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Extraction of Carboxylic Acids by Amine Extractants

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EXTRACTION OF CARBOXYLIC ACIDS BY AMINE EXTRACTANTS

Janet Ayako Tamada

ABSTRACT

This work examines the chemistry of solvent extraction by long-chain amines for recovery of carboxylic acids from dilute aqueous solution. Long-chain amines act as complexing agents with the acid, which facilitates distribution of the acid into the organic phase. This complexation is reversible, allowing for recovery of the acid from the organic phase and regeneration of the extractant.

Batch extraction experiments were performed to study the complexation of acetic, lactic, succinic, malonic, fumaric, and maleic acids with Alamine 336, an aliphatic, tertiary amine extractant, dissolved in various diluents. The diluents were selected from a variety of chemical classes, including halogenated hydrocarbons, alcohols, ketones, substituted aromatics, and alkanes.

The results of batch extraction experiments were interpreted by a "chemical" model, in which stoichiometric ratios of acid and amine molecules are assumed to form complexes in the solvent phase. From fitting of the extraction data, the stoichiometry of complexes formed and the corresponding equilibrium constants were obtained. The results of the model were combined with infrared spectroscopic experiments and results of past studies to analyze the chemical interactions that are responsible for extraction behavior.

Factors found to affect extraction include the acidity and structural characteristics of the acid extracted, the nature of the diluent, and temperature. Extraction increases with acid strength. Monocarboxylic acids form a higher ratio of multiacid to single acid complexes and show less aggregation of complexes than do dicarboxylic acids. The stoichiometries of complexes of dicarboxylic acids are influenced by intramolecular hydrogen bonding. Hydrogen-donating diluents, such as chloroform, promote formation of strong complexes with a single acid and amine, ketones promote multiacid per amine complexes, and inert diluents promote aggregation. An increase in temperature decreases the amount of acid extracted.

The information from the equilibrium studies was used to develop guidelines for large-scale staged extraction and regeneration schemes. A novel scheme, in which the diluent composition is shifted between extraction and regeneration, was developed which could achieve both high solute recovery and high product concentration.

To Dave

Two for the Road (reprise)

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TABLE OF CONTENTS

TABLE OF CONTENTS (CONT'D)

TABLE OF CONTENTS (CONT'D)

page

CHAPTER 4 (cont'd)

TABLE OF CONTENTS (CONT'D)

page

TABLE OF CONTENTS (CONT'D)

page

CHAPTER 8 (cont'd)

APPENDICES

LIST OF TABLES

LIST OF FIGURES

Chapter 2 Figures **page**

LIST OF FIGURES (CONT'D)

Chapter 2 Figures (cont'd) page

Chapter 3 Figures

LIST OF FIGURES (CONT'D)

Chapter 3 Figures (Cont'd) page

Chapter 4 Figures

Chapter 5 Figures

Chapter 6 Figures

LIST OF FIGURES (CONT'D)

Chapter 6 Figures (cont'd) page

Chapter 7 Figures

LIST OF FIGURES (CONT'D)

Chapter 7 Figures (cont'd) page

Chapter 8 Figures

LIST OF FIGURES (CONT'D)

Chapter 8 Figures (cont'd) page

Appendix C Figures

LIST OF FIGURES (CONT'D)

Appendix D Figures **page**

CHAPTER 1. INTRODUCTION

The selective recovery of carboxylic acids from dilute aqueous solutions has application to a number of processing situations. A major example is the production of carboxylic acids by fermentation, e.g., citric acid production (Kirk-Othmer, 1979). Separation and recovery of the products from the fermentation broth is a major factor in determining the economic viability of a fermentation process. Typical downstream processing costs for these fermentations constitute 40% or more of the final product cost (Stowell, 1986). Another application is removal and recovery of carboxylic acids from plant-effluent and waste streams, e.g., the removal of acetic acid from wastewaters from the manufacture of acetic acid (Ricker et al., 1979).

1.1 Feed Streams of Interest

The findings of this work apply to recovery of organic acids from any dilute, aqueous solution, although the impetus for the project is the development of energy-efficient recovery schemes for biologically-produced compounds. A great number of organic acids, including citric, succinic, fumaric, malic, lactic, propionic, acetic, and butyric acids, can be produced by microorganisms. More complex carboxyl-bearing compounds, including amino acids and the antibiotics penicillin and cephalosporin, are also produced by biological systems. In spite of this, industrial-scale biological production of organic acids is commercially attractive for very few of these acids. As an illustration, about 60 known kinds of organic acids are derived from microorganisms, but only six -- citric, gluconic, 2-keto-gluconic, itaconic, lactic, and tartaric acids -- are produced commercially by fermentation in Japan, a world leader in biological production technology (Yamada, 1977).

Usually fermentation broths contain less than 10 wt%, and more typically 1-5 wt%, of the desired product in a complex mixture of buffering agents, nutrients, cell debris, and other components (Busche, 1983). Separation of the acid from aqueous solution is difficult because the -COOH (carboxyl) group has a high affinity for water; i.e., the aqueous-phase activity coefficient is low. Separation by vaporization processes is difficult or precluded for most carboxylic acids because they have low volatilities relative to water.

Brief discussions of the manufacture and production of acids studied in this work -- lactic, succinic, fumaric, acetic, malonic, and maleic acids -- are given below. For comparison, citric acid, a high-volume chemical for which commercial-scale fermentations have been highly successful, is also discussed. If the price of petroleum feedstocks increases, commercial production of fumaric, lactic (Lockwood, 1979) and succinic (Kirk-Othmer, 1979) acids by fermentation will become increasingly attractive. Small amounts of acetic acid for food purposes are currently produced biologically, but large-scale industrial production is not currently economically feasible. Maleic and malonic acids are not, and are not likely to be, produced commercially by fermentation. They were studied so as to expand fundamental understanding of the extraction chemistry.

U.S. production of citric acid in 1981 exceeded 100,000 tons (Ng et al., 1983). Originally, citric acid was produced commercially by extraction from lemon and lime juice and from pineapple wastes. Currently, most commercial production of citric acid is achieved by fermentation with the fungus *Aspergillus niger* (Kirk-Othmer, 1979). The final concentration of citric acid in the broth is on the order of 10 wt% (Baniel et al., 1981), with the pH of the broth approximately 1.8 to 2.0 (Lockwood, 1979).

The usual method for recovery of the product acid is precipitation of calcium citrate by the addition of calcium hydroxide to the aqueous feedstream, which has been preheated to 60-100°C. The resultant crystals are filtered, washed, and subsequently reacidified with sulfuric acid to convert the salt to the free acid form. (Belter et al., 1988; Lockwood, 1979). The separation is followed by finishing steps, entailing filtration, carbon treatment, heavy metal precipitation, and finally evaporative crystallization to the final product. Although the chemistry of this recovery technique is straightforward, the engineering, separation, and unit operations are complicated and highly sophisticated (Kirk-Othmer, 1979). A recent alternative method of recovery is extraction by a solvent mixture of trilaurylamine, *n*-octanol and a C_{10} or C_{11} isoparaffin, followed by back extraction at an elevated temperature (Kirk-Othmer, 1979; Baniel et al., 1981). The aqueous acid solution then undergoes a diluent wash with a hydrocarbon solvent and is passed through activated-carbon columns. The final product crystals are formed by conventional evaporative crystallization.

The commercial manufacture of lactic acid is achieved by both biological and chemical means, with 85% of the U.S. production and most of the Japanese production by the chemical route (Lockwood, 1979; Yamada, 1977; Kirk-Othmer, 1979), while virtually all European production is by the biological route. The U.S. imports lactic acid because its fermentation is cheaper than its synthesis. World production capacity for lactic acid is approximately 29,000 metric tons/year (Kirk-Othmer, 1979).

The chemical synthesis of lactic acid is accomplished by several methods; among these are the hydrolysis of lactonitrile, alkaline degradation of sugar, and reaction of propylene and nitrogen oxides (Holten, 1971). Commercial biological production is

achieved by homolytic fermentation using various *Lactobacillus* bacteria. Concentrations of up to 12-15 wt% (more typically 10 wt%) lactic acid can be achieved (Roffler, 1986) at pH 5.0 to 5.5 (Kirk-Othmer, 1979). Acid is recovered from the broth by precipitation with calcium carbonate or calcium hydroxide, followed by acidification of the salt with sulfuric acid. The resultant 10% aqueous acid solution is concentrated to 50%, refined over carbon, treated with sodium ferrocyanide, and finally passed through an ion exchange column for final finishing.

Fumaric acid is prepared predominantly by either catalytic oxidation of aromatic hydrocarbons or isomerization of maleic acid (Kirk-Othmer, 1979). U.S. production in 1978 was 12,700 tons per year. In the past, fumaric acid was produced primarily by fermentation with strains of the fungus *Rhizopus*. The broth was kept at a pH of 5.0 to 6.5 to produce solutions with approximately 3.2 wt% fumaric acid (Kane et al., 1943).

Succinic acid is produced commercially by the hydrogenation of maleic anhydride or fumaric acid (Kirk-Othmer, 1979). The fermentive production of succinic acid has been studied extensively in Japan (Kirk-Othmer, 1979). In these processes, acid is recovered and purified from the broth by precipitation of the lead succinate salt, followed by ion exchange. This process is not presently commercially attractive.

Acetic acid had a 1981 U.S. production of 1.35 million tons (Ng et al., 1983). Most is produced chemically by either acetaldehyde oxidation, liquid-phase hydrocarbon (generally butane) oxidation, or methanol carbonylation. Food grade acetic acid (vinegar) is still produced by the centuries-old process of oxidation of ethanol with *Acetobacter aceti* (Ng et al., 1983). The high cost of the ethanol feedstock and the massive quantities of water involved in the process make it impractical for large-

scale glacial acetic acid production (Kirk-Othmer, 1979). The destructive distillation of wood, which produces pyroligneous acid of 5-6% acetic acid, 2.8% methanol, 2% tar and 2% wood oil (Kirk-Othmer, 1947), was the primary source of acetic acid in the U.S. for 75 years (Kirk-Othmer, 1979). It is still used in the Soviet Union for industrial production of acetic acid, but the high capital and operating costs are justified only by the value of the by-products. Fermentive production with forest wastes (e.g., pulp mill liquors, sawmill chips, or newsprint) as the carbohydrate source has been examined, and technologically acceptable routes have been developed. However, none have yet proven commercially viable because the cost of the concentration, purification, and high capital cost of the process (Kirk-Othmer, 1979). Recovery of acetic acid from dilute solutions is discussed by Busche et al. (1982) and King (1983), among others.

Maleic acid is made by the vapor-phase oxidation of benzene, butene, or butane with oxygen over V_2O_3 catalyst to yield a mixture of maleic anhydride and maleic acid (Kirk-Othmer, 1979). Free maleic acid is not a large-volume commercial product. A major use is as a precursor to the production of fumaric acid. Malonic acid is an intermediate in the preparation of its diesters. Purification is achieved through the calcium salt. Because malonic anhydride, like maleic anhydride, is the major commercial product, the production of free malonic acid is very small, less than 5 tons/year in 1978 (Kirk-Othmer, 1979).

1.2 Survey of Methods for the Separation of Carboxylic Acids from Dilute Aqueous Solution

The following section outlines some of the methods currently available and under

study for recovery of organic acids from dilute solution.

Precipitation. This process is currently used industrially for recovery of lactic and citric acid (see above). Recovery from the fermentation broth is achieved by precipitation of the insoluble calcium salt of the acid with $Ca(OH)_2$ or $CaCO_3$, followed by reacidification with H_2SO_4. Precipitation involves substantial cost for chemicals, difficulties in crystallization from the salt-containing solution, effluent disposal problems, and loss of the product acid because of substantial aqueous solubility of the calcium salt. Improvements of new processes over precipitation increase the potential for industrial production of carboxylic acids by fermentation.

Distillation. Volatile carboxylic acids, most notably acetic acid, may be distilled from aqueous solution. However, for low acetic acid concentrations, the relative volatility of the acid and water is close to one and water is the more volatile component, so conventional distillation is not the preferred recovery scheme (King, 1983). Energy requirements to separate a 5 wt% solution of acetic acid in water by distillation amount to about 21,000 Btu/lb of acid, over nineteen times the latent heat of water (Busche, 1983). Current commercialized alternatives include azeotropic distillation and solvent extraction followed by azeotropic distillation. Distillation of dilute aqueous solutions of non-volatile acids (including most of the acids of interest) is impractical because of the large energy cost for vaporization of large quantities of water to recovery a small amount of product. Furthermore, evaporation of the water leaves behind low-volatility impurities.

Sorption. Porous, solid sorbents with large surface areas, such as activated carbons and polymeric resins, are used extensively for removal of organic compounds from aqueous solution. Sorption is attractive in a number of ways. Solid sorbents

potentially have a major advantage over solvent extraction because they should not result in contamination of the effluent or recycle streams. Sorption is particularly effective for removing solutes from very dilute solutions; the limited capacity on the solid surface for the solute restricts its use for more concentrated solutions.

Sorption encompasses several subclasses:

Ion exchange. A cationic functional group, such as a quaternary ammonium cation, is attached to a polymeric resin. A counterion on the resin -- Cl^-, OH^-, or some other anion -- is exchanged for a carboxylate anion from the feed solution. The resin is regenerated by contact with a more concentrated solution of the original counterion. This method has the drawbacks of consumption of chemicals and production of salty waste streams.

Sorption with reversible complexation. So-called weak-base ion exchange resins, e.g. DOWEX MWA-1 (Dow Chemical) and Aurorez (Celanese Corporation), have been shown to be effective for removing acids from solution (Munson et al, 1987; Kuo et al., 1987; Garcia and King, 1989). These materials containing active sites, such as pyridyl, amide, imidazole, or amine functional groups, which complex with the solute. A major factor limiting the development of such sorption processes is that regeneration of the sorbent and recovery of the product have been found to be difficult for functionalized resins. Although removal of the acid from the sorbent by contact with aqueous NaOH solutions is effective, it involves chemical consumption and production of the acetate salt rather than acetic acid. Solvent regeneration (e.g., contacting the loaded sorbent with a solvent such as methanol) (Garcia and King, 1989), thermal regeneration to volatilize the acid from the solid (Ng, 1988), and esterification

followed by thermal regeneration (Sanchez et al., 1987) have all been studied as regeneration alternatives.

Non-wetting adsorption. Adsorbents without active functional groups, e.g. Amberlite XAD-4 (Rohm & Haas), have potential for carboxylic acid recovery and separation by use of the adsorbent in the non-wet state (Rixey and King, 1987). Solutes of surprisingly low volatility can be adsorbed by transport over short distances through the vapor phase in the pores.

Membranes. Electrodialysis, reverse osmosis, and carrier-mediated transport through polymeric membranes have been suggested as alternatives for carboxylic acid recovery (Busche, 1983). These methods are still in the early stages of development.

Liquid ion exchange. Quaternary ammonium salts are often used as liquid anion exchange materials (Roffler, 1986). They are often suggested as carrier molecules for liquid membranes. Like ion exchange resins, liquid ion exchangers consume salts or acid in the regeneration of the ion exchanger.

Conventional solvent extraction. Liquid-liquid (or solvent) extraction is a process in which a solute is transferred between an aqueous phase and a water-immiscible organic phase by physical contacting of the two phases. The phases are then separated, and the solute-rich phase is regenerated to recover the product. Extraction with conventional solvents, such as ether, is impractical for the recovery of most carboxylic acids because the low activity coefficient of the acid in the aqueous phase does not allow substantial transfer of the acid into the solvent. An exception is acetic acid, for which commercial processes using extraction with solvents such as isopropyl acetate have been developed (King, 1983).

Extraction by reversible chemical complexation. In this method, a liquid-phase complexing agent pulls the solute into the solvent phase by forming a complex with the functional group of the solute. Thus the distribution of acid into the solvent phase is substantially increased over conventional solvent extraction. The complexation is reversible, so that the solute can be recovered from the extract after phase separation. This method is the subject of the current research project.

1.3 Reasons for Investigation of Solvent Extraction by Reversible Chemical Complexation

For a separation to be practical it must be selective and economical. For the latter goal, it should minimize energy and chemical consumption. Addtionally, concentration of the product would be an advantage. Factors which favor the use of extraction by reversible chemical complexation over alternate methods are (King, 1987):

1. The presence of functional groups on the solute capable of complexation. The acidic functional group becomes a means of promoting selectivity and gaining uptake capacity.

2. Low solute concentration. For low solute concentrations there is a high driving force of free association sites on the complexing agent which is very favorable for extraction. Most other methods of separation do not derive similar advantages at low solute concentrations.

3. Low activity of the solute in water. Because complexation can lower the solute activity in the solvent phase substantially, it gains a relative advantage over competing methods.

4. Low solute volatility. Complexation gains a relative advantage over distillation for non-volatile solutes.

5. Low pH of feedstream. Reversible complexation is driven by the amount of un-ionized acid in solution and is thereby favored at low pH. The optimal pH for separation by complexation is related to the pK_A of the acid. There is no advantage to carrying out the separation at a pH more than one unit lower than the pK_A of the acid, because most of the acid is un-ionized at that point. Feed solutions with low pH may have the disadvantage of promoting extraction of other, competing acids. At high pH values, where the acid is mostly dissociated, ion exchange may be more favorable. In many cases, however, chemical complexation is capable of allowing essentially complete extraction even at relatively high pH values (4 to 5), and maintains its advantage of low chemical consumption over ion exchange.

6. Ease of regeneration. Most liquid extractants are more easily regenerated than solid sorbents. Regeneration is essential so that the complexing agent can be recycled and the product can be recovered. The cost of the regeneration step, which is tied to the energy and chemical consumption, is an important, if not the most important, factor in determining the economic viability of the separation.

Potential drawbacks of solvent extraction include:

1. Loss of solvent to the aqueous phase. To avoid the cost of solvent replacement, some means of solvent recovery from the aqueous streams or of preventing solvent loss will be necessary. These will entail sophisticated implementation schemes or additional separations, which may inflate the capital and operating costs of the process. Some alternative methods to reduce solvent loss are discussed below in Section 1.5

2. Solvent toxicity. Solvent dissolution or entrainment may contaminate the aqueous waste stream with potentially hazardous substances. For *in situ* extractions, solvent toxicity to the producing organism is a major difficulty in process implementation. Therefore, methods for solute removal or recovery from the aqueous stream may be necessary, even if the cost of solvent replacement is not significant.

3. Limited capacity. Because the maximum concentration of complexing sites is limited with the high molecular weight extractants, extraction by complexation works well only for dilute, < 1 mol/L, solutions.

1.4 The Solvent System

1.4.1 Terminology

The choice of solvent system is a basic consideration for an extraction process. For extraction by complexation, the solvent phase generally consists of the complexing agent itself, referred to as the extractant, dissolved in an organic solvent, referred to

as the diluent.

This work will focus primarily on forward extraction of the acid from the aqueous phase to the organic phase. The solute-depleted aqueous effluent from the extraction step is the "raffinate", and the solute-rich organic effluent is the "extract". The results of equilibrium studies of solvent extractions are generally reported as "distribution ratios". In this work, the distribution ratio will be reported in molar units as distribution of the acid from the aqueous to the organic phase, so that

$$D = C_{A,org}/C_{A,aq} \qquad \text{(Eq. 1-1)}$$

where,

D = molar distribution ratio (other common notations are K_D and K_C)

$C_{A,org}$ = molar concentration of solute in the organic phase

$C_{A,aq}$ = molar concentration of solute in the aqueous phase

1.4.2 Criteria for Selection of Extractant and Diluent

The complexation between the extractant and the solute should be strong enough to overcome the low activity of the solute in the aqueous phase, but not so strong as to render regeneration difficult or impossible. Two classes of basic extractants that have been effective for recovery of carboxylic acids are phosphorus-bonded oxygen-donor extractants and aliphatic amines.

Commonly used organophosphorus extractants include tributyl phosphate (TBP) and trioctylphosphine oxide (TOPO). Many workers (Ricker et al., 1979; Wardell and King, 1978; Wennersten, 1980; Roffler, 1986) have gathered equilibrium data for the extraction of various carboxylic acids by these extractants. A review is given by Kertes and King (1986). Phosphorus-bonded oxygen-donor extractants give significantly higher distribution ratios of the solute than the carbon-bonded oxygen-donor solvents (e.g., methyl isobutyl ketone).

Work by Wardell and King (1978), Ricker et al. (1979, 1980), and Baniel (1981) has indicated that long-chain, aliphatic amine extractants are particularly promising for recovery of carboxylic acids. The high basicity of the amine allows it to interact with the carboxylic acid functionality of the solute to form an acid-amine complex. The complexation has been shown to be reversible, allowing for regeneration of the solvent. Long-chain amines are minimally soluble in water, preventing costly losses of the extractant. They are thermally stable, allowing distillation or other high temperature regeneration methods to be implemented. Tertiary amines are generally favored over secondary or primary amines. Primary amines are too soluble in water to be of practical use. Secondary amines potentially undergo amide formation with carboxylic acids, which would cause loss of both product and extractant. Carbon chains between 8 and 12 appear to be optimal. Extractants with shorter chain lengths have excessive water solubility. Longer chain length reduces the molar concentration of extractant available for complexation and increases the alkyl character of the solvent, reducing extraction.

Commercially-available amine extractants are much less costly and are reported to give higher distribution ratios than phosphine oxide extractants (Michaels, 1978;

Kertes and King, 1986). On the whole, aliphatic amines appear to be the most satisfactory extractants for carboxylic acids. Alamine 336, a commercially-available tertiary amine (Henkel Corp.) with a reported molecular weight of 392 g/mol, was chosen for this work. A tertiary amine was chosen over a primary or secondary amine to reduce extractant loss from water solubility and to avoid the possibility amide formation with the carboxylic acid. The molecular weight is a compromise between a low molecular weight, which allows significant extractant solubility into the aqueous phase, and high molecular weight, which limits the number of basic complexation sites for a given volume or weight of extractant.

Traditionally, the diluent is an organic solvent used to control the physical qualities of the solvent, such as viscosity, density, interfacial tension, water uptake, and boiling point. The choice of diluent also plays another important and less obvious role in the extraction, in that it has a profound impact on the extracting power of the amine. Diluents which have functional groups that can interact with the complex are known as "active" diluents. Diluents without such functional groups are known as "inert" diluents. Diluent selection will be discussed further in Chapter 8.

1.5 Methods of Implementation

Conventionally, the separation step is downstream of the production step. *In situ* removal of carboxylic acids as they are produced has certain advantages, including lessening product inhibition and continuous recovery and recycle of the broth (Roffler, 1986; Bar and Gainer, 1987). Disadvantages include much more difficult process implementation and control.

Conventional extractors are probably the simplest way to incorporate reversible chemical complexation into a separation process. In conventional extractors, however, solvent loss, which is problematic from the cost of the lost solvent, and because solvent toxicity, both to the acid-producing organisms and as source of effluent contamination, is a concern. Additionally, for conventional extraction, the extraction capacity is limited by the maximum concentration of the high molecular weight amines.

There are a variety of possibilities for reducing these problems. The solvent can be recovered from the aqueous effluent by an additional separations step, such as activated-carbon adsorption or distillation. To reduce solvent loss, the extractant can be immobilized within a polymeric membrane (Smith, 1981; Sengupta, et al., 1988) or separated from the aqueous stream by hollow fiber membrane (Sepracor, 1988). Toxicity to the acid-producing organism can be reduced by immobilization of the microorganism in carrageenan beads (Bar and Gainer, 1987) or in alginate gels that contain castor oil as a protective agent (Honda et al., 1986). Liquid emulsion membranes, in which the extractant acts as a carrier molecule to transport the solute from an external feed aqueous phase through the organic-phase emulsion membrane to an interior aqueous product phase, reduce the capacity limitation because extraction and regeneration are achieved in one step (Thien et al., 1986; Halwachs et al., 1980; Matulevicius and Li, 1975).

Integration of the separation step into the overall carboxylic acid production scheme and the specifics of process implementation are particular to the type of process that is contemplated. These considerations are not explored further in this work.

1.6 Summary, Conclusions, and Overview of Dissertation

This work examines solvent extraction by long-chain amines as a process option for recovery of carboxylic acids from dilute aqueous solution. Long-chain aliphatic amine extractants have been chosen for study because of their ability to complex effectively yet reversibly with the solute. The objective of this project is to determine how factors, such as temperature, type of carboxylic acid and type of diluent, affect extraction equilibria. The nature of the chemical interactions between the amine, acid, and diluent will be examined to provide a molecular viewpoint of complexation. This in turn will enable rational interpretation of equilibrium data. Finally, the implications of the knowledge gained on complexation equilibria will be explored in relation to process design factors, such as diluent selection and regeneration alternatives.

The choice of systems to be studied in this work was based upon their potential for actual industrial processing and/or elucidation of the process chemistry. Acetic, lactic, succinic, and fumaric acids are actual or potential industrial fermentation products. Although malonic and maleic acids are unlikely to be produced biologically, including them provided fundamental understanding of certain aspects of extraction chemistry. Diluents were selected from a variety of chemical classes, including halogenated hydrocarbons, alcohols, ketones, substituted aromatics, and alkanes. A variety of solvents was chosen to probe the range of extraction behavior. A tertiary amine extractant was chosen because primary amines are too water soluble and tend to form emulsions, and secondary amines potentially form amide bonds with carboxylic acids. Alamine 336, a tertiary amine with linear chains of 8 to 10 carbons, was selected as the extractant because of its relatively high purity, low water solubility, and commercial availability.

Chapter 2 introduces the mass-action law approach to modeling extraction by chemical complexation and reports the results of batch extraction experiments performed in this work.

Chapter 3 reviews the findings of similar experiments by other workers. Based on the mass-action law approach, a comparison is made of different systems for the influence of acid and diluent type. The roles of hydroxyl groups, additional carboxyl groups, configuration, and pK_A on the extractability of the acid are discussed and the influence of the diluent functionality is examined.

Chapter 4 reports the results of infrared spectroscopic studies of carboxylic acid-amine systems. This, coupled with a review of more extensive work by previous investigators, helps elucidate the nature of species formed during complexation.

Chapter 5 correlates the findings of the batch extraction studies of Chapters 2 and 3 with the spectroscopic investigations of Chapter 4 to draw inferences on the nature of the chemical interactions which govern complex formation.

Chapter 6 describes the effect of temperature on extraction equilibria. The apparent enthalpies and entropies of complexation are calculated.

Chapter 7 reports data for the coextraction of water in carboxylic acid-amine systems.

Chapter 8 relates the findings from Chapters 2 through 7 to process engineering aspects of the separation. Methods of regeneration of the extract are discussed.

REFERENCES

Baniel, A. M., Blumberg, R., Hajdu, K., "Recovery of Acids from Aqueous Solutions", U. S. Patent No. 4,275,234 (Jun. 23, 1981); Chem. Abstr. Vol. 97, No. 109557 (1982).

Bar, R. and Gainer, J. L., "Acid Fermentation in Water-Organic Solvent Two-Liquid Phase Systems", *Biotechnol. Prog.*, 3(2), 109-114 (1987).

Belter, P. A., Cussler, E. W., and Hu, W.-S., *Bioseparations//Downstream Processing for Biotechnology*, John Wiley & Sons, New York (1988).

Busche, R. M., "Recovering Chemical Products from Dilute Fermentation Broths", *Biotechnol. Bioeng. Symp. No. 13*, John Wiley & Sons, 597-615 (1983).

Busche, R. M., Shimshick, E. J., and Yates, R. A., "Recovery of Acetic Acid from Dilute Acetate Solution", *Biotechnol. Bioeng. Symp. No. 12*, John Wiley & Sons (1982).

Garcia, A. A. and King, C. J., *Ind. Eng. Chem. Res.*, in press (1989).

Halwachs, W., Flaschel, E., and Schügerl, K., "Liquid Membrane Transport -- A Highly Selective Separation Process for Organic Solutes", *J. Membrane Sci.*, 6 33-44 (1980).

Holten, C. H., *Lactic Acid//Properties and Chemistry of Lactic Acid and Derivatives*, Verlag Chemie, Copenhagen (1971).

Honda, H., Taya, M., and Kobayashi, T., "Ethanol Fermentation Associated with Solvent Extraction Using Immobilized Growing Cells of *Saccharomyces Cerevisiae* and Its Lactose-Fermentable Fusant", *J. Chem. Eng. Jpn.*, **19**(4) 268-273 (1986).

Kane, J. H., Finlay, A., and Amann, P. F., "Production of Fumaric Acid", U.S. Patent No. 2,327,191 (Aug. 17, 1943); referenced in Prescott, S. C., *Industrial Microbiology*, 2nd ed., McGraw-Hill, New York (1949).

Kertes, A. S. and King, C. J., "Extraction Chemistry of Fermentation Product Carboxylic Acids", *Biotechnol. Bioeng.*, **28**, 269-282 (1986).

King, C. J., "Separation Processes Based on Reversible Chemical Complexation", *in Handbook of Separation Process Technology*, Rousseau, R. W., Ed., Wiley & Sons, New York, Chapter 15, 760-774 (1987).

King, C. J., "Acetic Acid Extraction", in *Handbook of Solvent Extraction*, T. C. Lo, H. Baird, and C. Hanson, Eds., Wiley & Sons, New York, Section 18.5, 567-573 (1983).

Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., John Wiley & Sons, New York, (1979). "Citric Acid", Vol. 6; "Acetic Acid", Vol. 1, "Malonic Acid", Vol. 14; "Maleic Anhydride, Maleic Acid, and Fumaric Acid, Vol. 14;, "Hydroxycarboxylic Acids", Vol. 13; "Succinic Acid and Succinic Anhydride", Vol. 21.

Kirk-Othmer Encyclopedia of Chemical Technology, 1st ed., Kirk, R.E. and Othmer, D. F., Eds., Interscience Encyclopedia, Inc., New York, "Acetic Acid", Vol. 1 (1947).

Kuo, Y., Munson, C. L., Rixey, W. G., Garcia, A. A., Frierman, M., and King, C. J.,

"Use of Adsorbents for Recovery of Acetic Acid from Aqueous Solutions. Part I-- Factors Governing Capacity", *Separ. Purif. Methods*, 16(1), 31-64 (1987).

Lockwood, L. B., "Production of Organic Acids by Fermentation", in *Microbial Technology*, 2nd ed., Vol. 1, Academic Press, Chapter 11, 356-386 (1979).

Matulevicius, E. S. and Li, N. N., "Facilitated Transport Through Liquid Membranes", *Separ. Purif. Methods*, 4(1), 73-96 (1975).

Michaels, J. N., "Selective of Solvents for Extraction of Wacker Process Wastewater", M.S. Thesis, Department of Chemical Engineering, University of California, Berkeley (1978).

Munson, C. L., Garcia, A. A., Kuo, Y., Frierman, M., and King, C. J., "Use of Adsorbents for Recovery of Acetic Acid from Aqueous Solutions. Part II -- Factors Governing Selectivity", *Separ. Purif. Methods*, 16(1), 91-101 (1987).

Ng, M., "Regeneration of Basic Sorbents Used in the Recovery of Acetic Acid from Dilute Aqueous Solutions", M.S. Thesis, Department of Chemical Engineering, University of California, Berkeley (1988).

Ng, T. K., Busche, R. M., McDonald, C. C., and Hardy, R. W. F., "Production of Feedstock Chemicals", *Science*, 219, 733-740 (11 February 1983).

Ricker, N. L., Michaels, J. N., and King, C. J., "Solvent Properties of Organic Bases for Extraction of Acetic Acid from Water", *J. Separ. Proc. Technol.*, 1(1), 36-41 (1979).

Ricker, N. L., Pittman, E. F., and King, C. J., "Solvent Extraction with Amines for Recovery of Acetic Acid from Dilute Aqueous Industrial Streams", *J. Separ. Proc. Technol.*, 1(2), 23-30 (1980).

Rixey, W. G. and King, C. J., "Non-wetting Adsorbents for Recovery of Solutes from Aqueous Solution", in *Fundamentals of Adsorption -- II*, A. I. Liapis, Ed., Engineering Foundation, New York (1987).

Roffler, S. R., "Extractive Fermentation -- Lactic Acid and Acetone/Butanol Production", Ph.D. Dissertation, Department of Chemical Engineering, University of California, Berkeley (1986).

Sanchez, P. A., Kawano, Y., and King, C. J., "Recovery of Biologically Produced Chemicals: Regeneration of Adsorber Beds by Entrainer Distillation and/or Esterification Directly on the Bed", *Ind. Eng. Chem. Res.* 26 1880-1887 (1987).

Sengupta, A., Basu, R., and Sirkar, K. K. "Separation of Solutes from Aqueous Solutions by Contained Liquid Membranes", *AIChE J.*, 34, 1698-1708 (1988).

Sepracor Inc., "MSX-500 System: Laboratory-scale development system for membrane-mediated solvent extraction applications", Sepracor Inc., Marlborough, MA (1988).

Smith, B. R, "Organic Acid Recovery with Coupled-Transport Membranes", Conf. on Advances in Fermentation Recovery Process Technology, Banff, Alberta, Canada (June 7-12, 1981).

Stowell, J. D., Bailey, P. J., and Winstanley, D. J., Eds., *Bioactive Microbial Products 3: Downstream Processing*, Academic Press, London (1986).

Thien, M. P., Hatton, T. A., and Wang, D. I. C., "Liquid emulsion membranes and their applications in biochemical separations", in *ACS Symp. Ser. (Separation, Recovery, and Purification in Biotechnology)*, Asenjo, J. A. and Hong, J., Eds., ACS, vol. 314, 67-77, Washington, D.C., (1986).

Wardell, J. M. and King, C. J., "Solvent Equilibria for Extraction of Carboxylic Acids from Water", *J. Chem. Eng. Data*, 23(2), 144-148 (1978).

Wennersten, R., "A New Method for the Purification of Citric Acid by Liquid-Liquid Extraction", *Int. Conf. Solv. Extr. Ion Exch.* (ISEC '80), vol 3, 1-7 (1980).

Yamada, K., "Bioengineering Report//Recent Advances in Industrial Fermentation in Japan", *Biotechnol. Bioeng.*, 19, 1563-1621 (1977).

CHAPTER 2. EXPERIMENTAL RESULTS FOR THE EXTRACTION OF CARBOXYLIC ACIDS BY TERTIARY AMINES

In this chapter, the extraction of carboxylic acids by a tertiary amine extractant in a variety of diluents is examined to compare the equilibrium behaviors of different systems. Equilibrium batch extraction experiments were performed on acetic acid, a monocarboxylic acid; lactic acid, an α-hydroxycarboxylic acid; succinic and malonic acids, aliphatic dicarboxylic acids; and fumaric and maleic acids, unsaturated dicarboxylic acids. The extractant used was Alamine 336 (Henkel Corp.), a commercially-available tertiary amine, with aliphatic chains that are 8 to 10 carbons in length. The diluents were chosen from distinct chemical classes. Active diluents studied were chloroform, a proton-donating halogenated hydrocarbon solvent; methylene chloride, another halogenated hydrocarbon solvent; methyl isobutyl ketone (MIBK), a proton acceptor; nitrobenzene, a highly polar, aromatic solvent; and 1-octanol, both a proton donor and acceptor. The inert diluent studied was *n*-heptane, an alkane solvent. Details of the experimental procedure of the extraction experiments and a tabulation of the experimental results are given in Appendix A. The pK_A of the acids and properties of the diluents used in this work, including diluent solubility in water, water solubility in diluent, density, and boiling point, are given in Appendix E.

2.1 General Trends

The most obvious mechanism of extraction for these systems is formation of an ion pair or complex between the undissociated acid, HA, and the basic amine, R_3N:

$$HA + R_3N = HA\text{-}R_3N \qquad \text{(Eq. 2-1)}$$

If this were the only complex formed, the molar distribution ratio, *D*, which is the equilibrium molar concentration of solute in the organic phase divided by the equilibrium molar concentration of solute in the aqueous phase, would be a maximum for the lowest concentration of HA and the highest extractant concentration.

Results of experiments for the extraction of succinic acid with Alamine 336 in chloroform, MIBK, and *n*-heptane, and for malonic acid with Alamine 336 in MIBK, at a solvent:water volumetric phase ratio of 1:1, are shown in Figs. 2-1 *a*, *b*, *c*, and *d* respectively. The results are given as the distribution ratio (the molar concentration of acid in the organic phase divided by the molar concentration of acid in the aqueous phase at equilibrium) versus the initial Alamine 336 molarity in the organic phase for various total acid concentrations. In the heptane diluent, a third phase was formed between the bulk aqueous and solvent phases, and *D* was taken as the amount of acid in both solvent phases divided by the amount of acid in the aqueous phase. Initial extractant concentration ranged from 0.0 mol/L (no amine) to 2.0 mol/L (100% amine).

The effect of acid concentration on distribution is dependent upon extractant concentration. In the active diluents, at low extractant concentration, the distribution ratio is highest for the lowest initial acid concentration. This trend reverses at high extractant concentration, where the distribution ratio is highest at high initial acid concentration. This reversal is due in part to acid dissociation. When pH is high, dissociation of the weak carboxylic acid reduces the undissociated acid concentration and reduces the effective extractive power of the extractant. In the absence of added acids or bases, high pH occurs when extractant concentration is

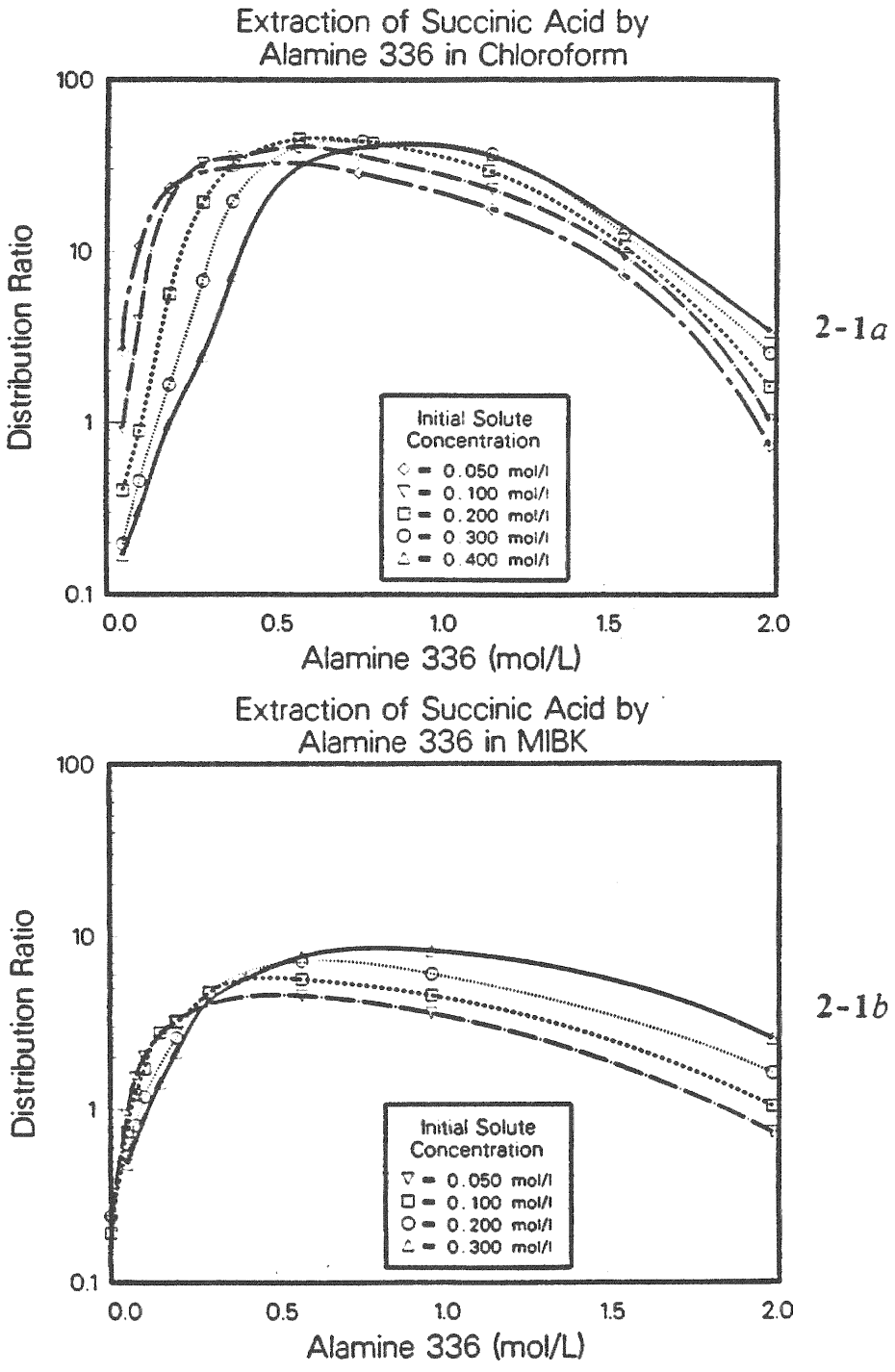
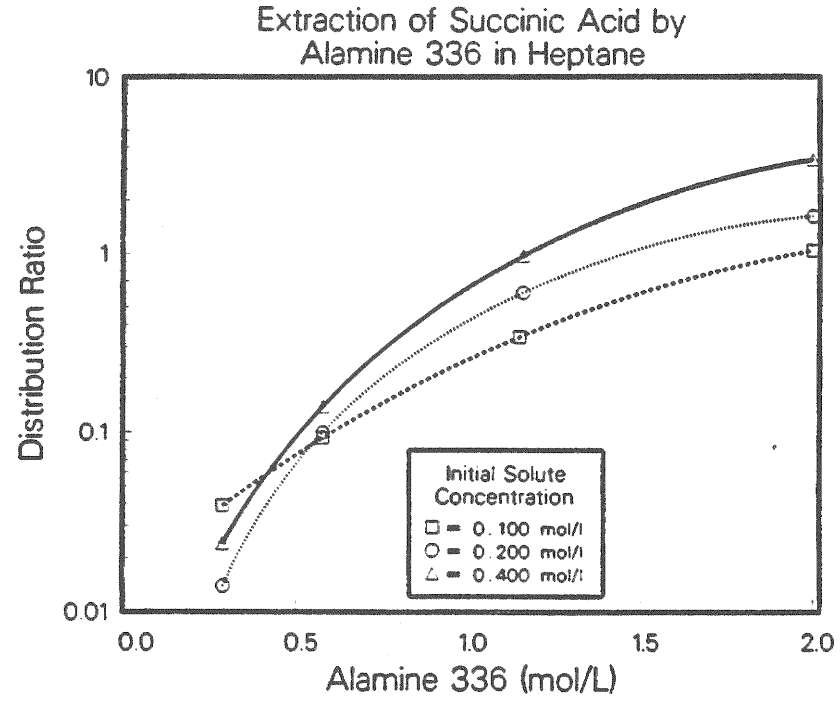
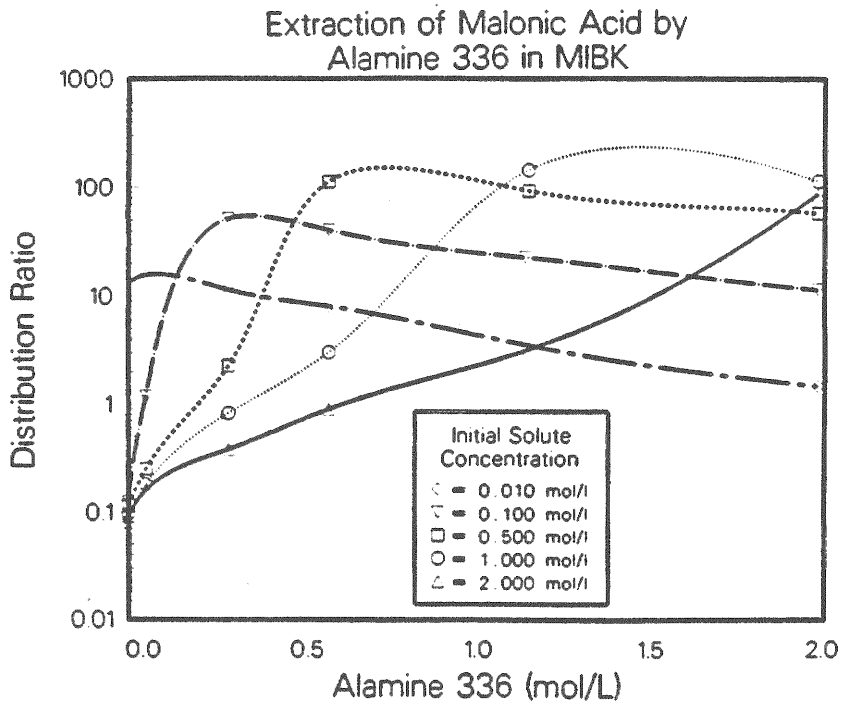


Fig. 2-1. Effect of Total Acid and Amine Concentration on the Distribution Ratio.

(*a*) Extraction of succinic acid by Alamine 336 in chloroform
(*b*) Extraction of succinic acid by Alamine 336 in methyl isobutyl ketone



2-1*c*



2-1*d*

Fig. 2-1. Effect of Total Acid and Amine Concentration on the Distribution Ratio (cont'd).

(*c*) Extraction of succinic acid by Alamine 336 in *n*-heptane
(*d*) Extraction of malonic acid by Alamine 336 in methyl isobutyl ketone

high and initial solute concentration is low. Thus at high extractant concentration, the dissociation of the acid creates low distribution ratios for the more dilute initial acid concentrations. A more complete explanation and an analysis of acid dissociation and its effects on distribution are given in Appendix C.

Figure 2-1 illustrates that the solvent characteristics have a major effect on the distribution of acid. MIBK by itself is capable of extracting small amounts of acid, indicated by a non-zero distribution ratio at zero amine concentration; chloroform and heptane by themselves extract very little acid. A solvent phase which contains both the extractant and an active diluent (chloroform or MIBK) produces larger distribution ratios than either the extractant or diluent alone; i.e., the distribution ratio exhibits a maximum at an intermediate amine concentration. A solvent which contains the extractant and an inert diluent (heptane) shows no such maximum. This difference strongly indicates that the active diluent interacts with the complex, stabilizing the complex more than the extractant itself does. Distribution ratios are dependent upon diluent, with chloroform as diluent showing the highest acid extraction and heptane the lowest. This establishes that the diluent-complex interaction is different in different diluents.

The above results demonstrate that complexes and interactions in addition to the acid-amine complex shown in Eq. 2-1 affect extraction behavior. What is the nature of these complexes and these interactions? Is it possible for more than one acid to form a complex with a single amine? Will a dicarboxylic acid complex with two bases, one for each carboxyl group? What about extending the reactions to include formation of even larger stoichiometric complexes or complexes with specific inclusion of the diluent? These concepts are formalized in the next section -- a mass-action law description of equilibrium.

2.2 Mass-Action Law Description of Equilibrium

2.2.1 Derivation

If "chemical" interactions between the components of the complex are strong compared to the "physical" interactions in the system, the equilibrium behavior can be modeled effectively by postulating the formation of various stoichiometric complexes of acid and amine. This method of description of a system as a series of stoichiometric reactions will be referred to as a mass-action law analysis (Connors, 1986).

An equilibrium description of the system can be written as a set of reactions of p acid, A, molecules and q amine, B, molecules to form various (p,q) complexes, with corresponding overall equilibrium constants, $\beta_{pq,true}$:

$$pA + q\overline{B} = \overline{A_pB_q} \qquad \beta_{pq,true} = \frac{\{\overline{A_pB_q}\}}{\{A\}^p\{\overline{B}\}^q} \qquad \text{(Eq. 2-2)}$$

where the species activities are denoted by braces, and organic-phase species are marked with an overbar.

For practical calculations, the activity coefficients of all species are assumed to be constant with respect to composition. Thus {A} is taken to be proportional to the concentration of undissociated acid (see Appendix C and Section 2.2.3 below for more discussion of this approximation), and the activities of the organic-phase species are taken to be proportional to their concentrations. Therefore, the equilibrium constant in Eq. 2-2 can be rewritten as

$$\beta_{pq} = \frac{[\overline{A_pB_q}]}{[A]^p[\overline{B}]^q} \qquad \text{(Eq. 2-3)}$$

where species concentrations are denoted by square brackets, and the constants of proportionality between species activities and concentrations are taken up in the equilibrium constant.

A material balance on the total (i.e. initial) concentration of amine in the organic phase, $C_{B,tot}$, completes the system description:

$$C_{B,tot} = [\overline{B}] + \Sigma q[\overline{A_pB_q}] \qquad \text{(Eq. 2-4)}$$

where the summation indicates the sum over all species present.

If reaction stoichiometry and the corresponding overall equilibrium constants are assumed, initial concentrations of amine are known, and extraction by the diluent alone is assumed to be negligible, the total concentration of acid extracted into the organic phase, $C_{A,org}$, can be determined by:

$$C_{A,org} = \Sigma p[\overline{A_pB_q}] = \Sigma p\beta_{pq}[A]^p[\overline{B}]^q \qquad \text{(Eq. 2-5)}$$

The loading of the extractant, Z, is defined as the total concentration of acid in the organic phase, divided by the total concentration of amine in the organic phase:

$$Z = \frac{C_{A,org}}{C_{B,tot}} = \frac{\Sigma p\beta_{pq}[A]^p[\overline{B}]^q}{C_{B,tot}} \qquad \text{(Eq. 2-6)}$$

If extraction by the diluent alone is significant, $C_{A,org}$ must be corrected to account for physical extraction by the diluent. Details of the correction used are given in Section 2.3.

2.2.2 Characteristics of Loading Curves

For a (1,1) acid-amine complex, the reaction and corresponding equilibrium constant are written as:

$$A + \overline{B} = \overline{AB} \qquad \beta_{11} = \frac{[\overline{AB}]}{[A][\overline{B}]} \qquad \text{(Eq. 2-7)}$$

If this were the only complex formed, the resultant expected loading can be shown to be:

$$Z = \frac{\beta_{11}[A]}{1 + \beta_{11}[A]} \qquad \text{(Eq. 2-8)}$$

In this case, loading increases rapidly with increasing [A] in proportion to β_{11} at low solute concentrations and asymptotically approaches unity at high [A], as the available extractant is exhausted. The solid curve in Fig. 2-2*a* shows the calculated "loading curve" -- the loading of the amine, Z, versus the logarithm of the undissosciated aqueous acid concentration, log[A] -- for this system. An inflection point occurs at $Z = 0.5$, corresponding to a $\log[A] = -\log(\beta_{11})$. Loading is independent of initial amine concentration.

The additional formation of a (2,1) acid-amine complex adds the following equation to the (1,1) case:

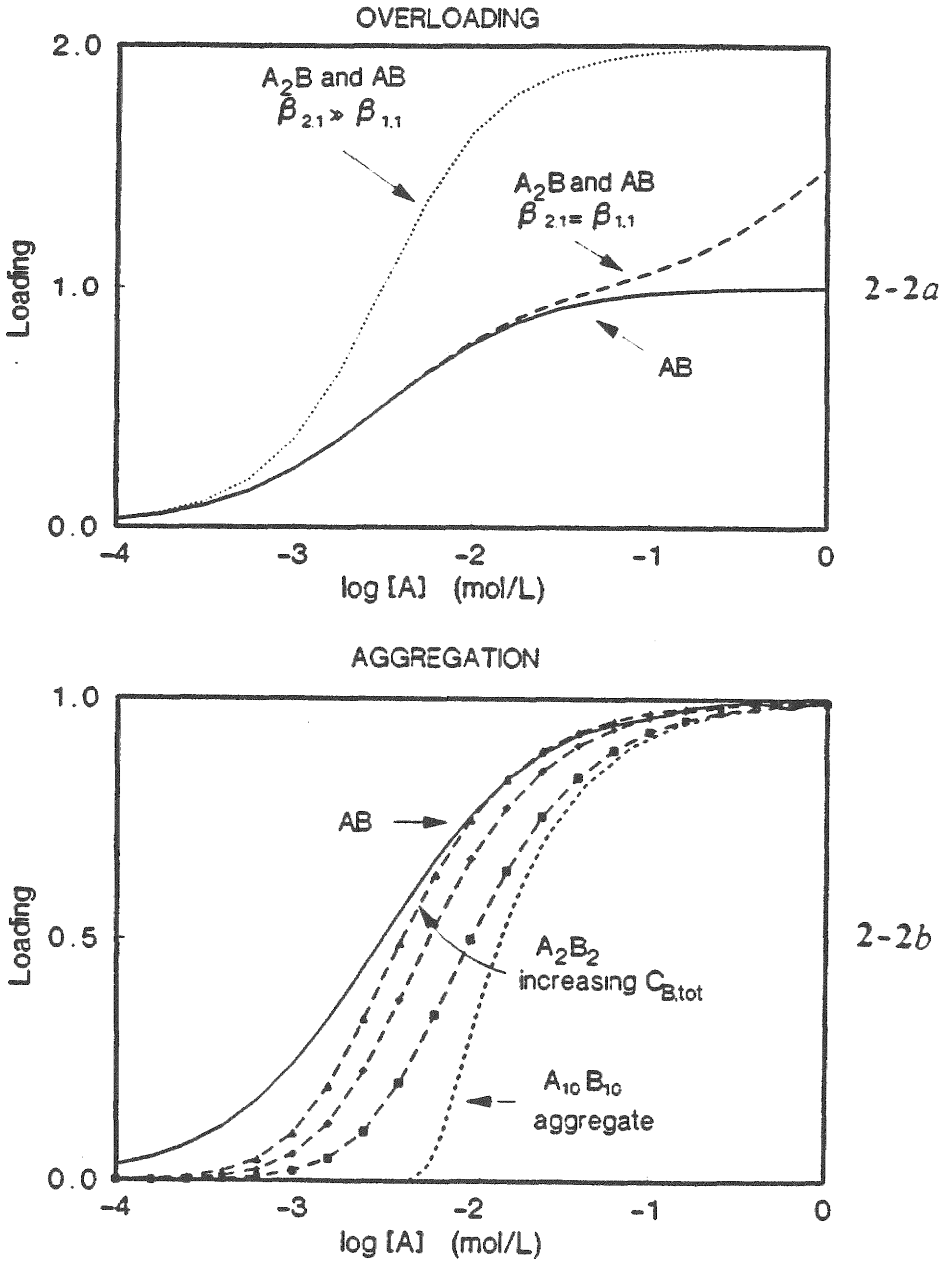
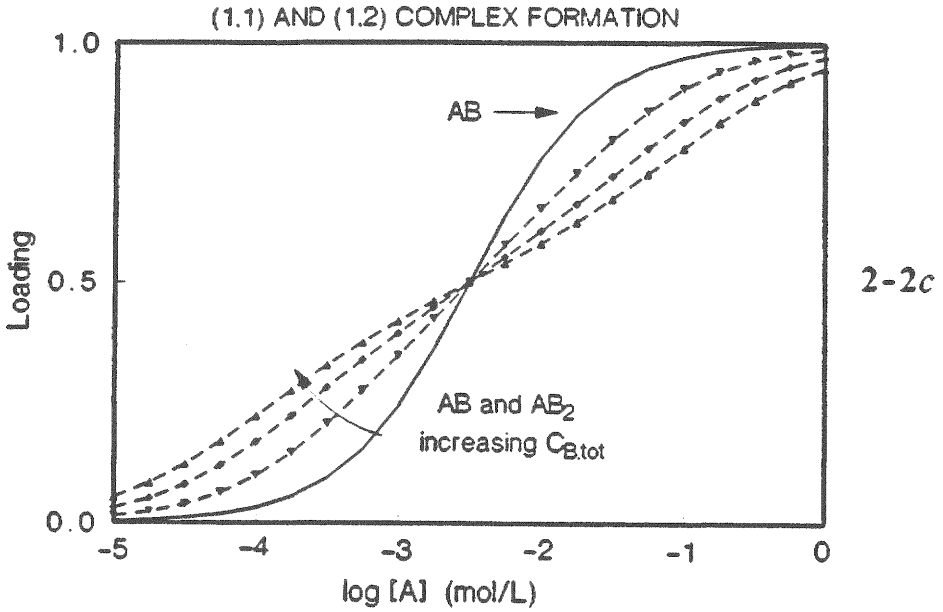


Fig. 2-2. Examples of Loading Curves.

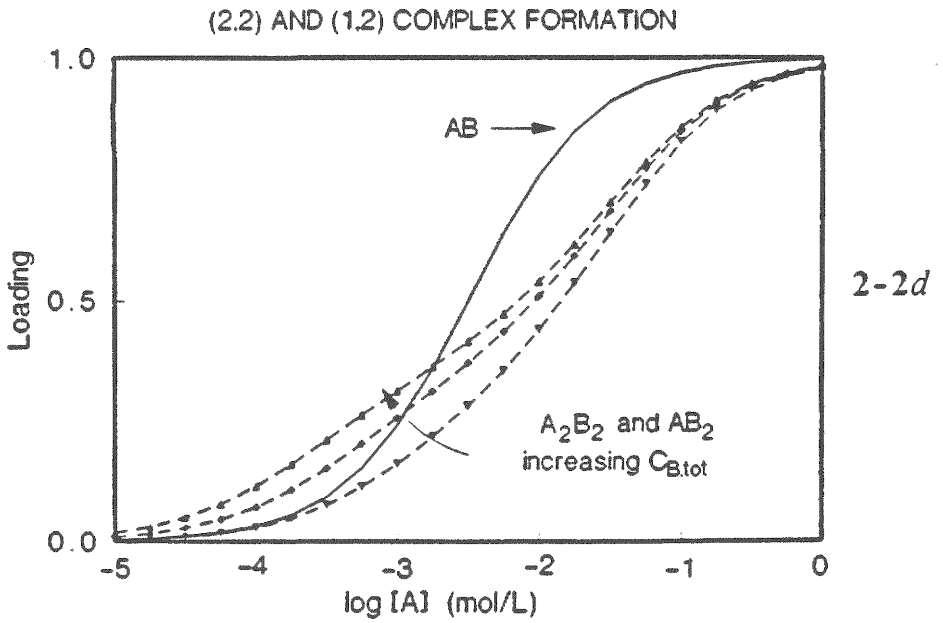
(*a*) Overloading.
- Solid curve, $\log(\beta_{11}) = 2.5$
- Dashed curve, $\log(\beta_{11}) = 2.5$, $\log(\beta_{21}) = 2.5$
- Dotted curve, $\log(\beta_{11}) = 2.5$, $\log(\beta_{21}) = 5.0$

(*b*) Aggregation
- Solid curve, $\log(\beta_{11}) = 2.5$
- Dashed curves, $\log(\beta_{22}) = 5.0$
  - (▲) $C_{B,tot}$ = 0.6 mol/L
  - (◆) $C_{B,tot}$ = 0.3 mol/L
  - (■) $C_{B,tot}$ = 0.1 mol/L

  Note increasing loading with increasing amine concentration.
- Dotted curve, $\log(\beta_{10,10}) = 20$



2-2c



2-2d

Fig. 2-2. Examples of Loading Curves (cont'd).

(*c*) (1,1) and (1,2).
- Solid curve, $\log(\beta_{11}) = 2.5$
- Dashed curves, $\log(\beta_{12}) = 3.0$
  $\log(\beta_{11}) = 2.5$
  (▲) $C_{B,tot}$ = 0.6 mol/L
  (◆) $C_{B,tot}$ = 0.3 mol/L
  (▼) $C_{B,tot}$ = 0.1 mol/L

Curves cross at $Z = 0.5$.

(*d*) (2,2) and (1,2)
- Solid curve, $\log(\beta_{11}) = 2.5$
- Dashed curves, $\log(\beta_{12}) = 3.0$
  $\log(\beta_{22}) = 5.0$
  (▲) $C_{B,tot}$ = 0.6 mol/L
  (◆) $C_{B,tot}$ = 0.3 mol/L
  (▼) $C_{B,tot}$ = 0.1 mol/L

Curves cross at $Z = 1.0$.

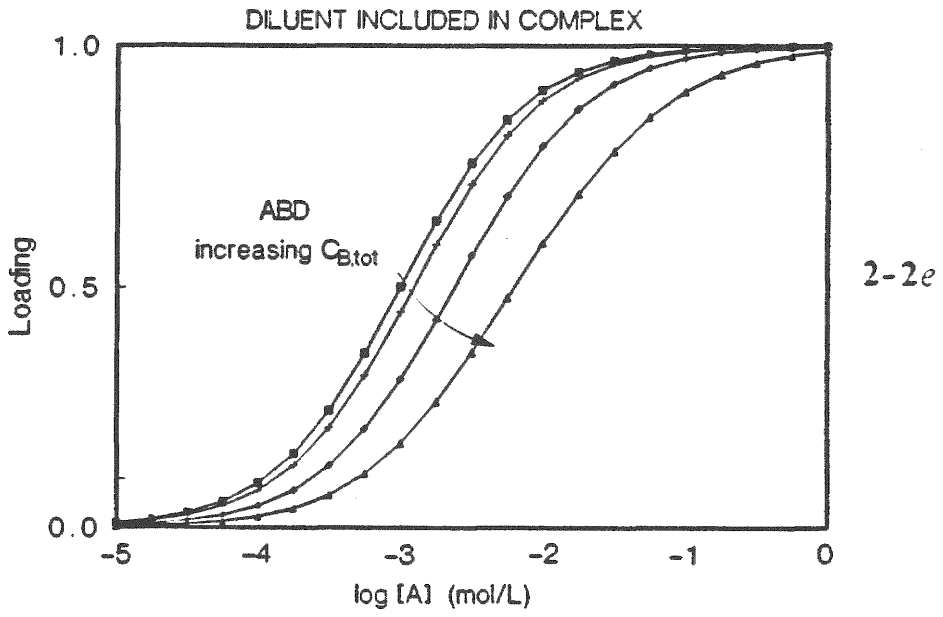


Fig. 2-2. Examples of Loading Curves (cont'd).

(e) Diluent included in complex.
$\log(\beta_{111}) = 2.0$
(▲) $C_{B,tot}$ = 1.6 mol/L
(◆) $C_{B,tot}$ = 1.2 mol/L
(+) $C_{B,tot}$ = 0.6 mol/L
(■) $C_{B,tot}$ = 0.3 mol/L
Note decreasing loading with increasing amine concentration.

$$2A + \overline{B} = \overline{A_2B} \qquad \beta_{21} = \frac{[\overline{A_2B}]}{[A]^2[\overline{B}]} \qquad \text{(Eq. 2-9)}$$

The formation of a (2,1) complex allows for the phenomenon of overloading, i.e., loading greater than unity, indicating multiple acids per amine in the organic phase (see Fig. 2-2*a*, dashed curve). If $\beta_{21} >> \beta_{11}$ the initial slope of the curve is larger than for the (1,1) case (see Fig. 2-2*a*, dotted curve). Loading for this and any other system with only a single amine per complex is independent of initial amine concentration.

In contrast, a (2,2) acid-amine system predicts a strong effect of amine concentration. For a given low aqueous acid activity, a system with multiple amines per complex results in increased loading for increased amine concentration (see Fig. 2-2*b*, dashed curves). Additionally, the initial slope of the curve is steeper than for the (1,1) case.

For (n,n) stoichiometries, as n increases, the steepness of the curve increases (Fig. 2-2*b*, dotted curve). Formation of complexes with large stoichiometries may be interpreted as aggregate formation. Extraction is low until there is a critical concentration, at which the amine and acid abruptly begin to aggregate together, drawing the acid into the organic phase. A critical micelle concentration is an extreme of such behavior.

With a (1,2) complex, the situation becomes more complicated. In Fig. 2-2*c*, the dashed curves illustrates a system with (1,2) and (1,1) complex formation, and in Fig. 2-2*d*, (1,2) and (2,2) complex formation. If the (1,2) complex formation constant

is sufficiently large, there is a plateau at $Z = 0.5$. For $Z < 0.5$, higher amine concentration promotes higher loading. However, for the (1,2) and (1,1) complex system, at $Z > 0.5$ the trend reverses, and the higher amine concentration gives lower loading. For the (1,2) and (2,2) system, the relative positions of the loading curves for different amine concentrations remain the same, and the curves converge at $Z = 1$.

If diluent interactions with the complex are very strong, it may be possible to represent the data by including r diluent, D, molecules specifically into the complex, with a corresponding equilibrium constant of β_{pqr}.

$$pA + q\overline{B} + r\overline{D} = \overline{A_pB_qD_r} \qquad \beta_{pqr} = \frac{[\overline{A_pB_qD_r}]}{[A]^p[\overline{B}]^q[\overline{D}]^r} \qquad \text{(Eq. 2-10)}$$

This is illustrated in Fig. 2-2*e*. Increased amine concentration decreases the diluent concentration, and thus decreases loading, in contrast with the trend for aggregation.

2.2.3 Limitations of the Mass-Action Law Approach

The use of a mass-action law approach to describe these systems does have some limitations. By ignoring "physical", or solvation, interactions between components, the model may be less realistic than models which account for organic phase nonidealities in other ways. Minimizing the error between the extraction data and a hypothetical model may imply that complexes of a specific stoichiometry are formed. Without independent evidence, such as spectroscopic data, the existence of these complexes must be viewed with caution, since they may be artifacts of the nature of the model. Despite the limitations of the mass-action law model, if complexation is strong, chemical modeling can be a useful tool in fitting data and in deepening understanding of the mechanism of extraction.

Another possible shortcoming of the approach taken in this work is the approximation of a constant aqueous-phase activity coefficient over the concentration ranges studied, i.e., aqueous-phase acid activity was assumed to be proportional to the undissociated aqueous-phase acid concentration. The difference between equilibrium constants based upon the use of activity and concentration driving forces (accounting for the "constant" activity coefficient which is absorbed into the equilibrium constant) was tentatively concluded to be minor for dilute concentration ranges (Appendix C). Nonetheless, in some cases there may be some deviation associated with the approximation of a constant aqueous-phase activity coefficient. A detailed evaluation of the effect of activity coefficients is left for future work.

It should be noted that corrections for activity coefficients make no difference in the qualitative evaluation of reaction stoichiometries, because the important parameter is the number of molecules of acid per molecule of amine (i.e. loading), which is based on concentration and not activity. Additionally, the results obtained by the mass-action law based on aqueous acid concentration fit well quantitatively with the actual experimental data, and therefore are useful in process modeling. Thus, the conclusions regarding molecular interactions and process implications, which are the emphasis of this work, are not affected by the use of concentration rather than activity.

2.3 Physical Extraction by the Diluent

Physical distribution can be modeled phenomenologically by the expression (Kertes and King, 1986):

$$C_{A,org} = P[A] + 2P^2K_d[A]^2 \qquad \text{(Eq. 2-11)}$$

where K_d is the dimerization constant of the acid in the organic phase, and P is the partition coefficient for acid monomer -- the concentration of monomer in the solvent phase divided by the concentration of undissociated aqueous acid. It is convenient to define an adjusted parameter K_d^* by $K_d^* = 2P^2K_d$. To determine K_d^* and P, a linear least-squares analysis of $C_{A,org}/[A]$ vs. [A] was performed using the results from experiments which examined extraction of acid by the diluent alone. The intercept of the line is P and the slope of the line is K_d^*. A summary of parameters for physical extraction calculated for several acid-solvent systems used in this study is given in Table 2-1. A more extensive discussion is given by Kertes and King (1986).

A correction was made for "physical" extraction by the diluent by subtracting out the amount of acid extracted by the diluent alone (calculated from the aqueous acid concentration and the P and K_d parameters) multiplied by the volume percent diluent in the solvent mixture. The use of volume percent rather than weight or mole percent is somewhat arbitrary, but the net difference among these methods is not great. Implicit in this type of correction procedure is that the organic-phase acid concentration in the acid-amine-diluent system is the sum of two binary interactions, acid-diluent and acid-amine.

The amount of acid extracted by most diluents is negligible compared to the amount extracted by amine-diluent solvent. However, the amount of acid extracted into ketone and alcohol diluents in some cases is significant compared to extraction by the amine-diluent mixture. A ternary interaction between the "free" acid in the organic phase and the acid-amine complex may be a non-negligible effect in these

Table 2-1. Physical Extraction Coefficients for Carboxylic Acids in Organic Solvents (25 °C)

$$C_{A,org} = P[A] + K_d^*[A]^2$$

Acid	Solvent	P	K_d^*
Acetic	Nitrobenzene	0.524	-
	15% (v/v) Chloroform in n-Heptane	0.0075	0.007
Lactic	*m*-Cresol	0.314	?
	MIBK	0.110	0.014
	Chloroform	0.010[a]	?
Malonic	MIBK	0.166	-
Succinic	1-Octanol	0.264	-
	MIBK	0.192	-
	Methylene Chloride	0.026	-
	Nitrobenzene	-	-
	Chloroform	-	-
	Heptane	-	-
Maleic	MIBK	0.354	-
	Chloroform	0.042	-
Fumaric	MIBK	2.2[b]	-
	Chloroform	-	-

[a] Holten, 1971
[b] Starr, 1988

cases, but it is difficult to quantify such an interaction. Fortunately, the results achieved with the binary acid-diluent interactions were found to be satisfactory for the purposes of this work.

2.4 Systems Following Simple Stoichiometric Complex Formation

The equilibrium behavior of systems at low amine concentrations in active diluents can often be modeled by sets of complexes with very simple stoichiometries. This "ideal" behavior may be interpreted as a result of the ability of the diluent to solvate the complex; i.e., the diluent prevents the complex from interacting strongly with other complexes so that the activity coefficient of the complex is relatively constant with respect to composition.

Experimental results and model predictions are plotted as the loading of the amine, corrected for extraction by the diluent alone, versus the logarithm of the undissociated acid concentration in the aqueous phase. Details of the numerical methods and computer results are given in Appendix B. The solid curves show the predicted results of the "best" model, i.e., the simplest model which gave low error between the experimental and predicted results (see Table B-1). If the error was not reduced significantly by inclusion of a particular complex, that complex was not considered to be part of the "best" model. An additional consideration was that the model should represent physically reasonable complex formation. Stress was placed on complexes whose existence has been inferred from spectroscopic experiments (see Chapter 4). Values of the equilibrium constants for the postulated complexes are shown in the figure captions.

2.4.1 Monocarboxylic Acids: Acetic and Lactic

Fig. 2-3*a* shows results for the extraction of acetic acid by Alamine 336 in a mixed diluent, in which chloroform comprised 15% of the total solvent volume, and the remaining volume was made up with *n*-heptane. Loading is independent of initial amine concentration, and overloading is very apparent. The extraction of acetic acid in nitrobenzene (Fig. 2-3*b*) is qualitatively similar, but the association constants in the polar nitrobenzene are much larger than in the relatively non-interacting heptane-chloroform mixture.

Lactic acid, a hydroxymonocarboxylic acid, behaves similarly to acetic acid in its ability to overload the amine. Figs. 2-4 *a* and *b* show the results of the extraction of lactic acid by Alamine 336 in chloroform and in MIBK, respectively. The data indicate significant formation of (2,1) and (1,1) lactic acid-amine complexes in chloroform. For lactic acid in MIBK, as for acetic acid in chloroform-heptane, a set of complexes with 1, 2, and 3 acids per amine must be hypothesized to account for the large amount of overloading.

2.4.2 Aliphatic Dicarboxylic Acids: Succinic and Malonic

Figs. 2-5 *a*, *b*, *c*, and *d* show the results for the extraction of succinic acid by low concentrations of Alamine 336 in chloroform, methylene chloride, nitrobenzene, and MIBK, respectively. The chloroform, methylene chloride, and nitrobenzene systems show much higher values of β_{11} than does the MIBK system, indicating that these solvents have greater abilities to solvate the complex than MIBK. (1,1) complex formation and very minor, if any, (2,1) complex formation is consistent with the chloroform and methylene chloride data, whereas significant (2,1) as well as (1,1)

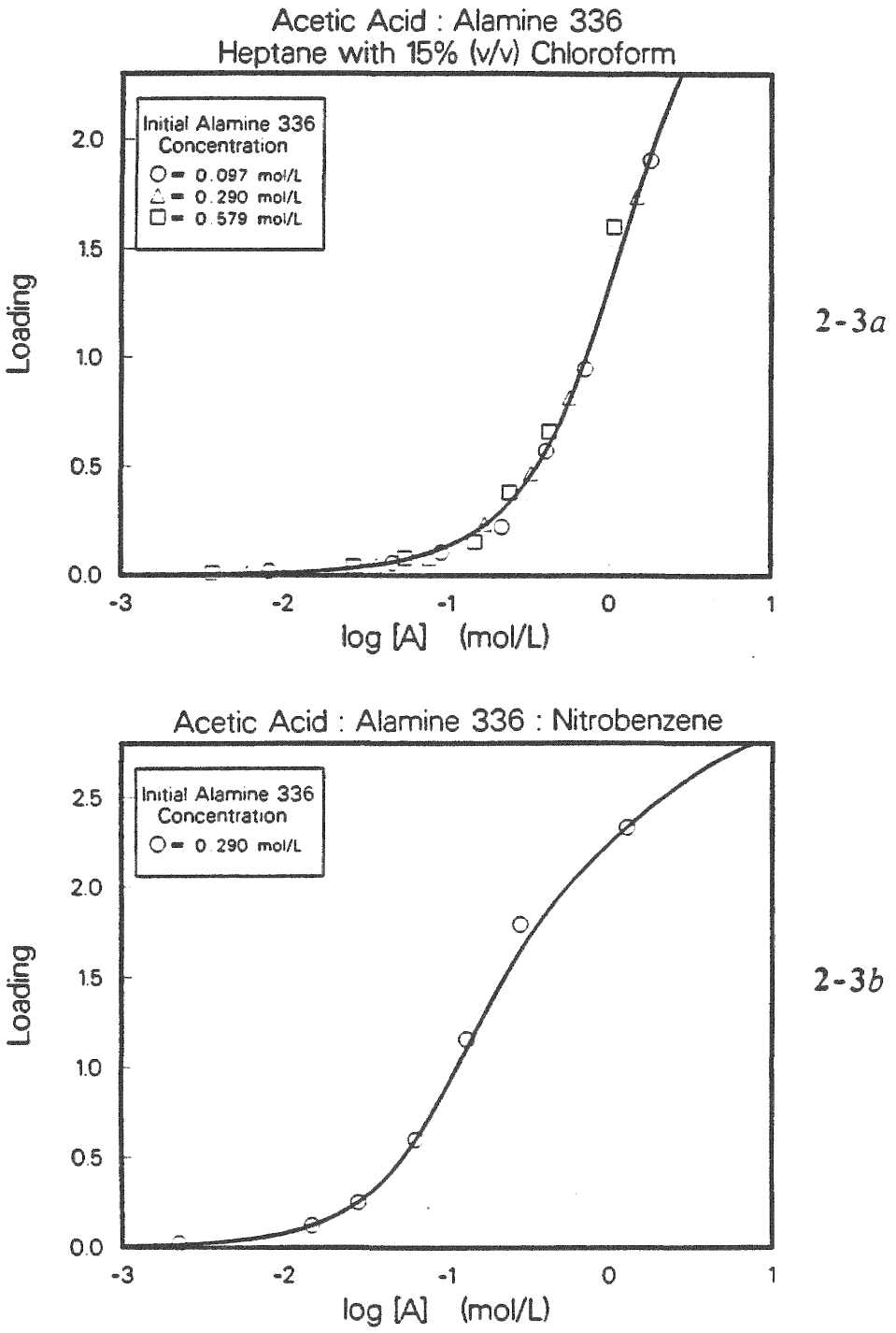


Fig. 2-3. Loading Curves for the Extraction of Acetic Acid by Alamine 336 in Various Diluents.

Diluent: (*a*) 15% (v/v) Chloroform in Heptane; vol% chloroform is vol% of total solvent volume; $\log(\beta_{11}) = 0.11$, $\log(\beta_{21}) = 0.02$, $\log(\beta_{31}) = -0.21$
(*b*) Nitrobenzene; $\log(\beta_{11}) = 0.86$, $\log(\beta_{21}) = 1.82$, $\log(\beta_{31}) = 1.55$

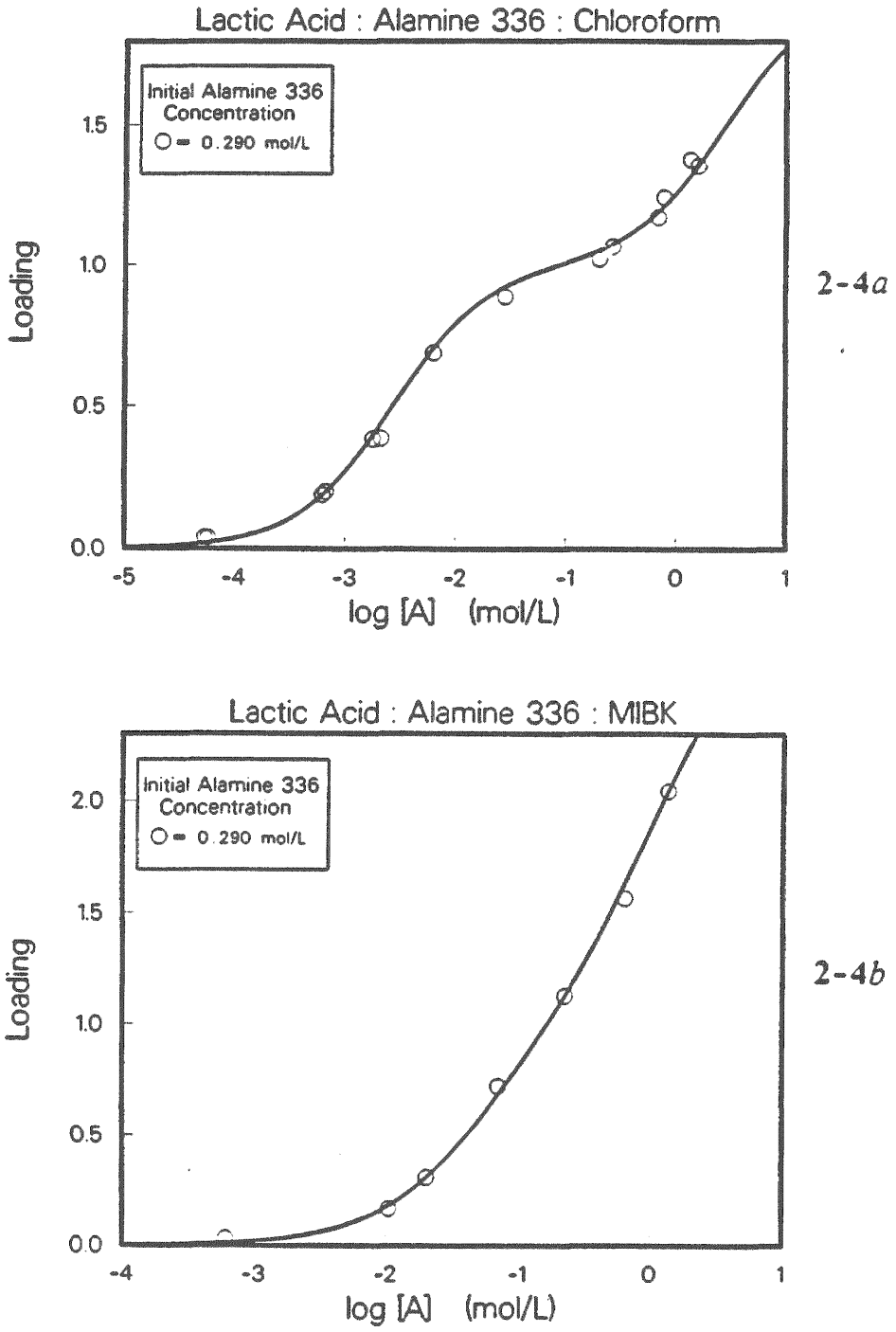


Fig. 2-4. Loading Curves for the Extraction of Lactic Acid by Alamine 336 in Various Diluents.

Diluent: (*a*) Chloroform; $\log(\beta_{11}) = 2.57$, $\log(\beta_{21}) = 2.12$
(*b*) MIBK; $\log(\beta_{11}) = 1.31$, $\log(\beta_{21}) = 1.52$, $\log(\beta_{31}) = 1.17$

complex formation is required to match the MIBK and nitrobenzene data. Overloading is most apparent for MIBK. The magnitudes of the (1,1) equilibrium constants are comparable to those for lactic acid in the same diluents. But the (2,1) complex formation is quite different, with succinic acid showing virtually no formation of a (2,1) complex in chloroform, but showing greater formation of a (2,1) complex in MIBK compared to lactic acid.

Another interesting attribute of these curves is that the loading is independent of the initial amine concentration. This indicates that any complexes formed have only a single amine molecule per complex, as multi-amine complexes would necessarily produce a dependence of loading on amine concentration. The dibasic character of the acid thus does not seem to engender complexes with multiple amines in these active-diluent systems, i.e., there is no significant formation of a (1,2) complex.

1-Octanol produces different behavior than the other diluents. In the extraction of succinic acid by Alamine 336 in octanol, an unusual, pseudo-third phase formed between the aqueous and organic phase. This was not a thermodynamically stable third phase as is observed with inert diluents, but a surface-area-dependent phenomenon known as a coacervate. This phase could was not broken by centrifugation at 3000 rpm. When this cloudy, bubbly-looking phase was transferred by pipet into a flask, it coalesced into a clear, normal organic phase. The composition of the coacervate did not appear to be significantly different from that of the bulk organic phase. However, coacervate formation may have affected acid concentration measurements. There was an unusually large experimental error, on the order of 10% or more, in the acid material balance for this system.

Fig. 2-5*e* shows the results for succinic acid extraction in 0.15 and 0.29 mol/L

Alamine 336 in octanol. The loading was calculated using the experimentally-determined organic-phase acid concentration, corrected for the appreciable extraction by the octanol alone. Loading increases with increasing amine concentration, and the loading curve has an unusual shape, flat at low loadings, and no obvious plateau at a loading of unity. None of the stoichiometries which were tested produced a satisfactory fit. Nonetheless, it is evident that the model must include complexes with multiple amines to achieve even moderate fit with the data. The model prediction for a (1,2) and (2,2) stoichiometry is shown.

In Fig. 2-5*f*, the results for the extraction of succinic acid by a mixed solvent of 40% (v/v) chloroform, 45% (v/v) 1-octanol, and 15% (v/v) Alamine 336 (0.29 mol/L) are presented. Three complexes, (1,2), (2,2), and (2,1), were fitted to the data, which may give a large uncertainty to the stoichiometry and equilibrium constants, as the amount of data was quite limited. Despite this, it can be seen that the loading curve for the mixed chloroform-octanol diluent system lies between the chloroform system and the octanol system. A direct comparison of the three systems is shown in Chapter 3, Fig. 3-3*b*.

Malonic acid extracted by Alamine 336 in MIBK diluent (Fig. 2-6) behaves similarly to succinic acid in the MIBK system; loading is independent of initial amine concentration, and formation of strong (2,1) and (1,1) complexes is necessary to fit the data. The high solubility of malonic acid in water, compared to that of succinic acid, allows examination of the high aqueous acid concentration region. Consequently, the extractant overloading region is very apparent. Malonic acid has a much higher value of pK_{A1} than does succinic acid (2.85 for malonic versus 4.21 for succinic), which produces higher equilibrium constants and a visible plateau at $Z = 1$.

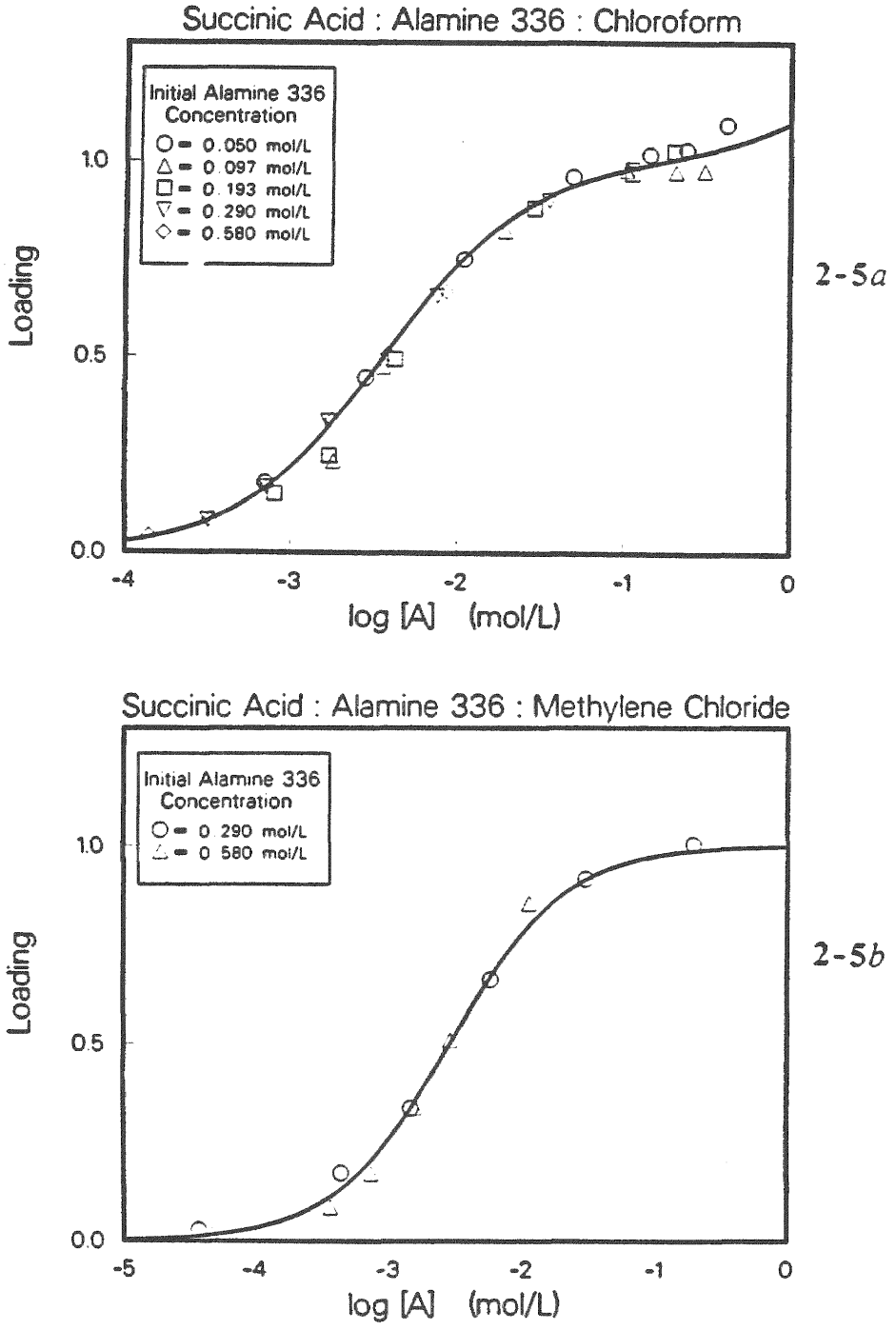
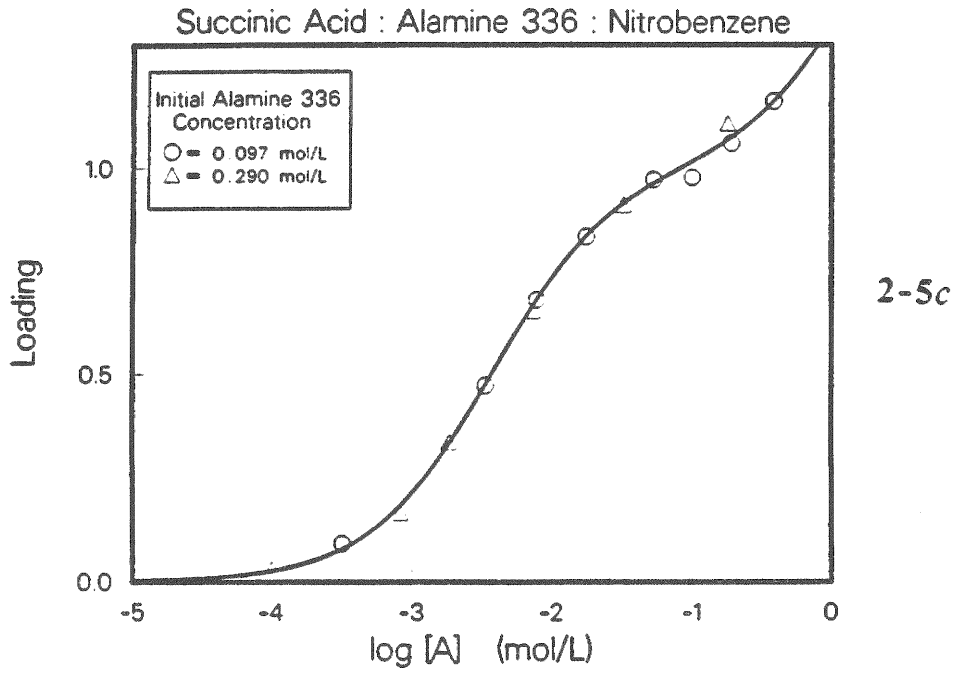


Fig. 2-5. Loading Curves for the Extraction of Succinic Acid by Alamine 336 in Various Diluents.

Diluent: (*a*) Chloroform; $\log(\beta_{11}) = 2.44$, $\log(\beta_{21}) = 1.49$
(*b*) Methylene Chloride; $\log(\beta_{11}) = 2.54$



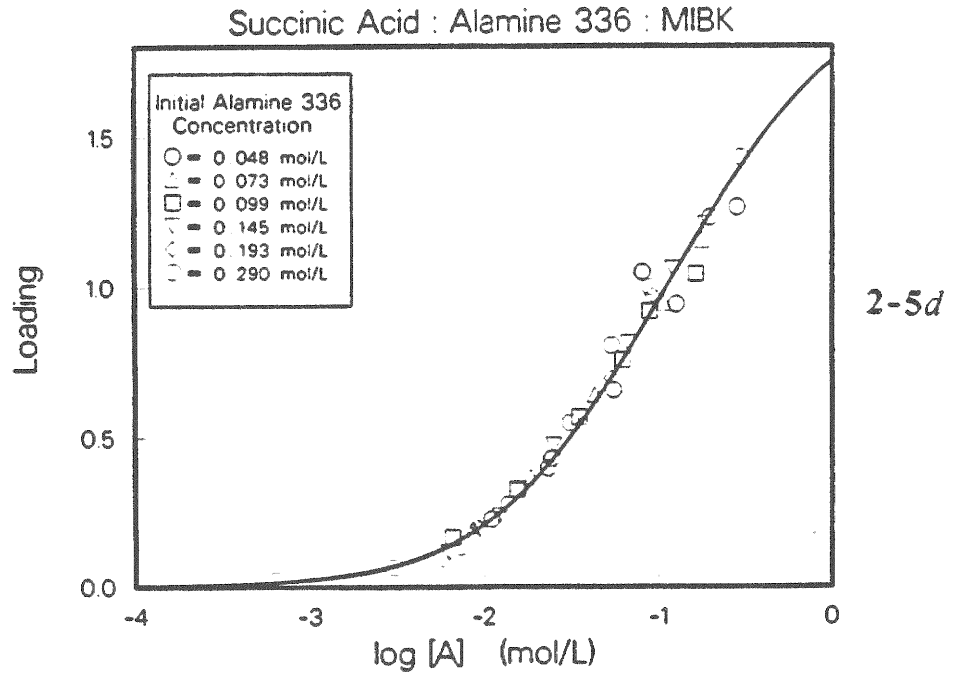


Fig. 2-5. Loading Curves for the Extraction of Succinic Acid by Alamine 336 in Various Diluents (cont'd).

Diluent: (*c*) Nitrobenzene; $\log(\beta_{11}) = 2.43$, $\log(\beta_{21}) = 2.16$
(*d*) MIBK; $\log(\beta_{11}) = 1.39$, $\log(\beta_{21}) = 1.91$

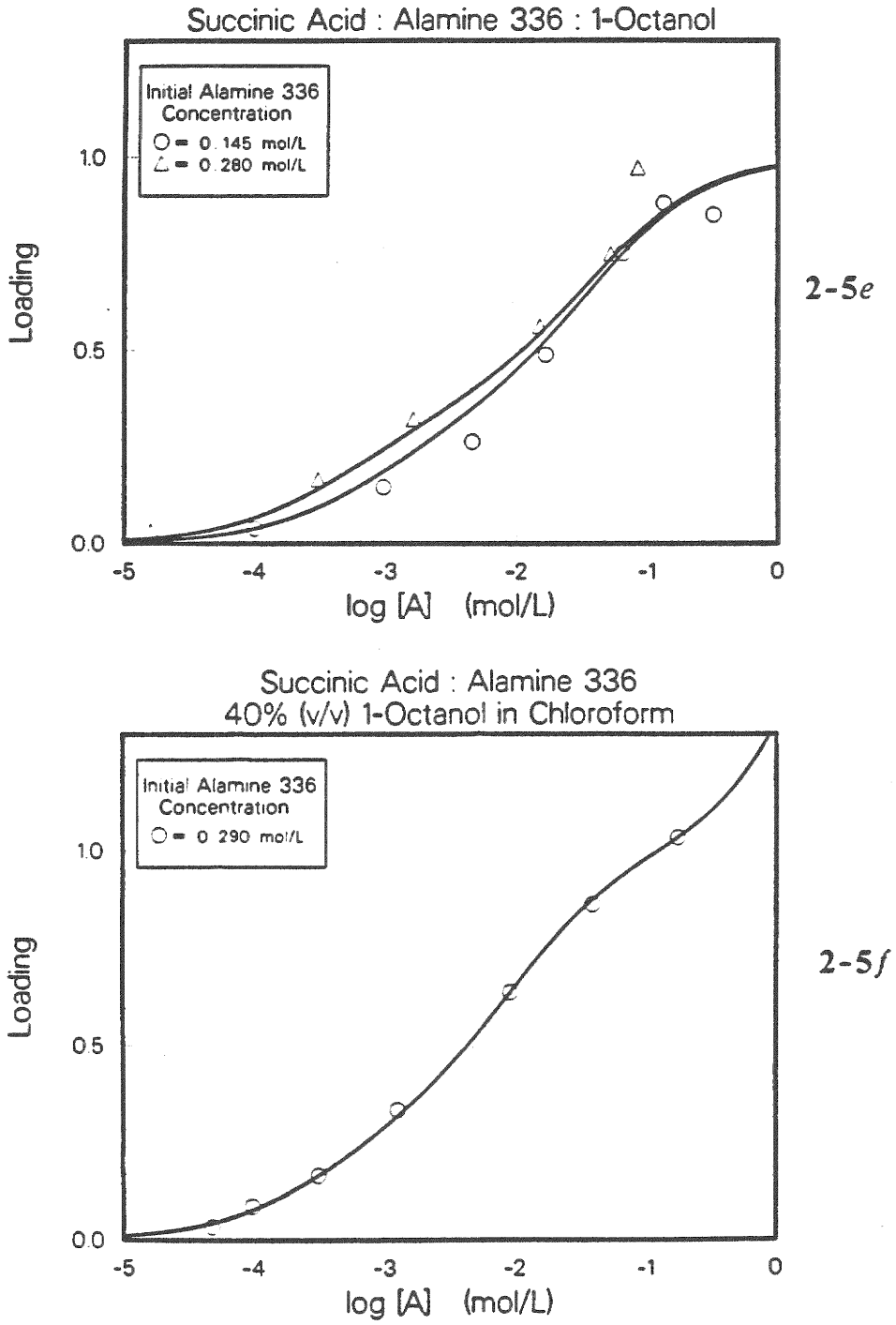


Fig. 2-5. Loading Curves for the Extraction of Succinic Acid by Alamine 336 in Various Diluents (cont'd).

Diluent: (*e*) 1-Octanol; $\log(\beta_{22}) = 4.91$, $\log(\beta_{12}) = 3.50$
(*f*) 40% (v/v) Chloroform, 45% (v/v) 1-Octanol;
$\log(\beta_{22}) = 5.59$, $\log(\beta_{12}) = 3.57$, $\log(\beta_{21}) = 2.29$

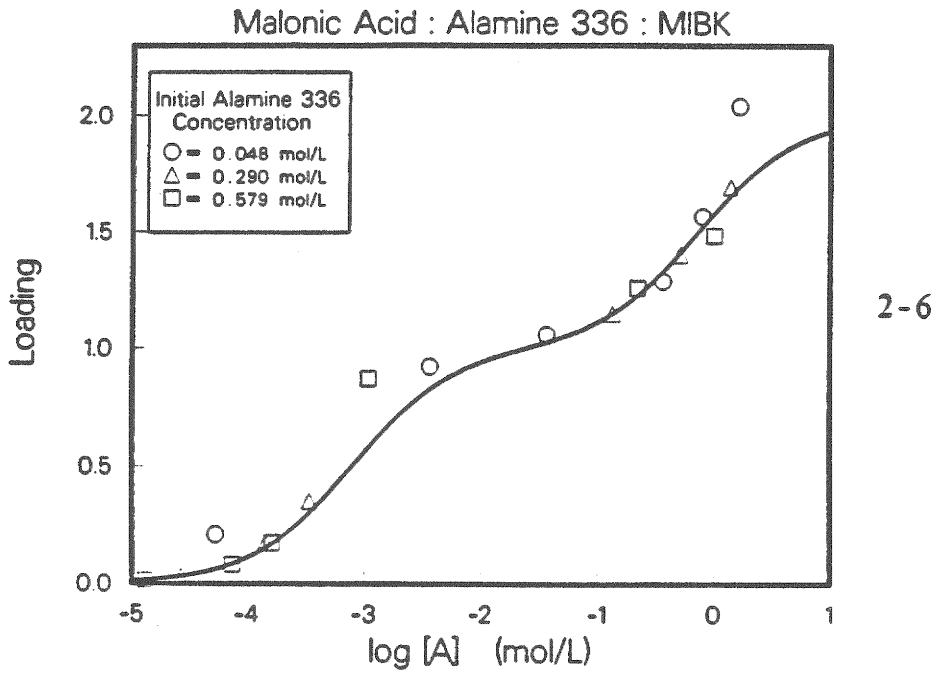


Fig. 2-6. Loading Curve for the Extraction of Malonic Acid by Alamine 336 in MIBK.

$\log(\beta_{11}) = 3.10$, $\log(\beta_{21}) = 3.24$

2.4.3 Unsaturated Dicarboxylic Acids: Maleic and Fumaric

Figs. 2-7*a* and *b* show the results for the extraction of maleic acid by Alamine 336 in chloroform and MIBK. Maleic acid is extracted very readily by Alamine 336 in both diluents, as would be expected on the basis of its high acidity (pK_{A1} = 1.91). Overloading occurs in both diluents at very high acid concentrations. There is a long plateau at Z = 1, which again may result from the low pK_A of the maleic acid. Slightly higher extraction at low acid concentrations occurred in chloroform, while MIBK allowed for slightly more overloading. Good fits were obtained with (1,1) and (2,1) complexes.

Fig. 2-8*a* shows results for the extraction of fumaric acid by Alamine 336 in chloroform. Fumaric acid exhibits quite different behavior from maleic acid. In chloroform, clear evidence of (1,2) and (2,2) complex formation is seen through the increase in loading with increasing amine concentration, and the convergence of the curves as loading approaches unity. Unfortunately, the limited solubility of fumaric acid in water at 25 °C prevented analysis of the overloading region.

Results obtained by Starr (1988), shown in Fig. 2-8*b*, indicate that fumaric acid extracted by Alamine 336 in MIBK exhibits significant overloading. The dependence of loading on the amine concentration and the convergence of the curves at Z = 1 are evidence of (1,2) and (2,2) complex formation. Inclusion of (1,1) stoichiometry reduces the error, but not significantly enough to establish the existence of a (1,1) complex without other evidence. The possible presence of significant quantities of four different complexes makes rational interpretation of the data troublesome, because, given a sufficient number of adjustable parameters, any set of data can be modeled. However, at low concentrations of amine (< 0.1 mol/L), where (1,2) and (2,2) complex

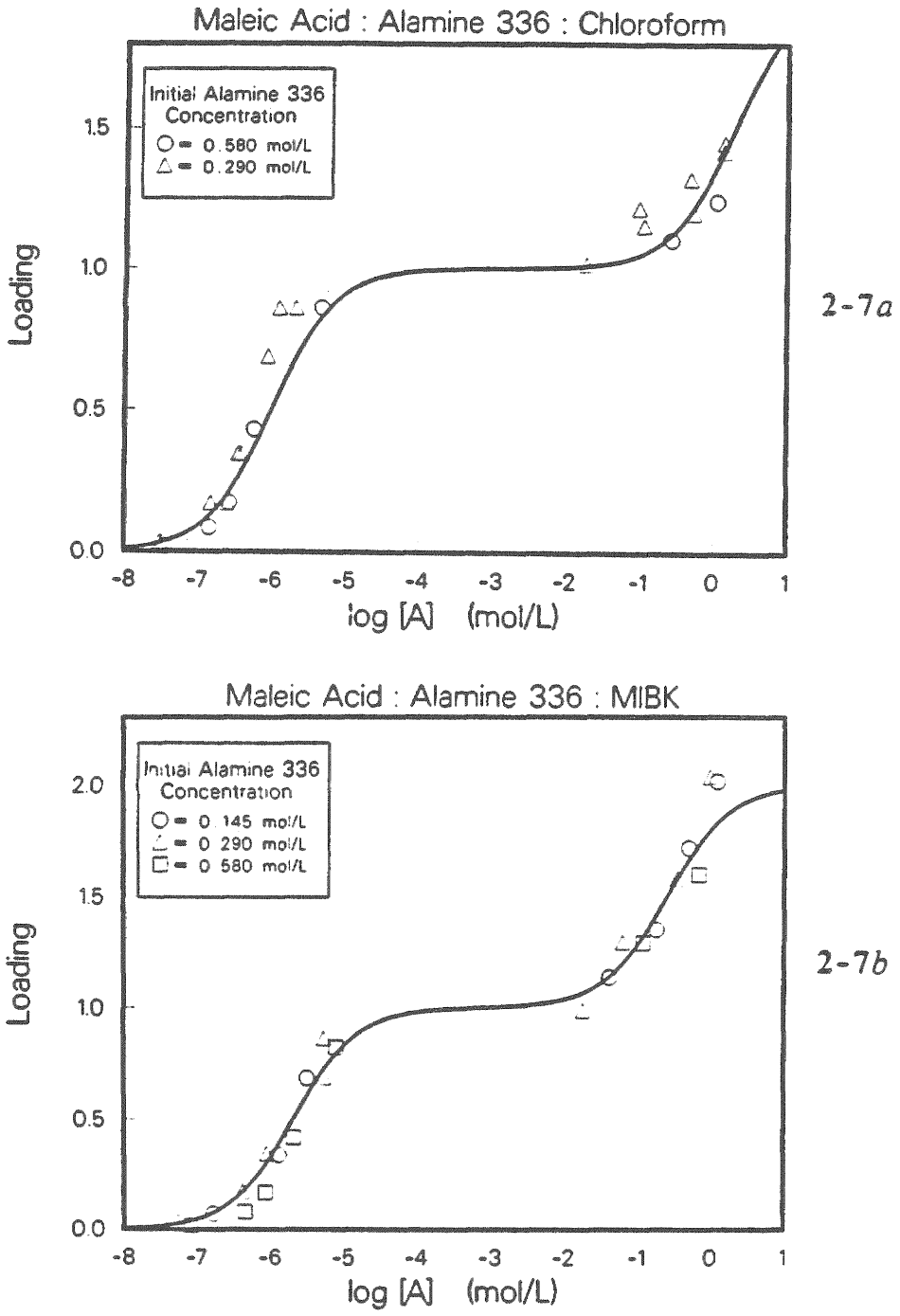


Fig. 2-7. Loading Curves for the Extraction of Maleic Acid by Alamine 336 in Various Diluents.

Diluent: (*a*) Chloroform; $\log(\beta_{11}) = 6.00$, $\log(\beta_{21}) = 5.72$
(*b*) MIBK; $\log(\beta_{11}) = 5.69$, $\log(\beta_{21}) = 6.29$. Note: The 0.58 mol/L data for MIBK are shown but were not used as input into the computer minimization program. There was noticeable deviation of the 0.58 mol/L data from the low amine concentration data, because of the lowered diluent concentration for the MIBK data.

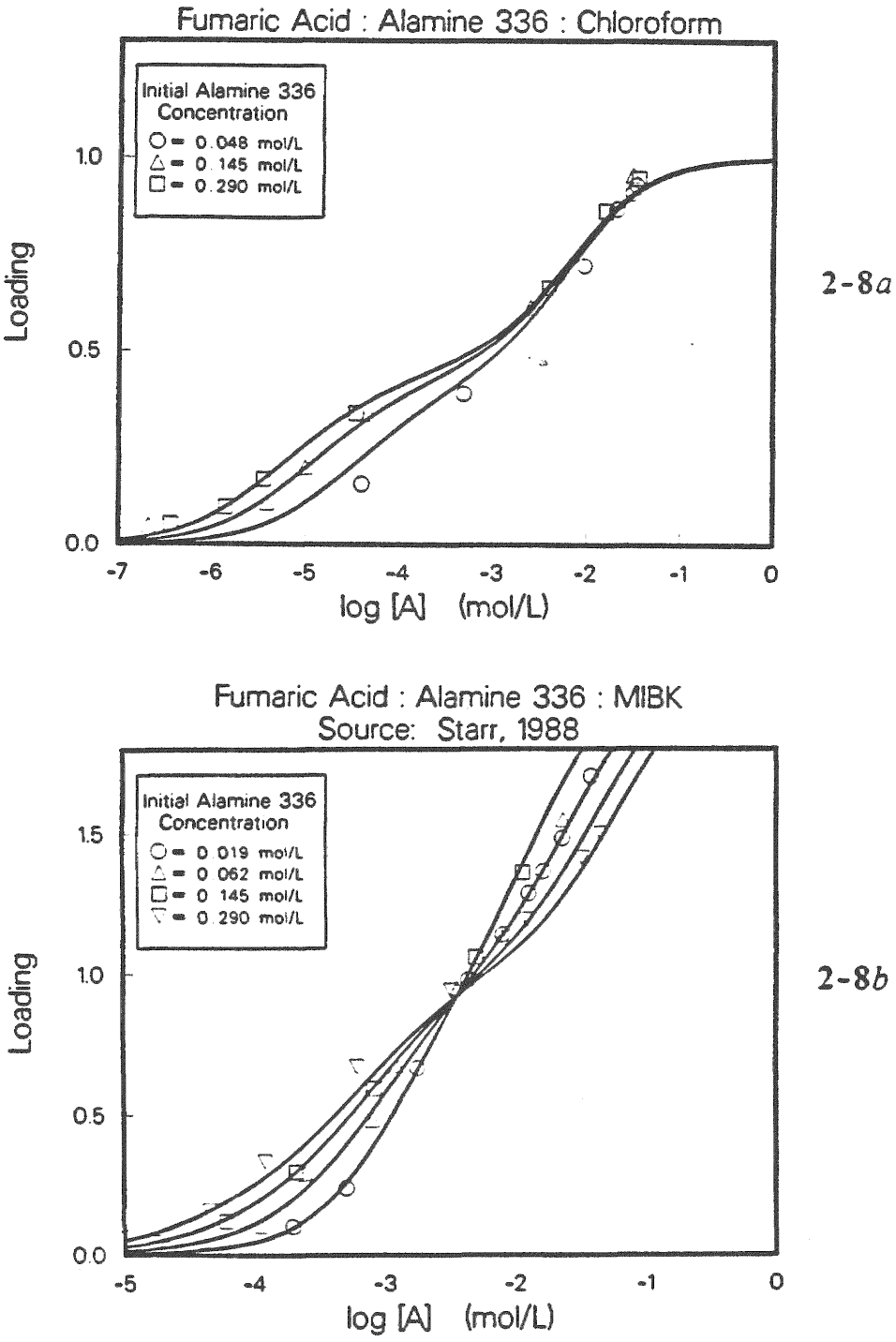


Fig. 2-8. Loading Curves for the Extraction of Fumaric Acid by Alamine 336 in Various Diluents.

Diluent: (*a*) Chloroform; $\log(\beta_{22}) = 7.74$, $\log(\beta_{12}) = 5.56$
(*b*) MIBK; $\log(\beta_{22}) = 7.52$, $\log(\beta_{12}) = 4.34$, $\log(\beta_{21}) = 4.82$
(Data for the MIBK diluent system were provided by Starr, 1988.)

formation would be expected to be low, there is very little effect of the concentration of amine on the experimental loadings. If the data for only 0.02 and 0.064 mol/L Alamine 336 are modeled, a good fit is obtained with only (2,1) and (1,1) complex formation (Starr, 1988). It appears qualitatively that the relative extent of multiple amine complex formation is lower in MIBK than in chloroform.

2.5 Systems Not Following Simple Stoichiometries

If the solvent is a poor solvating medium for the species formed, the system becomes highly non-ideal and difficult to describe by simple law-of-mass-action modeling. Data which fit complicated stoichiometries with large stoichiometric constants may indicate aggregate formation, where the polar complexes tend to cluster together, away from the low-polarity bulk solvent. A solvent system which contains an inert diluent, such as heptane, tends to show highly non-ideal behavior. Similarly, a system with a high amine concentration also behaves non-ideally, because the aliphatic amine by itself is a relatively poor solvating medium for the complexes. In an extreme case, the polar acid-amine complexes may form a separate phase or a precipitate. Such third-phase formation may be viewed as an extreme case of aggregation.

2.5.1 Inert Diluent

Results for the extraction of succinic acid by Alamine 336 in *n*-heptane show highly non-ideal behavior. In this system there is formation of a very viscous, white third phase between the bulk organic phase and the aqueous phase. Organic-phase analysis revealed that the third phase contains the majority of the extracted acid, and

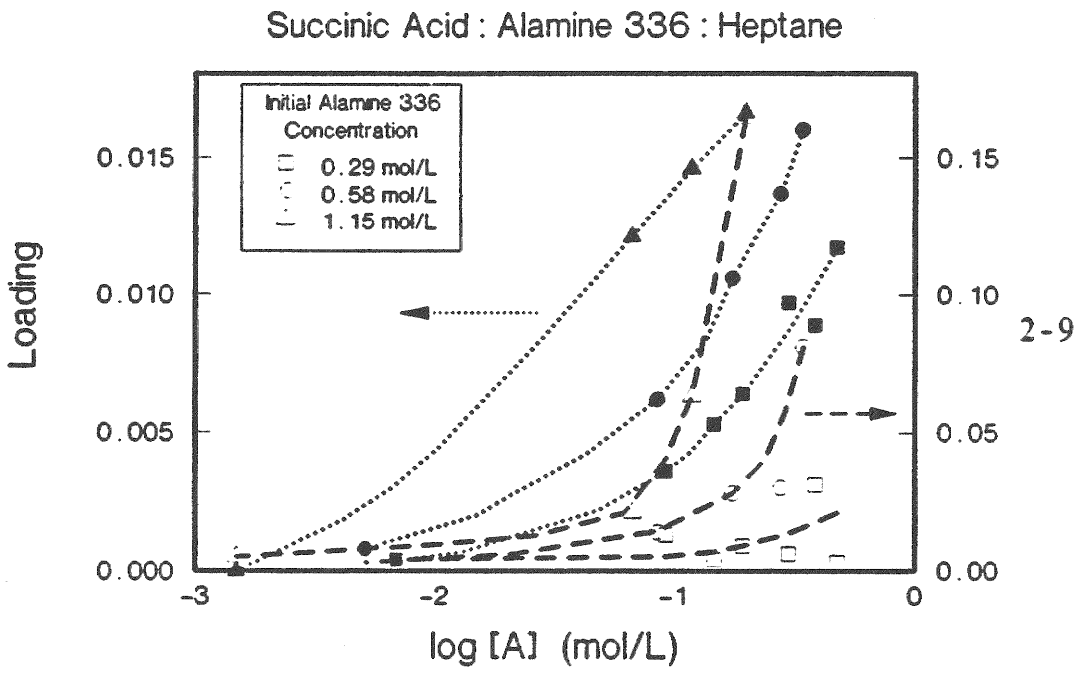


Fig. 2-9. Loading Curve for the Extraction of Succinic Acid by Alamine 336 in Heptane.

Filled symbols/dotted curves correspond the bulk (top) organic phase. Open symbols/dashed curves correspond to second (middle) organic phase. Note the different scales for the "loading" in the bulk (top) organic phase versus the "total loading" for both organic phases. Data were not fit because of high non-ideality.

the bulk solvent phase contains very little acid. Fig. 2-9 shows (1) the total acid in both organic phases divided by the total amine concentration and (2) the concentration of acid in the bulk (top) organic phase divided by the total amine concentration. Total distribution of acid into the organic phase was very low. The loading increased with increasing amine concentration throughout the entire amine concentration range. Because of the complications of third-phase formation, no modeling analysis was made of this system.

2.5.2 High Amine Concentration

In contrast to the inert diluent system, at high amine concentrations the active diluent systems showed that increasing the amine concentration decreases the loading of the organic phase. Figs. 2-10 *a* and *b* and 2-11 show data for the extraction of succinic acid by Alamine 336 in chloroform and in MIBK and malonic acid by Alamine 336 in MIBK over the full range of amine concentrations. At 100% amine, a third phase was formed, and loading is shown as the total moles of acid in both organic phases divided by the total moles of amine. 100% Alamine 336 corresponds to a concentration of 1.98 mol/L. All of the systems began to show signs of third-phase formation at high amine concentrations around 1.16 to 1.54 mol/L. For amine concentrations less than 0.29 to 0.58 mol/L, increasing amine concentration has little effect upon loading, but as the amine concentration is increased further, loading decreases.

The third phase had different appearances at different amine and acid concentrations. At lower acid concentrations, the "phase" was actually a nebulous, whitish gel, and not quite a separate, stable phase. But as acid concentration increased, the gel coalesced into a clear, viscous, stable phase, which could be

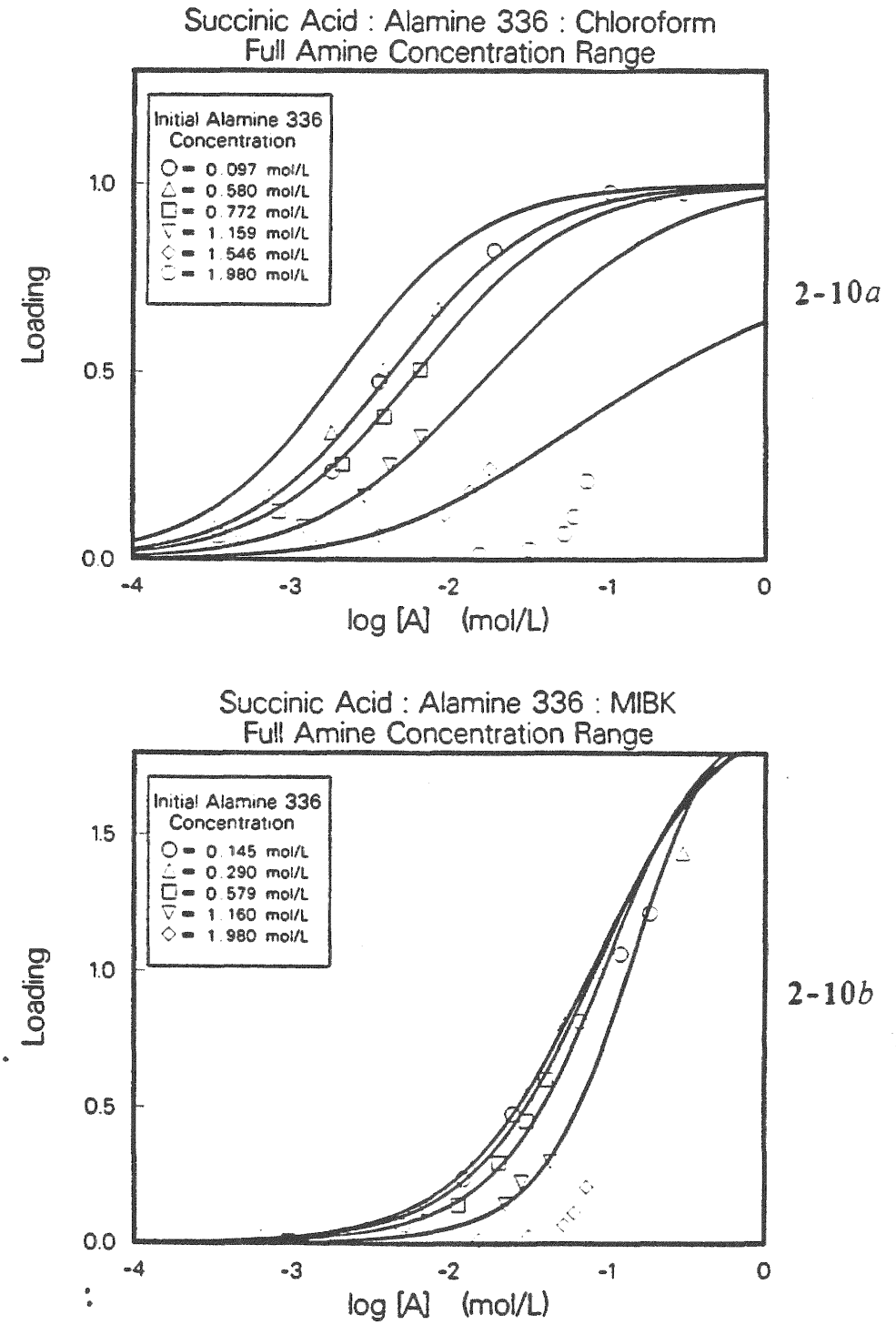


Fig. 2-10. Loading Curve for the Extraction of Succinic Acid by Alamine 336 in Various Diluents over the Full Amine Concentration Range.

Diluent: (*a*) Chloroform; $\log(\beta_{112}) = 0.54$
(*b*) MIBK; $\log(\beta_{211}) = 1.34$; $\log(\beta_{112}) = -0.35$
See comments for Fig. 2-11.

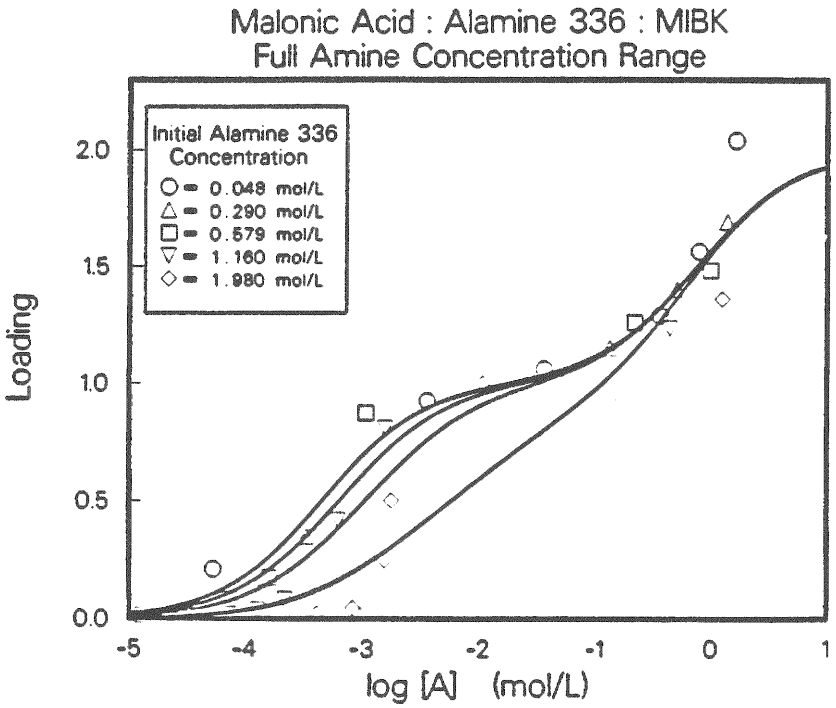


Fig. 2-11. Loading Curve for the Extraction of Malonic Acid by Alamine 336 in MIBK Over the Full Amine Concentration Range.

$\log(\beta_{112}) = 1.56$; $\log(\beta_{212}) = 1.68$

Note: For Figs. 2-10 and 2-11, the 1.98 mol/L (100%) Alamine 336 data are shown, but were not entered into the fitting program, because complexation with no diluent is not taken into account by the model.

All systems showed third-phase formation at 100% Alamine 336. Slight cloudiness in the organic phase, possibly a sign of the beginnings of third-phase formation, was seen for systems with MIBK diluent at 1.16 mol/L Alamine 336, and for the chloroform diluent system at 1.546 mol/L Alamine 336.

removed and analyzed. At higher acid concentrations, more third-phase formation was seen. For malonic acid at initial concentrations > 2.0 mol/L in 100% Alamine 336, the "third" phase volume had increased to be the entire organic phase volume, that is, the "normal" organic phase was not present. Details of the compositions of the third phases for the extraction of malonic acid and succinic acids by 100% Alamine 336 are given in Appendix A.

This behavior can be explained qualitatively by considering interactions between the diluent and the complex. For the active diluents, increasing the amine concentration entails decreasing the diluent concentration, and thus decreasing ability of the solvent phase to solvate the complex. Heptane has less ability than the amine itself to solvate polar species, and therefore loading and distribution increase as amine concentration increases over the full amine concentration range. The sharpness of the rise of the loading curves increases as amine concentration increases, becoming very abrupt for 100% amine systems. This suggests increasing aggregation as the solvent system becomes a less effective solvating agent for polar species.

In Figs. 2-10 and 2-11, the equilibria have been modeled by formation of $A_pB_qD_r$ complexes, which specifically include the diluent in the complex composition. At the higher amine concentrations, the slopes of the experimental loading curves increase, indicating aggregate formation, which has not been accounted for by the simple model presented. The simple acid-amine-diluent complexes shown overpredict the effect of increasing amine concentration at low amine concentrations. And, the model of course does not account for acid-base complex solvated by the amine itself or by non-stoichiometric assemblages of diluent molecules. Data for systems with no diluent present were not included in the fitting procedure; they are shown to illustrate the aggregation behavior. To describe this highly non-ideal behavior by mass-action-law

modeling would involve very large stoichiometric complexes, inclusion of which is probably not justified by the amount of data available.

2.5.3 Active-Inert Diluent Mixture

Another way of examining the diluent effect is to dissolve the extractant and active diluent into an inert diluent. Fig. 2-12*a* shows the results for succinic acid extracted by 0.29 mol/L Alamine 336 in varying ratios of chloroform (active) to heptane (inert) diluent. Almost identical results were obtained for succinic acid extracted by 0.29 mol/L Alamine 336 in methylene chloride and heptane (Fig. 2-12*b*). Third-phase formation was minor in these results. These systems have been modeled by specific acid-amine-diluent complex formation.

Fig. 2-13*a* shows the effect of amine concentration for the extraction of succinic acid by Alamine 336 in a chloroform-heptane mixed diluent system at low active diluent concentrations. Recall that at 100% active diluent (chloroform), the 0.29 and 0.58 mol/L Alamine 336 systems lay on the same loading curve; there was no discernible dependence of loading on amine concentration (see Fig. 2-5*a*). But at low active diluent concentration, 10% (v/v), loading depends strongly upon extractant concentration, increasing as extractant concentration increases. The 0.58 mol/L amine curve has a noticeably sharper slope than would be predicted from (1,1) stoichiometry. Aggregation is thus very evident and increases at higher amine concentrations where more complex is formed. Fig. 2-13*b* presents analogous results for a methylene chloride-heptane mixed diluent system with 100%, 70%, and 20% (v/v) methylene chloride in the diluent (not total solvent). At 100% and 70% methylene chloride, there is no effect of amine concentration on loading; but at 20% methylene chloride, loading is higher for the higher amine concentration. The characteristics of these succinic

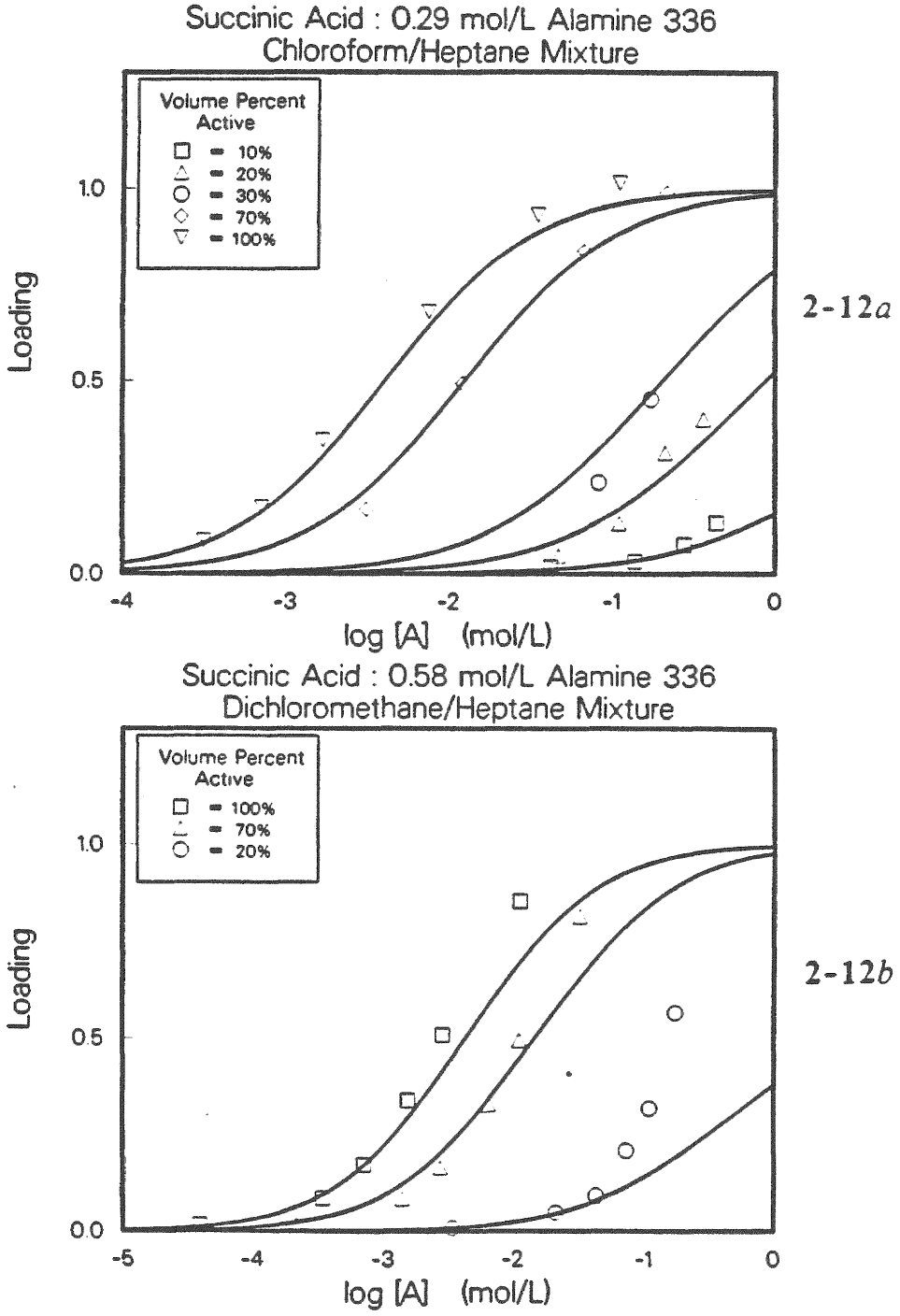


Fig. 2-12. Loading Curves for the Extraction of Succinic Acid by Alamine 336 in Active/Inert Mixed Diluents.

(*a*) Using chloroform as the active diluent and heptane as the inert diluent, 0.29 mol/L Alamine 336; $\log(\beta_{113}) = -0.63$

(*b*) Using methylene chloride as the active diluent and heptane as the inert diluent, 0.58 mol/L Alamine 336; $\log(\beta_{113}) = -0.32$

Volume percent active diluent refers to percent of diluent, not total solvent.

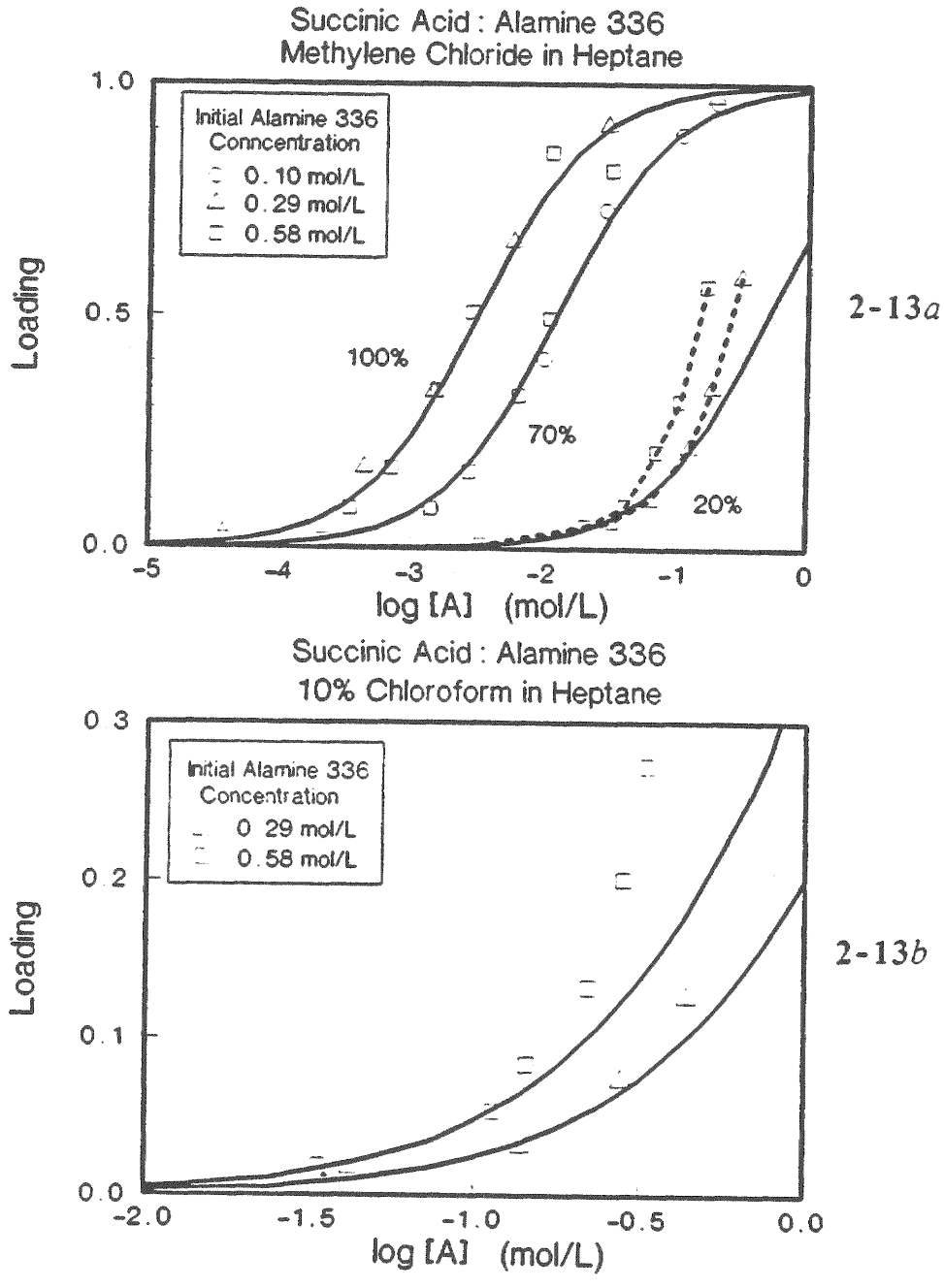


Fig. 2-13. Loading Curves Showing the Effect of Amine Concentration on the Extraction of Succinic Acid in Active/Inert Mixed Diluent Systems.

(*a*) Methylene Chloride (active) and heptane (inert)
100 vol% active, $\log(\beta_{11}) = 2.5$
70 vol% active, $\log(\beta_{11}) = 1.9$
20 vol% active, $\log(\beta_{11}) = 0.3$

(*b*) 10 vol% Chloroform (active) and heptane (inert)
0.29 mol/L, $\log(\beta_{11}) = -0.6$; 0.58 mol/L; $\log(\beta_{11}) = -0.3$

Solid curves for 10% and 20% active diluent do not represent best-fit results, they are for illustration purposes. Systems were too non-ideal to model effectively.

acid systems are a sharp contrast to the data for the extraction of acetic acid by Alamine 336 in the 15% (v/v) chloroform-heptane diluent, in which the loading curves for 0.29, 0.58 and 1.16 mol/L amine lie on the same curve (see Fig. 2-1*a*).

2.6 Summary and Conclusions

A number of carboxylic acid-amine-diluent systems were modeled with a mass-action law approach to infer stoichiometries and association constants of the complexes formed. Great differences were seen among different systems. Active diluents produce complex formation constants several orders of magnitude greater than inert diluents. Overloading, (2,1) complex formation, was extensive for the monocarboxylic acids, acetic and lactic acid, but far less so for dicarboxylic acids. Chloroform, methylene chloride, and nitrobenzene give the highest extraction at loadings less than unity, but MIBK promotes more overloading, and so gives higher extraction at loadings greater than unity. The use of an inert diluent resulted in aggregation and third-phase formation for succinic acid, but not for acetic acid. As increasing volumes of active diluents, chloroform or methylene chloride, were mixed into the inert diluent, heptane, extraction increased, and third-phase formation decreased. Different acids showed markedly different extractability into the same organic phase. Stronger acids, such as maleic acid, showed several order of magnitude greater (1,1) complexation constants than weaker acids, such as acetic acid. More discussion of these results in relation to the results of other workers is given in Chapter 3.

REFERENCES

Connors, K. A., *Binding Constants. A Measurement of Molecular Complex Stability*, John Wiley & Sons, New York (1987).

Holten, C. H., *Lactic Acid//Properties and Chemistry of Lactic Acid and Derivatives*, Chapter 4, Verlag Chemie, Copenhagen (1971).

Kertes, A. S. and King, C. J., "Extraction Chemistry of Fermentation Product Carboxylic Acids", *Biotechnol. Bioeng.*, **28**, 269-282 (1986).

Starr, J. N., University of Californa, Berkeley, personal communication (1988).

CHAPTER 3. COMPARISON WITH LITERATURE RESULTS

3.1 Qualitative Comparison of Literature Results

Several workers have performed batch extraction experiments similar to those described in Chapter 2 with other carboxylic acid-amine systems. A qualitative summary of these investigations is given in Table 3-1. The information is arranged by solute and then by the extractant, with the diluent indicated beneath. The second column, $C_{B,tot}$, shows the initial extractant concentration range (Low, < 0.5 mol/L, Medium, 0.5 to 1.0 mol/L, High, > 1.0 mol/L), at which the experiments were carried out. Where possible, the literature data were inspected for several qualitative characteristics -- overloading, third phase or precipitate formation, shape of loading curve relative to a (1,1) stoichiometry, and the effect on loading of the initial amine concentration. Where similar conditions were used, the data were also inspected for the relative order of solvent extracting power for the acid. The literature reference is noted in the final column.

3.1.1 Overloading

Overloading of the extractant indicates the presence of species with multiple acids per amine. The column entitled "Z>1?" was marked with a "Y" when loading, corrected for diluent extraction, exceeded unity at some aqueous acid concentration. (Most authors corrected for extraction by the diluent alone. For most of the systems, this correction is small.) Non-overloading, marked with a "N", was indicated when the loading asymptotically approached, but did not exceed, unity as acid concentration was increased. An N is somewhat qualified, as it is possible that overloading may still occur in these systems at higher acid concentrations. For example, if a system has a

large (1,1) versus (2,1) formation constant, there would be a long plateau at Z equal to one, which could appear to be maximum loading equal to one. The Z>1? column is marked with a "-" if experimental conditions were such that it was not possible to examine the overloading region (e.g., if the acid concentration was not high enough to load the amine fully).

3.1.2 Formation of a Precipitate or Third Phase

The formation of a precipitate or third phase in a system indicates that the complex is more stable as a solid or a separate phase than in the bulk solvent. Generally, this is an indication that the solvent is a poor solvating medium for the complex. However, it may also indicate that the acid forms a particularly stable solid salt. The "ppt or 3rd?" column is marked with a "P" or "3" if precipitate or third phase formation, respectively, was noted in the report. A "-" indicates that no third phase or precipitate was reported.

3.1.3 Shape of Loading Curve

Where possible, the shape of the loading curve was qualitatively examined in comparison to a (1,1) curve. If the curve had a steeper slope than a (1,1) curve, aggregation or multiple acid per amine complexes are indicated, and the "C?" column was marked with an "C". A steep curve accompanied by overloading is strong confirmation of significant multi-acid per amine complex formation. (If the formation constant for the (2,1) complex is small relative to that of the (1,1) complex, overloading is still possible, but the curve will resemble a (1,1) curve for $Z < 1$.) A steep curve accompanied by an increase in loading with increased amine concentration is a strong evidence of aggregation. An "N" indicates that the curve approximated a

(1,1) curve at loadings less than one. A "-" indicates that there was insufficient information to identify the shape of the loading curve.

3.1.4 Effect of Increasing Initial Amine Concentration on Loading

The effect of amine concentration is an indication of how the diluent interacts with the complex. If extraction increases as amine concentration increases, the presence of one or more complexes containing multiple amines per acid is indicated, and the Z as $C_{B,tot}\uparrow$ column was marked with an "I". If extraction decreases as amine concentration increases, strong diluent interaction with the complex is indicated, and the column was marked with "D". If there is no effect of amine concentration, the column is marked with an "N", strongly suggesting only one amine per complex. Some systems, especially those studied in this work, show no effect of increasing amine concentration on loading at low amine concentrations, but a further increase in amine content caused a decrease in loading. This is denoted by "N,D".

3.1.5 Order of Extracting Power

The extracting power of the diluent-extractant mixture is a measure of the positive interaction between the diluent and the complex. Within each text block with both the same extractant and author, the diluents are listed in approximate decreasing order of extraction; i.e., the diluents which allow for the most acid extraction are listed first and the diluents which allow for the least extraction are listed last. The effect of diluent on the order of extraction for a given acid-extractant system may vary, depending on the acid or amine concentration. Where possible, the data were compared at low acid concentrations and at the same amine concentration.

Table 3-1
Summary of Literature on Carboxylic Acid-Amine Systems

$C_{B,tot}$	Total Extractant Concentration (mol/L), L < 0.5; 0.5 < M < 1.0; 1.0 < H.
Z>1?	Y = Loading greater than 1; N = Loading approaches but does not exceed 1.
C?	Curve concave upward compared to a (1,1) curve.
ppt or 3rd?	P = precipitate formation; 3 = third-phase formation.
Z as $C_{B,tot}\uparrow$	I = Z increases as $C_{B,tot}$ increases, N = Z constant as $C_{B,tot}$ increases, D = Z decreases as $C_{B,tot}$ increases.

Extractant/Diluent	$C_{B,tot}$	Z>1?	ppt or 3rd?	C?	Z as $C_{B,tot}\uparrow$	Ref.
FORMIC (METHANOIC) ACID						
Amberlite LA-2 (II°)						KAW
Benzene	L	Y	-	-	I	(1)
Hexane	L	Y	-	-	I	(1,3)
Trilaurylamine						MAN
Chloroform	L	Y	-	-	-	
Benzene	L	Y	-	C	-	
Heptane	L	-	-	C	-	
Triisooctylamine						WAR
n-Hexanol/Heptane 2:1	L	-	-	-	-	
ACETIC (ETHANOIC) ACID						
Tridecylamine						CHA
Benzene	L,M	Y	-	C	N	
Carbon Tetrachloride	L,M	Y	-	C	N	
Trilaurylamine						HÖG
o-Xylene	L	Y	-	-	N	
n-Heptane	L	Y	-	-	N	

Table 3-1 (Cont'd)

Extractant/Diluent	$C_{B,tot}$	Z>1?	ppt or 3rd?	C?	Z as $C_{B,tot}\uparrow$	Ref.
ACETIC ACID (Cont'd)						
Amberlite LA-2 (II°)						KAW
Benzene	L	Y	-	-	N	(2)
Hexane	L	Y	-	-	N	(1)
Trioctylamine						
Hexane	L	Y	-	-	N	(3)
Alamine 336						RIC2
2-ethyl-1-hexanol	L,M,H	Y	-	-	D	
Chloroform	L,M,H	Y	-	-	D	
2-Heptanone	L,M,H	-	-	C	D	
TBP/2-Heptanone	L	-	-	-	-	
Cyclohexanone	L	-	-	-	-	
Di-isobutyl carbinol	M	-	-	-	-	
Di-isobutyl Ketone	L,M,H	Y	-	-	D	
Decane	L	-	-	-	-	
2-Ethyl-1-Hexanol in Chevron 410-H	M	Y	-	-	-	
Chevron 410-H	M	-	-	-	-	
none	H	-	-	-	-	
Adogen 283 (II°)						RIC2
Chloroform	M	-	-	-	-	
2-Heptanone	L,M,H	Y	-	C	D	
Chevron 25	M					
none						
Adogen 346D						
Methyl Isoamyl Ketone	M	-	-	-	-	RIC2
Adogen 387 D						
Methyl Isoamyl Ketone	M	-	-	-	-	RIC2
Adogen 381						RIC1
Chloroform	M	-	-	-	-	
2-Heptanone	M	-	-	-	-	
Adogen 364						RIC1
Chloroform	M	-	-	-	-	
2-Heptanone	M	-	-	-	-	

Table 3-1 (Cont'd)

Extractant/Diluent	$C_{B,tot}$	Z>1?	ppt or 3rd?	C?	Z as $C_{B,tot}$↑	Ref.
ACETIC ACID (Cont'd)						
Adogen 368						RIC1
Chloroform	M	-	-	-	-	
2-Heptanone	M	-	-	-	-	
Adogen 363						RIC1
Chloroform	M	-	-	-	-	
2-Heptanone	M	-	-	-	-	
Methyl Di-Tridecyl Amine						RIC1
Methyl Isoamyl Ketone	M	-	-	-	-	
Amberlite LA-1 (II°)						RIC1
Chloroform	M	-	-	-	-	
Chevron 25	M	-	-	-	-	
None	H	-	-	-	-	
Amberlite LA-2 (II°)						RIC1
Chloroform	M	-	-	-	-	
Chevron 25	M	-	-	-	-	
None	H	-	-	-	-	
Adogen 283-D (II°)						RIC1
Chloroform	M	-	-	-	-	
Chevron 25	M	-	-	-	-	
None	H	-	-	-	-	
Tribenzylamine						SOL1
Chloroform	L	-	P	C	-	
Alamine 336						SPA
Chloroform	M,H	Y	-	-	D	
Alamine 336						TAM
Nitrobenzene	L	Y	-	-	-	
Chloroform/Heptane (1:6)	L,M	Y	-	C	N	
Triisooctylamine						VIE3
Benzene	L	Y	-	C	-	
Xylene	L	Y	-	C	-	

Table 3-1 (Cont'd)

Extractant/Diluent	$C_{B,tot}$	Z>1?	ppt or 3rd?	C?	Z as $C_{B,tot}\uparrow$	Ref.
ACETIC ACID (Cont'd)						
Trioctylamine						WAR
n-Hexanol	L	-	-	-	-	
Chloroform	L	-	-	-	-	
n-Hexanol/Heptane (in various ratios)	L	-	-	-	-	
Nitrobenzene	L	-	-	-	-	
Chloroform/Heptane	L	-	-	-	-	
Chevron 25	L	-	-	-	-	
Tributylamine						WAR
Chloroform	L	-	-	-	-	
n-Hexanol	L	-	-	-	-	
Triisooctylamine						WAR
n-Hexanol	L	-	-	-	-	
Chloroform	L	-	-	-	-	
MONOCHLOROACETIC (CHLOROETHANOIC) ACID						
Tribenzylamine						SOL1
Methylene chloride	L,M,H?	Y	-	-	-	
Chloroform	L,M,H?	Y	-	-	-	
Benzene	L,M,H?	-	-	C	-	
Toluene	L,M,H?	-	-	C	-	
o-Xylene	L,M,H?	-	-	C	-	
Carbon tetrachloride	L,M,H?	-	-	C	-	
Hexane	L,M,H?	-	P	C	-	
TRICHLOROACETIC (TRICHLOROETHANOIC) ACID						
Trilaurylamine						KUC
o-Xylene	L	Y	-	-	N	
Tribenzylamine						SOL2
Hexane	L	Y	P	C	-	
Octane	L	Y	P	C	-	
Chloroform	L	Y	-	-	-	
Mesitylene	L	Y	P	C	-	
o-Xylene	L	Y	P	C	-	
Carbon tetrachloride	L	Y	P	C	-	
Benzene	L	Y	P	C	-	

Table 3-1 (Cont'd)

Extractant/Diluent	$C_{B,tot}$	Z>1?	ppt or 3rd?	C?	Z as $C_{B,tot}\uparrow$	Ref.
ACETIC ACID (Cont'd)						
Tribenzylamine						SOL1
Chloroform	L	Y	-	-	-	
Hexane	L	Y	P	-	-	
PROPIONIC (PROPANOIC) ACID						
Amberlite LA-2 (II°)						KAW
Benzene	L	Y	-	-	N	(1)
Hexane	L	Y	-	-	N	(1,3)
Trioctylamine						KAW2
Hexane	L	Y	-	-	N	
VALERIC (PENTANOIC) ACID						
Trioctylamine						MAN
Chloroform	L	Y	-	-	-	
Trilaurylamine						MAN
Chloroform	L	Y	-	-	-	
Benzene	L	Y	-	C	-	
BENZOIC (BENZENECARBOXYLIC) ACID						
Trilaurylamine						MAN
Chloroform	L	Y	-	-	-	
Benzene	L	Y	-	C	-	
BENZOIC ACID						PUT
SALICYLIC ACID						2,3,4
3-HYDROXYBENZOIC ACID						
4-HYDROXYBENZOIC ACID						
3,4-HYDROXYBENZOIC ACID						
2,5-HYDROXYBENZOIC ACID						
Triisooctylamine						
Chloroform	L	-	-	-	-	

Table 3-1 (Cont'd)

Extractant/Diluent	$C_{B,tot}$	Z>1?	ppt or 3rd?	C?	Z as $C_{B,tot}$↑	Ref.
DYES: TARTRAZINE, AMARANTH, PATENT BLUE						PUTI
Tri-n-Octylamine						
Methylene Chloride	L	-	-	-	-	
Chloroform	L	-	-	-	-	
Methyl Isobutyl Ketone	L	-	-	-	-	
Butyl Acetate	L	-	-	-	-	
Hexane	L	-	-	-	-	
LACTIC (2-HYDROXYPROPANOIC) ACID						
Triamylamine						RAT
2-Octanol	?	-	-	-	-	
Isoamyl Alcohol	?	-	-	-	-	
Chloroform	?	-	-	-	-	
Isobutyl Alcohol	?	-	-	-	-	
n-Amyl Alcohol	?	-	-	-	-	
sec-Amyl Alcohol	?	-	-	-	-	
3-Pentanol	?	-	-	-	-	
n-Butyl Alcohol	?	-	-	-	-	
2-Ethylhexanol	?	-	-	-	-	
Methyl Isobutyl carbinol	?	-	-	-	-	
tert-Amyl alcohol	?	-	-	-	-	
3-heptanol	?	-	-	-	-	
Ethyl Acetate	?	-	-	-	-	
Pinene	?	-	-	-	-	
Ether	?	-	-	-	-	
Carbon Tetrachloride	?	-	-	-	-	
Benzene	?	-	-	-	-	
Diethylbutylamine	?	-	-	-	-	RAT
Tributylamine	?	-	-	-	-	
Triamyamine	?	-	-	-	-	
Trioctylamine	?	-	-	-	-	
Octadecyldimethylamine	?	-	-	-	-	
Tribenzylamine	?	-	-	-	-	
Dimethylaniline	?	-	-	-	-	
Chloroform						
Di-*n*-butylamine (II°)	?	-	-	-	-	RAT
Di-*n*-decylamine (II°)	?	-	-	-	-	
Dicyclohexylamine (II°)	?	-	-	-	-	
Dibenzylamine (II°)	?	-	-	-	-	
Diphenylamine (II°)	?	-	-	-	-	
Chloroform						

Table 3-1 (Cont'd)

Extractant/Diluent	$C_{B,tot}$	Z>1?	ppt or 3rd?	C?	Z as $C_{B,tot}$↑	Ref.
LACTIC ACID (Cont'd)						
n-Octylamine (I°)	?	-	-	-	-	RAT
n-Decylamine (I°)	?	-	-	-	-	
n-Tetradecylamine (I°)	?	-	-	-	-	
n-Hexadecylamine (I°)	?	-	-	-	-	
Chloroform						
Adogen 283 (II°)						
Kerosene	M	-	-	-	-	ROF
Adogen 363						
Trichloroethylene	M	-	-	-	-	ROF
Trioctylamine						SAT
Xylene	L,M	Y	-	-	N	
Alamine 336						TAM
m-Cresol	L	-	-	-	-	
Chloroform	L	Y	-	-	-	
MIBK	L	Y	-	C	N	
PENICILLIN G						
Adogen 283 (II°)	L	-	-	-	-	RES
Dioctylamine (II°)	L	-	-	-	-	
Amberlite LA-2 (II°)	L	-	-	-	-	
Amberlite LA-1 (II°)	L	-	-	-	-	
n-Butyl Acetate						
Dimethylpalmitylamine	L	-	-	-	-	RES
Trioctylamine	L	-	-	-	-	
Adogen 383	L	-	-	-	-	
n-Butyl Acetate						
Amberlite LA-2 (II°)						RES
n-Butyl Acetate	L	-	-	-	-	
Isobutyl Acetate	L	-	-	-	-	
Isoamyl Acetate	L	-	-	-	-	
Xylol	L	-	-	-	-	
Diisopropyl Ether	L	-	-	-	-	
Dioctyl Ether	L	-	-	-	-	
Kerosene	L	-	-	-	-	

Table 3-1 (Cont'd)

Extractant/Diluent	$C_{B,tot}$	Z>1?	ppt or 3rd?	C?	Z as $C_{B,tot}\uparrow$	Ref.
PENICILLIN V						
Dioctylamine (II°)	L	-	-	-	-	RES
Amberlite LA-2 (II°)	L	-	-	-	-	
n-Butyl Acetate						
PHENYLACETIC ACID PHENOXYACETIC ACID						
Amberlite LA-2 (II°)	L	-	-	-	-	RES
n-Butyl Acetate						
OXALIC (ETHANEDIOIC) ACID						
Methyldioctylamine						BUL
Chloroform	M	N	-	-	-	
Amberlite LA-2 (II°)						KAW
Benzene	L	N	-	-	I	(1)
Hexane	L	N	-	-	I	(1,3)
Trioctylamine						LIP
Benzene	L	Y	-	-	-	
Trilaurylamine						MAN
Chloroform	L	N	-	-	-	
Chlorobenzene	L	N	-	-	-	
Benzene	L	N	-	C	-	
Toluene	L	N	-	C	-	
Mesitylene	L	N	-	C	-	
n-Heptane	L	N	P	C	-	
Trioctylamine						MAN
Benzene	L	N	-	C	-	
Trioctylamine						SME
?	L	N	-	-	P	

Table 3-1 (Cont'd)

Extractant/Diluent	$C_{B,tot}$	Z>1?	ppt or 3rd?	C?	Z as $C_{B,tot}\uparrow$	Ref.
OXALIC ACID (Cont'd)						
Triisooctylamine						VIE1
Chloroform	L	N?	-	-	-	
1,2-Dichloroethane	L	N?	-	-	-	
o-Dichlorobenzene	L	N?	P	-	-	
Benzene	L	-	P	-	-	
Xylene	L	-	P	-	-	
MALONIC (PROPANEDIOIC) ACID						
Trilaurylamine						MAN
Benzene	L	-	-	-	-	
Alamine 336						TAM
MIBK	L,M,H	Y	-	-	N,D	
None	H	Y	3	C	-	
Triisooctylamine						VIE1
1,2-Dichloroethane	L	N	-	-	-	
Chloroform	L	N	-	-	-	
o-Dichlorobenzene	L	N	-	-	-	
Benzene	L	-	-	-	-	
Xylene	L	-	-	-	-	
SUCCINIC (BUTANEDIOIC) ACID						
Trilaurylamine						MAN
Chloroform	L	N	-	-	-	
Benzene	L	N	-	-	-	
n-Heptane	L	-	-	-	-	
Trioctylamine						SAT
Xylene	L,M	-	-	C	I	

Table 3-1 (Cont'd)

Extractant/Diluent	$C_{B,tot}$	Z>1?	ppt or 3rd?	C?	Z as $C_{B,tot}$†	Ref.
SUCCINIC ACID (Cont'd)						
Alamine 336						TAM
1-Octanol	L	-	-	-	I	
1-Octanol/Chlororoform	L	-	-	-	-	
Methylene Chloride	L,M	N?	-	-	N,D	
Nitrobenzene	L	Y	-	-	N	
Chloroform	L,M,H	N?	-	-	N,D	
MIBK	L,M,H	Y	-	-	N,D	
CH_2Cl_2/Heptane	L,M	N?	-	-	N,I	
$CHCl_3$/Heptane	L,M	N?	-	-	N,I	
n-Heptane	L,M,H	-	3	C	I	
None	H	-	3	C	-	
Triisooctylamine						VIE1
Chloroform	L	N?	-	-	-	VIE2
1,2-Dichloroethane	L	N	-	-	-	
o-Dichlorobenzene	L	N	-	-	-	
Benzene	L	N?	-	-	-	
Xylene	L	-	-	-	-	
GLUTARIC (PENTANEDIOIC) ACID						
Trilaurylamine						MAN
Benzene	L	-	-	-	-	
Triisooctylamine						VIE2
1,2-Dichloroethane	L	-	-	-	-	
Chloroform	L	Y?	-	-	-	
o-Dichlorobenzene	L	Y?	-	-	-	
Benzene	L	Y?	-	-	-	
Xylene	L	-	-	-	-	
ADIPIC (HEXANEDIOIC) ACID						
Trilaurylamine						MAN
Benzene	L	-	-	-	C	

Table 3-1 (Cont'd)

Extractant/Diluent	$C_{B,tot}$	Z>1?	ppt or 3rd?	C?	Z as $C_{B,tot}\uparrow$	Ref.
MALEIC (*cis*-BUTENEDIOIC) ACID						
Alamine 336						TAM
Chloroform	L	Y	-	-	N	
MIBK	L	Y	-	-	N	
FUMARIC (*trans*-BUTENEDIOIC) ACID						
Alamine 336						TAM
Chloroform	L	N?	-	-	I	STA
MIBK	L	Y	-	-	I	
PHTHALIC (1,2-BENZENEDICARBOXYLIC) ACID						
Trilaurylamine						MAN
Chloroform	L	N	-	-	-	
Benzene	L	N	-	C	-	
Heptane	L	-	-	C	-	
TARTARIC (2,3-DIHYDROXYBUTANEDIOIC) ACID						
Trioctylamine						SAT
Xylene	L,M	-	-	C	I	
CITRIC (2-HYDROXY-1,2,3-PROPANETRICABOXYLIC) ACID						
Tridecylamine						BAN
Nitrobenzene	M	-	-	-	-	
Xylene	M	-	-	-	-	
Oil/Octanol	M	-	-	-	-	
Oil, bp. 140-210	M	-	3	-	-	
Amberlite LA-1 (II°)						
Oil, bp. 140-210	M	-	-	-	-	
Triethylamine						PYA2
Triamylamine						
Octylamine						
Dioctylamine						
Tribenzylamine						
Chloroform	L,M	-	-	-	-	

Table 3-1 (Cont'd)

Extractant/Diluent	$C_{B,tot}$	Z>1?	ppt or 3rd?	C?	Z as $C_{B,tot}$↑	Ref.
CITRIC ACID (Cont'd)						
Trioctylamine						PYA1
Methyl Isobutyl Ketone	L	-	-	-	-	
Amyl Acetate	L	-	-	-	-	
Dichloroethane	L	-	-	-	-	
Carbon Tetrachloride	L	-	-	-	-	
Chlorobenzene	L	-	-	-	-	
Xylene	L	-	-	-	-	
Toluene	L	-	-	-	-	
Benzene	L	-	-	-	-	
Cyclohexane	L	-	-	-	-	
Hexane	L	-	-	-	-	
Tributylamine						PYA3
Chloroform	L	-	-	-	-	
Hostarex A324	?	-	-	-	-	RÜC
Isodecanol						
Alamine 336						WEN
n-Butyl Chloride	M	N?		-	-	-
Isopar H/MIBK (1:1)	M	N?	-	-	-	
Isopar H	M	N?	-	-	-	
n-Butanol	M	-	-	-	-	
Nitrobenzene	M	-	-	-	-	
Dichloromethane	M	-	-	-	-	
Isoamyl alcohol	M	-	-	-	-	
2-Ethylhexanol	M	-	-	-	-	
Cyclohexanone	M	-	-	-	-	
MIBK	M	-	-	-	-	
Ethyl acetate	M	-	-	-	-	
1,1,1-Trichloroethane	M	-	-	-	-	
Toluene	M	-	-	-	-	
n-Hexane	M	-	-	-	-	
None	H	-	P	-	-	
Toluene/Isopar H (4:1)	M	-	-	-	-	
Toluene/Isopar H (3:2)	M	-	-	-	-	
Toluene/Isopar H (2:3)	M	-	P	-	-	
Toluene/Isopar H (1:4)	M	-	P	-	-	
Isopar H	M	-	P	-	-	

Table 3-1 (Cont'd)

Extractant/Diluent	$C_{B,tot}$	Z>1?	ppt or 3rd?	C?	Z as $C_{B,tot}\uparrow$	Ref.
CITRIC ACID (cont'd)						
MIBK/Isopar H (2:3)	M	-	-	-	-	WEN
MIBK/Isopar H (1:4)	M	-	P	-	-	
Shellsol A	M	-	-	-	-	
Trilaurylamine						WEN
2-ethylhexanol	M	-	-	-	-	
Chloroform	M	-	-	-	-	
MIBK	M	-	-	-	-	
Toluene	M	-	-	-	-	
Hostarex A327						WOJ
TOPO/n-Dodecane (2:3)	M	-		-	-	-
Methyl isobutyl ketone	M	-	-	C	-	
None	H	-	-	C	-	
Trioctylamine						SAT
Xylene	L,M	N	-	C	I	
Trilaurylamine						VAN
Toluene	L	N	-	-	I	

3.2 Quantitative Comparison of Literature Results

Some of the previous studies included data which were analyzed quantitatively by the mass-action-law modeling approach. A summary of the quantitative results for systems which followed simple (p,1) stoichiometries is given in Table 3-2. The information is arranged by solute, extractant, and diluent, as before. Extractant-diluent systems are listed in approximate decreasing order of extracting power for a given acid. The logarithms (base 10) of the overall equilibrium constants for the (p,1) complexes are shown. The source of data and the method (C, computer minimization program; G, graphical analysis) used to calculate the equilibrium constants is given in the last column. An asterisk indicates that determination of the complex stoichiometries and equilibrium constants was done in this work; otherwise, the values were taken from the published work.

C* denotes that the computer minimization routine outlined in Appendix B was applied to systems studied experimentally in this work. In some cases, data from previous studies for which no mass-action law analysis had been performed were entered into the same minimization program to determine best-fit stoichiometries and apparent equilibrium constants. Usually no pH data were available, so undissociated acid concentration was calculated from pK_A values and aqueous acid concentration, assuming no other effects upon pH. Appendix B reports results obtained by using the computer minimization program from this work to analyze data reported in the literature.

C is entered for cases in which the authors performed their own computer calculations of best-fit stoichiometries and association constants. Results of the published calculations, converted into units and definitions of this work, are shown.

The particular error minimization procedures used in these calculations probably differ from the one used here, so different values of the equilibrium constants may be obtained. The magnitude of the difference depends on the scatter and adequacy of the data, as well as the minimization procedure. Appendix B gives more information on the effect of the error minimization procedure on calculation of equilibrium constants.

G* indicates that graphical plots which enable determination of (1,1) equilibrium constant, assuming (1,1) stoichiometry, were provided in the original paper, although the authors did not report the actual values for the constant. For this work, values of the (1,1) equilibrium constant were estimated directly from the published plots by taking the intercept of the log(D) vs. log[B] plot, where D is the distribution ratio and [B] is the "free" amine concentration (taken as the difference between the total amine concentration and the equilibrium organic-phase acid concentration). A more complete analysis was not possible because of the limited data provided. G indicates that the authors reported values which they had obtained by graphical analysis in the published work.

Determination of equilibrium constants by purely graphical means often obscures some of the important characteristics of these systems. The graphical analyses used in most of the works reviewed here are based on the assumption of (1,1) stoichiometry. The data were plotted in a form, either as log(D) vs. log[B] or $Z/(1-Z)$ vs. [A], which should result in linear plots if the stoichiometry is (1,1). Deviations from linear behavior were used as indications of more complex stoichiometries. Unfortunately, these deviations may be extremely difficult to detect. Therefore, the conclusion of (1,1) stoichiometry and the value of the equilibrium constant determined by graphical methods should be viewed with skepticism. Nevertheless, the reported

Table 3-2
Summary of Mass-Action Law Modeling Results for Carboxylic Acid-Tertiary Amine Systems at 25 °C

Extractant (Conc., mol/L)	Diluent	log(β_{pq}) (1,1)	(2,1)	(3,1)	(4,1)	Source (Method)
ACETIC ACID $pK_A = 4.76$						
Adogen 283 (0.429)	2-Heptanone	2.09	2.59	2.52		RIC2 (C*)
Alamine 336 (0.02 to 0.10)	2-Ethyl-1-Hexanol	1.83	1.82			RIC2 (C*)
Alamine 336 (0.68)	Chloroform	1.25	1.90			SPA (C*)
Alamine 336 (0.29)	Nitrobenzene	0.86	1.82	[1.55]		TAM (C*)
Alamine 336 (0.39 and 0.69)	Diisobutyl Ketone	0.25	-0.28			RIC2 (C*)
Amberlite LA-2 (?)	Benzene	0.5	1.23	1.14	1.04	KAW1 (?)
Tridecylamine (0.186 to 0.745)	Benzene	0.13	0.20	0.85		CHA (?)
Triisooctylamine (0.10)	Benzene	[0.2]	[0.4]	[[0.1]		VIE3 (C*)
Triisooctylamine (0.10)	Xylene	[0.1]	[0.2]	[0.1]		VIE3 (C*)
Alamine 336 (0.1 to 0.58)	15% CHCl3 in n-Heptane	0.11	0.02	-0.21		TAM (C*)
Tridecylamine (0.372 to 1.49)	Carbon Tetrachloride	0.1		0.25		CHA (?)
Trilaurylamine (0.08 to 0.32)	*o*-Xylene	-0.6	0.38	-0.19		HÖG (C)
Amberlite LA-2 (0.044 to 0.510)	Hexane	-0.2	0.42	-0.88	-0.63	KAW3 (?)

Note: Brackets [] indicate large uncertainty in value of β_{pq}.

Table 3-2 (Cont'd)

Extractant (Conc., mol/L)	Diluent	$\log(\beta_{pq})$ (1,1)	(2,1)	(3,1)	(4,1)	Source (Method)
ACETIC ACID (Cont'd)						
Trilaurylamine (0.08 to 0.32)	*n*-Heptane		-0.68	-3.0	-2.0	HÖG (C)
Trioctylamine (0.05 to 0.20)	Hexane	-0.85	-1.2	-2.8	-2.1	KAW2 (?)
TRICHLOROACETIC ACID $pK_A = 0.52$						
TLA (0.0154 to 0.161)	o-Xylene	6.93	9.44			KUC (C)
PROPIONIC ACID $pK_A = 4.874$						
Amberlite LA-2 (0.054 to 0.20)	Benzene	0.87	2.35	3.05		KAW1 (?)
Amberlite LA-2 (0.044 to 0.21)	Hexane	0.18	1.32	1.30	1.55	KAW3 (?)
TOA (0.05 to 0.20)	Hexane	-0.13	-0.03	0.14	0.40	KAW2 (?)
LACTIC ACID $pK_A = 3.858$						
Alamine 336 (0.29)	Chloroform	2.12	2.57			TAM (C*)
Alamine 336 (0.29)	MIBK	1.31	1.52	1.17		TAM (C*)
Alamine 336 (0.1 to 1.0)	Xylene	-0.11	-0.13	-1.42		SAT (C*)

Table 3-2 (Cont'd)

Extractant (Conc., mol/L)	Diluent	log(β_{pq}) (1,1)	(2,1)	(3,1)	(4,1)	Source (Method)
OXALIC ACID pK_{A1} = 1.271, pK_{A2} = 4.272)						
Trilaurylamine (0.05)	Chloroform	[3.0]				MAN (G)
Triisooctylamine (0.05)	1,2-Dichloro-ethane	[3.0]				VIE2 (G*)
Triisooctylamine (0.05)	*o*-Dichloro-benzene	[2.4]				VIE2 (G*)
MALONIC ACID pK_{A1} = 2.826, pK_{A2} = 5.696						
Alamine 336 (0.048 to 0.58)	MIBK	3.10	3.24			TAM (C*)
Triisooctylamine (0.10)	*o*-Dichloro-benzene	[2,4]				VIE2 (G*)
Triisooctylamine (0.10)	Benzene	[1.7]				VIE2 (G*)
SUCCINIC ACID pK_{A1} = 4.207, pK_{A2} = 5.635						
Alamine 336 (0.29 and 0.58)	Methylene Chloride	2.54				TAM (C*)
Alamine 336 (0.048 to 0.58)	Chloroform	2.44	[1.49]			TAM (C*)
Alamine 336 (0.10 to 0.29)	Nitrobenzene	2.43	2.16			TAM (C*)
Trioctylamine (0.05)	Chloroform	2.35				MAN (G)
Triisooctylamine (0.05 and 0.10)	1,2-Dichloro-ethane	[2.0]				VIE1 (G*)
Alamine 336 (0.048 to 0.29)	MIBK	1.39	1.91			TAM (C*)

Table 3-2 (Cont'd)

Extractant (Conc., mol/L)	Diluent	log(β_{pq}) (1,1)	(2,1)	(3,1)	(4,1)	Source (Method)
SUCCINIC ACID (Cont'd)						
Triisooctylamine (0.05 and 0.10)	*o*-Dichloro-benzene	[0.8]				VIE1 (G*)
Triisooctylamine (0.05)	Benzene	[0.1]				VIE1 (G*)
Trilaurylamine (0.05)	Benzene	[0.0]				MAN (G)
GLUTARIC ACID pK_{A1} = 4.34, pK_{A2} = 5.41						
TIOA (0.05 and 0.10)	Chloroform	[1.6]				VIE1 (G*)
TIOA (0.05 and 0.10)	*o*-Dichloro-benzene	[0.5]				VIE1 (G*)
TIOA (0.05)	Benzene	[0.0]				VIE1 (G*)
MALEIC ACID pK_{A1} = 1.91, pK_{A2} = 6.33						
Alamine 336 (0.29 and 0.58)	Chloroform	6.00	5.72			TAM (C*)
Alamine 336 (0.15 and 0.29)	MIBK	5.69	6.29			TAM (C*)
PHTHALIC ACID pK_{A1} = 2.95, pK_{A2} = 5.408						
Trilaurylamine (0.01)	Chloroform	[3.7]				MAN (G)
Trilaurylamine (0.01)	Benzene	[3.2]				MAN (G)
Trilaurylamine (0.01)	*n*-Heptane	[2.6]				MAN (G)

constants do have utility in evaluating of the relative extracting powers of solvents and the extractabilities of the acids.

Table 3-3 summarizes best-fit stoichiometries for systems which showed more complicated behavior. The solute, extractant, and diluent are shown with the corresponding best-fit stoichiometric coefficients and equilibrium constants.

3.3 Survey of Literature Data

3.3.1 Acetic Acid

Chaikhorskii et al. (1966) performed studies of the extraction of acetic acid by tridecylamine (TDA) in carbon tetrachloride and benzene. The authors corrected loadings by subtraction of results they obtained for extraction by the diluent alone. Both loading curves were steep, with a final plateau at $Z = 3$ at high, approximately 8 mol/L, acetic acid concentrations. No effect of amine concentration was observed for concentration ranges used, 0.37 to 1.49 mol/L for CCl_4 and 0.37 to 0.745 mol/L for benzene. Their published values for formation constants, adjusted to the definitions in this work, are shown in Table 3-2. For comparison, their data were put into the error minimization routine developed in this work, and similar results were obtained (see Appendix B). It is interesting that the best-fit stoichiometries for carbon tetrachloride diluent provides for no (2,1) complex.

Högfeldt and Fredlund (1966) studied the extraction of acetic acid by 5%, 10%, 15%, and 20% (v/v) (0.079, 0.158, 0.236, and 0.315 mol/L) trilaurylamine (TLA) in *o*-xylene and *n*-heptane. A correction was made for the amount of acid extracted by

Table 3-3
Summary of Mass-Action Law Modeling Results
For Systems Not Showing (p,1) Stoichiometry

Extractant (Conc., mol/l)	Diluent	(p,q) or (p,q,r) $\log(\beta_{pq})$ or $\log(\beta_{pqr})$			Source (Method)
FORMIC ACID $pK_A = 3.751$					
Amberlite LA-2 (0.05 and 0.10)	Benzene	(1,1) 0.89	(2,1) 1.97	(3,1) 1.74	KAWI (?)
		(4,1) 1.35	(1,2) 1.36	(2,2) 4.11	
Amberlite LA-2 (0.05 and 0.10)	Hexane	(1,1) -0.3	(2,1) 0.0	(3,1) -0.06	KAWI (?)
		(1,2) 0.73			
SUCCINIC ACID $pK_{A1} = 4.21$; $pK_{A2} = 5.64$					
Alamine 336 (0.15 and 0.29)	1-Octanol	(1,2) [3.50]	(2,2) [4.91]		TAM (C*)
Alamine 336 (0.29)	40% 1-Octanol in Chloroform	(1,2) 3.28	(1,1) 2.27	(2,1) 2.42	TAM (C*)
Alamine 336 (0.05 to 2.0)	Chloroform	(1,1,2) 0.54			TAM (C*)
Alamine 336 (0.29)	Chloroform in Heptane	(1,1,3) -0.63			TAM (C*)
Alamine 336 (0.58)	Dichloromethane in Heptane	(1,1,3) -0.32			TAM (C*)
Alamine 336 (0.05 to 2.0)	MIBK	(2,1,1) 1.34	(1,1,2) -0.35		TAM (C*)

Note: Brackets [] indicate large uncertainty in value of β.

Table 3-3 (Cont'd)

Extractant (Conc., mol/l)	Diluent	(p,q) or (p,q,r) $\log(\beta_{pq})$ or $\log(\beta_{pqr})$			Source (Method)
MALONIC ACID pK_{A1} = 2.83; pK_{A2} =5.64					
Alamine 336 (0.05 to 2.0)	MIBK	(2,1,2) [1.68]	(1,1,2) [1.56]		TAM (C*)
FUMARIC ACID pK_{A1} = 3.1; pK_{A2} = 4.6					
Alamine 336 (0.05 to 0.29)	Chloroform	(1,2) 5.54	(2,2) 7.74		TAM (C*)
Alamine 336 (0.02 to 0.29)	MIBK	(1,2) 4.33	(2,2) 7.49	(2,1) 4.81	STA (C*)
TARTARIC ACID pK_{A1} = 3.22; pK_{A2} = 4.81					
Trioctylamine (0.05 to 1.0)	Xylene	(1,2) [1.0]	(6,7) [8.9]		SAT (C*)
CITRIC ACID pK_{A1} = 3.128; pK_{A2} = 4.761, pK_{A3} = 6.396					
Trilaurylamine (0.016 to 0.31)	Toluene	(1,2) 1.35	(2,3) 3.06	(5,6) 8.94	VAN (C)
Trioctylamine (0.05 to 1.0)	Xylene	(1,2) [1.1]	(6,7) [11.1]		SAT (C*)

the diluent alone. Loading curves were steep, and loading was independent of initial amine concentration. At the highest acid concentrations, around 1 or 2 mol/L, the loading was approximately 2.2 in *o*-xylene and 1.2 in heptane. The authors postulated the formation of several sets of (p,1) complexes, for p = 1 to 4. The errors obtained using only two complexes with (4,1) and (2,1) stoichiometry were of the same order as those obtained postulating all four (4,1), (3,1), (2,1), and (1,1) complexes. The equilibrium constants reported by the authors for the fit using all four complexes are given in Table 3-2. However, there is some confusion as to whether the constants are for overall or stepwise association; it appears that their published results are consistent with constants for overall association, although they stated that the constants were given for stepwise association.

Kawano and co-workers (1982, 1983*a,b*) investigated the extraction of acetic acid by Amberlite LA-2 (a highly branched, secondary amine) in hexane and in benzene, and by trioctylamine (TOA) in hexane. In all cases loading was independent of amine concentration from 0.05 to 0.20 mol/L amine, and the amine overloaded with acid to a maximum of around 3 to 3.5. The authors' reported equilibrium constants are shown in Table 3-2. The secondary amine shows significantly higher equilibrium constants than the tertiary amine.

Vieux (1969) studied the extraction of acetic acid by 0.1 mol/L TLA in benzene and xylene. A maximum loading around four was reported. The author determined equilibrium constants for the (1,1) complex only, which is of questionable utility when the loading clearly exceeded unity. The data from the paper were treated by the methods used in this work, and the equilibrium constants calculated are shown in Table 3-2. There were few data points, so the values should be considered approximate.

The above results for the extraction of acetic acid by tertiary amines in inert diluents -- hexane, heptane, benzene, and xylene -- have much in common. All show significant overloading, and there was no evidence of an effect of initial amine concentration on loading. For the aromatic diluents, the (1,1) equilibrium constants were of the order of unity, i.e., $\log(\beta_{11}) = 0$. Extraction was lower for the alkane diluents.

There are some differences among the data, especially among different investigators. The most disturbing is that the Chaikhorskii et al. data, which compose by far the most complete set of data, clearly show a maximum loading of three in carbon tetrachloride and benzene, while the results of Kawano et al. in benzene and hexane and of Vieux in benzene and xylene have a few points that appear to exceed a loading of three. Högfeldt found good fits with inclusion of a (4,1) complex, although the maximum loading achieved experimentally was around 2.2. Chaikhorskii et al. presented independent spectroscopic evidence of stable (3,1) complexes (see Chapter 4 for discussion), which rationalizes the finding of a maximum loading of three. It is difficult to determine if experimental error, inadequate accounting for the extraction by the diluent alone, or actual differences among the systems account for the differences in these results.

The variations in the values of the equilibrium constants and stoichiometries can most likely be attributed to differences in fitting procedure and the inherent limitations of a mass-action-law analysis. For example, the results by Högfeldt imply that no (1,1) or (3,1) complexes exist, but this is more likely an artifact of using a mass-action law model and the particular fitting procedure. As the authors themselves stated, with the limited range of data and the large number of adjustable equilibrium

constants (four constants plus the stoichiometries), there are several sets of complexes which are consistent with the data. Thus, it is not advisable to obtain stoichiometries solely from mass-action law fitting without considering the chemical and physical factors involved, especially when a large number of equilibrium constants are required.

Ricker (1978) made a comprehensive study of the extraction of acetic acid by amines in a variety of diluents. Several systems were studied in detail. The extraction of acetic acid by Alamine 336 in 2-ethyl-1-hexanol, by Alamine 336 in diisobutyl ketone (DIBK), and by Adogen 283, an aliphatic secondary amine, in 2-heptanone was studied at various amine concentrations. Selected results from Ricker (1978) plotted with the best-fit curve calculated in this work, are shown in Figs. 3-1 *a*, *b*, and *c*. The loadings were corrected for diluent extraction as in the present work, by subtraction of the product of the volume fraction of diluent and the amount extracted by the diluent alone at the appropriate concentration of undissociated acid (also provided in Ricker's experimental data). Treatment of the Ricker data by this method indicates that, at high amine concentrations, loading decreased as amine concentration increased for all of these systems. In all of these acetic acid systems, overloading was evident. Unfortunately, there is some difficulty in absolute confirmation of these results; all of these diluents by themselves are capable of extracting an appreciable amount of acid, so the correction factor for diluent extraction was often large compared to the amount attributed to extraction by the amine. Table 3-2 shows quantitative results for only low amine concentrations. No attempt was made to include the diluent specifically into the complex. The secondary amine, Adogen 283, appears to extract significantly more acid than the tertiary amine, Alamine 336.

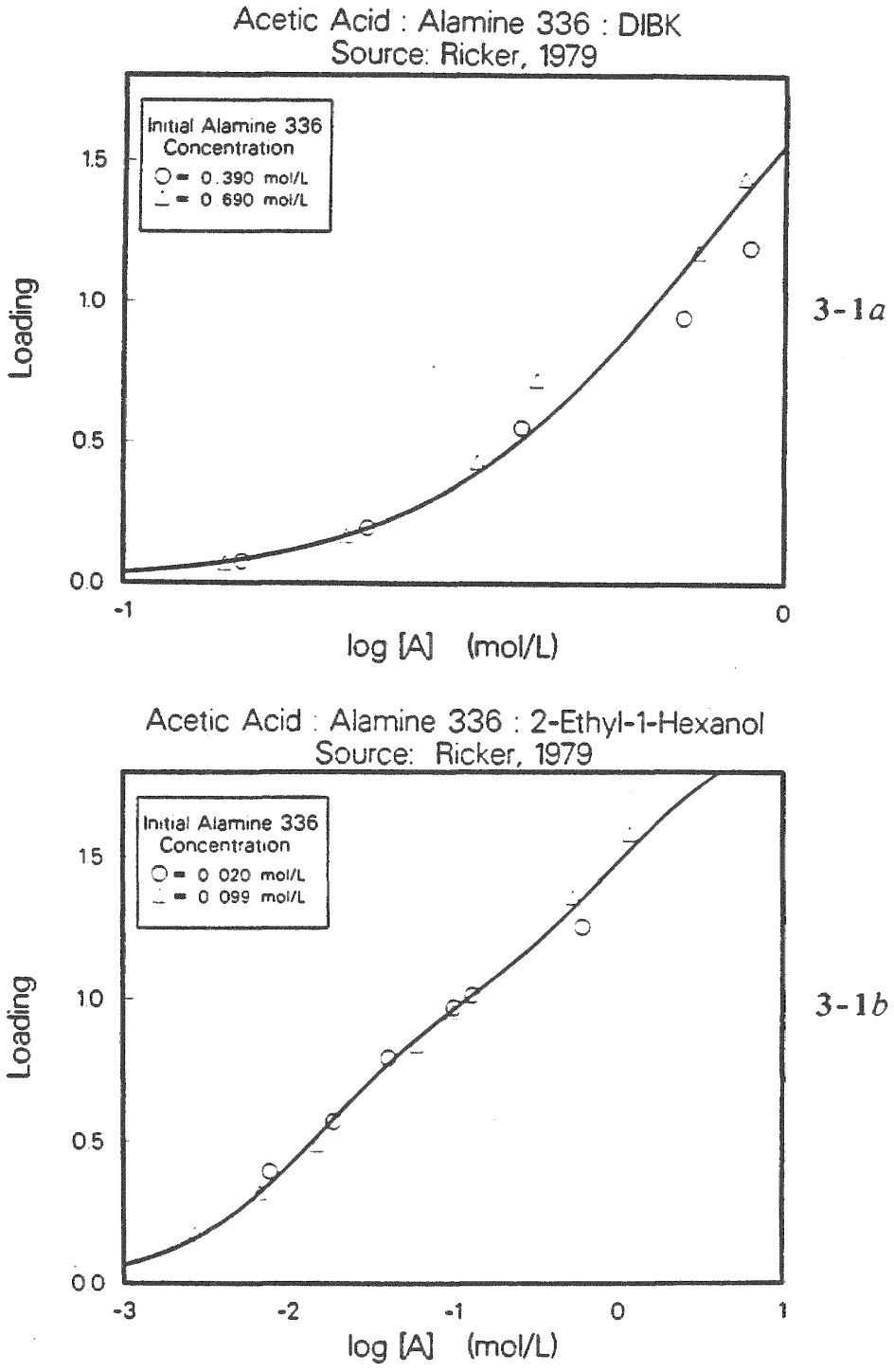
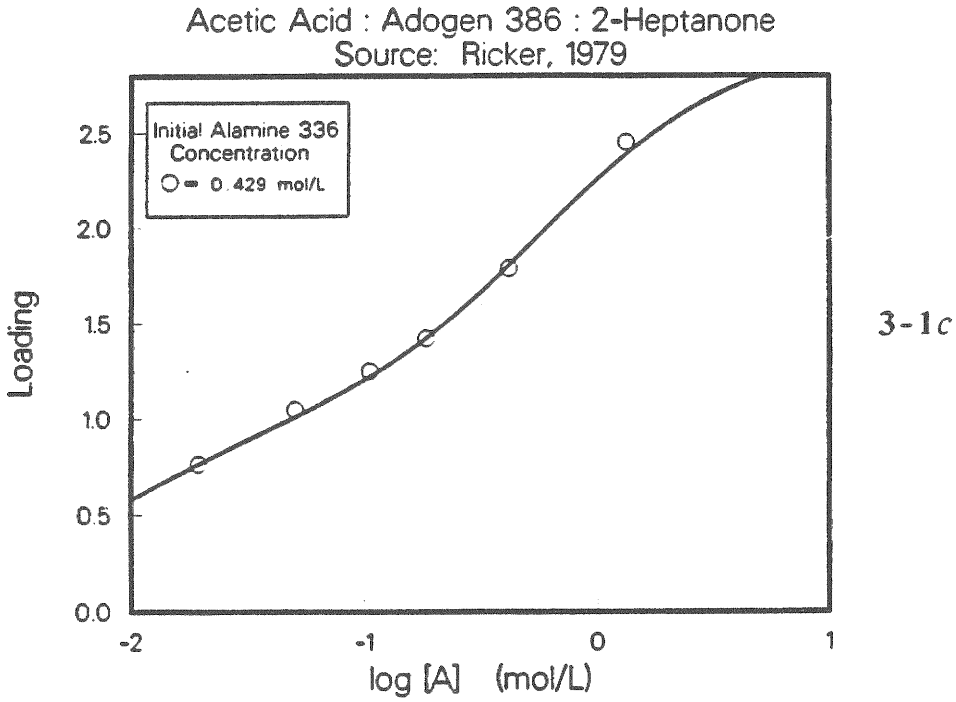
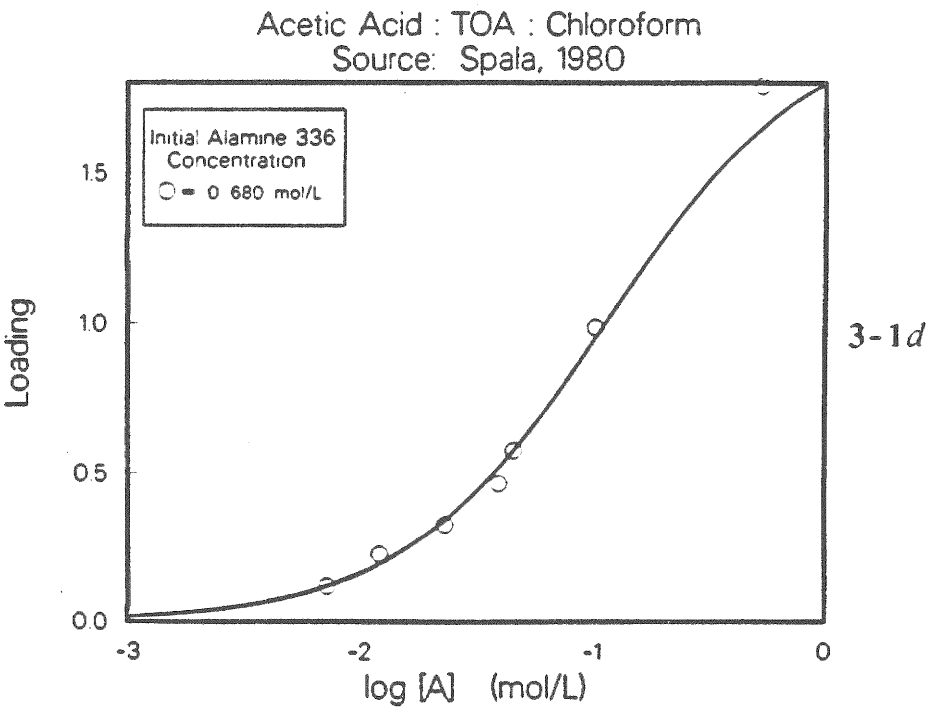


Fig. 3-1. Loading Curves for the Extraction of Acetic Acid by Amines in Various Diluents.

Diluent/Amine: (*a*) diisobutyl ketone/Alamine 336; $\log(\beta_{11})$ =-0.28, $\log(\beta_{21})$ = 0.25
(*b*) 2-ethyl-1-hexanol/Alamine 336; $\log(\beta_{11})$ = 1.83, $\log(\beta_{21})$ = 1.82



3-1*c*



3-1*d*

Fig. 3-1. Loading Curves for the Extraction of Acetic Acid by Amines in Various Diluents (cont'd).

Diluent/Amine:

(*c*) 2-heptanone/Adogen 283; $\log(\beta_{11}) = 2.09$, $\log(\beta_{21}) = 2.59$, $\log(\beta_{31}) = 2.53$

(*d*) chloroform/trioctylamine; $\log(\beta_{11}) = 1.25$, $\log(\beta_{21}) = 1.90$

Spala (1980) performed related experiments on the extraction of acetic acid by trioctylamine (TOA) in chloroform at 0.68 and 1.7 mol/L of amine. Results for the lower amine concentration are shown in Fig. 3-1*d*. Loading was reduced at the higher amine concentration. Overloading of the extractant was again evident.

A comparison of the available acetic acid data shows that acetic acid at low concentrations was extracted by tertiary amines from most to least in the diluent order: 2-ethyl-1-hexanol > chloroform > nitrobenzene > benzene > xylene > DIBK > 15% (v/v) chloroform in *n*-heptane = carbon tetrachloride > heptane = hexane, assuming that the slight difference in extractant chain length had negligible effect on the extraction. The active diluents generally showed (1,1) equilibrium constants which were one to two orders of magnitude greater than those for the inert diluents. All systems showed overloading of the amine by acetic acid. But, the alcohol and chloroform show more stabilization of the (1,1) complex relative to (2,1) or (3,1) complexes than do the ketone and the less active diluents.

For the active diluents, increasing amine concentration brought about a decrease in loading, whereas for the alkane and simple aromatic diluents, there was no effect of amine concentration on loading, even at fairly high amine concentrations. This is consistent with the concept of diluent interaction with the complex. The less active diluents are relatively similar to the amine in solvating ability for the complex, and thus the amine concentration should have little effect upon loading. The more active diluents solvate the complex, and as amine concentration increases, the solvent solvating capacity decreases.

3.3.2 Acetic Acid Derivatives

Soldatov and Manenok (1979) examined the extraction of monochloroacetic acid by tribenzylamine (TBA) in several diluents. Extracting power decreased in the order methylene chloride > chloroform > benzene > toluene > *o*-xylene > carbon tetrachloride > hexane (precipitate of composition A_2B forms). Overloading was apparent in the methylene chloride and chloroform diluents; the overloading region could not be examined for the other diluents because the degree of extraction was quite low. The authors reported than an investigation of the effect of amine concentration (0.1, 0.5, and 2.0 mol/l) showed that the extraction of monochloroacetic acid is independent of amine concentration. However, no data to this effect were presented, and it was not stated on which systems these experiments were performed.

Soldatov et al. (1978) analyzed the extraction of trichloroacetic acid by tribenzylamine (TBA) in a variety of diluents. The extent of extraction was substantially greater for trichloroacetic acid than for monochloroacetic acid in comparable solvent systems. In all of the diluents, except for chloroform, there was a precipitate formed during the extraction, unlike for monochloroacetic acid, which showed precipitate formation only in the alkane diluent. In all cases, overloading of the amine was evident. (Loading was considered as the total amount of acid in both the precipitate and the bulk organic phase.) It is interesting that no precipitate was reported in the trichloroacetic acid-TLA-xylene systems of Kuca and Högfeldt (see below), presumably because of the difference between the aliphatic groups of trilaurylaminė and the aromatic groups of tribenzylamine.

An intriguing finding from the work of Soldatov et al. was that the effect of diluent on extractability of the acid differed between overloaded and non-overloaded

extractant. For the non-overloaded extractant, the authors found the total acid extractability decreased in the series: hexane-octane > chloroform > mesitylene > *o*-xylene > carbon tetrachloride = benzene. On the other hand, for the region where loading exceeded unity, the extractability series was almost reversed: benzene > chloroform > *o*-xylene > mesitylene > hexane-octane. Solubility of dried precipitate of the (1,1) salt in dry organic diluent decreased in the series: chloroform > benzene > *o*-xylene > carbon tetrachloride > mesitylene > hexane, and the solubilities of (2,1) and (3,1) dried precipitates were in the order: chloroform > benzene > *o*-xylene > mesitylene ≥ carbon tetrachloride > hexane. Increasing the number of methyl groups on an aromatic ring from benzene to xylene to mesitylene decreases the solvating ability of the solvent, presumably because of the increasing alkane character of the solvent.

The authors explained the reversal in extractability qualitatively as a compromise between different positive effects on total acid extraction that occur with high and low solvating power of the diluent. Low solvating power of the solvent favors precipitate formation and thus accommodates high extractant loading in the form of precipitate. On the other hand, high solvating power of the solvent favors high loadings of unprecipitated acid. So the total extraction is a combination of the precipitate and dissolved complex.

It is also noteworthy that the order of solvating power of the solvents for the dried trichloroacetic acid-amine precipitates corresponds to the order of extracting power of the diluent-extractant for monochloroacetic acid. That is, if it is assumed that diluent solubilization of mono- and trichloroacetic acid salts is similar, the solubility of dried precipitate in a given solvent indicates the solvating power and hence extracting power of a diluent-extractant system.

Kuca and Högfeldt (1967) investigated the extraction of trichloracetic acid by trilaurylamine (TLA) in *o*-xylene in great detail. Activity coefficients of the aqueous acid and water were calculated from freezing point data. Extraction by the diluent alone was determined experimentally, and used to calculated the corrected loading. Data for several amine concentrations, from 0.0154 to 0.161 mol/L TLA, were obtained. No effect of amine concentration was observed, and overloading was evident. The plotted results of Z vs. log[A] showed clear plateaus at Z = 1 and Z = 2, indicating the formation of stable (1,1) and (2,1) complexes. The authors used the computer program LETAGROPVRID to calculate the (1,1) and (2,1) equilibrium constants. The values they determined for the constants, 6.93 and 9.44, are large, probably related to the high acidity (pK_A = 0.5) for trichloroacetic acid.

3.3.3 Other Monocarboxylic Acids

Kawano and co-workers (1982, 1983*a,b*) studied the extraction of propionic acid by Amberlite LA-2, an aliphatic secondary amine, in *n*-hexane and benzene at an amine concentration range of 0.05 to 0.20 mol/l, and by trioctylamine (TOA) in hexane. Loading appeared to reach or exceed three in all cases. The formation constants calculated by Kawano et al. are shown in Table 3-2. As with the other monocarboxylic acids in alkane or aromatic diluents, significant (2,1) and (3,1) formation constants, relative to the (1,1) formation complex, are seen. The secondary amine showed significantly higher equilibrium constants than the tertiary amine.

Kawano and co-workers also studied the extraction of formic acid by Amberlite LA-2 in *n*-hexane and benzene. Formic acid behaves quite differently than other monocarboxylic acids. Loading increases with increasing amine concentration. The

authors described this effect by including (1,2) complexes into their system.

Sato et al. (1985) studied the extraction of lactic acid by 0.1 to 1.0 mol/L trilaurylamine (TLA) in xylene. Data from their studies were analyzed in the present work (see Table 3-2). Results are shown in Fig. 3-2. The lactic acid system showed no effect of amine concentration on loading, and overloading of the acid was considerable. The extraction of lactic acid could be modeled by a simple (1,1), (2,1), and (3,1) model. Extraction was considerably less than extraction using chloroform or MIBK as the diluent.

Manenok et al. (1979) performed studies for a variety of acids, including valeric, formic, and benzoic acids, extracted by trilaurylamine (TLA) in chloroform and benzene. Overloading was noted in all cases. Marked upward concavity of the curves was noted in benzene. No attempt was made to fit the data to any model, so the concavity could be from extensive overloading or from aggregation.

3.3.4 Aromatic Monocarboxylic Acids

Puttemans and co-workers (1985, 1984*a,b,c*) performed a series of studies of the influence of a number of factors -- pH, ionic strength, competition with strong acids, amine and acid concentration, and organic phase composition -- on the extraction of benzoic acid, its hydroxylated derivatives, and various dyes, with tri-*n*-octylamine (TNOA).

In the first set of experiments (Puttemans et al, 1984*a*), the extraction of 5×10^{-5} mol/L aqueous acid solutions of benzoic, salicylic, 3-hydroxybenzoic, 4-hydroxybenzoic, 3,4-dihydroxybenzoic, and 2,5-dihydroxybenzoic acids with 0.1 mol/L

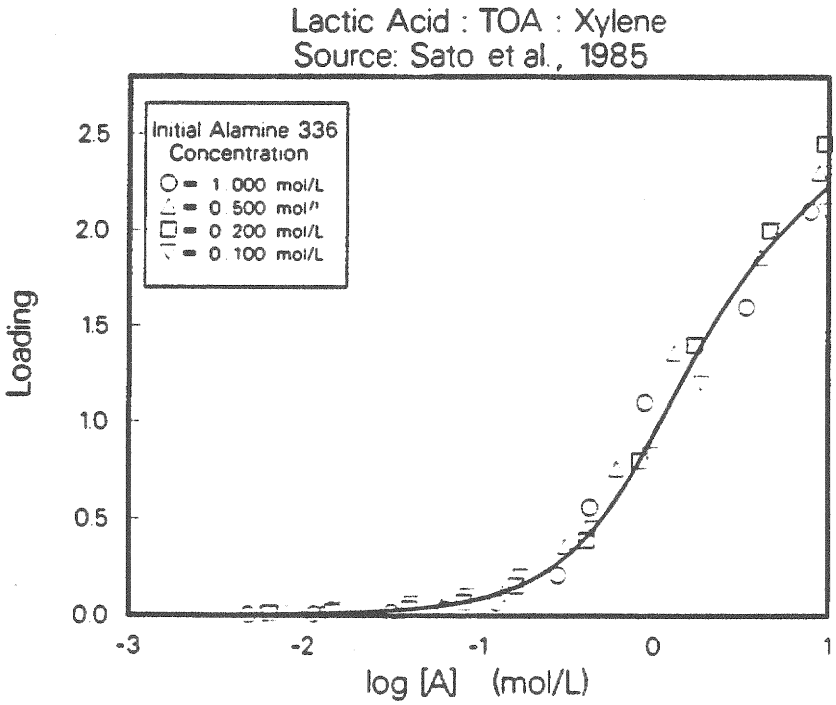


Fig. 3-2. Loading Curve for the Extraction of Lactic Acid by Trilaurylamine in Xylene.

$\log(\beta_{11})$ =-0.11, $\log(\beta_{21})$ =-0.12, $\log(\beta_{31})$ = -1.42

TNOA in chloroform was studied at an ionic strength of 0.1 mol/L and various pH values. The pH was controlled with a phosphate buffer. Results were presented as a plot of percent of acid extracted vs. pH.

Correction for extraction by the diluent alone was accomplished by subtracting the value of percent extraction from data on extraction by the diluent alone from the total percent extraction at the pH of the data point. Unfortunately, this method of diluent correction is not meaningful under the conditions of the experiment because it does not use an appropriate driving force to correct for the diluent. That is, at the same pH, the diluent-correction experiment and amine-extraction experiment have different aqueous acid concentrations, and thus a different driving force for distribution of acid into the solvent. For example, salicylic and benzoic acids were essentially completely extracted at pH less than 5, where extraction by chloroform just begins to become significant. The authors subtracted extraction of 70-80% by chloroform alone from 100% by the amine system. The 0.1 mol/L amine almost certainly still had capacity for more extraction than 20-30% of the 5×10^{-5} mol/L of solute. Fortunately, extraction by chloroform alone was significant only for salicylic and benzoic acids.

In the plot of the results, percent extraction was low at high pH (where the acid is dissociated), increased sharply as pH decreased (as the concentration of undissociated acid rises), and decreased at low pH. For salicylic and benzoic acids, the decrease in corrected extraction occurred at relatively high values of pH, but this is probably an artifact of the correction procedure mentioned above. The pH at which the sharp increase in extraction occurred (an inflection point in the curve of percent extraction vs. pH) decreased in the order: salicylic, benzoic, 2,5-hydroxybenzoic, 3-hydroxybenzoic, 4-hydroxybenzoic, and 3,4-dihydroxybenzoic.

Except for the benzoic acid, this in order of increasing pK_A. That is, greater acid extractability, which corresponds to an inflection at higher pH, corresponds to greater acidity of the acid. The exception is benzoic acid, probably because of greater hydrophobicity due to its lack of hydroxyl groups. The authors did not comment on the decrease in percent extraction at high pH, but it is presumably attributable to competition by the buffering agent for the amine.

The authors examined the influence of ionic strength on the extraction of 3-hydroxybenzoic, 4-hydroxybenzoic, and 3,4-dihydroxybenzoic acids by TNOA in chloroform. As the ionic strength of the aqueous solution increased from near zero to 0.5 mol/L, the distribution ratio decreased, reached a minimum, and then increased. The authors explained the initial decrease in distribution ratio as a decrease in aqueous phase activity coefficients with increasing in ionic strength. At high ionic strengths, they concluded that the free volume of water is reduced because ions are hydrated, causing the activity coefficients of the acids to increase.

The second paper (Puttemans et al., 1984*b*) reported back-extraction of benzoic and sorbic (2,4-hexadienoic) acids, and amaranth and quinoline yellow, two food dyes, from TNOA-chloroform solutions with sodium salts of chloride, bromide, iodide, nitrate, and perchlorate. For most of the substances investigated, displacing ions back-extracted with increasing effectiveness in the order: chloride < bromide < iodide < perchlorate. The authors reported that this is the same order as extractability of the strong acids by amine solutions. As expected, the acid which is extracted more easily by the amine solution is a better competitor for association with the amine in the displacement reaction. Nitrate differed in its displacing ability, depending on the carboxylic acid displaced. This may be because nitric acid shows complicated behavior patterns in extraction experiments, such as substantial overloading. A good review of

the extractability of strong mineral acids is given by Shmidt (1971).

The effect of acid and amine concentration in the extraction of penicillins, benzoic acid and hydroxyl derivatives, and other acids by TNOA in chloroform was the subject of the third paper (Puttemans, 1984*c*). The authors used a graphical analysis, which assumed the existence of either (1,1), (1,*n*), or (*m*,1) complexes, to determine equilibrium constants. An extensive tabulation of their results was provided in the paper. The (1,1) complex formation constant was compared with a hydrophobicity parameter for various classes of solutes.

The final paper (Puttemans et al., 1985) examined mixtures of hexane and chloroform, methylene chloride, MIBK, butyl acetate, and pentanol used as diluents for amine extractants in the extraction of tartrazine, amaranth, and patent blue. As the volume percent of active diluent increased from 0 to 100%, the distribution ratio increased. Extraction decreased in the diluent order: dichloromethane > chloroform > MIBK > butyl acetate > hexane.

The authors examined extraction with a diluent mixture of chloroform with an alcohol modifier to "combine the solvating effects of both solvents". 4-Hydroxybenzoic and 2,4-dihydroxybenzoic acids were extracted by TNOA in a mixture of chloroform and pentanol. As the volume percent of pentanol in chloroform increased from 0 to 20%, the percent extraction increased. Patent blue was extracted by TNOA in mixtures of chloroform and pentanol. Extraction increased with increasing pentanol concentration. The authors concluded that the pentanol had "modified" the chloroform to increase the extraction.

These results should not be taken as implication that chloroform with an alcohol

modifier somehow combines the solvating powers of each diluent to produce a superior diluent. Rather, the effect is probably an averaging of the high solvating powers of each diluent. Alcoholic diluents, in general, promote extremely high acid extraction. In the experiments of Puttemans et al., addition of the alcohol to the chloroform most likely increased extraction because the alcohol alone as a diluent promoted extraction more than did chloroform at the concentration of the acid used. Furthermore, it is unclear how increased phase miscibility from the highly water-soluble pentanol may have affected the distribution. Additional evidence is in the present work, shown below in Fig. 3-3*b*, which shows the extraction of succinic acid by Alamine 336 in an octanol-chloroform mixture, as compared with chloroform and octanol alone. The mixture results lie almost directly in between the results for chloroform and octanol alone.

Reschke and Schügerl (1984*a*,*b*) performed a detailed analysis of factors which affect the extraction of penicillins G and V and phenylacetic and phenoxyacetic acids (precursors to biological production of penicillins G and V, respectively) by Amberlite LA-2 and other amines in various diluents. The authors examined the effect of pH, amine concentration, amine type, and diluent type and modeled the results with mass-action law equilibrium expressions. Secondary amines extracted more acid than the tertiary amines studied. Extraction decreased in the diluent order: chloroform > *n*-butyl acetate > isobutyl acetate > isoamyl acetate, > xylol > diisopropyl ether > dioctyl ether > kerosene. Penicillin V (pK_A = 2.70) was extracted more efficiently than penicillin G (pK_A = 2.75), both by physical extraction into the diluent alone and by complexation with amines. Phenoxyacetic acid (pK_A = 3.14) was extracted more readily than phenylacetic acid (pK_A = 4.28).

3.3.5 Dicarboxylic Acids

Manenok et al. (1979) also examined the extraction of several dicarboxylic acids by trilaurylamine (TLA) in various diluents. For oxalic acid the extraction decreased in the diluent order: chloroform > chlorobenzene > toluene > mesitylene > *n*-heptane, which corresponded to the decreasing solubility of the dried precipitate into the solvents. Extraction of oxalic acid by amine in heptane resulted in extensive precipitate formation. Extractability of acids by TLA using a benzene diluent was in the sequence: oxalic > malonic > adipic > succinic > glutaric, which, with the exception of adipic acid, corresponds to decreasing acidity as measured by pK_A. The adipic acid loading curve shows pronounced upwards concavity, possibly indicating aggregate formation. Extractability of acids by TLA in chloroform diluent was in the order: oxalic > succinic > glutaric, again in the order of decreasing acidity as represented by pK_A. Extraction of phthalic acid by TLA in chloroform and in benzene was greater than that of the aliphatic dicarboxylic acids, although its pK_A lies between that of succinic and oxalic. The greater hydrophobicity of phthalic acid probably confers its high extractability compared to the other acids studied.

Manenok et al. calculated equilibrium constants by graphical means for (1,1) complex formation of succinic acid in chloroform and benzene, oxalic acid in chloroform, glutaric acid in benzene, and phthalic acid in chloroform, benzene, and heptane. Their results are shown in Table 3-2. The authors assumed (1,1) complex formation and plotted $Z/(1-Z)$ vs. [A] to determine equilibrium constants. Close examination of the data for succinic and glutaric acids in benzene reveals that the relationships may be slightly curved, rather than linear. This would suggest that the complex formation for succinic and glutaric acids in benzene is not simply (1,1). Whether or not there is curvature cannot be confirmed because of the low level of

acid extraction.

Qualitative inspection of the data of Manenok et al. yields a number of interesting results. The authors concluded that no overloading occurred for any of the dicarboxylic acids studied, which included oxalic, malonic, succinic, and phthalic acids, in diluents which included chloroform, *n*-heptane, benzene, and toluene. However, monocarboxylic acids, including formic, valeric, and benzoic, showed overloading in chloroform and benzene. The authors thus concluded that dicarboxylic acids do not overload, while monocarboxylic acids do.

Vieux and co-workers (1974, 1977) extracted a homologous series of dicarboxylic acids -- oxalic, malonic, succinic, and glutaric -- with triisooctylamine (TIOA) in benzene, chloroform, *o*-dichlorobenzene, xylene, and 1,2-dichloroethane. No overloading was observed for the oxalic, malonic, and succinic acid systems. The glutaric acid system may have shown slight overloading of the amine, but this is difficult to determine from the data provided. Acid extractability using benzene diluent decreased in the sequence: malonic > succinic > glutaric; using 1,2-dichloroethane diluent gave oxalic > succinic; and using o-dichlorobenzene gave oxalic = malonic > succinic > glutaric. These orders correspond to decreasing acidity of the acids, which accompanies increasing chain length. Solvating ability of the diluent was in the order: chloroform > 1,2-dichloroethane > *o*-dichlorobenzene > benzene > xylene.

Two methods of graphical analysis were used to determine that (1,1) stoichiometries modeled the system equilibrium -- the isomolar series approach and a plot of log(D) vs. log[B]. On the basis of these graphical methods, Vieux and co-workers reported that (1,1) stoichiometry was consistent with their results for all the systems they studied. However, results reported by Sato et al. (1985) (see below) for

succinic acid extraction by trilaurylamine in xylene diluent strongly counterindicate (1,1) stoichiometry. Their results show a marked increase in loading with increased amine concentration. Also, as mentioned above, close examination of the Z/(1-Z) plot of Manenok et al. for succinic acid in benzene shows possible curvature, which also is contrary to exclusive (1,1) complex formation. Therefore, it is probable that in benzene, xylene, and other inert diluents careful examination of several amine concentrations would reveal aggregation behavior.

Table 3-2 shows the apparent equilibrium constants which were determined in this work from the graphs presented by Vieux et al. (1974, 1977), assuming that (1,1) stoichiometry was a valid approximation for the systems. Although these may not represent actual system stoichiometries, they give a quantitative estimate of the relative extractabilities of the acids. It was not possible to resolve the data from the paper precisely enough to carry out computerized fitting calculations.

Comparing the available data for succinic acid extracted by tertiary amines at low acid concentration, the extraction decreases in diluent order: octanol > nitrobenzene = methylene chloride > chloroform > 1,2-dichloroethane > MIBK > *o*-dichlorobenzene > benzene. The order is similar to that for acetic acid, except that the order of nitrobenzene and chloroform is reversed.

3.3.6 Hydroxycarboxylic Acids

Wennersten (1983) investigated the extraction of citric acid by Alamine 336 and TLA in a wide variety of diluents. Three systems were studied in detail--Alamine 336 in Isopar H, a paraffinic kerosene (1:1, v/v), Alamine 336 in Isopar H and MIBK (2:1:1, v/v), and Alamine 336 in *n*-butyl chloride (1:1, v/v). The systems were

too highly non-ideal to allow for reliable modeling by a mass-action-law approach. Extracting power of the diluent decreased in the order MIBK-Isopar H = *n*-butyl chloride > Isopar H.

Vanura and Kuca (1976) performed a detailed study on the extraction of citric acid by trilaurylamine in toluene. Aqueous-phase activities were controlled through use of an isomolar combination of sodium citrate and citric acid. By means of LETAGROP, an error minimization program, the equilibrium constants for various stoichiometries were calculated, and specific reaction stoichiometry was assigned. For comparison, the authors' raw data were analyzed by the computer program developed in this work, and essentially identical results were obtained (see Appendix B). No overloading was evident, and extraction decreased with increasing amine concentration. A set of complexes of stoichiometry (1,2), (2,3), and (5,6) were found to fit the data best. The authors also developed a model that included water in the complex, which described data where aqueous acid activities were not kept constant.

Sato et al. (1985) studied the extraction of succinic, tartaric, and citric acids by 0.05 to 1.0 mol/l TLA in xylene. Data from their studies were used in mass-action-law calculations made in this work. As mentioned above, the lactic acid system showed no effect of amine concentration on loading, and significant overloading. In contrast, the di- and tricarboxylic acid systems all showed a marked increase in loading with increased amine concentration. No overloading was evident. Sets of complexes with the general form $(p,q) = (1,2), (i,i+1), (j,j+1)$ seem to fit the data best, although no specific "best" stoichiometry could be determined. Acid extractability decreased in the order: citric > tartaric > succinic, corresponding to increasing pK_A.

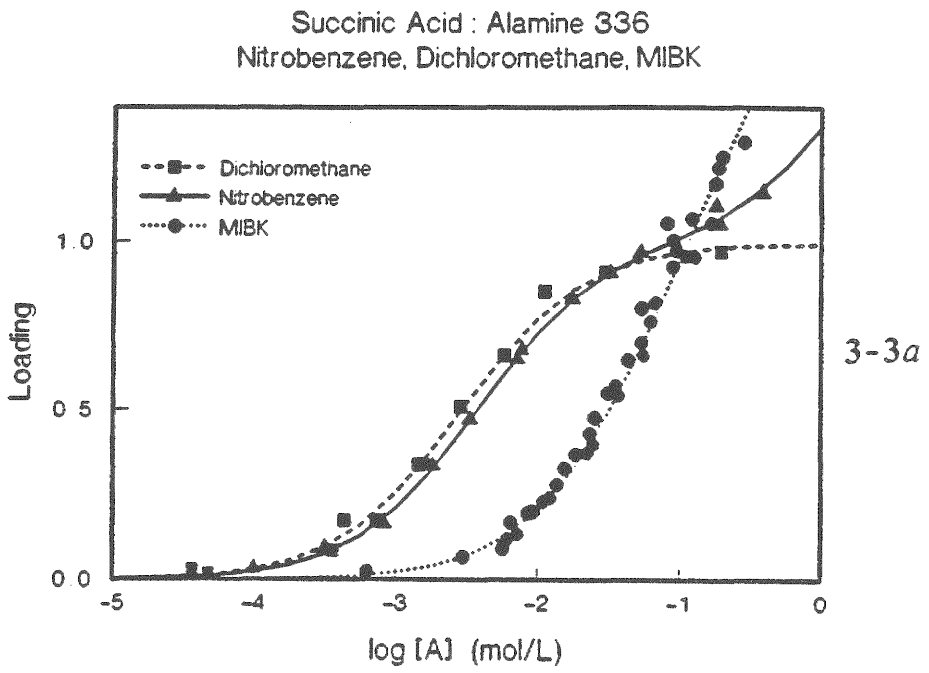
3.4 Summary and Conclusions

To enable easier comparison of different systems, replotted data for several carboxylic acid-amine-diluent systems are provided. The first set of plots show the effect of different diluents on the same acid; the second set shows how acids differ in behavior in the same diluent. Data are from the present work unless otherwise indicated.

Fig. 3-3 compares the extraction of succinic acid by Alamine 336 in (*a*) methylene chloride, nitrobenzene, and MIBK and (*b*) chloroform, octanol, and an octanol-chloroform mixture. Fig. 3-4 compares the extraction of acetic acid by Alamine 336, TOA, or TLA in (*a*) 2-ethyl-1-hexanol (Ricker, 1978), chloroform (Ricker, 1978), nitrobenzene, and DIBK (Ricker, 1978), and (*b*) benzene (Chaikhorskii et al, 1966), carbon tetrachloride (Chaikhorskii et al., 1966), and 15% (v/v) chloroform in heptane. Fig. 3-5 compares the extraction of lactic acid by Alamine 336 in chloroform, MIBK, and xylene (Sato et al., 1985). Figure 3-6 compares the extraction of succinic and acetic acids by Alamine 336 in nitrobenzene. Fig. 3-7 compares the extraction of (*a*) maleic and succinic acids and (*b*) fumaric (Starr, 1988) and lactic acids by Alamine 336 in MIBK and acetic acid in DIBK (Ricker, 1978). Fig. 3-8 compares the extraction of (*a*) maleic and succinic acids and (*b*) acetic, lactic, and fumaric acids in chloroform.

The following points summarize some of the trends found in the survey of carboxylic acid extraction literature:

1. Overloading of the Extractant. Formation of complexes with more than one acid per amine is the usual behavior for monocarboxylic acids. For the most part,



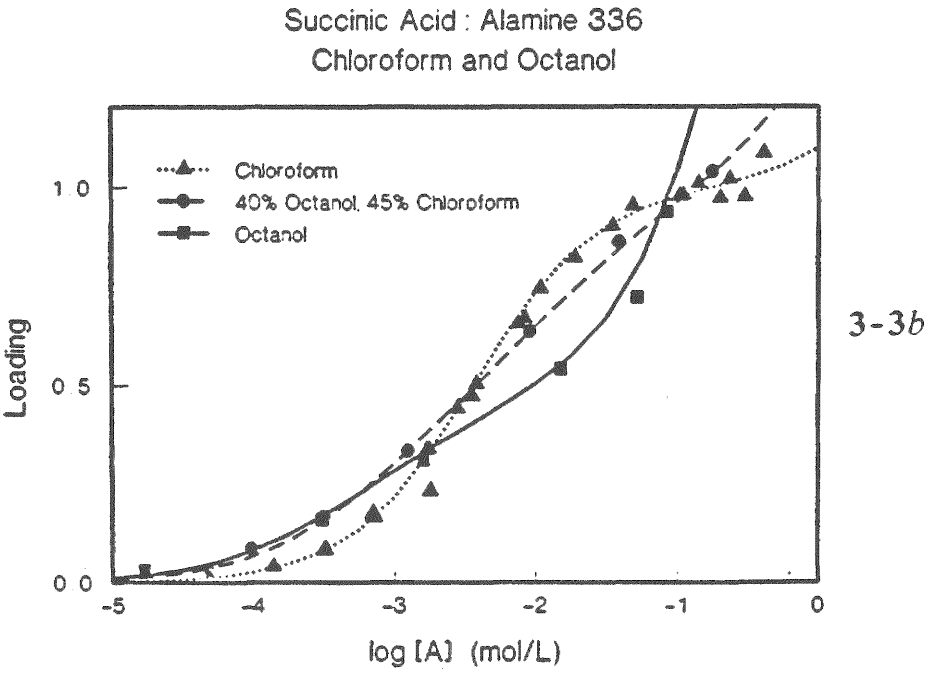
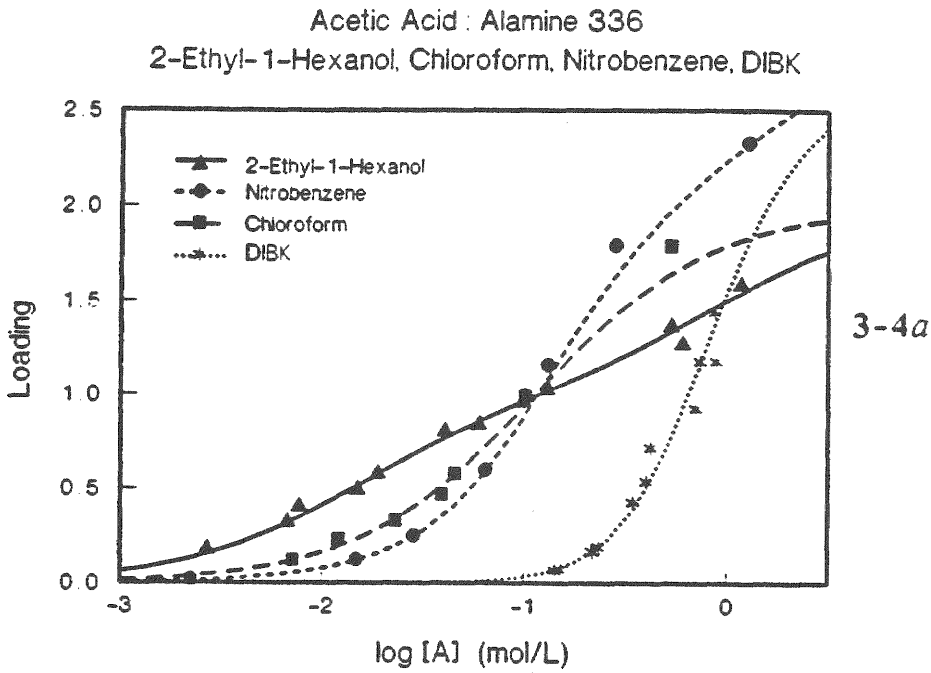


Fig. 3-3. Comparison of the Extraction of Succinic Acid by Alamine 336 in Various Diluents.

Diluent: (*a*) nitrobenzene, methylene chloride, and methyl isobutyl ketone
(*b*) chloroform, 40% (*v*/v) 1-octanol and 45% (*v*/v) chloroform, 1-octanol



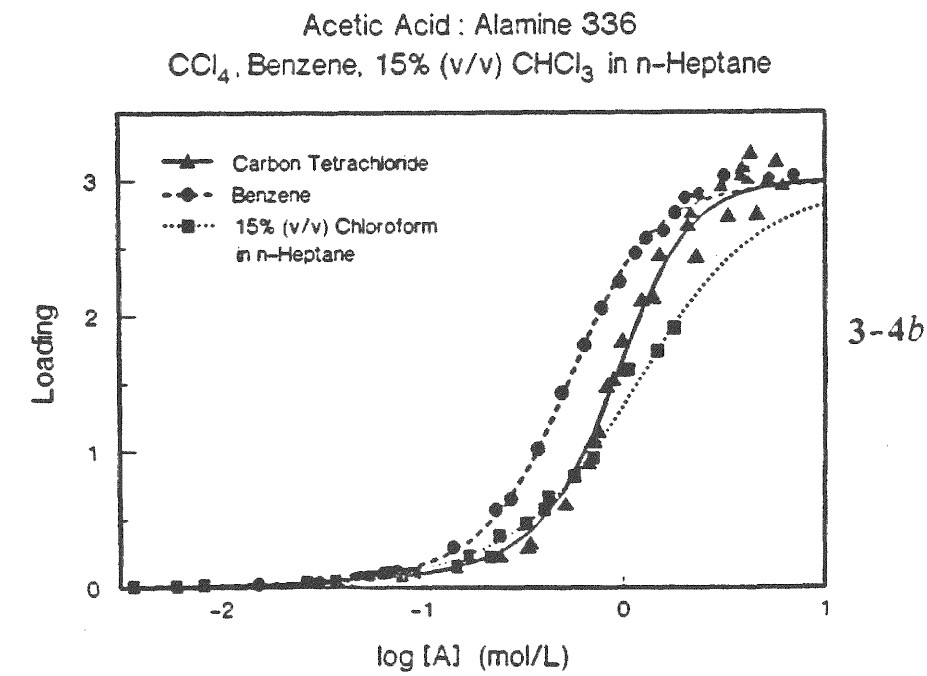


Fig. 3-4. Comparison of the Extraction of Acetic Acid by Tertiary Amines in Various Diluents.

Diluent/Amine: (*a*) 2-ethyl-1-hexanol/Alamine 336, nitrobenzene/Alamine 336, chloroform/TOA, and diisobutyl ketone/Alamine 336 (Ricker, 1978)

(*b*) carbon tetrachloride/TLA, Benzene/TLA, and 15% (v/v) chloroform in heptane/Alamine 336 (Chaikhorskii et al., 1966)

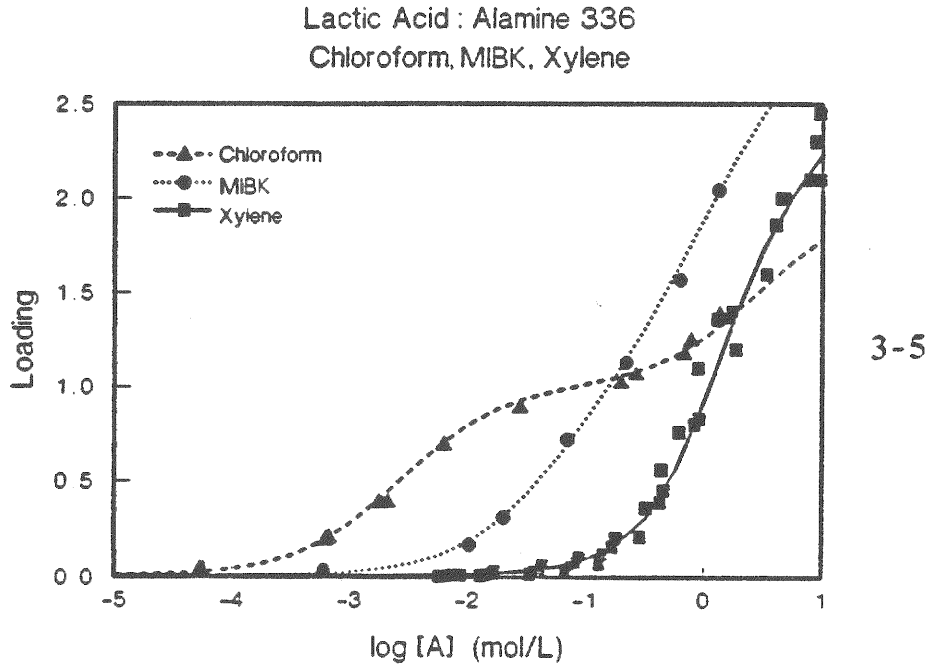


Fig. 3-5. Comparison of the Extraction of Lactic Acid by Tertiary Amines in Various Diluents

Diluent/Amine: chloroform/Alamine 336, MIBK/Alamine 336, xylene/trilaurylamine (Sato et al., 1985)

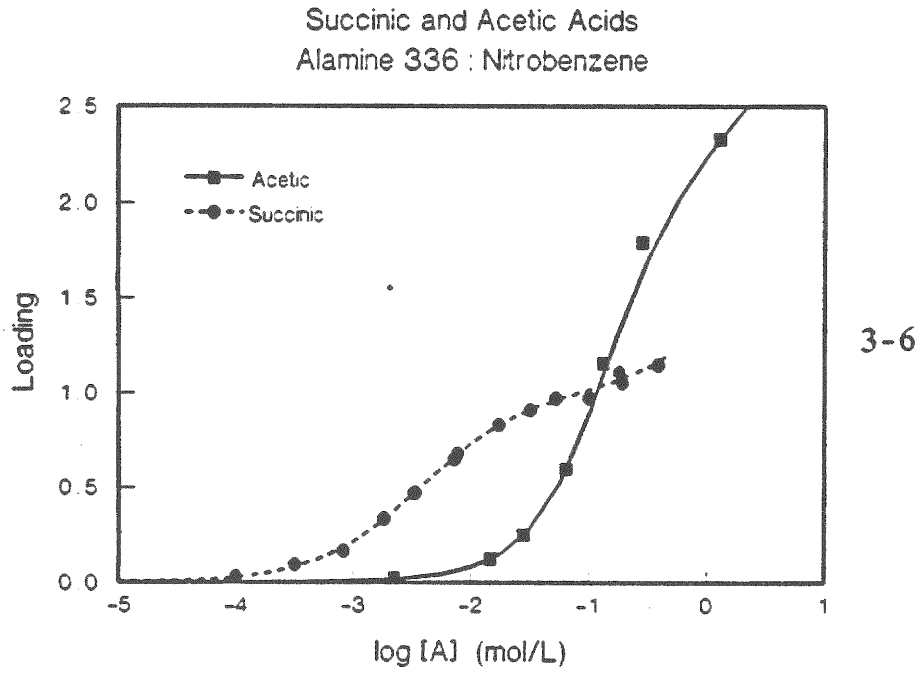
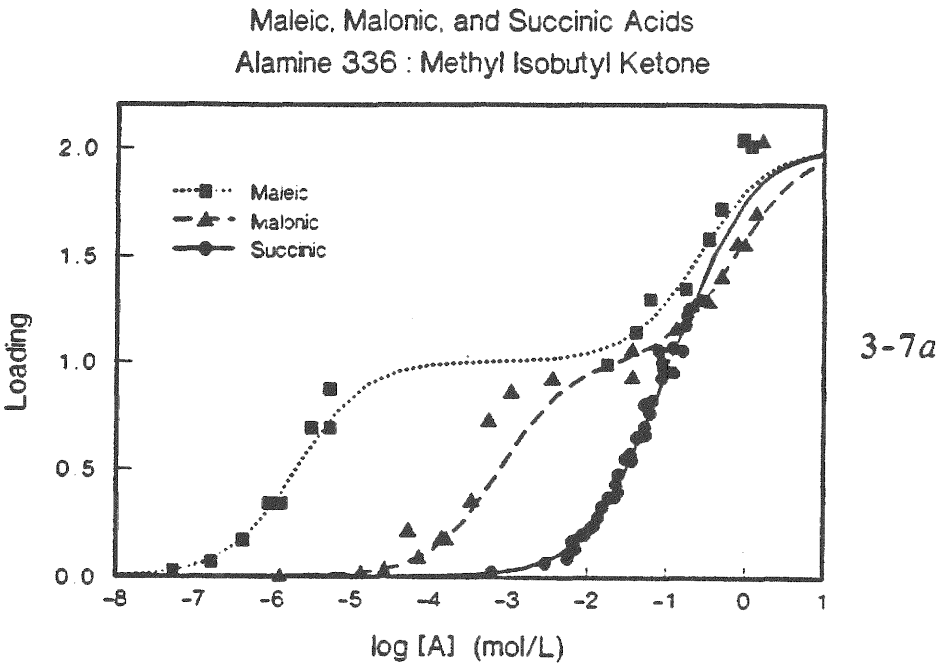


Fig. 3-6. Comparison of the Extraction of Acetic and Succinic Acids by Alamine 336 in Nitrobenzene.



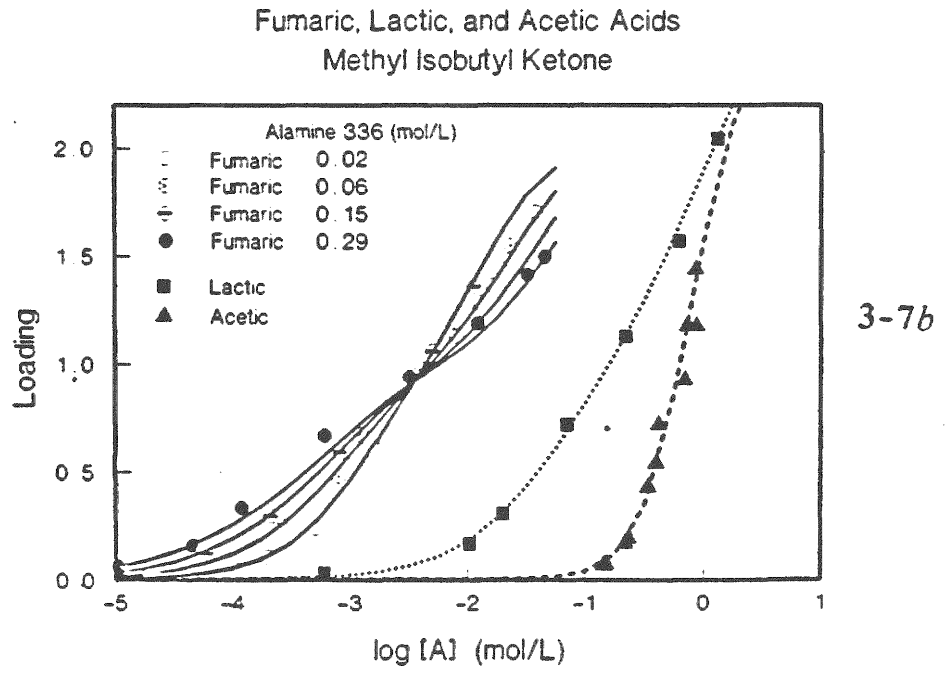


Fig 3-7. Comparison of the Extraction of Various Acids by Alamine 336 in Methyl Isobutyl Ketone.

Acid: (*a*) maleic, malonic, and succinic
(*b*) lactic and fumaric; acetic with diisobutyl ketone diluent (Ricker, 1978)

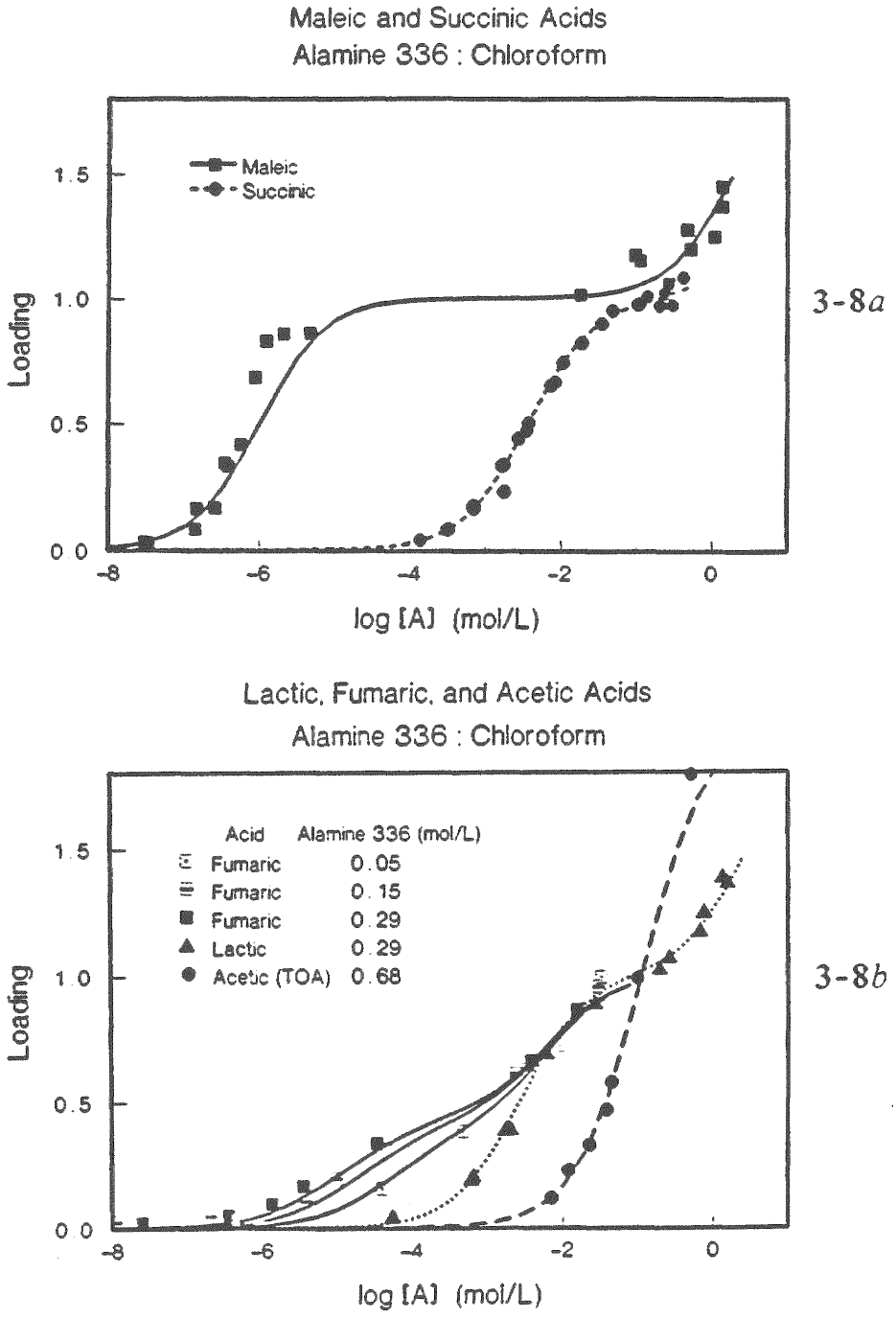


Fig. 3-8. Comparison of the Extraction of Various Acids by Alamine 336 in Chloroform.

Acid: (*a*) maleic and succinic
(*b*) fumaric, lactic, and acetic

dicarboxylic acid-amine-diluent systems do not show significant overloading behavior at the concentrations studied, although dicarboxylic acids in ketone diluents do overload significantly. The ratio of (1,1) to (2,1) complex formation is diluent dependent -- ketone diluents promote overloading and halogenated hydrocarbons inhibit overloading.

2. Number of Amines per Acid. At the concentrations studied in non-aggregating systems, there was no detectable formation of one acid to two amine complexes, as might be expected for dicarboxylic acids. Two significant exceptions were fumaric acid in chloroform and MIBK diluents and succinic acid in octanol diluent.

3. Extractability of the Acid. Generally, the more acidic the acid, as measured by pK_A, the more it is extracted, given the same solvent system. For acids with similar pK_A values, more hydrophobic acids are more readily extracted. Since the monocarboxylic acids studied show more tendency to overload, they often show higher extractability at high loadings, when compared to dicarboxylic acids of the same strength. Also, extractability of the acid is affected by amine concentration when multi-amine complexes are present, such as for systems of dicarboxylic acids in low-polarity diluents.

4. Effect of Diluent on Solvation of Complex. For most of the acids studied, the amount of solvation by the diluent decreases in the order: alcohol (e.g. 2-ethyl-1-hexanol) $\geq$ nitrobenzene $\geq$ halogenated hydrocarbon (e.g. methylene chloride, chloroform, 1,2-dichloroethane) > ketone (e.g. MIBK, DIBK) > halogenated aromatic (e.g. dichlorobenzene, chlorobenzene) > benzene > alkyl aromatic (e.g. toluene, xylene) > aliphatic hydrocarbon (e.g. hexane, heptane, octane).

5. Effect of Amine Concentration. When active diluents are employed, increasing amine concentration decreases the diluent concentration, and the solvent becomes a less favorable solvating medium for the polar complex. Thus, at a given aqueous acid activity, loading decreases with increasing amine concentration. For non-aggregating systems in inert diluents (monocarboxylic acids in alkane or aromatic diluents) there was no effect of amine concentration on loading. For aggregating systems (dicarboxylic acids in inert diluents) increasing amine concentration increased loading. A few non-aggregating systems -- fumaric acid in chloroform or MIBK, formic acid in hexane and benzene, and succinic acid in 1-octanol -- also showed increasing loading with increased amine concentration.

6. Aggregation. Amine complexes of di- and tricarboxylic acids show a much greater tendency to aggregate than do those of monocarboxylic acids. In fact, there was little overt aggregation behavior for any of the monocarboxylic acids studied, except in the form of precipitation. The more inert diluents, especially hexane, heptane, and octane, had a greater tendency to produce aggregation of the complexes, often with third-phase or precipitate formation.

The chemical interactions which lead to these behaviors are the subject of the next two chapters.

REFERENCES

(The three-letter abbreviations are those used in Tables 3-1, 3-2 and 3-3.)

BAN Baniel, A. M., Blumberg, R., and Hajdu, K., "Recovery of Acids from Aqueous Solutions", U.S. Patent No. 4,275,234, (Jun 23, 1981); *Chem. Abstr.* Vol. 97, No. 109557 (1982).

BUL Bullock, J. I., Choi, S. S., Goodrick, D. A., Tuck, D. G., and Woodhouse, E. J., "Organic Phase Species in the Extraction of Mineral Acids by Methyldioctylamine in Chloroform", *J. Phys. Chem.*, **68**, 2687-2696 (1964).

CHA Chaikhorskii, A. A., Nikol'skii, B. P., and Mikhailov, B. A., "Complex Formation in Nonaqueous Solutions X. Interaction of Tridecylamine with Acetic Acid", *Sov. Radiochem.* (Engl. Transl.), **8**, 152-158 (1966); *Radiokhimiya*, **8**, 163-171 (1966).

HÖG Högfeldt, E. and Fredlund, F., "Aggregation of Long-Chain Amine Salts Studied by Two-Phase EMF Titrations. Some Results for the Extraction of Acetic Acid by Trilaurylamine Dissolved in Heptane and o-Xylene", *Proc. Int. Solv. Ext. Conf. '66*, Gothenburg, Sweden, *Solvent Extraction Chemistry*, North Holland Publishing, Amsterdam (1967).

KAW1 Kawano, K., Kusano, K., Inoue, K., and Nakashio, F., "Extraction Equilibria of Aqueous Solution of Lower Carboxylic Acid (*sic*) with Benzene Solution of Long-Chain Alkylamine, Amberlite LA-2", *Kagaku Kogaku Ronbunshu*, 9(4), 473-475 (1983*a*).

KAW2 Kawano, Y., Kazushito, K., and Nakashio, F., "Extraction and Interfacial Adsorption Equilibria of Aqueous Acetic Acid and Propionic Acid with Tri-*n*-Octylamine in Hexane", *Kagaku Kogaku Ronbunshu*, 9(2), 211-213 (1983*b*).

KAW3 Kawano, Y., Kusano, K., Takahashi, T., Kondo, K., and Nakashio, F., "Extraction Equilibria of Lower Carboxylic Acids with Long-Chain Alkylamine", *Kagaku Kogaku Ronbunshu*, 8(4), 404-409 (1982).

Kertes, A. S. and King, C. J., "Extraction Chemistry of Fermentation Product Carboxylic Acids", *Biotechnol. Bioeng.*, **27**, 269-682 (1986).

KUC Kuca, L. and Högfeldt, E., "On Extraction with Long Chain Tertiary Amines VIII. Extraction of Trichloroacetic Acid and Water by Trilaurylamine Dissolved in *o*-Xylene", *Acta Chem. Scand.*, **21**, 1017-1027 (1967).

LIP Lipovskii, A. A. and Kuzina, M. G., "Infrared Spectra and Structure of Compounds Formed in the Extraction of Oxalic Acid by Solutions of Trioctylamine", *Sov. Radiochem.* (Engl. Transl.), **10**, 169-174 (1967); *Radiokhimiya*, **10**, 165-181 (1967).

MAN Manenok, G. S., Korobanova, V. I. Yudina, T. N., and Soldatov, V. S., "Influence of the Nature of the Solvent on Extraction of Certain Mono- and Dicarboxylic Acids by Amines", *Russ. J. Appl. Chem.* (Engl. Transl.), **52**, 156-160; *Zh. Prikl. Khim.* **52**, 173-183 (1979).

PUT1 Puttemans, M., Dryon, L., and Massart, D. L., "Extraction of Organic Acids by Ion-Pair Formation with Tri-n-Octylamine, Part 4. Influence of Organic Phase Composition", *Anal. Chim. Acta*, **178**, 189-195 (1985).

PUT2 Puttemans, M., Dryon, L., and Massart, D. L., "Extraction of Organic Acids by Ion-Pair Formation with Tri-n-Octylamine, Part 1. Extraction Rate and Influence of pH and Ionic Strength", *Anal. Chim. Acta*, **161**, 221-229 (1984*a*).

PUT3 Puttemans, M., Dryon, L., and Massart, D. L., "Extraction of Organic Acids by Ion-Pair Formation with Tri-n-Octylamine, Part 2. Back-extraction", *Anal. Chim. Acta*, **161**, 381-386 (1984*b*).

PUT4 Puttemans, M., Dryon, L., and Massart, D. L., "Extraction of Organic Acids by Ion-Pair Formation with Tri-n-Octylamine, Part 3. Influence of Counter-ion and Analyte Concentrations", *Anal. Chim. Acta*, **165**, 245-256 (1984*c*).

PYA1 Pyatnitskii, I. V., Tabenskaya, T. V., and Markachuk, T. L., "Effect of the Solvent on the Extraction of Citric Acid and the Iron Citrate Complex by Trioctylamine", *Russ. J. Anal. Chem.* (Engl. Transl.), **28**, 484-488 (1973); *Zh. Anal. Khim.*, **28**, 550-554 (1973).

PYA2 Pyatnitskii, I. V. and Tabenskaya, T. V., "Effect of the Nature of the Amine on the Extractability of the Iron Citrate Complexes", *Russ. J. Anal. Chem.* (Engl. Transl.), **25**, 2060-2064 (1970); *Zh. Anal. Khim.*, **25**, 2390-2395 (1970).

PYA3 Pyatnitskii, I. V. and Kharchenko, R. S., "Ekstraktsiya Citranova Compleksiya Zheleza f Prisytsvii Tri-n-butylamina (Extraction of Iron (III) Citrate Complexes in the Presence of Tri-*n*-Butylamine", *Ukraine Khim. Zh.*, **30**, 635-636 (1964).

RAT Ratchford, W. P. Harris, E. H., Jr., Fisher, C. H., and Willits, C. O, "Extraction of Lactic Acid from Water Solution by Amine Solvent Mixtures", *Ind. Eng. Chem. Eng. Process Dev.*, **43**, 778-781 (1951).

RES Reschke, M. and Schügerl, K., "Reactive Extraction of Penicillin. II: Distribution Coefficients and Degrees of Extraction", *Chem. Eng. J.*, **28**, B11-B20 (1984*a*).

Reschke, M. and Schügerl, K., "Reactive Extraction of Penicillin. I: Stability of Penicillin G in the Presence of Carriers and Relationships for Distribution Coefficients and Degress of Extraction", *Chem. Eng. J.*, **28**, B1-B9 (1984*b*).

RIC1 Ricker, N. L., Michaels, J. N., and King, C. J., "Solvent Properties of Organic Bases for Extraction of Acetic Acid from Water", *J. Sep. Proc. Technol.*, **1**(1), 36-41 (1979).

RIC2 Ricker N. L., "Recovery of Carboxylic Acids and Related Organic Chemical from Wastewaters by Solvent Extraction", Ph.D. Dissertation, Department of Chemical Engineering, University of California, Berkeley (1978).

ROF Roffler, S. R., "Extractive Fermentation", Quarterly Report, Section 3, The Center for Biotechnological Research, Department of Chemical Engineering, Berkeley, (June, 1984).

RÜC Rückl, W., Siebenhofer, M., and Marr, R., "Separation of Citric Acid from Aqueous Fermentation Solutions by Extraction-Reextraction Processes", *Proc. Int. Solv. Ext. Ion. Exch.* (ISEC '86), III-653-658, Dechema, Munich, Germany, (1986).

SAT Sato, T., Watanabe, H., and Nakamura, H., "Extraction of Lactic, Tartaric, Succinic, and Citric Acids by Trioctylamine", *Bunseki Kagaku*, 34, 559-563 (1985). Transl. provided by Polyglot Language Service, San Francisco.

Shmidt, V. S., "Chapter IV. Extraction of Acids", *Amine Extraction* (Engl. Transl.), Israel Program for Scientific Translations, Jerusalem (1971).

SME Smelov, B. C., Strakhova, A. V., "Ekstraktsiya Shchavelevoi Kisloti Trioktylaminom (Extraction of Oxalic Acid by Trioctylamine)", *Radiokhimiya*, 4, 509-510 (1963).

SOL1 Soldatov, V. S. and Manenok, G. S., "Extraction of Monochloroacetic Acid by Tribenzylamine Solutions", *Russ. J. Appl. Chem.* (Engl. Transl.), 52, 1764-1767 (1979); *Zh. Prikl. Khim.* 52, 1856-1860 (1979).

SOL2 Soldatov, V. S., Manenok, G. S., and Korobanova, V. I., "Distribution of Trichloroacetic Acid Between Aqueous Solutions and Solutions of Tribenzylamine in Organic Solvents", *Russ. J. Appl. Chem.* (Engl. Transl.), 51, 631-634 (1978); Zh. Prikl. Khim., 51, 646-651 (1978).

SPA Spala, E. E., "A Thermodynamic Model for Solvating Solutions with Physical Interactions", M.S. Thesis, Department of Chemical Engineering, University of Washington, Seattle (1980).

STA Starr, J. N., University of California at Berkeley, unpublished results (1988).

TAM Tamada, J., this work (1989).

VAN Vanura, P. and Kuca, L., "Extraction of Citric Acid by the Toluene Solutions of Trilaurylamine", *Collect. Czech. Chem. Commun.*, 41, 2857-2877 (1976).

VIE1 Vieux, A. S., Rutagengwa, N., Rulinda, J. B., and Balikungeri, A., Extraction of Some Dicarboxylic Acids by Tri-Isooctylamine", *Anal. Chim. Acta*, 68, 415-424 (1974).

VIE2 Vieux, A. S. and Rutagengua, N., "Extraction of Glutaric and Succinic Acids by Tri-Isooctylamine", *Anal. Chim. Acta*, 91, 359-363 (1977).

VIE3 Vieux, A. S., "No. 575 -- Sur l'extraction de l'acetate d'uranyle par la tri-iso-octylamine en solution dans des solvants organiques divers. (Note preliminaire)", *Bull. Soc. Chim. Fr.*, 9, 3364-3367 (1969).

WAR Wardell, J. M. and King, C. J., "Solvent Equilibria for Extraction of Carboxylic Acids from Water", *J. Chem. Eng. Data*, 23, 144-148 (1978).

WEN Wennersten, R., "The Extraction of Citric Acid from Fermentation Broth Using a Solution of a Tertiary Amine", *J. Chem. Technol. Biotechnol.*, 33B, 85-94 (1983).

WOJ Wojtech, B. and Mayer, M., "Synergistische Effekte bei der Extraktion mit Tertiaren Aminen", *Chem.-Ing.-Tech.*, 57(2), 134-136 (1985).

CHAPTER 4. INFRARED SPECTROSCOPIC STUDIES

The mass-action law calculations of Chapters 2 and 3 revealed interesting patterns for the effects of acid and diluent on the stoichiometries of the complexes and the magnitudes of the equilibrium constants. Unfortunately, the mass-action-law analysis is based on looking at only the net results of a complicated mixture of interactions. It may or may not give accurate information on the structure of the species present, depending on how closely the system actually obeys simple stoichiometric behavior. Spectroscopic studies provide independent evidence for the structure of species in solution, and thus can provide more fundamental understanding of the chemistry of extraction.

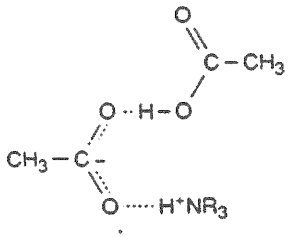
In this chapter some of the findings reported in the literature for IR, NMR, and UV spectroscopic studies on acid-amine systems are discussed. These studies have investigated the nature of the interactions among the carboxylic acid, amine, complexes, and diluent, which control the extraction equilibria. Additionally, an infrared spectroscopic investigation of dicarboxylic acids and Alamine 336 in chloroform was performed in this work. These experiments display the differences among maleic, fumaric, and succinic acids in their interactions with the amine.

4.1 Complex Stoichiometry

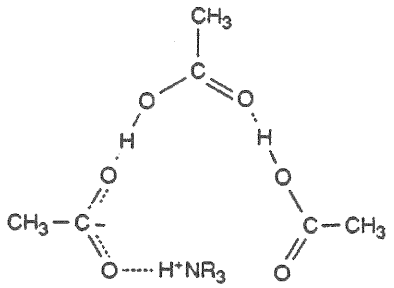
4.1.1 Number of Acids per Amine (Overloading)

A number of spectroscopic studies have confirmed the results from the mass-action-law analysis which indicate that monocarboxylic acids form complexes with

multiple acids per amine. The presence of both (2,1) and (1,1) acid-amine complexes for acetic acid and triethylamine in carbon tetrachloride and in chloroform was inferred from infrared spectroscopic data by Barrow and Yerger (1954). Greater detail of their study is given below in Section 4.2.1. They found that a conjugated -C-O group of the carboxylate (COO^-) group of the first acid, which is ion-paired with the amine, forms a hydrogen bond with the -OH of the carboxyl (COOH) group of the second acid (structure **4-1**). The findings of Smith and Vitoria (1968) on haloderivatives of acetic acid and tri-*n*-propylamine in carbon tetrachloride and chloroform, Duda and Szafran (1978) on haloderivatives of acetic acid and triethylamine in benzene, Detar and Novak (1970) on benzoic acid and triethylamine in chloroform, and Chibizov and Komissarova (1984) on octanoic acid and primary amines in benzene also support this type of bonding.



4-1. (2,1) complex
acetic acid - 3° amine



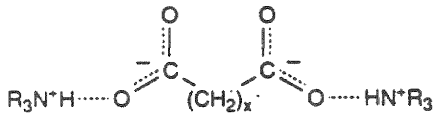
4-2. (3,1) complex
acetic acid - 3° amine

Chaikhorskii et al. (1966) studied the IR spectra of acetic acid and tridecylamine in carbon tetrachloride. The authors proposed an additional overloaded complex, structure **4-2**, in which one additional acid is complexed to form a cyclic arrangement around the amine nitrogen. This would be in agreement with the stable (3,1) complex observed in their batch extraction experiments (see Section 3.3.1).

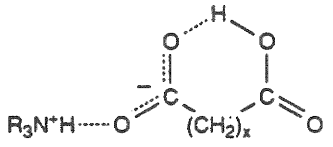
For either complex, the spectroscopic evidence has established that the first acid interacts directly with the amine, and the -OH of the succeeding acids interact with the conjugated -C-O of the acid before it.

4.1.2 Number of Amines per Acid

In Chapters 2 and 3 it was found that dicarboxylic acids tend not to form (1,2) complexes with tertiary amines (structure 4-3). Electrostatic attraction of the carboxylate anion for the second proton makes removal of the second proton much more difficult than that of the first for short-chain dicarboxylic acids (Roberts and Caserio, 1977). This may discourage formation of the neutralized (1,2) complex. Furthermore, there is the possibility that intramolecular hydrogen bonding (structure 4-4) plays an important role in discouraging (1,2) complex formation. It is known that dicarboxylic acids, especially malonic, succinic, and maleic acids, form intramolecular hydrogen bonds in organic solvents (Gusakova et al., 1986). The carboxylate group may compete with the amine for the proton of the second carboxyl group.



4-3. (1,2) complex for dicarboxylic acids



4-4. (1,1) complex with intramolecular hydrogen bonding for dicarboxylic acids

Gusakova et al. (1986) performed IR investigations of the interactions of malonic acid with a secondary and a tertiary amine in various solvents. In deuterated methanol, malonic acid formed (1,2) complexes in excess amine with both dibutylamine

and tributylamine. In chloroform, dioxane, and acetonitrile, malonic acid formed some (1,2) complex when excess dibutylamine was present. However, in these same solvents only (1,1) complexes were formed between malonic acid and tributylamine, even with a thirtyfold excess of the tertiary amine. The authors also concluded that intramolecular hydrogen bonding of the bimalonate occurred in the (1,1) complex in all of the solvents. On the other hand, Kabwe (1971) reported that malonic acid and triisooctylamine in chloroform produced both the (1,1) bimalonate salt and a (1,2) neutralized malonate. The author did not discuss the possibility of intramolecular hydrogen bonding.

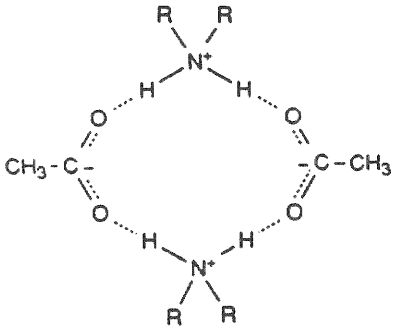
Lipovskii and Kuzina (1968) studied oxalic acid-trioctylamine complexes in carbon tetrachloride, benzene, and chloroform. They found that there was no evidence of the neutralization (1,2) product in carbon tetrachloride or benzene, although they did not study conditions with a large excess of amine. In chloroform, at a ten-fold excess of amine, complete reaction to the (1,2) product was observed. The authors further concluded that there was strong evidence that no intramolecular hydrogen bonding occurred in the oxalic acid systems. Bullock et al. (1964) found that oxalic acid formed almost stoichiometric (1,2) complexes with methyldioctylamine in chloroform.

There is quite a diversity of opinion on (1,2) complex formation. This diversity may result from experimental differences, such as the presence or absence of water in the system or the type of amine. Or, the diverse conclusions may be different interpretations of the spectra, as it is difficult to correlate unambiguously the peaks obtained from IR experiments with a particular chemical species. In an effort to clarify the issue of (1,2) complex formation and intramolecular hydrogen bonding, especially with respect to systems studied in this work, a brief IR investigation of fumaric, succinic, and maleic acids was performed. This study and more details of the

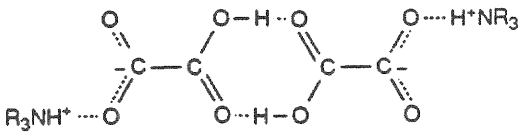
Lipovskii et al., Kabwe, and Gusakova et al. studies are discussed in Section 4.4 below.

4.1.3 (2,2) Dimeric Complexes

Yerger and Barrow (1955*a*) concluded from IR studies that acetic acid and diethylamine can form ion-pair dimers (a (2,2) complex) in carbon tetrachloride (structure 4-5). This structure was formed for relatively concentrated (0.1 to 0.3 mol/L) stoichiometric solutions of acetic acid and diethylamine; in very dilute solutions the equilibrium was shifted toward a (1,1) complex. The authors proposed that this dimeric structure is possible with secondary amines because the secondary ammonium cation can bridge the two carboxylate anions. Tertiary amines cannot form a similar cation bridge, and therefore do not form these dimers. Furthermore, the authors concluded that in chloroform, acetic acid and diethylamine do not form the (2,2) complex. The authors reasoned that the interaction of chloroform with the ion pair may discourage dimer formation.



4-5. Dimer of acetic acid-diethylamine with cation bridge



4-6. Dimer of oxalic acid-trioctylamine with intermolecular hydrogen bond

Lipovskii and Kuzina (1968) concluded from IR studies that crystalline bioxalate-trioctylamine salts form dimers of structure 4-6. This structure involves intermolecular hydrogen bonds between the carboxyl groups which are not bound to

the amine, unlike structure 4-5, which involves a cation bridge. This type of dimer could only occur with dicarboxylic acids. No dimer was found when the bioxalate-amine salt was dissolved in water-saturated solutions of benzene or carbon tetrachloride, nor was the presence of a dimer indicated in chloroform.

4.2 The Nature of the Acid-Amine Bond

It is obvious that the basic nitrogen of the amine and acidic proton of the carboxyl group interact. Spectroscopic studies have revealed a less obvious phenomenon, that the nature of the acid-amine interaction changes, depending on the solvent and the concentrations of species present. In the next section the findings of spectroscopic investigations on the nature of the acid-amine bond will be reviewed.

Infrared spectroscopic studies are particularly useful for examining the characteristics of the -COOH group of the acid (Nakanishi, 1977; Parikh, 1974; Silverstein et al., 1974). Two of the most useful peaks are the asymmetric carboxylate stretch, $\nu_{as}(COO^-)$ at 1550-1620 cm^{-1} and the carbonyl stretch, $\nu(C=O)$ peak of the carboxyl (-COOH) group at 1700-1780 cm^{-1}. The so-called $\nu_{as}(COO^-)$ peak actually arises from a situation in which the bonding of the two oxygens from the central carbon atom is the same, and is not necessarily associated with ionization of the carboxyl group (Barrow and Yerger, 1954). Nonetheless, this peak usually is attributed to the presence of a carboxylate ($-COO^-$) group. In a carboxylic acid, the carbonyl (-C=O) peak can arise from a carboxyl (-COOH) group or from a carboxylate (COO^-) in which the bonding from the central carbon is not the same, and is not necessarily associated with an un-ionized carboxyl group. For aliphatic carboxylic acids, a carbonyl band at 1700-1720 cm^{-1} is associated with a hydrogen-bonded

carbonyl, especially that of a dimeric acid; a carbonyl band at 1760-1780 is associated with a non-hydrogen-bonded carbonyl, as in a monomeric acid. However, a variety of carbonyl groups appear to give the same band at 1700-1780 cm^{-1} (Barrow and Yerger, 1954), so its presence cannot be associated with any particular species.

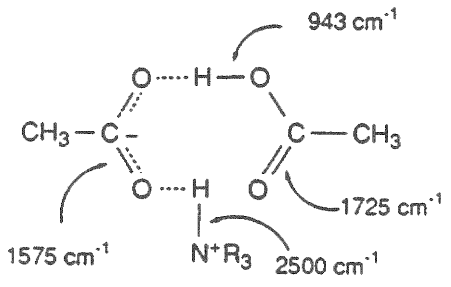
The carboxyl and carboxylate groups give rise to peaks in addition to those mentioned above. The carboxyl group gives two bands arising from the -C-O stretch coupled with -O-H in-plane deformation, ν(C-O)+δ(O-H), a weak band at 1350-1440 cm^{-1} and a stronger band at 1210-1320 cm^{-1}. The O-H stretch may appear at 3500-3550 cm^{-1} for a free -OH group or as a broad band at 2500-3300 cm^{-1} for a hydrogen-bonded -OH group. A band for out-of-plane -OH deformation, δ(O-H), arises with variable intensity at 890-955 cm^{-1}. These carboxyl bands are all generally associated with an acid dimer. Another so-called carboxylate band occurs for symmetric stretching, $\nu_s(COO^-)$, at 1350-1450 cm^{-1}, with less intensity than the 1550-1620 cm^{-1} ν_{as}(COO-).

There are several peaks of interest for the amine or ammonium ion. The N-H stretch, $\nu(N^+-H)$, of the tertiary ammonium salt gives a broad band at 2250-2700 cm^{-1}, which signals that the amine has been protonated. Salts of secondary amines may give an N^+-H_2 bending vibration, δ(N-H), in the 1560-1620 cm^{-1} range, and salts of primary amines give this band at 1500-1550 cm^{-1}. The C-N stretch, ν(C-N), of an aliphatic amine at arises at 1020-1200 cm-1. A band at 1400-1440 cm^{-1} sometimes appears when an aliphatic amine is protonated, because the $-CH_2-$ adjacent to the N^+ is shifted to a lower frequency (Nakanishi, 1977).

4.2.1 The "Carbonyl" and "Carboxylate" Forms of the Acid-Amine Complex

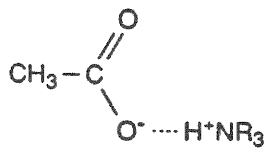
The work by Barrow and Yerger (1954) on the interactions of acetic acid with triethylamine in carbon tetrachloride and chloroform was one of the early studies on acid-amine complex formation. Their interpretations are very valuable in understanding several aspects of acid-amine interactions, and will be summarized in some detail here. The authors prepared 0.1 mol/L acetic acid solutions with successively increasing concentrations of triethylamine in carbon tetrachloride. As the amine concentration increased from 0 to 0.05 mol/L (2:1 acid:amine), the intensity of the carboxylate band at 1575 cm^{-1} increased from zero to its maximum value, the dimer bands of the carboxyl ν(C-O)+δ(O-H) at 1289 cm^{-1} and δ(OH) at 943 cm^{-1} decreased to zero, and the carbonyl band at 1725 cm^{-1} decreased to approximately half of its original value.

The authors proposed structure 4-7, which is shown with its peak assignments in below. The first acetic acid is ionized and ion-paired to the protonated amine. The -OH of a second non-ionized acetic acid molecule is hydrogen-bonded to the -C-O of the first molecule.



4-7. Carboxylate and carbonyl shifts for a (2,1) complex of acetic acid and triethylamine

Further increase of the amine concentration to full neutralization of the acid (1:1 acid:amine) brought about a decrease in the intensity of the carboxylate band. The intensity of the -H-N^+ salt band at 2500 cm^{-1} continued to rise, and the intensity of the 1725 cm^{-1} carbonyl peak remained roughly constant. The authors proposed structure 4-8, in which the carboxylate group is ionized, but a second acid no longer interacts with the unbonded oxygen. The triethylammonium ion is bonded preferentially to one of the carboxylate oxygens, causing the negative formal charge to lie on the bonded oxygen. Instead of a 1575 cm^{-1} $\nu_{as}(COO^-)$ of a carboxylate with electron delocalization, a carbonyl-like band is present at 1725 cm^{-1}, coincidentally the same place as the carbonyl bands of the acid dimer and of the second acid in the (2,1) complex.

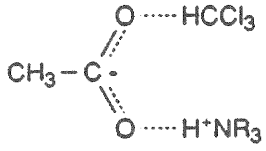


4-8. (1,1) "Carbonyl" complex of acetic acid and triethylamine in carbon tetrachloride. Negative formal charge lies on the oxygen that is hydrogen-bonded to the ammonium cation.

4.2.2 Chloroform Interaction with the Complex

Barrow and Yerger also produced evidence of specific interaction of chloroform with an acetic acid-triethylamine complex. In chloroform, an increase in amine concentration from zero to one half of the acid concentration (2:1 acid:amine) brought about a decrease in intensity of the carbonyl band at 1725 cm^{-1} and an increase in intensity of a carboxylate band at 1563 cm^{-1}, the same behavior as in carbon tetrachloride (structure 4-7).

However, as the amine concentration increased further, the intensity of the 1563 cm^{-1} carboxylate band decreased, reaching zero at approximately 1 mol/L amine; the carbonyl band continued to decrease, also reaching zero at approximately 1 mol/L amine; and, a new carboxylate band at 1613 cm^{-1} developed, attaining its maximum intensity at 1 mol/L amine. As an explanation, the authors proposed formation of structure 4-9 from structure 4-7 as the acid-to-amine ratio decreases. Increased amine concentration drives the equilibrium toward structure 4-9, with complete neutralization of the acid at 1 mol/L of amine. In structure 4-9 interaction of the acidic hydrogen of the chloroform with the unbonded oxygen creates an effectively symmetric carboxylate group with a resonance at 1613 cm^{-1}. This resonance is slightly different from the 1563 cm^{-1} peak in structure 4-7 of the carboxylate which is hydrogen-bonded to the acidic hydrogen of the second acid, presumably because the hydrogen bond strengths are different.



4-9. Chloroform interaction with (1,1) acetic acid-triethylamine complex to give rise to "carboxylate" form.

Further interesting behavior was seen in great excess of amine. As the amine concentration rose above 1 mol/L, the carbonyl band reappeared at 1725 cm^{-1} and the 1613 cm^{-1} carboxylate band shrank to zero. The authors reasoned that the symmetric carboxylate became an asymmetric carboxylate (structure 4-8) as the proton-donating

power of the solvent diminished with decreasing chloroform concentration. Furthermore, the chloroform is tied up by preferential hydrogen bonding to the amine.

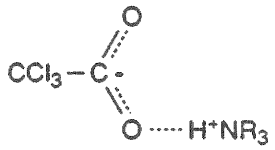
4.2.3 Equilibrium Between the Carbonyl and Carboxylate Forms of the Acid-Amine Complex

Investigations of highly acidic haloderivatives of acetic acid have extended the Barrow and Yerger interpretation of the carbonyl/carboxylate band behavior. Smith and Vitoria (1968) studied haloderivatives of acetic acid complexed with tri-*n*-propylamine in carbon tetrachloride and chloroform. Duda and Szafran (1978) performed IR investigations of haloderivatives of acetic acid complexed with triethylamine in benzene.

For the purposes of this discussion, the acids will be categorized as strong--trichloroacetic, trifluoroacetic, dichloroacetic, intermediate -- monochloroacetic, and weak -- acetic and trimethylacetic. The results for the weak acids were qualitatively similar to the Barrow and Yerger acetic acid results; i.e., the (2,1) complex gives carboxylate and carbonyl peaks (structure **4-7**), and increasing amine concentration gives decrease in carboxylate and increase in carbonyl peak intensities (structure **4-8**). Detar and Novak (1970) obtained similar results for benzoic acid and triethylamine in carbon tetrachloride, cyclohexane, and carbon disulfide. All of the acids in chloroform gave results qualitatively similar to the Barrow and Yerger experiments; i.e., the (2,1) complex gives carboxylate and carbonyl peaks (structure **4-7**), and the (1,1) complex gives a different carboxylate peak (structure **4-9**), which is shifted 30-50 cm^{-1} higher in frequency, and no carbonyl peak. However, the strong acids behaved quite differently from the weaker acids in the inert solvents, carbon tetrachloride and benzene.

Like the weak acids, in an inert solvent 2:1 strong acid:amine solutions yielded peaks for carbonyl stretch, from 1745-1780 cm^{-1}, and carboxylate, ranging from 1610-1680 cm^{-1}. However, 1:1 and 1:2 mixtures of the strong acid-amine solutions produced no peaks in the 1700-1780 cm^{-1} carbonyl frequency range. The carboxylate signals increased in intensity and appeared to be shifted 20-40 cm^{-1} higher in frequency to a range of 1650-1690 cm^{-1}. It should be noted that is quite possible the that carboxylate signal did not actually shift to a new frequency; rather, the original band may have diminished and a new one developed, as was seen in the chloroform studies of Barrow and Yerger mentioned above. The experiments did not include acid:amine ratios where this would have been possible to observe.

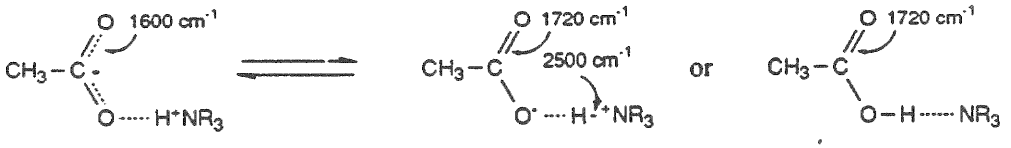
The discovery of carboxylate peaks at (1,1) complexes for the strong acids suggests structure **4-10**. Thus, in inert diluents a carboxylate peak can occur for the (1,1) species, provided the acid is sufficiently strong. It is not necessarily specific hydrogen bonding of the chloroform to the (1,1) complex which produces a carboxylate peak. However, this finding does not discount the possibility that chloroform hydrogen bonding with the complex occurs and facilitates carboxylate formation.



4-10 (1,1) "Carboxylate" complex of strong acids and amines

With the additional information on the carboxylate/carbonyl peak behavior, it has been proposed that an equilibrium between a species giving a carboxylate peak and a

species giving a carbonyl peak exists in solution (Duda and Szafran, 1978; Chibizov and Komissarova, 1984).



4-10 **4-8** **4-11**

Equilibrium between the "carboxylate" and "carbonyl" forms of a (1,1) complex (Eq. 4-1)

For strong acids the equilibrium is shifted towards the carboxylate form. For weak acids in inert diluents, the equilibrium is shifted toward the carbonyl form. Chloroform allows both strong and weak acids to shift toward the carboxylate form.

In several cases, spectra of (1,1) complexes which are intermediate between mostly carboxylate and mostly carbonyl forms are reported. Duda and Szafran (1978) and Smith and Vitoria (1968) reported that monochloroacetic acid behaves somewhere between weak and strong acids. In an inert solvent, at 1:1 acid:amine, there are both substantial carboxyl and substantial carbonyl peaks, with the carboxylate larger than those for weak acids, and the carbonyl peak larger than those for strong acids. This indicates that at 1:1 acid:amine, significant amounts of both forms exist in equilibrium.

A change in temperature shifts the equilibrium between the two forms. Chibizov and Komissarova (1984) studied octanoic acid-primary amine-benzene systems. IR spectra of a 1:1 mixture of octanoic acid and amine at 20, 40, 60, and 90 °C were recorded. As the temperature increased, the intensities of the carboxylate bands, $\nu_{as}(COO^-)$ at 1580 cm^{-1} and $\nu_s(COO^-)$ at 1410 cm^{-1}, fell, and the weak $\nu(C=O)$ band

at 1710 cm^{-1} became stronger. Smith and Vitoria (1968) performed temperature studies of monochloroacetic acid and tri-*n*-propylamine at -25, 25, and 50 °C on both 2:1 acid:amine mixtures and mixtures with excess amine. In both cases, at higher temperature, the carboxylate band is smaller and the carbonyl band is larger. Both sets of authors ascribed the changes to the equilibrium in Eq. 4-1, in which the carboxylate form is energetically favored. Thus higher temperature shifts the equilibrium toward the carbonyl form. Additionally, equilibria among the acid dimer, (2,1), and (1,1) complex may cause a shift in relative carboxyl-to-carboxylate peak intensity.

Duda and Szafran (1978) also observed that decreasing acid pK_A corresponded to greater carboxylate and lower carbonyl peak intensities. They reasoned that greater acidity shifted the equilibrium toward the carboxylate form. Batch extraction experiments in Chapter 3 indicate that greater acidity, as measured by lower pK_A, corresponds to higher equilibrium constants for (1,1) complex formation. It may be that the ratio of carboxylate to carbonyl intensities is correlated to the strength of the acid-amine bond, which, in turn, is related to pK_A. A quantitative evaluation to correlate batch equilibrium constants with IR results would be interesting and remains for future work.

4.2.4 Proton Transfer or Hydrogen Bonding?

An unresolved question from the IR studies reviewed here is whether the proton on the (1,1) complex which gives the carbonyl peak, i.e., the (1,1) complex of weak acid and amine in inert diluents, is associated with the acid or the amine. That is, does the carbonyl frequency result from a carboxylate anion (with electrons localized on the bonded oxygen) and ammonium cation ion-pair (structure 4-8) or a carboxyl

and amine hydrogen-bonded molecular complex (structure 4-11 of Eq. 4-1)? Both Barrow and Yerger and Smith and Vitoria reported the presence of an increasing NH^+ peak as amine concentration rises, implying that the hydrogen is associated with the amine and that the carboxyl must therefore be ionized (structure 4-8). Duda and Szafran (1978) and Chibizov and Komissarova (1984) identify the carbonyl peak with the hydrogen-bonded carboxyl (structure 4-11). These authors made no mention of the presence or absence of an NH^+ peak, nor for their rationale for identifying the complex as uncharged.

The issue is complicated further by the work of Barrow (1956) on the interaction of acetic acid and its haloderivatives with pyridine in carbon tetrachloride. By examination of the pyridinium ion and carbonyl absorption peaks, Barrow concluded that there is an equilibrium between an ion-paired carbonyl form (as suggested by structure 4-12) and a hydrogen-bonded carbonyl form (as suggested by structure 4-13). Research by Gusakova et al. (1970) on dichloroacetic acid and pyridine in benzene confirms these findings.

4-12 4-13

Equilibrium between ion-pair and hydrogen-bonded carbonyl form of the (1,1) complex of acetate and pyridinium / acetic acid and pyridine (Eq. 4-2)

Barrow added, however, that it does not follow that amines, such as triethylamine, exhibit the same type of equilibrium as pyridine. Pyridine is a weaker base than triethylamine. Other differences between the pyridine and triethylamine

systems were observed. Barrow noted that it is difficult to determine the nature of the proton in amine-acid complexes by IR investigations.

Other methods including UV and NMR spectroscopy and determination of dipole moments have been used to examine the proton in acid-amine complexes. Some of these are discussed briefly below.

Sobczyk and Pawelka (1973) used dielectric permittivity measurements on carboxylic acids and triethylamine in benzene and the Hedestrand extrapolation formula to determine the percent proton transferred. They concluded that even the weakest acids formed mostly proton-transfer complexes.

Nakanishi et al. (1977) used near and vacuum UV absorption spectra to measure acetic acid-aliphatic amine systems. The authors observed a band characteristic of a charge-transfer mechanism of hydrogen bonding. Yamabe et al. (1976) also observed a UV charge-transfer band between thioacetic acid and triethylamine. In methylene chloride and ethanol, two charge transfer bands were observed, while only one was present in carbon tetrachloride. However, the value of these results for addressing the specific question of ion-pair vs. hydrogen-bonded complex is probably limited. It has been noted (Jensen, 1980) that charge-transfer bands are not unique to molecular complexes, but are found in virtually all acid-base adducts, whether molecular or ionic.

Duda and Szafran (1976) performed NMR experiments on the labile proton between acetic acid and its derivatives and triethylamine in benzene. As triethylamine concentration increased from zero, the NMR signal of the labile proton of strong acids showed a distinct pattern of downfield shift to a maximum shift at 2:1

acid:amine, then an upfield shift as amine concentration increased further. The weak acids showed different behavior, giving a steady downfield shift with increasing amine concentration, which leveled off at high amine concentrations. The authors concluded that stronger acids showed a greater downfield shift for the (2,1) complex and a smaller downfield shift for the (1,1) complex than the weaker acids. They further concluded that for strong acids, the shift for the (2,1) complex is larger than that of the (1,1) complex. For weak acids, the shift for the (2,1) complex is smaller than that of the (1,1) complex.

The results affirm the existence of a distinct (2,1) complex. No conclusions could be drawn for the differences in the (1,1) complex for weak and strong acids in inert diluents, as the magnitude of a proton shift is difficult to correlate with species proton transfer between the acid and amine. The authors did find a correlation between acid strength and proton shift; greater acid strength correlated with greater downfield shift for the (2,1) complex and a smaller shift for the (1,1) complex.

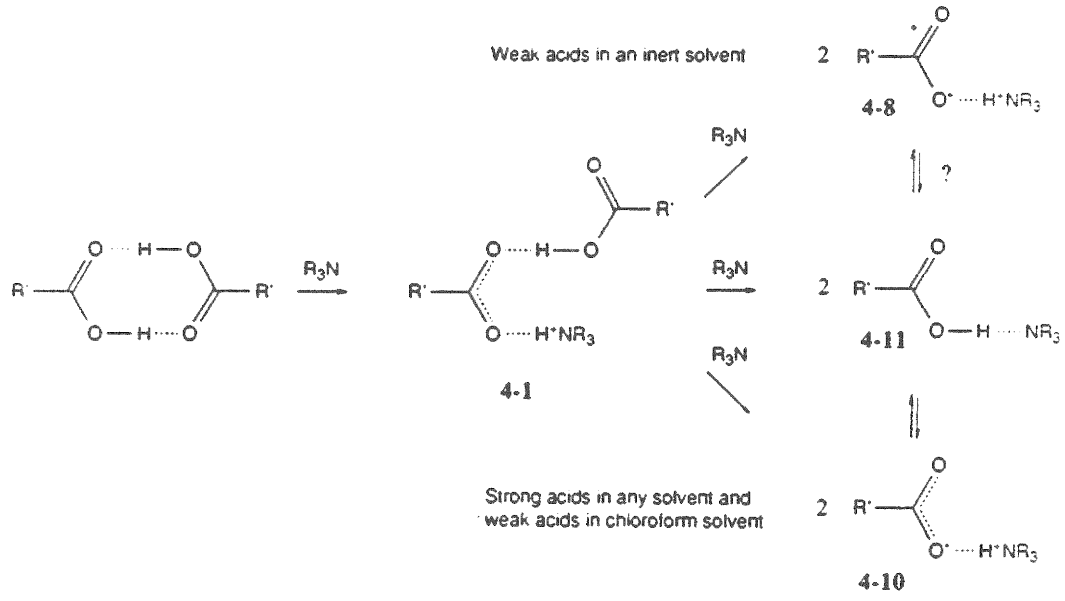
From the literature reviewed here, it is not possible to ascertain whether the "carbonyl" band in the (1,1) complex of weak acids and amines in inert diluents arises from an asymmetric carboxylate which forms an ion-pair with the amine or from a carboxyl which is hydrogen-bonded to the amine. This question remains for further work.

4.2.5 Summary of the Acid-Amine Bond

Carboxylic acids involved in (2,1) acid:amine complexes in both active and inert solvents form a species of structure 4-7, in which the -OH of the second acid interacts with the unbonded oxygen of the first acid to give a symmetric carboxylate

anion. In both chloroform and inert solvents the (1,1) complexes of strong acids give signals for a symmetric carboxylate anion (structure **4-10**), but at a frequency 20-40 cm^{-1} higher than in the (2,1) complex. The (1,1) complexes of weak acids in chloroform give symmetric carboxylate peaks shifted 30-50 cm^{-1} higher than the (2,1) complex. It is probable that interaction of chloroform with the complex promotes stability of the carboxylate ion-pair. The (1,1) complexes of weak acids in inert solvents give peaks at the carbonyl stretching frequency at 1700-1750 cm^{-1} (structure **4-8** or **4-11**). From the studies discussed here a controversy remains as to whether the (1,1) complex of weak acids and amine in inert solvent is an ion-pair (structure **4-8**) or a molecular hydrogen-bonded complex (structure **4-11**).

Thus, the addition of amine to an organic solution of carboxylic acids follows the equilibrium



(Eq. 4-3)

4.3 Determination of Equilibrium Constants by Infrared Spectroscopic Studies

IR measurements have been used to determine the equilibrium constants for complex formation quantitatively. Barrow and Yerger (1954) and Yerger and Barrow (1955*a.b*) included quantitative results for reactions of acetic acid with triethyl-, diethyl-, and *n*-butylamines in carbon tetrachloride and chloroform. The authors calculated the constants for the following reactions:

$$\overline{A} + \overline{B} = \overline{AB} \qquad K_I = \frac{[\overline{AB}]}{[\overline{A}][\overline{B}]} \qquad \text{(Eq. 4-4)}$$

$$\overline{A_2B} + \overline{B} = 2(\overline{AB}) \qquad K_{II} = \frac{[\overline{AB}]^2}{[\overline{A_2B}][\overline{B}]} \qquad \text{(Eq. 4-5)}$$

Hibbert and Satchell (1968) determined the organic-phase equilibrium constant for the (1,1) reactions of acetic acid and chloropropionic acid with *n*-butylamine. Detar and Novak (1970) calculated a contour plot of possible organic-phase equilibrium constants for the (1,1) and (2,1) reactions of benzoic acid and triethylamine in chloroform. Bullock et al. (1964) determined the constant for the reaction of the (1,2) complex of oxalic acid and trioctylamine with free trioctylamine to form two (1,1) complexes. The results of these studies are summarized in Table 4-1.

Translation of the organic-phase constants to the heterogeneous equilibrium constants used in this work requires the transformations $\beta_{11} = P \cdot K_I$ and $\beta_{21} = P^2 \cdot K_1^2 / K_{II}$, where P is the distribution ratio for acid monomer between the organic and aqueous phases, $[\overline{A}]/[A]$. Table 4-2 shows the equilibrium constants calculated by Barrow and Yerger, their constants adjusted to the definitions of this

Table 4-1. Equilibrium Constants From IR Studies

(Source: Barrow and Yerger, 1954; Yerger and Barrow, 1955a,b; Detar and Novak, 1970; Hibbert and Satchell, 1968; Bullock, et al., 1964)

Reactions:

I. $\overline{A} + \overline{B} = \overline{AB}$

II. $\overline{A_2B} + \overline{B} = 2(\overline{AB})$

III. $2\overline{A} + \overline{B} = \overline{A_2B}$

IV. $\overline{AB_2} + A = 2(\overline{AB})$

	K_I	K_{II}	K_{III}	K_{IV}
Acetic Acid : TEA Chloroform	3000	22		
Acetic Acid : TEA Carbon Tetrachloride	800	1.6		
Acetic Acid : DEA Chloroform	3000	22		
Acetic Acid : DEA Carbon Tetrachloride	2800	16		
Acetic Acid : *n*-BA Chloroform	600			
Acetic Acid : *n*-BA Carbon Tetrachloride	2800			
Acetic Acid : *n*-BA Diethyl Ether	69			
Chloropropionic : *n*-BA Diethyl Ether	481			
Benzoic Acid : TEA Chloroform	5×10^4		2.5×10^7	
Oxalic Acid : TOA Chloroform				10

Note: Values of K are for molar units.

work, and the analogous equilibrium constants for acetic acid and long-chain tertiary amines calculated from batch extractions studies given in Table 3-2).

Table 4-2. Comparison of Equilibrium Constants Calculated from IR and Batch Extraction Studies

	As Determined From IR Studies with Triethylamine (Barrow and Yerger, 1954)			As Determined From Batch Studies with Trioctylamine (Present work)	
	β_{11}	β_{21}	P	β_{11}	β_{21}
Acetic Acid-Amine Chloroform	220	2300	0.074[a]	18	8.1
Acetic Acid-Amine Carbon Tetrachloride	3.6	7.9	0.0045[b]	1.0	0.0

[a] Othmer and Ku, 1960

[b] Chaikhorskii, et al., 1966

The correlation between results from the spectroscopic work and results from similar batch extraction systems is poor. There are a number of possible causes. Most IR studies are done in anhydrous solvents, whereas batch experiments saturate the solvent phase with water. Water is believed to affect the acid-base equilibria (Lipovskii and Kuzina, 1968). There is error associated with calculation of equilibrium constants by both the batch extraction experiments and IR experiments. With batch extraction, the stoichiometry of the species is an unknown, and must be determined

by a combination of data fitting and chemical plausibility. With IR experiments, the absorptivity for a particular species is unknown, and must be determined either by additional fitting or by an assumption that the concentration of a species is known under particular conditions. Finally, the short-chain amines used in the spectroscopic studies may differ in complexation properties from the long-chain amines used in batch extraction experiments. There is potential for use of IR measurements to study acid-amine systems quantitatively if the question of correlation with batch extraction studies can be addressed.

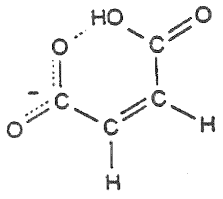
4.4 Spectroscopic Studies for Fumaric, Maleic, and Succinic Acids

The batch extraction results and mass-action law calculations in Chapter 3 for the extraction of fumaric, maleic, and succinic acids in chloroform indicate that these four-carbon dicarboxylic acids behave very differently. In chloroform, fumaric acid showed probable (1,2) and (2,2) complex formation; maleic acid showed probable (1,1) and (2,1), but no detectable (1,2), complex formation; succinic acid showed definite (1,1), possible (2,1), but no detectable (1,2) or (2,2), complex formation.

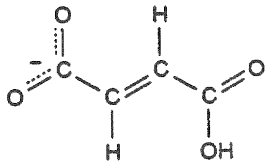
Intramolecular hydrogen bonding may be playing an important role in the complex formation. The bimaleate anion can form very strong intramolecular hydrogen bonds, because the double bond fixes the proton-donating and proton-accepting groups in close proximity to each other (structure **4-14**). This stabilizes the singly deprotonated form of the acid, so that removal of the first proton is favored and removal of the second proton is discouraged. Some investigators (Evans and Goldstein, 1968) have proposed that this contributes to the large difference in pK_A between the first and second carboxyl groups (pK_{A1} = 1.9, pK_{A2} = 6.3), although

others (Kolthoff and Chantooni, 1975) have concluded that in an aqueous medium, intramolecular hydrogen bonding is absent because of bonding of the water to the carboxylate and carboxyl groups. There is general agreement, nevertheless, that the intramolecularly hydrogen-bonded complex of dicarboxylic acids is stabilized in organic solvents, where the solvent proton-donor/acceptor ability is much lower than that of water.

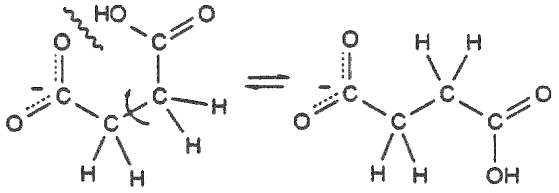
In the bifumarate anion, the carboxyl groups are fixed on opposite sides of the double bond (structure 4-15), and cannot form intramolecular hydrogen bonds. The pK_A of the first carboxyl group is not as large as for maleic acid (pK_{A1} = 3.1), and the differential between first and second acid dissociation constants is not nearly as large (pK_{A2} = 4.6). The bisuccinate ion can orient itself to form intramolecular hydrogen bonds, but the central single bond allows floppiness of carboxyl and carboxylate groups (structure 4-16). Thus the tendency for intramolecular hydrogen bond formation is not nearly as strong as for maleic acid.



4-14 Bimaleate Anion



4-15 Bifumarate Anion



4-16 Bisuccinate Anion

4-14 to 4-16. Intramolecular hydrogen bonding in maleic, fumaric, and succinic acids

4.4.1 Experimental Methods

Solutions of 0.05 mol/L maleic and fumaric acids (Aldrich Chemical Co.) with 0.05, 0.10, and 0.20 mol/L Alamine 336 (Henkel Corp.) in chloroform (Mallinkrodt Corp., spectral grade) and solutions of 0.05 mol/L Alamine 336 in chloroform with 0.05, 0.025, 0.113 mol/L succinic acid were prepared by adding measured quantities of acid crystals directly to the dry solvent phase. A small amount of fumaric acid crystals remained undissolved in the 0.05 mol/L amine sample. The solution was decanted prior to use in the investigation. The acids are virtually insoluble in chloroform, so no spectra of the undisturbed acid in solvent were obtainable.

Spectra for succinic acid were recorded on a Perkin-Elmer Model 1420 ratio recording, double-beam, infrared spectrophotomer, with a 0.02 cm NaCl window. Chloroform was used as the reference solvent. Spectra for maleic and fumaric acids were recorded on a Digilab Model FTS-50 Fourier Transform infrared spectrometer with a triglycine sulfate detector at 4 cm^{-1} wavelength resolution and 64 scans using a 0.02 cm NaCl window. A Biorad-Digilab division 3200 Data Station associated with this spectrometer allowed digital subtraction of the reference solvent spectra (the appropriate solution of Alamine 336 in chloroform) from the solvent-amine-acid spectra. All spectra were recorded at room temperature.

4.4.2 Results

The peaks obtained for Alamine 336 in chloroform referenced against chloroform, for maleic and fumaric acids in Alamine 336 and chloroform, referenced against the appropriate Alamine 336 and chloroform solution, and for succinic acid and Alamine 336 in chloroform, referenced against chloroform, are tabulated in Table 4-3.

Table 4-3. Peak Assignments for Infrared Studies Performed in This Work

Solvent: **Alamine 336 Chloroform** Reference: Chloroform		Key for Peak Intensity
2967-2855vs	$\nu_{as}(CH_3,CH_2)$, $\nu_s(CH_3,CH_2)$	vs = very strong
1467s	$\delta_s(CH_2)$	s = strong
1450?	$\delta_{as}(CH_2)$	m = medium
1377m,w	$\delta(CH_3)$	w = weak
1330vw	?	vw = very weak
1095m	ν(C-N)	

Fumaric Acid Alamine 336 Chloroform	**Maleic Acid Alamine 336 Chloroform**	**Succinic Acid Alamine 336 Chloroform**	**Assignment**
3300w	3300vw	3400vw	δ(O-H)
2480vw	2334-2465vw	2400-2500vw	$\nu(N^+-H)$
1701m,w	**1703m**	**1730s**	**ν(C=O)**
1635m,w	**1622s,1675vw**		**$\nu_{as}(COO^-)$**
1593-1599m,s	**1500-1600vs**	**1500-1610s**	**$\nu_{as}(COO^-)$**
1467w,m	1473m	1480	$\delta(CH_2)$?
1379-1381w	1380w	1390w	$\nu_s(COO^-)$?
1354-1359m	1352s	1340m	$\nu_s(COO^-)$?
1285-1289m		1315w	**ν(C=O)+δ(O-H)**(dimer)
1251m	1234vw	1180w	ν(C=O)+δ(O-H)?
983m		950w	?
866s	850w		δ(O-H)?
663vs	650-660s	670m	$\delta(COO^-)$

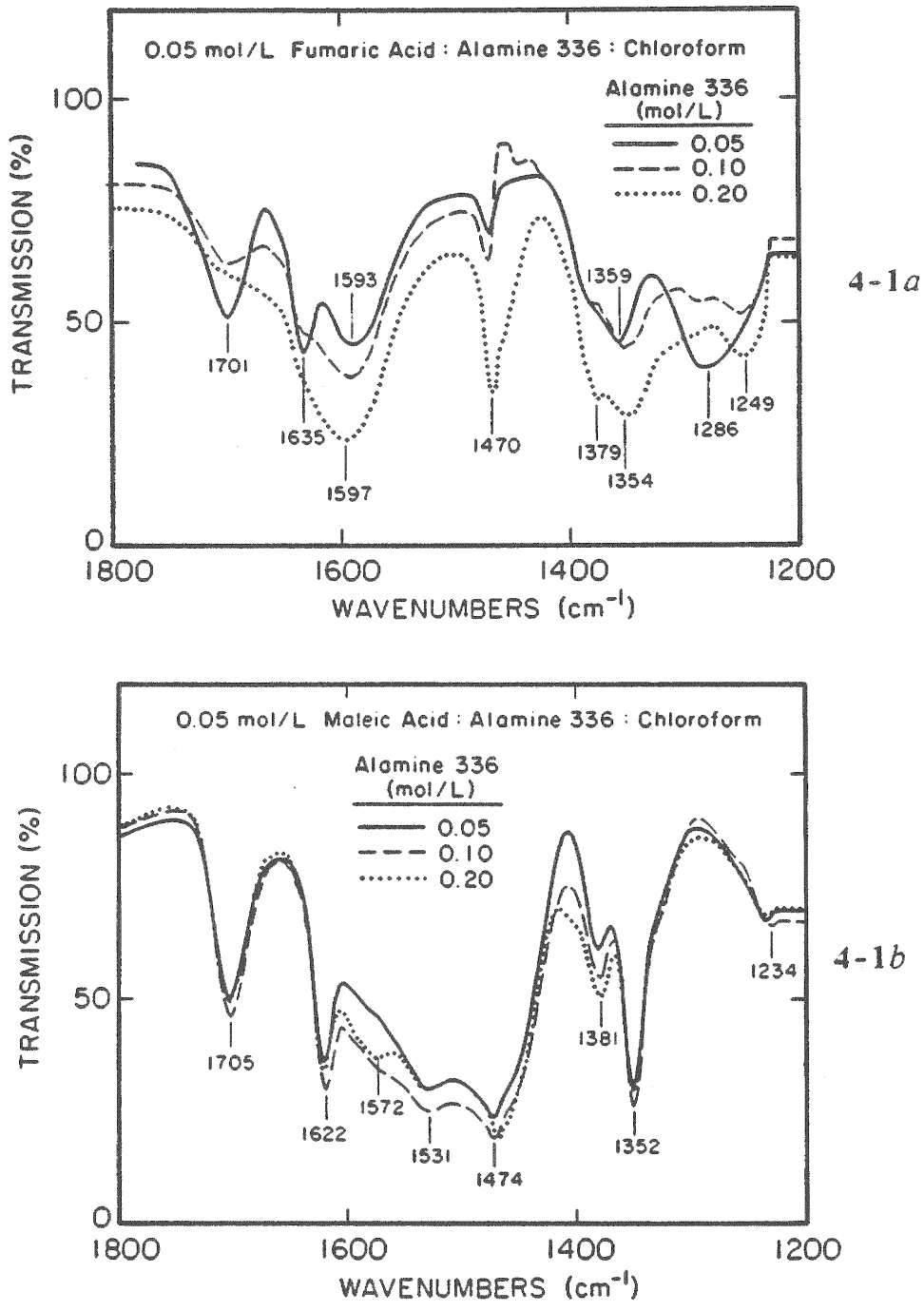
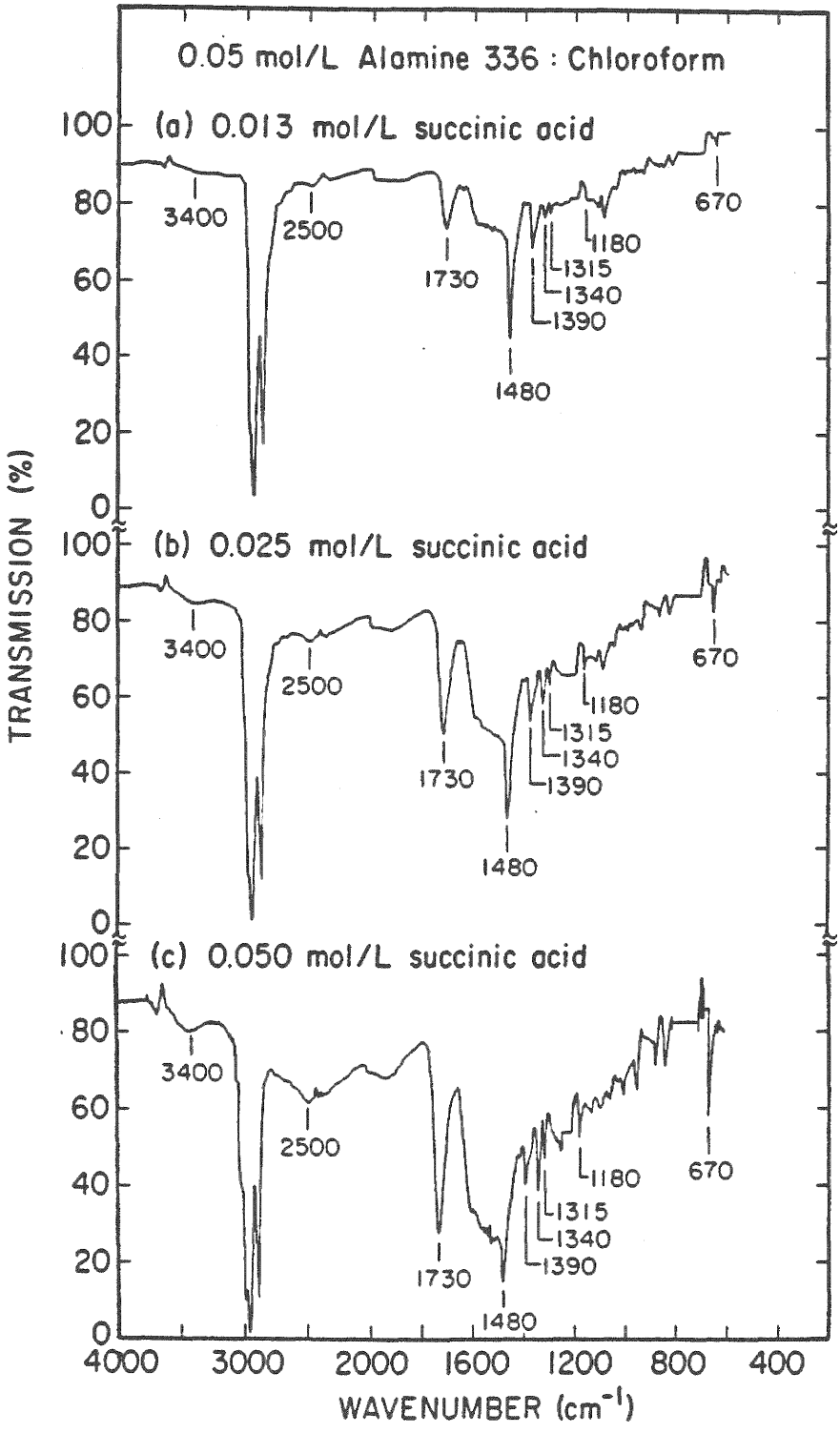


Fig. 4-1. IR Spectra for Solutions Containing Fumaric or Maleic Acids and Alamine 336 in Chloroform.

(*a*) Fumaric acid and (*b*) maleic acid
Samples referenced against solutions of Alamine 336 and chloroform.



4-2

Fig. 4-2. IR Spectra for Solutions Containing Succinic Acid and Alamine 336 in Chloroform.

Samples referenced against chloroform.

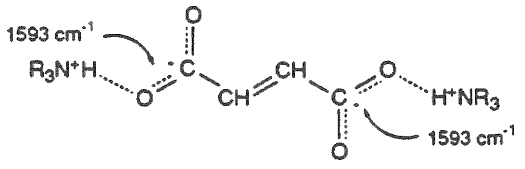
The peak assignments are also given. Fig. 4-1 shows the spectra in the 1200-1800 cm^{-1} region resulting from the (*a*) fumaric and (*b*) maleic acid experiments, with the amine in chloroform solution as the reference. Fig. 4-2 shows the spectra of the succinic acid experiments with chloroform as the reference.

Fumaric Acid

The fumaric acid spectra undergo a gradual change as the amine concentration increases. At a 1:1 acid:amine ratio, a band is present at 1701 cm^{-1}, assigned to the ν(C=O) of a carboxyl, and two bands appears at 1597 and 1635 cm^{-1}, assigned to two distinct $\nu_{as}(COO^-)$. As the ratio of amine to acid increases, there is a marked decrease in the carbonyl peak at 1701 cm^{-1}, which shrinks to a small shoulder at 1:4 acid:amine ratio. There is a corresponding increase in the carboxylate peak intensity at 1593 cm^{-1}. The 1635 cm^{-1} carboxylate peak appears to diminish in intensity, but this is somewhat obscured by the broadening and growth of the 1593 cm^{-1} band. With increasing amine concentration, a medium, broad band at 1285 cm^{-1}, assigned to ν(C-O)+δ(O-H) decreases in intensity. The region around 1400 cm^{-1} where the second ν(C-O)+δ(O-H) would be expected is obscured by the carboxylate and amine bands. At the same time, a weak, broad band at 1370-1380 cm^{-1}, assigned to $\nu_s(COO^-)$ appears to increase in intensity, but may be obscured by the amine band at 1380 cm^{-1}. Another weak, broad band, possibly another $\nu_s(COO^-)$, appears at 1354-1359 cm^{-1}. A band at 1467 cm^{-1} increases with increasing amine concentration, and is tentatively assigned to the amine $-CH_2-$ groups adjacent to a protonated nitrogen.

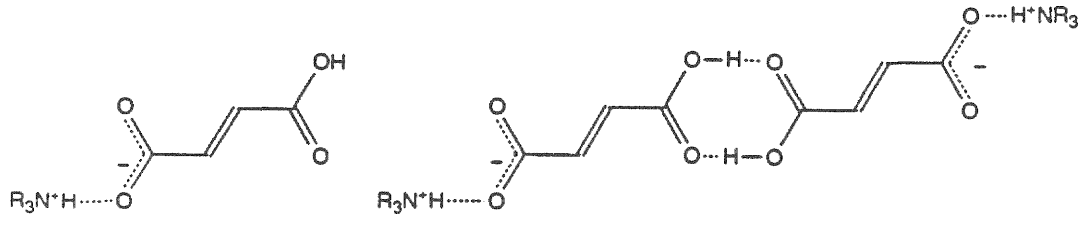
The disappearance of the carbonyl and increase in carboxylate bands with increasing amine concentration is a strong confirmation of formation of (1,2)

complexes. The 1593 cm^{-1} peak seen at high amine concentration almost certainly is associated with carboxylate of the (1,2) complex (structure **4-17**).

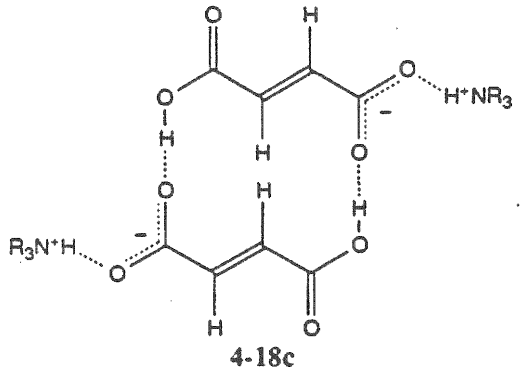


4-17 (1,2) fumaric acid - Alamine 336 complex
Carboxylate peak at 1593 cm^{-1}.

It is more difficult to determine the origin of the 1635 cm^{-1} carboxylate peak. Three possible candidates are shown in structure **4-18**.



4-18a **4-18b**



4-18c

4-18 Possible (1,1) and (2,2) bifumarate - Alamine 336 complexes
Carboxylate peak at 1635 cm^{-1}, carbonyl peak at 1701 cm^{-1}
possible dimer peak at 1285 cm^{-1}

The dimer structures are attractive from the standpoint of satisfying the second carboxyl group by hydrogen bond formation with the carboxyl group of a second acid. Structure **4-19b** is a classical dimeric acid structure with amine interaction with the undimerized carboxyl group. It is especially attractive in terms of allowing interaction of chloroform with the unbonded oxygen, similar to structure **4-9**, and because the hydrogen bonding between the "free" carboxyl groups would be expected to give a strong ν(C-O)+δ(O-H) peak in the 1210-1320 cm^{-1} region. In structure **4-16c**, the large ring formation is entropically disfavored because formation of the ring involves fixing the orientation of the four =C-COO- bonds.

From the batch extraction studies it was concluded that fumaric acid-amine complexes with (1,2) and (2,2) stoichiometries are formed in chloroform. This would correspond to the 1635 cm^{-1} band being associated with a (2,2) complex. The spectroscopic experiments performed here do not help in identifying the complex. In theory, it would be possible to determine the stoichiometry of the acid-amine complex with more certainty by observing the concentration dependence of the peaks and performing a best-fit calculation, as was done by Barrow and Yerger (1954). Experiments and calculations of this type were beyond the scope of this work, but could prove valuable for more positive identification of the complexes involved.

The appearance of two carboxylate peaks for dicarboxylic acid-amine systems has been noted in the literature. Gusakova et al. (1986) studied malonic acid and dibutylamine in a variety of solvents, including chloroform, dioxane, CH_3OD, and acetonitrile. The authors found that at 1:1 acid:amine ratios, the complex gives a $\nu_{as}(COO^-)$ at 1593-1610 cm^{-1}. As the concentration of amine increases to promote formation of a (1,2) complex, a $\nu_{as}(COO^-)$ at 1570-1580 cm^{-1} appears, and the 1593-

1610 cm^{-1} band disappears. Kabwe (1971) also noted two carboxylate bands for malonic acid-triisooctylamine in chloroform at 1600 and 1625 cm^{-1}. Thus, it appears that the equimolar complex has an asymmetric stretch of the carboxylate at 25-40 cm^{-1} higher in frequency than does the (1,2) complex.

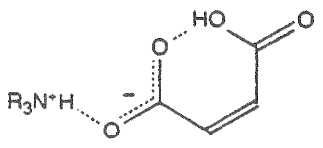
Maleic and Succinic Acids

The maleic acid spectra are quite different from the fumaric acid spectra. Maleic acid in amine gives virtually no change in peak intensity or position as the acid to amine ratio is changed from 1:1, 1:2, and 1:4. The strong peak at 1703 cm^{-1} is assigned to a ν(C=O) of the carboxyl. A strong, sharp peak at 1622 cm^{-1} is tentatively assigned to ν_{as} of the carboxylate; however, it could be a C=C stretching vibration, which sometimes occurs in *cis*-$\alpha\beta$-unsaturated C=O groups. It is interesting that this peak is not observed on the succinic acid spectra (Fig. 4-2). A medium, sharp peak at 1381 cm^{-1} and a strong, sharp peak at 1352 cm^{-1} are tentatively assigned to the ν_s of the carboxylate, but interference from the amine obscures this region somewhat. A weak peak amid the broad high absorption is present at 1473 cm^{-1}, and is tentatively assigned to the $-CH_2-$ next to a protonated nitrogen, as in the fumaric acid analysis. A barely visible carboxylate peak at 1575 cm^{-1} develops at high amine concentration amid the broad high absorption in this region. There are no apparent peaks in the 1200-1300 cm^{-1} region for the ν(C-O)+δ(O-H) of the acid dimer as there are for fumaric acid.

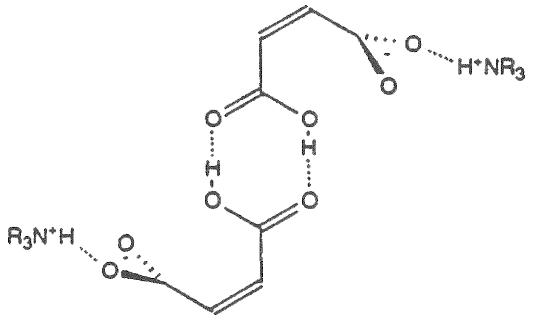
An unusual feature of the maleic acid spectra is the broad, intense absorption in the entire 1470-1600 cm^{-1} region, with a weak peak at 1522 cm^{-1}. The 1522 cm^{-1} peak is substantially lower than the normally observed carboxylate shifts at 1550-1620 cm^{-1}. However, interaction and coupling with other groups can alter peaks from their

normally observed frequency and shape. Several species with slightly different characteristic shifts may be present in solution and give the appearance of a single, broad band. Therefore, this broad region is assigned to the $\nu_{as}(COO^-)$.

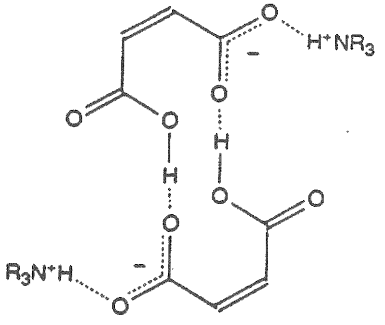
For maleic acid, increasing amine concentration does not result in increase of the carboxylate and decrease of the carboxyl, which would be expected for formation of (1,2) complexes. This suggests a stable equimolar complex, probably with a (1,1) or (2,2) stoichiometry. A few of the possibilities are shown in structures 4-19 **a**,**b**, and **c** below. Again, it would be necessary to do a detailed analysis of the concentration dependence in order to differentiate (1,1) from (2,2) stoichiometry.



4-19a



4-19b



4-19c

4-19 Possible (1,1) and (2,2) bimaleate - Alamine 336 complexes
Carboxylate peak at 1470-1600 cm^{-1} region, carbonyl peak at 1703 cm^{-1}

4-19b and **c** are analogous to **4-18b** and **c**. Entropic effects would disfavor the existence of **4-19c** as they do for **4-18c**. Structure **4-19b** would be unfavorable because of the close proximity of the electronegative oxygen atoms of the carboxyl and carbonyl of each bimaleate anion. The (1,1) complex, **4-19a**, is favorable for maleic acid, unlike **4-16a** for fumaric acid, because the intramolecular interactions can satisfy the -OH of the carboxyl group.

Qualitatively, succinic acid gives results very similar to those for the maleic acid. A carbonyl peak appears at 1730 cm^{-1}, and the unusual broad absorption seen in maleic acid at 1480-1600 cm^{-1} appears for succinic acid also. The carbonyl stretch of the carboxyl for succinic acid is at a higher frequency than for maleic or fumaric acids, presumably because there is no conjugation with the C=C bond in the molecule. Its location at 1730 cm^{-1} implies a hydrogen-bonded carboxyl group, rather than a free carboxyl, which would be expected at a higher frequency. The ratio of carboxyl to carboxylate peak intensity does not change significantly with decreasing acid:amine content. (In the succinic acid experiment, the concentration of acid was changed to alter the acid:amine ratio, so the relative absorption intensities for the carboxyl and carboxylate peaks is the pertinent consideration.)

There are minor differences between the maleic and succinic spectra. In the succinic acid spectra, the sharp 1622 cm^{-1} peak is notably absent. The succinic acid-amine complex gives a small peak at 1320 cm^{-1}, which may be the ν(C-O)+δ(O-H) of a carboxyl dimer. The carbonyl/carboxylate peak height is somewhat larger for succinic than maleic acid, possibly related to the higher pK_A of succinic acid. The similarities far outweigh the differences, however, and it appears that succinic acid also forms stable equimolar complexes.

The batch extraction data for maleic and succinic acids concur strongly with the lack of (1,2) complex formation. Batch extraction results for succinic acid strongly suggest that (1,1) rather than (2,2) complexes predominate in chloroform. The batch data for maleic acid are not extensive enough to allow this distinction; there a slight discrepancy between predicted and experimental results for (1,1) complexation, but these could be the result of experimental procedure or activity coefficient changes. Spectroscopic data do not give much more information on the equimolar complex, because a (1,1) complex and (2,2) complex appear identical in terms of the carboxylate and carbonyl bands. The lack of peaks in the 1210-1320 cm^{-1} range may be taken as an indication that there is no dimeric hydrogen bond formation of the unbonded carboxyl groups as would be expected for the dimer in **4-19b**, but this would be rather weak evidence.

As noted above, Gusakova et al. (1986) found (1,1), but no (1,2), complexes with malonic acid and tributylamine in chloroform, dioxane, and acetonitrile. Even a thirtyfold excess of tertiary amine did not result in decrease of the carbonyl or increase of the carboxylate peak. However, Gusakova et al. found that secondary amines allow more (1,2) complex formation. It would be interesting to determine if the (1,2) complex formation is also indicated by batch extraction experiments with secondary amines and dicarboxylic acids.

4.4.3 Discussion and Conclusions

Spectroscopic evidence affirms the existence of (1,2) acid-amine complexes for fumaric acid and the lack of (1,2) complexes for maleic and succinic acids in chloroform. Although it is not possible to detect intramolecular hydrogen bonding

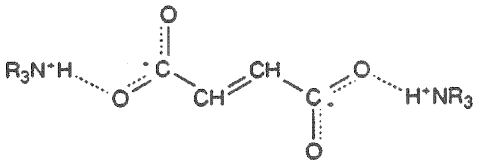
from IR spectra directly, the difference in spectra between fumaric acid, which cannot form intramolecular hydrogen bonds, and succinic and maleic acids, which can form intramolecular hydrogen bonds, is strong evidence that intramolecular hydrogen bonding is an important determinant of reaction stoichiometry. Intramolecular hydrogen bonding reduces the availability of the second carboxyl group for bonding to the amine. It may also reduce the availability of the second carboxyl group for dimer formation in equimolar complexes.

The IR evidence does not discount the possibility that stable dimer formation of some type that is particular to succinic or maleic acid may prevent (1,2) complex formation. The studies performed here do not allow positive identification of the equimolar complex, as (1,1) and (2,2) complexes most likely give similar IR spectra. However, it does not seem that dimeric complexes, structures **4-19bc**, for maleic acid-amine would have any greater relative stability than analogous complexes, structures **4-18bc**, for fumaric acid-amine, whereas intramolecular hydrogen bonding should have a large effect in stabilizing a (1,1) complex. Furthermore, no significant dimer band in the 1210-1320 cm^{-1} range was seen for maleic and succinic acids.

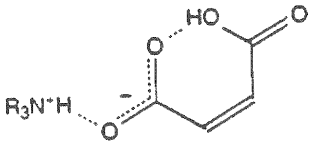
4.5 Summary and Conclusions

Results from the spectroscopic investigation of the complexation of succinic, maleic, and fumaric acids with Alamine 336 in chloroform strongly support the complex stoichiometries that were determined by the mass-action-law analysis of batch extraction results. Fumaric acid forms (1,2) acid-amine complexes (Structure **4-17**) with excess amine in chloroform diluent, while succinic and maleic acids do not. Intramolecular hydrogen bonding between the carboxylate bonded to the ammonium

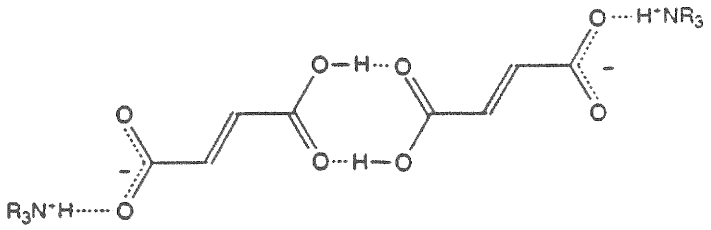
cation and the "free" carboxyl has been proposed to rationalize this difference (Structure **4-19a**). Based on the spectroscopic investigation, tentative structures for the predominant equimolar species were proposed. For fumaric acid, structure **4-18b**, a dimeric structure with intermolecular hydrogen bonding between the uncomplexed carboxyl groups seems the most likely candidate. For succinic and maleic acids, a (1,1) complex with intramolecular hydrogen bonding, structure **4-19a** for maleic acid and the analogous structure for succinic acid, is thought to be favored.



4-17. (1,2) fumaric acid-amine complex



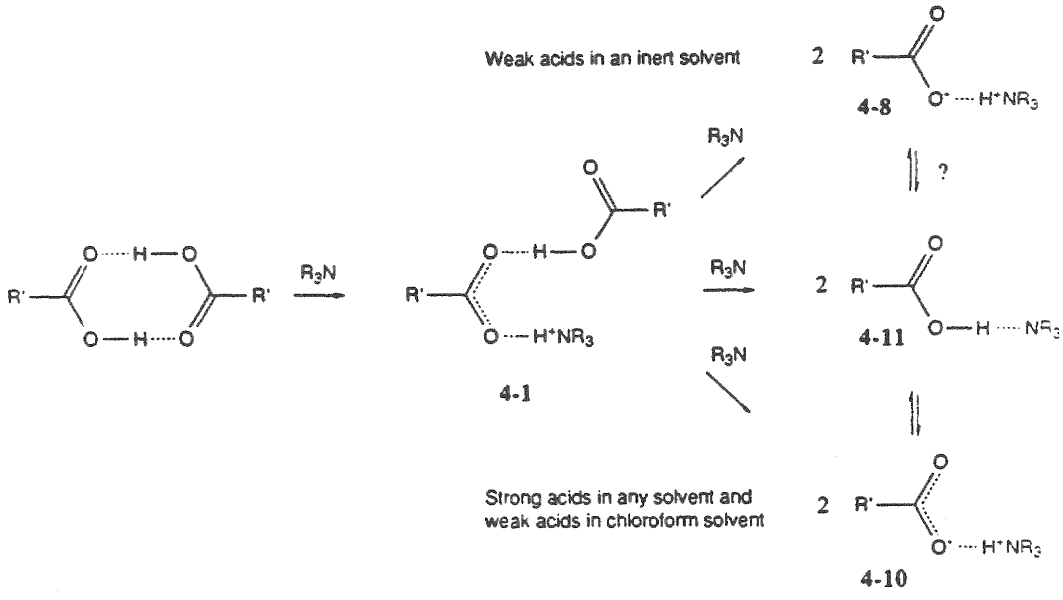
4-19a. (1,1) maleic acid-amine complex



4-18b. (2,2) fumaric acid-amine complex

A review of the literature gives insight into acid-amine interactions. (2,1) complexes form species of structure **4-1**, in which the first acid is ion-paired to the ammonium ion, and the second acid is hydrogen-bonded to the oxygen of the first acid. The nature of the (1,1) complex differs, depending on the strength of the acid and the type of solvent. For strong acids or in chloroform solvent, formation of the carboxylate ion-pair (**4-10**) is favored. Chloroform is believed to form a hydrogen bond with the carboxylate oxygen. For weak acids in an inert solvent, formation of

either a hydrogen-bonded acid-amine complex or a ion-pair with a negative formal charge localized on the oxygen that is bonded to the amine is favored (**4-8** or **4-11**).



(Eq. 4-3)

Spectroscopy is a valuable tool for analysis of acid-amine-diluent systems. It can be used to confirm the findings of batch extraction experiments and to give deeper insight into the nature of the acid-amine interactions. IR investigations have uncovered an equilibrium between a carbonyl and carboxylate form which is not detectable by batch extraction studies. Evaluation of this equilibrium has potential utility in correlation with acid-amine bond strength. Differences in the equilibrium between carboxyl and carboxylate also illustrate the differences among solvents in their interaction with the complex. There is potential for integrating the spectroscopic results more completely with batch extraction studies in further work.

REFERENCES

Barrow, G. M., "The Nature of Hydrogen Bonded Ion-Pairs: The Reaction of Pyridine and Carboxylic Acids in Chloroform", *J. Am. Chem. Soc.*, **78**, 5802-5806 (1956).

Barrow, G. M. and Yerger, E. A., "Acid-Base Reactions in Non-dissociating Solvents. Acetic Acid and Triethylamine in Carbon Tetrachloride and Chloroform", *J. Am. Chem. Soc.*, **76**, 5211-5216 (1954).

Bullock, J. I., Choi, S. S., Goodrick, D. A., Tuck, D. G., and Woodhouse, E. J., "Organic Phase Species in the Extraction of Mineral Acids by Methyldioctylamine in Chloroform", *J. Phys. Chem.*, **68**, 2687-2696 (1964).

Chaikhorskii, A. A., Nikol'skii, B. P., and Mikhailov, B. A., "Complex Formation in Nonaqueous Solutions X. Interaction of Tridecylamine with Acetic Acid", *Sov. Radiochem.* (Engl. Transl.), **8**, 152-158 (1966); *Radiokhimiya*, **8**, 163-171 (1966).

Chibizov, V. P. and Komissarova, L. N., "Study of Complex Formation in Octanoic Acid-Amine-Benzene Systems by Means of NMR and IR Spectroscopy", *J. Gen. Chem. USSR* (Engl. Transl.), **54**, 2377-2380; *Zhurnal Obshchei Khimii*, **54**, 2659-2633 (1984).

Detar, D. F. and Novak R. W., "Carboxylic Acid-Amine Equilibria in Nonaqueous Solvents", *J. Am. Chem. Soc.*, **92**, 1361-1365 (1970).

Duda, T. and Szafran, M., "PMR and IR Studies of Hydrogen Bond and Proton Transfer in Complexes of Triethylamine and Dimethylaniline with Acetic Acids", *Bull. de l'Acad. Pol. Sci.. Ser. Sci. Chim.*, **26**(3), 207-215 (1978).

Evans, H. G. and Goldstein, J. H., "An investigation of intramolecular hydrogen bonding in some malonic acids using NMR techniques", *Spectrochim. Acta Part A*, **24A**, 73-79 (1968).

Gusakova, G. V., Denisov, G. S., and Smolyanskii, A. L., "Infrared Spectra and Structures of Complexes Formed for Dibasic Carboxylic Acids with Amines in Nonaqueous Solvents: Malonic Acid", *J. Gen. Chem. USSR* (Engl. Transl.), **56**, 531-536; *Zh. Obshch. Khim.*, **56**, 600-607 (1986).

Gusakova, G. V., Denisov, G. S., Smolyanskii, A. L., and Shraiber, V. M., "Hydrogen Bonding and Proton Transfer in Carboxylic Acid-Amine Systems. Spectroscopic Investigation of the Equilibrium Between a Molecular Complex and an Ion Pair", *Proc. Acad. of Sci. USSR* (Engl. Transl.), **193**, 577-579; *Dokl. Akad. Nauk SSSR*, **193**, 1065-1068 (1970).

Hibbert, F. and Satchell, D. N. P., "Equilibria Between Carboxylic Acids and n-Butylamine in Diethyl Ether Solution", *J. Chem. Soc. (B) Phys. Org.*, 573-575 (1968).

Jensen, W. B., *The Lewis Acid-Base Concepts: An Overview*, John Wiley & Sons, New York, Chapter 5, 179-185 (1980).

Kabwe, C., "Neutralisation de la tri-iso-octylamine en solution chloroformique par l'acide malonique", *Anal. Chim. Acta*, **54**, 343-349 (1971).

Kolthoff, I. M. and Chantooni, M. K., "Intramolecular Hydrogen Bonding in Monoanions of *o*-Phthalic Acid and the Homologous Oxalic Acid Series in Acetonitrile", *J. Am. Chem. Soc.*, **97**, 1376-1381, (1975).

Lipovskii, A. A. and Kuzina, M. G., "Infrared Spectra and Structure of compounds Formed in the Extraction of Oxalic Acid by Solutions of Trioctylamine", *Sov. Radiochem.* (Engl. Transl.), **10**, 169-174; *Radiokhimiya*, **10**, 175-181 (1968).

Nakanishi, H., Morita, H, and Kagakura, S., "Charge-Transfer Bands Observed with the Intermolecular Hydrogen-Bonded Systems between Acetic Acid and Some Aliphatic Amines", *J. Mol. Spectrosc.*, **65**, 295-305 (1977).

Nakanishi, K., *Infrared Absorption Spectroscopy*, 2nd ed., Holden-Day, San Francisco, Chapter 2, 10-45 (1977).

Othmer, D. and Ku, P. L., "Solubility Data for Ternary Liquid Systems//Acetic Acid and Formic Acid Distributed between Chloroform and Water", *J. Chem. Eng. Data*, **5**(1), 42-44 (1960).

Parikh, V. M., *Absorption Spectroscopy of Organic Molecules*, Addison-Wesley, Reading, MA, Chapter 3, 34-90 (1974).

Roberts, J. D. and Caserio, M. C., *Basic Principles of Organic Chemistry*, W. A. Benjamin, Inc., Menlo Park, California, Section 18-10, 846-847 (1977).

Silverstein, R. M., Bassler, G. C., and Morrill, T. C., *Spectrometric Identification of Organic Compounds*, 3rd ed., John Wiley & Sons, New York, Chapter 3, 74-119 (1974).

Smith, J. W. and Vitoria, M. C., "Infrared Spectroscopic Investigations of Acid-Base Interactions in Aprotic Solvents. Part 1. The Interaction of Tri-n-propylamine and Some Carboxylic Acids", *J. Chem. Soc. (A) Inorg. Phys. Theor.*, 2468-2474 (1968).

Sobczyk, L. and Pawelka, Z., "IR-Spectra and Dipole Moments of Hydrogen-Bonded Complexes. Part IV. Proton-Transfer in Carboxylic Acid-Trialkylamine Adducts", *Rocz. Chem., Ann. Soc. Chim. Polonorum*, **47**, 1523-1531 (1973).

Yamabe, T., Akagi, K., Kagata, S., Kato, H., and Fukui, K., "Charge Transfer Interaction Between Thioacetic Acid or its Ethyl Ester and Triethylamine", *J. Phys. Chem.*, **80**, 611-617 (1976).

Yerger, E. A. and Barrow, G. M., "Acid-Base Reactions in Non-dissociating Solvents. Acetic Acid and Diethylamine in Carbon Tetrachloride and Chloroform", *J. Am. Chem. Soc.*, **77**, 4474-4481 (1955*a*).

Yerger, E. A. and Barrow, G. M., "Acid-Base Reactions in Non-dissociating Solvents *n*-Butylamine and Acetic Acid in Carbon Tetrachloride and Chloroform", *J. Am. Chem. Soc.*, **77**, 6206-6207 (1955*b*).

CHAPTER 5. CHEMICAL INTERACTIONS

In Chapter 3 it was shown that mass-action law analysis can be an effective tool for determining reaction stoichiometry, from which chemical interactions can be inferred; however, artifacts from the data treatment methods and deviations of the actual system from simple stoichiometric behavior may confuse interpretation. In Chapter 4 it was shown how spectroscopic methods can detect the nature of individual chemical interactions; yet, these methods have limitations, as the results are frequently ambiguous and difficult to interpret. The goal of this chapter is to correlate the findings of the mass-action law approach with findings from spectroscopic experiments and to appraise these results for chemical plausibility. Thus a fuller understanding of the interactions among the acid, amine, diluent, and complexes which control complexation equilibria shall be developed.

5.1 More Discussion of the Mass-Action Law

The magnitudes of the equilibrium constants calculated in Chapters 2 and 3 are governed by a combination of the strength of the acid-amine or acid-acid bond formation and the activity coefficients of the complexes. In Chapter 2, the overall equilibrium constant, β_{pq}, was defined as

$$\beta_{pq} = \frac{[\overline{A_pB_q}]}{[A]^p[\overline{B}]^q} \qquad \text{(Eq. 2-3)}$$

In cases where there is a single amine per complex, as in $(p,1)$ stoichiometries, where p = 1, 2, 3, or 4, it is convenient to recast the complexation reactions into stepwise associations of the form

$$A + \overline{A_{p-1}B} = \overline{A_pB} \qquad K_{p1,true} = \frac{\{\overline{A_pB}\}}{\{A\}\{\overline{A_{p-1}B}\}} \qquad \text{(Eq. 5-1)}$$

where the braces denote species activities. The experimentally accessible apparent equilibrium constant, K_{p1}, is defined as

$$K_{p1} = \frac{[\overline{A_pB}]}{[A][\overline{A_{p-1}B}]} \qquad \text{(Eq. 5-2)}$$

where the square brackets indicate the analytical concentration of the species. The apparent stepwise association constant, K_{p1}, is the ratio of the overall association constants, $\beta_{p1}/\beta_{p-1,1}$, and K_{11} is equal to β_{11}. The true thermodynamic equilibrium constant, $K_{p1,true}$, is related to the apparent constant by

$$K_{p1,true} = K_{p1} \frac{\gamma_{ApB}}{\gamma_A \gamma_{Ap-1B}} \qquad \text{(Eq. 5-3)}$$

where γ_i is the activity coefficient of species i. It has been assumed as a first approximation that the activity coefficients are constant for a given system, i.e., independent of acid and complex concentrations. The stepwise constant is more useful in the discussion of this chapter because it refers to the interaction of a single acid molecule with the amine or amine-acid complex.

To separate the effects that contribute to K, the complexation can be taken as a series of paths which bring about the overall change of state. The standard state is specified as pure liquid components at 25 °C and one atmosphere pressure (Raoult's Law). For a reaction carried out at 25 °C and one atmosphere, the overall change of state may be divided into: (*a*) "Unmixing" of reactants (A, $A_{p-1}B$, and B) from their

equilibrium concentrations in solution to pure components. (*b*) Reaction at 25 °C of the pure reactants to form pure product, A_pB. (*c*) Dilution at 25 °C of pure product to equilibrium concentration in solution.

Transition (*b*) is the standard state reaction; hence the association constant for this reaction is the true thermodynamic constant, $K_{p1,true}$. This constant, being for the reaction of pure components, will depend on the acid and amine and will be independent of the diluent.

Transitions (*a*) and (*c*) reflect deviations of K from K_{true} due to the non-idealities of dilution of the aqueous and organic phases, that is, the activity coefficients, γ_A, γ_B, $\gamma_{Ap\text{-}1B}$, and γ_{ApB}, in Eq. 5-3. Diluent interactions with the species govern the magnitudes of these values. If the extractant is concentrated enough to affect the overall solvent properties, it too will affect the magnitude of these values.

5.2 Discussion the Mass-action Law Analysis in Comparison with Information From Spectroscopic Studies on the Stoichiometry

5.2.1 Overloading

Spectroscopic evidence outlined in Chapter 4 indicated that (2,1) complex formation occurs when the hydroxyl group of the second acid forms a hydrogen bond with the carboxylate of the first acid. The strength of this interaction can be inferred from batch extraction results. Table 5-1 shows selected data from Table 3-2 that have been recast in the stepwise form to make the relationship between first and

Table 5-1. Comparison of (2,1) and (1,1) Complexation Constants for Carboxylic Acid-Tertiary Amine Systems

(Calculated from values given in Table 3-2)

Solvent	$\log_{10}$	Acetic	Lactic	Fumaric[a]	Succinic	Malonic	Maleic
MIBK/DIBK	K_{21}		0.19	1.62	0.72	0.14	0.55
	K_{11}		1.31	3.02	1.27	3.11	5.69
	Δ	>0[b]	**-1.12**	**-1.50**	**-0.55**	**-2.97**	**-5.14**
Benzene/Xylene	K_{21}	0.10	-0.02				
	K_{11}	0.14	-0.11				
	Δ	**-0.04**	**0.09**				
Nitrobenzene	K_{21}	0.90			-0.27		
	K_{11}	0.87			2.43		
	Δ	**0.03**			**-2.70**		
Chloroform	K_{21}	0.63	-0.45		-0.95		-0.28
	K_{11}	1.25	2.57		2.44		6.00
	Δ	**-0.62**	**-3.02**		**-3.39**		**-6.28**
2-Ethyl-1-Hexanol	K_{21}	-0.13					
	K_{11}	1.83					
	Δ	**-1.96**					

[a] Values for calculations for fumaric acid that were done at low amine concentrations, where the influence of (2,2) complexation is small.

[b] A value of negative infinity for $\log(K_{11})$, i.e. $K_{11} = 0$, was found to fit the data best. Thus K_{21} is not defined, but it must be a large, positive number.

second acid binding constants more apparent. If $\Delta = \log(K_{21}) - \log(K_{11}) << 0$, then the (1,1) complex is stabilized in preference to the (2,1) complex. Visually, this was seen in plots of Z vs. log[A] as a long plateau at $Z = 1$.

The effect of acid or diluent on the apparent equilibrium constant for (2,1) complexation can be derived from Eq. 5-3 as shown below.

$$K_{21} = \frac{\gamma_{AB}\gamma_A}{\gamma_{A2B}} \times K_{21,true} \qquad \text{(Eq. 5-4)}$$

For different acids in the same diluent, the difference in K_{21} values is proportional to the difference in $\gamma_A \cdot K_{21,true}$. An assumption is that the activity coefficients of the (1,1) and (2,1) complexes for different acids are affected similarly in the same diluent. For different diluents with the same acid, the difference in K_{21} values is proportional to the difference in γ_{AB}/γ_{A2B}. This carries the assumption that "general" solvation for polar species will affect the activities of (2,1) and (1,1) complexes to a similar extent. But, if one complex has a more "specific" interaction with the diluent than the other, the activity coefficient ratios will be dissimilar in the different diluents.

It should be noted that "general" and "specific" are arbitrary divisions of the range of forces which may occur between solvent and complex. In this section, "specific" will generally refer to interactions which depend on the structure and functionality of the particular molecules involved, e.g. hydrogen bonding. "General" will refer to forces which relate to the overall solvation ability of a solvent, e.g. dipole-dipole interactions or dispersion forces.

Effect of Type of Acid on Overloading

In general, the ratio of formation constants for (2,1) to those for (1,1) complexes for dicarboxylic acids is small compared with the same ratio for monocarboxylic acids. This behavior can be attributed in large measure to the fact that dicarboxylic acids are generally stronger than monocarboxylic acids. Table 5-1 shows that Δ, the difference in the logarithm of the (2,1) and (1,1) equilibrium constants, decreases in the order: acetic > succinic > lactic > fumaric > malonic > maleic, the same order as decreasing pK_A. It is also evident that K_{11} increases with increasing strength (lower pK_A) of the acid. Therefore, if K_{21} is not related to acid strength, it is logical that the difference between K_{21} and K_{11} will be greater for a more acidic acid. This is consistent with the spectroscopic findings that different mechanisms control (2,1) and (1,1) complex formation. (2,1) complexation occurs by hydrogen bond formation, which should not be directly dependent on acid strength. (1,1) complexation is controlled by an acid-base reaction and depends greatly on acid strength.

Additionally, there appears to be not only a trend in the difference in values of the (1,1) and (2,1) constants, but also the actual values of the (2,1) constants themselves are smaller for dicarboxylic than monocarboxylic acids. This behavior may be rationalized in part as competition between intramolecular and intermolecular hydrogen bond formation. It is known that in some organic solvents bimalonate, bisuccinate, bimaleate, biphthalate, and possibly bioxalate undergo appreciable internal hydrogen bonding between the carboxyl and carboxylate groups (Kolthoff and Chantooni, 1975; Evans and Goldstein, 1968). Possibly this impedes the interaction of the carboxylate group of the first acid, which is complexed to the amine, with the hydroxyl of the second acid, thus suppressing (2,1) complex formation. Table 5-1

shows that the magnitudes of K_{21} for acids in MIBK (or DIBK) decrease in the order: malonic < maleic < succinic < fumaric < acetic. This is approximately in order of decreasing tendency to form intramolecular hydrogen bonds, taking the pK_A difference between the first and second carboxyl group as a first approximation of intramolecular hydrogen bond strength, and reasoning that fumaric and acetic acid cannot form intramolecular hydrogen bonds. Such a trend helps support the speculation that internal hydrogen bonding in the (1,1) complex competes with (2,1) complex formation. This evidence, however, is far from conclusive; the trend may also be related to the differences in aqueous-phase activity coefficients. Therefore, the effect of intramolecular hydrogen bonding on (2,1) complexation is speculative at this time.

No significant overloading was detectable for the extraction of fumaric acid by Alamine 336 in chloroform at the concentrations and temperatures studied, even though fumaric acid cannot form intramolecular hydrogen bonds. An additional factor that may impede (2,1) complex formation for fumaric acid in chloroform is simply that two acid groups rather than one must be satisfied for each amine. In other words, (1,2) complex formation uses up two amines per acid. Therefore, loading greater than one for a dicarboxylic acid may be analogous to loading greater than two for a monocarboxylic acid. In MIBK, (1,2) complex formation is less favored, because the basic carbonyl group of the ketone can compete with the amine for the second carboxyl group. Hence, overloading is possible for fumaric acid in the ketone diluent.

Lactic acid exhibits unexpectedly little overloading behavior for a monocarboxylic acid, much less than acetic acid. It may be speculated that, in both chloroform and MIBK, there is internal hydrogen bonding of the hydroxyl of the lactic acid to the carboxylate group, albeit such an interaction would be expected to form an extremely strained ring. Interestingly, an internally-bonded structure for α-hydroxyisobutyric

acid has been deduced by NMR experiments (Mori et al., 1969), which would also be a very strained cyclic structure. Nevertheless, such an internal interaction for lactic acid is speculative.

Effect of Diluent on Overloading

The diluent also affects the stability of the (2,1) complex. Table 5-1 compares (2,1) equilibrium constants for different diluents. For acetic acid, chloroform and 2-ethyl-1-hexanol, both proton-donating solvents, stabilize the (1,1) complex in preference to (2,1) complexes, in comparison with non-proton-donating solvents. (Acetic acid in benzene shows little (2,1) complex formation, but does show significant (3,1) complex formation, and thereby exhibits a large net amount of overloading.) For lactic acid, K_{21} in chloroform is much smaller than K_{21} in MIBK or xylene. For succinic and maleic acids, K_{21} is smaller in chloroform than in MIBK. Thus it is seen that y_{AB}/y_{A2B} is smaller in proton-donating diluents.

This behavior can be rationalized as competition between the solvent proton and the second acid carboxyl proton for the carboxylate binding site on the first acid. Ketones, aromatic, and other non-proton-donating solvents cannot compete effectively for the binding site, and therefore allow for multi-acid complexes. Consequently, interaction of the solvent proton with the carboxylate stabilizes the (1,1) complex and destabilizes the (2,1) complex. From spectroscopic studies by Barrow and Yerger (1954), it was inferred than chloroform indeed interacts specifically with the complex at the carboxylate (see Section 4.2.2 for more discussion). The hydroxyl group of an alcohol would be expected to interact similarly.

Interestingly, it appears that ketone diluents promote overloading more than other non-proton donating diluents, such as benzene or nitrobenzene. This behavior can be justified for dicarboxylic acids if internal hydrogen bonding is assumed to be a factor in complex stoichiometry. It is logical that ketones (and perhaps other basic solvents) promote overloading for dicarboxylic acids because of their ability to interact with the second carboxyl group. This interaction may both inhibit internal hydrogen bonding, freeing the binding site for a second acid, and satisfy the second carboxyl group, repressing the need for a second amine. However, this does not explain why (2,1) formation constants are larger in ketones than in other diluents for acetic and lactic acids, which are monocarboxylic acids. Perhaps the ketone somehow stabilizes the (2,1) complex by influencing the hydrogen bonding of the second acid to the first.

Intramolecular bonding has been shown to be less in dimethyl sulfoxide, DMSO, a basic solvent, than in acetonitrile, a non-proton donor or acceptor (Kolthoff and Chantooni, 1976). This supports the conjecture that solvents with basic functional groups, such as ketones, may interfere with intramolecular hydrogen bonds. However, an additional complication is that water has also been found to compete with internal hydrogen bonding of dicarboxylate monoanions in organic solvents (Evans and Goldstein, 1968).

In this work, it was not determined with certainty whether an alcohol diluent helps or hinders the formation of (2,1) complexes for dicarboxylic acids. It is logical that the hydroxyl group would reduce (2,1) complexation by interaction with the (1,1) complex. However, the hydroxyl group could interfere with intramolecular hydrogen bonding, thereby encouraging (2,1) complex formation. On the other hand, it apparently is not basic enough to compete with the amine for the second acid, which

would discourage (2,1) complex formation (see Section 5.2.2 below). Unfortunately, the overloading region for the extraction of succinic acid by Alamine 336 in octanol could not be studied in detail because of the limited solubility of succinic acid in water. Nevertheless, the lack of overloading at the concentrations studied suggests that (2,1) complex formation is rather limited. Testing of a more water-soluble dicarboxylic acid in an alcohol diluent is required to gain more complete information on the effect of an alcohol hydroxyl group on overloading of dicarboxylic acids.

5.2.2 Multi-Amine Complex Formation

Dicarboxylic acids potentially can form (1,2) complexes, but the presence of such complexes was rarely indicated by the data from the batch extraction studies. No evidence of (1,2) complex formation with Alamine 336 was seen for succinic acid in chloroform, nitrobenzene, MIBK, or methylene chloride, for malonic acid in MIBK, or for maleic acid in MIBK or chloroform. (1,2) complex formation was manifested for succinic acid in octanol, and fumaric acid in chloroform and MIBK.

In Section 4.4, an IR spectroscopic investigation reported a comparison of succinic, maleic, and fumaric acids. It was concluded that intramolecular hydrogen bonding discourages the formation of (1,2) complexes; thus fumaric acid has a greater tendency for form (1,2) complexes. Similar effects of the type of acid should be extensible to other solvents.

For fumaric acid, the equilibrium constant for (1,2) complex formation is approximately an order of magnitude higher in chloroform than in MIBK. In MIBK, the basic carbonyl group of the solvent can provide for stabilization of the second carboxyl group, possibly reducing (1,2) complex formation, while in chloroform, no

such interaction is possible. It is interesting that the formation constants for fumaric acid-amine (2,2) complexes were calculated to be of similar magnitude in chloroform and MIBK. If the above argument that the ketone interacts with the second carboxyl group were correct, it would be expected that (2,2) complex formation would also be impeded in the ketone diluent, which was not the case.

Octanol allows for significant (1,2) complex formation with succinic acid and Alamine 336. This is consistent with the study by Gusakova et al. (1986) who showed that malonic acid and triethylamine in methanol formed a (1,2) complex, whereas malonic acid and triethylamine in chloroform, acetonitrile, and dioxane did not. Gusakova et al. concluded that the alcohol hydroxyl group interferes with the intramolecular hydrogen bond. Apparently, it is not basic enough to satisfy the second carboxyl group to prevent (1,2) complex formation.

Prior investigations have shown that the nature of the amine also affects formation of complexes with multiple amines. Gusakova et al. (1986) concluded from spectroscopic studies that secondary amines are more able to form (1,2) complexes than tertiary amines. Kawano et al. (1983*b*) fit the data for formic acid, which has only one carboxyl group, and Amberlite LA-2, a secondary amine, to stoichiometries which included (1,2) complex formation. Yerger and Barrow (1955) found from spectroscopic studies that secondary and primary amines form (2,2) complexes with acetic acid, whereas tertiary amines do not. This phenomenon could be examined in more detail by performing batch extraction experiments to compare the stoichiometries obtained with secondary and tertiary amines. Such an examination was not attempted here.

5.3 Aggregation

Di- and tricarboxylic acids show a much more pronounced tendency to aggregate and form third phases when extracted by amines than do monocarboxylic acids. This may be because dicarboxylic acids have two potential binding sites, so they can act as a link between other amines and acids to form a large complex or aggregate. Monocarboxylic acids, having only one site, cannot link two amines together. Further evidence of this is the odd stoichiometries inferred for citric, succinic, and tartaric acids extracted by trilaurylamine in aromatic hydrocarbons (Table 3-3). Sets of complexes with $(i,i+1)$ stoichiometries fit the data best, suggesting, perhaps, a chain-like structure, with each acid sandwiched between two amines. If this were the case, one might expect secondary amines, with their tendency to form bridged structures (see Section 4.1.3) would show a greater tendency toward aggregation. Such speculation was not examined further and remains for future work.

The more inert the diluent, the more favorable it will be for the polar complexes to form aggregates, and thus shield themselves from the non-polar environment. Aggregation also increases as the acid-amine complex concentration increases, as is indicated by the law of mass action and was seen in the present work for succinic acid extracted with 0.29 and 0.58 mol/L Alamine 336 in a heptane-chloroform mixture and a heptane-dichloromethane mixture (see Figs. 2-13 *a* and *b* and surrounding discussion). A larger concentration of polar complexes increases the ability to form a separate phase.

Aggregation is a difficult phenomenon to describe quantitatively by a mass-action law model. Formation of acid-amine complexes with large stoichiometric coefficients, such as proposed Vanura and Kuca (1976), can quantitatively describe some systems

quite successfully. In fact, a mass-action law analysis can model any set of data, given enough adjustable stoichiometric coefficients and equilibrium constants. Unfortunately, these increasing numbers of adjustable parameters are increasingly unwieldy for use in empirical models and have doubtful basis in reality.

Experimental methods for determinations of average molecular weight, which use colligative properties, such as vapor pressure osmometry (Clark, 1941) or freezing point depression (Vieux et al., 1974), could provide additional information to describe aggregates. For example, an acetic acid-amine system could be compared with a succinic acid-amine system to determine if there is a large difference in average molecular weight. This would give additional evidence for aggregate formation. Measurements of freezing point depression have also been used to detect evidence of dimer formation in the complexation of oxalic acid with trioctylamine in nitrobenzene (Vieux et al., 1974).

Using concepts of molecular thermodynamics to calculate activity coefficients for simple species, rather than using multiple complexes with large stoichiometric coefficients, may be a more physically justifiable way to describe the data. To model the shapes of the loading curves for dicarboxylic acids in inert diluents, these activity coefficients must be functions of the concentration of the complex in the solvent phase. The concave upward shape of the data in Fig. 2-14 indicates that the activity coefficient of the complex decreases with increasing complex concentration. However, interactions between complexes are likely to be quite strong. A description of the solvation of the complexes would require either a large number of empirically-based parameters or a very sophisticated theory of physical solvation.

5.4 Factors Affecting the Acid-Amine (1,1) Reaction

5.4.1 Type of Acid (Acidity, Hydrophilicity/Hydrophobicity)

Two major parameters affecting (1,1) equilibrium constant are the acidity and hydrophobicity of the acid. Clearly, the greater the acidity of the acid, the stronger the complex it will form, and the greater the extraction. And, the greater the hydrophobicity of the acid, the more distribution, both by solvation and by complexation, into the organic phase will be favored. Acidity is a stronger influence that hydrophobicity for the acids studied in the present work. For example, malonic acid is extracted more easily than succinic acid by Alamine 336 in MIBK, although malonic acid is clearly less hydrophobic, and shows smaller distribution ratios into the diluent alone than succinic acid (see Table 2-1). For acids with similar pK_A values, hydrophobicity would determine which acid is extracted preferentially. The effect of hydrophobicity may also be more important for more complex solutes, which could show a greater range of hydrophobicities than the simple solutes studied in the present work.

Fig. 5-1 shows the effect of pK_A of the acid on the logarithm of the (1,1) equilibrium constant, K_{11}, in various diluents. The constant decreases with increasing pK_A (decreasing aqueous-phase acidity) of the acid. This can be rationalized by splitting the complexation reaction into three separate reactions. The overall reaction is given as

$$\overline{B} + \overline{HA} = \overline{BHA} \qquad K_{11} = \frac{[\overline{BHA}]}{[\overline{B}][HA]} \qquad \text{(Eq. 2-7)}$$

The equations

$$HA = H^+ + A^- \qquad K_A = \frac{[HA]}{[H^+][A^-]} \qquad \text{(Eq. 5-5)}$$

$$\overline{BH^+} = \overline{B} + H^+ \qquad K_B = \frac{[H^+][\overline{B}]}{[\overline{BH^+}]} \qquad \text{(Eq. 5-6)}$$

$$\overline{BH^+} + A^- = \overline{BHA} \qquad K_P = \frac{[\overline{BHA}]}{[\overline{BH^+}][A^-]} \qquad \text{(Eq. 5-7)}$$

combine to give the relation

$$K_{11} = K_P \times K_A/K_B \qquad (5\text{-}8)$$

Thus,

$$\log(K_{11}) = -pK_A + pK_B - pK_P \qquad (5\text{-}9)$$

K_A is determined by the type of acid. K_B depends on the basicity of the amine in the diluent and is independent of acid type. K_P is governed by acid-diluent and acid-ammonium ion interactions. *If* it were assumed that the last of these interactions are similar for all carboxylic acids (constant K_P), Fig. 5-1 would give a straight line with a slope of negative one and an intercept at $pK_B - pK_P$. The data in Fig. 5-1 qualitatively follow Eq. 5-9, but the relationship is not an adequate tool for quantitative prediction of K_{11}.

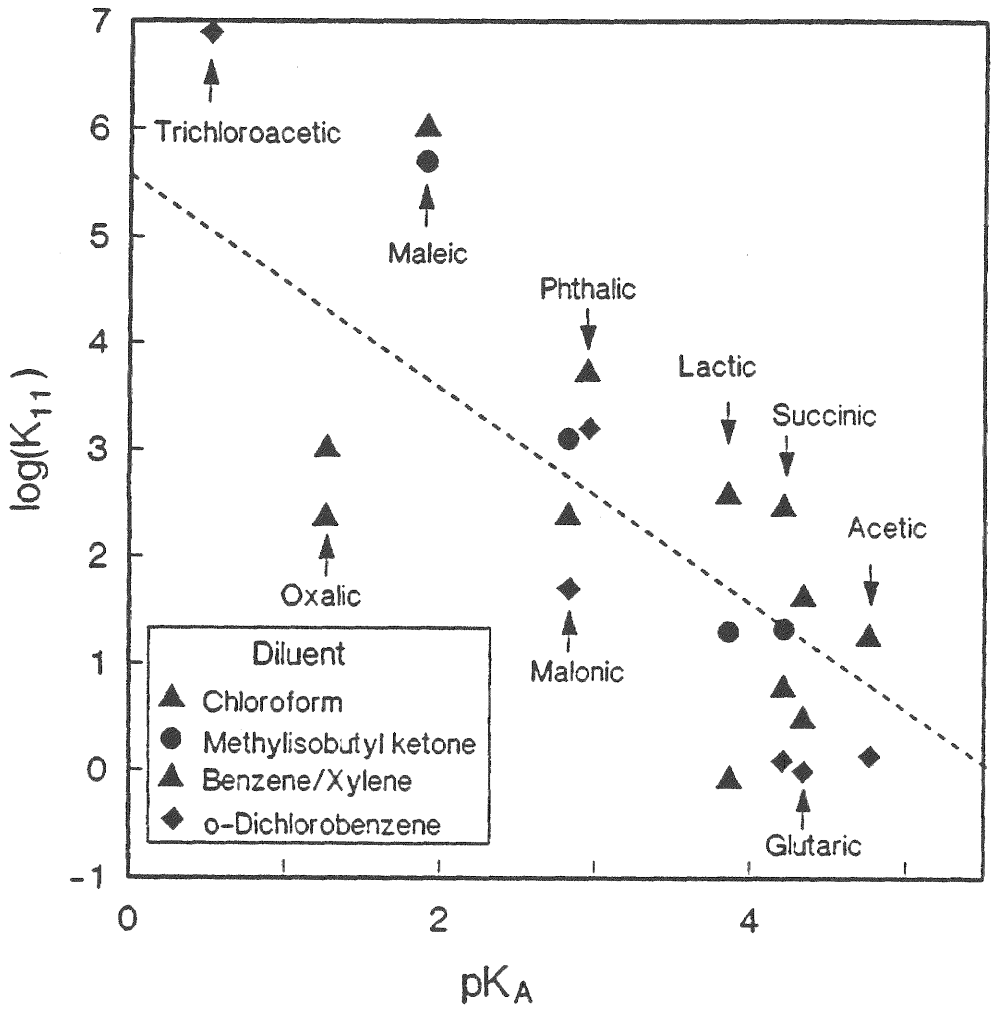


Fig. 5-1. Influence of pK_A on the (1,1) Equilibrium Constant.

Comparison of the data with the relationship

$$\log(K_{11}) = -pK_A + pK_B - pK_P \qquad \text{(Eq. 5-9)}$$

Dashed line indicates a slope of negative one.

The major problem with this approach is that K_P is *not* constant for each acid. The tendency for an acid to form the salt with the ammonium ion will be affected by class of amine, diluent, and the structure of the acid itself. Acid-diluent interactions may be characterized by the distribution of acid into the solvent alone, which is related directly to acid hydrophobicity, but acid-ammonium ion behavior in the organic phase is difficult to characterize.

An alternative approach is to predict ion-pair stability by a combination of some measure of solute acidity in the organic-phase with the physical partitioning of the acid into the solvent. This derivation postulates that organic-phase acidity characterizes the anion stability in a particular diluent. This avoids the difficulty with ternary interactions of K_P because the organic-phase acidity is assumed to depend on the anion and diluent and to be independent of base type.

$$HA = \overline{HA} \qquad P = \frac{[\overline{HA}]}{[HA]} \qquad \text{(Eq. 5-10)}$$

$$\overline{HA} = \overline{H^+} + \overline{A^-} \qquad K_{A,org} = \frac{[\overline{HA}]}{[\overline{H^+}][\overline{A^-}]} \qquad \text{(Eq. 5-11)}$$

$$\overline{BH^+} = \overline{B} + \overline{H^+} \qquad K_B^* = \frac{[\overline{H^+}][\overline{B}]}{[\overline{BH^+}]} \qquad \text{(Eq. 5-12)}$$

If it is assumed that $[\overline{BH^+}]$ corresponds to the amount of "complexed" acid then

$$K_{11} = P \times K_{A,org}/K_B^* \qquad (5\text{-}13)$$

This derivation separates the equilibrium constant into three parts, each of which is dependent only upon binary interactions. P is governed by the hydrophobicity of the acid and the type of diluent; $K_{A,org}$, the acid and diluent; K_B^*, amine and diluent. Unfortunately, organic phase acidity data are not generally available for carboxylic acids. Because of the limited data base available, there was no attempt in this work to pursue this derivation further.

5.4.2 Amine Class and Type (I°, II°, III°, Branched/Linear, Chain Length)

An experimental study of the effects of different amines was beyond the scope of this work; however, information from the literature suggests that amine type may be an important influence in an acid extraction process. Accordingly, a brief discussion of literature results is given below.

Kawano et al. (1983*a*) compared Amberlite LA-2, a secondary amine, and trioctylamine, a tertiary amine, for their extracting power for acetic and propionic acids in hexane and benzene. The authors found that the secondary amine allowed more extraction than the tertiary amine (see Table 3-2). Ricker (1978) studied the extraction of acetic acid by Amberlite LA-2 in methyl isobutyl ketone and Alamine 336 in diisobutyl ketone. The secondary amine allowed for significantly higher extraction than the tertiary amine, if the difference in the diluent chain-length is ignored. From IR studies, Yerger and Barrow (1955) found that for acetic acid in carbon tetrachloride diluent, diethylamine produced a much greater (1,1) complex formation constant than triethylamine. Additionally, the authors found that the effect of amine is coupled with the type of diluent. In chloroform, diethylamine and triethylamine gave approximately equal (1,1) complex formation constants.

Reschke and Schügerl (1984) studied the extraction of penicillin G in *n*-butyl acetate diluent with secondary amines -- Amberlite LA-2 (a mixture of secondary amines, $C_{12}H_{25}$-NH-$R_1R_2R_3$, with R_1+R_2+R_3 equal to 11-13 carbon atoms, molecular weight 351-393 g/mol), dioctylamine, Amberlite LA-1 (another mixture of secondary amines), and Adogen 283 (a symmetric secondary amine with two branched C_{13} chains), tertiary amines -- dimethylpalmitylamine, trioctylamine, and primary amines-- *n*-octylamine, n-dodecylamine, and decylamine, Amberlite LA-3, and Adogen 115-D. The primary amines were found to be unsuitable for extraction because they exhibit low distribution coefficients and tend to form stable emulsions. The secondary amines were found to have significantly more extracting power than the tertiary amines, and also show more variation within the amine class in extracting power.

Grinstead (1967) studied the behavior and base strengths of various amine types and classes for the extraction of hydrochloric acid in toluene diluent. The base strength decreased in the order primary > secondary > tertiary. He found that aggregation occurred less readily for the tertiary amine-acid complexes than for primary or secondary amine-acid complexes. For all amine classes, increased branching on the alkyl group(s) lowered the effective base strength of the amine. Secondary and tertiary amines with linear alkyl chains showed three orders of magnitude greater complexation constant than the highly-branched forms. The effect of branching was less for the primary amines studied, which was thought to reflect the lower steric crowding around the nitrogen of a single alkyl group. Trihexylamine and trioctylamine were found to have identical base strengths, supporting the idea that chain length is not of great consequence.

Grinstead proposed several explanations for the effect of branching on amine strength. The first is that the anion of the ion pair will encounter steric hindrance

with more highly branched amines, and thus bond less effectively. Secondly, the anion may restrict the freedom of rotation of the alkyl groups on the nitrogen atom, reducing the stability of the salt. Finally, the steric effect may be related to the ease with which the amine salt complexes can aggregate together. If aggregation is more facile, the apparent extraction of the acid will be greater, and the apparent base strength of the amine will be greater. Alkyl chains with more branching would be expected to aggregate less easily, and thus have lower effective basicities.

Rieux et al. (1964) examined the effect of chain length, class of amine (primary, secondary, or tertiary), and diluent on amine basicity. The authors determined the complexed acid concentration spectrophotometrically, using 2,4-dinitrophenol as the reacting acid for all cases. From the fraction of acid ionized, they calculated the amine basicity. In benzene and chloroform, the basicities of the amines followed the order, secondary = tertiary > primary; in ketones, secondary > tertiary > primary; in ethers and esters, secondary > primary > tertiary; in chlorobenzene, tertiary > secondary > primary. The length of the alkyl chain from butyl to dodecyl was found to have negligible effect on amine basicity for any class of amine.

It is clear that the effect of amine type is complicated by diluent interaction, and cannot be summarized by simple generalities. Yerger and Barrow (1955) concluded that the diluent influence varies with amine class because the three classes of amine differ in their interaction with the acid. The differences in these interactions change the relative influence of diluent interaction with the complex. For example, secondary ammonium ions are capable of forming two hydrogen bonds with acetic acid, while a tertiary ammonium ion can form only one. The effect of "extra" hydrogen bonding of the complex with chloroform does not affect the secondary amine-acid complex as much as the tertiary amine-acid complex. Hence the formation constant for the acid-

tertiary amine complex increases greatly between carbon tetrachloride and chloroform, whereas the formation constant for the acid-secondary amine complex does not change significantly.

It would be interesting to perform batch extraction experiments in order to examine more closely the effect of amine class. The results could be correlated with the findings from IR studies to determine if different amine structures allow for different amine-acid interactions, and if these correspond to different amine extracting powers. This study remains for future work.

5.4.3 Diluent

Diluent Properties

It has been suggested that the diluent effect can be characterized by a comparison of equilibrium constants which are based on the concentration of acid in the organic rather than aqueous phase (Chaikhorskii et al., 1966; Rieux et al., 1964). This basis was not used in this work. The activity of free acid in the organic phase is equal to the activity of acid in the aqueous phase. Using organic-phase acid concentrations adds an additional complication, because the activity coefficients of a given acid in the organic phase are unknown and differ in different diluents. On the other hand, the activity coefficients in the aqueous phase are the same for a given acid in different diluents, since the diluent does not affect the relationship between aqueous acid concentration and activity (at least insofar as the diluent is water-immiscible.) In this way, for a given acid the effect of diluent can be compared more directly.

It has been argued that using the organic-phase acid concentration accounts for the acid-diluent interaction, allowing direct comparison of the acid-amine interactions in different diluents. However, spectroscopic experiments showed convincingly that interaction of the diluent with the acid-amine complex, not just the acid itself, has a strong effect (Barrow and Yerger, 1954). Given the high acid distribution into amine with a chloroform diluent, where partitioning into the solvent is low, and the lower distribution into amine with MIBK diluent, where partitioning into the solvent is high, it is clear that the diluent-complex interaction is not correlated well with the diluent-acid interaction. Thus, a parameter for diluent-complex interactions (i.e. y_{AB}) rather than diluent-acid interactions (i.e. activity of free acid in the organic phase) is used in this work to characterize the diluent effect. (Although the derivation leading to Eq. 5-13 uses the organic-phase acid concentration, it requires acidity values in the organic phase to characterize the acid anion-diluent interaction.)

The large differences among K values for the same acid in different diluents (see Table 3-2) indicate that solvation of the complex by the diluent is a critical factor in the overall process (transition c). Consider (1,1) complex formation at 25 °C. The difference in K_{11} is inversely proportional to the difference in y_{AB}/y_B, since y_A is a constant depending only on the type of acid and $K_{11,true}$ depends only on the acid and amine. Increased interaction between diluent and complex decreases y_{AB} and thus increases the distribution of acid to the organic phase.

Inert diluents -- alkanes and unsubstituted aromatic hydrocarbons -- give very low distribution of acid into the solvent phase. This is easily understood, as alkanes, being non-polar, provide for very little solvation of the polar complexes. The (1,1) equilibrium constants for the extraction of acetic and propionic acids by tertiary amines in alkane diluents were all less than unity (i.e., $\log(K_{11}) < 0$). Aromatic

diluents produce slightly higher K_{11} values, with acetic and lactic acid-amine complexes showing formation constants of the order of unity. The slightly higher extraction by aromatic solvents has been rationalized as solvation due to interaction of the aromatic π electrons with the complexes (Vieux et al., 1974). In Table 3-1 it was seen that alkyl substituted aromatics (xylene and toluene) extract slightly less acid than benzene. This is logical because xylene and toluene have more alkyl character than benzene and thus slightly less ability to solvate the complexes.

Active diluents have functional groups which enable greater solvation of the complex. The chlorinated aromatics promote about a fivefold greater equilibrium association constant than unsubstituted aromatics, probably because their greater polarity allows for better solvation of polar complexes. The ketone diluents give formation constants tenfold larger than the unsubstituted aromatics. Nitrobenzene, chlorinated hydrocarbons, and alcohols give the highest distribution ratios, with an additional order of magnitude increase in K_{11}.

Nitrobenzene is an extremely polar solvent, and can promote extraction by providing a good solvating medium for the ion-pair. However, polarity (or polarizability) alone does not account for the behavior of some of the solvents. Halogenated hydrocarbons and alcohol diluents give unusually high equilibrium constants, higher than would be expected from polarity arguments alone. For these solvents, specific hydrogen bonding between the proton of the diluent and the acid-amine complex is thought to explain the extra solvation by these diluents (Manenok et al., 1979). Such hydrogen bonding interactions have been inferred for acetic acid in triethylamine and chloroform by spectroscopic studies (Barrow and Yerger, 1954), where chloroform acts as a proton donor to the carboxylate anion. It is reasonable that an alcohol can also donate a proton to the ion-pair.

It is difficult to establish whether ketones, which are proton acceptors, interact specifically with the complex, or simply solvate it. On the basis of results from a UNIFAC modeling scheme (see below) Spala and Ricker (1982) concluded that diisobutyl ketone did not interact specifically with an acetic acid-amine complex. They found that parameters for binary systems were capable of describing the quaternary acid-amine-diluent-water system, and so concluded that specific diluent-complex interactions were negligible. Methylene chloride is also difficult to characterize as either specific interaction or general solvation. It is not as strong a proton donor as chloroform, and it has higher solvating ability for polar molecules.

Several authors (Manenok et al., 1979; Wardell and King, 1978; Soldatov et al, 1978) have suggested to use of the Hildebrand solubility parameter, δ, as a measure of solvation of the complex by the diluent. Table 5-2 compares the values of δ with K_{11} for various acids. For some groups of diluents, the solubility parameter qualitatively describes the effect of diluent on extracting power. For instance, the sequence, alkane < aromatic < chlorinated aromatic < nitrobenzene, corresponds to increasing acid distribution. However, for diluents which interact specifically with the complex, e.g. chloroform, the order is not followed.

The solubility parameter is the square root of the cohesive-energy density, i.e., the energy change upon isothermal vaporization of saturated liquid to the ideal gas state divided by the molar volume (Prausnitz, 1969). According to regular solution theory, the square of the difference in solubility parameters between two substances is proportional to the logarithm of the activity coefficient of each substance. Therefore, if δ for the acid-amine complex is large, the decrease in complex activity with increasing δ of the solvent makes sense. However, the regular solution theory is valid only for regular solutions of nonpolar fluids, not for polar mixtures.

Table 5-2. Relationship Between the Solubility Parameter and Extraction of Carboxylic Acids by Tertiary Amines

(Values for $\log(K_{11})$ from Table 3-2.)

Solvent	$\log(K_{11})$ (L/mol)	δ $(cal/cm^3)^{1/2}$
Acetic Acid		
2-Ethyl-1-Hexanol	1.9	9.5[K]
Chloroform	1.3	9.16
Nitrobenzene	1.0	10.40
Benzene	0.1	9.16
Carbon Tetrachloride	0.0	8.55
n-Hexane	-0.85	7.27
Lactic Acid		
Chloroform	2.1	9.16
MIBK (3-Pentanone)[a]	1.3	9.06
o-Xylene	-0.2	9.06
p-Xylene		8.83
Oxalic Acid		
Chloroform	3.0	9.16
1,2-Dichloroethane	3.0	9.86
o-Dichlorobenzene	2.4	10.04
Malonic Acid		
MIBK (3-Pentanone)	3.2	9.06
o-Dichlorobenzene	2.4	10.04
1,2-Dichloroethane	1.7	9.86
Succinic Acid		
Dichloromethane	2.5	9.88
Chloroform	2.4	9.16
Nitrobenzene	2.4	10.40
1,2-Dichloroethane	2.0	9.86
MIBK (3-Pentanone)	1.3	9.06
o-Dichlorobenzene	0.8	10.04
Benzene	0.1	9.16

[a] No value for MIBK, so value for 3-pentanone given.

Source of value for solubility parameter: Chastrette et al., 1985
[K] source of value for solubility parameter: Kojima et al., 1985

More sophisticated theories for solvent characterization which account for solvent polarity, acidity, and basicity are discussed by Kamlet et al. (1983). These may provide better predictions for the effect of diluent on extracting ability, since they can differentiate between specific solvation due to hydrogen bonding, and general solvation from electrostatic, dispersion, or other forces. This was not pursued further in this work.

Linear Free Energy Relationships

In a series of works, Shmidt and co-workers used linear free energy relationships to describe the effects of solute, extractant and diluent on extraction equilibria. Their semi-empirical approach was developed for general adduct-forming extraction systems, with main emphasis on the extraction of mineral acids. Nonetheless, their derivation may also be useful for carboxylic acid-amine systems.

For acid-amine-diluent systems (Shmidt et al., 1978*a*) the (1,1) equilibrium constant is described by

$$\log(K_{11}) = \log(K_o) + aDP + b\Delta G \qquad \text{(Eq. 5-14)}$$

where,

K_o = equilibrium constant for a standard solute and diluent

= K_o(extractant)

a = sensitivity coefficient = a(solute, extractant)

DP = diluent parameter = DP(diluent)

b = sensitivity coefficient = b(diluent, extractant)

ΔG = free energy of hydration = ΔG(solute)

The parameters, other than the free energy of hydration, are determined empirically from extraction data. The authors proposed an approximation that, for non-specifically interacting diluents, the parameters a and b depend only on the extractant. Thus K_o, a, and b are constants for a given extractant, DP depends on the diluent only, and ΔG depends on the solute only. For the extraction of various mineral acids by trioctylamine, the best-fit values gave the equation

$$\log(K_{11}) = 16.37 + 1.20DP + 0.181\Delta G \qquad \text{(Eq. 5-15)}$$

and for trilaurylamine,

$$\log(K_{11}) = 12.76 + 1.47DP + 0.148\Delta G \qquad \text{(Eq. 5-16)}$$

with ΔG given in units of kcal/mol. A tabulation of diluent parameters calculated from equilibrium data for mineral acid extraction by amines in various solvents is given by Shmidt et al. (1983*a*); a tabulation of values for the free energies of hydration of mineral acids and acetic acid is given by Shmidt et al. (1983*b*).

Shmidt et al. noted several factors which cause deviations from Eq. 5-14. Tertiary amines were the only class of amine which fit a linear relationship between

DP and $\log(K_{11})$; primary and secondary amines do not. The authors concluded that factors other than those taken into account by the diluent parameter influence the value of the equilibrium constant for non-tertiary amines. This is consistent with observations made by Yerger and Barrow (1955), which illustrated that primary and secondary amines interact differently with the acid than do tertiary amines. Shmidt et al. also observed that the parameter b is smaller for chloroform and alcohol/alkane mixtures than for other diluents. Thus a linear relationship between b and $\log(K_{11})$ is applicable only for systems with no specific solvation of the complex by the diluent. Finally, certain anions do not follow a linear relationship between $\log(K_{11})$ and ΔG. For example, ClO_4^- forms a more polar salt than I^-, Cl^-, Br^-, and NO_3^- anions, which indicates a lower solvation energy in the low polarity solvent, and results in smaller equilibrium constants than predicted by Eq. 5-14.

Fig. 5-2 shows the results obtained from experimental measurements of the extraction of acetic and succinic acid compared to the prediction of Eq. 5-14. The equation was examined only for the effect of diluent; $K_o + b\Delta G$ was combined into a single constant, K_o^*. It was assumed that the amine did not significantly influence the value of K_o^*, within the tertiary amine class. The parameter a was calculated separately for the two different carboxylic acids. The values of K_{11} given in Table 3-2 were fit with a linear least-squares analysis to the diluent parameters given by Shmidt (1983*a*). Values of a for acetic and succinic acids differed from those calculated for strong acids by Shmidt et al., with $a = 0.28$ for acetic acid and 0.76 for succinic acid, compared to values of 1.20-1.47 for the strong acids. Values of K_o^* for acetic and succinic acids were -0.517 and -1.199, respectively.

Although the systems show significant average deviations from a linear model (r^2 values for the least squares fits were 0.894 and 0.844 for the acetic and succinic acid

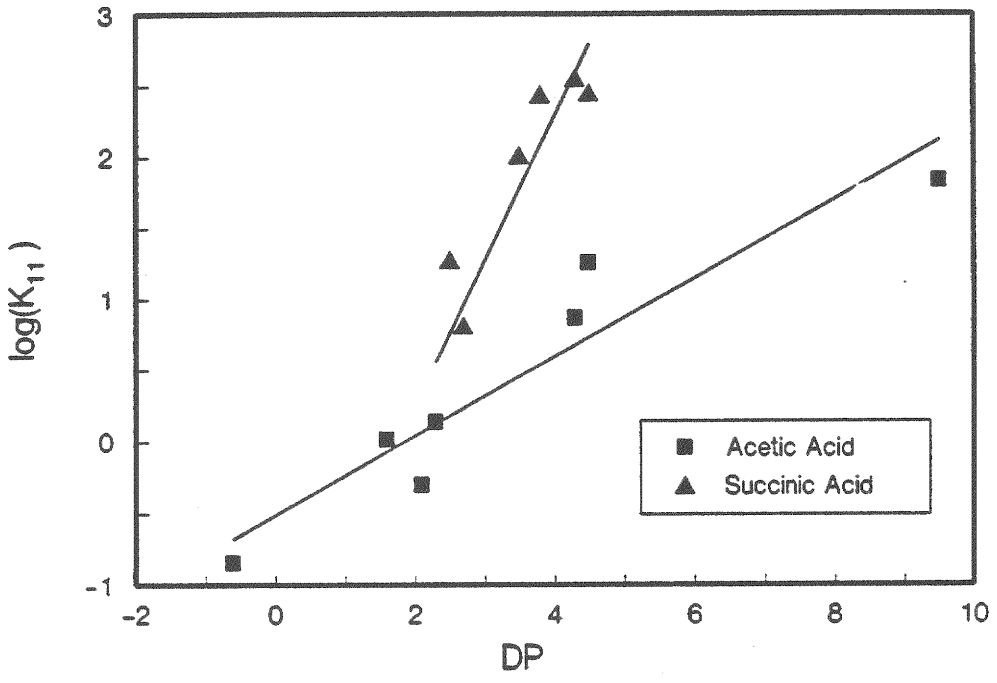


Fig. 5-2. Linear Free Energy Relationship for the Effect of Diluent on the (1,1) Equilibrium Constant.

Extraction of acetic and succinic acid by tertiary amines. Lines show the best-fit to the relationship given by Shmidt et al., (1978*a*).

$$\log(K_{11}) = K_o^* + aDP \qquad \text{(Eq. 5-14)}$$

For acetic acid $a = 0.28$, $K_o^* = -0.52$ for succinic acid $a = 0.76$, $K_o^* = -1.2$

	DP		*DP*
n-heptane	-0.6	benzene	2.3
carbon tetrachloride	1.6	*o*-dichlorobenzene	2.7
o-xylene	2.1	1,2-dichlorobenzene	3.5
benzene	2.3	methylene chloride	3.8
nitrobenzene	4.3	nitrobenzene	4.3
chloroform	4.5	chloroform	4.5
2-ethylhexanol	9.5		

systems, respectively), Eq. 5-14 gives a good first-approximation of how the diluent will affect the magnitude of the equilibrium constant. The semi-empirical *DP* parameters are of greater predictive value than other diluent properties which have been examined. Because they are based on data for acid-amine-diluent or acid-quaternary ammonium ion-diluent, they successfully combine the factors which affect the interaction between the complex and diluent into one parameter. Thus, the linear free energy relationships allow data obtained for one system to be meaningfully applied to other systems.

Shmidt and co-workers examined other extraction systems that are related to the extraction of acids by amines. Anion exchange reactions with quaternary ammonium salts are described by Eq. 5-14, using the same diluent and solute parameters derived for acid-amine extraction systems (Shmidt et al, 1983*b*, 1983*c*, 1980). Systems with more than one acid per amine have also been examined (Shmidt and Rybakov, 1974). The effect of inductive and steric effects of substituents of the nitrogen atom of the amine extractant were described by Shmidt and Rybakov (1978*c*). These authors have also proposed an alternative diluent parameter to take into account not only general but specific solvation of the nucleophilic extractant (Shmidt, 1983*a*).

5.5 Combination of the "Chemical" and "Physical" Theory of Solutions

So far, a "chemical" theory of solutions has been used to characterize the systems studied in this work. This approach is appropriate for systems in which the chemical interactions of species formation are much stronger than forces of solvation. In these cases, the nature of the chemical species generated by a law of mass action model is physically reasonable. From freezing point depression measurements,

Chaikhorskii et al. (1966) concluded that activity coefficients of the (1,1), (2,1), (3,1) complexes and the amine itself were close to unity for acetic acid complexed with trilaurylamine in benzene. However, some systems deviate from this "ideal" behavior. In these cases it may be useful to make an arbitrary division between complexation and solvation effects so that they may be combined into a hybrid model. In such a model, simple complexes are assumed to exist, and deviations from simple stoichiometric behaviors are simulated by assigning activity coefficients to the reactants and/or complexes.

A division between chemical and "physical" (i.e. solvation) interactions may be defensible and useful for carboxylic acid-amine systems. Spectroscopic studies have illustrated that acid-amine complexes can be considered to exist stoichiometrically, whereas interaction of the complex with the solvent may not be strong enough to be attributed to stable species formation. A particularly appropriate use for this type of modeling is to characterize the change in equilibria as the concentration of active diluent is varied, either by change of amine concentration or the active/inert diluent ratio. Thus the effects of solvent composition can be attributed to changes in the activity coefficient of the complex, γ_{AB}.

In Chapter 3, it was shown that modeling by the mass-action law with specific inclusion of diluent in the complex can qualitatively account for the effects of amine concentration and active/inert diluent ratio. Modeling by this "chemical" theory simulates the decrease in loading as amine concentration increases at high amine concentrations. (See Fig. 2-11 showing the extraction of succinic acid by Alamine 336 in chloroform and in MIBK over a full range of amine concentrations.) Inclusion of the diluent in the complex also reproduces the decrease in loading as the volume fraction of active diluent is reduced (Figs. 2-12 *a* and *b* showing the

extraction of succinic acid by Alamine 336 in chloroform and heptane and in dichloromethane and heptane in various ratios). However, limitations of the mass-action law approach are apparent from these plots. First, in Fig. 2-12 the model overpredicts the effect of active diluent concentration at low amine concentrations. Second, at higher amine concentrations or in mostly inert diluent, the experimental results deviate significantly from the simple (p,q,r) model. The experimental data show a much more concave upward shape than the prediction (Fig. 2-11 and Fig. 2-12), presumably because of aggregation of the complex. Finally, it is at least somewhat counterintuitive to include specific numbers of diluent molecules into a complex. It is rather unlikely that the interaction is strong enough to create strong, specific complexes with an exact number of chloroform molecules per complex. At best, the stoichiometric coefficient r can represent an average number of diluent molecules in the complex.

If the above systems are interpreted in terms of a hybrid model, the true (1,1) equilibrium constant remains constant and the activity coefficient of the complex changes with solvent composition. The data shown in Figs. 2-11*a* and 2-12*a* were remodeled, giving each individual amine concentration or active/inert diluent ratio a separate equilibrium constant for the (1,1) reaction. Since the true K_{11} is theoretically identical for these systems, the differences in K_{11} are proportional to the differences in γ_{AB}/γ_B. Fig. 5-3 shows the effect of chloroform (active diluent) concentration on K_{11} for the extraction of succinic acid by (1) Alamine 336 in chloroform and (2) 0.29 mol/L Alamine 336 in a chloroform/heptane mixture. There was no attempt in this work to develop a quantitative molecular thermodynamic model for the activity coefficients of the complexes. The results are shown to illustrate the magnitude of the change in the activity coefficient of the complex with concentration of the active diluent.

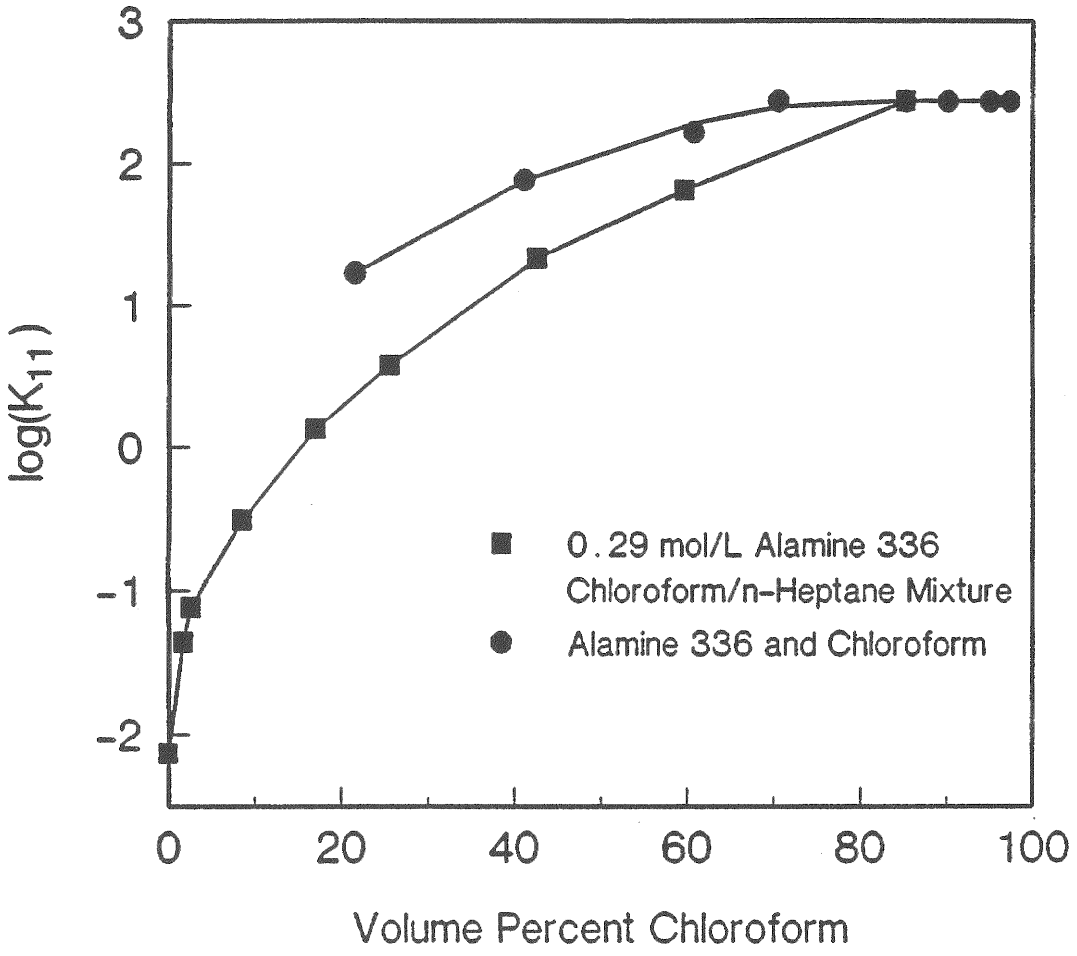


Fig. 5-3. Effect of Active Diluent Concentration on the (1,1) Equilibrium Constant.

Extraction of succinic acid by (1) various concentrations of Alamine 336 in chloroform and (2) 0.29 mol/L Alamine 336 in mixtures of chloroform and heptane. Volume percent chloroform refers to volume percent of the total solvent mixture. For the 0.29 mol/L amine-chloroform-heptane mixture, 85% is the maximum possible chloroform content.

There is a four order-of-magnitude difference in the (1,1) equilibrium constant for the amine-chloroform-heptane mixture for the range of the chloroform content. The amine-chloroform solvent shows higher equilibrium constants than the amine-chloroform-heptane solvent, indicating that the amine itself is a better solvating agent for the complex than heptane.

It should also be noted that the data curve is more concave upward than the theoretical curve for the (1,1) model at high amine concentrations and high inert diluent contents (see Fig. 2-14). This is expected behavior considering the system chemistry -- aggregation favors increasing extraction with increasing complex concentration, relative to simple (1,1) stoichiometry. In terms of activity calculations, increased acid or complex content in the solvent phase increases the ability of the solvent to solubilize polar species, and thus decreases the activity coefficient of the complex, γ_{AB}.

Spala and Ricker (1982) have developed a quantitative hybrid model to describe the extraction of acetic acid by trioctylamine and Alamine 336 in chloroform, 2-ethyl-1-hexanol, and diisobutyl ketone. The authors used the UNIFAC (Fredenslund et al., 1975) model to calculate the activity coefficients of the species. The model was successful in reproducing the decrease in distribution ratio with increasing amine concentration, such as the type of behavior seen in Fig. 2-1. This is a significant accomplishment, as the alternate approach to describing this behavior requires that the diluent be included specifically into the complex.

One difficulty found in implementation of the Spala and Ricker model was that the available binary parameter data, i.e., data for interactions between two components, did not describe the full acid-amine-diluent-water system for chloroform or 2-ethyl-hexanol diluent. It was necessary to use the full multicomponent data to back out the "binary" parameters in order obtain good agreement with the experimental extraction data (Spala, 1980). The authors concluded that the major cause of discrepancy in binary parameters between data from two-component and multicomponent systems was from the complex-diluent interactions, especially for chloroform and 2-ethyl-1-hexanol diluents. In the model, complex parameters are

derived from the free acid and amine parameters. The amine-diluent interaction parameters were set to zero. Hence, complex-diluent interactions were determined by acid-diluent interactions, which apparently do not predict the behavior of the complex-diluent system. This is supported by spectroscopic studies by Barrow and Yerger (1954), who concluded that complex-diluent interactions occur between a carboxylate anion and chloroform, whereas acid-diluent interactions involve the interaction of undissociated, dimeric carboxyl groups with the diluent. Therefore, acid-diluent interactions would not predict complex-diluent interactions because they are so dissimilar. Conversely, it was found, that the DIBK system was modeled well with the two-component binary interaction parameters, suggesting no strong, specific diluent-complex interaction.

Interestingly, significant (2,1) equilibrium constants were not necessary for good fit of the chloroform and 2-ethyl-1-hexanol diluent systems in the work of Spala and Ricker (1982). Instead of using a chemical interpretation with formation of (2,1) complexes, the Spala-Ricker model has used a physical interpretation, lowering the activity of the acid in the organic phase with increasing complex concentration. In contrast, the ketone system required significant (2,1) and (3,1) complex formation to achieve a fit of the data. UNIFAC activity coefficients and a (1,1) complex alone were not sufficient to account for the lowering of acid activity with increasing acid concentration in the organic phase. This latter situation agrees with the spectroscopic studies, which indicated that (2,1) and (3,1) complexes are stable, identifiable species.

Spala and Ricker discussed some limitations of their implementation of the combination physical and chemical model. The values of K_{11} were found to be dependent on the diluent, and therefore do not represent true thermodynamic values.

Hence, the activity coefficients did not fully describe the rest of the system chemistry. In the end, to fit the data the UNIFAC modeling required a considerable number of adjustable parameters, which were empirically determined from the extraction data. Currently, empirical mass-action law modeling is much easier to implement, requires fewer adjustable parameters, and is as accurate as the approach which combines mass-action law and physical solvation modeling. Other hybrid modeling approaches have been implemented for other systems (Nagata et al., 1977/1978; Harris and Prausnitz, 1969; Grenzheuser and Gmehling, 1986). Nonetheless, it is apparent that for carboxylic acid-amine systems the hybrid modeling approach will require more development of species activity coefficient calculations to be useful for practical calculations.

5.5 Summary and Conclusions

Qualitative

1. The interaction of the first acid and the amine is different from the interaction of the second acid with the (1,1) complex. Spectroscopically, it was seen that the first acid forms an ion-pair or hydrogen bond with the amine, and the second acid forms a hydrogen bond to the carboxylate of the first acid. This was manifested in the mass-action law analysis by the close relationship between the (1,1) complexation constant and the acidity of the acid, and the relative lack of dependence of the stepwise (2,1) complexation constant on the acidity of the acid. Furthermore, the (1,1) complexation constant is usually larger than the stepwise (2,1) equilibrium constant, indicating that the attraction of the first acid for the amine is much stronger than the attraction of the second acid for the (1,1) complex.

2. Intramolecular hydrogen bonding of dicarboxylic acids affects complex stoichiometry. There is strong evidence from the spectroscopic studies that intramolecular hydrogen bonding impedes formation of (1,2) complexes. This is confirmed by the mass-action law analysis through the presence of (1,2) complexes for fumaric acid and amine, and the absence of (1,2) complexes for succinic and maleic acids. It is speculated that internal bonding of the second carboxyl group to the carboxylate group also discourages (2,1) complexation and (2,2) dimer formation. In the case of (2,1) complexation, the carboxyl of the first acid may compete with the carboxyl of the second acid for the carboxylate binding site. In the case of (2,2) complex dimerization, the carboxylate of the first acid may compete with the carboxyl group of the second acid for the hydrogen-bonding site on the carboxyl group of the first acid.

3. Solvent interaction with the complex affects stoichiometry. Chloroform and other proton-donating diluents interact with the oxygen on the carboxylate group of the acid-amine ion pair, and thus impede (2,1) complex formation by competing with the second acid for the binding site on the (1,1) complex. Ketone diluents enhance (2,1) complex formation. For dicarboxylic acids, it is speculated that this arises from the ability of the basic carbonyl of the ketone to interact with the acidic carboxyl group of the acid. This inhibits internal hydrogen bonding, freeing the binding site for a second acid, and satisfies the second carboxyl group, repressing the need for two amines per complex. For monocarboxylic acids, it is unclear why ketone diluents enhance overloading. Alcohol diluents allow (1,2) complex formation for dicarboxylic acids, which was not seen in the other diluents. It is speculated that interference of the alcohol with internal hydrogen bonding is responsible for this behavior.

Quantitative

1. The magnitude of the (1,1) equilibrium constant is strongly related to the aqueous-phase pK_A of the acid, increasing approximately one order of magnitude for each unit decrease in pK_A (Fig. 5-1). For the acids studied in the present work, the effect of the hydrophobicity of the solute on the distribution of acid was small compared to the effect of acidity.

2. Diluents affect complexation in a variety of ways. Some diluents are believed to interact specifically with the complex; examples are chloroform and other proton-donating solvents, which are thought to form hydrogen bonds with the carboxylate of the (1,1) complex. Other diluents enhance extraction by general solvation, manifested by the high extraction observed in polar diluents (e.g., nitrobenzene). Inert diluents provide a very poor solvating medium for the complex, and aggregation results as the complex seeks to "solvate" itself. The effect of the diluent on the (1,1) complex formation constant has been characterized by a linear free energy relationship and Hildebrand solubility parameters.

REFERENCES

Barrow, G. M. and Yerger, E. A., "Acid-Base Reactions in Non-dissociating Solvents. Acetic Acid and Triethylamine in Carbon Tetrachloride and Chloroform", *J. Am. Chem. Soc.*, **76**, 5211-5216 (1954).

Chaikhorskii, A. A., Nikol'skii B. P., and Mikhailov, B. A., "Complex Formation in Nonaqueous Solutions X. Interaction of Tridecylamine with Acetic Acid", *Sov. Radiochem.*, **8**, 152-158 (1966); *Radiokhimiya*, **8**, 163-171 (1966).

Chastrette, M., Rajzmann, M, Chanon, M, and Purcell, K. F., "Approach to a General Classification of Solvents Using a Multivariate Statistical Treatment of Quantitative Solvent Parameters", *J. Am. Chem. Soc.*, **107**, 1-11 (1985).

Clark, E. P. ,"The Signer Method for Determining Molecular Weights", *Ind. Eng. Chem.. Anal. Ed.*, **13**, 820-821 (1941).

Evans, H. G. and Goldstein, J. H., "An investigation of intramolecular hydrogen bonding in some malonic acids using NMR techniques", *Spectrochim. Acta. Part A*, **24A**, 78-79 (1968).

Fredenslund, A., Jones, R., and Prausnitz, J. M., "Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures", *AIChE J.*, **21**, 1086-1099 (1975).

Grenzheuser, P. and Gmehling, J., "An Equation of State for the Description of Phase Equilibria and Caloric Quantities on the Basis of the "Chemical Theory", *Fluid Phase Equilib.*, **25**, 1-29 (1986).

Grinstead, R. R., "Base Strengths of Amines in Liquid-Liquid Extraction Systems", *Solv. Extr. Chem.* (ISEC '67), North-Holland, Amsterdam, 426-432 (1967).

Gusakova, G. V., Denisov, G. S., and Shraiber, V. M., "Infrared Spectra and Structures of Complexes Formed by Dibasic Carboxylic Acids with Amines in Nonaqueous Solvents: Malonic Acid", *J. Gen. Chem. USSR* (Engl. Transl.), **56**, 531-536 (1986); *Zh. Obshch. Khim.*, **56**, 600-607 (1986).

Harris, H. G. and Prausnitz, J. M., "Thermodynamics of Solutions with Physical and Chemical Interactions", *Ind. Eng. Chem. Fundam.*, **8**, 180-188 (1969).

Kamlet, M. J., Abboud, J. L. M., and Taft, R. W., "An Examination of Linear Solvation Energy Relationships", *Prog. Phys. Org. Chem.*, **13**, 485-630 (1983).

Kawano, Y., Kusano, K., and Nakashio, F., "Extraction and Interfacial Adsorption Equilibria of Aqueous Acetic Acid and Propionic Acid with Tri-*n*-Octylamine in Hexane", *Kagaku Kogaku Ronbunshu*, **9**, 211-213 (1983*a*).

Kawano, Y., Kusano, K., Inoue, K., and Nakashio, F., "Extraction Equilibria of Aqueous Solution of Lower Carboxylic Acid with Benzene Solution of Long-Chain Alkylamine, Amberlite LA-2", *Kagaku Kogaku Ronbunshu*, **9**, 473-475 (1983*b*).

Kojima, I. and Davis, S., "Prediction of the Distribution Constant of Some Solutes Containing Hydrophilic Functional Groups from Data of the Solubility of Water in Organic Solvents", *Sep. Sci. Technol.*, **20**(2&3), 131-151 (1985).

Kolthoff, I. M. and Chantooni, M. K., Jr., "Intramolecular Hydrogen Bonding in Monoanions of *o*-Phthalic Acid and the Homologous Oxalic Acid Series in Acetonitrile", *J. Am. Chem. Soc.*, **97**, 1376-1381 (1975).

Kolthoff, I. M. and Chantooni, M. K., "Intramolecular Hydrogen Bonding Involving Hydroxyl Groups in Mono- and Dianions of Diprotic Acids in Acetonitrile and Dimethyl Sulfoxide", *J. Am. Chem. Soc.*, **98**, 5063-5068 (1976).

Manenok, G. S., Korobanova, V. I., Yudina, T. N., and Soldatov, V. S., "Influence of the Nature of the Solvent on Extraction of Certain Mono- and Dicarboxylic Acids by Amines", *Russ. J. Appl. Chem.* (Engl. Transl.) **52**, 156-160 (1979); *Zh. Prikl. Khim.*, **52**, 173-183 (1979).

McCoy, L. L., "The Geometry of Intramolecular Hydrogen Bonding in 1,2-Dicarboxylic Acids", *J. Am. Chem. Soc.*, **89**, 1673-1677 (1967).

Mori, N., Asano, Y, Irie, T., and Tsuzuki, Y., "Intramolecular Hydrogen Bonds. XIII. The Preferable Conformation of α-Hydroxy-carboxylic and *o*-Hydroxybenzoic Acids", *Bull. Chem. Soc. Jpn.*, **42**, 482-487 (1969).

Mori, N., Asano, Y., and Tsuzuki, Y., "Intramolecular Hydrogen Bonds. XIV. Correlation of the Hydroxyl and the Carbonyl Frequencies of Methyl Salicylates with Hammett's Substituent Constants", *Bull. Chem. Soc. Jpn.*, **42**, 488-491 (1969).

Nagata, I., Kita, H., and Nakamiya, Y., "Ternary Liquid-Liquid Equilibria: The Associated Solution Theory", *Fluid Phase Equilib.*, **1**, 267-275 (1977/1978).

Prausnitz, J. M., *Molecular Thermodynamics of Fluid-Phase Equilibria*, Prentice-Hall, Englewood Cliffs, New Jersey (1969).

Reschke, M. and Schügerl, K., "Reactive Extraction of Penicillin II: Distribution Coefficients and Degrees of Extraction", *Chem. Eng. J.*, **28**, B11-B20 (1984).

Ricker, N. L., "Recovery of Carboxylic Acids and Related Organic Chemicals from Wastewaters by Solvent Extraction", Ph.D. Dissertation, Chemical Engineering, University of California, Berkeley (1978).

Rieux, A., Rumeau, M., and Tremillon, B., "No. 185 -- Etude spectrophotometrique de la basicite des amines aliphatiques a longues chaines dans des solvants peu dissociants", *Bull. Soc. Chim. Fr.*, 1053-1057 (1964).

Rumeau, M. and Tremillon, B., "No. 184 -- Etude spectrophotometrique de reactions acides-bases dans le chloroforme", *Bull. Soc. Chim. Fr.*, 1049-1053 (1964).

Shmidt, V. S., Mezhov, E. A., and Rybakov, K. A., and Rubisov, V. N., "Use of Two-Parameter Equations to Describe Data on the Influence on the Extraction Equilibrium of the Diluent and the Anion of the Acid Extracted by an Amine", *Russ. J. Inorg. Chem.* (Engl. Transl.), **23**, 1526-1527 (1978*a*); *Zh. Neorg. Khim.*, **23**, 2756-2760 (1978*a*).

Shmidt, V. S., Mezhov, E. A, and Rybakov, K. A, "Quantitative Description of the Mutual Influence of Changes in the Structure of the Extraction Reagent and the Nature of the Diluent on Extraction Using Two-Parameter Equations Based on the Linear Relationships of Free Energies (LFE), *Sov. Radiochem.* (Engl. Transl.), **20**, 224-227 (1978*b*); *Radiokhimiya*, **20**, 265-268 (1978*b*).

Shmidt, V. S. and Rybakov, K. A., "Possibility of Predicting Extraction of Various Monobasic Acids from Aqueous Solutions by Nucleophilic Extractants", *Sov. Radiochem.*, **16**, 434-437 (1974); *Radiokhimiya*, **16**, 440-445 (1974).

Shmidt, V. S. and Rybakov, K. A., "Use of a Three-Parameter Linear Equation to Describe Data on the Extraction of Nitric Acid by Amine Nitrates", *Russ. J. Inorg. Chem.* (Engl. Transl.), **23**, 1528-1531 (1978*c*); *Zh. Neorg. Khim.*, **23**, 2761-2765 (1978*c*).

Shmidt, V. S., Rybakov, K. A., and Rubisov, V. N., "The Use of Linear Free Energy Relationships to Describe the Anion-Exchange Extraction of Various Monobasic Acids by Salts of Quaternary Ammonium Bases", *Russ. J. Inorg. Chem.* (Engl. Transl.), **25**, 1062-1064 (1980); *Zh. Neorg. Khim.*, **25**, 1915-1919 (1980).

Shmidt, V. S., Rybakov, K. A., and Rubisov, V. N., "Quantitative Prediction of the Extractability of Various Anions Through Anion-Exchange or Ionic-Associate-Formation Reactions", *Russ. J. Anal. Chem.*, **38**, 896-900 (1983*b*); *Zhurnal Analiticheskoi Khimii*, **38**, 1182-1187 (1983*b*).

Shmidt, V. S., Smelov, V. S., Rybakov, K. A., and Kondrat'ev, B. A., "Effect of the Diluent Effect (DE) Parameters DE and DE* on the Extraction Equilibria for Various Types of Extraction Systems", *Sov. Radiochem.*, **25**, 179-184 (1983*a*).

Soldatov, V. S., Manenok, G. S., and Korobanova, V. I., "Distribution of Trichloroacetic Acid between Aqueous Solutions and Solutions of Tribenzylamine in Organic Solvents", *Russ. J. Appl. Chem.* (Engl. Transl.), **51**, 631-634 (1978); *Zh. Prikl. Khim.*, **51**, 646-651 (1978).

Spala, E. E. and Ricker, N. L., "Thermodynamic Model for Solvating Solutions with Physical Interactions", *Ind. Eng. Chem. Process Des. Dev.*, **21**, 409-415 (1982).

Spala, E. E., "A Thermodynamic Model of Solvating Solutions with Physical Interactions", M.S. Thesis, Chemical Engineering, University of Washington (1980).

Tremillon, B., "No. 186. -- Remarque sur la relation entre la force basique des amines aliphatiques a longues chaines et leur pouvoir d'extraction", *Bull. Soc. Chim. Fr.*, 1057-1060 (1964).

Vanura, P. and Kuca L., "Extraction of Citric Acid by the Toluene Solutions of Trilaurylamine", *Collect. Czech. Chem. Commun.*, **41**, 2857-2877 (1976).

Vieux, A. S., Rutagengwa, N., Rulinda, J. B., and Balikungeri A., "Extraction of Some Dicarboxylic Acids by Tri-Isooctylamine", *Anal. Chim. Acta*, **68**, 415-424 (1974).

Wardell, J. M. and King, C. J., "Solvent Equilibria for Extraction of Carboxylic Acids from Water", *J. Chem. Eng. Data*, 23(2), 144-148 (1978).

Yerger, E. A. and Barrow, G. M., "Acid-Base Reactions in Non-dissociating Solvents *n*-Butylamine and Acetic Acid in Carbon Tetrachloride and Chloroform", *J. Am. Chem. Soc.*, 77, 6206-6207, (1955).

CHAPTER 6. EFFECT OF TEMPERATURE

This chapter describes the effect of temperature on the extraction of succinic and lactic acids by Alamine 336 in chloroform and MIBK. These systems were chosen because of their contrasting extraction behaviors in the ambient temperature experiments as described in Chapter 2. Overloading was more evident for lactic acid than for succinic acid. Extraction of the acids was greater in chloroform at loadings less than unity, but more overloading occurred in MIBK. From studies of the effect of temperature, apparent values of enthalpies and entropies of reaction of the acid and amine can be obtained. A comparison of these values for the different systems will give insight into the underlying chemical interactions involved in acid extraction by chemical complexation. Furthermore, the data are useful for evaluation of regeneration by temperature swing (see Chapter 8).

Previous investigators have shown that temperature strongly affects the extraction of carboxylic acids by amine extractants. Baniel et al. (1981) studied the effect of temperature on the extraction of citric acid by tridecylamine in petroleum fractions with an alcohol modifier, in xylene, and in nitrobenzene. The distribution of acid into the solvent phase decreases sharply with increasing temperature. The decrease is large enough to allow efficient back-extraction of the acid from the solvent into a fresh aqueous phase. Wennersten (1983) studied the extraction of citric acid by Alamine 336 a variety of diluents at 25 and 60 °C. Detailed sets of data were collected for Isopar H (a paraffinic kerosene), a 1:1 (v/v) mixture of Isopar H and MIBK, and *n*-butyl chloride at 25 and 60 °C. For the 35 C° increase in temperature, distribution ratios decreased by as much as a factor of six in these diluents. Sato et al. (1985) examined the extraction of lactic, tartaric, succinic, and citric acids by trilaurylamine in xylene at 20, 30, 40, and 50 °C. Over the 30 C°

temperature increase, distribution ratios decreased by factors between two and ten, depending on the type of acid and its concentration.

6.1 Thermodynamics

6.1.1 Calculation of the Apparent Enthalpy and Entropy of Complexation

In Chapter 3 it was found that for lactic and succinic acids formation of complexes with stoichiometries of $(p,1)$, where p = 1, 2, and 3, quantitatively described the experimental results. As in Chapter 5, it is convenient to recast the equations into stepwise associations of the form:

$$A + A_{p-1}B = A_pB \qquad K_{p1,true} = \frac{\{\overline{A_pB}\}}{\{A\}^p\{\overline{A_{p-1}B}\}} \qquad \text{(Eq. 5-1)}$$

where the stepwise association constant, $K_{p1,true}$, is the ratio of the overall association constants, $\beta_{p1,true}/\beta_{p-1,1,true}$, and $K_{11,true}$ is equal to $\beta_{11,true}$. As before, an experimentally accessible apparent equilibrium constant K_{p1} is defined as:

$$K_{p1} = \frac{[\overline{A_pB}]}{[A][\overline{A_{p-1}B}]} \qquad \text{(Eq. 5-2)}$$

where the square brackets indicate the analytical concentration of the species. The true thermodynamic equilibrium constant is related to the apparent constant by

$$K_{p1,true} = K_{p1} \frac{\gamma_{ApB}}{\gamma_A \gamma_{Ap-1B}} \qquad \text{(Eq. 5-3)}$$

where γ_i is the activity coefficient of species *i*.

The complexation reactions in the organic phase involve hydrogen bond formation and are expected to be exothermic. Formation of a complex makes the system more ordered, and thus decreases the entropy. LeChatelier's Principle indicates that as temperature is increased, the extent of reaction, and therefore the amount of acid extracted, should decrease. If the enthalpy and entropy of reaction are assumed to be constant over the temperature range, the expression

$$\ln(K) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \qquad \text{(Eq. 6-1)}$$

shows that a plot of $\ln(K)$ vs. $1/T$ should give a straight line. The slope will be proportional to the enthalpy of reaction (the van't Hoff equation), and the intercept is proportional to the entropy.

6.1.2 Standard State

As in Chapter 5, it is helpful to consider the complexation as a series of paths which bring about the overall change of state. For a reaction carried out at temperature T and one atmosphere, the overall change of state may be divided into (*a*) Cooling (or heating) of reactants (A, $A_{p-1}B$, B) in solution at their equilibrium concentrations from temperature T to 25 °C. (*b*) "Unmixing" reactants at 25 °C from their equilibrium concentrations in solution to pure components. (*c*) Reaction at 25 °C of the pure reactants to form pure product, A_pB. (*d*) Dilution at 25 °C of pure product to equilibrium concentration in solution. (*e*) Heating (or cooling) products in solution from 25 °C to temperature T.

Recall that transitions (*b*) and (*d*) reflect deviations of the apparent K from K_{true} due to the non-idealities of mixing in the aqueous and organic phases, the y_A, y_B, $y_{Ap\text{-}1B}$, and y_{ApB} terms in Eq. 5-3, and that these values have been assumed to be independent of concentration of the components. These transitions have been discussed in Chapter 5. Transition (*c*) is the standard state reaction, and hence the association constant for this reaction is the true thermodynamic constant, $K_{p1,true}$.

Transitions (*a*) and (*e*) account for the effect of temperature on the activity coefficient, which will cause deviations of the apparent ΔH and ΔS from the true standard state values. For a pure-liquid standard state, this factor can theoretically be calculated from

$$R \frac{d\ln y_i}{d(1/T)} = \Delta\overline{H}_i = \overline{H}_i - H_{pure\ i} \qquad \text{(Eq. 6-2)}$$

where $\Delta\overline{H_i}$ is the partial molar heat of mixing (a.k.a. partial excess enthalpy), $\overline{H_i}$ is the partial molar enthalpy of species i, and $H_{pure\ i}$ is the enthalpy of pure i (Smith and Van Ness, 1975).

Combining Eqs. 6-1 and 6-2 gives the following expression for the true thermodynamic enthalpy, $\Delta H_{11,true}$, for the (1,1) complexation:

$$\Delta H_{11,true} = \Delta H_{11} - \Delta\overline{H_{AB}} + \Delta\overline{H}_A + \Delta\overline{H}_B \qquad \text{(Eq. 6-3)}$$

where ΔH_{11} is the apparent heat of complexation for the (1,1) reaction, and $\Delta\overline{H_{AB}}$, $\Delta\overline{H_B}$, and $\Delta\overline{H_A}$ are the partial molar heats of mixing of the complex in the diluent, the free amine in the diluent, and the acid in water, respectively.

6.2 Effect of Temperature on Extraction and Complexation of Lactic and Succinic Acids by Alamine 336 in MIBK and in Chloroform

6.2.1 Experimental

Batch extraction experiments were performed at various temperatures as described in Appendix A. Extraction experiments without amine were also performed at various temperatures in MIBK, for which extraction by the diluent alone is significant. The temperature of the thermostatted shaker bath was maintained within ±2 °C of the setpoint.

Temperature affects the dissociation constants of the acids and water in the aqueous phase. However, the change in pK_A is small over the temperature range in these experiments, and calculations show that the effect of temperature on the solution pH values should be less than 0.04 pH units. To check the effect of temperature on pH, for several runs, pH measurements of the separated, centrifuged aqueous phases were made both at the temperature of extraction and after the solutions had cooled (or warmed) to ambient temperature. Table 6-1 shows the results. The difference between pH measurements at T, the temperature of the experiment, and 25 °C is small, generally less than the error associated with the pH measurement itself (±0.03 pH units).

Organic-phase acid concentrations were corrected for extraction by the diluent alone at the appropriate temperature in the same way as for the ambient-temperature experiments. Best-fit equilibrium constants were determined as described in Appendix B. Values of the apparent ΔH and ΔS of reaction were calculated from these values of the association constants by a linear least-squares fit of Eq. 6-1.

Table 6-1. Comparison of the pH of Aqueous Solutions at Different Temperatures.

Each set of data shows results for the same initial organic phase, but different acid concentrations.

Succinic Acid-MIBK
No Alamine 336
T = 0 °C

pH	
0°C	25°C
2.39	2.42
2.51	2.54
2.68	2.70
2.84	2.83
3.17	3.15

Succinic Acid-MIBK
No Alamine 336
T = 50 °C

pH	
50°C	25°C
2.62	2.60
2.70	2.69
2.81	2.79
2.89	2.86
3.20	3.22

Succinic Acid-Chloroform
0.29 mol/L Alamine 336
T = 0 °C

pH	
0°C	25°C
2.79	2.81
3.28	3.27
4.21	4.18
4.77	4.76
5.08	5.04
5.25	5.25
5.55	5.52

Succinic Acid-MIBK
0.29 mol/L Alamine 336
T = 75 °C

pH	
75°C	25°C
2.49	2.51
2.67	2.67
2.79	2.81
3.01	3.01
3.26	3.27
3.93	3.92

Lactic Acid-Chloroform
0.29 mol/L Alamine 336
T = 55 °C

pH	
55°C	25°C
1.96	1.91
2.17	2.14
2.43	2.41
2.66	2.66
3.00	2.95
3.28	3.25
3.52	3.52
4.20	4.06

6.2.2 Extraction by MIBK Alone

Table 6-2 gives the best-fit partition coefficients and dimerization constants for the extraction of succinic and lactic acids by MIBK without the presence of amine. No dimerization constant was apparent for succinic acid at the concentrations studied. The acids exhibit contrasting behavior; as temperature increases, extraction of succinic acid decreases, while extraction for lactic acid increases. The dimerization constant of the lactic acid decreases with increasing temperature.

Prior investigations of the effect of temperature on the extraction of lactic acid into other solvents have shown that distribution coefficients generally increase as temperature increases, as in the MIBK case studied here (Holten, 1971; Leonard et al, 1948). Pentasol (an amyl alcohol mixture), cyclohexanol, *n*-butyl lactate, methyl *n*-amyl ketone, cyclohexanone, MIBK, and ethyl acetate were among the solvents which showed this increase. However, in butyl acetate and 2-methyl-2-propanol, lactic acid exhibits distribution coefficients which decrease with increasing temperature. Distribution ratios of succinic acid extracted by ether also decreased as temperature increased (Forbes and Coolidge, 1918). More information on the effect of temperature on the distribution of other acids into conventional solvents is given by Kertes and King (1986).

It is unclear why increasing the temperature increases the distribution ratio of lactic acid, but decreases the distribution ratio for succinic acid, in the solvents studied. It will be concluded below in Section 6.3.3 that the effect of temperature on the aqueous-phase activity coefficients of succinic and lactic acid is very similar. Therefore, the difference between the two acids lies in the effect of temperature on the organic-phase activity coefficients. It is reasonable that a carboxylic acid

Table 6-2
Effect of Temperature on
Partition and Dimerization Constants for
Lactic and Succinic Acids in MIBK

$$C_{A,org} = P[A] + 2K_d P^2[A]^2$$

Acid	T (°C)	P	K_d
Lactic Acid	0	0.09	0.75
	25	0.11	0.56
	50	0.13	0.43
	75	0.14	0.45
Succinic Acid	0	0.28	
	25	0.19	
	50	0.16	
	75	0.15	

Table 6-3
Effect of Temperature on the Stepwise Formation Constants for
Complexes of Lactic and Succinic Acids with 0.29 mol/l Alamine 336
in Chloroform and MIBK

System	T (°C)	$\log(K_{11})$	$\log(K_{21})$	$\log(K_{31})$
Lactic Acid	0	1.68	0.07	-0.07
Alamine 336	25	1.31	0.21	-0.35
MIBK	50	1.12	-0.04	-0.26
	75	0.67	0.08	-0.15
Lactic Acid	0	3.37	-0.62	
Alamine 336	25	2.57	-0.46	
Chloroform	55	1.74	-0.36	
Succinic Acid	0	2.06	0.86	
Alamine 336	25	1.35	0.75	
MIBK	50	0.85	0.47	
	75	0.46	0.09	
Succinic Acid	0	3.60		
Alamine 336	25	2.45		
Chloroform	40	1.85		
	55	1.40		

interacts with the basic carbonyl of the ketone, so that increasing temperature drives this "reaction" back toward "free" acid and ketone. So, why does lactic acid experience an increase in physical partitioning with increasing temperature? Arenson (1989) has found that distribution ratios for ethanol into a variety of solvents increase with increasing temperature. Possibly, the influence of the -OH group of the lactic acid is the major contribution to partitioning behavior. Another possibility is that coextracted water becomes greater at higher temperatures for lactic acid, and the coextracted water facilitates accommodation of lactic acid into the organic phase. Water measurements for the extraction of lactic acid by Alamine 336 in MIBK was not examined in this work.

6.2.3 Extraction by Tertiary Amine in Diluent

Figs. 6-1 (*a-d*) shows the experimental results for the extraction of lactic and succinic acids by Alamine 336 in MIBK (0 to 75 °C) and in chloroform (0 to 55 °C). The data are displayed as Z vs. log[A]. The solid curves show the results of calculations from the model with best-fit association constants. Table 6-3 summarizes the equilibrium constants (note that log is logarithm to the base 10). For a given [A], as temperature increases, the loading decreases, indicating less acid extraction.

Figs. 6-2 *a* and *b* present the plot of log(K) vs. $1/T$ for lactic and succinic acids, respectively, with the solid lines corresponding to derived values for the apparent enthalpies and entropies of stepwise formation of (1,1), (2,1) and (3,1) complexes, as calculated from a linear least-squares fit of these plots (Tables 6-4 and 6-5). There is large scatter in the data for lactic acid in MIBK which pertain to the (2,1) and (3,1) complexes, probably because of the relatively large number of equilibrium constants (three) used to model each curve compared to the relatively small number of

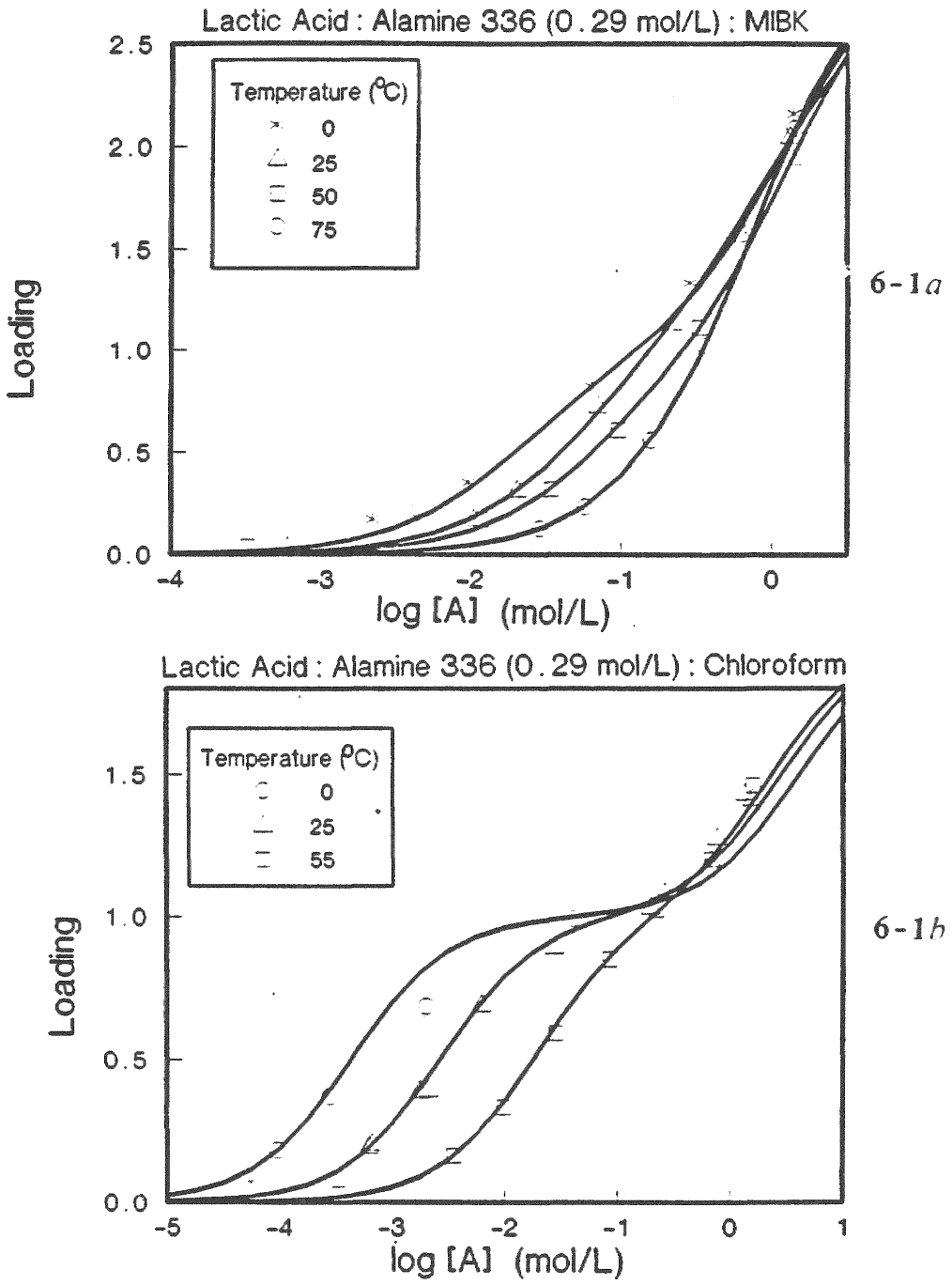


Fig. 6-1. Effect of Temperature on the Loading Curves for the Extraction of Lactic and Succinic Acids by Alamine 336 in MIBK and Chloroform.

(*a*) Lactic Acid : Alamine 336 : MIBK
(*b*) Lactic Acid : Alamine 336 : Chloroform

Solid lines show the curves calculated from the equilibrium constants given in Table 6-3.

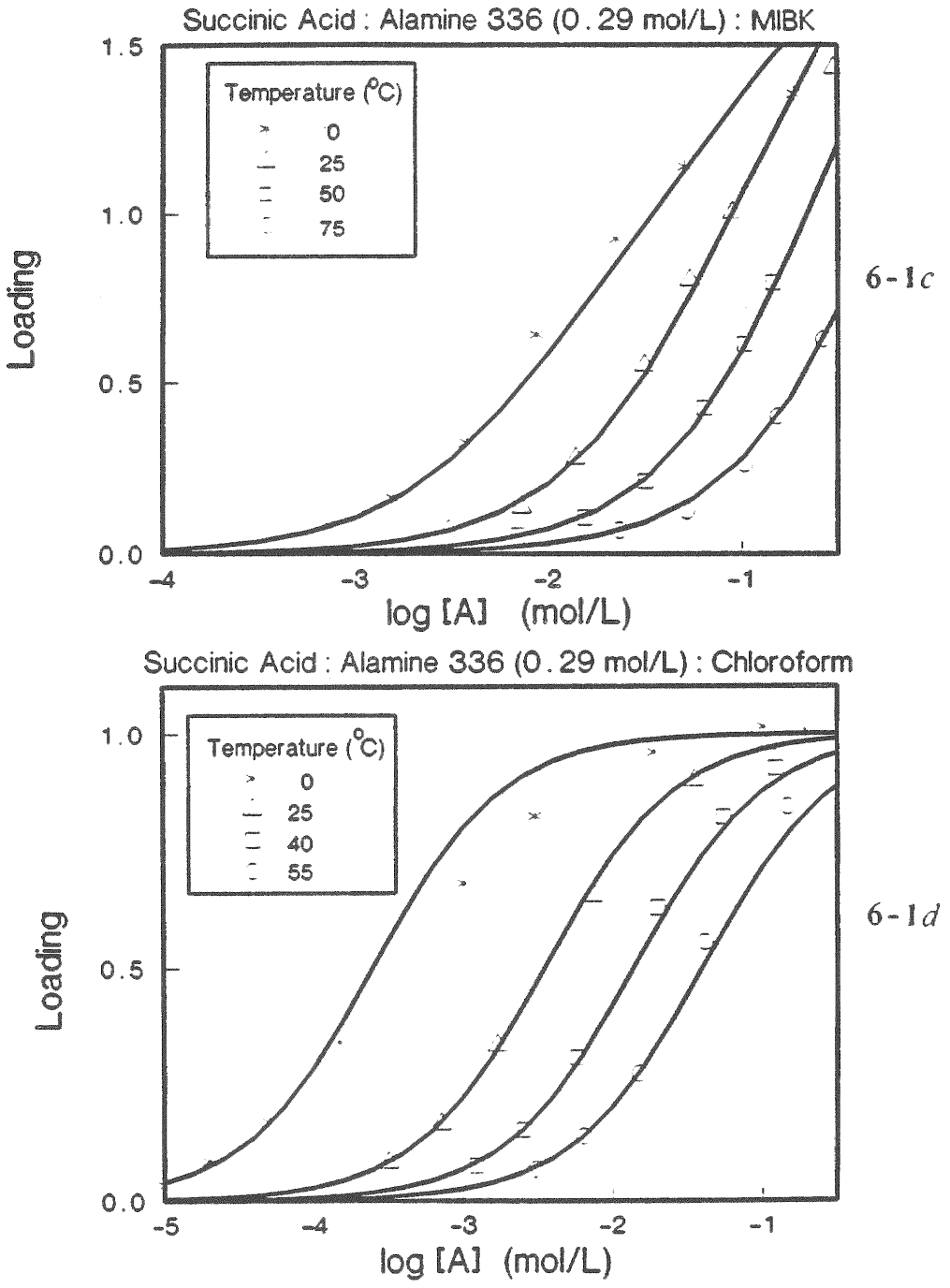


Fig. 6-1. Effect of Temperature on the Loading Curves for the Extraction of Lactic and Succinic Acids by Alamine 336 in MIBK and Chloroform (cont'd).

(*c*) Succinic Acid : Alamine 336 : MIBK
(*d*) Succinic Acid : Alamine 336 : Chloroform

Solid lines show the curves calculated from the equilibrium constants given in Table 6-3.

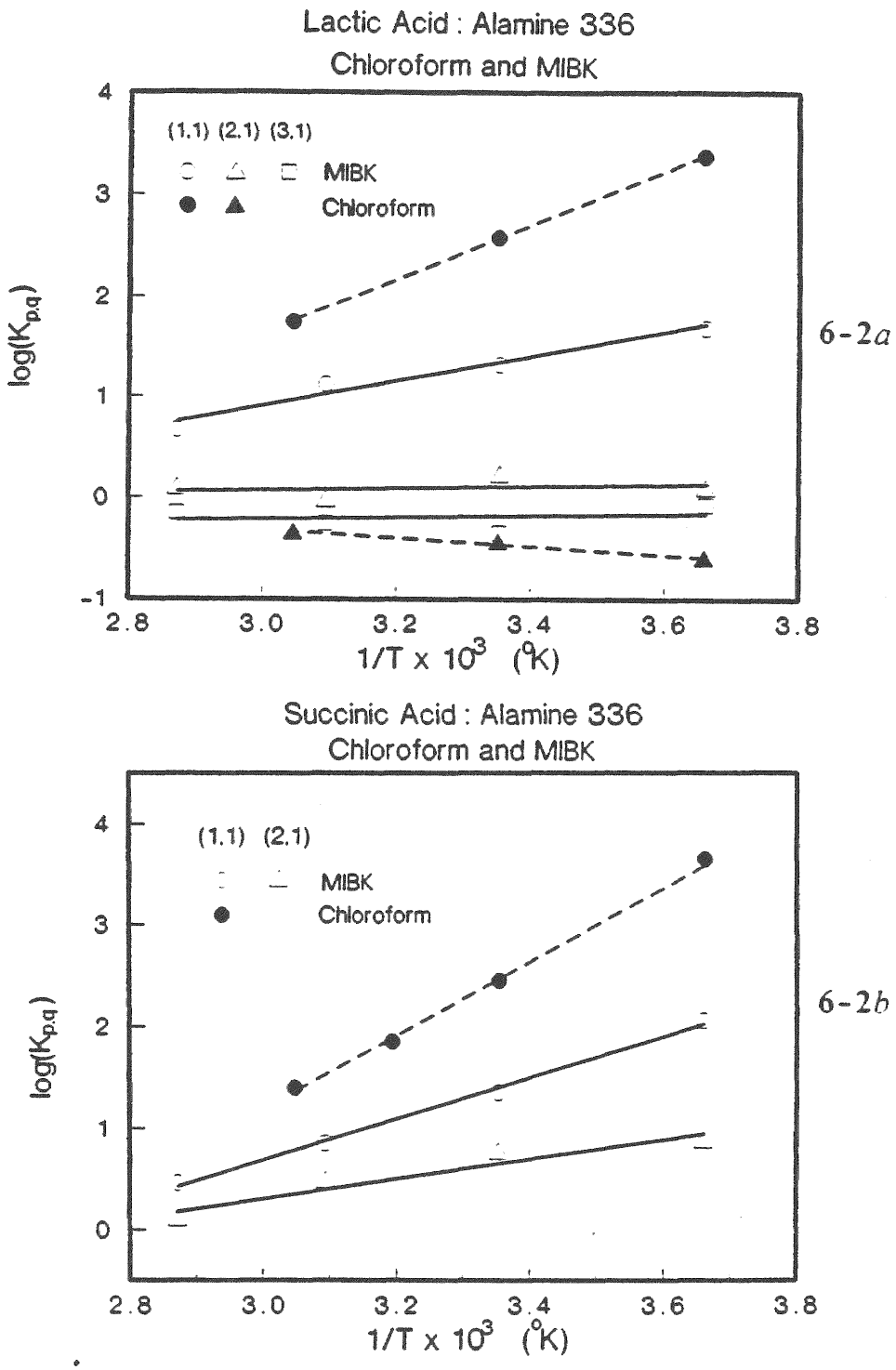


Fig. 6-2. van't Hoff Plots for the Complexation Reactions of Succinic and Lactic Acids with Alamine 336 in MIBK and Chloroform.

(*a*) Lactic Acid
(*b*) Succinic Acid

Table 6-4
Apparent Enthalpies of Complex Formation with Alamine 336

System	ΔH (kcal/mol) (1,1)	(2,1)	(3,1)	ΔH Transfer
Lactic Acid ΔH_{dil} = -1.0 kcal/mol				
MIBK	-5.6 ± 0.4	-0.4 ± 0.9	-0.4 ± 1.1	+1.1 ± 0.1
Chloroform	-12.1 ± 0.2	+1.9 ± 0.3		
Succinic Acid $\Delta \bar{H}_{mix}$ = -0.66 kcal/mol				
MIBK	-9.2 ± 0.4	-4.4 ± 1.0		-1.7 ± 0.3
Chloroform	-16.5 ± 0.4			

Table 6-5
Apparent Entropies of Complex Formation with Alamine 336

System	ΔS (cal/mol·K°) (1,1)	(2,1)	(3,1)	ΔS Transfer
Lactic Acid				
MIBK	-12.6 ± 0.4	-0.9 ± 0.5	-2.09 ± 0.7	-0.7 ± 0.1
Chloroform	-29.0 ± 0.1	+4.2 ± 0.1		
Succinic Acid				
MIBK	-24.6 ± 0.2	-11.9 ± 0.6		-8.7 ± 0.2
Chloroform	-44.2 ± 0.2			

(± values are the standard errors of estimate.)

data points. However, three complexes are necessary to describe the extensive overloading. The apparent enthalpies of association are more exothermic for succinic than for lactic acid, and more exothermic in chloroform than in MIBK. The apparent entropy decrease is greater in chloroform than in MIBK and greater for succinic acid than for lactic acid.

6.3 Discussion

6.3.1 Comparison of (1,1) with (2,1) and (3,1) Complexation

For the systems studied here, (1,1) complexation is much more exothermic and involves a much greater loss of entropy than formation of (2,1) or (3,1) complexes. This is expected from results of previous chapters, where it was concluded that (1,1) complexation involves formation of an ion-pair, but higher complexes involve hydrogen bond formation. The large difference in energies conforms with the concept of distinct mechanisms of complex formation.

6.3.2 Effect of Diluent (Same Acid, Different Diluent)

ΔH_{true} and the partial molar heat of mixing of the aqueous-phase acid in Eq. 6-3 depend only on the type of acid. Therefore, for a given acid, the following expression can be written for the apparent enthalpy of (1,1) complexation:

$$\Delta H_{11} = \Delta\overline{H_{AB}} - \Delta\overline{H_{B}} + \text{Constant} \qquad \text{(Eq. 6-4)}$$

The quantity $\Delta\overline{H_{AB}} - \Delta\overline{H_{B}}$ is more negative in chloroform than in MIBK for the (1,1) complexation. For lactic acid, ΔH_{11} is 6.5 kcal/mol more negative (reaction is

more exothermic) in chloroform than in MIBK; for succinic acid, 7.3 kcal/mol. The term $\Delta\bar{H}_B$ would be expected to be more negative for chloroform, because chloroform is acidic and MIBK is basic. That is, one would expect that, if temperature were increased, chloroform interaction with the amine would decrease, the amine would become more readily available to form complexes, and ΔH_{11} would become less exothermic from the $\Delta\bar{H}_B$ term. However, ΔH_{11} is more exothermic in chloroform; hence, in chloroform the $\Delta\bar{H}_{AB}$ term must be a substantial exothermic contribution.

A comparison of the apparent entropy of (1,1) complexation, ΔS_{11}, shows that, for lactic acid, there is 16.2 cal/mol-K° more entropy lost in chloroform than in MIBK, and, for succinic acid, there is 19.6 cal/mol-K° more entropy lost in chloroform than in MIBK. Therefore, there is also a substantial entropy loss associated with accommodation of the complex in chloroform diluent.

The large enthalpy and entropy losses involved in the mixing of the complex in the diluent are consistent with the conclusions from previous chapters: Diluent interaction with the complex is significant for chloroform. This may be rationalized in a physical sense as hydrogen bonding of the chloroform molecules with the complex. There is an exothermic "reaction" of chloroform with the complex, which increases order (decreases entropy) of the solvent molecules.

A comparison of the thermodynamic quantities for (2,1) complex formation for lactic acid in chloroform and MIBK reveals a contrast to the (1,1) behavior. In chloroform, ΔH_{21} is a small, positive quantity, indicating an endothermic reaction, and ΔS_{21} is positive, indicating an increase in system entropy upon formation of hydrogen bonds. This is consistent with the hypothesis that chloroform orders itself around the (1,1) complex. Addition of the second acid disrupts the chloroform-complex

interaction, which requires energy to break the hydrogen bonds and increases the overall randomness of the system. As illustrated in Eq. 6-5 (analogous to Eq. 6-4) below, a negative contribution of the partial molar heat of solution of the (1,1) complex produces a positive contribution (more endothermic) to ΔH_{21}.

$$\Delta H_{21} = \Delta\overline{H_{A2B}} - \Delta\overline{H_{AB}} + \text{constant} \qquad \text{(Eq. 6-5)}$$

In MIBK, ΔH_{21} and ΔS_{21} were found to have negative values close to zero, but these results are tentative because of the scatter in the data. Qualitatively, the interaction of MIBK with the (1,1) complex is not as strong as in chloroform, so addition of the second acid involves less endothermic interaction.

6.3.3 Effect of Acid (Same Diluent, Different Acid)

For a given diluent, $\Delta\overline{H_B}$ is constant and Eq. 6-3 becomes

$$\Delta H_{11} = \Delta H_{11,true} + \Delta\overline{H_{AB}} - \Delta\overline{H_A} + \text{constant} \qquad \text{(Eq. 6-6)}$$

A comparison of ΔH_{11} indicates the (1,1) complexation is more exothermic for succinic than for lactic acid by 4.4 kcal/mol in chloroform and 3.6 kcal/mol in MIBK. Likewise, the entropy loss is greater for succinic acid by 15.2 cal/mol·K° in chloroform and 12.0 cal/mol·K° in MIBK. Are these variations due to dissimilarities between succinic and lactic acid in $\Delta H_{11,true}$, $\Delta\overline{H_{AB}}$, $\Delta\overline{H_A}$, or a combination of all three? A discussion of the possible contributions of these factors, given information on the partial molar heats of mixing of aqueous acids, the partition coefficients of the acids into the diluent alone, and the effect of temperature on pK_A is given below.

The contribution of the partial molar heat of mixing of the aqueous acid can

theoretically be calculated from the heat evolved or required in the dissolution of the solute $\Delta H_{soln,tot}$, (total heat required to dissolve crystalline acid to acid in solution) and the enthalpy of fusion, ΔH_{fus} (heat required per mole of solute to melt the acid from the crystalline state to the pure liquid state). From the total enthalpy of solution, a partial molar enthalpy of solution, $\Delta \bar{H}_{soln,}$ can be calculated by taking the partial derivative of the $\Delta H_{soln,tot}$ with respect to the number of moles of solute, keeping temperature, pressure, and moles of water constant. The partial molar heat of mixing of the acid, $\Delta \bar{H}_A$, (heat required per mole of acid to dilute acid from the pure liquid state to the concentration in solution) can then be determined from the relation $\Delta \bar{H}_A = \Delta \bar{H}_{soln} - \Delta H_{fus}$.

Detailed literature data for succinic acid on heats of solution have shown a partial molar heat of solution of +6860 cal/mol (dissolving crystals is endothermic), which was found to be constant for concentrations from 0 to 0.03 mol/L (Apelblat, 1986). The heat of fusion has been experimentally determined to be 7520 cal/mol (Khetarpal et al, 1980). Therefore, the partial molar heat of mixing is -660 cal/mol for dilute acid solutions. The reported molar heat of solution of lactic acid is +1868 cal/(mol of lactic acid) for dilution of crystalline lactic acid with large quantities of water (Saville, 1959); the heat of fusion is +2710 cal/(mol of lactic acid) (Holten, 1971). Therefore, the heat of dilution of the acid, which equals the partial molar heat of mixing for very dilute solutions, is -940 cal/mol. Although these figures apply only to very dilute solutions and the accuracy of the data is not well established, a difference of 0.28 kcal/mol in the partial heats of mixing of lactic and succinic acids suggests that this factor probably is not a significant contribution to the variation in the heat of complexation with acid for the concentrations studied in this work.

A comparison of the effects of temperature on the partition coefficients, P, for

extraction of the acids by the diluent alone may yield information on the organic-phase heat of mixing. Since $P = y_A/y_{Aorg}$, it follows from Eq. 6-2 that

$$\frac{d\ln P}{d(1/T)} = R\frac{d\ln y_A}{d(1/T)} - R\frac{d\ln y_{Aorg}}{d(1/T)}$$

$$= \Delta\bar{H}_A - \Delta\overline{H_{Aorg}} = (\bar{H}_A - H_A) - (\overline{H_{Aorg}} - H_{Aorg}) \qquad \text{(Eq. 6-7)}$$

$$= \bar{H}_A - \overline{H_{Aorg}} = -\Delta H_{trans}$$

where ΔH_{trans} the is the heat of transfer from the organic to the aqueous phase. Although it was shown in Chapter 5 that the activity coefficient of the complex in the organic phase is not correlated with the partition coefficient of acid into the diluent, it is possible that the change in activity coefficient with temperature is related to change in the partition coefficient with temperature. That is, one could speculate that, in the same diluent, the heat of mixing of the complex in the diluent is closely related to the heat of mixing of "free" acid in the diluent alone.

Values for the heats of transfer of the acid from the aqueous to a organic phase of MIBK for lactic and succinic acids are +1.1 and -1.7 kcal/mol, respectively. Thus, In MIBK, the mixing of lactic acid is endothermic, whereas mixing of succinic acid is exothermic. If it is assumed that $\Delta\bar{H}_{AB} = \Delta\bar{H}_{Aorg}$, then the $\Delta\bar{H}_{AB} - \Delta\bar{H}_A$ term of Eq. 6-6 in MIBK diluent is 2.8 kcal/mol less exothermic for lactic than for succinic acid. This is a substantial portion of the 3.6 kcal/mol difference in ΔH_{11} of the two acids in MIBK. This is much greater than the estimated 0.3 kcal/mol difference in the aqueous-phase heats of mixing between lactic and succinic acids. Likewise, the difference in the entropy of transfer from the aqueous to organic phases is 7 cal/mol·K°, a substantial fraction of the 12 cal/mol·K° difference in ΔS_{11}.

Analogous calculations cannot be performed in chloroform diluent because the distribution of acid into the solvent phase is too low to be measured accurately.

Finally, in Chapter 5 it was shown that larger acid dissociation constants (lower pK_A values) are correlated with higher equilibrium constants for (1,1) complexation. It can be speculated that the heat of dissociation is related to the heat of complexation. The influence of temperature on the dissociation constants of different carboxylic acids is different from acid to acid. Fig. 6-3 shows plots of the pK_A for the first dissociation vs. $1/T$ for succinic and lactic acids (Lange's Handbook, 1985). Note the behavior of lactic acid. At 0 °C the slope of the line is positive, indicating an endothermic dissociation reaction, at 25 °C the slope is close to zero, and at 50 °C the slope of the line is negative, indicating an exothermic dissociation reaction. On the other hand, succinic acid gives an endothermic heat of dissociation over the 0 to 50 °C temperature range.

If one assumes a direct correlation between the heat of dissociation and the heat of complexation, then ΔH_{11} is probably not constant for the temperature ranges studied as was assumed in the linear fit of $\ln(K)$ vs. $1/T$. The heat of dissociation is small compared to the heat of reaction for the (1,1) complex, so it should not be a large factor in the value of the ΔH_{11} calculated from these lines. Nevertheless, it may affect the comparison of heats of reaction between succinic and lactic acids. Qualitatively, the exothermic dissociation at high temperature for lactic acid would mean that the complexation reaction is more favorable than would be predicted on the assumption of a constant, average heat of reaction. Conversely, at low temperature, the more endothermic dissociation means that the complexation is less favorable than would be expected. Thus lactic acid may show higher values of K_{11} at high T and lower ones at low T, and the slope of $\log(K_{11})$ vs. $1/T$ would be shallower than

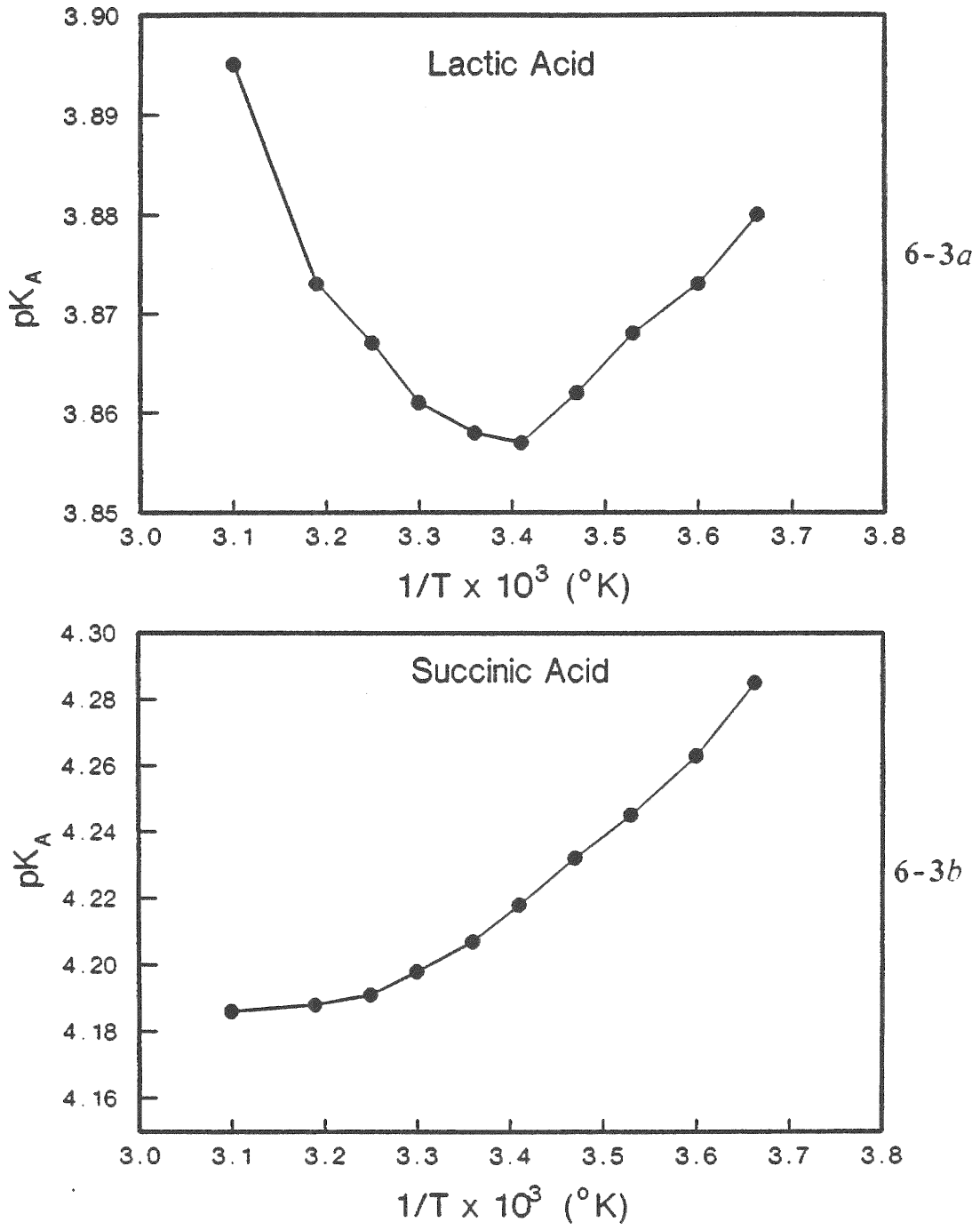


Fig. 6-3. Effect of Temperature on pK_A.

(*a*) Lactic Acid
(*b*) Succinic Acid

Data from Lange's Handbook, Dean, J. A. (Ed.), 13th ed., McGraw-Hill, New York, pp. 5-62 to 5-67 (1985).

expected. This may account for some of the difference in the apparent thermodynamic values between succinic and lactic acid.

Both of these explanations for the larger enthalpy of complexation of succinic acid compared to lactic acid -- a difference in the enthalpy of mixing in the organic phase, and a heat of (1,1) complexation that varies over the temperature range -- should be considered to be very speculative.

In MIBK, the (2,1) succinic acid-amine complex exhibits an apparent enthalpy of complexation that is 4.0 kcal/mol more negative than the (2,1) lactic acid-amine complex; the entropy decrease is 11 cal/mol·K° greater for succinic than for lactic acid. These are about the same differences as for the (1,1) complexation in MIBK.

$$\Delta H_{21} = \Delta H_{21,\text{true}} + \Delta \overline{H}_{\text{A2B}} - \Delta \overline{H}_{\text{A}} - \Delta \overline{H}_{\text{AB}} \qquad \text{(Eq. 6-8)}$$

For (2,1) complexation, acid dissociation is not expected to relate to complex strength, because (2,1) complexation involves hydrogen bonding of the second acid to the first, and not ion-pair formation. Thus differences in acid dissociation would not be expected to affect ΔH_{21}, although dissimilarities in hydrogen bonding capability would. Therefore the explanation of non-constant enthalpies of reaction would not apply to the (2,1) reaction. The explanation of differences in the enthalpy of mixing in the organic phase is also difficult to evaluate, since it is not known how the enthalpies of mixing for the (2,1) complex compare with those for the (1,1) complex. Somehow, whether by coincidence or a fundamental distinction between succinic and lactic acids, the net effect is that the variation between acids is similar for (2,1) and (1,1) complex formation.

The above discussion gives a partial understanding of factors which cause the differences between acids. More study is needed of different acid systems in different diluents to draw more firm conclusions regarding the effect of the nature of the acid.

6.4 Summary and Conclusions

Temperature is an important parameter in the extraction of carboxylic acids by amine extractants. An increase in temperature drives the complexation reaction back toward the reactants, resulting in lower extraction. The (1,1) reactions studied were much more exothermic and involved greater entropy loss than the (2,1) or (3,1) reactions, which is expected from the different mechanisms of (1,1) complex formation, as opposed to (2,1) and (3,1) complex formation. Apparent enthalpies of reaction are more exothermic in chloroform than in MIBK, and more exothermic for succinic than for lactic acids. An exception is the (2,1) complexation reaction for lactic acid in chloroform, which was found to be slightly endothermic. These results are consistent with the conclusions gained from the mass-action law model and spectrometric analyses of previous chapters. Chloroform, an active diluent, interacts strongly with the complex, making the overall reaction more exothermic and decreasing the system entropy because of ordering of diluent molecules around the complex. Unanswered questions remain as to why succinic acid shows a more exothermic reaction than lactic acid. There is need for more study in this area.

REFERENCES

Apelblat, A., "Enthalpy of solution of oxalic, succinic, adipic, maleic, malic, tartaric, and citric acids, oxalic acid dihydrate, and citric acid monohydrate in water at 298.15 K", *J. Chem. Thermodyn.*, **18**, 351-357 (1986).

Arenson, D. R., Ph.D. Dissertation, Department of Chemical Engineering, University of California, Berkeley (1989).

Baniel, A. M., Blumberg, K. H., and Hajdu, K., "Recovery of Acids from Aqueous Solutions", U.S. Patent No. 4,275,234 (Jun. 23, 1981), *Chem. Abstr.* Vol. 97, No. 109557 (1982).

Lange's Handbook of Chemistry, 13th ed., Dean, J. A., Ed., McGraw-Hill, New York, pp. 5-62 to 5-67 (1985).

Forbes, G. S. and Coolidge, A. S., "Relations Between Distribution Ratio, Temperature and Concentration in System: Water, Ether, Succinic Acid", *J. Amer. Chem. Soc.*, **41**, 150-166 (1919).

Holten, C. H., *Lactic Acid: Properties and Chemistry of Lactic Acid and Derivatives*, Verlag Chemie, Copenhagen, Chapter 4 (1971).

Kertes, A. S. and King, C. J., "Extraction Chemistry of Fermentation Product Carboxylic Acids", *Biotechnol. Bioeng.*, **28**, 269-282 (1986).

Khetarpal, S. C., Lal, K., and Bhatnagar, H. L., "Thermodynamic Studies on Melting of Aliphatic Dicarboxylic Acids", *Indian J. Chem.*, **19A**, 516-519 (1980).

Leonard, R. H., Peterson, W. H., and Johnson, M. J., "Lactic Acid from Fermentation of Sulfite Waste Liquor", *Ind. Eng. Chem.*, **40**, 57-67 (1948).

Saville, G. and Gundry, H. A., "The Heats of Combustion, Solution and Ionization of Lactic Acid", *Trans. Faraday Soc.*, **55**, 2036-2038 (1959).

Sato, T., Watanabe, H., and Nakamura, H., "Extraction of Lactic, Tartaric, Succinic, and Citric Acids by Means of Trioctylamine", *Bunseki Kagaku*, **34**, 559-563 (1985). Engl. Transl. provided by Polyglot Language Service.

Smith, J. M. and Van Ness, H. C., *Introduction to Chemical Engineering Thermodynamics*, 3rd ed, McGraw-Hill Book Company, New York, 335 (1975).

Wennersten, R., "The Extraction of Citric Acid from Fermentation Broth Using a Solution of Tertiary Amine", *J. Chem. Technol. Biotechnol.*, **33B**, 85-94 (1983).

CHAPTER 7. WATER COEXTRACTION

As acid molecules transfer from the aqueous to the organic phase during extraction, they may be accompanied by molecules of water. Determining the amount of this "coextracted water" is useful because organic-phase water potentially affects the distribution of acid into the solvent by interaction with the acid-amine complex. Furthermore, to the extent that the amount of water extracted into the organic phase is high, the product acid will require further concentration, thereby influencing process economics. The extent of water coextraction in relation to the nature of the of acid and diluent is the subject of this chapter.

7.1 Experimental Results

Details of the experimental procedures for the determination of the concentration of water in the organic phase by Karl Fischer titration and gas chromatography are given in Appendix A. The results of these measurements are presented as the molar concentration of water in the organic phase plotted against the molar concentration of acid in the organic phase ($C_{A,org}$). The slope of the line tangent to the curve at any given $C_{A,org}$ is the average number of water molecules coextracted into the solvent per molecule of acid which is extracted at that $C_{A,org}$. This slope will be referred to here as the water/acid ratio. Points for $C_{A,org}$ equal to 0 indicate the solubility of water into the solvent alone, i.e., for no acid in the system.

Data from Spala (1980) for the extraction of acetic acid by trioctylamine in chloroform are reproduced in Fig. 7-1*a*. Fig. 7-1 also gives results from the present work for the extraction of (*b*) succinic, (*c*) fumaric, (*d*) maleic and (*e*) lactic acids by

various concentrations of Alamine 336 in chloroform. Water solubility in the solvent alone is low in all cases. The water/acid ratio is low with chloroform as a diluent, typically in the range of 0.25 to 0.5. Generally, a higher amine concentration results in a higher water/acid ratio. Higher $C_{A,org}$ results in a lower water/acid ratio; that is, the curves have a concave downward shape. There is significant scatter in the experimental results for low acid concentrations, making it is difficult to assess trends in the low acid region.

Fig. 7-2*a* reproduces data from Ricker (1978) for the extraction of acetic acid by Alamine 336 in DIBK. In Fig. 7-2, results from the present work for the extraction of (*b*) succinic, (*c*) fumaric (*d*) malonic, (*e*) maleic acids by various concentrations of Alamine 336 in MIBK are presented. Because ketones interfere with Karl Fischer analysis, systems that contained ketones were analyzed by gas chromatography. Gas chromatography was found to be less precise than Karl Fischer analysis, so the experimental data for ketones show more scatter than do other results.

For the MIBK systems, it can been seen that higher amine content in the solvent decreases the solubility of water. This is expected from the relatively high solubility of water in MIBK alone (0.8 mol/L) versus the low solubility in Alamine 336 alone (< 0.1 mol/L). Generally, the water/acid ratio is quite high, typically on the order of 2. For maleic and malonic acids, higher amine concentration results in a lower water/acid ratio; for acetic acid, amine concentration has no effect on the water/acid ratio; for succinic acid, the effect of amine concentration is difficult to determine from the available data. Most of the curves are nearly linear, although for malonic acid the curves appear to be concave downward at high $C_{A,org}$, and for fumaric acid the curve is concave downward throughout.

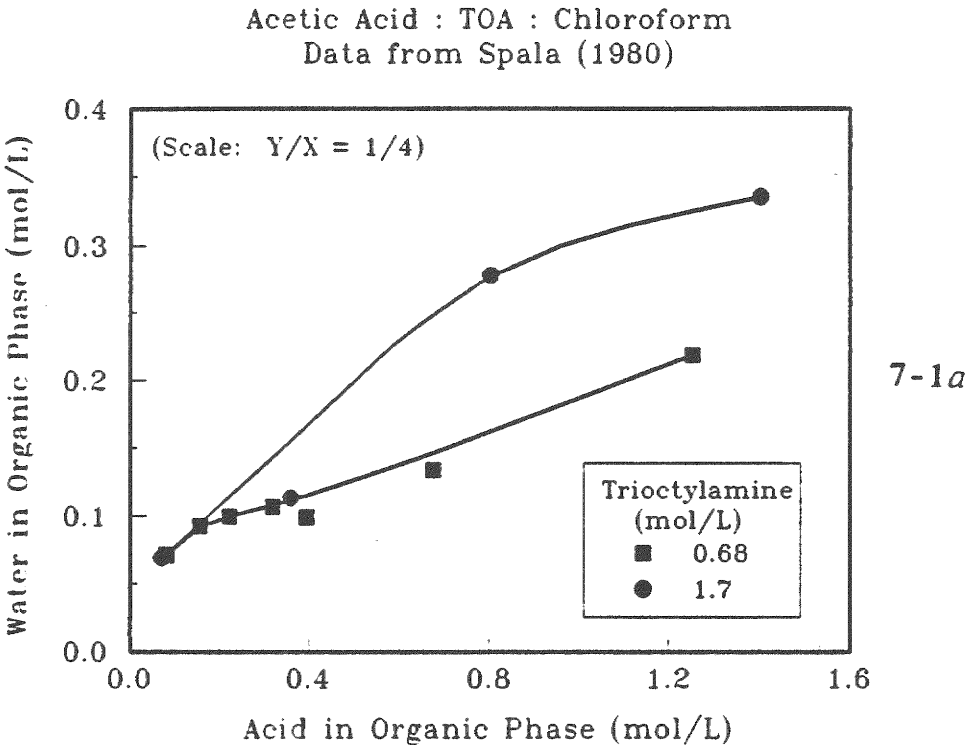
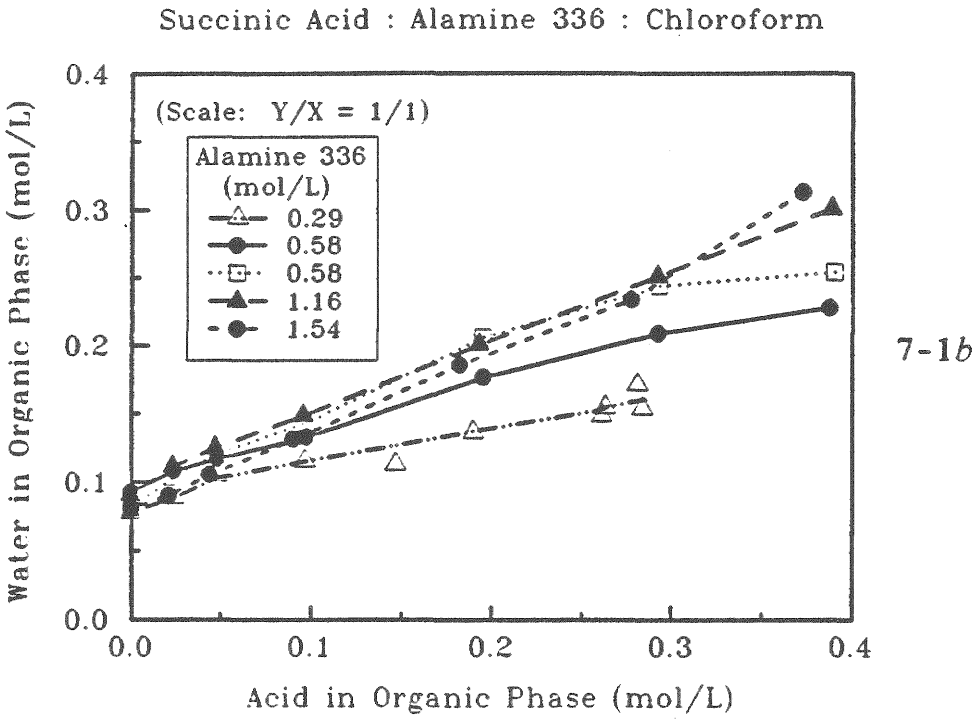


Fig. 7-1. Water Coextraction for Various Acids and Alamine 336 in $CHCl_3$.

(*a*) acetic acid - trioctylamine (data from Spala, 1980)



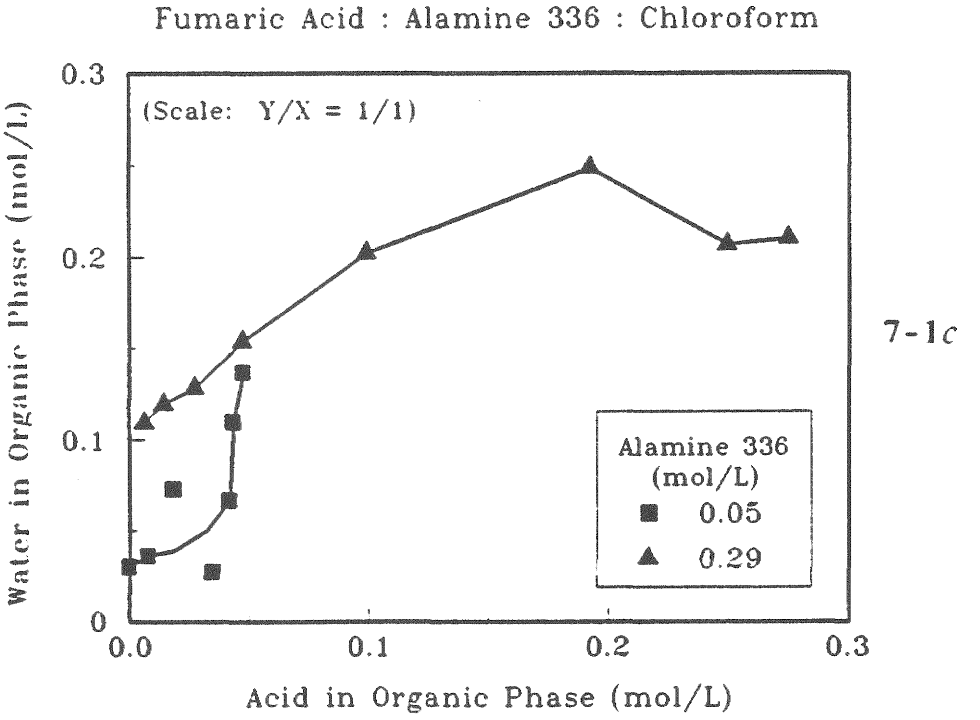
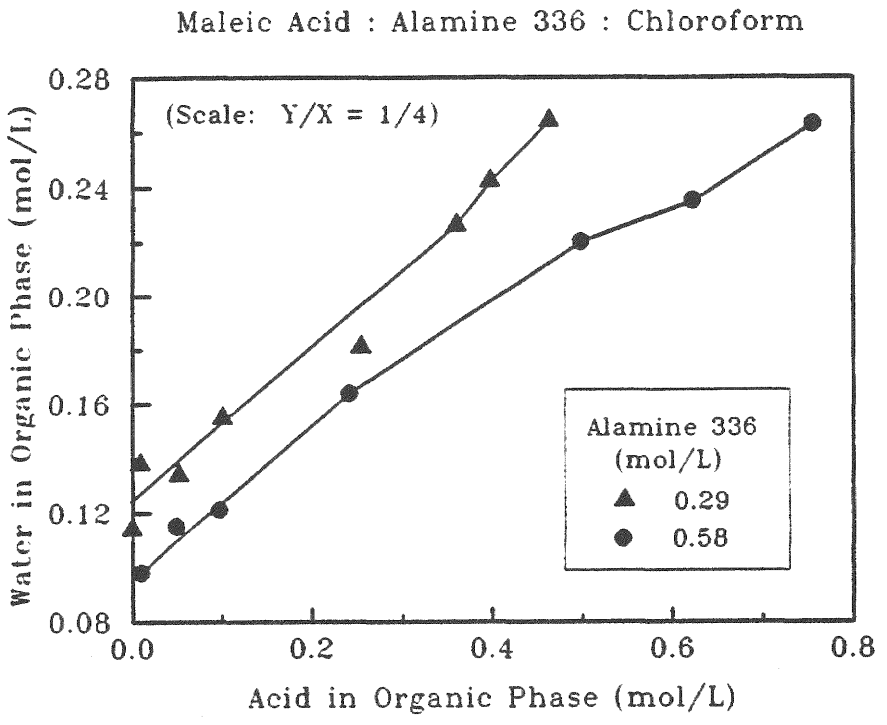
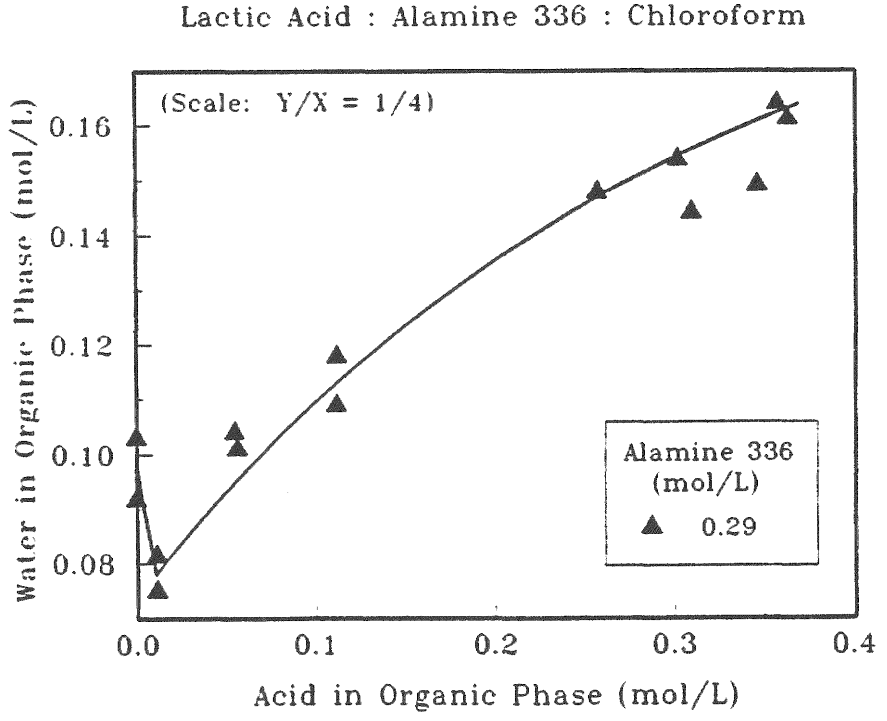


Fig. 7-1. Water Coextraction for Various Acids and Alamine 336 in $CHCl_3$ (cont'd).

(*b*) succinic acid and (*c*) fumaric acid



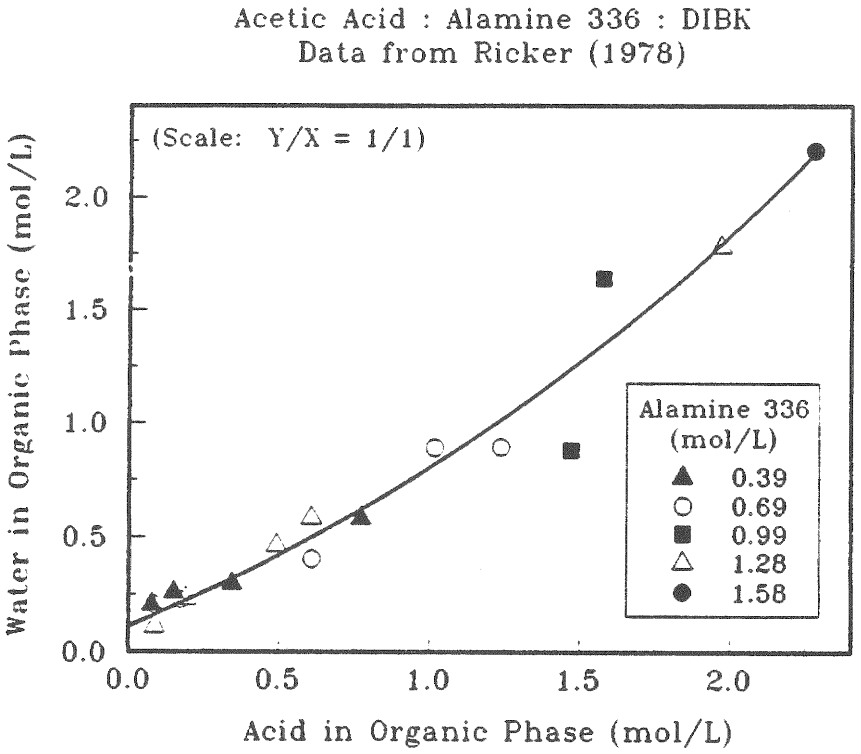
7-1*d*



7-1*e*

Fig. 7-1. Water Coextraction for Various Acids and Alamine 336 in $CHCl_3$ (cont'd).

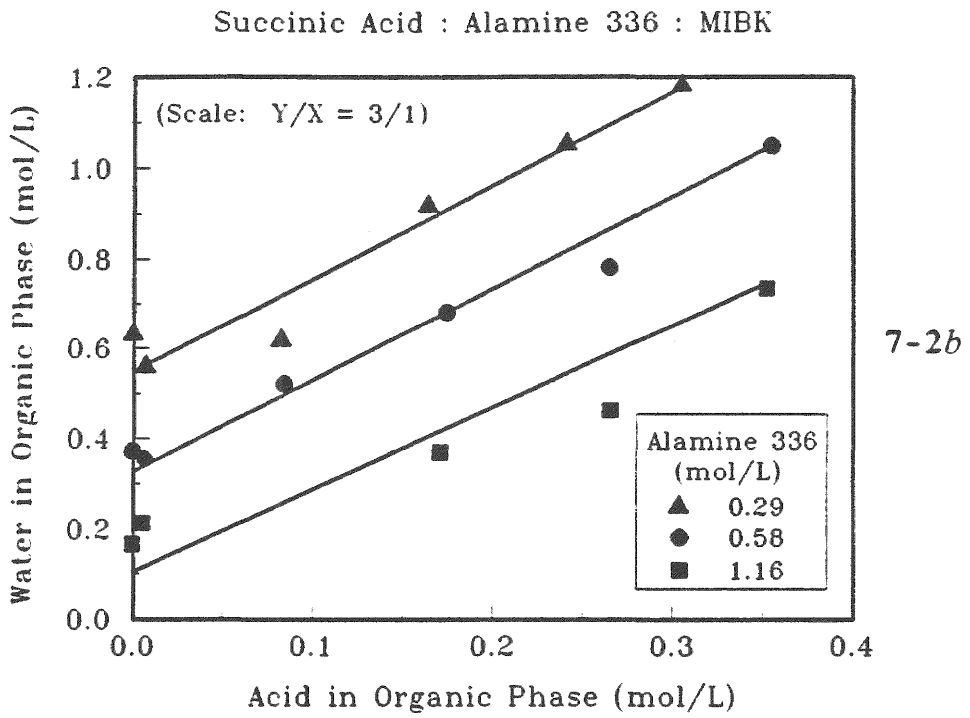
(*d*) maleic acid and (*e*) lactic acid



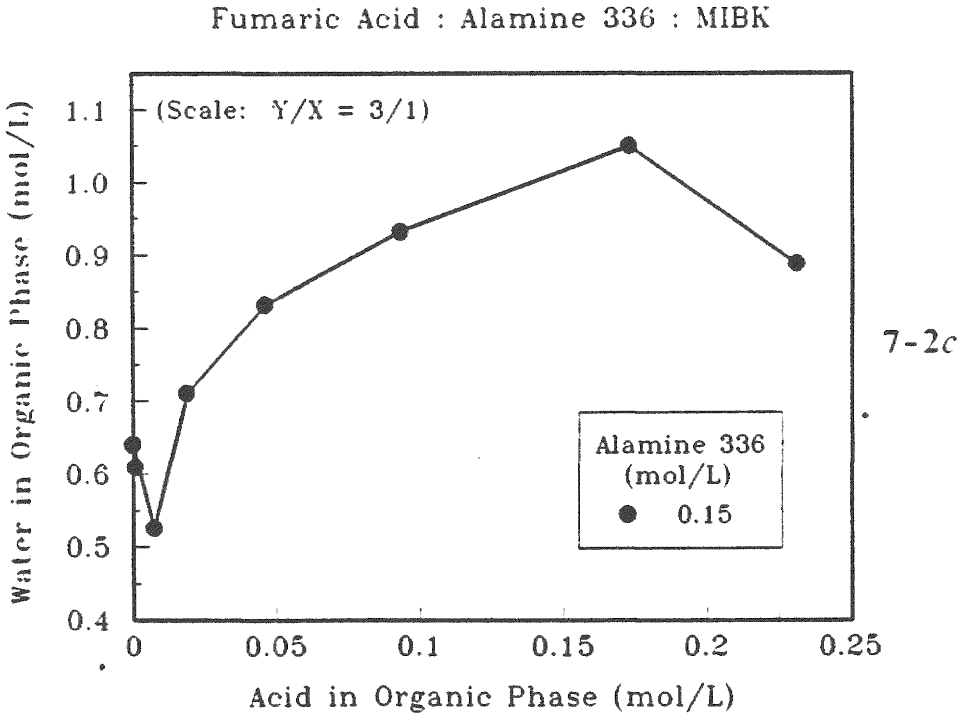
7-2*a*

Fig. 7-2. Water Coextraction for Various Acids and Alamine 336 in Ketones.

(*a*) acetic acid in DIBK (data from Ricker, 1978)



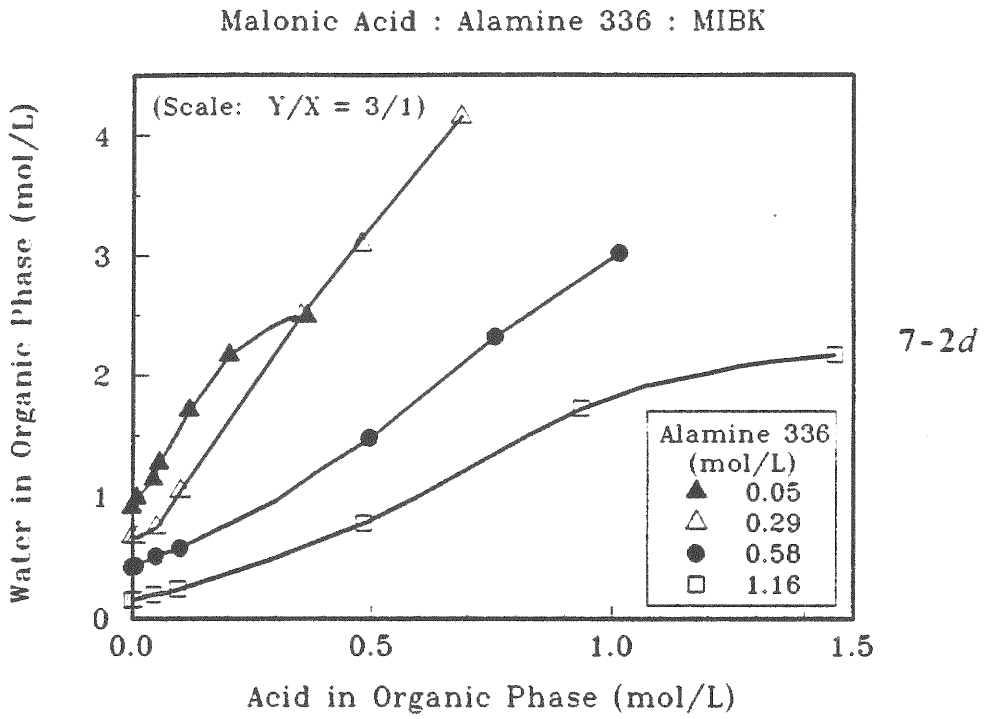
7-2*b*



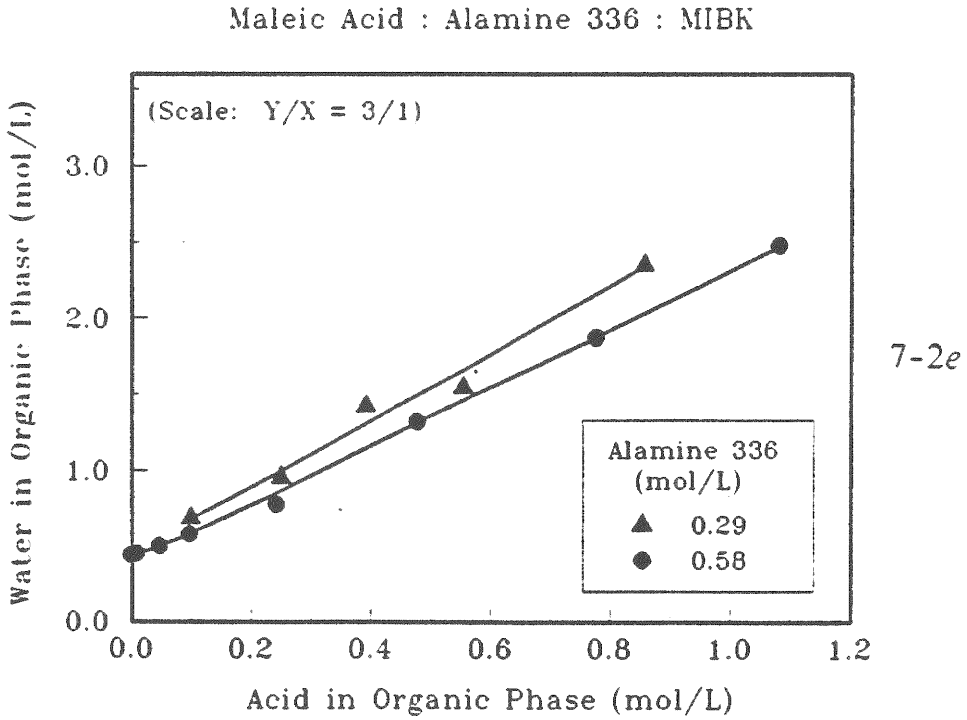
7-2*c*

Fig. 7-2. Water Coextraction for Various Acids and Alamine 336 in Ketones (cont'd).

(*b*) succinic acid and (*c*) fumaric acid



7-2*d*



7-2*e*

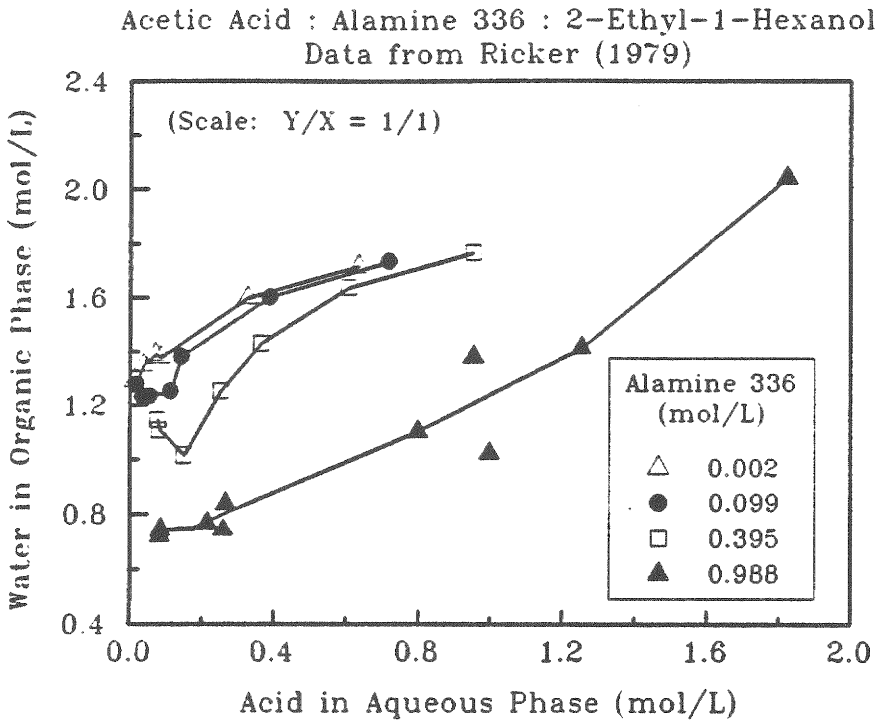
Fig. 7-2. Water Coextraction for Various Acids and Alamine 336 in Ketones (cont'd).

(*d*) malonic acid and (*e*) maleic acid

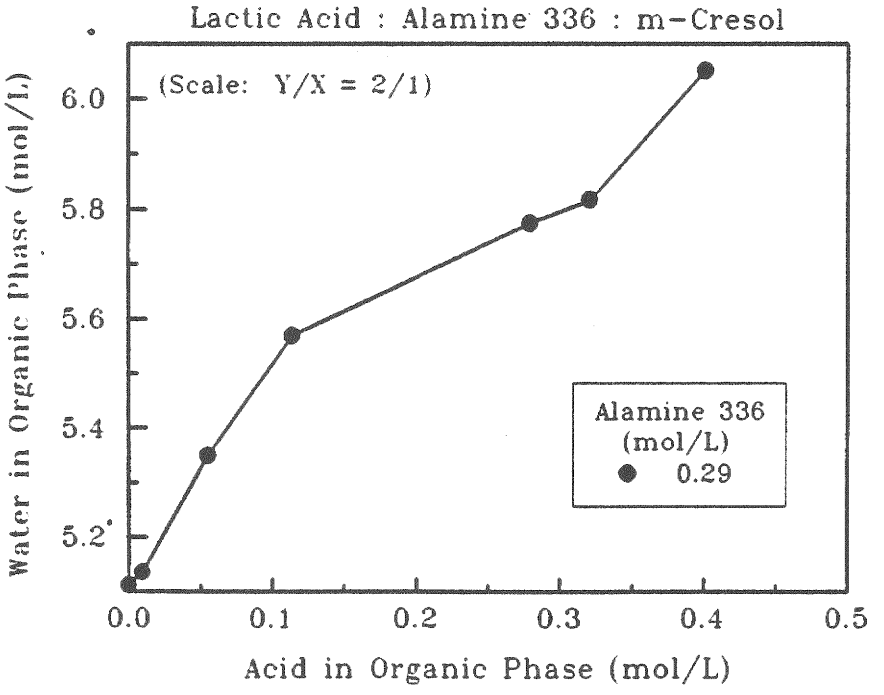
Fig. 7-3 gives the results for the extraction of several acids by Alamine 336 at various concentrations in hydroxyl-bearing diluents: (*a*) acetic acid with 2-ethyl-1-hexanol diluent (data from Ricker, 1978); (*b*) lactic acid with *m*-cresol diluent; (*c*) succinic acid in 1-octanol diluent. Figs. 7-3 *b* and *c* are from the present work. In diluents with an -OH group, water extraction is high; there is both high water solubility in the solvent alone and a high water/acid ratio. All the systems give curves that are concave downward, except for acetic acid at the highest amine concentration. Succinic acid exhibits an extremely high water/acid ratio (on the order of 5) at low $C_{A,org}$, which decreases significantly at high values of $C_{A,org}$.

Fig. 7-4 compares water coextraction for the extraction of succinic acid by 0.29 mol/L Alamine 336 in chloroform, in a chloroform-octanol mixture, and in octanol. The water extracted by the solvent alone was subtracted from the total organic-phase water concentration to facilitate direct comparison of coextracted water for the three diluents. Addition of chloroform to the octanol diluent significantly reduces the amount of coextracted water.

Fig. 7-5 shows the results for the extraction of (*a*) acetic and (*b*) succinic acids by various concentrations of Alamine 336 in diluent mixtures of *n*-heptane and (*a*) 15% (v/v) chloroform and (*b*) 8% (v/v) chloroform (vol% indicates volume percent of total solvent volume). Water solubility in the solvent is extremely low and increases slightly with increased amine concentration. The water/acid ratio is low, on the order of 0.25. Increased amine concentration appears to increase the water/acid ratio slightly, but it is difficult to establish this with certainty from the data available. Fig. 7-6 shows the effect of the volume percent of chloroform in 0.29 mol/L Alamine 336 and heptane on water coextraction for succinic acid (vol% refers to percent of total solvent volume). Water coextraction is low in all cases, with a



7-3*a*



7-3*b*

Fig. 7-3. Water Coextraction for Various Acids and Alamine 336 in Solvents Containing a Hydroxyl Group.

(*a*) acetic acid in 2-ethyl-1-hexanol (data from Ricker, 1978),
(*b*) lactic acid in *m*-cresol

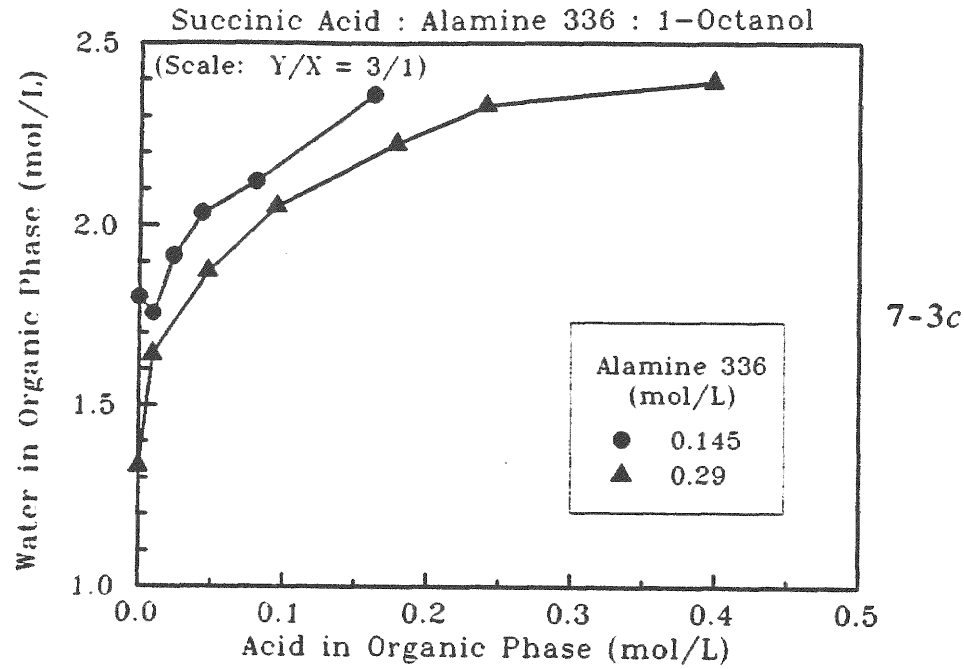


Fig. 7-3. Water Coextraction for Various Acids and Alamine 336 in Solvents Containing a Hydroxyl Group (cont'd).

(*c*) succinic acid in 1-octanol.

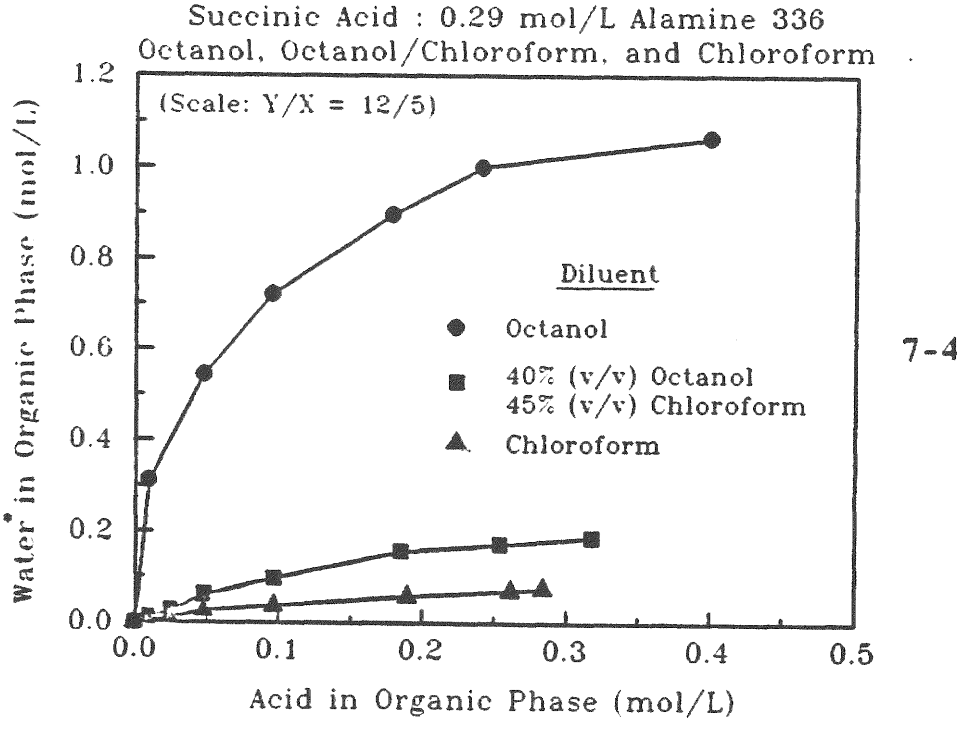


Fig. 7-4. Water Coextraction for Succinic Acid and 0.29 mol/L Alamine 336 in 1-Octanol/Chloroform Mixtures.

* Solubility of water in solvent alone has been subtracted from all data points.

water/acid ratio on the order of 0.25. The proportion of chloroform in the solvent has little effect on the water/acid ratio. Fig. 7-7 shows results for the extraction of succinic acid by 0.29 mol/L Alamine 336 in *n*-heptane. Similar plots for 0.58 and 1.16 mol/L Alamine 336 gave extreme scatter in the data; however, it was apparent that water content was extremely low in all cases. There is an unusual trend of decreasing water content with increasing organic-phase acid concentration; however, this trend must be considered uncertain because there is a high relative error in water analysis at the low water content.

Figs. 7-8 and 7-9 give results analogous to Figs. 7-5 and 7-6 for the extraction of succinic acid by Alamine 336 in a mixed diluent of methylene chloride and heptane. The water/acid ratio increases slightly with increased amine concentration in solvents with both high and low volume percentages of methylene chloride in the solvent. No effect of the proportion of methylene chloride to heptane was seen. The water/acid ratio was slightly higher than for the chloroform-heptane system, typically on the order of 0.7.

Figs. 7-10 and 7-11 present water coextraction results for the extraction of succinic acid by Alamine 336 in methylene chloride and nitrobenzene, respectively. Water coextraction in methylene chloride follows a pattern similar to that of water coextraction in chloroform. The curves are concave downward and the water/acid ratio increases with increased amine concentration. In methylene chloride, the water/acid ratio is less than 0.50. In nitrobenzene, the curve is approximately linear for the concentrations studied, and the water/acid ratio is near 1.0.

In Fig. 7-12, the effect of temperature is shown for extraction with 0.29 mol/L Alamine 336 of (*a*) lactic acid in chloroform, (*b*) succinic acid in chloroform, and

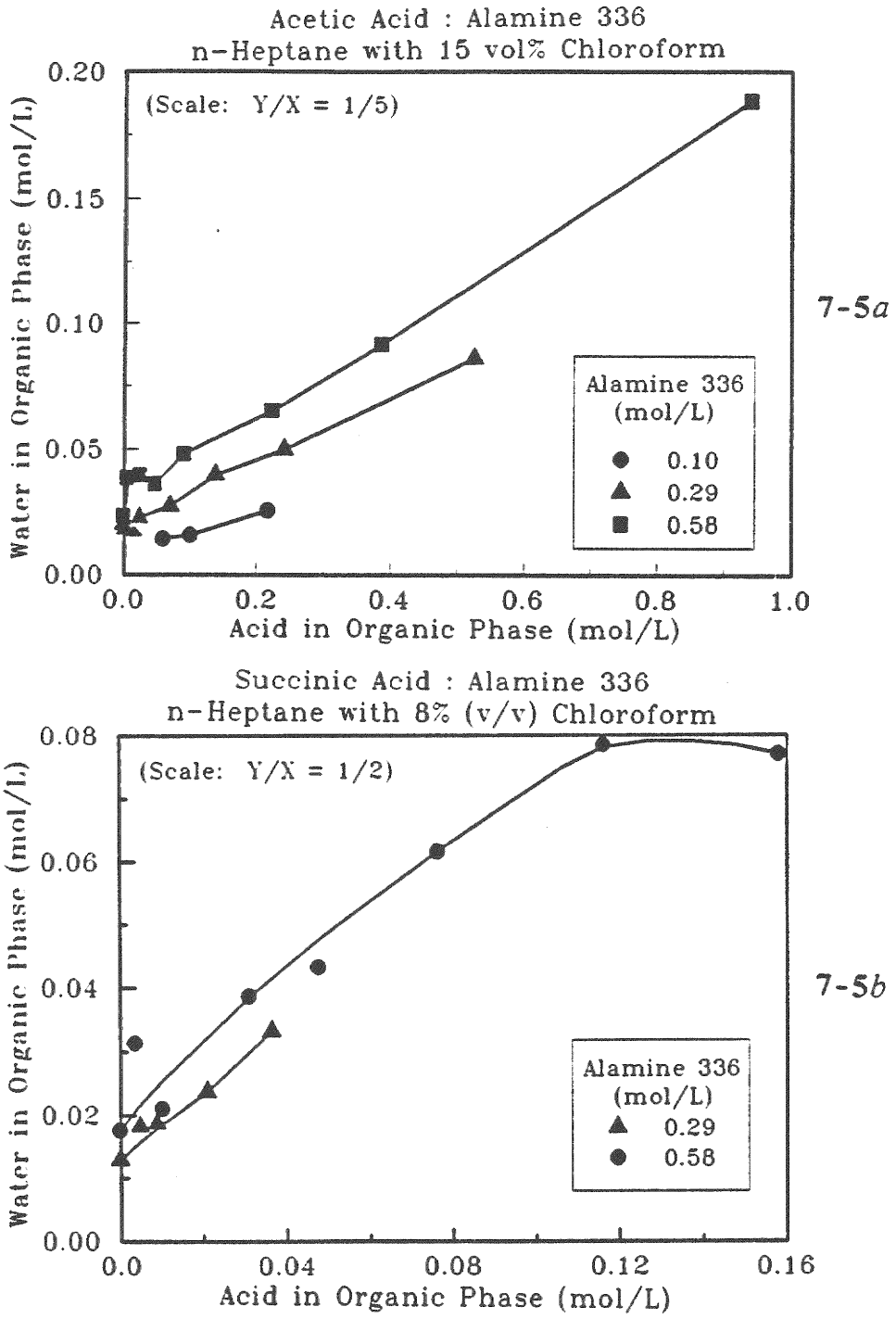
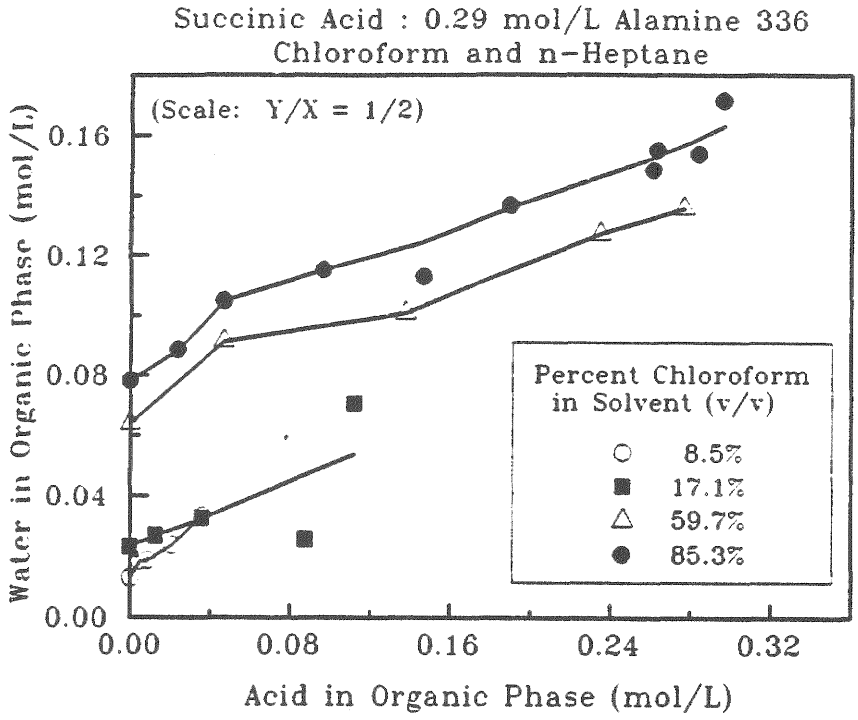


Fig. 7-5. Water Coextraction for Various Acids and Various Concentrations of Alamine 336 in an n-Heptane/Chloroform Mixed Diluent.

(*a*) acetic acid with 15% (v/v) chloroform and (*b*) succinic acid with 8% (v/v) chloroform.

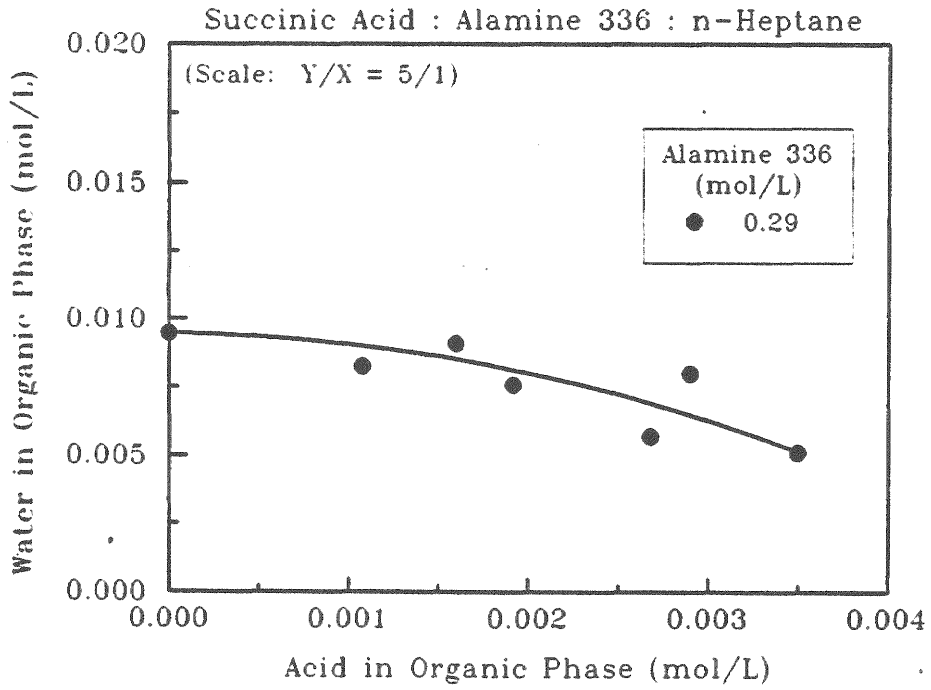
(Note: vol% refers to percent of total solvent volume).



7-6

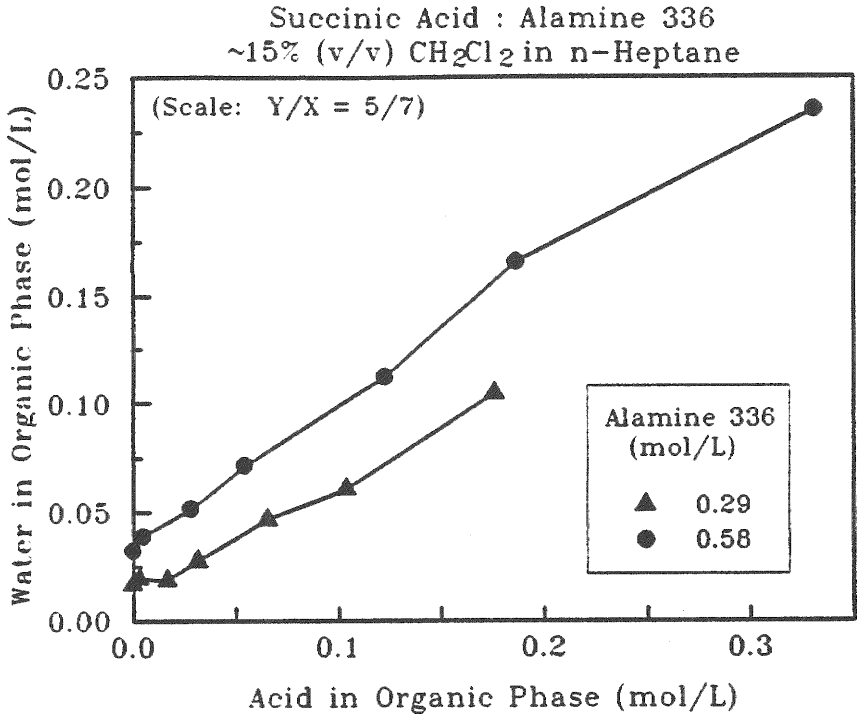
Fig. 7-6. Water Coextraction for Succinic Acid and 0.29 mol/L Alamine 336 in Various n-Heptane/Chloroform Mixed Diluents.

(Note: vol% indicates percent of total solvent volume.)

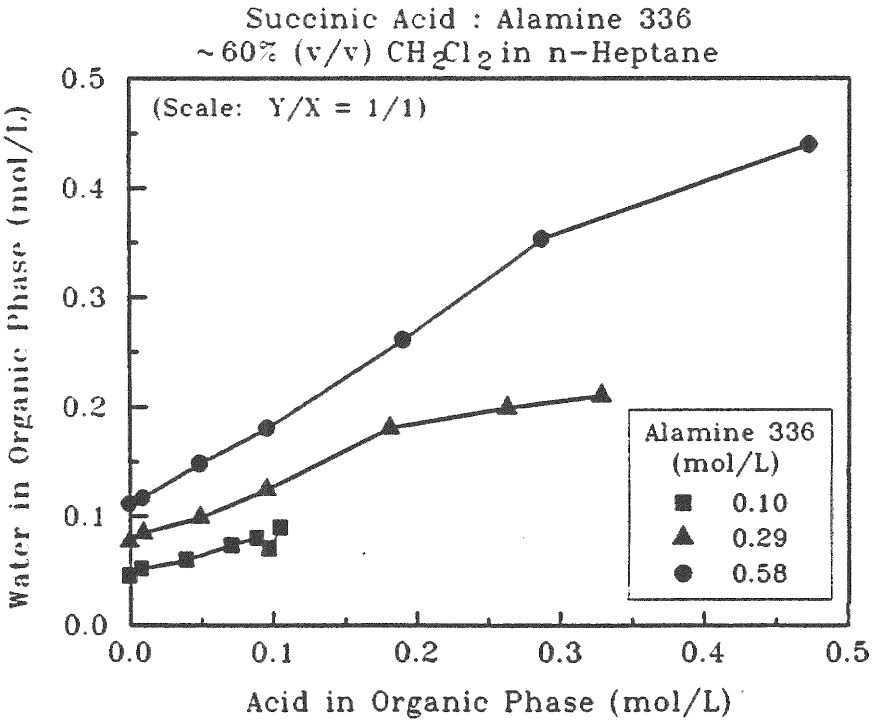


7-7

Fig. 7-7. Water Coextraction for Succinic Acid and Alamine 336 in n-Heptane.



7-8*a*

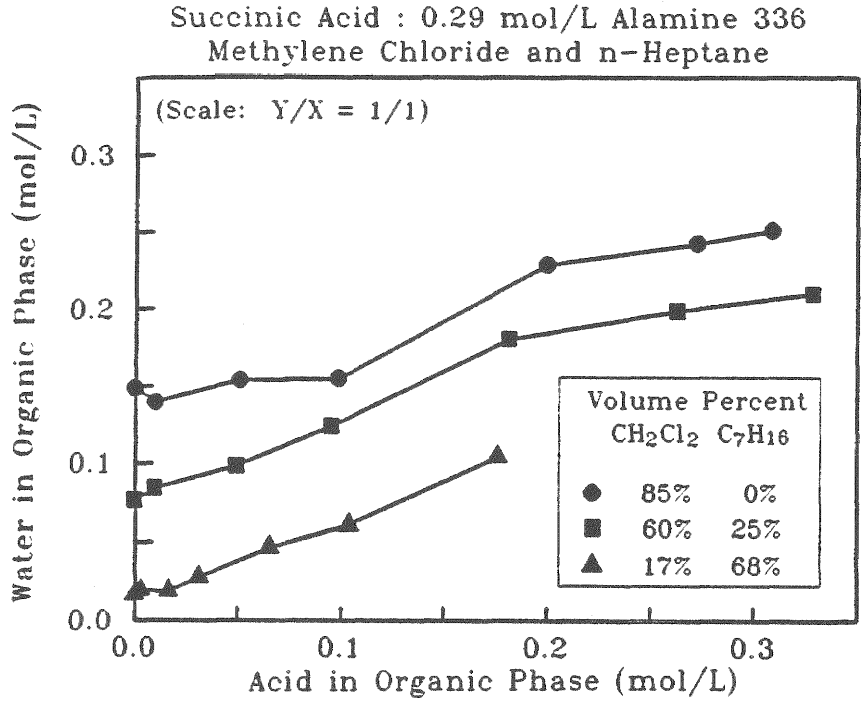


7-8*b*

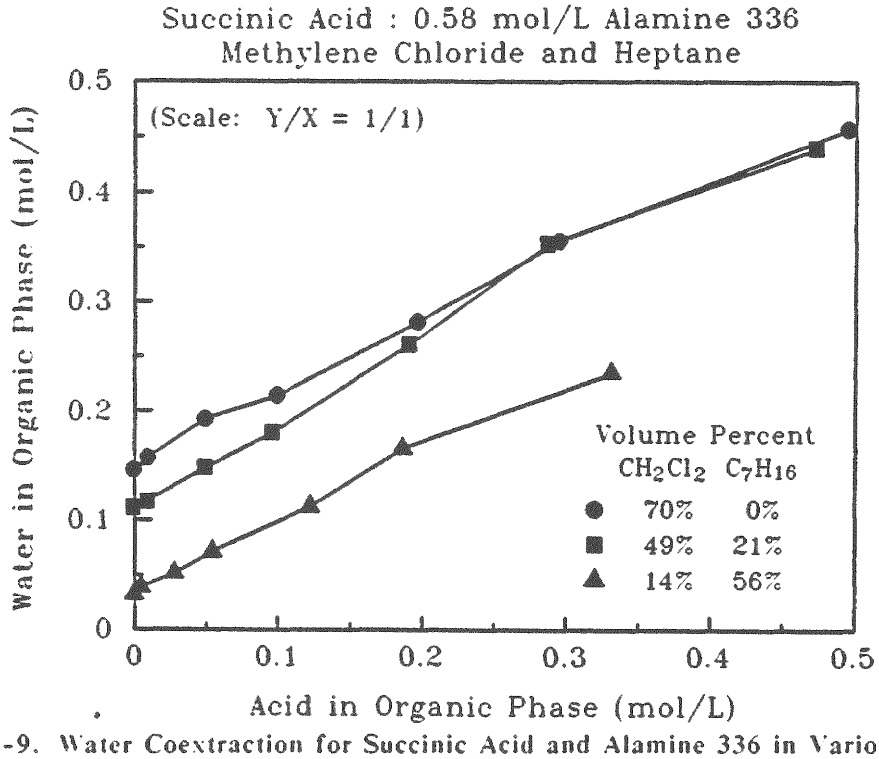
Fig. 7-8. Water Coextraction for Succinic Acid and Various Concentrations of Alamine 336 in an n-Heptane/Methylene Chloride Mixed Diluent.

(*a*) ~15% (v/v) methylene chloride and (*b*) ~60% (v/v) methylene chloride.

(Note: vol% indicates percent of total solvent volume.)



7-9*a*



7-9*b*

Fig. 7-9. Water Coextraction for Succinic Acid and Alamine 336 in Various n-Heptane/Methylene Chloride Mixed Diluents.

(*a*) 0.29 mol/L Alamine 336 and (*b*) 0.58 mol/L Alamine 336.

(Note: vol% indicates percent of total solvent volume.)

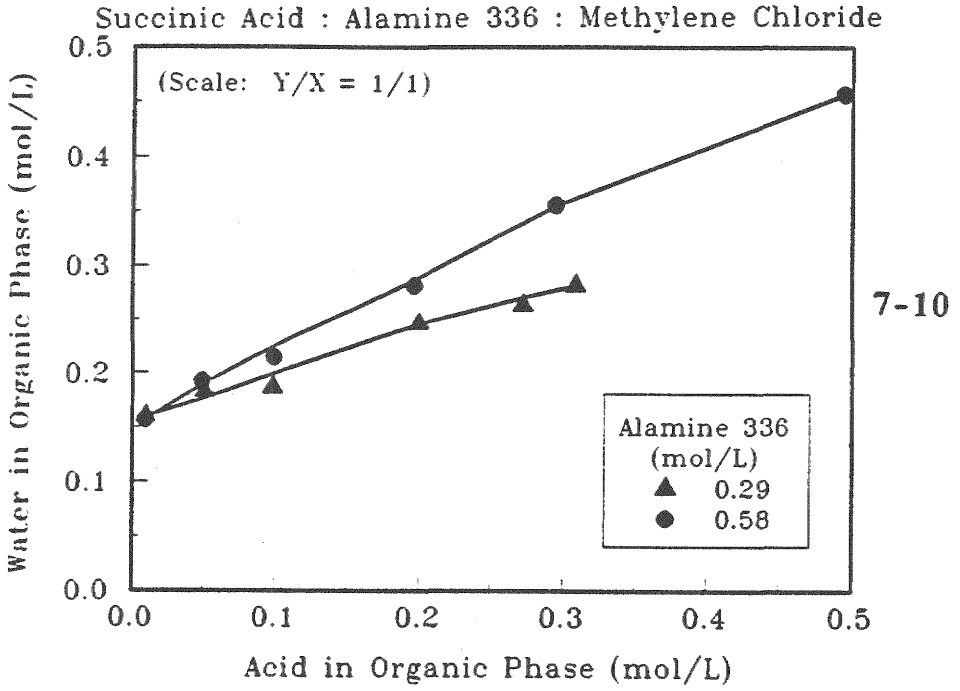


Fig. 7-10. Water Coextraction for Succinic Acid and Alamine 336 in Methylene Chloride.

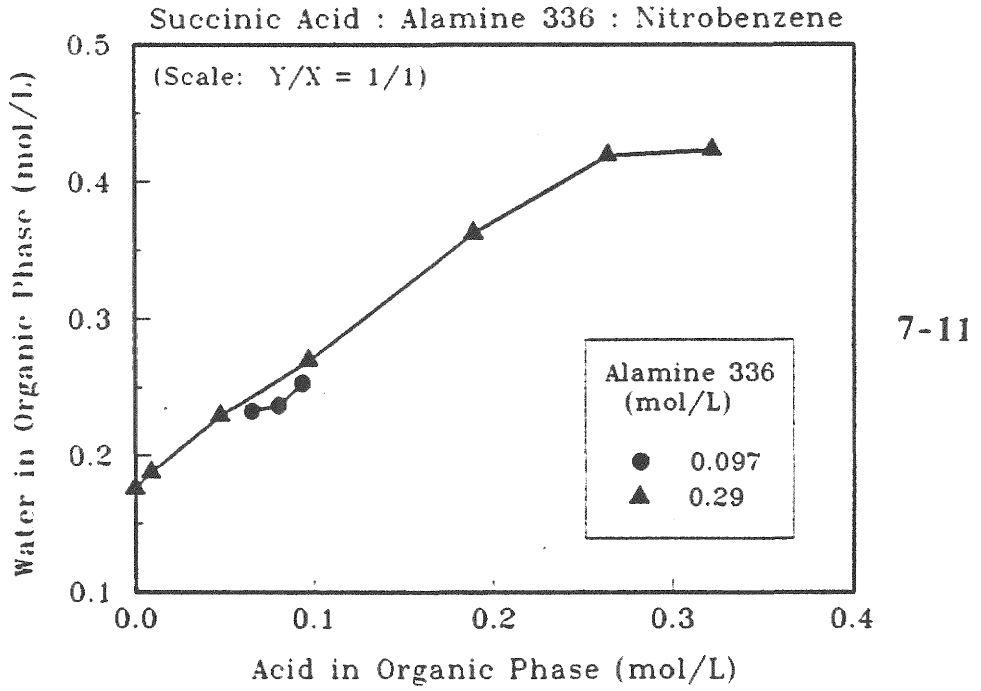
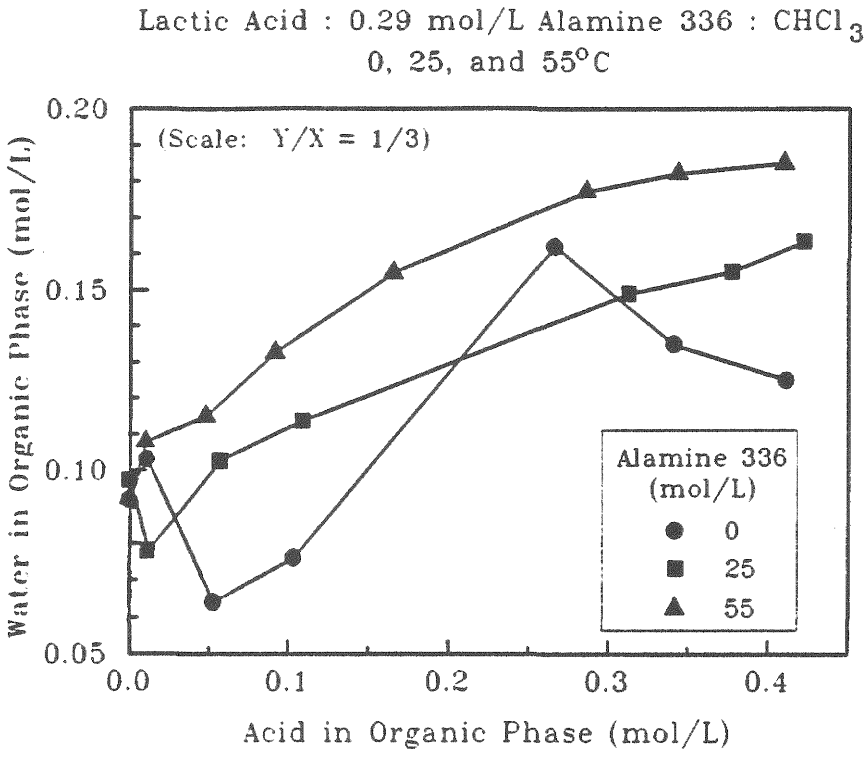


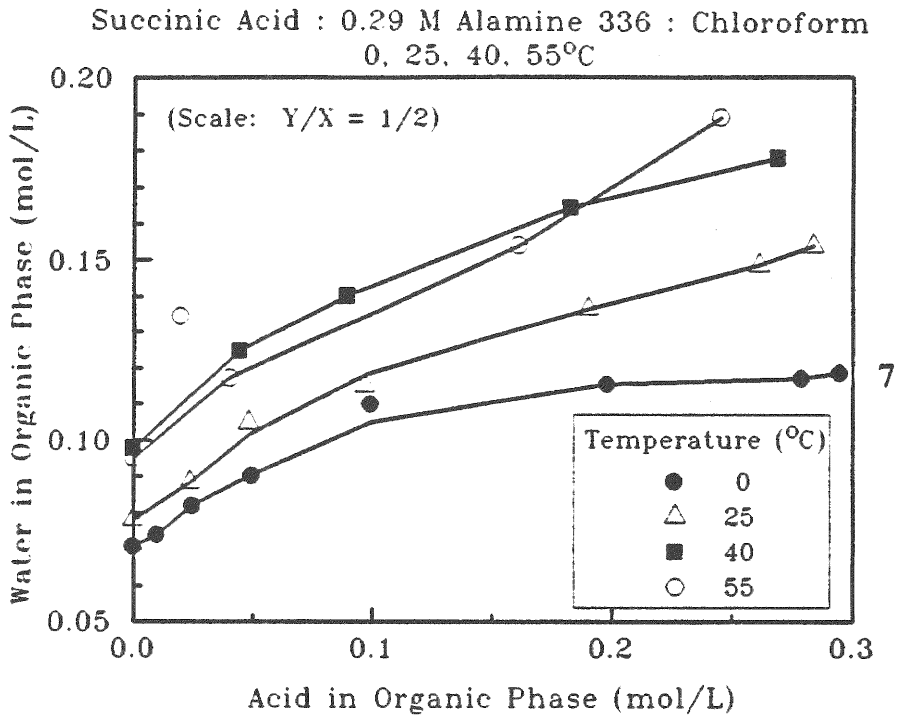
Fig. 7-11. Water Coextraction for Succinic Acid and Alamine 336 in Nitrobenzene.



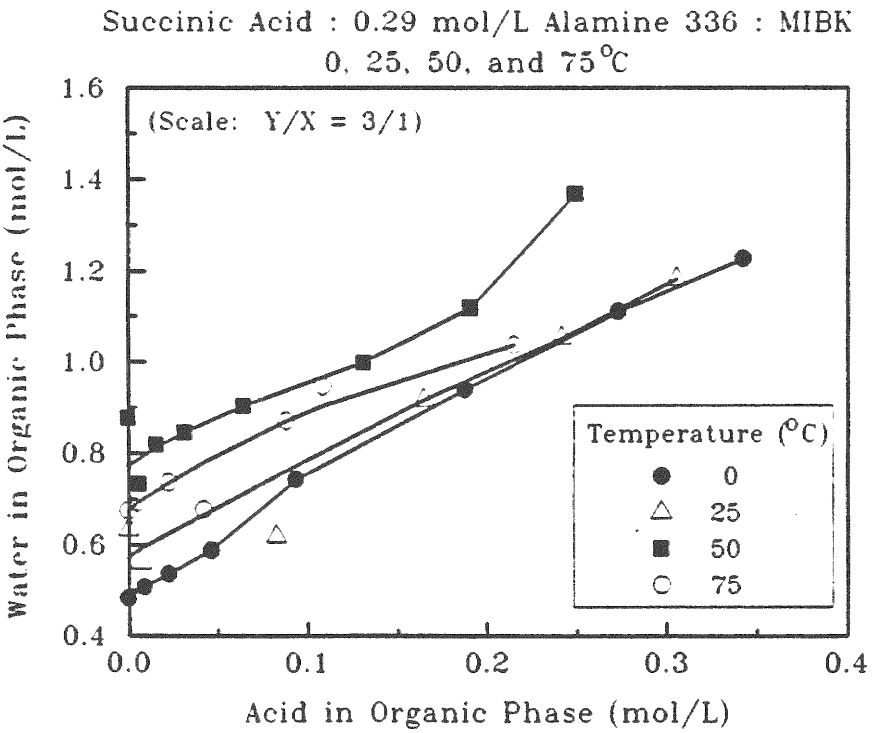
7-12*a*

Fig. 7-12. Effect of Temperature on Water Coextraction.

(*a*) lactic acid and Alamine 336 in chloroform



7-12*b*



7-12*c*

Fig. 7-12. Effect of Temperature on Water Coextraction (cont'd).

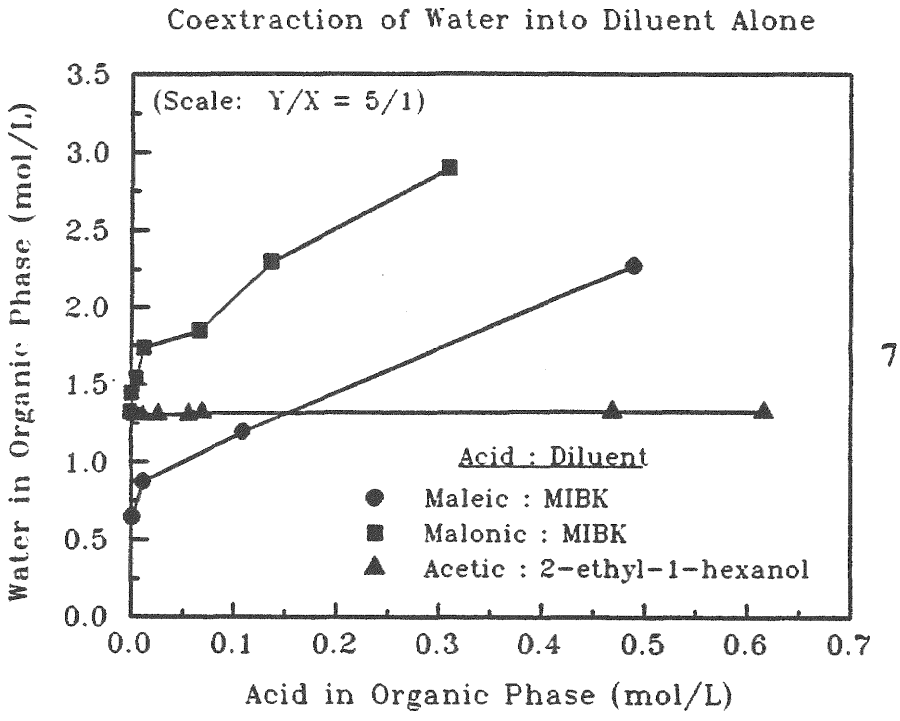
(*b*) succinic acid and Alamine 336 in chloroform and (*c*) succinic acid and Alamine 336 in MIBK

(*c*) succinic acid in MIBK. For succinic acid in chloroform, the curves are concave downward at low temperature, but become increasingly linear as temperature increases. As temperature increases from 0 °C, the solubility of water into the solvent alone increases until the temperature reaches 40 °C, and then is roughly the same at 55 °C. Thus water coextraction increases with increased temperature, especially at high $C_{A,org}$. Data for lactic acid in chloroform are more scattered, but appear to follow similar trends. For succinic acid in MIBK, there was no effect of temperature on the water/acid ratio detectable at the level of precision of the analysis. Solubility of water into the solvent increased with increasing temperature until 50 °C, and then decreased at 75 °C.

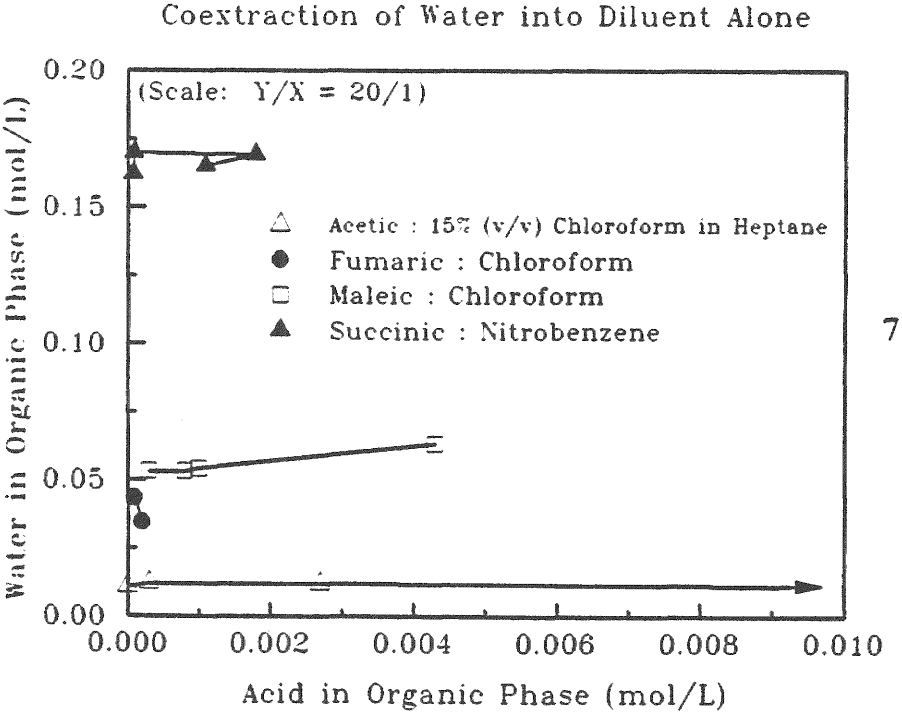
Water coextraction associated with the extraction of acids by the diluent with no amine present is given in Fig. 7-13 *a* and *b*. The flat lines for acetic acid in 2-ethyl-1-hexanol and 15% (v/v) chloroform in heptane suggest that no water accompanies acetic acid into the alcohol diluent. In contrast, maleic and malonic acids in MIBK show a steep slope, indicating a large amount of water coextraction. The amount of acid extracted by chloroform or nitrobenzene alone is so low that it is not possible to judge water coextraction.

7.2 Discussion

The topic of water coextraction has not been covered extensively in the literature, although there have been a few investigations to characterize the effect of water on carboxylic acid extraction. Vanura and Kuca (1976) performed as mass-action law analysis which included water explicitly in complexes of citric acid and trilaurylamine in toluene. The water/acid ratio was unity for low concentrations of



7-13*a*



7-13*b*

Fig. 7-13. Coextraction of Water into Diluent Alone.

(*a*) solvents which extract more acid
(*b*) solvents which extract less acid

acid, but decreased as acid concentration increased. Sato et al. (1985) measured water content in the extraction of lactic, succinic, tartaric, and citric acids by trilaurylamine in xylene. The authors reported that the water/acid ratio decreased with increasing acid concentration, but did not present data for the actual values of organic-phase water content.

Lipovskii and Kuzina (1968) found that preparations of trioctylamine and oxalic acid at 2:1 and 4:1 ratios did not dissolve in anhydrous carbon tetrachloride or benzene, but did dissolve in water saturated solutions of these solvents. From this, the authors concluded that water is essential for the formation of an extractable compound. The water/acid ratio for these systems was reported to be close to 2. Additionally, the authors found that preparations of trioctylamine and oxalic acid in chloroform did not require the presence of water for solution of the complex.

Obviously, water accompanies the complex into the organic phase because it somehow increases the stability of the system. Presumably, the water hydrates the carboxyl groups (and -OH groups for hydroxycarboxylic acids) to increase the complex stability in the solvent.

Figs. 7-14 to 7-16 compare different acids in chloroform, -OH group bearing solvents, and MIBK, respectively. Water coextraction at low acid concentrations decreases in the order: fumaric > malonic > maleic = succinic > lactic > acetic. Thus it is seen that monocarboxylic acids carry less water with them than do dicarboxylic acids. The most obvious explanation is that each carboxyl group, whether free or complexed, requires a certain amount of interaction with water molecules in order for it to be stable in the solvent. However, in the cases of succinic, malonic, maleic acid, intramolecular hydrogen bonding may displace some of the water. Fumaric acid,

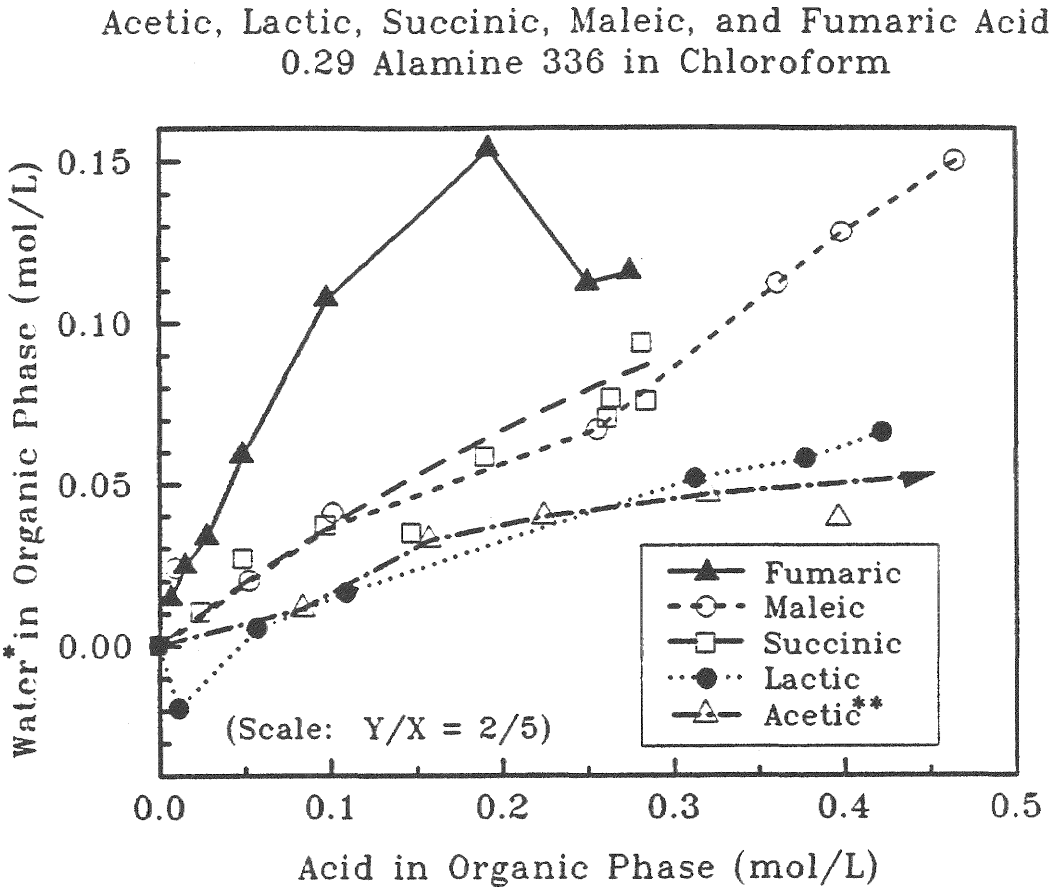


Fig. 7-14. Comparison of Water Coextraction for Various Acids in Chloroform.

* Solubility of water in solvent alone has been subtracted from all data points.
**Data for acetic acid in 0.68 instead of 0.29 mol/L trioctylamine.

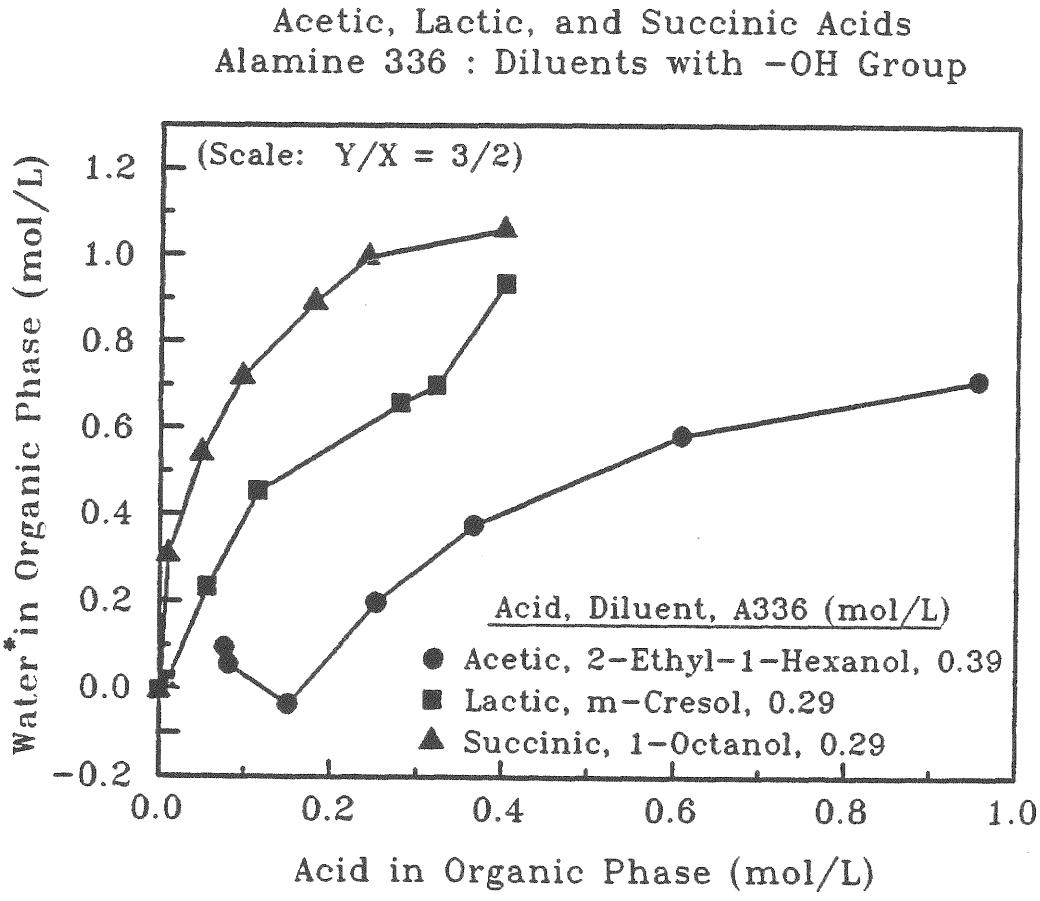


Fig. 7-15. Comparison of Water Coextraction for Various Acids in Alcohols.

* Solubility of water in solvent alone has been subtracted from all data points.

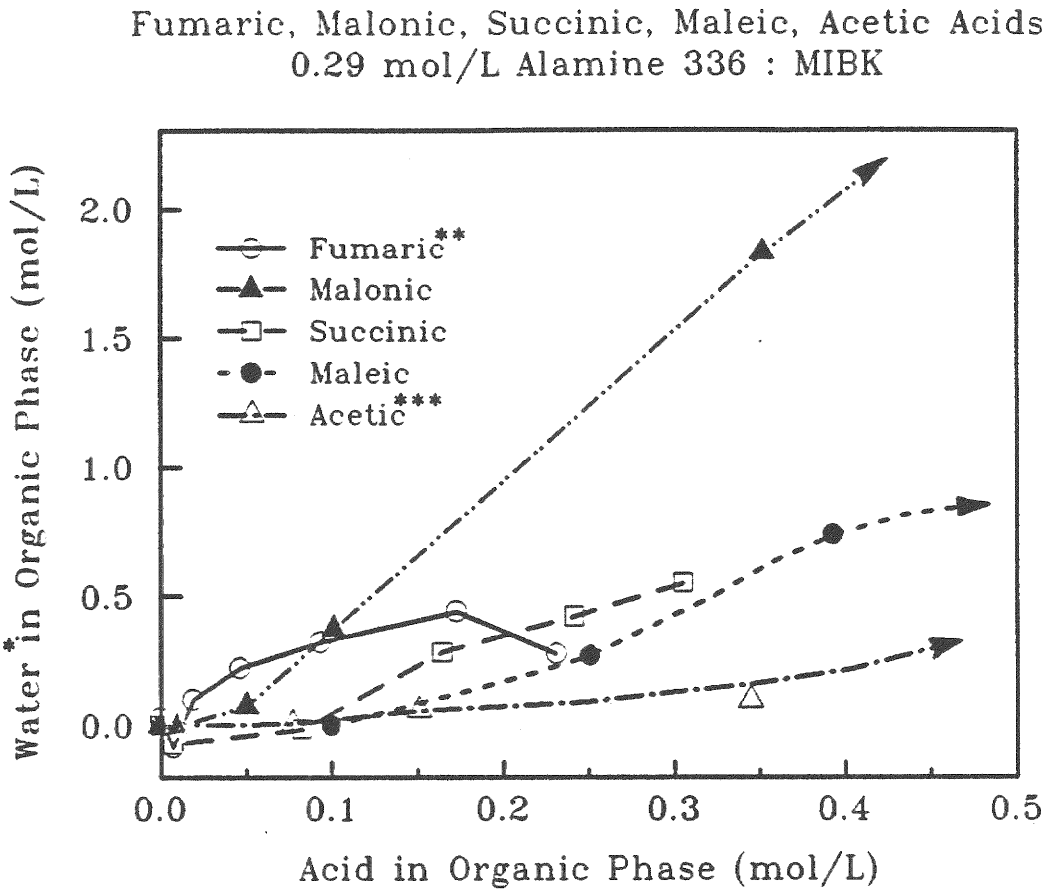


Fig. 7-16. Comparison of Water Coextraction for Various Acids in MIBK.

(*a*) 0.29 mol/L Alamine 336

* Solubility of water in solvent alone has been subtracted from all data points.
** Data for fumaric acid in 0.15 instead of 0.29 mol/L Alamine 336.
***Data for acetic acid for 0.39 mol/L Alamine 336 in DIBK instead of 0.29 mol/L Alamine 336 in MIBK.

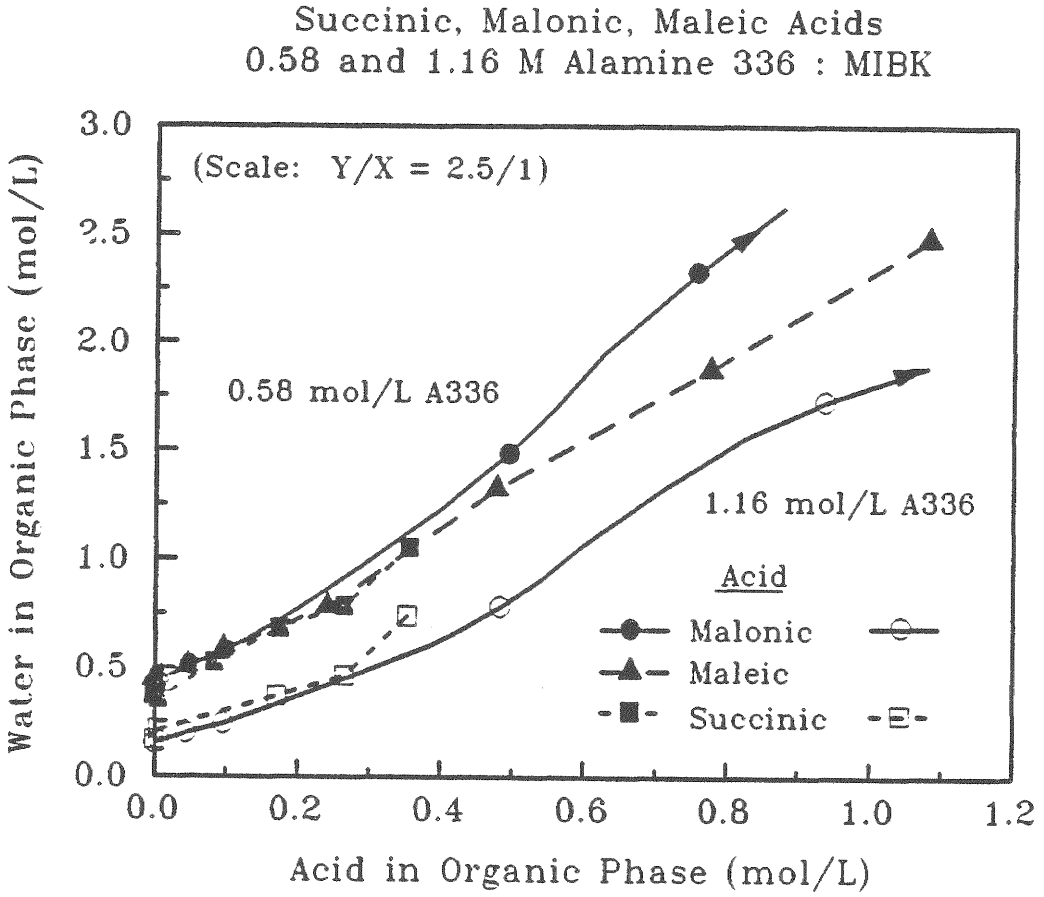


Fig. 7-16. Comparison of Water Coextraction for Various Acids in MIBK (cont'd).

(b) 0.58 and 1.16 mol/L Alamine 336

* Solubility of water in solvent alone has been subtracted from all data points.

which forms no intramolecular hydrogen bonds, may require water for each carboxyl group independently, therefore exhibiting the highest water/acid ratio.

The concave downward shape of the curves in alcohols and in chloroform can be rationalized from a physical or chemical standpoint. From a physical standpoint, as acid concentration increases, the solvent phase as a whole becomes more polar and less water is needed to satisfy the complex. Using a chemical rationale, at higher organic-phase acid concentrations it becomes easier for the polar complexes to interact with each other rather than with water molecules.

These simple explanations do not account for differences which may exist among physically solvated acid, the (2,1) complex, and the (1,1) complex in interactions with water. Clearly this will have some effect. The extraction of maleic and malonic acid by MIBK alone (physical solvation) produces high water coextraction, higher than when amine is present. On the other hand, acetic acid in 2-ethyl-1-hexanol alone shows no water coextraction, whereas coextraction of water is high with amine present. The results in ketone diluents frequently show a concave upward shape. Perhaps this phenomenon is connected to the high (2,1) complex formation seen in ketone diluents.

Fig. 7-17 compares water coextraction with succinic acid and 0.29 mol/L Alamine 336 in the various diluents. The water concentration in the organic phase has been adjusted by subtracting the amount of water soluble in the solvent alone. Water coextraction decreases in the order: 1-octanol > MIBK > nitrobenzene > methylene chloride > chloroform > heptane (not shown). The solubility of water into the diluent alone follows the order (see Appendix E): 1-octanol, 1.74 mol/L > MIBK, 0.776 mol/L > methylene chloride, 0.145 mol/L > chloroform, 0.074 mol/L > heptane

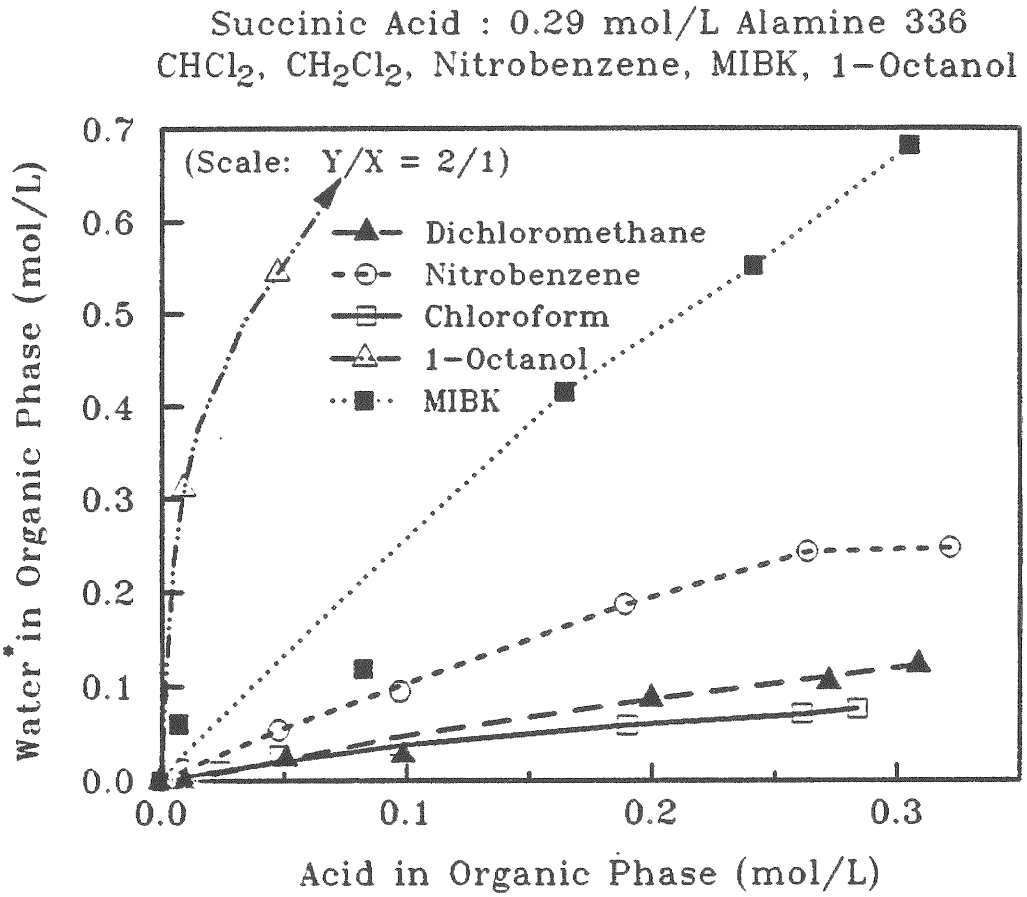


Fig. 7-17. Comparison of Water Coextraction for Succinic Acid in Various Diluents.

* Solubility of water in solvent alone has been subtracted from all data points.

0.003 mol/L. Thus, the coextracted water follows the same order as the solubility of water in the diluent alone. Apparently, forces which allow the diluent to solvate water molecules effectively also allow the diluent to solvate the water molecules surrounding or attached to a complex.

7.3 Summary and Conclusions

Water is pulled into the organic phase as acid-amine complexes are formed. The type of diluent is the major factor determining the extent of water coextraction into the organic phase. For example, water coextraction for succinic acid decreases in the order: 1-octanol > MIBK > nitrobenzene > methylene chloride > chloroform > heptane. The higher the water solubility in the diluent alone, the more water is taken into the corresponding acid-amine-diluent extract. Acid type has a lesser effect on water coextraction, with monocarboxylic acids showing less water coextraction than dicarboxylic acids. In alcohols, ketones, and chloroform diluent, water coextraction at low acid concentrations decreases in the order: fumaric > malonic > maleic = succinic > lactic > acetic. The effect of temperature on water coextraction varies with the acid and diluent. For the extraction of lactic and succinic acids by Alamine 336 in chloroform, water coextraction increases with increasing temperature. For the extraction of succinic acid by Alamine 336 in MIBK, there does not appear to be an effect of temperature on water coextraction.

REFERENCES

Lipovskii, A. A. and Kuzina, M. G., "Infrared Spectra and Structure of Compounds Formed in the Extraction of Oxalic Acid by Solutions of Trioctylamine", *Sov. Radiochem.* (Engl. Transl.), **10**, 169-174 (1968); *Radiokhimiya*, **10**, 175-181 (1968).

Ricker, N. L., "Recovery of Carboxylic Acids and Related Organic Chemicals from Wastewaters by Solvent Extraction", Ph.D. Dissertation, Chemical Engineering, University of California, Berkeley (1978).

Sato, T., Watanabe, H., and Nakamura, H., "Extraction of lactic, tartaric, succinic, and citric acids by trioctylamine", *Bunseki Kagaku*, **34**, 559-563 (1985).

Spala, E. E., "A Thermodynamic Model of Solvating Solutions with Physical Interactions", M.S. Thesis, Chemical Engineering, University of Washington (1980).

Vanura, P. and Kuca, L., "Extraction of citric acid by the toluene solutions of trilaurylamine", *Collect. Czech. Chem. Commun.*, **41**, 2857-2877 (1976).

CHAPTER 8. PROCESS IMPLICATIONS

Previous chapters have reported experimental equilibrium and spectroscopic data for the extraction of carboxylic acids by tertiary amine extractants. From examination and interpretation of the effect of temperature, acid type, and diluent on extraction, a greater understanding was reached of the chemical interactions that are responsible for chemical complexation. How can the knowledge gained from these discussions aid in the development and improvement of large-scale carboxylic acid recovery processes? This chapter discusses how the chemistry of extraction relates to some of the engineering design considerations for acid recovery by chemical complexation.

8.1 General Considerations

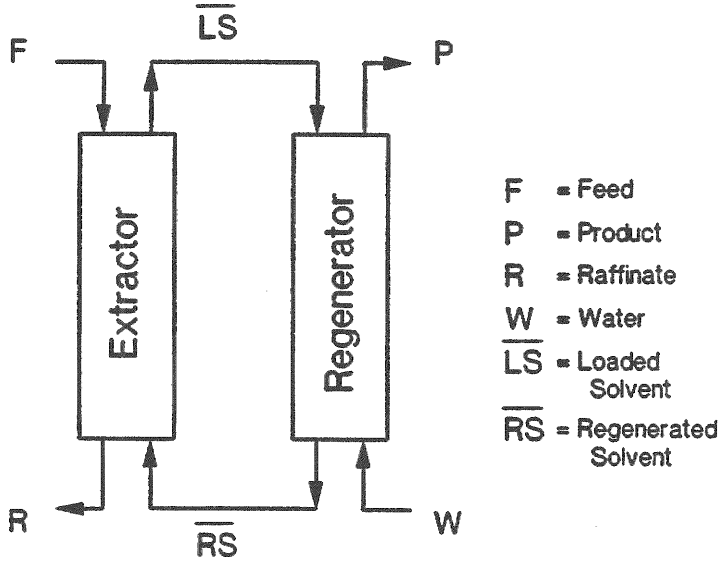
8.1.1 General Design

There are two stages to a practical extractive recovery process (Fig. 8-1*a*). The first is the extraction of the acid into the solvent to produce the acid-loaded extract and the relatively acid-free aqueous raffinate. The second stage transfers the acid from the solvent into a product phase and regenerates the solvent, which is recycled back to the extractor. Regeneration of the solvent is often overlooked in the study of extraction processes, but it is crucial in development of a practical operation. In this work, we will focus mainly on back-extractive regeneration methods, in which the regenerator is an extractor working in reverse to recover the acid into an aqueous product phase.

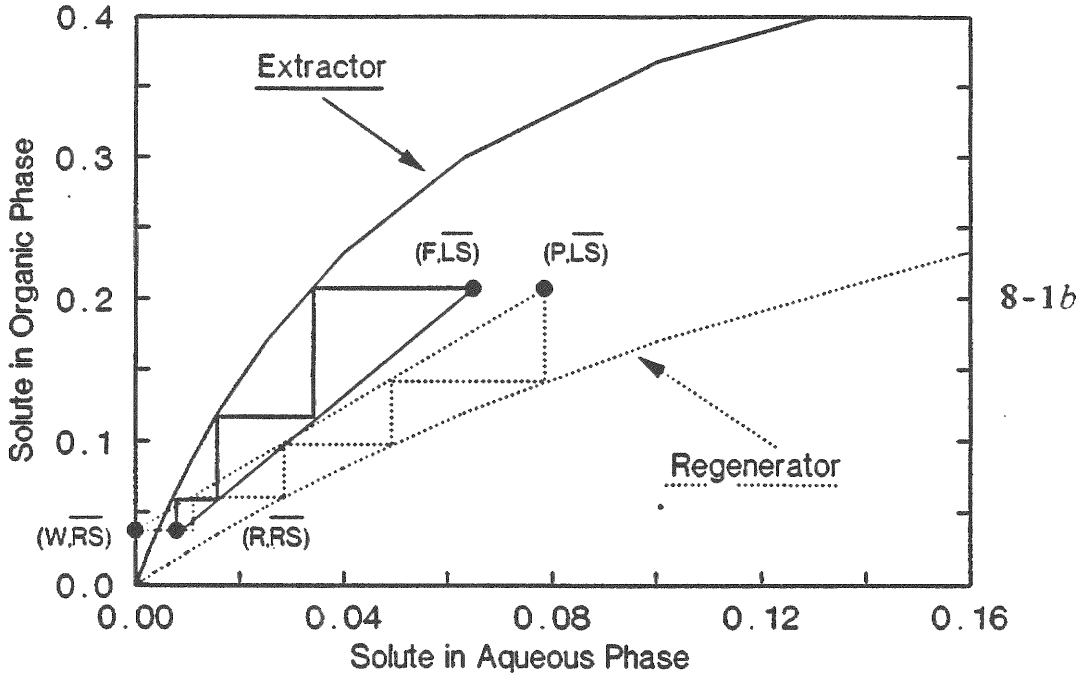
A McCabe-Thiele operating diagram for dilute solutions (Fig. 8-1*b*) outlines the general form of an extraction/back-extraction acid recovery process (King, 1980). The equilibrium curve of a McCabe-Thiele diagram is closely related to the loading curves of previous chapters. On the McCabe-Thiele diagram, the vertical axis is the concentration of acid in the organic phase. This is equal to the product of the loading and the total amine concentration (plus any acid extracted by the diluent alone). The horizontal axis on the McCabe-Thiele diagram is the total concentration of acid in the aqueous phase, rather than the logarithm of the undissociated acid concentration used on a loading curve. The operating curve is a straight line for dilute solutions, with a slope equal to the W/S (water/solvent) flow ratio.

During the extraction stage, the equilibrium curve must lie above the operating line. A low solvent flow rate corresponds to a relatively large slope of the operating line. Thus high equilibrium distribution of acid into the solvent phase is necessary in order to achieve good product recovery at reasonable solvent flow rates. During regeneration, the situation is reversed -- the equilibrium curve must lie below the operating line. The slope of the regenerator operating curve must be relatively small, corresponding to low water flow rates, to avoid dilution of the product. Thus the equilibrium distribution of the acid into the organic phase must be low so that most of the solute can be recovered from the solvent into an aqueous product of reasonable product concentration. Therefore, for a back-extractive regeneration to be a practical process, it is important to effect a downward shift in the equilibrium line between the extraction and regeneration stages. Such processes are known as "swing" processes, some of which are discussed below.

Limiting conditions for operation occur where the operating and equilibrium line meet to form a "pinch point". Usually, limiting conditions occur at the ends of the



8-1*a*



8-1*b*

Fig. 8-1. General Extraction-Regeneration Process.
(*a*) Process flow diagram and (b) McCabe-Thiele-type staged process diagram. The equilibrium curve relates the composition of one outlet stream to the composition of the other outlet stream. The operating line relates the compositions of streams passing each other between stages. Slope of operating line = W/S.

column, as in the example shown in Fig. 8-1. However, an internal or tangent pinch may occur for non-ideal systems and will be illustrated in some of the examples below.

Note that a mass balance dictates that the amount of solute in the solvent phase leaving the extractor must equal the amount of solute in the loaded extract entering the regenerator, and that the amount of solute in the solvent entering the extractor must equal the amount of solute in the regenerated solvent leaving the regenerator. If the solvent flow rate is constant, the organic-phase concentrations on the McCabe-Thiele diagram must be equal at the ends of the columns, as shown in Fig. 8-1.

8.1.2 Factors Affecting Optimal Process Design

In designing a process, one must characterize the desired concentration of solute in the feed and effluent streams to determine the optimal flow configuration and solvent composition. Extraction by chemical complexation is most effective for dilute feed streams (< 10% (w/w) solute), because of the limited capacity of the extractant. However, it will be shown that some extractive recovery configurations will work best for very dilute solutions (< 1% w/w), while others are suitable for treatment of more concentrated feed streams.

The desired effluent concentration depends on the specific objectives of the separation. The relative importance of selectivity, product recovery, acid concentration in the raffinate, and product concentration determines the permissible solute concentrations in the effluent streams. For example, in a wastewater treatment process, the purpose is to reduce the concentration of the solute, so it is important for concentration of the acid in the aqueous raffinate to be low. Also, in separation

of high-value fermentation products, nearly complete recovery is essential to avoid loss of the product to a waste stream. In recovery from very dilute solutions, concentration of the product may be important for practical, economic operation. Still other operations may merely require the ability to separate the acid selectively from the other components.

Factors that influence the selection of the appropriate solvent and regeneration method include loss of extractant or diluent by solubility or entrainment in the aqueous phase or by decomposition, energy consumption, and consumption of chemicals. Other workers (Baniel et al., 1981; Ricker, 1978; Ritcey and Ashbrook, 1980) have analyzed losses of solvent, so that issue will not be discussed in detail here. A brief summary of some of their findings is given below. Regeneration is the major contributor to chemical and energy consumption. Section 8.4 will discuss regeneration alternatives, and their relationship to the energy and chemical consumption of the process.

Extractant losses by solubility are minimal for amines with sufficiently long aliphatic chains. Baniel et al. (1981) concluded that solubility of an amine with greater than a total of 20 carbons was sufficiently low for consideration in a practical application. The manufacturer's reported solubility of Alamine 336 is less than 5 ppm (Henkel, 1984). Ricker (1978) performed GC analysis of aqueous mixtures of acetic acid and water which had been contacted with Alamine 336 and found the solubility of the amine was less than 10 ppm. Ritcey and Ashbrook (1980) reviewed studies of the solubility of amine extractants in a recycle process. For bench-scale continuous operations, in the first few cycles of solvent regeneration, low-molecular-weight impurities dissolve in the aqueous phase, but after more cycles, amine loss settles to a low, steady level of less than 10 ppm. Commercial operations reported that amine

losses were greater than 10 ppm, but still less than 40 ppm.

Appendix D contains data on concentrations of organic nitrogen found in the aqueous raffinates of extraction experiments. Nitrogen levels were present which would indicate higher amine solubilities than those reported from other works; however, this loss is almost certainly attributable to solubilization of a low molecular weight amine and not to the extractant itself. In any event, the loss of amine from solubility in the aqueous phase is certainly less than losses from entrainment or other factors. Loss of diluent by solubility in the aqueous phase can be approximated by the solubility of the diluent in water. Appendix E gives available literature values of aqueous solubilities of the diluents used in this work.

Ricker (1978) examined losses of extractant and diluent through decomposition and entrainment. The reader is referred to Ricker's dissertation for details. In summary, Ricker examined the heat stability of amine extractants to predict loss from thermal decomposition. It was concluded that secondary amines and acetic acid formed an amide bond, which is undesirable for both recycle of the extractant and recovery of the product. Tertiary amines do not have this problem. Heating of a mixture of Alamine 336, acetic acid, and diisobutyl ketone under nitrogen produced no measurable degradation of the amine at temperatures up to 184°, as measured by gas chromatographic analysis. However, alcohol diluents potentially form covalent bonds with carboxylic acids, which would result in undesirable loss of product and solvent. Ricker concluded that regeneration methods involving heating of the solvent should not pose a problem relating to the stability of tertiary amines. Entrainment was concluded to be the major factor contributing to solvent loss. Ricker also describes methods to reduce entrained solvent droplets in extraction processes.

Additional factors to be considered in selection of a solvent system include solvent toxicity, phase-separation characteristics, density, viscosity, cost, effect on selectivity, and effect on third-phase formation. Toxicity of the solvent can be a concern, both through contamination of eventual waste streams and through growth inhibition in extractive fermentation systems. In order to determine the feasibility of *in situ* solvent extraction, Roffler (1986) studied the toxicity to lactate-producing organisms of aqueous phases which had been contacted with amine solutions. He found that, despite the low aqueous solubility of the amine, growth of the organisms was severely inhibited by the presence of the amine solution. Because there was no mention of prewashing of the amine prior to these experiments, it is not clear if the toxicity is from the extractant itself or the low-molecular-weight impurities in the extractant. Methods of circumventing problems associated with toxicity were briefly discussed in Chapter 1, Section 1.5. Wennersten (1983) concluded that non-polar organic solvents gave the most desirable physical properties, such as phase separation, viscosity, and density, to the solvent mixture, as well as minimizing extraction of the non-acidic components of the feed. Third-phase formation is generally considered to be undesirable. Alcohol modifiers are often used to suppress third-phase formation in inert diluents. However, Leonard et al. (1983) have successfully operated a continuous extractor with a three-phase system by keeping the two organic phases together. This may promote enhanced extraction over two-phase extractions in inert diluents because of the high concentration of solute found in the third phase.

8.2 Use of Batch Extraction Data in Process Design

8.2.1 Utility of the Mass-Action Law Approach

Interpretation of equilibrium data for extraction by chemical complexation is more complicated than it is for conventional solvent extraction. In conventional extraction, the distribution ratio usually does not vary much with acid concentration. Therefore, only a few data points are required to predict the equilibrium relationship. Extraction by chemical complexation usually gives a large dependence of the distribution ratio on the acid concentration, resulting in highly non-linear equilibrium curves that are generally not predictable with a few data points. In extraction by complexation, the concentration of amine is an additional, and very important, variable. Recall Fig. 2-1, which showed the large variation in the distribution ratio with changing amine concentration.

These observations illustrate the following point: Information based on extrapolation from a few experimental data points for extraction by complexation may be inappropriate for the range of conditions expected in a continuous process. The effect of acid and amine concentration will vary greatly, influenced by factors such as high overloading, (1,2) complex formation, or formation of aggregates. For example, compare the extraction of acetic (Fig. 2-3*b*) and succinic (Fig. 2-5*c*) acids by 0.29 mol/L Alamine 336 in nitrobenzene. For acid concentrations less than 0.1 mol/L, where the loading is less than unity, the distribution ratios for acetic acid are much lower than for succinic acid. But for larger acid concentrations, acetic acid is extracted more readily than succinic acid, because acetic acid forms (2,1) complexes more easily. As a second example, compare the extraction of succinic acid by Alamine 336 in octanol diluent (Fig. 2-5*e*) with the results for MIBK diluent (Fig. 2-5*d*). At

low acid concentrations, distribution ratios were higher in octanol, apparently because of high (1,2) complexation. But, at high acid concentrations MIBK allows higher distribution ratios, because of its ability to promote (2,1) loading. Finally, compare the effect of amine concentration on the extraction of succinic (Fig. 2-13*a*) and acetic (Fig. 2-3*a*) acids by Alamine 336 in 8 and 15% (v/v of total solvent volume) chloroform in heptane. For acetic acid, doubling the amine concentration from 0.29 to 0.58 mol/L doubles the concentration of acid in the organic phase at a given concentration of acid in the aqueous phase. For succinic acid, doubling the amine concentration more than doubles the concentration of acid extracted at a given aqueous acid concentration, because multiple amines are involved in the complex.

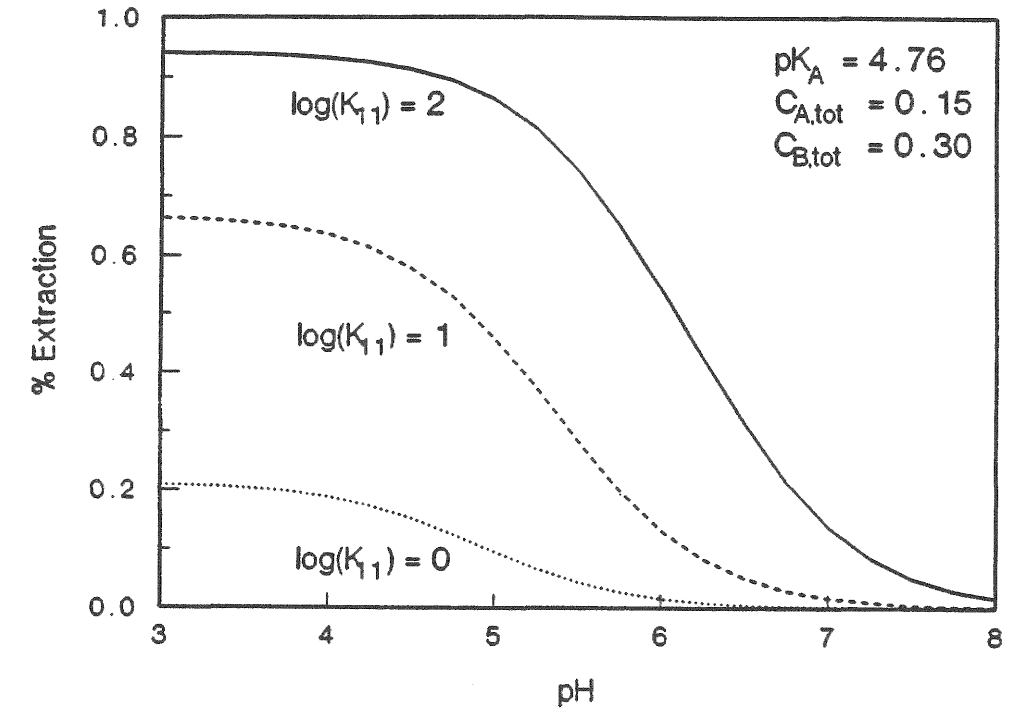
Information gained from the study of chemical interactions suggests some strategies for making efficient use of experimental data. For systems which obey relatively simple stoichiometries, the mass-action-law approach provides a simple way to model the equilibrium curves quantitatively for detailed computer simulations of staged processes. Interpolation of equilibrium curves over a range of amine or acid concentrations is easily implemented, and rational extrapolation of limited data is possible. For example, if it is known that the system obeys (1,1) stoichiometry, the equilibrium curves over a range of amine and acid concentrations can theoretically be predicted by data taken at just one amine concentration and acid. (Of course, one would not know that a system obeyed (1,1) stoichiometry if there was only one data point). Knowledge of chemical interactions can also indicate where extrapolation would be inappropriate, such as extrapolating distribution data at one amine concentration to another if it is suspected that each acid molecule interacts with more than one amine.

8.2.2 Appropriate Diluent Selection for the Acid

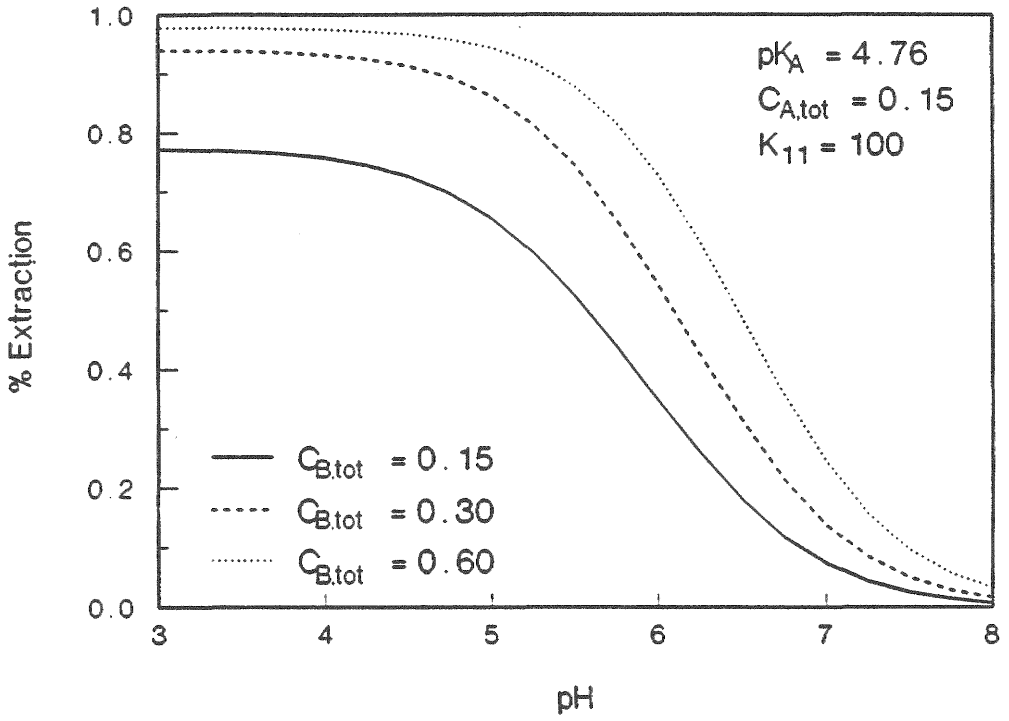
Previous chapters have shown that the effect of diluent on the extracting power of the solvent is profound and must be taken into consideration in diluent selection and process design. Furthermore, the nature of the diluent presents an important degree of freedom in a process. It is desirable to use a diluent which promotes extraction, but not to the extent that regeneration of the solute is restricted. Different acids will require different diluents for optimal extraction/regeneration. For example, previous investigators found that for citric acid extraction inert diluents or inert diluents with an alcohol modifier work well (Baniel et al, 1981), and some workers have concluded that these diluents are the optimal choice (Wennersten, 1983) for citric acid extraction. Citric acid is reasonably acidic (pK_A = 3.128) and thus readily extracted. On the other hand, an inert diluent would be ineffective for the extraction of weaker acids, such as succinic or lactic acid. A more active diluent would be required to promote greater acid extraction.

8.2.3 Effect of pH

A rise in pH drives the acid toward the dissociated form, which reduces the driving force for complexation. This produces a sharp drop in the percent of acid extracted around some pH value. The value at which this drop occurs is determined by the amine concentration and the equilibrium complexation constants; large equilibrium constants or high amine concentrations will allow better extraction at higher pH values. Figs. 8-2 *a* and *b* illustrate these effects, showing curves calculated from the acid dissociation (Eq. C-1) and (1,1) complexation (Eq. 2-8) equations. Extraction at pH > pK_A means that regeneration at pH < pK_A will be difficult. Since most fermentations work best at pH ≥ pK_A (fermentive production of citric acid is an



8-2*a*



8-2*b*

Fig. 8-2. Calculation of the Effect of pH on Extraction.
(*a*) Effect of the magnitude of the equilibrium constant
(*b*) Effect of the amine concentration

exception, see Chapter 1), production of an acidic product at pH < pK_A can be difficult.

Puttemans et al. (1983) studied the effect of pH on the extraction of benzoic acid and hydroxy derivatives by trioctylamine in various diluents. No theoretical predictions based on acid dissociation and mass-action law reaction were made, but qualitatively the results followed expected behavior for high pH values. At low values of the pH, the curves deviated from expected behavior, presumably because competition from the buffering agent reduced extraction of the solute.

Reschke and Schügerl (1984) performed detailed investigations of the effect of pH and amine concentration on the extraction of penicillin G, penicillin V, phenylacetic acid and phenoxyacetic acid by Amberlite LA-2 in n-butyl acetate and other solvents. The experimental results corresponded closely with the authors' predictions based on acid dissociation and the law of mass action. The authors found very little interference in the extraction of the penicillin from competition by citrate and phosphate ions used as buffering agents.

8.2.4 Effect of Other Extractor Feed Components

In an actual operation, the desired solute is often part of a complex aqueous mixture. For example, a fermentation broth would be expected to contain sugars, cell debris, buffering agents, nutrients, and many other compounds. The other components may affect distribution of the acid by changing the ionic strength of the medium, acting as surface active agents, or competing with the desired solute for the extractant. Amines are advantageous in that they are selective for acids. Baniel, et al, (1981) did not report interference from non-acidic components of actual

fermentation broth feeds to be a problem in amine extraction experiments. Wennersten (1983) reported that non-polar diluents minimize interference from non-acidic components.

Competition from other acidic metabolites produced in the medium complicate the separation. For example, small quantities of oxalic acid are produced with citric acid and must be removed during regeneration, or else they will accumulate in the solvent and limit the product citric acid extraction (Baniel et al., 1981). In the processing of penicillin fermentation broths, it is desirable to remove the residual precursor acids because of their high cost and potential toxicity (Reschke and Schügerl, 1984).

On the basis of present knowledge of chemical interactions it can be predicted that a variety of interactions will influence extraction with two or more acids present. For example, two acids will compete for the amine site. In the absence of other complicating factors, the competing (1,1) reactions should be predictable from the (1,1) equilibrium constants obtained from single-solute batch extraction studies and an appropriate mass balance. Jagirdar and Sharma (1980) have performed investigations of the competitive extraction of several pairs of acids, including acetic-monochloroacetic, monochloroacetic-dichloroacetic, dichloroacetic-trichloroacetic, formic-oxalic, and glycolic-oxalic acids, by tri-n-octylamine in o-xylene, 2-ethyl-hexanol, and benzene. Separation factors between 2 and 38 were observed, with the more acidic acid extracted more readily.

Complexation with multiple acids per amine will be complicated by the choice of two acids which can add onto the (1,1) complex. Simultaneous extraction of two different acids was studied by Shmidt and Rybakov (1978, 1977), who presented convincing evidence of extraction by "addition", the formation of mixed complexes

with one or more carboxylic acids attached to a mineral acid-amine salt. The authors studied the extraction of monochloroacetic, acetic, formic, and oxalic acids added onto acid-amine salts of hydrochloric or hydrobromic acid and trioctylamine. However, a search of the literature did not yield any reports of investigations of the formation of analogous mixed carboxylic acid-amine complexes. The study of competitive extraction behavior has application to process evaluation and offers fundamental insight into chemical complexation chemistry, but is left for future investigators.

8.2.5 Water Coextraction

Chapter 7 presented data for water extraction into the solvent phase. Appendix E gives available literature data for the solubility of water in the diluents studied in this work. In general, selectivity of the acid over water in extraction by amine extractants is very high, and the water carried into the solvent would be minimal compared to the water in an aqueous back-extraction. In a few specific applications, such as liquid membrane extractions with an amine carrier, water carried into the interior aqueous phase of the emulsion membrane could create and affect transport and other properties (Thien et al., 1986). However, in general, water is not expected to be a major consideration in the design of these extraction systems.

8.3 Effect of Stoichiometry on Extraction-Regeneration

In Fig. 8-3, McCabe-Thiele diagrams for hypothetical systems illustrate how complexation stoichiometry can affect an extraction or regeneration process. For simplicity, the same equilibrium curve is shown for both forward and backward extraction. In the (1,1) stoichiometry case (Fig. 8-3*a*), the equilibrium extraction

curve has a steep initial rise at low acid concentration, where there is a high driving force of free amine, and asymptotically approaches the extractant concentration, where the amine has been exhausted. The extraction equilibrium curve is well above the extraction operating line, and is especially advantageous for very dilute acid solutions, where the slope of the equilibrium curve is steepest. The potential pinch points lie at the inlet and outlet of the extractor. However, for back-extractive regeneration, the same equilibrium curve produces an internal pinch in the system. A high degree of regeneration is difficult to achieve, requiring high water flow rates for good recovery of the acid from the extract. The resultant product acid would be dilute.

The equilibrium curve for a system with (2,1) stoichiometry (Fig. 8-3*b*) has a concave upward region at low solute concentrations. This potentially creates an internal pinch in the extraction, which would limit solute recovery and/or force the use of high solvent flow rates to attain good recovery of the solute. However, the regeneration requires a lower aqueous flow rate than the (1,1) case, especially in the low concentration region. An advantage of a system which shows (2,1) stoichiometry is that more acid is recovered per amine used. Therefore a lower extractant concentration can be used, which could be important if losses from amine solubility or entrainment are high.

The equilibrium curve for a situation involving aggregation of complexes is shown in Fig. 8-3*c*. The extraction is extremely pinched at low solute concentrations. A high degree of recovery of the solute would be virtually impossible. On the other hand, regeneration of the solvent requires only a low aqueous flow rate and the operating line lies well above the equilibrium curve.

(*a*) (1,1) stoichiometry
$\log(\beta_{11}) = 2.0$
$C_{B,tot} = 0.3$ mol/L
(e.g. in chloroform)

(*b*) (2,1) stoichiometry
$\log(\beta_{21}) = 2.0$
$C_{B,tot} = 0.3$ mol/L
(e.g. in ketones)

(*c*) Aggregation
$\log(\beta_{10,10}) = 10.0$
$C_{B,tot} = 1.0$ mol/L
(e.g. in heptane)

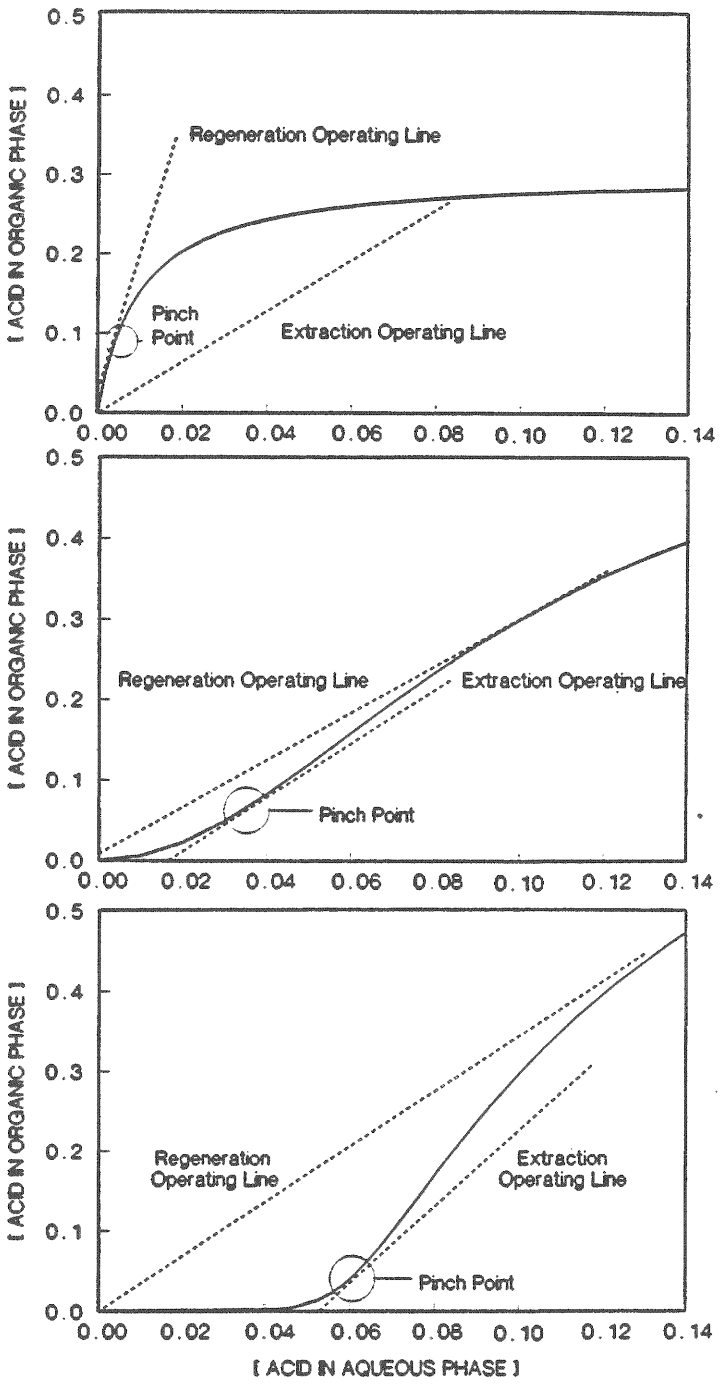


Fig. 8-3. Effect of Stoichiometry on Extraction Regeneration.

Previous chapters have shown than the nature of the diluent affects stoichiometry greatly. Strong (1,1) complexation was observed for the extraction of dicarboxylic acids by amines in chloroform diluent (e.g., the extraction of succinic acid by Alamine 336 in chloroform or methylene chloride, Figs. 2-5*a* and *b*). Significant (2,1) and higher stoichiometries were found for monocarboxylic acid extraction in ketones, aromatic solvents, and some other diluents (e.g., the extraction of acetic acid by Alamine 336 in chloroform/heptane and the extraction of lactic acid by Alamine 336 in MIBK, Figs. 2-3*a* and 2-4*b*). In performing a detailed process analysis for the extraction of acetic acid by Alamine 336 in DIBK, Ricker et al. (1980) reported that the equilibrium curve was concave upward (consistent with the extensive (2,1) complex formation), which created a potential pinch point in the operation. Aggregation is more pronounced in inert diluents for dicarboxylic acids (e.g., the extraction of succinic acid by Alamine 336 in heptane, Fig. 2-9). Siebenhofer and Marr (1983) noted that the extraction of acids in pure Hostarex A, a tertiary amine, gave a concave upward shape to the curve at low acid concentrations. The authors suggested the use of an isodecanol modifier to remove the concave upward region, and stressed the importance of considering diluent and modifier in equilibrium calculations.

It should be noted that at low loadings of the amine, the equilibrium curves are more nearly linear. In these cases, internal pinch points would be less of a factor in process design. It is also possible to mix diluents so that more nearly linear equilibrium curves are obtained. For example, chloroform, which gives strongly concave downward equilibrium curves, and heptane, which gives concave upward equilibrium curves mix to give a more linear curve (Fig. 8-8).

8.4 Regeneration Alternatives

Several alternatives for regeneration of the solute have been discussed by other workers. Ricker (1978) discussed back extraction of the extract with an aqueous base, such as $CaCO_3$ or NaOH. Experimentally, back extraction by a strong base allows quantitative recovery of the acid salt (see Appendix A). However, the consumption of chemicals is expensive, and the process generates a salt rather than product acid. The salt could be acidified to produce an acid product, but this would result in additional chemical consumption and a salty waste stream, which would require disposal. Ricker et al. (1980) concluded that development of a regeneration method which recycles all reagents is important for an economic process.

If the product acid is volatile, distillation directly from the extract is an alternative. Ricker et al. (1980) performed detailed experiments and an economic assessment of an acetic acid recovery process utilizing extraction by Alamine 336 in DIBK and subsequent distillation of the extract. However, most carboxylic acid metabolites of commercial interest are nonvolatile.

There have been a number of methods proposed for recovery of nonvolatile acids. Rückl et al. (1986) proposed a product recovery step in which the extract is contacted with volatile "stripping" acid, which drives the product solute from the extract to the aqueous product phase. In the authors' configuration, an aqueous citric acid feed solution is contacted with an amine-diluent solvent. The citric acid-loaded solvent from the extraction is contacted with an aqueous acetic acid solution in a reextraction column, where the exchange of citric and acetic acid occurs. The raffinate is a mixture of citric and acetic acids. The solvent loaded with acetic acid enters a distillation operation, where the volatile acetic acid is removed for recycle to

the reextraction column. The regenerated solvent is recycled back to the extractor.

Poole (1989) has examined a regeneration technique employing recycle of a volatile base. Aqueous-phase trimethylamine is contacted with the extract to pull the acid into the aqueous phase. The trimethylammonium-carboxylic acid salt is heated to drive off excess water and the volatile amine, leaving the non-volatile acid in the aqueous phase. If the acid has low water solubility, it precipitates from the bottoms upon cooling to room temperature. Starr (1988) has investigated recovery of acids with lower water solubility by direct precipitation from the extract. The solvent phase containing the loaded amine and a volatile diluent is placed under vacuum and heated. Crystallization of the product acid occurs as the diluent is driven off.

In this work, we examine two back-extractive regeneration methods that are based on the shifts in the equilibrium. A rule-of-thumb for conventional extractions with nearly linear equilibrium relationships is that $1.2 < D \times S/W < 2.0$ is optimal for a high degree of solute removal (King, 1980). Thus for the solute to be concentrated in the extract (S/W small), D must be large. Conversely, for regeneration, $1.2 < W/(D \times S) < 2.0$ is optimal. Thus for the solute to be concentrated in the aqueous product (W/S small), D must be small. Therefore, to double the concentration of solute in the extraction/regeneration operation, D must shift by a factor of approximately 4 to 6. Although extraction by complexation results in highly variable values of D, these values give order-of-magnitude estimates of the amount of decrease in distribution ratio necessary to achieve product concentration.

8.4.1 Temperature-Swing Regeneration

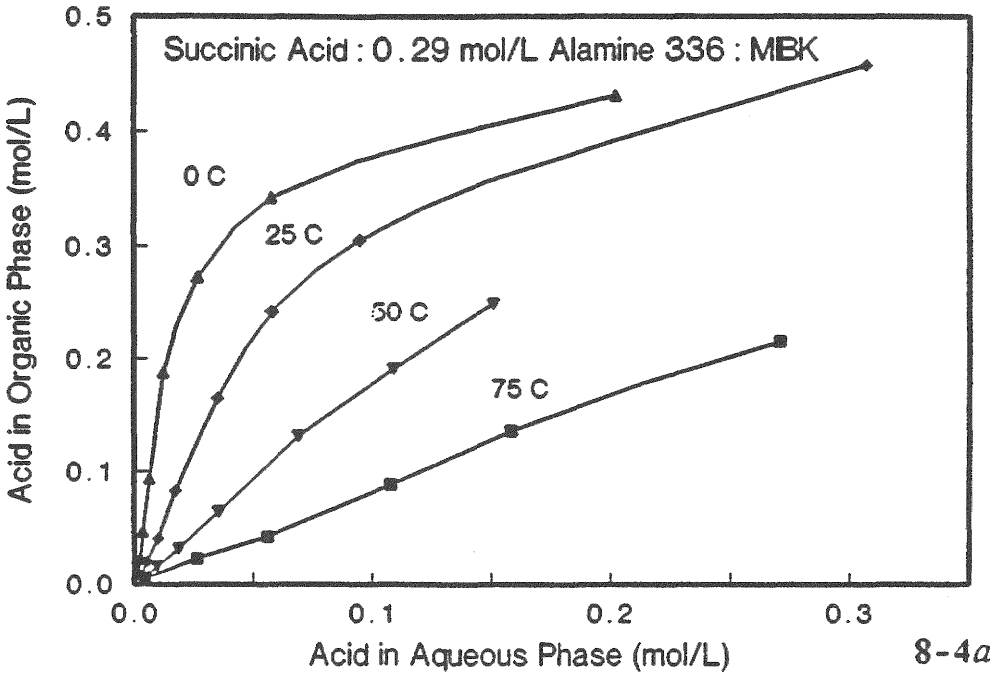
Baniel et al. (1981) have developed a process for citric acid recovery based on

the shift of equilibrium with temperature. The acid is extracted at a low temperature, where equilibrium favors the solvent phase, and regenerated at a higher temperature, where equilibrium favors transfer of the acid to the aqueous phase. For citric acid, relatively inert diluents, such as petroleum fractions with alcohol modifiers, and aromatic solvents, were found to give equilibrium distribution ratios that were an appropriate magnitude for extraction and regeneration.

Fig. 8-4 shows the results for effect of temperature on the extraction of succinic acid by Alamine 336 in (*a*) MIBK and (*b*) chloroform, plotted in a McCabe-Thiele form. The equilibrium curves are significantly lowered by the temperature increase.

MIBK is a suitable diluent for use in temperature-swing regeneration of succinic acid. Distribution ratios for extraction are lower than they are for chloroform, but are high enough for facile extraction. At the high temperature, the acid readily distributes back into the aqueous phase.

However, chloroform would probably not be as good a choice for a diluent for temperature-swing regeneration of succinic acid. There is a tangent pinch midway along the operating line for regeneration, because of the severe concavity of the equilibrium curve. Although the heat of reaction for the (1,1) complexation is large (-16.6 kcal/mol, see Chapter 6) a temperature increase of 55 C° does not lower the equilibrium line enough for practical back-extraction. For operations at atmospheric pressure, the boiling point of chloroform, 63 °C, restricts the swing in temperature; however, the equipment could run under a higher pressure to effect a larger temperature and hence equilibrium swing.



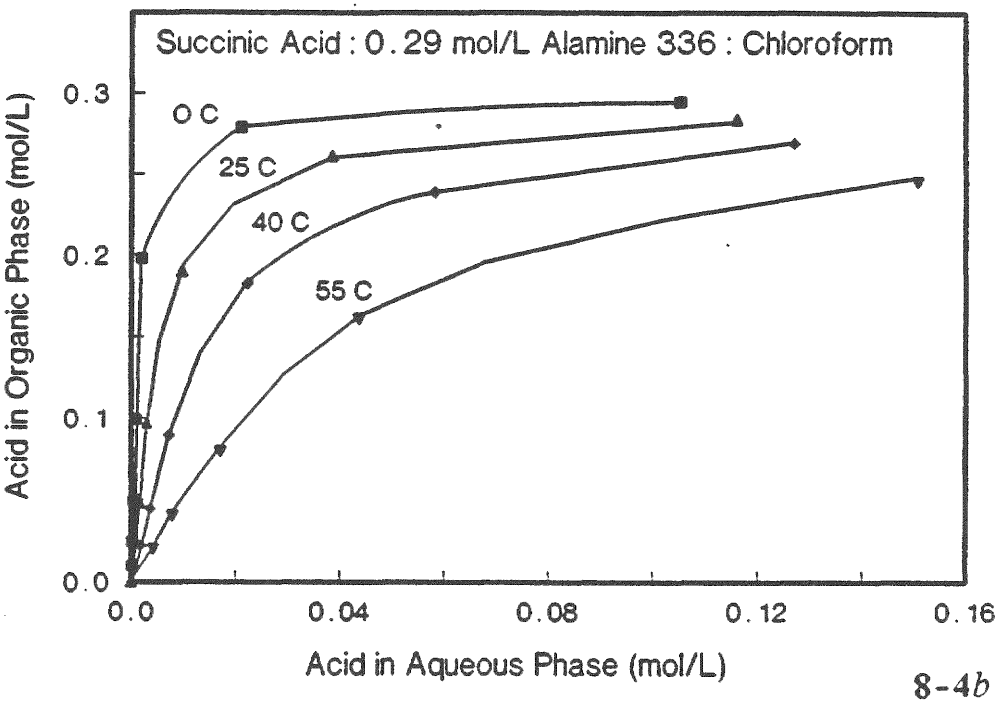


Fig. 8-4. Effect of Temperature on the Extraction of Succinic Acid.
(*a*) MIBK diluent and (*b*) chloroform diluent.

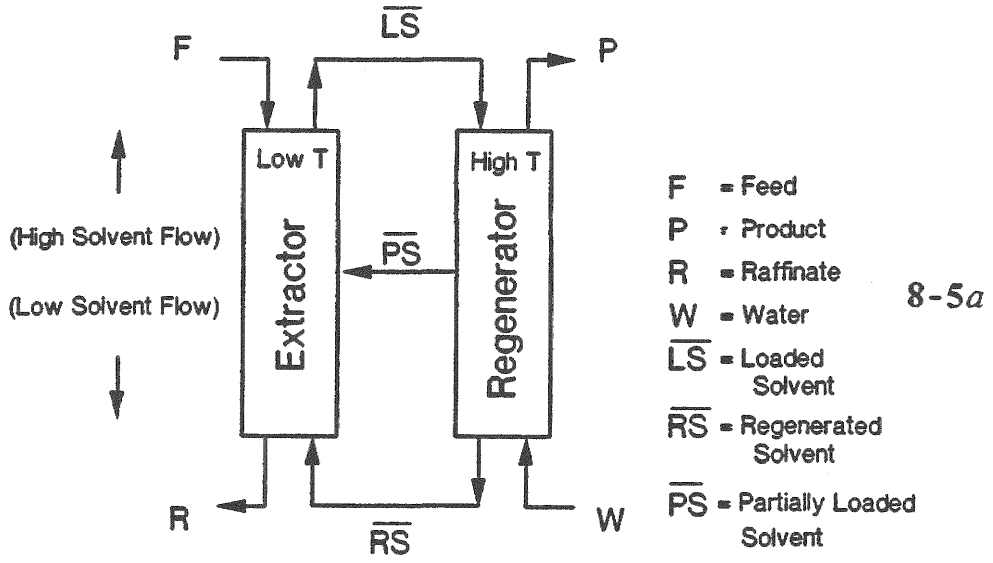
An alternative is to mix chloroform (or some other active diluent) with an inert diluent to lower the magnitudes of the distribution ratios. This is a very flexible way to bring both the extraction and regeneration equilibrium into appropriate distribution ranges. It may also be a way to reduce curvature of the equilibrium relationship. Another possibility is to use a split-flow configuration to move the operating curve around the pinch point (Fig. 8-5). Midway along the regenerator, partially-regenerated solvent is removed and added midway along the extractor to the partially-loaded solvent.

Fig. 8-6 shows equilibrium curves for the extraction of lactic acid by Alamine 336 in (*a*) MIBK and (*b*) chloroform. Recall from Chapter 6 that the heat of reaction of lactic acid is less than that of succinic acid. This translates into a weaker shift in equilibrium, and less effective temperature-swing regeneration.

8.4.2 Diluent-Swing Regeneration

Another approach for shifting the equilibrium relationship between extraction and regeneration involves removal or addition of a component of a mixed diluent prior to the extraction and regeneration stages. The primary extraction is performed with high active diluent content in the solvent, so as to promote large distribution ratios. The regeneration is performed with low active diluent content and relatively high inert diluent content in the solvent, so as to facilitate back-extraction of the solute into an aqueous product.

Equilibrium data for succinic acid extracted by Alamine 336 in a diluent composed of varying ratios of chloroform (active) to heptane (inert) are shown in Fig. 8-7. Removal of the active diluent has a very strong effect on the equilibrium



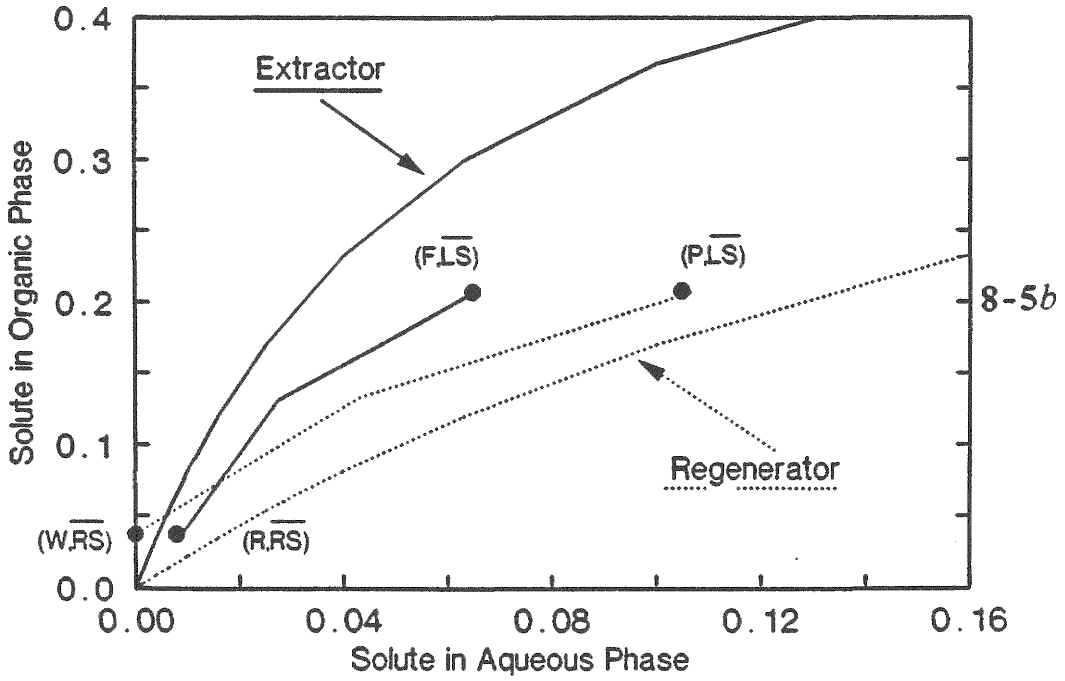
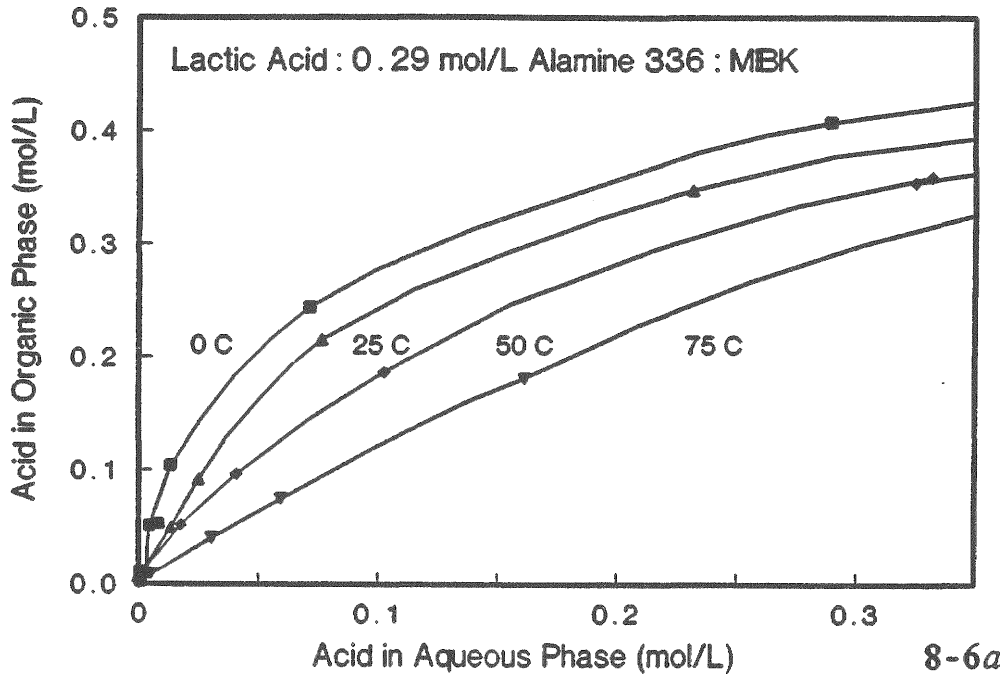
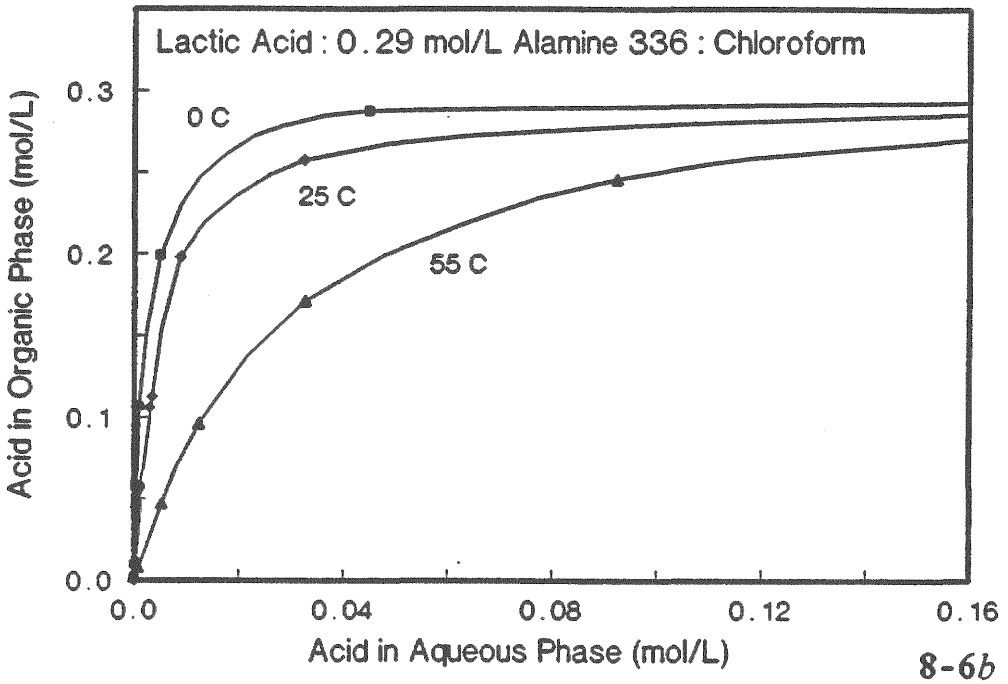


Fig. 8-5. Temperature Swing with Split Flow.
(*a*) Flow diagram and (*b*) McCabe-Thiele operating diagram

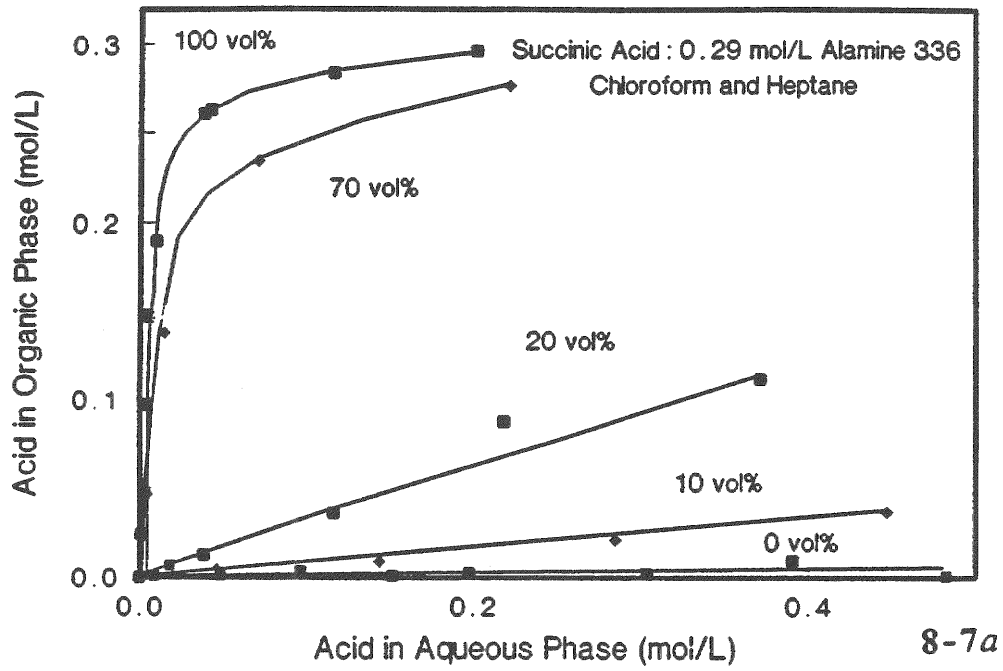


8-6*a*



8-6*b*

Fig. 8-6. Effect of Temperature on the Extraction of Lactic Acid.
(*a*) MIBK diluent and (*b*) chloroform diluent



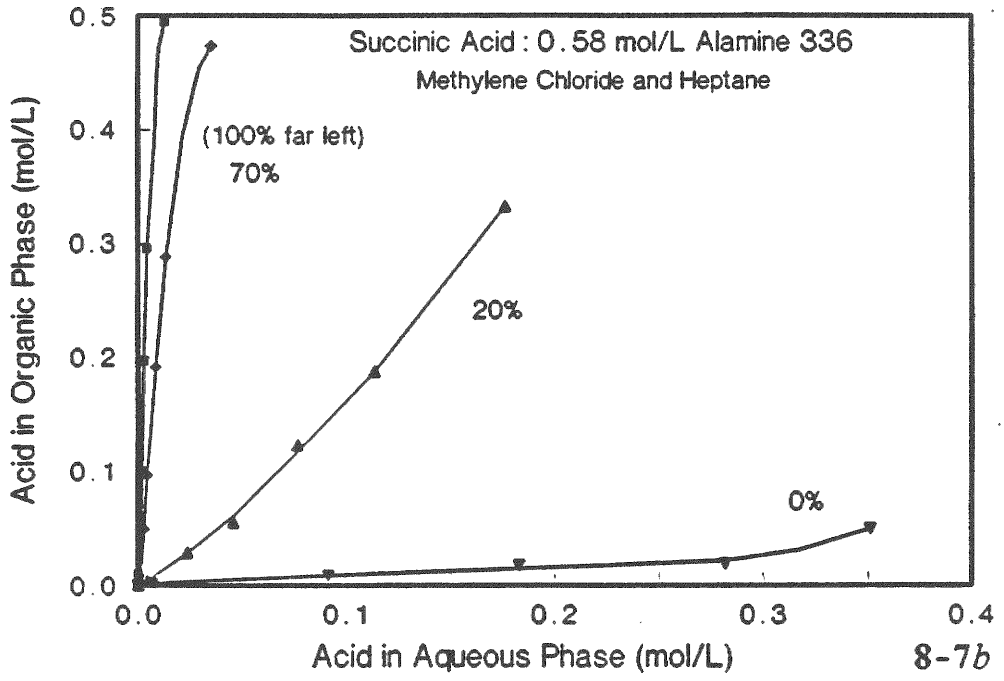


Fig. 8-7. Effect of Active-Inert Diluent Composition on the Extraction of Succinic Acid.

(*a*) 0.29 mol/L Alamine 336. Active = chloroform, inert = heptane.
(*b*) 0.58 mol/L Alamine 336. Active = dichloromethane, inert = heptane.

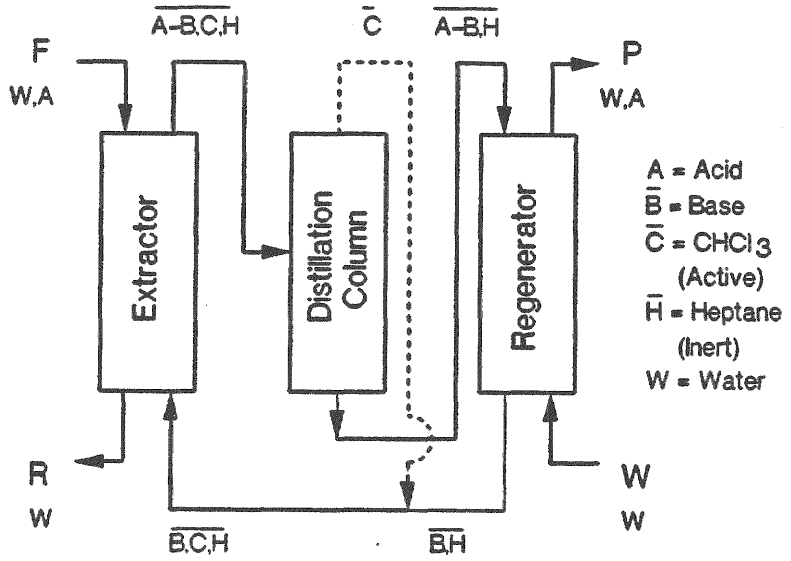
vol% indicates volume percent active diluent of total diluent volume (not total solvent volume).

distribution of the acid. The equilibrium curve at high inert diluent concentration is no longer concave downward, as it was for the extraction at high active diluent concentration. Thus the tangent pinch for the regeneration process is removed, or at least ameliorated.

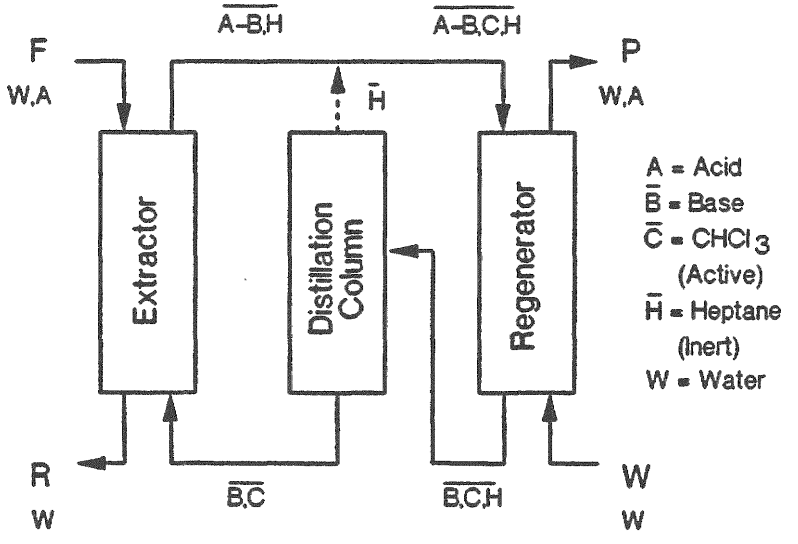
In one example scheme (Fig. 8-8*a*), the active diluent is distilled from the extract leaving the primary extractor, and is recycled to join the regenerated solvent leaving the regenerator. Note that the distillation of the extract has the additional advantage of preconcentration of the product acid before regeneration; thus the concentration of extractant and acid entering the regenerator is higher than that leaving the extractor from the removal of the diluent.

Another possibility (Fig. 8-8*b*) involves use of a relatively non-volatile active diluent (e.g. an alcohol) in the extractor. A volatile inert diluent is added to the loaded extract prior to regeneration, and then removed from the regenerated extract by distillation before reentering the extractor. This has the disadvantages of dilution of the product stream and distillation of larger amounts of solvent to get the same shift in active/inert diluent ratio. However, this configuration has a subtle compensating advantage in equilibrium. Recall that the loading of dicarboxylic acids in inert diluents decreases with decreasing amine concentration (Figs. 2-13 *a* and *b*). Therefore, halving the amine concentration more than halves the equilibrium amount acid extracted at a given aqueous acid concentration. A greater shift in equilibrium is achieved for the same shift in active/inert diluent ratio.

The schemes could be combined so that the active diluent is distilled from the extract leaving the primary extractor, and the inert diluent is distilled from the regenerated solvent leaving the regenerator. This is a more difficult configuration to



8-8*a*



8-8*b*

Fig. 8-8. Diluent Swing Regeneration Process Flow Diagrams.
(*a*) Distillation of active diluent
(*b*) Distillation of inert diluent

implement, because it requires both the active and inert diluent to be volatile, and therefore involves a more difficult separation between the two diluents. However, it potentially provides the largest practical shift in equilibrium.

8.4.3 Evaluation of Temperature- and Diluent-Swing Regeneration

Both temperature and diluent swing provide full recycle of chemicals; the only consumption of chemicals would be from entrainment, solubility, or degradative losses. Energy consumption, product concentration, and capital and operating costs are important factors in determining process viability. Some of the advantages and disadvantages of each method are given in Table 8-1 below.

Fig. 8-9 shows an operating diagram for extraction of succinic acid by Alamine 336 in MIBK at 25 °C, with regeneration by back-extraction at 85 °C. The equilibrium curves were calculated through the use of the apparent enthalpies and entropies of (1,1) and (2,1) complexation given in Chapter 6 (Tables 6-4 and 6-5). Fig. 8-10 shows the operating diagram for the extraction of succinic acid by Alamine 336 in chloroform and heptane, in which half of the solvent volume is removed before entering the regenerator (configuration in Fig. 8-8*a* of the sample schemes). The extractor solvent composition is 55% (v/v) chloroform 30% (v/v) heptane, and 15% (v/v) amine (0.3 mol/L). The equilibrium curve was calculated from the plot of the effect of volume percent chloroform on the (1,1) equilibrium constant given in Chapter 5 (Fig. 5-3). As a first approximation, it was assumed that all of the removed solvent in the distillation was the more volatile component, chloroform, bp 63 °C. Thus the regenerator solvent composition is 10% (v/v) chloroform, 60% (v/v) heptane and 30% (v/v) amine (0.6 mol/L).

Table 8-1. Considerations for Temperature- and Diluent-Swing Regeneration

Temperature Swing	Diluent Swing
Simple implementation, requires only heat exchanger for regeneration column.	More complicated implementation, requires additional unit operation (the distillation column).
More flexible diluent alternatives.	Restricts variety of diluents.
Must balance needs of extraction and regeneration, therefore, diluent cannot promote too much extraction.	Can use diluent which promotes extraction, allowing low solvent flows, and still effect regeneration.
Energy is required to heat the extract and product aqueous phase.	Energy is required to distill the solvent.
If the aqueous product flow rate is low, the energy use is low.	If solvent flow is low, energy use is low.
Probably requires a regeneration temperature of >85 °C. However, pressurization of regenerator could allow larger temperature swing.	Distillation temperature will only need to be a little above boiling point of volatile active diluent and can be even lower, if a reduced pressure system is used. May be useful for thermally labile solutes.
May still have tangent pinch. Split flow configuration would alleviate pinch.	Can eliminate or reduce tangent pinch. Favorable shape of regeneration equilibrium curve.
Shifts in equilibrium are large at relatively high solute concentrations.	Shifts in equilibrium are large for low solute concentrations.

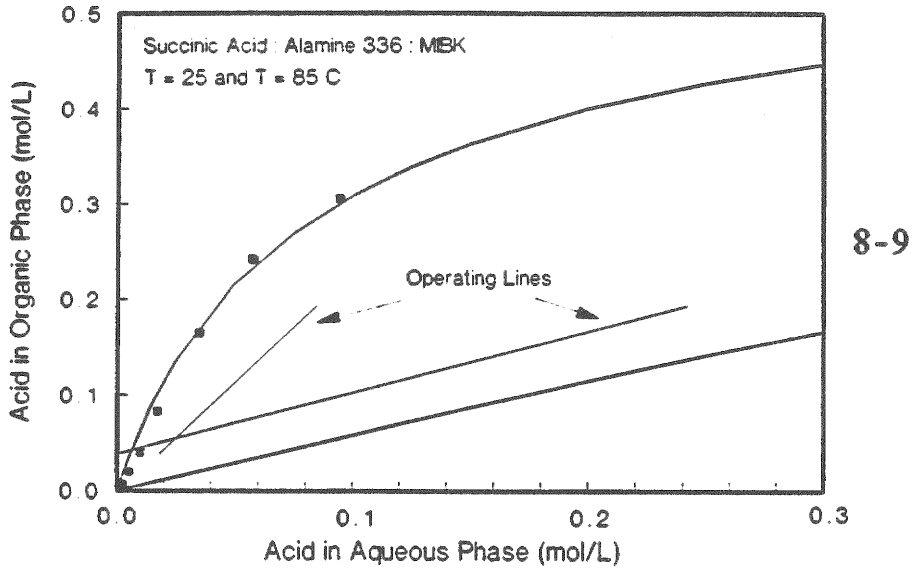


Fig. 8-9. Temperature-Swing for the Extraction of Succinic Acid by Alamine 336 in MIBK at 25 and 85 °C.

Equilibrium curves calculated by β values obtained from ΔH and ΔS values in Chapter 6. For 25 °C, $\log(\beta_{11})$ = 1.40, $\log(\beta_{21})$ = 2.05; for 85°C, $\log(\beta_{11})$ = 0.269, $\log(\beta_{21})$ = 0.373

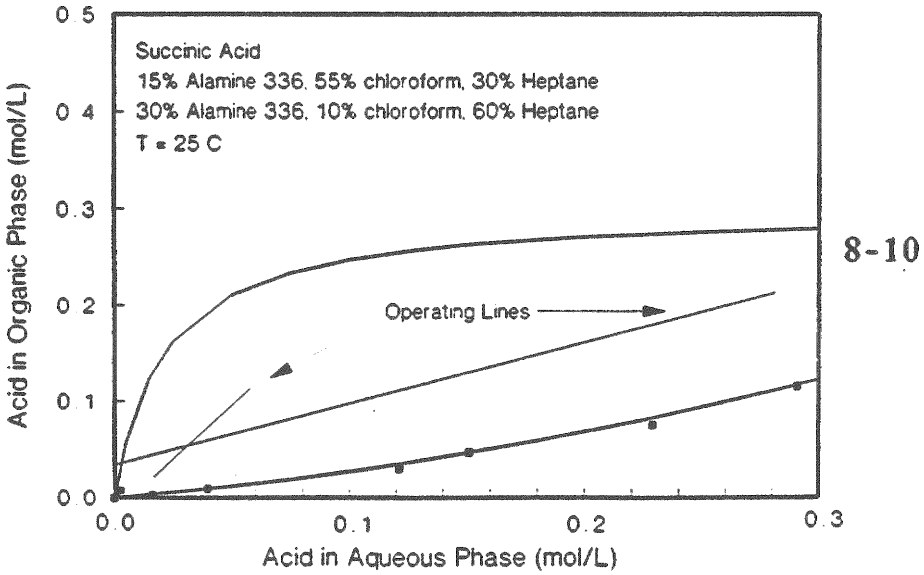


Fig. 8-10. Diluent Swing for the Extraction of Succinic Acid by Alamine 336 in Chloroform and Heptane.

Configuration 8-8*a*. Equilibrium curve for 0.3 mol/L Alamine 336 (15%), 55% chloroform, 30% heptane was interpolated from Fig. 5-3, $\log(\beta_{11})$ = 1.68. Equilibrium curve for 0.6 mol/L Alamine 336 (30%), 10% chloroform, 60% heptane was empirically fit to the data as an equation of the form:

$$C_{A,org} = 0.205\cdot[A] + 0.680\cdot[A]^2$$

Evaluations of the expected performances of these processes were carried out through the use of several simplifying assumptions. For the first approximation, infinite stages for both the extractor and regenerator were assumed. For the diluent-swing process, complete separation and minimum reflux in the distillation column were assumed. The dissociation of acid was not taken into account. A feed flow rate of 1 liter per unit time and 95% recovery of the acid were used for a base case. Calculations yielded the minimum energy consumption and maximum product concentration that are possible with these two methods. An actual process, of course, will require more energy and will not achieve as high a product concentration.

From the values of the concentration of solute in the feed stream and the assumption of 95% recovery, the aqueous raffinate acid concentration was easily determined. The concentration of solute in the extract was calculated as the concentration of acid in the organic phase at equilibrium with the concentration of acid in the aqueous feed. The concentration of solute in the solvent feed to the extractor (i.e. the concentration of solute leaving the regenerator) was calculated as the concentration of acid in the organic phase at equilibrium with the desired aqueous raffinate acid concentration. From this, the water/solvent flow ratio in the extractor, and thus the solvent flow rate, could be calculated by material balance. The product concentration was calculated as the concentration of acid in the aqueous phase at equilibrium with the concentration of acid in the organic-phase extract. This gives the aqueous product flow rate from the regenerator.

For temperature-swing regeneration, it was assumed that there were no internal pinch points, because the regeneration equilibrium curve shown in Fig. 8-9 is close to linear. It should be noted that the operating and equilibrium curves for temperature-swing regeneration lie very close together, so that an actual process must have a

lower water/solvent flow ratio. For diluent-swing regeneration, the regenerator equilibrium curve lies farther from the operating line. For diluent-swing regeneration, because of the distillation of the one-half of the solvent volume, the concentration of solute entering (or leaving) the regenerator in the solvent phase is twice that of the solute leaving (or entering) the extractor.

Fig. 8-11 shows the concentration factor (concentration of solute in the product divided by concentration of solute in the feed) for ideal, infinite-stage processes at different solute feed concentrations. At low feed concentrations, diluent-swing provides better concentration, whereas at high feed concentrations, temperature-swing is superior in this aspect. This is predictable from the slightly concave downward shape of the temperature-swing regeneration equilibrium curve and the concave upward shape of the diluent-swing regeneration equilibrium curve.

The minimum energy consumption for a temperature-swing extraction-regeneration process is given by the sensible heat required to raise the temperature of the aqueous feed which enters the regenerator and the extract from the extractor temperature to the regenerator temperature. This is given by:

$$E = W_R C_{p,W}(T_R - T_E) + S C_{p,S}(T_R - T_E) \qquad \text{(Eq. 8-1)}$$

where,

W_E = water flow rate in extractor = feed flow rate (1.0 L/hr)

W_R = water flow rate in regenerator = product flow rate (L/hr)

S = solvent flow (L/hr), same for both extractor and regenerator

T_E = temperature of extractor (25 °C)

T_R = temperature of regenerator (85 °C)

$C_{p,W}$ = heat capacity of water (1.0 kcal/L)

$C_{p,S}$ = heat capacity of solvent (0.41 kcal/L, Reid et al., 1987)

In practice, a heat exchanger would probably be used between the regenerated solvent and the loaded solvent. However, this is ignored for the purposes of this calculation.

The minimum energy consumption for a diluent-swing extraction-regeneration process with an ideal distillation column is given by the heat required to create the necessary vapor flow in the reboiler plus the sensible heat of raising the solvent temperature. If the heat capacity of the solvent before and after distillation is assumed to be approximately constant, an enthalpy balance shows that energy consumption is given by:

$$E = SC_{p,S}(T_f - T_c) + S_R C_{p,S}(T_r - T_c) + \Delta H_{vap}(S_D + L_{min}) \qquad \text{(Eq. 8-2)}$$

where,

ΔH_{vap} = heat of vaporization of the active diluent

(for chloroform, ΔH_{vap} = 93.2 kcal/L, CRC, 1984)

T_r = temperature of the reboiler ≈ bp of heptane (98.4 °C, CRC, 1984)

T_f = temperature of the feed = T_E (25 °C)

T_c = temperature of the condenser ≈ bp of chloroform (61.7 °C)

L_{min} = minimum reflux (L/time) ≈ $S/(\alpha-1)$ (King, 1980, p. 417)

$\ln\alpha \approx C_{p,S}(1/T_c - 1/T_r)/R$ (King, 1980, p. 680)

R = gas constant

S_R = column bottoms flow rate into regenerator (0.5S L/hr)

S_D = active diluent flow rate leaving top of distillation column (0.5S L/hr)

($S_R + S_D = S$)

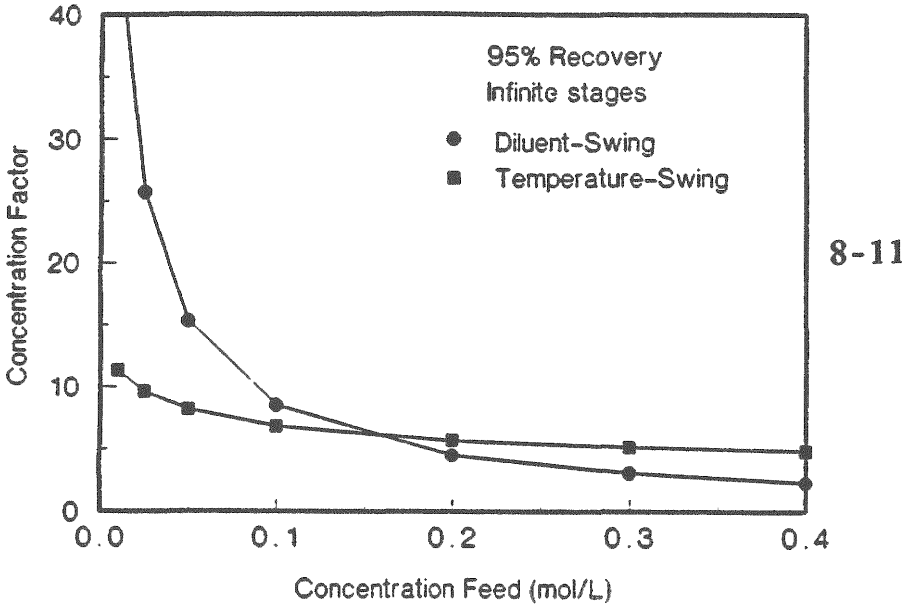


Fig. 8-11. Comparison of the Maximum Possible Concentration Factor for Temperature- and Diluent-Swing Regeneration.

Calculation assumes infinite stages for the systems shown in Fig. 8-9 and 8-10. The concentration factor is the concentration of the aqueous product divided by the feed concentration.

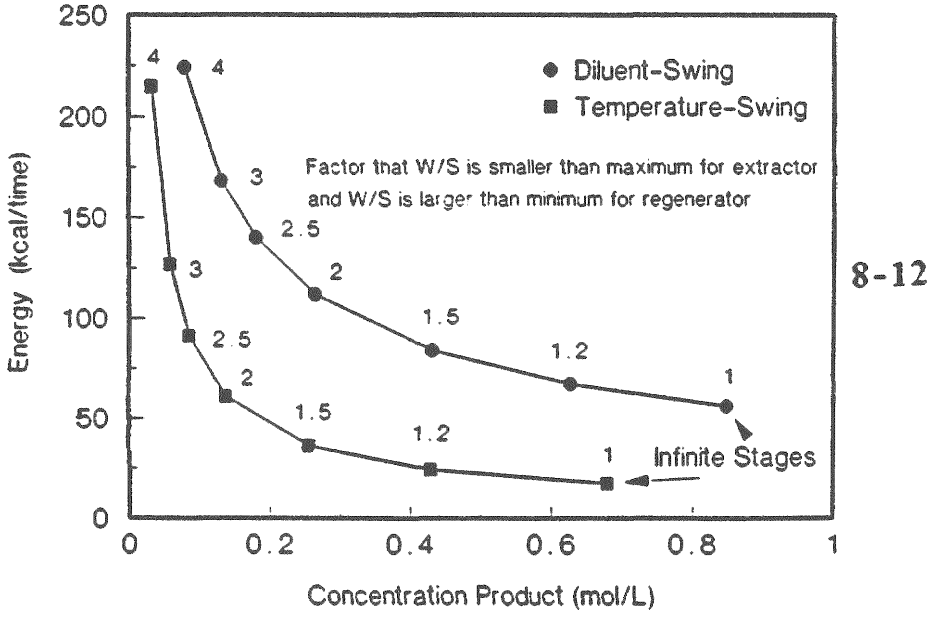


Fig. 8-12. Comparison of the Energy Consumption for Different Solvent/Water Ratios for Temperature- and Diluent-Swing Regeneration.

Calculations were performed using equilibrium curves given in Fig. 8-9 and Fig. 8-10, a base case of $C_{A_1 tot}$ = 0.1 mol/L, 95% recovery, and Eqs. 8-1 and 8-2. Numbers refer to the factor that W/S is smaller than maximum for the extractor and W/S is larger than minimum for the regenerator.

Fig. 8-12 shows the results for a base case of 0.10 mol/L (1.2% w/w) succinic acid in the aqueous feed solution and a recovery of 95%. In this figure, extraction and regeneration units of different efficiencies (i.e. non-infinite stage processes) were compared, although the distillation was still assumed to be ideal. The numbers by the markers indicate the multiple of the minimum flow rate, the flow rate factor, that was used for both extraction and regeneration calculations. That is, the minimum flow rate for an infinite-stage process was calculated, and the flow rate of the appropriate phase (the solvent phase for extraction, aqueous phase for regeneration) was multiplied by the flow rate factor. Thus, points marked with a 1 are for infinite-stage processes. For the particular case studied, temperature-swing is more energy efficient. However, the two cases are not directly comparable, because diluent-swing offers higher concentration of the product.

The energy cost of temperature-swing regeneration decreases with decreasing flow rate of water in the regenerator, and thus high product concentration is associated with low energy cost. Therefore, if there is a large shift in equilibrium, allowing for good product concentration, the temperature-swing will be efficient. For diluent-swing regeneration, the flow rate of water in the regenerator, and hence the product concentration, does not directly relate to the energy cost of the process. The solvent flow rate is the most important factor in determining energy costs because most of the energy consumption is in the heat of vaporization of the diluent. Therefore, a high concentration of solute in the extract will allow for a more efficient process.

Coupling of diluent- and temperature-swing regeneration methods could utilize the advantages of both. The additional energy cost of the distillation over simple temperature swing may be offset by the greater concentration of the product and the

fact that diluent swing offers less pinched, more favorable equilibrium curves. In particular, feedstreams with low concentration of solute would benefit from the addition of diluent-swing to a temperature-swing process, because of the favorable equilibrium shift at low solute concentrations. Studies of the effect of temperature on acid extraction at different diluent compositions are left for future work.

8.5 Summary and Conclusions

The mass-action law description of equilibrium developed in the previous chapters gives insight into factors which will be important in design of full-scale, continuous processes. Complexation stoichiometry and the magnitude of the equilibrium constants strongly affect the shape of the equilibrium curve. For the extraction step, strong (1,1) complexation provides favorable conditions for good product recovery, and (2,1) stoichiometry imparts higher capacity to the extractant. Aggregation creates an internal pinch point in the operating diagram, limiting the amount of solute which can be recovered from the feed. During a back-extractive regeneration step, strong (1,1) complexation may create an internal pinch, which may result in low product concentration. Systems which show aggregation, however, have favorable equilibrium curves for removal of the solute from the extract, especially at low solute concentrations.

Regeneration of the solvent is a crucial part of a practical process for recovery of carboxylic acids by amine extractants. A balance must be made between high distribution ratios, which allow for good recovery of the acid, and low distribution ratios, which allow for recovery of the acid from the solvent. Two "swing" processes, temperature-swing and diluent-swing, have been examined as means of effecting a

change in equilibrium between the extraction and back-extraction stage. In temperature-swing regeneration, the extraction is performed at a low temperature, and regeneration at a high temperature. In diluent-swing regeneration, extraction is carried out with a solvent containing a high concentration of active diluent, and the regeneration is carried out with a solvent containing a low concentration of active diluent. These schemes, used either separately or together, can provide effective and practical means of regenerating the solvent and recovering the product acid.

REFERENCES

Baniel, A. M., Blumberg, R., and Hajdu, K., "Recovery of Acids from Aqueous Solutions", U.S. Patent No. 4,275,234 (Jun. 23, 1981); Chem. Abstr. Vol. 97, 109557 (1982).

CRC Handbook of Chemistry and Physics, 65th ed., Weast, R. C., Ed., CRC Press, Boca Raton, FL (1984).

Henkel Corp., RED LINE technical Bulletin "Alamine 336", Henkel Technical Center, Minneapolis, MN (1984).

Jagirdar, G. C. and Sharma, M. M., "Recovery and Separation of Mixtures of Organic Acids from Dilute Aqueous Solutions", *J. Separ. Proc. Technol.*, 1(2), 40-43 (1980).

King, C. J., *Separation Processes*, 2nd ed., McGraw-Hill Book Company, New York, Chapters 6 and 8, (1980).

Leonard, R. A., Ziegler, A. A., Wigeland, R. A., Bane, R. W., and Steindler, M. J., "Operation with Three Liquid Phases in a Staged Liquid-Liquid Contactor", *Sep. Sci. Technol.*, **18**, 1563-1579 (1983).

Poole, L. J., Ph.D. Dissertation, Department of Chemical Engineering, University of California, Berkeley (1989).

Puttemans, M., Dryon, L., and Massart, D. L., "Extraction of Organic Acids by Ion-Pair Formation with Tri-n-Octylamine", *Anal. Chim. Acta*, **161**, (221-229 (1984).

Reid, R. C., Prausnitz, J. M., and Poling, B. E., *The Properties of Gases & Liquids*, 4th ed., McGraw-Hill Book Company, New York, 136-143, (1987).

Reschke, M. and Schügerl, K., "Reactive Extraction of Penicillin. II: Distribution Coefficients and Degrees of Extraction", *Chem. Eng. J.*, **28**, B11-B20 (1984).

Ricker, N. L, Pittman, E. F., and King, C. J., "Solvent Extraction with Amines for Recovery of Acetic Acid from Dilute Aqueous Industrial Streams", *J. Separ. Proc. Technol.*, 1(2), 23-30 (1980).

Ricker, N. L., "Recovery of Carboxylic Acids and Related Organic Chemicals from Wastewaters by Solvent Extraction", Ph.D. Dissertation, University of California, Berkeley (1978).

Ritcey, G. M. and Ashbrook, A. W., *Solvent Extraction//Principles and Applications to Process Metallurgy*, Part II, Chapter 6, 230-287, Elsevier, New York (1980).

Roffler, S. R., "Extractive Fermentation--Lactic Acid and Acetone/Butanol Production", Ph.D. Dissertation, Department of Chemical Engineering, University of California, Berkeley (1986).

Rückl, W., Siebenhofer, M., and Marr, R., "Separation of Citric Acid from Aqueous Fermentation Solutions by Extraction-Reextraction Processes", *Int. Solv. Extr. Ion Exch. Conf. (ISEC '86)*, Preprints, vol. III., Dechema, Munich, Germany, III-653 to III-658 (1986).

Shmidt, V. S. and Rybakov, K. A., "Extraction of Monochloroacetic, Acetic, and Formic Acids by Tri-n-Octylamine from Solutions of Hydrochloric and Hydrobromic Acids", *Russ. J. Appl. Chem.* (Engl. Transl.), **51**, 637-640; *Zh. Prikl. Khim.*, **51**, 654-658 (1978).

Shmidt, V. S. and Rybakov, K. A.,"Extraction of Oxalic Acid with Tri-n-Octylammonium from Hydrochloric Acid Solutions", *Russ. J. Anal. Chem.*, **32**, 283-286 (1977); *Zh. Anal. Khim.*, **32**, 357-361 (1977).

Siebenhofer, M. and Marr, R., "Auswirkung der Extraktionmittel-Zusammensetzung auf den Stoffaustausch und die Apparateauswah am Beispiel der Essigsaure-Extraktion", *Chem.-Ing.-Tech.*, **57**, 558-559 (1985).

Siebenhofer, M. and Marr, R., "Acid Extraction by Amines", *Int. Solv. Extr. Conf. (ISEC '83)*, Denver, Colorado, 26 Aug. - 2 Sept., Paper 18c, Fuel and Chemical Extraction Processes -- 1, 219-220 (1983).

Starr, J. N., University of California, Berkeley, personal communication (1988).

Thien, M. P., Hatton, T. A., and Wang, D. I. C., "Liquid Emulsion Membranes and Their Applications in Biochemical Separations", *Separation, Recovery, and Purifications in Biotechnology*, American Chemical Society Symp. Ser. 314, Washington, D. C., 67 (1986).

Wennersten, R., "The Extraction of Citric Acid from Fermentation Broth Using a Solution of a Tertiary Amine", *J. Chem. Technol. Biotechnol.*, **33B**, 85-94 (1983).

APPENDIX A. PROCEDURE FOR BATCH EXTRACTION EXPERIMENTS

A.1 Materials

Alamine 336 (Henkel Corporation), an aliphatic, straight-chain tertiary amine, was used as received from the manufacturer. The alkyl groups are a C_8-C_{10} mixture, with the C_8 carbon chain predominating about 2 to 1. The manufacturer's reported average molecular weight of the amine is 392 gm/mol (Henkel, 1984). From organic-phase potentiometric titrations of the amine dissolved in 1-propanol (Baker reagent grade) using approximately 0.1 mol/L HCl dissolved in 1-propanol (Baker, reagent grade) and taking the endpoint to be the inflection of the titration curve, the effective molecular weight was determined to be 406 gm/mol. The experimentally determined molecular weight of 406 gm/mol was used in all further calculations.

All solutions were prepared by dilution of the appropriate acid into distilled water, which had been further purified by passage through a Mille-Q water filtration system (Millipore). Lactic acid (Mallinkrodt, analytical reagent grade, 85%) was diluted with Mille-Q water to approximately 15% (w/w) and refluxed for 10 hours to hydrolyze any dimers or multimers present in the concentrated solution. A concentration of 15% (w/w) was considered to be low enough so that essentially all the lactic acid is in the monomeric form at equilibrium (Holten, 1971). HPLC of the lactic acid before and after heating confirmed success of transformation into a monomeric solution. De-esterification is extremely important for analysis of lactic acid systems, since the presence of esterified acid can greatly alter the experimental results (Holten, 1971). Malonic (Aldrich Chemical Company, Inc., 99%), succinic (Mallinkrodt, analytical reagent grade), acetic (Fisher Scientific, reagent grade), fumaric (Aldrich), and maleic (Aldrich) acids were used as received. Methyl isobutyl

ketone (MIBK) (Mallinkrodt, 99%), *n*-heptane (Baker, reagent grade), methylene chloride (Fisher), nitrobenzene (Aldrich), and 1-octanol (Aldrich) were used as received. In the initial experiments, chloroform (Mallinkrodt, analytical reagent grade) was washed three times with water immediately prior to use to remove the ethanol stabilizer. Experiments with washed and unwashed chloroform showed that the presence of ethanol stabilizer had no significant effect on the equilibrium data, and later experiments were done without prewashing of the chloroform.

A.2 Equilibrium Measurements

Known volumes of aqueous and organic solutions of known concentration were added to Erlenmeyer flasks and equilibrated in a temperature-controlled shaker bath at the temperature setpoint ±2 °C for at least 12 hours, which preliminary tests demonstrated to be sufficient time for equilibration. Experiments were performed at 25 °C, using 50 ml each of the aqueous and organic phase solutions, unless noted otherwise. The aqueous and organic phases were removed by pipet, and each phase was centrifuged on a Damon/IEC centrifuge at 3000 rpm for at least five minutes. Good separation into two distinct phases was achieved, unless otherwise noted. No significant volume change of the phases was observed. A blank run, in which water was equilibrated with the organic phase, was analyzed and the apparent amount extracted was subtracted from the amount measured for acid extractions. This correction was found to be negligible in virtually all cases examined.

Aqueous-phase pH measurements were performed using an Orion 601A pH meter equipped with an Orion Ross pH electrode. Aqueous-phase acid concentrations were determined by colorimetric titration with 0.001, 0.01, or 0.1 mol/l NaOH, using phenolphthalein as an indicator. Titrant concentration and sample volume were varied

in order to give approximately the same relative precision to low-concentration measurements as to high-concentration measurements.

In most cases, organic-phase acid concentrations were determined with two-phase titration with aqueous NaOH, using phenolphthalein as an indicator. However, potentiometric organic phase titrations were used in cases where the indicator color change was not visible. Potentiometric organic-phase titrations were performed by dissolving the organic phase in methylene chloride and titrating with KOH (Mallinkrodt) in 1-propanol. Material balances were within 5%, and generally within 2%.

In most cases, organic-phase water concentrations were determined with a Quintel model MS-1 automatic Karl Fischer titrator. Since ketones interfere with Karl Fischer analyses, water analyses of samples with MIBK present were done by gas chromatography with a Varian model 3700 gas chromatograph equipped with a thermal conductivity detector and a 1 m x 3.17 mm stainless steel column packed with Porapak Q (Varian, Inc.) at 120 °C.

A.3 Tabulation of Experimental Data

Results of the batch extraction experiments are given in Table A-1. The experimentally measured quantities are:

$C_{A,tot}$ = initial aqueous-phase acid concentration, mol/L

$C_{A,aq}$ = equilibrium aqueous-phase acid concentration, mol/L

$C_{A,org}$ = equilibrium organic-phase acid concentration, mol/L

pH = -log{H+}

$C_{W,org}$ = equilibrium organic-phase water concentration, mol/L

Values calculated from these data are:

log[A] = logarithm of undissociated aqueous-phase acid

Z = loading, corrected for diluent extraction

D = distribution coefficient = $\frac{C_{A,org}}{C_{A,aq}}$ or $\frac{C_{A,tot}-C_{A,aq}}{C_{A,aq}}$

Methods for calculation of log[A] from the is give in Appendix C. Z, corrected for extraction by the diluent alone, was calculated by

$$Z = \frac{[\, C_{A,org} - (\text{vol\% diluent in solvent}) \times (P \cdot [A] + K_d^* \cdot [A]^2)\,]}{C_{B,org}}$$

where $C_{B,org}$ is the amine concentration and P and K_d^* were calculated from least squares fit as described in Chapter 2. Note that D given in the table is not corrected for acid dissociation or extraction by the diluent alone. Phase ratios were 1:1 by volume unless otherwise noted.

REFERENCES

Henkel Corporation, Red Line Technical Bulletin, "Alamine 336", Minneapolis, MN (1984).

Holten, C. H., *Lactic Acid: Properties and Chemistry of Lactic Acid and Derivatives*, Verlag Chemie, Copenhagen, 20-86 (1971).

Table A-1. Tabulation of Experimental Data

ACETIC ACID

Alamine 336 (Various Concentrations), 15% (v/v) Chloroform; Remaining Volume *n*-Heptane, 25 °C

Alamine 336 (Various Concentrations), Nitrobenzene, 25 °C

FUMARIC ACID

Alamine 336 (Various Concentrations), Chloroform (Trichloromethane), 25 °C

Alamine 336, Methyl Isobutyl Ketone, 25 °C

LACTIC ACID

Alamine 336 (0.29 mol/L), Chloroform (Trichloromethane), 0, 25, 55 °C

Alamine 336 (0.29 mol/L), *m*-Cresol and *m*-Cresol/Toluene, 25 °C

Alamine 336 (0.29 mol/L), Methyl Isobutyl Ketone (4-Methyl-2-Pentanone), 0, 25, 50, 75 °C

MALEIC ACID

Alamine 336 (Various Concentrations), Chloroform (Trichloromethane), 25 °C

Alamine 336 (Various Concentrations), Methyl Isobutyl Ketone, 25 °C

MALONIC ACID

Alamine 336 (No Diluent), 25 °C

Alamine 336 (Various Concentrations), Methyl Isobutyl Ketone, (4-Methyl-2-Pentanone), 25 °C

SUCCINIC ACID

Alamine 336 (No Diluent), 25 °C

Alamine 336 (Various Concentrations), Chloroform (Trichloromethane), 25 °C

Alamine 336 (0.29 mol/L), Chloroform, 0, 25, 40, 55 °C

SUCCINIC ACID (cont'd)

Alamine 336 (Various Concentrations), Chloroform and *n*-Heptane Mixed Diluent, 25 °C

Alamine 336 (Various Concentrations), *n*-Heptane, 25 °C

Alamine 336 (Various Concentrations), Methylene Chloride (Dichloromethane), 25°C

Alamine 336 (Various Concentrations), Methylene Chloride and *n*-Heptane Mixed Diluent, 25 °C

Alamine 336 (Various Concentrations), Methyl Isobutyl Ketone (4-Methyl-2-Propanone), 25 °C

Alamine 336 (0.29 mol/L), Methyl Isobutyl Ketone, 0, 25, 50, and 75 °C

Alamine 336 (Various Concentrations), Nitrobenzene, 25 °C

Alamine 336 (Various Concentrations), 1-Octanol, 25 °C

Alamine 336 (0.29 mol/L), 40% (v/v) 1-Octanol and 45% (v/v) Chloroform, 25 °C

Acetic Acid
Alamine 336 (Various Concentrations)
15% (v/v) Chloroform; Remaining Volume *n*-Heptane

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	$C_{W,org}$	log[A]	Z	D
No Alamine 336							
2.0200	1.9799		2.30	0.012			0.020
0.8200	0.8099		2.53	0.012			0.012
0.2450	0.2423		2.80	0.012			0.011
0.0540	0.0537		3.11	0.012			0.006
0.0000			6.88	0.011			
0.097 mol/L Alamine 336 (4.9 vol%)							
2.0200	1.8030	0.24795	2.43	0.025	0.254	1.908	0.138
0.8200	0.7200	0.11995	2.70	0.016	-0.146	0.950	0.167
0.4733	0.4140	0.06845	2.84	0.014	-0.388	0.573	0.165
0.2450	0.2215	0.03075	2.85		-0.660	0.224	0.139
0.1060	0.0951	0.01222	3.08		-1.031	0.106	0.129
0.0540	0.0482	0.00605	3.27		-1.330	0.056	0.125
0.0108	0.0090	0.00096	3.73		-2.085	0.018	0.107
0.0000			6.88				
0.29 mol/L Alamine 336 (14.9 vol%)							
2.0200	1.4938	0.60784	2.36	0.086	0.173	1.741	0.407
0.8200	0.5778	0.27784	2.65	0.050	-0.242	0.817	0.481
0.4733	0.3348	0.14884	2.86	0.040	-0.481	0.469	0.445
0.2450	0.1753	0.07084	3.07	0.027	-0.765	0.236	0.404
0.1060	0.0823	0.02824	3.34	0.022	-1.101	0.080	0.343
0.0540	0.0398	0.01434	3.55	0.018	-1.427	0.048	0.361
0.0108	0.0074	0.00256	4.12	0.018	-2.221	0.012	0.346
0.0000			6.90	0.020			
0.58 mol/L Alamine 336 (29.4 vol%)							
2.0200	1.0800	1.00000	2.53	0.188	0.031	1.604	0.926
0.8200	0.4333	0.40560	2.87	0.092	-0.369	0.662	0.936
0.4733	0.2504	0.20500	3.06	0.065	-0.610	0.382	0.819
0.2450	0.1550	0.11000	3.30	0.048	-0.825	0.154	0.710
0.1060	0.0597	0.04750	3.60	0.036	-1.253	0.079	0.796
0.0540	0.0303	0.02380	3.84	0.040	-1.568	0.041	0.784
0.0108	0.0055	0.00503	4.44	0.039	-2.434	0.009	0.921
0.0000			6.96	0.023			

* P = 0.00754 and K_d^* = 0.00652 used to calculate Z.

Data by Tong.

Acetic Acid
Alamine 336 (Various Concentrations)
Nitrobenzene
25 °C

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	$C_{W,org}$	log[A]	Z	D
<u>No Alamine 336</u>							
2.02	1.940		2.29	0.223	0.286		0.041
0.477	0.453	0.02172	2.65	0.174	-0.347		0.048
0.0540	0.0524	0.00228	3.15	0.166	-1.292		0.045
0.0108	0.0102	0.00072	3.58	0.158	-2.019		0.075
<u>0.29 mol/L Alamine 336</u>							
2.02	1.288		2.49		0.107	2.29	2.53
0.820	0.288		2.97		-0.548	1.78	1.84
0.477	0.136		3.26		-0.879	1.15	1.18
0.245	0.0685		3.53		-1.189	0.597	0.609
0.106	0.0321		3.85		-1.544	0.250	0.255
0.0540	0.0179		4.07		-1.828	0.122	0.125
0.0108	0.00404		4.66		-2.648	0.023	0.023

* P = 0.0524 used in calculation of Z.

Fumaric Acid
Alamine 336 (Various Concentrations)
Chloroform (Trichloromethane)
25 °C

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	$C_{W,org}$	log[A]	Z	D
No Alamine 336 (data by McKinley)							
0.0200	0.020	0.0001	2.52	0.043	-1.80		0.007
0.0480a	0.047	0.0003	2.33	0.034	-1.40		0.005
0.05 mol/L Alamine 336 (data by McKinley)							
0.0480a	0.0400	0.0447	2.38	0.137	-1.47	0.960	1.12
0.0480b	0.0370	0.0437	2.40	0.110	-1.51	0.880	1.18
0.0480c	0.0270	0.0417	2.51	0.067	-1.67	0.840	1.54
0.0480	0.0130	0.0347	2.68	0.027	-2.03	0.700	2.67
0.0200	0.00140	0.0187	3.34	0.073	-3.31	0.372	13.36
0.0080	0.00039	0.0075	3.95	0.036	-4.39	0.152	19.23
0.0000			5.92	0.030			
0.145 mol/L Alamine 336 (data by Leong)							
0.244 d	0.0369	0.139	2.35		-1.51	0.925	3.8
0.148 d	0.0235	0.125	2.48		-1.72	0.833	5.3
0.100 d	0.00580	0.0915	2.91		-2.46	0.610	15.8
0.096 d	0.00423	0.0889	2.95		-2.61	0.593	21.0
0.0480	0.000542	0.0489	4.02		-4.33	0.326	90.2
0.0280	0.000328	0.0288	4.39		-5.00	0.192	87.9
0.0150	0.000199	0.0155	4.53		-5.41	0.103	77.8
0.0070	0.000100	0.0072	5.13		-6.67	0.048	71.5
0.0040	0.000062	0.0039	5.70		-7.94	0.026	63.4
0.29 mol/L Alamine 336 (data by Leong)							
0.318 d	0.0429	0.275	2.37	0.211	-1.44	0.917	6.4
0.270 d	0.0203	0.251	2.54	0.207	-1.80	0.835	12.3
0.200 d	0.00753	0.193	3.04	0.248	-2.40	0.642	25.6
0.100 d	0.000625	0.0980	4.19	0.202	-4.46	0.327	156.8
0.0480	0.000278	0.0488	4.65	0.154	-5.44	0.163	175.4
0.0280	0.000200	0.0280	4.83	0.129	-5.86	0.093	140.0
0.0150	0.000109	0.0153	5.02	0.120	-6.44	0.051	139.9
0.0070	0.000094	0.0070	5.61	0.110	-7.59	0.023	73.9

* Extraction by diluent alone is negigible.

a 6:1 O:A phase ratio
b 4:1 O:A phase ratio
c 2:1 O:A phase ratio
d Organic phase was pre-loaded with an appropriate amount of fumaric acid and contacted with 0.48 mol/L aqueous fumaric acid.

Fumaric Acid
Alamine 336
Methyl Isobutyl Ketone
25 °C

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	$C_{W,org}$	log[A]	Z	D
<u>No Alamine 336 (Data from Starr, 1988)</u>							
0.049c	0.02760	0.0463	2.45		-1.65		1.68
0.049	0.01965	0.0300	2.54		-1.81		1.53
0.020	0.00848	0.0124	2.73		-2.23		1.46
0.008	0.00372	0.0048	2.94		-2.66		1.28
0.004	0.00193	0.0024	3.08		-3.01		1.25
0.001	0.00052	0.0004	3.41		-3.79		0.85
0.000	0.00015	0.0000	4.66				
<u>0.0145 mol/L Alamine 336 (Data by McKinley)</u>							
0.048a	0.01530	0.2320	2.61	0.888	-1.94	1.547	15.2
0.048b	0.00740	0.1740	2.77	1.050	-2.30	1.160	23.5
0.048c	0.00214	0.0944	3.26	0.932	-3.07	0.629	44.1
0.048	0.00130	0.0474	3.73	0.832	-3.65	0.316	36.5
0.020	0.00085	0.0200	4.06	0.711	-4.18	0.133	23.5
0.008	0.00060	0.0084	4.35	0.526	-4.68	0.056	14.0
0.001	0.00020	0.0010	5.30	0.641	-6.68	0.007	5.0
0.000			6.18	0.610			

a = 1/6 O:A ratio
b = 1/4 O:A ratio
c = 1/2 O:A ratio

* P = 2.243 used to calculate Z.

Lactic Acid
Alamine 336 (0.29 mol/L)
Chloroform (Trichloromethane)
0, 25, 55 °C

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	$C_{W,org}$	Log[A]	Z	D
T = 0 °C							
2.026	1.6150	0.3950	1.89	0.125	0.204	1.307	0.24
1.044	0.7025	0.3383	2.13	0.135	-0.161	1.143	0.48
0.517	0.2500	0.2970	2.41	0.162	-0.617	1.016	1.19
0.334	0.0450	0.2880	2.87		-1.389	0.992	6.40
0.199	0.00501	0.1994	4.02		-2.689	0.688	39.8
0.104	0.00096	0.1072	4.24	0.076	-3.551	0.370	112
0.053	0.00051	0.0528	4.50	0.064	-4.019	0.182	103
0.011	0.00009	0.0098	5.00	0.103	-5.216	0.034	109
0.000			5.98	0.092			
T = 25 °C							
2.014	1.6050	0.4310	1.91	0.163	0.201	1.356	0.27
1.044	0.6980	0.3880	2.15	0.149	-0.165	1.169	0.56
0.505	0.2068	0.3146	2.42	0.144	-0.700	1.021	1.52
0.209	0.00879	0.1983	3.45		-2.199	0.689	22.56
0.115	0.00293	0.1060	3.67	0.109	-2.749	0.386	36.12
0.057	0.00127	0.0560	3.87	0.104	-3.202	0.190	44.11
0.012	0.00026	0.0118	4.41	0.075	-4.240	0.039	45.12
0.000			6.65	0.103			
1.737	1.3800	0.4130	2.07	0.164	0.133	1.377	0.30
1.158	0.7950	0.3678	2.26	0.161	-0.110	1.241	0.46
0.579	0.2770	0.3118	2.53	0.154	-0.577	1.066	1.13
0.290	0.0325	0.2578	3.07	0.148	-1.554	0.888	7.94
0.116	0.00347	0.1128	3.66	0.118	-2.673	0.389	32.54
0.058	0.00140	0.0582	3.89	0.101	-3.172	0.201	41.69
0.012	0.00026	0.0114	4.45	0.081	-4.271	0.039	43.36
0.000			6.55	0.092			
T = 55 °C							
2.026	1.6159	0.4223	1.91	0.185	0.204	1.401	0.26
1.044	0.6999	0.3467	2.14	0.182	-0.163	1.172	0.50
0.517	0.2299	0.2959	2.41	0.177	-0.654	1.013	1.29
0.334	0.0925	0.2459	2.66	0.270	-1.061	0.845	2.66
0.198	0.0326	0.1714	2.95	0.155	-1.537	0.590	5.26
0.104	0.0124	0.0963	3.25	0.133	-2.003	0.332	7.78
0.053	0.00516	0.0472	3.52	0.115	-2.451	0.163	9.15
0.011	0.00087	0.0082	4.06	0.108	-3.473	0.028	9.38
0.000			5.06	0.092			

* P = 0.01 used in calculation of Z (virtually neglible correction).
Data by Grewal, Starr, and Tamada.

Lactic Acid
Alamine 336 (0.29 mol/L)
m-Cresol and *m*-Cresol/Toluene

Cresol (mol/L)	$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	$C_{W,org}$	log[A]	D
0.29 mol/L Alamine 336 in m-Cresol/Toluene Mixture							
0	0.562	0.5742	0.00055	2.16	0.0137		0.001
1	0.562	0.5697	0.0102	2.14	0.1247		0.018
3	0.562	0.5603	0.0175	2.14	0.9268		0.031
5	0.562	0.5415	0.0429	2.16	2.1728		0.079
7	0.562	0.5171	0.0792	2.17	3.8831		0.153
9.5	0.562	0.4718	0.1483	2.18	7.3602		0.314

A mixed diluent of toluene and cresol was prepared with the indicated molar concentration of cresol.

0.29 mol/L Alamine 336 in m-Cresol						
1.1580	0.7566	2.29	6.051	-0.13	0.53
0.5790	0.2580	2.51	5.816	-0.61	1.24
0.2895	0.0100	3.29	5.774	-2.10	27.95
0.1158	0.0016	4.72	5.569	-3.71	71.38
0.0579	0.0025	4.98	5.349	-3.75	22.16
0.0116	0.0022	5.42	5.135	-4.23	4.26
0.0000		6.05	5.112		

Cresol extracts significant lactic acid by itself. Because a detailed analysis of extraction by the diluent alone was not performed, accurate values of Z could not be calculated. Cresol was found to interfere with aqueous phase titrations at low acid concentrations because it is a weak acid and has appreciable solubility in water. Thus log[A] values are approximate at the three lowest acid concentrations.

Lactic Acid
Alamine 336 (0.29 mol/L)
Methyl Isobutyl Ketone (4-Methyl-2-Pentanone)
0, 25, 50, 75 °C

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	log[A]	Z	D
T = 0 °C						
No Alamine 336						
2.0770	1.8695	0.22109	1.88	0.267		0.118
0.6920	0.6295	0.06089	2.14	-0.209		0.097
0.1380	0.1225	0.01169	2.52	-0.930		0.095
0.0138	0.0125	0.00104	2.94	-1.950		0.083
0.29 mol/L Alamine 336						
2.0770	1.3900	0.715	1.81	0.139	2.160	0.6264
1.1580	0.6700	0.515	2.20	-0.183	1.612	0.4674
1.0440	0.5598	0.487	2.22	-0.261	1.540	0.4466
0.6920	0.2890	0.407	2.44	-0.555	1.330	0.3856
0.2895	0.0714	0.243	2.98	-1.198	0.822	0.2382
0.1158	0.0131	0.103	3.45	-2.020	0.353	0.1025
0.0579	0.0081	0.0520	3.78	-2.345	0.178	0.0516
0.0533	0.0044	0.0501	3.88	-2.661	0.172	0.0499
0.0116	0.0033	0.00813	4.45	-3.162	0.028	0.0081
0.0109	0.0003	0.00986	4.34	-4.071	0.034	0.0099

* P = 0.0939 and K_d^* = 0.0133 used in calculation of Z at 0 °C.
pH taken at 0 °C; pK_A = 3.88 used in calculation of [A].

T = 25 °C						
No Alamine 336						
2.0770	1.8495	0.24734	1.63	0.265		0.134
0.2895	0.2615	0.02914	2.04	-0.589		0.111
0.0138	0.0124	0.00078	2.61	-1.929		0.063
0.29 mol/L Alamine 336						
2.0770	1.3486	0.69605	2.00	0.124	2.043	0.5925
1.1580	0.6436	0.50855	2.20	-0.201	1.567	0.4544
0.5790	0.2306	0.34755	2.43	-0.653	1.129	0.3274
0.2895	0.0754	0.21555	2.72	-1.153	0.721	0.2091
0.1158	0.0238	0.09155	3.10	-1.694	0.309	0.0897
0.0579	0.0136	0.04955	3.34	-1.982	0.168	0.0486
0.0116	0.0015	0.00965	4.02	-3.216	0.033	0.0096

* P = 0.1096, K_d^* = 0.0135 used in calculation of Z at 25 °C.
pH taken at 25 °C; pK_A = 3.858 used in calculation of [A].

Lactic Acid
Alamine 336 (0.29 mol/L)
Methyl Isobutyl Ketone (4-Methyl-2-Pentanone)
0, 25, 50, 75 °C (Cont'd)

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	log[A]	Z	D
T = 50 °C						
No Alamine 336						
2.077	1.7697	0.28315	1.63	0.246		0.160
0.692	0.6077	0.08415	1.88	-0.220		0.138
0.2895	0.2597	0.03465	2.03	-0.591		0.133
0.138	0.1207	0.01635	2.17	-0.926		0.135
0.29 mol/L Alamine 336						
2.0770	1.3862	0.6953	2.00	0.136	1.949	0.5651
0.6920	0.3277	0.3568	2.48	-0.501	1.112	0.3224
0.2895	0.1022	0.1868	2.90	-1.032	0.608	0.1764
0.1380	0.0410	0.0963	3.26	-1.478	0.319	0.0926
0.0692	0.0178	0.0513	3.60	-1.928	0.172	0.0500
0.0138	0.0022	0.0109	4.68	-3.503	0.037	0.0109

* P = 0.133 and K_d^* = 0.0154 used in calculation of Z at 50 °C.
pH taken at 50 °C; pK_A = 3.895 used in calculation of [A].

T = 75 °C						
No Alamine 336						
2.077	1.72	0.295	1.68	0.233		0.172
0.692	0.614	0.0929	1.91	-0.216		0.151
0.0138	0.0126	0.00054	2.64	-1.922		0.043
0.29 mol/L Alamine 336						
2.0770	1.4298	0.74614	1.74	0.152	2.088	0.6056
0.6920	0.3628	0.33714	2.09	-0.447	1.021	0.2960
0.3460	0.1618	0.18114	2.29	-0.802	0.560	0.1625
0.1380	0.0598	0.07454	2.53	-1.242	0.233	0.0677
0.0692	0.0308	0.04014	2.69	-1.538	0.126	0.0367
0.0138	0.0058	0.00824	3.32	-2.341	0.027	0.0077

* P = 0.142 and K_d^* = 0.0179 used in calculation of Z at 75 °C.
pH taken at 75 °C; pK_A = 3.9 used in calculation of [A].

Data by Grewal.

Maleic Acid
Alamine 336 (Various Concentrations)
Chloroform (Trichloromethane)
25 °C

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	$C_{W,org}$	log[A]	Z	D
No Alamine 336							
2.000	1.980	0.0043	0.93	0.0627	0.253		0.010
0.500	0.484	0.0010	1.33	0.0544	-0.417		0.033
0.100	0.097	0.0008	1.70	0.0528	-1.222		0.031
0.010	0.010	0.0003	2.24	0.0533	-2.505		0.020
0.29 mol/L Alamine 336 (Data by Leong, McKinley, and Tamada)							
2.00	1.531		0.96		0.139	1.45	0.31
2.00	1.540	0.465	0.99	0.264	0.138	1.39	0.30
1.00	0.634		1.21		-0.277	1.20	0.58
1.00	0.600	0.399	1.32	0.242	-0.321	1.27	0.67
0.500	0.161		1.55		-0.950	1.15	2.10
0.500	0.144	0.361	1.60	0.226	-1.015	1.19	2.47
0.333	0.0377	0.299	1.93		-1.735	1.03	7.84
0.250	0.00075		4.45		-5.672	0.859	332.3
0.250	0.00080	0.256	4.70	0.181	-5.898	0.852	311.5
0.200	0.00064	0.204	4.75		-6.046	0.704	311.5
0.100	0.00060	0.101	5.07	0.155	-6.405	0.338	165.7
0.100	0.00052		5.05		-6.447	0.343	191.3
0.050	0.00050		5.17		-6.590	0.171	99.0
0.050	0.00050	0.0523	5.38	0.134	-6.817	0.174	99.0
0.010	0.00026	0.0095	5.71	0.138	-7.478	0.032	37.5
0.010	0.00022		5.68		-7.515	0.034	44.5
0.000			6.82	0.114			
0.58 mol/L Alamine 336 (Data by Leong)							
2.00	1.248	0.757	1.06	0.263	0.039	1.249	0.603
1.00	0.352	0.624	1.43	0.235	-0.578	1.061	1.841
0.500	0.00151	0.500	4.40	0.220	-5.317	0.861	330.1
0.250	0.00091	0.242	5.08	0.164	-6.234	0.417	272.8
0.100	0.00069	0.0970	5.28	0.121	-6.568	0.167	143.9
0.050	0.00055	0.0492	5.44	0.115	-6.842	0.085	89.9
0.010	0.00023	0.0104	5.63	0.098	-7.437	0.018	42.5

* P = 0.0417 used in calculation of Z.

Maleic Acid
Alamine 336 (Various Concentrations)
Methyl Isobutyl Ketone
25 °C

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	$C_{W,org}$	log[A]	Z	D
No Alamine 336 (data by McKinley)							
2.000	1.5330	0.4900	1.02	2.275	0.180		0.32
0.500	0.3900	0.1100	1.38	1.194	-0.414		0.28
0.100	0.0810	0.0120	1.75	0.874	-1.097		0.15
0.010	0.0092	0.0016	2.32	0.647	-2.042		0.17
0.145 mol/L Alamine 336 (data by Leong)							
2.00	1.37	0.660	1.02		0.084	2.014	0.5
1.00	0.606	0.401	1.23		-0.300	1.716	0.7
0.500	0.243	0.251	1.45		-0.744	1.351	1.0
0.250	0.0745	0.178	1.81		-1.382	1.137	2.4
0.100	0.00074	0.0996	4.27		-5.498	0.687	135.0
0.050	0.00059	0.0494	4.56		-5.887	0.340	83.6
0.010	0.00038	0.0103	5.23		-6.776	0.071	27.2
0.29 mol/L Alamine 336 (data by McKinley)							
2.00	1.16	0.857	1.22	2.351	-0.016	2.036	0.72
1.00	0.436	0.555	1.30	1.546	-0.456	1.580	1.29
0.500	0.0960	0.393	1.63	1.422	-1.201	1.295	4.21
0.333	0.0379	0.292	1.96		-1.748	0.990	7.79
0.250	0.00120	0.251	4.25	0.955	-5.266	0.866	207.
0.200	0.00071	0.200	4.02		-5.264	0.690	281.
0.100	0.00089	0.100	4.89	0.685	-6.047	0.345	111.
0.050	0.00075	0.0500	5.13		-6.372	0.172	65.8
0.010	0.00036	0.0100	5.64		-7.256	0.034	26.9
0.58 mol/L Alamine 336 (data by Leong)							
2.00	0.7995	1.081	1.16	2.479	-0.168	1.593	1.4
1.00	0.169	0.776	1.54	1.874	-0.927	1.291	4.6
0.500	0.00172	0.478	4.24	1.322	-5.100	0.824	278.
0.250	0.00147	0.2425	4.75	0.779	-5.685	0.418	165.
0.100	0.00127	0.0969	5.06	0.582	-6.069	0.167	76.3
0.050	0.00107	0.04675	5.25	0.503	-6.345	0.081	43.7
0.010	0.00057	0.00973	5.66	0.451	-7.078	0.017	17.1
0.000				0.443			

* P = 0.354 used in calculation of Z.

Malonic Acid
Alamine 336 (No Diluent)
25 °C

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	log[A]	Z	D
4.000	1.3072	2.6928	1.52	0.096	1.314	2.06
2.000	0.0226	1.9774	2.86	-1.962	0.965	87.34
1.000	0.0087	0.9913	3.41	-2.745	0.484	114.34
0.500	0.0084	0.4916	3.47	-2.807	0.240	58.45
0.100	0.0080	0.0920	3.76	-3.079	0.045	11.47
0.050	0.0080	0.0420	4.08	-3.382	0.021	5.27
0.010	0.0041	0.0059	4.81	-4.427	0.003	1.46
0.000			7.03			

Significant formation of a clear, viscous second organic phase was observed in these runs. The values shown immediately above are for $C_{A,org} = C_{A,tot} - C_{A,aq}$; thus values for Z and D shown above are calculated for the combined organic phases.

$C_{A,tot}$	$C_{A,org}$	$C_{W,org}$	Density	$C_{B,org}$	$C_W:C_A$	Z
4.000	2.425	2.137	0.9769	1.7	0.88	1.39
2.000	1.685	2.325	0.8778	1.7	1.38	1.00
1.000	1.504	2.100	0.8958	1.8	1.40	0.83
0.500	1.376	2.050	0.8855	1.8	1.49	0.77

In some cases, there was sufficient "middle" (2nd org) phase to determine its $C_{A,org}$, $C_{W,org}$, and density (gm/ml) experimentally (values shown immediately above). As the initial acid concentration increased, the volume of this "middle" phase increased, until, for 4.0 and 2.0 $C_{A,tot}$ samples, there was no normal "top" organic phase. From the density, $C_{A,org}$, and $C_{W,org}$ in the second organic phase, calculations were made of the concentration of amine, $C_{B,org}$ (mol/L), the ratio of water to acid, $C_W:C_A$, and the effective Z for the second organic phase.

$C_{A,tot}$	$C_{A,org}$	$C_{W,org}$
1.000	0.0041	0.0232
0.500	0.0046	0.0293
0.100	0.0060	0.0270
0.050	0.0049	0.0280
0.010	0.0013	0.0534
0.000		0.0600

$C_{A,org}$ and $C_{W,org}$ in the "top" (first organic) phase were determined experimentally (values given above).

Malonic Acid
Alamine 336 (Various Concentrations)
Methyl Isobutyl Ketone (4-Methyl-2-Pentanone)
25 °C

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	$C_{W,org}$	log[A]	Z	D
No Alamine 336							
2.002	1.8317	0.3101	1.46	2.90	0.245		0.169
0.998	0.9122	0.1371	1.60	2.30	-0.065		0.150
0.509	0.4487	0.0671	1.75	1.84	-0.383		0.150
0.101	0.0890	0.0131	2.04	1.73	-1.116		0.147
0.050	0.0451	0.0060	2.20	1.54	-1.437		0.133
0.010	0.0093	0.0010	2.52	1.44	-2.205		0.108
0.000			3.81	1.32			
0.048 mol/L Alamine 336 (2.45 vol%)							
2.002	1.7274	0.3638	1.52	2.49	0.217	2.028	0.211
0.998	0.8474	0.2027	1.69	2.17	-0.102	1.556	0.239
0.509	0.3999	0.1202	1.86	1.71	-0.442	1.282	0.301
0.101	0.0458	0.0568	2.23	1.27	-1.436	1.054	1.24
0.050	0.0060	0.0449	2.64	1.14	-2.438	0.918	7.48
0.010	0.0006	0.0101	3.83	0.984	-4.269	0.209	16.83
0.000			5.25	0.911			
0.29 mol/L Alamine 336 (14.7 vol%)							
2.002	1.4485	0.6856	1.53	4.15	0.140	1.695	0.473
0.998	0.5490	0.4783	1.73	3.09	-0.294	1.403	0.871
0.509	0.1527	0.3523	1.98	2.50	-0.874	1.151	2.31
0.312	0.0479	0.2745	2.26		-1.424	0.928	5.74
0.202	0.0027	0.2095	3.41		-3.248	0.722	76.88
0.101	0.0019	0.1015	3.49	1.04	-3.469	0.350	53.42
0.050	0.0014	0.0503	3.77	0.744	-3.846	0.174	35.93
0.010	0.0008	0.0096	4.27	0.663	-4.568	0.033	12.00
0.000			4.84	0.669			
0.58 mol/L Alamine 336 (29.4 vol%)							
2.002	1.0556	1.0153	1.62	3.02	-0.002	1.552	0.962
0.998	0.2492	0.7568	1.97	2.32	-0.660	1.262	3.04
0.509	0.0044	0.4953	3.31	1.48	-2.962	0.855	112.6
0.103	0.0024	0.0999	3.96	0.574	-3.788	0.172	41.6
0.050	0.0020	0.0498	4.23	0.508	-4.130	0.086	24.9
0.010	0.0011	0.0080	4.69	0.428	-4.865	0.014	7.27
0.000			5.21	0.421		0.000	

Malonic Acid
Alamine 336 (Various Concentrations)
Methyl Isobutyl Ketone (4-Methyl-2-Pentanone)
25 °C (Cont'd)

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	$C_{W,org}$	log[A]	Z	D
1.16 mol/L Alamine 336 (58.8 vol%)							
2.002	0.4774	1.4623	1.78	2.18	-0.358	1.236[c]	3.06
1.005	0.0069	0.9363	3.35	1.72	-2.797	0.808[c]	135.7
0.501	0.0053	0.4838	3.70	0.779	-3.204	0.418[c]	91.3
0.103	0.0042	0.0963	4.08	0.243	-3.660	0.083[c]	22.9
0.052	0.0039	0.0449	4.28	0.198	-3.890	0.039[c]	11.5
0.010	0.0022	0.0067	4.87	0.158	-4.761	0.006[c]	3.05
0.000			6.24	0.150			

[c] Cloudiness between phases -- may indicate third phase formation.

* P = 0.166 used in calculation of Z.
Data by Soroush.

Succinic Acid
Alamine 336 (No Diluent)
25 °C

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$ (Bulk)	$C_{A,org}$ (Total)	pH	vol 3rd	log[A]	D	Z
0.486	0.0873	0.0216	0.4127	3.46	10a	-1.13	4.73	0.209
0.400	0.0910	0.0344	0.3090		a		3.40	0.156
0.300	0.0845	0.0337	0.2155		a		2.55	0.109
0.294	0.0748	0.0266	0.2252	3.52	4a	-1.21	3.01	0.114
0.200	0.0762	0.0278	0.1238		c		1.62	0.063
0.196	0.0655	0.0262	0.1345	3.56	3b	-1.27	2.05	0.068
0.150	0.0653	0.0329	0.0847		c		1.30	0.043
0.100	0.0489	0.0263	0.0511		c		1.04	0.026
0.098	0.0464	0.0213	0.0537	3.73		-1.46	1.16	0.027
0.050	0.0269	0.0146	0.0231		c		0.86	0.012
0.050	0.0263		0.0237				0.90	0.012
0.049	0.0248	0.0111	0.0252	3.98	5c	-1.81	1.02	0.013
0.025	0.0103	0.0060	0.0147		c		1.42	0.007
0.010	0.0025	0.0013	0.0075	5.26	3c	-3.70	3.01	0.004
0.000				7.50				

$C_{A,org}$ (bulk) was the experimentally determined acid concentration in the top organic phase. $C_{A,org}$ (total) = $C_{A,tot}$-$C_{A,aq}$. The difference between these gives the amount of acid in the middle organic phase (the third phase).

vol 3rd is the approximate volume of the third (middle) phase after centrifugation of the sample.

a Third phase is clear, viscous liquid.
b Third phase is a cloudy gel.
c Third phase is a white gel.

* Z is for $C_{A,org}$ (total)/$C_{B,org}$ (total).

Succinic Acid
Alamine 336 (Various Concentrations)
Chloroform (Trichloromethane)
25 °C

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	$C_{W,org}$	log[A]	Z	D
0.050 mol/L Alamine 336							
0.4895	0.4195	0.0546	2.35		-0.383	1.085	0.17
0.2953	0.2417	0.0514	2.52		-0.626	1.022	0.22
0.1962	0.1456	0.0508	2.63		-0.848	1.010	0.35
0.0992	0.0512	0.0480	2.89		-1.311	0.954	0.94
0.0492	0.0121	0.0375	3.24		-1.962	0.746	3.06
0.0258	0.00346	0.0223	3.56		-2.550	0.443	6.44
0.0104	0.00109	0.0089	3.92		-3.148	0.177	8.59
0.0966 mol/L Alamine 336							
0.400	0.3057		2.36		-0.521	0.943	0.308
0.300	0.2060		2.46		-0.694	0.940	0.457
0.200	0.1056		2.61		-0.987	0.944	0.894
0.100	0.0204		3.03		-1.718	0.796	3.891
0.050	0.0043		3.47		-2.443	0.457	10.686
0.025	0.0025		3.76		-2.740	0.225	9.050
						0.000	
0.193 mol/L Alamine 336							
0.400	0.2022				-0.694	0.989	0.978
0.300	0.1130				-0.947	0.935	1.654
0.200	0.0300				-1.523	0.850	5.665
0.100	0.0047				-2.325	0.476	20.114
0.050	0.0021				-2.688	0.240	23.390
0.025	0.0010				-2.985	0.120	23.159
0.29 mol/L Alamine 336							
0.483	0.2018		2.60	0.172	-0.706	0.939	1.40
0.400	0.1160		2.83	0.154	-0.954	0.947	2.45
0.306	0.0423		3.10	0.155	-1.407	0.878	6.23
0.300	0.0385		3.18	0.148	-1.454	0.872	6.78
0.200	0.0098		3.66	0.137	-2.119	0.634	19.39
0.153	0.0054		3.81	0.113	-2.418	0.490	27.24
0.100	0.0030		4.07	0.115	-2.771	0.327	49.00
0.050	0.0017		4.30	0.105	-3.143	0.161	28.94
0.025	0.0010		4.48	0.088	-3.498	0.080	24.77
0.000			6.44	0.078		0.000	

Succinic Acid
Alamine 336 (Various Concentrations)
Chloroform
25 °C (Cont'd)

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	$C_{W,org}$	log[A]	Z	D
0.386 mol/L Alamine 336							
0.400	0.0481				-1.318	0.880	7.32
0.300	0.0146				-1.837	0.714	19.59
0.200	0.0061				-2.213	0.485	31.65
0.100	0.0028				-2.561	0.243	35.36
0.050	0.0016				-2.804	0.121	30.83
0.025	0.0009				-3.027	0.060	25.60
0.58 mol/L Alamine 336							
0.400	0.0125		3.86	0.228	-2.068	0.646	30.9
0.300	0.0072		4.13	0.209	-2.417	0.488	40.7
0.200	0.0044		4.33	0.177	-2.745	0.326	44.9
0.100	0.0024		4.52	0.133	-3.135	0.163	40.8
0.050	0.0015		4.70	0.117	-3.487	0.081	32.6
0.025	0.0010		4.86	0.108	-3.829	0.040	25.3
0.000			6.20	0.092			
0.772 mol/L Alamine 336							
0.400	0.0097		3.88	0.254	-2.184	0.488	40.1
0.300	0.0067		4.05	0.244	-2.410	0.367	43.6
0.200	0.0046		4.25	0.206	-2.675	0.244	42.6
0.100	0.0027		4.51	0.143	-3.076	0.122	36.2
0.050	0.0017		4.73	0.121	-3.457	0.060	28.6
0.025	0.0011		4.89	0.103	-3.779	0.030	20.9
0.000	0.0000		6.50	0.081		0.000	
1.16 mol/L Alamine 336							
0.400	0.0109		4.00	0.301	-2.179	0.324	35.7
0.300	0.0075		4.14	0.251	-2.405	0.244	39.1
0.200	0.0066		4.28	0.201	-2.537	0.161	29.4
0.100	0.0042		4.56	0.149	-2.922	0.080	22.9
0.050	0.0027		4.79	0.125	-3.312	0.039	17.7
0.025	0.0018		5.00	0.111	-3.694	0.019	12.9
0.000			5.59	0.091		0.000	

Succinic Acid
Alamine 336 (Various Concentrations)
Chloroform
25 °C (Cont'd)

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	$C_{W,org}$	log[A]	Z	D
1.55 mol/L Alamine 336							
0.400	0.0271		3.89	0.313	-1.744	0.233[c]	13.79
0.300	0.0222		4.00	0.234	-1.870	0.174[c]	12.51
0.200	0.0172		4.11	0.186	-2.030	0.114[c]	10.65
0.100	0.0096		4.40	0.131	-2.448	0.057[c]	9.44
0.050	0.0060		4.66	0.105	-2.846	0.027[c]	7.32
0.025	0.0040		4.85	0.090	-3.200	0.013[c]	5.33
0.000	0.0000		6.70	0.081		0.000	

[c] Cloudiness between phases -- may indicate slight third phase formation.

* Extraction by diluent alone is neglible.

Succinic Acid
Alamine 336 (0.29 mol/L)
Chloroform
0, 25, 40, 55 °C

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	$C_{W,org}$	log[A]	Z	D
T = 0 °C							
0.490	0.1972	0.3003	2.59		-0.716	1.008	1.5
0.400	0.1053	0.2829	2.81	0.119	-0.995	1.014	2.8
0.300	0.0211	0.2796	3.27	0.117	-1.724	0.960	13.2
0.245	0.00434	0.2390	3.84		-2.522	0.829	55.4
0.200	0.00202	0.2029	4.18	0.116	-2.992	0.682	97.9
0.100	0.00078	0.1017	4.76	0.110	-3.817	0.342	127.4
0.050	0.00046	0.0503	5.04	0.090	-4.319	0.171	107.0
0.025	0.00028	0.0262	5.25	0.082	-4.780	0.085	88.7
0.010	0.00021	0.0100	5.52	0.074	-5.261	0.034	47.4
0.000			6.34	0.071			
T = 25 °C							
0.400	0.1160		2.83	0.154	-0.954	0.978	2.4
0.300	0.0385		3.18	0.148	-1.454	0.900	6.8
0.200	0.00981		3.66	0.137	-2.119	0.655	19.4
0.100	0.00299		4.07	0.115	-2.770	0.334	32.4
0.050	0.00167		4.30	0.105	-3.142	0.166	28.9
0.025	0.00097		4.48	0.088	-3.496	0.083	24.8
0.000			6.44	0.078			
T = 40 °C							
0.396	0.1270	0.2799	2.78	0.178	-0.912	0.926	2.1
0.297	0.0582		2.99		-1.261	0.822	4.1
0.205	0.0223	0.1829	3.24	0.164	-1.697	0.629	8.2
0.0967	0.00729	0.0914	3.59	0.140	-2.233	0.308	12.3
0.0484	0.00372	0.0437	3.85	0.125	-2.593	0.154	12.0
0.0240	0.00186		3.89		-2.906	0.076	11.9
0.0000			4.63	0.098			
T = 55 °C							
0.396	0.1508	0.2615	2.61	0.189	-0.833	0.844	1.6
0.205	0.0437	0.1721	2.98	0.154	-1.385	0.555	3.7
0.0967	0.0171		3.31		-1.819	0.274	4.6
0.0484	0.00796	0.0453	3.57	0.117	-2.191	0.139	5.1
0.0240	0.00429	0.0259	3.79	0.134	-2.512	0.068	4.6
0.0000			4.86	0.095			

* Extraction by diluent alone is negligible.
pH taken at 25 °C.

Succinic Acid
Alamine 336 (Various Concentrations)
Chloroform and *n*-Heptane Mixed Diluent
25 °C

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	$C_{W,org}$	log[A]	D	Z
0.29 mol/L Alamine 336 (14.7% v/v)							
1.7% (v/v) Chloroform and 83.6% (v/v) n-Heptane, i.e. 2% C/(C+H)							
0.4834	0.4778	0.0061	2.44	0.0060	-0.328	0.0117	0.0193[3]
0.29 mol/L Alamine 336 (14.7% v/v)							
3.4% (v/v) Chloroform and 81.9% (v/v) n-Heptane, i.e. 4% C/(C+H)							
0.4834	0.4738	0.0122	2.44	0.0099	-0.332	0.0203	0.0331[3]
0.3058	0.3014	0.0084	2.63	0.0169	-0.532	0.0146	0.0152[3]
0.1525	0.1492	0.0039	2.80	0.0167	-0.843	0.0221	0.0114[3]
0.29 mol/L Alamine 336 (14.7% v/v)							
8.5% (v/v) Chloroform and 76.8% (v/v) n-Heptane, i.e. 10% C/(C+H)							
0.4834	0.4468	0.0565	2.44	0.0332	-0.357	0.0819	0.1262
0.3058	0.2848	0.0176	2.63	0.0237	-0.557	0.0737	0.0724
0.1525	0.1436	0.0116	2.80	0.0187	-0.860	0.0620	0.0307
0.0515	0.0466	0.0038	3.21	0.0183	-1.374	0.1041	0.0167
0.0000	0.0000	0.0001	6.76	0.0129			0.0000
0.29 mol/L Alamine 336 (14.7% v/v)							
17.1% (v/v) Chloroform and 68.2% (v/v) n-Heptane, i.e. 20% C/(C+H)							
0.4834	0.3714	0.1428	2.46	0.0703	-0.438	0.3016	0.3862
0.3058	0.2180	0.1054	2.66	0.0255	-0.674	0.4028	0.3028
0.1525	0.1161	0.0384	2.82	0.0323	-0.953	0.3135	0.1255
0.0515	0.0386	0.0123	3.17	0.0267	-1.452	0.3329	0.0443
0.0000	0.0000	0.0003	6.55	0.0232			0.0000

[3] Third-phase formation. Z includes both organic phases.

* Extraction by diluent alone is negibile.

Succinic Acid
Alamine 336 (Various Concentrations)
Chloroform and *n*-Heptane Mixed Diluent
25 °C (Cont'd)

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	$C_{W,org}$	log[A]	D	Z
0.29 mol/L Alamine 336 (14.7% v/v)							
25.6% (v/v) Chloroform and 59.7% (v/v) n-Heptane, i.e. 30% C/(C+H)							
0.3058	0.1792	0.1373	2.70	0.0695	-0.760	0.7065	0.4366
0.1525	0.0862	0.0710	2.90	0.0514	-1.086	0.7691	0.2286
0.29 mol/L Alamine 336 (14.7% v/v)							
42.6% (v/v) Chloroform and 42.6% (v/v) n-Heptane, i.e. 50% C/(C+H)							
0.4834	0.2475	0.2751	2.55	0.1151	-0.616	0.9531	0.8134
0.29 mol/L Alamine 336 (14.7% v/v)							
59.7% (v/v) Chloroform and 25.6% (v/v) n-Heptane, i.e. 70% C/(C+H)							
0.4983	0.2214	0.2768	2.60	0.1357	-0.666	1.25	0.9548
0.3058	0.0709	0.2423	2.95	0.1272	-1.173	3.31	0.8100
0.1525	0.0147	0.1475	3.53	0.1008	-1.917	9.37	0.4752
0.0515	0.0047	0.0480	3.91	0.0911	-2.513	10.00	0.1613
0.0000	0.0000	0.0025	5.93	0.0638			
0.58 mol/L Alamine 336 (29.4% v/v)							
7.1% (v/v) Chloroform and 65.5% (v/v) n-Heptane, i.e. 10% C/(C+H)							
0.4983	0.3403	0.1192	2.58	0.0770	-0.479	0.4644	0.2724[c]
0.4073	0.2910	0.1074	2.64	0.0784	-0.548	0.3995	0.2004[c]
0.3058	0.2294	0.0796	2.74	0.0616	-0.654	0.3332	0.1318[c]
0.1993	0.1515	0.0453	2.91	0.0433	-0.841	0.3155	0.0824
0.1529	0.1218	0.0333	3.01	0.0387	-0.942	0.2559	0.0537
0.0501	0.0400	0.0109	3.77	0.0209	-1.537	0.2546	0.0175
0.0199	0.0163	0.0037	3.44	0.0313	-1.859	0.2240	0.0063
0.0000	0.0000	0.0000	6.75	0.0176			

[c] Cloudy organic phase. May indicate slight third-phase formation.

* Extraction by diluent alone neglible.
Data by Chan.

Succinic Acid
Alamine 336 (Various Concentrations)
n-Heptane
25 °C

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$ (bulk ph)	pH	$C_{W,org}$	log[A]	Z	D
0.29 mol/L Alamine 336							
0.4834	0.4824	0.0035	2.44	0.0051	-0.324	0.0021	0.0034
0.4000	0.3906	0.0027	2.47	0.0057	-0.416	0.0240	0.0323
0.3058	0.3039	0.0029	2.62	0.0080	-0.529	0.0063	0.0066
0.2000	0.1973	0.0019	2.66	0.0076	-0.717	0.0139	0.0095
0.1525	0.1514	0.0016	2.79	0.0091	-0.836	0.0073	0.0038
0.1000	0.0963	0.0011	2.85	0.0083	-1.036	0.0390	0.0129
0.0500	0.0484		3.09		-1.347	0.0322	0.0054
0.0250	0.0181		3.88		-1.914	0.3801	0.0237
0.0100	0.0089	0.0001	3.66		-2.160	0.1186	0.0037
0.0000			6.59	0.0095			
0.58 mol/L Alamine 336							
0.400	0.3513	0.00963	2.65	0.006	-0.466	0.081	0.1388
0.300	0.2819	0.00825	2.57	0.011	-0.560	0.030	0.0643
0.200	0.1830	0.00638	2.95	0.006	-0.761	0.028	0.0929
0.100	0.0915	0.00375	3.08	0.021	-1.070	0.014	0.0929
0.010	0.0081	0.00050	3.96	0.009	-2.291	0.003	0.2308
0.000			6.74	0.006			
1.16 mol/L Alamine 336							
0.400	0.2033	0.02100	2.68	0.014	-0.705	0.164	0.9680
0.200	0.1250	0.01863	2.99	0.010	-0.929	0.063	0.6000
0.100	0.0746	0.01563	3.28	0.015	-1.177	0.021	0.3400
0.010	0.0044	0.00113	4.47	0.009	-2.834	0.005	1.2727
0.000			6.83	0.008			

* Extraction by diluent alone is neglible.

Two organic phases are formed in all cases. $C_{A,org}$ is given for the upper organic phase (the bulk phase).

Succinic Acid
Alamine 336 (Various Concentrations)
Methylene Chloride (Dichloromethane)
25°C

CA,tot	CA,aq	CA,org	pH	CW,org	log(A)	Z	D
Methylene chloride only							
0.5078	0.496		2.17		-0.308		0.02
0.2994	0.291		2.48		-0.544		0.028
0.1993	0.194		2.35		-0.717		0.025
0.1013	0.0990		2.44		-1.01		0.023
0.0503	0.0500		2.86		-1.32		0.006
0.0099	0.00970		2.85		-2.03		0.025
0.29 mol/L Alamine 336							
0.4900	0.199		2.62		-0.712	0.972	1.46
0.2978	0.0325		3.13		-1.523	0.911	8.15
0.1995	0.00754		3.67		-2.235	0.662	25.5
0.1005	0.00274		4.14		-2.834	0.337	35.7
0.0515	0.00130		4.49		-3.356	0.173	38.6
0.0085	0.00030		5.05		-4.430	0.028	27.3
0.58 mol/L Alamine 336							
0.5078	0.0130	0.492	3.38	0.457	-1.948	0.853	38.2
0.2994	0.00423	0.301	3.87	0.355	-2.540	0.509	69.7
0.1993	0.00272	0.199	4.06	0.282	-2.803	0.339	72.4
0.1013	0.00177	0.103	4.35	0.214	-3.132	0.172	56.3
0.0504	0.00103	0.0510	4.47	0.193	-3.439	0.085	47.7
0.0099	0.00035	0.0108	5.00	0.157	-4.319	0.017	27.4

Z corrected using P = 0.026

Succinic Acid
Alamine 336 (Various Concentrations)
Methylene Chloride and *n*-Heptane Mixed Diluent
25 °C

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	$C_{W,org}$	log[A]	Z	D
0.097 mol/L Alamine 336, 60 vol% Dichloromethane, 35.1 vol% n-Heptane							
0.5078	0.40268	0.1020	2.16	0.0893	-0.399	1.028	0.261
0.2994	0.20197	0.1037	2.30	0.0707	-0.700	0.979	0.482
0.1993	0.11061	0.0969	2.43	0.0799	-0.964	0.902	0.802
0.1013	0.03010	0.0744	2.64	0.0734	-1.533	0.733	2.37
0.0504	0.01069	0.0403	2.92	0.0599	-1.993	0.409	3.71
0.0099	0.00166	0.0083	3.40	0.0518	-2.843	0.086	4.98
0.0000			5.53	0.0456			
0.29 mol/L Alamine 336, 59.7 vol% Dichloromethane, 25.6 vol% n-Heptane							
0.498	0.16930		2.59	0.2098	-0.782	1.13	1.94
0.498	0.17485		2.59		-0.768	1.11	1.85
0.5078	0.21195		2.19		-0.678	1.01	1.40
0.3005	0.03738		2.97	0.1986	-1.452	0.906	7.04
0.3005	0.04063		2.96		-1.415	0.894	6.40
0.2994	0.05165		2.50		-1.296	0.852	4.80
0.1995	0.01782	0.2221	3.15	0.1803	-1.786	0.626	10.2
0.10035	0.00476	0.0995	3.61	0.1242	-2.422	0.329	20.1
0.05188	0.00242	0.0569	3.88	0.0985	-2.789	0.170	20.5
0.01011	0.00058	0.0097	4.39	0.0843	-3.660	0.033	16.5
0.00000			6.28	0.0765			
0.29 mol/L Alamine 336, 17.1 vol% Dichloromethane, 68.2 vol% n-Heptane							
0.498	0.32197	0.1790	2.49	0.1045	-0.501	0.603	0.547
0.3005	0.19647	0.1012	2.62	0.0605	-0.718	0.356	0.529
0.1995	0.13387	0.0672	2.73	0.0466	-0.888	0.224	0.490
0.10035	0.06879	0.0312	2.88	0.0274	-1.183	0.108	0.459
0.05188	0.03514	0.0150	3.08	0.0186	-1.486	0.057	0.476
0.01011	0.00694	0.0033	3.58	0.0192	-2.253	0.011	0.456
0.00000			5.06	0.0167			

Succinic Acid
Alamine 336 (Various Concentrations)
Methylene Chloride and *n*-Heptane Mixed Diluent
25 °C (Cont'd)

0.58 mol/L Alamine 336, 49.4 vol% Dichloromethane, 21.1 vol% n-Heptane

0.5078	0.03519	0.4629	3.16	0.4394	-1.492	0.814	13.4
0.3005	0.01342	0.2894	3.52	0.3527	-1.955	0.495	21.4
0.1995	0.00856	0.1964	3.70	0.2612	-2.188	0.329	22.3
0.10035	0.00441	0.0998	3.97	0.1800	-2.561	0.165	21.8
0.05188	0.00279	0.0535	4.18	0.1477	-2.853	0.085	17.6
0.01011	0.00095	0.0098	4.68	0.1165	-3.664	0.016	9.6
0.00000			6.66	0.1108			

0.58 mol/L Alamine 336, 14.1 vol% Dichloromethane, 56.4 vol% n-Heptane

0.5078	0.17650	0.3267	2.56	0.2351	-0.763	0.570	1.88
0.3005	0.11390	0.1814	2.72	0.1657	-0.958	0.321	1.64
0.1995	0.07692	0.1054	2.86	0.1122	-1.133	0.211	1.59
0.10035	0.04599	0.0508	3.03	0.0713	-1.366	0.093	1.18
0.05188	0.02375	0.0239	3.27	0.0515	-1.673	0.048	1.18
0.01011	0.00513	0.0019	3.89	0.0388	-2.466	0.009	0.97
0.00000			6.22	0.0323			

* Extraction by diluent alone is negligible.
Data by Kamimura.

Succinic Acid
Alamine 336 (Various Concentrations)
Methyl Isobutyl Ketone (4-Methyl-2-Propanone)
25 °C

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$*	pH	$C_{W,org}$	log[A]	Z	D
No Alamine 336							
			(calc)				
0.200	0.1680	0.0320	2.49		-0.775		0.190
0.100	0.0838	0.0162	2.64		-1.089		0.199
0.050	0.0428	0.0073	2.79		-1.386		0.176
0.050	0.0408	0.0092	2.80		-1.406		0.235
0.020	0.0169	0.0031	3.00		-1.799		0.195
0.048 mol/L Alamine 336							
			(calc)				
0.400	0.2838	0.1162	2.38		-0.547	1.267	0.409
0.300	0.2020	0.0980	2.45		-0.702	1.233	0.485
0.200	0.1298	0.0702	2.55		-0.896	0.944	0.541
0.150	0.0835	0.0665	2.65		-1.090	1.051	0.796
0.100	0.0574	0.0426	2.73		-1.256	0.659	0.742
0.050	0.0247	0.0253	2.91		-1.629	0.430	0.973
0.050	0.0260	0.0240	2.90		-1.606	0.398	0.923
0.025	0.0119	0.0131	3.08		-1.956	0.227	1.101
0.072 mol/L Alamine 336							
			(calc)				
0.300	0.1820	0.1180	2.47		-0.748	1.157	0.65
0.200	0.1106	0.0894	2.58		-0.967	0.949	0.81
0.100	0.0451	0.0550	2.78		-1.363	0.644	1.22
0.050	0.0198	0.0302	2.96		-1.728	0.368	1.53
0.025	0.0094	0.0156	3.13		-2.065	0.193	1.67
0.145 mol/L Alamine 336							
			(calc)				
0.400	0.1901	0.2099	2.46		-0.729	1.212	1.10
0.300	0.1238	0.1763	2.56		-0.917	1.063	1.42
0.200	0.0694	0.1306	2.69		-1.172	0.816	1.88
0.100	0.0265	0.0735	2.90		-1.598	0.475	2.77
0.050	0.0132	0.0368	3.06		-1.910	0.239	2.79
0.025	0.0069	0.0181	3.20		-2.206	0.117	2.65

* P = 0.192 used in calculation of Z.
$C_{A,org}$* for this set of runs is $C_{A,tot}$-$C_{A,aq}$.

(calc) indicates pH was predicted from pK_A and $C_{A,aq}$ and Eq. D-1.
(expt) indicates pH value was determined experimentally.

Succinic Acid
Alamine 336 (Various Concentrations)
Methyl Isobutyl Ketone (4-Methyl-2-Propanone)
25 °C (continued)

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$*	pH	$C_{W,org}$	log[A]	Z	D
0.099 mol/L Alamine 336							
			(calc)				
0.303	0.1680	0.1350	2.49		-0.783	1.045	0.80
0.200	0.0916	0.1084	2.62		-1.050	0.921	1.18
0.152	0.0646	0.0874	2.70		-1.203	0.760	1.35
0.100	0.0368	0.0632	2.83		-1.452	0.569	1.72
0.052	0.0166	0.0354	3.00		-1.807	0.326	2.13
0.025	0.0072	0.0178	3.19		-2.183	0.167	2.47
0.193 mol/L Alamine 336							
			(calc)				
0.300	0.0957	0.2043	2.62		-1.030	0.972	2.13
0.200	0.0557	0.1443	2.73		-1.269	0.697	2.59
0.150	0.0385	0.1115	2.82		-1.432	0.543	2.90
0.100	0.0238	0.0762	2.92		-1.646	0.374	3.20
0.050	0.0103	0.0397	3.11		-2.021	0.197	3.85
0.050	0.0099	0.0401	3.12		-2.038	0.199	4.04
0.025	0.0064	0.0186	3.22		-2.240	0.091	2.93
0.290 mol/L Alamine 336							
			(expt)				
0.500a	0.3067	0.4645	2.47		-0.521	1.432	1.51
0.400	0.0949	0.3051					3.22
0.400	0.0946	0.3054	2.95	1.181	-1.048	1.002	3.23
0.300	0.0576	0.2425					4.21
0.300	0.0584	0.2416	3.09	1.052	-1.266	0.803	4.14
0.200	0.0351	0.1649					4.70
0.200	0.0353	0.1647	3.29	0.916	-1.503	0.550	4.67
0.100	0.0175	0.0826					4.73
0.100	0.0173	0.0827	3.60	0.618	-1.860	0.277	4.78
0.050	0.0099	0.0401					4.04
0.050	0.0100	0.0400	3.75		-2.135	0.134	4.02
0.025	0.0053	0.0197	4.06		-2.519	0.066	3.73
0.010	0.0028	0.0072	4.69	0.560	-3.199	0.024	2.53
0.000				0.631			

a 1:2 O:A phase ratio used.
* P = 0.192 used in calculation of Z.
$C_{A,org}$* for this set of runs is $C_{A,tot}$-$C_{A,aq}$.

(calc) indicates pH was predicted from pK_A and $C_{A,aq}$ and Eq. D-1.
(expt) indicates pH value was determined experimentally.

Succinic Acid
Alamine 336 (Various Concentrations)
Methyl Isobutyl Ketone (4-Methyl-2-Propanone)
25 °C (continued)

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$*	pH	$C_{W,org}$	log[A]	Z	D
0.396 mol/L Alamine 336							
0.381	0.0580	0.3230				0.792	5.57
0.303	0.0440	0.2590				0.636	5.89
0.250	0.0366	0.2134				0.524	5.83
0.225	0.0343	0.1907				0.468	5.56
0.191	0.0260	0.1650				0.406	6.35
0.175	0.0263	0.1487				0.365	5.65
0.152	0.0220	0.1300				0.319	5.91
0.095	0.0150	0.0803				0.197	5.35
0.048	0.0086	0.0390				0.095	4.53
0.024	0.0048	0.0190				0.046	3.96
0.579 mol/L Alamine 336							
			(expt)				
0.400	0.0444	0.3556	3.14	1.049	-1.389	0.603	8.01
0.300	0.0349	0.2651				0.449	7.60
0.300	0.0344	0.2657	3.25	0.782	-1.510	0.451	7.73
0.200	0.0245	0.1755				0.297	7.16
0.200	0.0249	0.1752	3.51	0.681	-1.686	0.297	7.05
0.150	0.0212	0.1288				0.217	6.08
0.100	0.0151	0.0849				0.143	5.62
0.100	0.0155	0.0845	3.72	0.521	-1.935	0.142	5.45
0.050	0.0091	0.0409				0.069	4.52
0.050	0.0093	0.0408	4.09		-2.289	0.068	4.41
0.050	0.0090	0.0410				0.069	4.53
0.025	0.0054	0.0196	4.31		-2.637	0.033	3.61
0.020	0.0047	0.0153				0.025	3.26
0.010	0.0032	0.0068	4.53	0.356	-3.019	0.011	2.15
0.000			6.44	0.372			

* P = 0.192 used in calculation of Z.
$C_{A,org}$* for this set of runs is $C_{A,tot}$-$C_{A,aq}$.

(calc) indicates pH was predicted from pK_A and $C_{A,aq}$ and Eq. D-1.
(expt) indicates pH value was determined experimentally.

Succinic Acid
Alamine 336 (Various Concentrations)
Methyl Isobutyl Ketone (4-Methyl-2-Propanone)
25 °C (continued)

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$*	pH	$C_{W,org}$	log[A]	Z	D
0.97 mol/L Alamine 336							
0.400	0.0383	0.3617				0.371	9.44
0.300	0.0337	0.2663				0.272	7.90
0.300	0.0324	0.2676				0.274	8.26
0.200	0.0283	0.1717				0.175	6.07
0.200	0.0269	0.1732				0.177	6.45
0.150	0.0229	0.1271				0.129	5.55
0.100	0.0191	0.0809				0.082	4.22
0.100	0.0180	0.0820				0.083	4.56
0.050	0.0109	0.0391				0.039	3.59
0.050	0.0114	0.0386				0.039	3.37
0.025	0.0073	0.0177				0.018	2.43
1.16 mol/L Alamine 336							
			(expt)				
0.400	0.0471	0.3529	3.10	0.735	-1.360	0.301[c]	7.49
0.300	0.0343	0.2658	3.50	0.329	-1.545	0.227[c]	7.76
0.200	0.0288	0.1712	3.62	0.369	-1.642	0.146[c]	5.94
0.050	0.0122	0.0378	4.33		-2.297	0.032[c]	3.09
0.025	0.0071	0.0179	4.44		-2.602	0.015[c]	2.50
0.010	0.0043	0.0058	4.69	0.213	-3.022	0.005[c]	1.35
0.000			6.44	0.166			

[c] Slight cloudiness between phases -- may indicate third phase formation.

* P = 0.192 used in calculation of Z.
$C_{A,org}$* for this set of runs is $C_{A,tot}$-$C_{A,aq}$.

(calc) indicates pH was predicted from pK_A and $C_{A,aq}$ and Eq. D-1.
(expt) indicates pH value was determined experimentally.

Succinic Acid
Alamine 336 (0.29 mol/L)
Methyl Isobutyl Ketone
0, 25, 50, and 75 °C

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	$C_{W,org}$	log[A]	Z	D
T = 0 °C							
No Alamine 336							
0.400	0.2634	0.0710	2.39		-0.585		0.269
0.200	0.1554	0.0464	2.51		-0.816		0.299
0.100	0.0784	0.0218	2.68		-1.116		0.278
0.050	0.0393	0.0106	2.84		-1.421		0.269
0.010	0.0081	0.0019	3.17		-2.126		0.234
0.000			3.47				
0.29 mol/L Alamine 336							
0.490	0.1972		2.59		-0.714	1.353	2.22
0.400	0.0576		3.27		-1.280	1.138	5.94
0.300	0.0269		3.50		-1.636	0.923	10.14
0.200	0.0123		3.84		-2.046	0.640	15.31
0.100	0.0064		4.07		-2.407	0.320	14.72
0.050	0.0036		4.36		-2.791	0.159	12.77
0.025	0.0026		4.61		-3.108	0.077	8.72
0.010	0.0012		4.79		-3.584	0.030	7.31
0.000			5.23				
T = 25 °C							
No Alamine 336							
0.200	0.1680				-0.775		0.190
0.100	0.0838				-1.077		0.193
0.050	0.0428				-1.369		0.170
0.050	0.0408				-1.389		0.225
0.020	0.0169				-1.772		0.183

* P = 0.280 used in calculation of Z at 0 °C.
pH taken at 0 °C; pK_{A1} = 4.285, pK_{A2} = 5.674 used to calculate [A].

Succinic Acid
Alamine 336 (0.29 mol/L)
Methyl Isobutyl Ketone
0, 25, 50, and 75 °C (Cont'd)

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	$C_{W,org}$	log[A]	Z	D
T = 25 °C (Cont'd)							
0.29 mol/L Alamine							
		(calc)					
0.500a	0.3067	0.4645	2.47		-0.521	1.432	1.51
0.400	0.0946	0.3054	2.95		-1.047	1.002	3.23
0.300	0.0584	0.2416	3.09		-1.266	0.803	4.14
0.200	0.0353	0.1647	3.29		-1.502	0.550	4.67
0.100	0.0173	0.0827	3.60		-1.859	0.277	4.78
0.050	0.0100	0.0400	3.76		-2.136	0.134	4.02
0.025	0.0053	0.0197	4.06		-2.516	0.066	3.73
0.010	0.0028	0.0072	4.69		-3.191	0.024	2.53
0.000			5.28				

a 1:2 O:A phase ratio.
* P = 0.192 used to calculate Z at 25 °C.
pK_{A1} = 4.206, pK_{A2} = 5.640 at 25 °C.

T = 50 °C

No Alamine 336

0.299	0.2590	0.0404	2.60		-0.598		0.156
0.199	0.1682	0.0263	2.69		-0.788		0.157
0.101	0.0865	0.0133	2.79		-1.080		0.154
0.050	0.0427	0.0056	2.86		-1.390		0.131
0.010	0.0086	0.0009	3.22		-2.112		0.103
0.000	0.0002		3.99				

0.29 mol/L Alamine 336

0.400	0.1509		2.73		-0.836	0.793	1.65
0.300	0.1091		2.83		-0.981	0.611	1.75
0.200	0.0689		2.99		-1.189	0.423	1.90
0.100	0.0356		3.23		-1.494	0.207	1.81
0.050	0.0185		3.46		-1.807	0.101	1.70
0.025	0.0096		3.73		-2.151	0.050	1.62
0.010	0.0040		4.05		-2.639	0.020	1.49
0.000							

* P = 0.155 used in calculation of Z at 50 °C.
pH taken at 50 °C; pKA1 = 4.186, pKA2 = 5.680 used to calculate [A].

Succinic Acid
Alamine 336 (0.29 mol/L)
Methyl Isobutyl Ketone
0, 25, 50, and 75 °C (Cont'd)

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	$C_{W,org}$	log[A]	Z	D
T = 75 °C							
No Alamine 336							
0.486	0.4059	0.0588	2.33		-0.398		0.145
0.294	0.2418	0.0326	2.45		-0.625		0.135
0.196	0.1600	0.0238	2.55		-0.806		0.149
0.098	0.0786	0.0112	2.70		-1.119		0.142
0.049	0.0390	0.0057	2.86		-1.429		0.145
0.010	0.0084	0.0007	3.19		-2.119		0.079
0.000	0.0004	0.0017	3.86				
0.29 mol/L Alamine 336							
0.486	0.2709		2.51		-0.577	0.628	0.794
0.294	0.1585		2.67		-0.814	0.401	0.855
0.196	0.1079		2.81		-0.987	0.260	0.817
0.0981	0.0560		3.01		-1.283	0.123	0.753
0.0488	0.0264		3.26		-1.631	0.067	0.848
0.0098	0.0047		3.93		-2.535	0.016	1.081
0.0000			5.82				

* P = 0.147 used in in calcultion of Z at 75 °C.
pH taken at 25 °C.

Succinic acid
Alamine 336 (Various Concentrations)
Nitrobenzene
25 °C

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	$C_{W,org}$	log[A]	Z	D
No Alamine 336							
0.4996	0.4985		2.31	0.165	-0.308		0.0022
0.2994	0.2976		2.44	0.169	-0.534		0.0062
0.1013	0.1012		2.69	0.170	-1.008		0.0010
0.0099	0.0099		3.17	0.162	-2.045		0.0089
0.0966 mol/L Alamine 336							
0.508	0.396		2.67		-0.415	1.15	0.284
0.299	0.197		2.68		-0.718	1.05	0.520
0.199	0.105		2.86		-0.999	0.973	0.900
0.150	0.0562		2.97	0.253	-1.276	0.970	1.67
0.100	0.0196		3.29	0.237	-1.758	0.832	4.10
0.0750	0.0094		3.52	0.233	-2.112	0.679	7.01
0.0504	0.0048		3.82		-2.475	0.472	9.56
0.0099	0.0011		4.53		-3.496	0.092	8.38
0.0000			6.28				
0.29 mol/L Alamine 336							
0.508	0.186	0.319	2.74	0.424	-0.745	1.11	1.73
0.299	0.0357	0.264	3.23	0.419	-1.492	0.909	7.40
0.199	0.0101	0.188	3.78	0.363	-2.140	0.653	18.8
0.101	0.0040	0.0973	4.24	0.270	-2.735	0.336	24.6
0.0504	0.0024	0.0513	4.45	0.229	-3.079	0.165	19.8
0.0099	0.0010	0.00976	5.03	0.188	-3.999	0.031	9.35
0.0000				0.176			

Succinic Acid
Alamine 336 (Various Concentrations)
1-Octanol
25 °C

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	$C_{W,org}$	log[A]	Z	D
No Alamine 336							
0.4895	0.409	0.1026	2.32		-0.39		0.251
0.2953	0.242	0.0531	2.46		-0.62		0.219
0.1962	0.158	0.0405	2.56		-0.81		0.257
0.0992	0.0807	0.0177	2.71		-1.11		0.219
0.0492	0.0403	0.0111	2.87		-1.41		0.275
0.0256	0.0205	0.0054	3.01		-1.72		0.263
0.0104	0.00855	0.0025	3.23		-2.11		0.288
0.145 mol/L Alamine 336 in Octanol							
0.4895	0.32600	0.18914	2.43	2.359	-0.49	0.853	0.58
0.2953	0.13760	0.15521	2.64		-0.87	0.883	1.13
0.1962	0.06760	0.12207	2.79		-1.19	0.751	1.81
0.0992	0.01820	0.07421	3.14	2.121	-1.78	0.489	4.08
0.0492	0.00544	0.03916	3.46	2.034	-2.34	0.264	7.20
0.0256	0.00150	0.02139	3.94	1.916	-3.02	0.146	14.26
0.0104	0.00048	0.00567	4.72	1.756	-4.00	0.039	11.89
0.0000			6.27	1.803			
0.29 mol/L Alamine 336 in Octanol							
0.4860	0.08663	0.28799	2.62	2.394	-1.07	0.940	3.32
0.2940	0.05508	0.21940	2.92	2.329	-1.28	0.724	3.98
0.1960	0.01700	0.15985	3.31	2.225	-1.82	0.542	9.40
0.0981	0.00275	0.09059	4.02	2.052	-2.79	0.312	32.94
0.0488	0.00104	0.04626	4.54	1.874	-3.51	0.159	44.59
0.0098	0.00036	0.00889	5.32	1.640	-4.77	0.031	24.85
0.0000				1.330			

* P = 0.264 used in calculation of Z.
Data by Tong and Tamada.

Succinic Acid
Alamine 336 (0.29 mol/L)
40% (v/v) 1-Octanol and 45% (v/v) Chloroform
25 °C

$C_{A,tot}$	$C_{A,aq}$	$C_{A,org}$	pH	$C_{W,org}$	log[A]	Z	D
0.29 mol/L Alamine 336 (14.9 vol%)							
0.4985	0.1803	0.3214	2.57	0.634	-0.75	1.033	1.76
0.2953	0.04135	0.2586	2.98	0.619	-1.41	0.861	6.14
0.1962	0.01072	0.1884	3.42	0.604	-2.04	0.636	17.30
0.0992	0.00224	0.0988	4.08	0.543	-2.90	0.334	43.29
0.0492	0.00097	0.0486	4.49	0.507	-3.50	0.166	49.62
0.0258	0.00055	0.0273	4.80	0.474	-4.01	0.087	45.84
0.0104	0.00064	0.0108	5.15	0.457	-4.31	0.034	15.27
0.0000			6.55	0.446			

* Value of P = 0.264 used in calculation of Z.

APPENDIX B. NUMERICAL METHODS FOR DETERMINATION OF EQUILIBRIUM CONSTANTS

A computer program was developed to minimize the error between the experimental data points and points calculated from the mass-action law equations (Eqs. 2-3 to 2-5) . The program uses a Newton-Raphson multivariable minimization routine. The data inputs were the undissociated aqueous acid concentration, total amine concentration, and organic-phase acid concentration, taken either as the difference between initial and equilibrium acid concentrations or, when available, the experimental organic-acid concentration (corrected for physical extraction). Sets of stoichiometries of the complex(es) formed were postulated, and the minimization routine was performed for each set of stoichiometries to determine the corresponding best-fit equilibrium constants and the total error.

The minimization parameter used was the sum of the absolute value of $(Z_{pred}-Z_{expt})/Z_{expt}$ where the subscript "pred" denotes the value predicted by the mass-action law equations, and the subscript "expt" denotes the experimentally-determined value. Equilibrium constants obtained using this parameter are given in Table B-1 under the Method 1 column. This parameter was examined on the assumption that the relative (percentage) error in the organic-phase acid concentration, $C_{A,org}$, was constant for the measurements within each data set. Experimentally, an effort was made to vary the sample volume and titrant concentrations so as to maintain approximately the same relative error in all cases. The percent material balance non-closure was relatively constant over the entire acid concentration range for a given system, except at very low acid concentrations. This result tends to bear out the assumption, because the organic-phase acid concentration measurements were generally greater sources of error than the aqueous-phase acid

concentration measurements. The low concentration points were removed from the data-fitting procedure if they showed a large experimental material balance error and did not fit with the rest of the data. Values which were omitted from fitting are indicated in Table B-1.

On occasion, an alternate parameter was minimized, the sum of the squares of

$$\log \frac{(D_{expt} + 1)}{(D_{pred} + 1)} \tag{B-1}$$

Equilibrium constants derived using this parameter are shown in the Method 2 column of Table B-1. This parameter was examined on the assumption that the relative error in the aqueous-phase acid measurements is constant. Therefore,

$$\log \frac{(C_{A,aq\ pred})}{(C_{A,aq\ expt})} \tag{B-2}$$

would weight each point according to its approximate experimental accuracy. From the definition of distribution ratio and the fact that the initial solute concentration $C_{A,tot}$ is equal to $C_{A,aq} + C_{A,org}$, it is easily shown that

$$C_{A,aq} = \frac{C_{A,tot}}{(D + 1)} \tag{B-3}$$

From this, the parameter for least-squares minimization is derived, assuming that $C_{A,tot}$ is known exactly.

The Method 2 parameter was not used for the majority of the data fitting because the undissociated acid concentration rather than the aqueous acid

concentration was used as the data input. Thus, the modified *D* (see Appendix C) tended to weight the low concentration points too heavily. However, this method gave faster computation of the error minimization, and proved more convenient for rapid estimations. In most cases the choice of minimization procedure had little impact upon the value of the equilibrium constants obtained from the programs, especially if there were many data points or the data fit a postulated stoichiometry closely.

Table B-1 compares the errors calculated for the various assumed sets of stoichiometries for data collected in this work. The table shows the set of stoichiometries (p,q,r are stoichiometric coefficients of acid, amine, and diluent, respectively) of the model that was postulated and the corresponding error by Method 1 and Method 2, normalized by the total number of data points. The asterisk indicates the value that was used in discussions in this work.

Table B-2 shows similar results for data from other workers which were used in the analyses of this work. The symbol "#" indicates Method 2 was used to calculated the results; otherwise, Method 1 was used. The published data of Chaikhorskii et al. (1966) and Vanura and Kuca (1976) were entered into the minimization program used in this work, so as to compare the results of previous workers with those obtained in this work. The values obtained in this work were quite close to those of the published works, despite the use of different computer routines and different minimization parameters. Table B-2 shows the published values of the equilibrium constants compared to the results calculated in this work.

Table B-1
Numerical Results of Models

- All experiments done at 25 °C unless noted otherwise
- N_T = total number of data points
* indicates value deemed most appropriate

System	Model (p,q,r)	Method 1: $\log\frac{(D_{expt}+1)}{(D_{pred}+1)}$ $\log(\beta_{pqr})$	error	Method 2: $\frac{\Delta Z}{Z_{pred}}$ $\log(\beta_{pqr})$	error
SUCCINIC ACID					
METHYL ISOBUTYL KETONE					
- Low amine concentration					
Alamine 336: 0.0483, 0.0725, 0.0995, 0.145, 0.193, 0.290 mol/L					
N_T = 40	2,1,0	1.96	0.008	1.91	0.076 *
	1,1,0	1.39		1.39	
	1,1,0	1.45	0.018		
- Effect of temperature					
Alamine 336: 0.29 mol/L					
75°C	2,1,0	-0.74	0.014	0.55	0.127 *
N_T = 6	1,1,0	0.55		0.46	
50°C	2,1,0	1.29	0.003	1.33	0.048 *
N_T = 7	1,1,0	0.87		0.85	
25°C	2,1,0	2.01	0.019	2.10	0.097 *
N_T = 8	1,1,0	1.42		1.35	
0°C	2,1,0	2.97	0.005	2.92	0.059 *
N_T = 8	1,1,0	2.06		2.06	
- Full amine concentration range					
Alamine 336: 0.048, 0.073, 0.099, 0.15, 0.19, 0.29, 0.58, 1.16 mol/L					
N_T = 53	2,1,1	1.28	0.012	1.08	0.101
	1,1,2	-0.33		-0.34	

Table B-1 (Cont'd)

System	Model (p,q,r)	Method 1 $\log(\beta_{pqr})$	Method 1 error	Method 2 $\log(\beta_{pqr})$	Method 2 error
SUCCINIC ACID METHYL ISOBUTYL KETONE (Cont'd)					
- Full amine conentration range, weighted toward high concentrations. Alamine 336: 0.145, 0.290, 0.579, 1.159 mol/L					
N_T = 27	2,1,1	1.35	0.017	1.34	0.108 *
	1,1,2	-0.32		-0.35	
	2,1,2			0.49	0.142
	1,1,2			-0.34	
	2,1,2			0.63	0.159
	1,1,1			0.36	
	2,1,1	1.28	0.044	1.18	0.172
	1,1,1	0.39		0.38	
	2,1,1			1.43	0.169
	1,1,3			-1.13	
SUCCINIC ACID CHLOROFORM					
- Low amine concentration Alamine 336: 0.05, 0.099, 0.195, 0.29, 0.58 mol/L					
N_T = 30	2,1,0	1.19	0.008	1.49	0.059 *
	1,1,0	2.42		2.44	
	1,1,0	2.42	0.008	2.44	0.060
- Effect of Temperature Alamine 336: 0.29 mol/L					
0°C N_T = 6	1,1,0	3.64	0.026	3.60	0.139 *
25°C N_T = 6	1,1,0	2.45	0.000	2.45	0.017 *
40°C N_T = 6	1,1,0	1.85	0.002	1.85	0.041 *

Table B-1 (Cont'd)

System	Model (p,q,r)	Method 1 $\log(\beta_{pqr})$	Method 1 error	Method 2 $\log(\beta_{pqr})$	Method 2 error
SUCCINIC ACID					
CHLOROFORM (Cont'd)					
- Effect of Temperature (Cont'd)					
55°C	1,1,0	1.40	0.002	1.40	0.037 *
N_T = 6					
	1,1,0	1.39	0.001		
	2,1,0	1.26			
- Full amine concentration range					
Alamine 336: 0.05, 0.097, 0.19, 0.29, 0.58, 0.77, 1.16, 1.55 mol/L					
N_T = 42	1,1,1	1.28	0.111	1.22	0.278
	1,1,2	0.52	0.023	0.54	0.126
	1,1,3	-0.19	0.147	-0.32	0.282
- Full amine concentration range, weighted toward higher concentration.					
Alamine 336: 0.0966, 0.58, 0.772, 1.159, 1.546 mol/L					
N_T = 30	1,1,1			1.19	0.317
	1,1,2			0.54	0.103 *
	1,1,3			-0.29	0.271
- Each amine concentration modeled separately.					
Alamine 336: 0.772 mol/L					
N_T = 6	1,1,0	2.24	0.009	2.22	0.079
Alamine 336: 1.159 mol/L					
N_T = 6	1,1,0	1.90	0.013	1.88	0.085
Alamine 336: 1.546 mol/L					
N_T = 6	1,1,0	1.28	0.031	1.23	0.149

Table B-1 (Cont'd)

System	Model (p,q,r)	Method 1 $\log(\beta_{pqr})$	Method 1 error	Method 2 $\log(\beta_{pqr})$	Method 2 error
SUCCINC ACID NITROBENZENE					
- Alamine 336: 0.966, 0.29 mol/L					
N_T = 14	2,1,0	2.17	0.003	2.16	0.039 *
	1,1,0	2.46		2.43	
SUCCINIC ACID METHYLENE CHLORIDE					
- Alamine 336: 0.29, 0.58 mol/L					
N_T = 12	1,1,0	2.60	0.061	2.54	0.123 *
SUCCINIC ACID 1-OCTANOL					
- Only one concentration considered Alamine 336: 0.29 mol/L					
N_T = 6	1,1,0			2.46	0.346
	1,2,0			3.52	0.143
	1,1,0			2.09	
	1,2,0			3.65	0.102
	2,2,0			5.08	
	1,2,0			3.67	0.092 *
	2,2,0			4.97	
	2,1,0			2.78	
	1,2,0			3.56	0.096
	1,1,0			1.93	
	2,1,0			2.80	

Table B-1 (Cont'd)

System	Model (p,q,r)	Method 1 log(β_{pqr})	Method 1 error	Method 2 log(β_{pqr})	Method 2 error
SUCCINIC ACID					
1-OCTANOL (Cont'd)					
- Using $C_{A,org} = C_{A,tot} - C_{A,aq}$					
Alamine 336: 0.145, 0.29 mol/L					
N_T = 13	1,2,0	3.80	0.040	3.75	0.194 *
	2,2,0	5.25		5.17	
	1,2,0	3.74	0.063		
	1,1,0	2.07			
	1,2,0	3.81	0.051		
	2,1,0	3.05			
	1,2,0	3.80	0.051		
	1,1,0	1.16			
	2,1,0	3.01			
	1,2,0	3.80	0.040		
	2,2,0	5.20			
	2,1,0	2.17			
- Using $C_{A,org}$ determined by titration					
Alamine 336: 0.145, 0.29 mol/L					
N_T = 13	1,2,0	3.66	0.049	3.50	0.141 *
	2,2,0	4.94		4.91	
	1,2,0	3.62	0.068		
	1,1,0	1.83			
	1,2,0			3.50	0.141
	2,2,0			4.93	
	2,1,0			-10.00	
	1,2,0				
	1,1,0				
	2,1,0				
	1,2,0	3.67	0.044		
	3,3,0	8.07			
	1,2,0	3.67	0.042	3.50	0.125
	4,4,0	11.24		11.05	

Table B-1 (Cont'd)

System	Model (p,q,r)	Method 1 $\log(\beta_{pqr})$	Method 1 error	Method 2 $\log(\beta_{pqr})$	Method 2 error
SUCCINIC ACID					
1-OCTANOL (Cont'd)					
	1,2,0	3.76	0.042		
	5,5,0	14.44			
	1,2,0	3.67	0.042		
	6,6,0	17.66			
	1,2,0	3.65	0.073		
	2,3,0	6.55			
	1,2,0	3.67	0.046		
	5,6,0	16.42			
	1,2,0	3.67	0.042		
	6,6,0	17.66			
	2,1,0	< -6			
SUCCINIC ACID					
40% OCTANOL AND CHLOROFORM					
- Alamine 336: 0.29					
N_T = 7	1,1,0	2.85	0.044	2.80	0.182
	1,2,0	3.33	0.009	3.26	0.067 *
	1,1,0	2.46		2.42	
	2,1,0			2.20	0.075
	1,1,0			2.80	
	1,2,0			3.57	0.075
	2,2,0			5.60	
	1,2,0			3.61	0.284

Table B-1 (Cont'd)

System	Model (p,q,r)	Method 1 $\log(\beta_{pqr})$	Method 1 error	Method 2 $\log(\beta_{pqr})$	Method 2 error	
SUCCINIC ACID						
CHLOROFORM (ACTIVE) AND HEPTANE (INERT)						
- Effect of vol% active diluent as % of diluent Alamine 336: 0.29 mol/L						
0% Active N_T = 7	1,1,0	-0.88	0.002	-2.13	0.727	*
2% Active N_T = 1		-1.36	-	-1.36	-	*
4% Active N_T = 3		-1.15	0.000	-1.12	0.158	*
10% Active N_T = 4		-0.52	0.000	-0.50	0.096	*
20% Active N_T = 4		0.15	0.003	0.13	0.191	*
30% Active N_T = 2		0.61	0.001	0.58	0.062	*
50% Active N_T = 1		1.33	-	1.33	-	*
70% Active N_T = 4		1.84		1.81	0.051	*
- 10, 20, 70, 100% chloroform, include diluent in complex Alamine 336: 0.29 mol/L						
N_T = 18	1,1,2			-0.45	0.431	
	1,1,3			-0.63	0.199	*
	1,1,4			-1.53	0.414	
SUCCINIC ACID						
METHYLENE CHLORIDE (ACTIVE) AND HEPTANE (INERT)						
- 20, 70, and 100 vol% active, include diluent into complex Alamine 336: 0.58						
N_T = 18	1,1,2			0.26	0.394	
	1,1,3			-0.32	0.231	*
	1,1,4			-1.17	0.384	

Table B-1 (Cont'd)

System	Model (p,q,r)	Method 1 $\log(\beta_{pqr})$	Method 1 error	Method 2 $\log(\beta_{pqr})$	Method 2 error
MALONIC ACID					
METHYL ISOBUTYL KETONE					
- Using $C_{A,org} = C_{A,tot} - C_{A,aq}$					
Alamine 336: 0.048, 0.29, 0.58 mol/L (CALCULATED)					
N_T = 21	2,1,0	3.37	0.061		
	1,1,0	3.21			
- Using CA,org determined from titration					
Alamine 336: 0.048, 0.29, 0.58 mol/L					
N_T = 21	2,1,0	3.34	0.059	3.25	0.090 *
	1,1,0	3.20		3.11	
- Full amine concentration range					
Alamine 336: 0.048, 0.29, 0.579, 1.16 mol/L					
N_T = 24	2,1,1			2.49	0.170
	1,1,2			1.56	
	2,1,2			1.68	0.156 *
	1,1,2			1.56	
	2,1,2			1.60	0.211
	1,1,1			2.71	
	2,1,1			2.41	0.214
	1,1,1			2.27	
	2,1,2			1.78	0.226
	1,1,3			0.87	
	2,1,3			0.80	0.219
	1,1,1			2.27	
	1,1,0			1.89	0.166
	1,1,2			1.54	
	2,1,1			2.49	
	2,2,0			6.04	0.392
	2,1,0			2.88	

Table B-1 (Cont'd)

System	Model (p,q,r)	Method 1 $\log(\beta_{pqr})$	Method 1 error	Method 2 $\log(\beta_{pqr})$	Method 2 error
MALONIC ACID					
METHYL ISOBUTYL KETONE					
- Full amine concentration range (cont'd).					
	1,1,0			2.52	0.314
	2,1,0			2.86	
	2,2,0			5.54	
	1,1,0			2.62	0.328
	1,2,0			-6.74	
	2,1,0			2.79	
	2,1,3			0.90	0.159
	1,1,2			1.56	
LACTIC ACID					
CHLOROFORM					
- Alamine 336: 0.29 mol/L					
N_T = 7	2,1,0	2.22		2.20	0.100
	1,1,0	2.72		2.57	
- Removed lowest acid concentration point, which did not fit rest of data					
Alamine 336: 0.29 mol/L					
N_T = 6	2,1,0	2.10	0.002	2.14	0.035
	1,1,0	2.54		2.50	
- Effect of Temperature					
Alamine 336: 0.29 mol/L					
0°C	2,1,0	2.84	0.062	2.75	0.116
N_T = 8	1,1,0	3.56		3.37	
25°C	2,1,0	2.16	0.035	2.12	0.093 *
N_T = 14	1,1,0	2.71		2.57	
55°C	2,1,0	1.15	0.015	1.38	0.067
N_T = 8	1,1,0	1.82		1.74	

Table B-1 (Cont'd)

System	Model (p,q,r)	Method 1 log(β_{pqr})	Method 1 error	Method 2 log(β_{pqr})	Method 2 error
LACTIC ACID					
METHYL ISOBUTYL KETONE					
- Effect of temperature					
Alamine 336: 0.29 mol/L					
0°C	3,1,0	2.14	0.289	1.51	0.169 *
N_T = 10	2,1,0	-16.63		1.75	
	1,1,0	2.01		1.68	
	2,1,0	2.05	0.292	2.05	0.182
	1,1,0	2.01		1.67	
25°C	3,1,0	1.63	0.059	1.17	0.115 *
N_T = 7	2,1,0	-5.78		1.52	
	1,1,0	1.55		1.31	
	2,1,0	1.45	0.063	1.70	0.130
	1,1,0	1.54		1.29	
50°C	3,1,0	1.43		0.82	0.189 *
N_T = 6	2,1,0	-11.97		0.11	
	1,1,0	1.79		1.12	
	2,1,0	-6.78	0.244	1.24	0.222
	1,1,0	1.79		1.10	
75°C	3,1,0	0.81	0.002	0.59	0.038 *
N_T = 6	2,1,0	0.43		0.75	
	1,1,0	0.73		0.67	
	2,1,0	0.82	0.003	0.93	0.088
	1,1,0	0.71		0.65	

Table B-1 (Cont'd)

System	Model (p,q,r)	Method 1 $\log(\beta_{pqr})$	Method 1 error	Method 2 $\log(\beta_{pqr})$	Method 2 error
ACETIC ACID					
15% (VOL% of TOTAL SOLVENT) CHLOROFORM IN HEPTANE					
- Alamine 336: 0.0966, 0.29, 0.58 mol/L					
N_T = 21	3,1,0	0.20	0.005	-0.21	0.148 *
	2,1,0	-11.45		0.02	
	1,1,0	0.23		0.11	
	2,1,0	0.13	0.007	0.23	0.181
	1,1,0	0.20		0.05	
	3,1,0	0.20	0.005	0.18	0.163
	1,1,0	0.23		0.18	
ACETIC ACID					
NITROBENZENE					
- Alamine 336: 0.29 mol/L					
N_T = 7	2,1,0	1.84	0.006		
	1,1,0	0.93			
	3,1,0	2.12	0.003	1.55	0.058 *
	2,1,0	1.61		1.82	
	1,1,0	0.96		0.86	
MALEIC ACID					
CHLOROFORM					
- Alamine 336: 0.29, 0.58 mol/L					
N_T = 23	2,1,0	5.83	0.060	5.72	0.188 *
	1,1,0	6.00		6.00	
	2,2,0	13.29	0.254	12.81	0.259
	2,1,0	6.32		5.91	
	2,1,0	5.96	0.054	5.77	0.174
	2,2,0	12.10		12.27	
	1,1,0	5.92		5.76	

Table B-1 (Cont'd)

System	Model (p,q,r)	Method 1 $\log(\beta_{pqr})$	error	Method 2 $\log(\beta_{pqr})$	error
MALEIC ACID					
METHYL ISOBUTYL KETONE					
- Alamine 336: 0.145, 0.29 mol/L					
N_T = 16	2,1,0	6.35	0.009	6.29	0.083 *
	1,1,0	5.72		5.69	
FUMARIC ACID					
CHLOROFORM					
- Alamine 336: 0.048, 0.145, 0.29					
N_T = 24	1,2,0	7.06	0.651	5.54	0.207
	2,2,0	9.11		7.74	
	1,2,0			5.53	0.247
	1,1,0			3.33	
- Removed lowest acid concentrations, data did not fit with rest of data					
Alamine 336: 0.048, 0.145, 0.29					
N_T = 21	1,2,0	5.83	0.083	5.56	0.101 *
	2,2,0	7.95		7.74	
	1,2,0			5.56	0.098
	1,1,0			-2.80	
	2,2,0			7.71	
	2,1,0			3.16	
FUMARIC ACID					
METHYL ISOBUTYL KETONE					
- Very low amine concentration. Data from Starr.					
Alamine 336: 0.0193, 0.062					
N_T = 18	2,1,0			4.64	0.119 *
	1,1,0			3.02	
	2,1,0			4.67	
	1,2,0			3.97	
	1,1,0			2.93	
	2,1,0			4.62	0.091
	1,2,0			4.31	
	1,1,0			2.19	
	2,2,0			7.40	

Table B-1 (Cont'd)

System	Model (p,q,r)	Method 1 $\log(\beta_{pqr})$	Method 1 error	Method 2 $\log(\beta_{pqr})$	Method 2 error
FUMARIC ACID					
METHYL ISOBUTYL KETONE					
- Low amine concentration. Data from Starr. Alamine 336: 0.0193, 0.062. 0.145, 0.29					
N_T = 32	1,2,0			4.42	0.241
	2,1,0			4.80	
	1,2,0			4.34	0.087
	2,1,0			4.82	
	2,2,0			7.52	
	1,2,0			4.33	0.085 *
	2,1,0			4.81	
	2,2,0			7.49	
	1,1,0			1.72	
	1,2,0			4.21	0.141
	2,1,0			4.72	
	1,1,0			2.93	
	2,2,0			7.64	0.180
	2,1,0			4.33	

Table B-2
Numerical Results of Models that Use Data from Previous Workers

- All experiments done at 25 °C unless noted otherwise
- N_T = total number of data points

SYSTEM	p,q,r	$\log(\beta_{pqr})$	error

Ricker, N. L., "Recovery of Carboxylic Acids and Related Organic Chemicals from Wastewaters by Solvent Extraction", Ph.D. Dissertation, Department of Chemical Engineering, University of California, Berkeley (1978).

ACETIC ACID
DIISOBUTYL KETONE

- Alamine 336: 0.39, 069 mol/L

N_T = 11	2,1,0	0.29	0.102
	1,1,0	-20.68	
	3,1,0	-0.28	0.086
	2,1,0	0.25	
	1,1,0	-18.42	

ACETIC ACID
CHLOROFORM

- Alamine 336: 0.68 mol/L

N_T = 7	2,1,0	1.90	0.060
	1,1,0	1.25	

ACETIC ACID
2-HEPTANONE

- Adogen 283: 0.429 mol/L

N_T = 6	3,1,0	2.53	0.016
	2,1,0	2.59	
	1,1,0	2.09	

2-ETHYL-1-HEXANOL

- Alamine 336: 0.02, 0.99 mol/L

N_T = 14	2,1,0	1.82	0.006
	1,1,0	1.83	

Table B-2 (Cont'd)

# indicates sum of squares of log[(Dcalc+1)/(Dexpt+1)] used as error.

SYSTEM	p,q,r	$\log(\beta_{pqr})$	error

Sato, T., Watanabe, H., and Nakamura, H., "Extraction of Lactic, Tartaric, Succinic, and Citric Acids by Trioctylamine", *Bunseki Kagaku*, 34, 559-563 (1985).

CITRIC ACID
XYLENE

- Trilaurylamine: 0.5, 0.2,. 0.1, and 0.05 mol/L

N_T = 28	1,2,0	0.98	0.018 #
	2,3,0	3.02	
	1,2,0	1.09	0.006 #
	2,3,0	-6.68	
	5,6,0	8.97	
	1,1,0	0.36	0.032 #
	1,2,0	1.01	
	1,1,0	0.02	0.017 #
	1,2,0	0.85	
	2,3,0	2.94	
	1,2,1	0.33	0.010 #
	3,3,0	4.33	
	2,3,0	5.30	
	1,2,0	1.06	0.011 #
	2,3,0	-6.72	
	3,4,0	4.95	
	1,2,0	1.08	0.008 #
	4,5,0	6.95	
	1,2,0	1.10	0.006 #
	6,7,0	11.06	

Table B-2 (Cont'd)

SYSTEM	p,q,r	log(β_{pqr})	error
Sato (1985) cont'd			
TARTARIC ACID XYLENE			
- Trilaurylamine: 0.5, 0.2, 0.1, 0.05 mol/L			
N_T = 27	1,1,0	0.10	0.032 #
	1,2,0	0.89	
	1,2,0	1.00	0.026 #
	3,4,0	3.94	
	1,2,0	1.01	0.024 #
	5,6,0	7.25	
	1,2,0	1.03	0.025 #
	6,6,0	8.16	
	1,2,0	1.02	0.032 #
	3,6,0	4.85	
	1,2,0	1.03	0.025 #
	3,6,0	< -5	
	6,6,0	8.16	
	1,2,0	1.01	0.024 #
	6,7,0	8.91	
LACTIC ACID XYLENE			
- Trilaurylamine: 0.5, 0.2, 0.1, 0.05 mol/L			
N_T = 40	3,1,0	-1.42	0.201
	2,1,0	-0.13	
	1,1,0	-0.11	

Table B-2 (Cont'd)

# indicates sum of squares of log[(Dcalc+1)/(Dexpt+1)] used as error.

SYSTEM	p,q,r	$\log(\beta_{pqr})$	error
Sato (1985) cont'd			
SUCCINIC ACID			
XYLENE			
Trilaurylamine: 1.0, 0.5, 0.2, 0.1 mol/L			
N_T = 24	1,2,0	-	0.029 #
	1,1,0	-0.18	
	1,1,0	-0.54	0.015 #
	2,2,0	0.61	
	1,1,0	-0.43	0.010 #
	2,2,0	-7.70	
	3,3,0	1.44	
	1,1,0	-0.39	0.008 #
	4,4,0	2.31	
	1,1,0	-0.43	0.008 #
	2,1,0	-0.32	
	4,4,0	2.23	
	1,2,0	-0.32	0.014 #
	5,6,0	3.43	
	2,1,0	0.43	0.014 #
	1,1,0	-1.15	
	1,2,0	-0.55	

Table B-2 (Cont'd)

SYSTEM	p,q,r	log(βpqr)	error

Vieux, A. S., "Sur l'extraction de l'acetate d'uranyle par la tri-iso-octylamine en solution dans des solvants organiques divers, (Note preliminaire), *Bull. Soc. Chim. Fr.*, No. 9, 3364-3365 (1969).

ACETIC ACID
XYLENE

- Trioctylamine: 0.10 mol/L

N_T = 11	3,1,0	0.13	0.12
	2,1,0	0.16	
	1,1,0	0.10	
	4,1,0	-0.34	0.09
	3,1,0	-4.30	
	2,1,0	0.30	
	1,1,0	0.05	

ACETIC ACID
BENZENE

- Trioctylamine: 0.10 mol/L???

N_T = 10	3,1,0	0.12	0.18
	2,1,0	0.36	
	1,1,0	0.21	
	4,1,0	0.26	0.14
	3,1,0	-3.43	
	2,1,0	0.35	
	1,1,0	0.23	

Table B-2 (Cont'd)

SYSTEM	p,q,r	$\log(\beta_{pqr})$	error	Literature $\log(\beta_{pqr})$
Chaikhorskii, A. A., Nikol'skii, B. P., and Mikhailov, B. A., "Complex Formation in Nonaqueous Solutions X. Interaction of Tridecylamine with Acetic Acid", *Sov. Radiochem.* (Engl. Trans.), 8, 152-158 (1966); *Radiokhimiya*, 8, 163-171 (1966).				
ACETIC ACID BENZENE				
- Trilaurylamine: 0.037, 0.186, 0.557, 0.745 mol/L				
N_T = 40	3,1,0	0.86	0.071	0.80
	2,1,0	0.24		0.33
	1,1,0	0.14		0.19
ACETIC ACID CARBON TETRACHLORIDE				
- Trilaurylamine: 0.37, 0.745, 1.12, 1.49 mol/L				
N_T = 29	3,1,0	0.17	0.063	-0.07
	2,1,0	-		-
	1,1,0	-0.08		0.21
Vanura, P. and Kuca, L., "Extraction of Citric Acid by the Toluene Solutions of Trilaurylamine", *Collect. Czech. Chem. Commun.*, 41, 2857-2877 (1976).				
CITRIC ACID TOLUENE				
- Trilaurylamine:				
N_T = 47	1,2,0	1.39	0.089	1.42
	4,5,0	7.29		7.28
	1,2,0	1.32	0.085	1.26
	2,3,0	3.15		3.22
	5,6,0	8.94		8.95

APPENDIX C. DETERMINATION OF AQUEOUS ACID ACTIVITY, {A}

C.1 Calculation of Fraction Dissociated

The appropriate reactant concentration for the reaction given in Eq. 2-2 is the activity of the undissociated acid in the aqueous phase at equilibrium. The pK_A values of the acids (see Appendix E) and the experimentally determined pH values of the equilibrium aqueous solutions (see Appendix A) were used to determine the concentration of undissociated acid in the aqueous phase, [A], from the equation

$$[A] = \frac{C_{A,aq}}{1 + \frac{K_{A1}}{[H^+]} + \frac{K_{A1}K_{A2}}{[H^+]^2}} \qquad \text{(Eq. C-1)}$$

where $C_{A,aq}$ is the analytical acid concentration in the aqueous phase at equilibrium.

At relatively high pH and for stronger acids, the fraction dissociated is large, and pH becomes a critical factor in determining [A]. To illustrate the effect of acid dissociation, Fig. C-1*a* compares the experimentally determined distribution coefficient, $D = C_{A,org}/C_{A,aq}$, vs. $\log[C_{A,aq}]$ (solid lines and filled symbols) with a modified distribution coefficient, modified $D = C_{A,org}/[A]$, vs. log[A] (dashed lines and unfilled symbols) for succinic acid extracted by low concentrations of Alamine 336 in chloroform. The actual D is lower than the modified D because the acid dissociation decreases the net aqueous phase reactant concentration. The difference between D and modified D is greater for lower acid concentrations because at low acid concentrations pH is higher, and therefore a larger fraction of acid dissociates. For the 0.3 and 0.6 mol/L Alamine 336 concentrations, as $\log(C_{A,aq})$ increases, D increases, attains a maximum, and then decreases. This behavior is inconsistent with

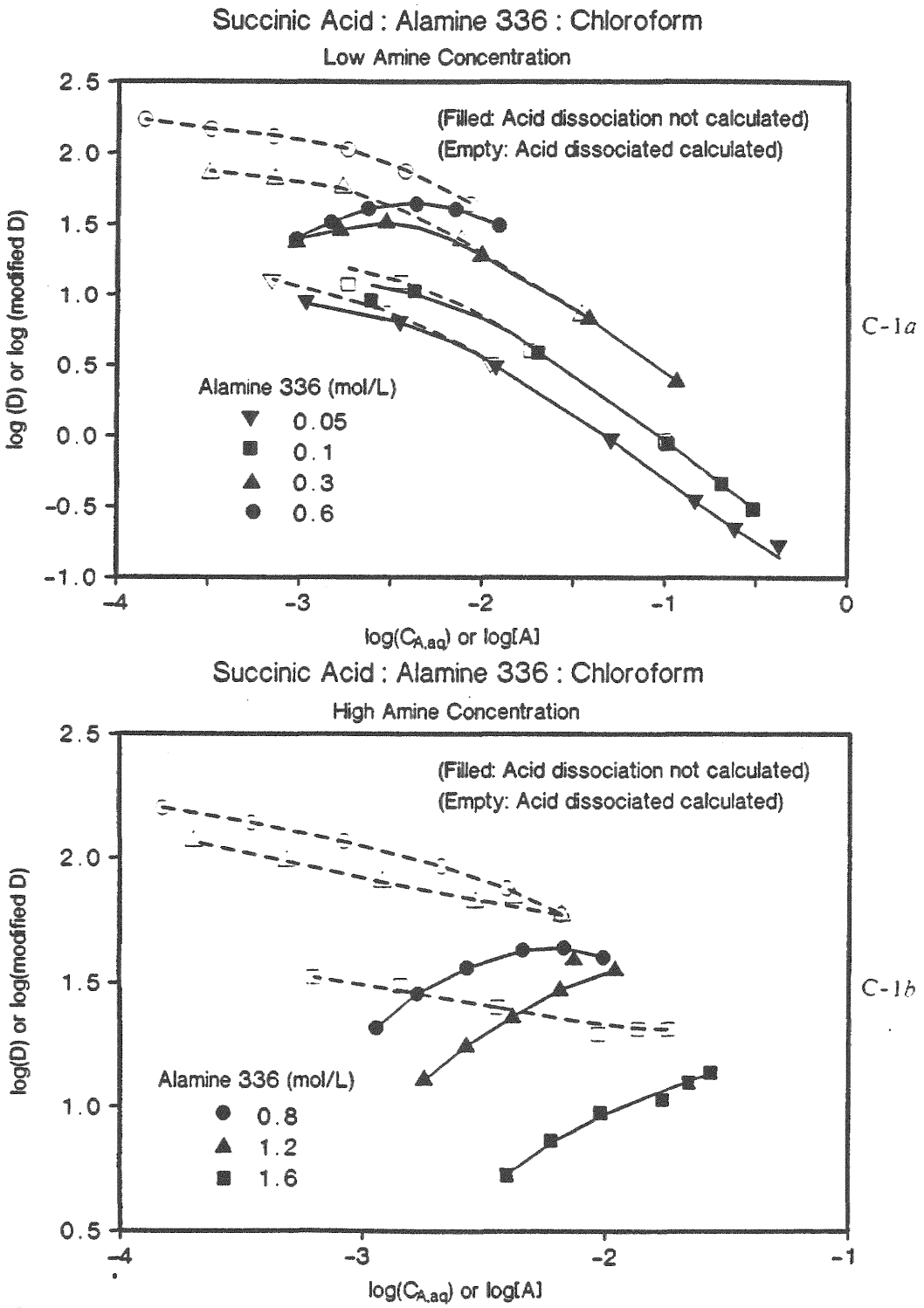


Fig. C-1. Comparison of the Distribution Ratio (Effect of Acid Dissociation Not Included) and the Modified Distribution (Effect of Acid Dissociation Included). (*a*) Low amine concentrations (*b*) High amine concentrations

Note that dissociation increases at low acid and high amine concentrations.

(1,1) complex formation. In contrast, the modified D decreases monotonicly with increasing log[A], as would be predicted for (1,1) complex formation. Thus, it can be seen that account must be taken of acid dissociation in developing the mass-action law models.

Fig. C-1*b* shows the relationship between D and modified D for succinic acid extracted by Alamine 336 in chloroform, the same system as Fig. C-1*a*, at higher amine concentrations. The difference between D and modified D is large, and increases as the initial amine concentration increases. It is probable that a water-soluble, basic impurity in the amine is responsible for the pH increase which leads to a large fraction dissociated. As amine concentration increases, the amount of dissolved basic impurity increases, raising the pH of the aqueous solution and consequently reducing the aqueous-phase driving force. Therefore, it is important to measure the pH in the equilibrium aqueous solution, because it will not be the same as the pH predicted by the analytical aqueous acid concentration and pK_A. This phenomenon is discussed more fully in Appendix D.

Acid dissociation partially explains the behavior shown in Fig. 2-1, which shows log(D) vs. $C_{B,tot}$ for the extraction of succinic acid by Alamine 336 and chloroform. At low amine concentration, D decreases as acid concentration increases, and at high amine concentration, D increases as acid concentration increases. Consequently, the curves of constant $C_{A,tot}$ cross each other. The relevance of acid dissociation is demonstrated by Fig. C-1. At low $C_{B,tot}$ acid dissociation is minor, as seen in the 0.05 and 0.10 mol/L $C_{B,tot}$ curves of Fig. C-1, and D decreases with increasing $C_{A,aq}$ (and therefore with increasing $C_{A,tot}$). At high $C_{B,tot}$, acid dissociation is significant, as seen in Fig. C-1*b*, where D increases with increasing acid concentration. Thus the crossing of the curves in Fig. 2-1 is due to acid dissociation

resulting from low acid concentration and a water-soluble, basic impurity.

C.2 Activity Coefficients of Aqueous-Phase Species

Recall that an "average" value of the aqueous activity coefficient over the experimental acid concentration range is absorbed into the equilibrium constants, because the aqueous-phase undissociated acid concentration rather than activity is used as the driving force. Hence, the differences in aqueous-phase acid activity between different acids (e.g. from differences in hydrophilicity) are incorporated into the equilibrium constant. Changes in aqueous-phase activity coefficients with concentration, however, were not appraised quantitatively in this work because information on aqueous-phase activity coefficients for most carboxylic acids is not readily available. This may cause deviations of the calculated equilibrium constants from the real values if activity coefficients vary greatly over the concentration ranges studied.

If there were changes in aqueous-phase activity coefficients with concentration, the calculated curves would be expected to deviate from the experimental curves. Experimental data for succinic acid gave very good fits for the simple stoichiometry systems (diluents: MIBK, Fig. 2-5*d*; chloroform, Fig. 2-5*a*; and nitrobenzene, Fig. 2-5*c*), whereas experimental data for maleic acid with chloroform diluent (Fig. 2-7*a*) and malonic acid in MIBK diluent (Fig. 2-6) appeared to have a slightly steeper slope than would be predicted from (1,1) stoichiometry. It is not known if this arose from slight variation in experimental technique, or if aqueous-phase activity coefficients varied with concentration in some cases to cause a slight discrepancy. It is also possible that the organic-phase activity coefficients of the complexes vary over the concentration range. Nonetheless, for the most part, the deviations of theoretical and

experimental results for the simple stoichiometries was very small. On this basis the change in activity coefficient with concentration was not deemed to be a significant influence in the calculations.

Another complication is that the calculation of the fraction of undissociated acid should also incorporate activity coefficients. Moreover, it must include activities not only of the undissociated acid, but the ionic, dissociated species as well, which may be even more complicated functions of aqueous-phase composition. Fortunately, the error involved in calculation of acid dissociation somewhat mitigates the error involved in not using activity as the driving force for complexation. This is because a greater undissociated acid activity coefficient drives the dissociation reaction further, reducing the concentration of undissociated acid. Then the actual concentration of undissociated acid is lower than calculated, but its activity coefficient is higher than calculated. Therefore the product of the actual concentration and activity coefficient (normalized by the "average" activity coefficient over the concentration range) may end up being close to the calculated undissociated acid concentration.

Data available for carboxylic acid activity coefficients are presented below. There were insufficient data to use in equilibrium calculations. Fig. C-2 shows the activity coefficients calculated by isopiestic studies of succinic, maleic, malic, and malonic acids (Davies and Thomas, 1955). The standard state was taken as 0.5 molal for succinic acid, and 1.0 molal for the other acids. These studies established that there is a slight decrease in activity coefficient as acid concentration increases, which levels off at higher concentrations. Fig. C-3 shows the activity coefficients determined from isopiestic studies for citric acid (Vanura and Kuca, 1976; Levien, 1955). An increase in activity coefficient with increasing concentration was seen for

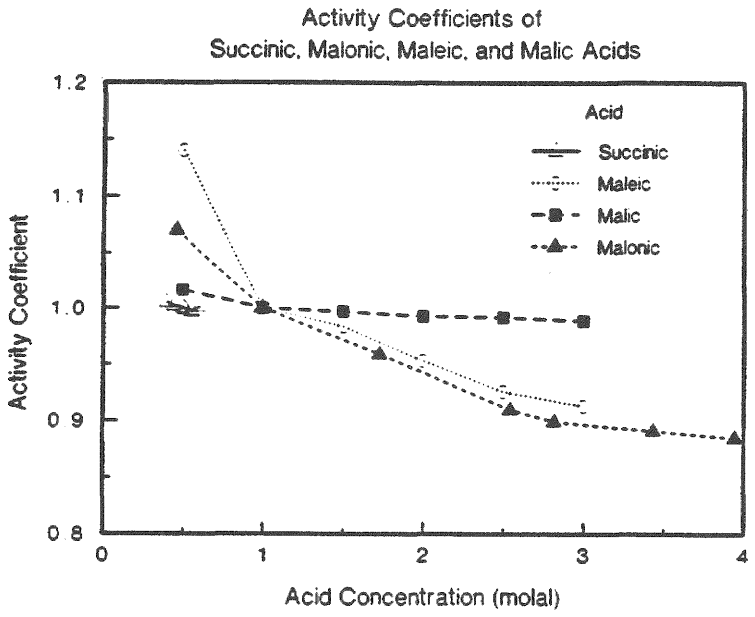


Fig. C-2. Activity Coefficients for Various Carboxylic Acids as a Function of Acid Concentration. (Data from Davies and Thomas, 1955.)

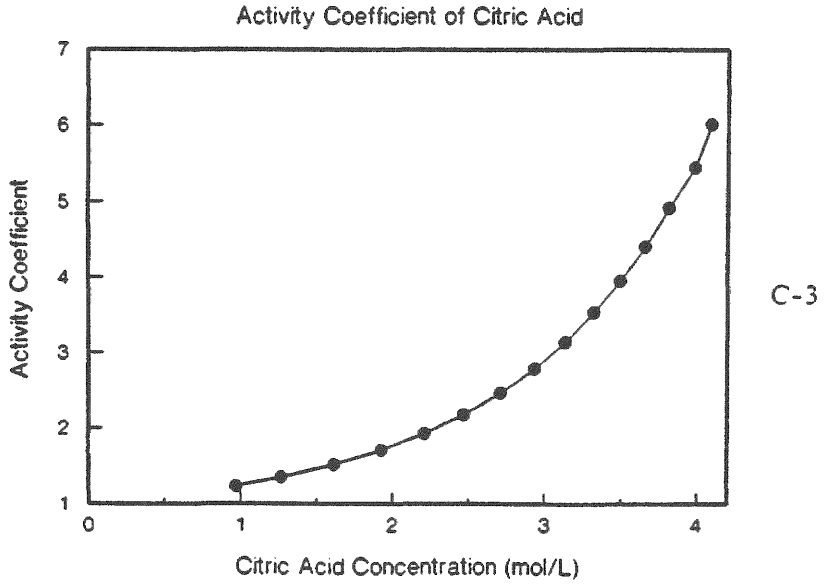


Fig. C-3. Activity Coefficients for Citric Acid as a Function of Acid Concentration. (Data from Vanura and Kuca, 1976 and Levien, 1955.)

solute concentrations greater than 1 mol/L. The activity coefficient for succinic acid varied less than 0.5% over the concentration range of 0.399 to 0.602 molal; the activity coefficient for malonic acid varied from 1.14 at 0.5 molal to 0.953 at 2.0 molal, a difference of approximately ±10%.

Activity coefficients can, in principle, be controlled by maintaining a constant ionic strength in solution. Shah and Tiwari (1981) studied the effect of sodium sulfate concentration (5 to 25%) on the distribution of acetic acid into ethyl acetate, 2-ethylhexanol, and methyl ethyl ketone. The authors concluded that there was "salting-out" of acetic acid from the aqueous phase; that is, the aqueous-phase activity coefficient of acetic acid increased with salt concentration. Unfortunately, for extraction by amine extractants, addition of a mineral acid salt to control ionic strength may cause competition of the mineral acid with the carboxylic acid for the amine. Notwithstanding, the effects of ionic strength and salt content of the aqueous phase on extraction by tertiary amines have been studied. Puttemans et al. (1984) examined the effect of ionic strength on the extraction of hydroxylated derivatives of benzoic acid by trioctylamine in chloroform. As ionic strength increased to approximately 0.1, distribution decreased; as ionic strength increased further, distribution increased. The authors claimed that the phosphate buffer ions are very badly extracted by ion pair formation with amines, and so should not have interfered with the analysis.

Vanura and Kuca (1976) used an isomolar series of citric acid and sodium citrate to maintain approximately constant ionic strength and species' activity coefficients in solution. The sum of the concentrations of citric acid and sodium citrate were maintained at 1.0 mol/L. This method circumvents any possible interference from buffer ions, but is less effective for activity coefficient control.

REFERENCES

Davies, M. and Thomas, D.K., "Isopiestic studies of Aqueous Dicarboxylic Acid Solutions", *J. Phys. Chem.*, **60**, 41-44 (1956).

Levien, B. "A Physicochemical Study of Aqueous Citric Acid Solutions", *J. Phys. Chem.*, **59**, 640-644 (1955).

Puttemans, M., Dryon, L., and Massart, D., "Extraction of Organic Acids by Ion-Pair Formation with Tri-*n*-Octylamine//Part 1. Extraction Rate and Influence of pH and Ionic Strength", *Anal. Chim. Acta*, **16**, 221-229 (1984).

Vanura, P. and Kuca, L., "Extraction of Citric Acid by the Toluene Solutions of Trilaurylamine", *Collect. Czech. Chem. Commun.*, **41**, 2857-2887 (1976).

APPENDIX D. SOLUBILITY OF EXTRACTANT IN AQUEOUS PHASE

The manufacturer's reported solubility of Alamine 336 in water is very small, less than 5 ppm (Henkel, undated). However, small amounts of impurities, 2-5% (w/v), are reported in the product literature. These can be primary, secondary, or low-molecular-weight tertiary amines, which may be soluble in water. These impurities may affect the pH of the aqueous phase. Additionally, the acid-amine complex, being more polar than the amine itself, may have a greater water solubility than the uncomplexed amine, and thereby also affect the aqueous-phase pH.

D.1 Experimental vs. Predicted pH

The experimentally determined pH values were found to deviate up to one pH unit from the pH values that would be expected based on the aqueous acid concentration and pK_A values of the acid, as calculated from the solution of Eq. D-1 (Stumm and Morgan, 1981).

$$[H^+]^4 + [H^+]^3 K_{A1} + [H^+]^2 (K_{A1}K_{A2} - C_{A,aq}K_{A2} - K_W) - [H^+]K_{A1}(2C_{A,aq}K_{A2} + K_W) - K_{A1}K_{A2} = 0 \qquad \text{(Eq. D-1)}$$

Fig. D-1 shows the pH calculated from the aqueous acid concentration vs. the pH measured experimentally for several of the systems studied in this work. The experimental pH values are slightly higher than the calculated values, with the deviation increasing with increasing initial amine concentration and high pH (i.e., decreasing aqueous acid concentration). The pattern was identical for different acids and diluents. Temperature did not seem to affect the curves. Calculated and experimental pH values were within 0.03 pH units when no amine was present. This

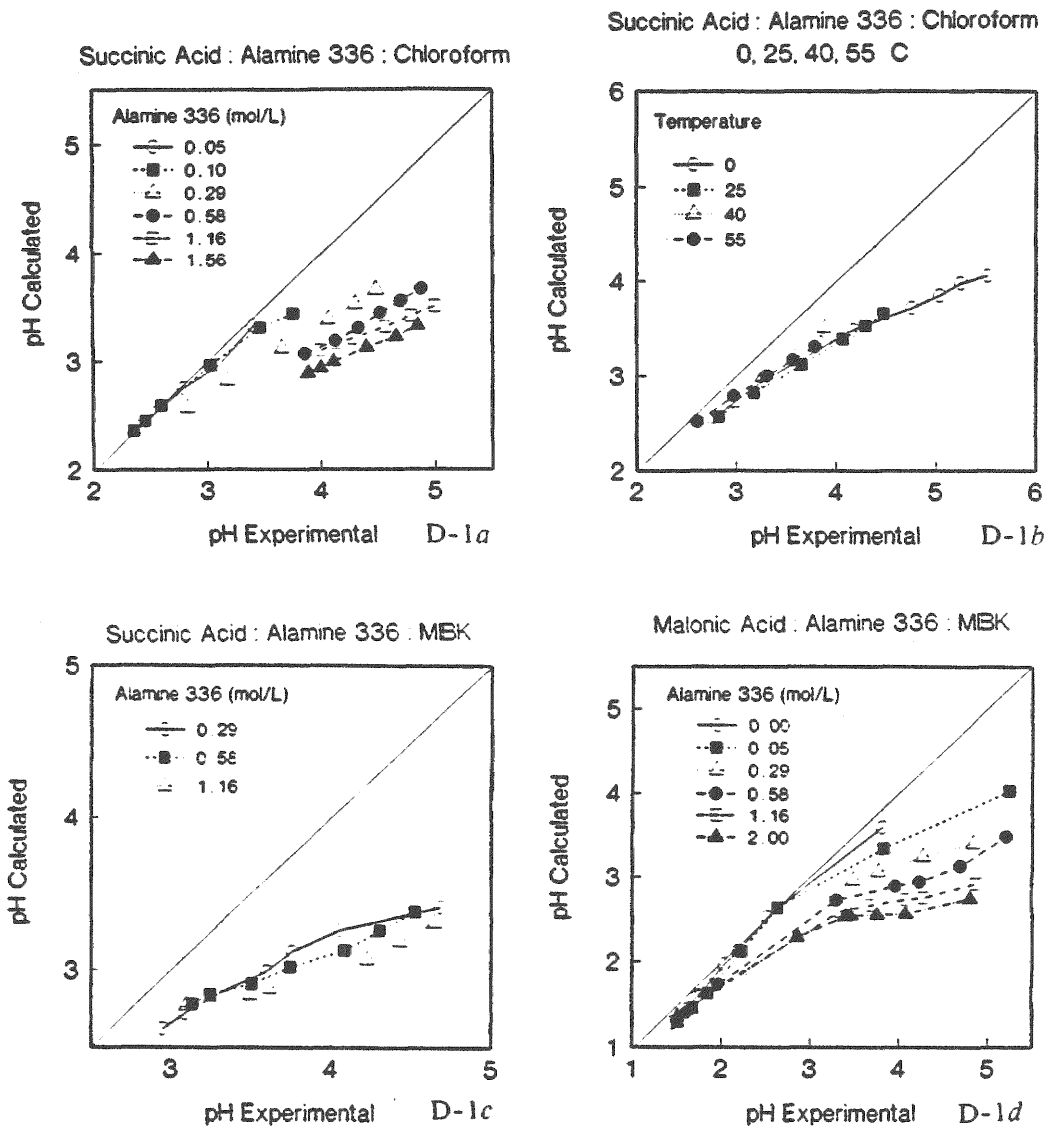


Fig. D-1. Comparison of the pH Values Calculated from the Concentration of Acid in the Aqueous Phase and pK_A to the pH Values Determined Experimentally.

(*a*) Succinic acid : Alamine 336 : chloroform
As amine concentration increases and a higher pH (lower acid concentration), the deviation of theoretical from predicted increases.

(*b*) Succinic acid : Alamine 336 : chloroform at various temperatures. Temperature does not appear to affect the relationship.

(*c*) Succinic acid : Alamine 336 : MIBK
Effect is the same for different diluents

(*d*) Malonic acid : Alamine 336 : MIBK
Effect is the same for different acids

behavior is consistent with a small amount of a basic impurity, such as a low molecular weight amine, being soluble in the aqueous phase.

D.2 Potentiometric Titration of the Aqueous Raffinate

Previous investigators have performed potentiometric NaOH titrations of the aqueous product phases to detect the presence of amine salt in the aqueous phase (Wardell and King, 1978). For this work, similar titrations were performed on selected samples. Resulting titration curves are shown in Figs. D-2 and D-3. The x-axis is the volume of NaOH solution added, converted and normalized to units of the equivalent molarity of solute. During titration, the stirred water phase became cloudy. Wardell and King attributed this cloudiness to the presence of an acid-amine salt. Titration of the acid frees the amine from the amine salt, and the water-insoluble amine produces cloudiness in the solution. This cloudpoint and the phenolphthalein colorimetric endpoint are indicated on the curve.

Fig. D-2*a* shows the titration curve for the aqueous-phase product of the contact of 0.05 mol/L succinic acid solution with 100% Alamine 336. A relatively broad cloudpoint-endpoint region was observed, which could be interpreted as two inflection points, one at the cloudpoint and one at the endpoint. According to Wardell and King, the first inflection, at the cloudpoint, corresponds to the "free acid" concentration. The difference between the phenolphthalein endpoint and the cloudpoint corresponds to either the concentration of acid in the "salt" form or one-half the concentration of acid in the salt form, depending on whether the salt is neutralized acid or the bisuccinate. That is, if the bisuccinate salt is water-soluble, the salt concentration is twice the difference between the cloudpoint and endpoint because the x-axis is normalized to two carboxyl groups and the bisuccinate salt has

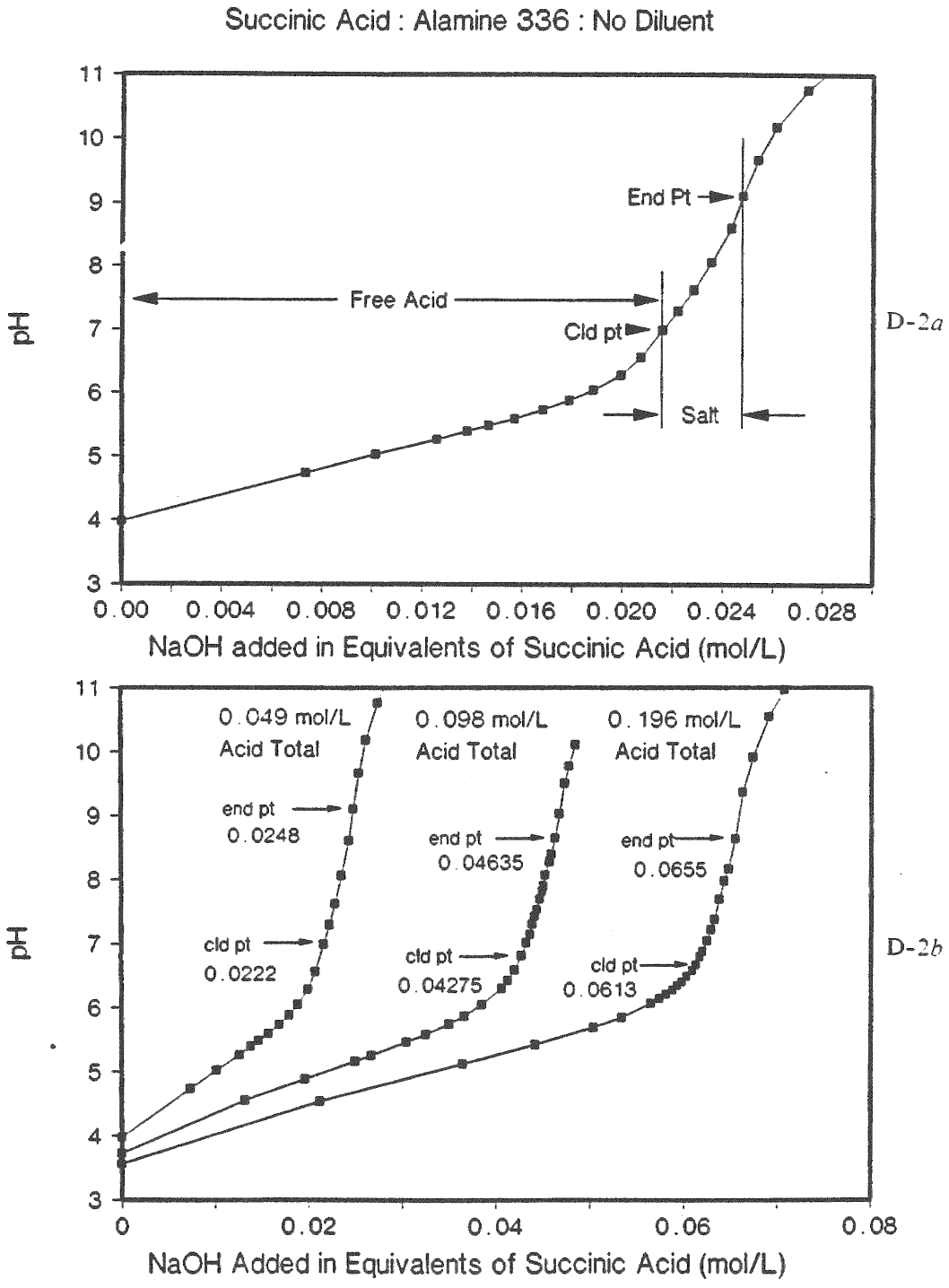


Fig. D-2. Sample Aqueous-Phase Titration Curves for Extraction by 100% Alamine 336.

(*a*) $C_{A,tot}$ = 0.049 mol/L succinic acid
(*b*) $C_{A,tot}$ = 0.049, 0.098, and 0.196 mol/L succinic acid

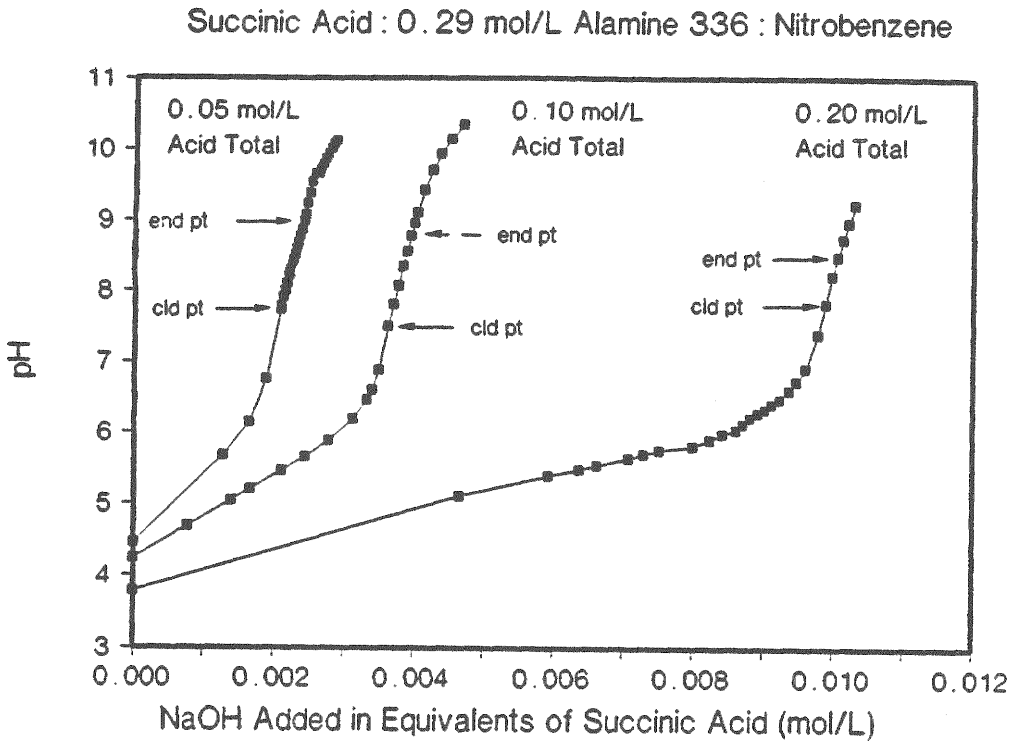


Fig. D-3. Sample Aqueous-Phase Titration Curves for Extraction by 0.29 mol/L Alamine 336 Diluted in Nitrobenzene.

$C_{A,tot}$ = 0.05, 0.10, 0.20 mol/L succinic acid

only one carboxyl deprotonate at high pH. If the salt is a neutralized, succinate form, then the difference simply corresponds to the concentration of acid in the salt form.

Fig. D-2*b* compares this curve with similar titration curves for 0.10 and 0.20 mol/L succinic acid contacted with Alamine 336. The slopes of the curves near the endpoint are similar, suggesting that the amount of salt is roughly independent of acid concentration, and the relative amount of acid in the salt form decreases as acid concentration increases. At higher acid concentrations the endpoint and cloudpoint are virtually indistinguishable.

Fig. D-3 shows the titration curve for 0.05, 0.10, and 0.20, mol/L succinic acid contacted with 0.29 mol/L Alamine 336 in nitrobenzene. A comparison of Fig. D-3 with Fig. D-2 (note the much smaller x-axis scale for Fig. D-3) shows that the amount of salt present is much lower at the lower amine concentration. Again, as the aqueous acid concentrations increase, the relative amount of acid in the salt form decreases, and at initial acid concentrations of greater than 0.30, the fraction in the salt form is negligible.

A problem in the above interpretation of titration curves is that there is no way of determining if the salt is composed of the extractant itself or of the more water-soluble amine impurities in the extractant. Wardell and King implied that the extractant trioctylamine was responsible for the cloudiness and fuzzy endpoint; however, it seems as likely that these titration effects result from basic impurities in the extractant, which are pulled into the aqueous phase by the acid and cloud the sample as the acid is titrated away.

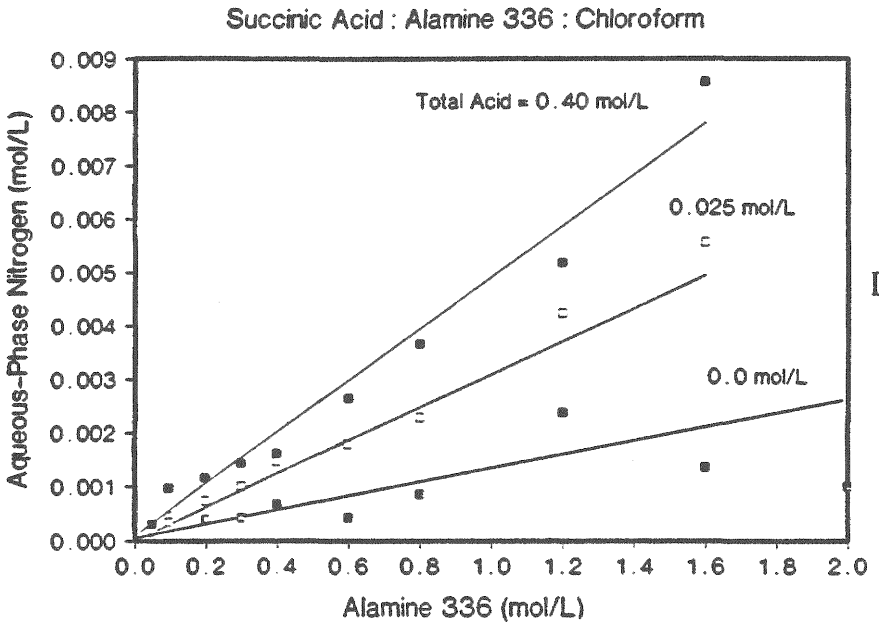
Another difficulty with titration is that it is not possible to obtain sufficiently precise measurements for quantitative evaluation of amine solubility. Even worse, the presence of an amine salt in the aqueous phase produces a small error in the aqueous-phase acid concentration, because the endpoint is less distinct and includes acid in both the salt and free form. The figures referenced above include the samples with the greatest endpoint ambiguity of all samples titrated. In general, the error caused by salt solubility is negligible.

D.3 Kjeldahl Analysis to Determine the Nitrogen Content of the Aqueous Phase

Kjeldahl analyses for determination of organic nitrogen in the aqueous phase were performed by the Microanalytical Laboratory of the College of Chemistry, University of California, Berkeley. Results showing the concentration of nitrogen in the aqueous phase are given in Table D-1 and Figs. D-4 and D-5. Fig. D-4 shows the concentration of nitrogen in the aqueous phase vs. the initial amine concentration for constant $C_{A,tot}$. The concentration of nitrogen in the aqueous phase is roughly proportional to the amine concentration, and increases with increasing acid concentration. Figure D-5 shows the concentration of nitrogen in the aqueous phase vs. the concentration of acid in the solvent phase. The solubility increases sharply, then levels off. If the nitrogen was from the Alamine 336-succinic acid salt, it would be expected that nitrogen content would be approximately proportional to the concentration of acid in the organic phase. This suggests that the nitrogen content is primarily due not to the extractant-acid salt itself, but to an impurity. Figure D-6 shows the aqueous nitrogen concentration (mol/L) divided by the amine concentration vs. pH. As pH decreases, the normalized nitrogen content increases, which would be expected for a basic substance.

Table D-1. Results of Kjeldahl Analysis for Aqueous-Phase Nitrogen Succinic Acid : Alamine 336: MIBK or Chloroform

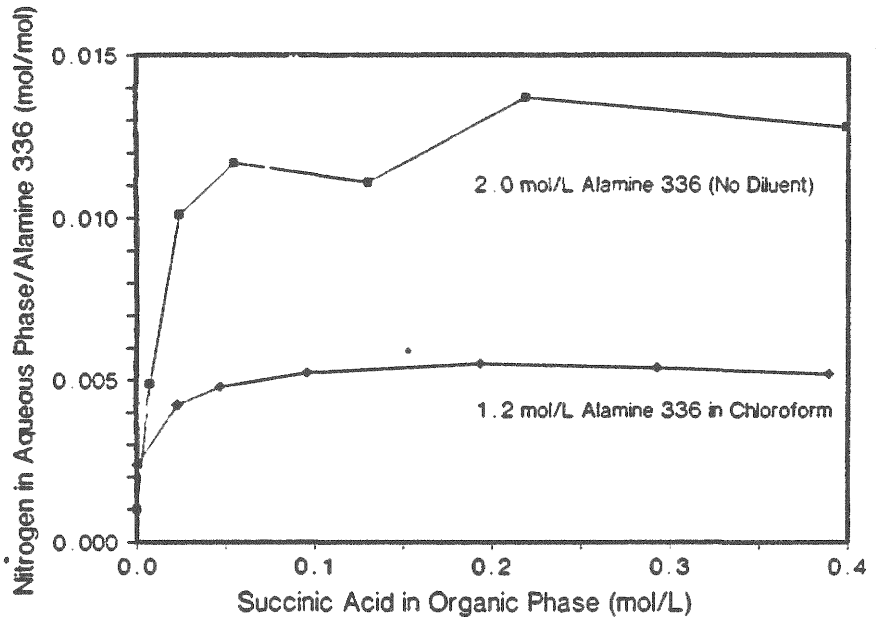
$C_{A,tot}$	$C_{N,aq}$
2.0 mol/L Alamine 336 (No Diluent)	
0.486	0.0128
0.294	0.0137
0.196	0.0111
0.098	0.0117
0.049	0.0101
0.010	0.0049
0.000	0.0010
0.000	0.0014
0.29 mol/L Alamine 336 in MIBK	
0.400	0.0041
0.025	0.0011
0.000	0.0014
0.58 mol/L Alamine 336 in MIBK	
0.400	0.0033
0.025	0.0026
0.000	0.0014
1.16 mol/L Alamine 336 in MIBK	
0.400	0.0042
0.025	0.0087
0.000	0.0010
0.048 mol/L Alamine 336 in $CHCl_3$	
0.400	0.0003
0.025	0.0003
0.000	0.0002
0.096 mol/L Alamine 336 in $CHCl_3$	
0.400	0.0010
0.025	0.0005
0.000	0.0004
0.19 mol/L Alamine 336 in $CHCl_3$	
0.400	0.0012
0.025	0.0007
0.000	0.004
0.29 mol/L Alamine 336 in $CHCl_3$	
0.400	0.0014
0.025	0.0010
0.000	0.0004
0.38 mol/L Alamine 336 in $CHCl_3$	
0.400	0.0016
0.025	0.0015
0.000	0.0007
0.58 mol/L Alamine 336 in $CHCl_3$	
0.400	0.0026
0.025	0.0018
0.000	0.0004
0.77 mol/L Alamine 336 in $CHCl_3$	
0.400	0.0037
0.025	0.0023
0.000	0.0009
1.16 mol/L Alamine 336 in $CHCl_3$	
0.400	0.0052
0.300	0.0054
0.200	0.0055
0.100	0.0052
0.050	0.0048
0.025	0.0042
0.000	0.0024
1.54 mol/L Alamine 336 in $CHCl_3$	
0.400	0.0086
0.025	0.0056
0.000	0.0014



D-5

Fig. D-4. Effect of Acid and Amine Concentration on the Aqueous-Phase Nitrogen Concentration as Determined by Kjeldahl Analysis.

Nitrogen content increases with increasing acid and amine content.



D-4

Fig. D-5. Effect of Organic-Phase Acid Concentration on Aqueous-Phase Nitrogen Concentration as Determined by Kjeldahl Analysis.

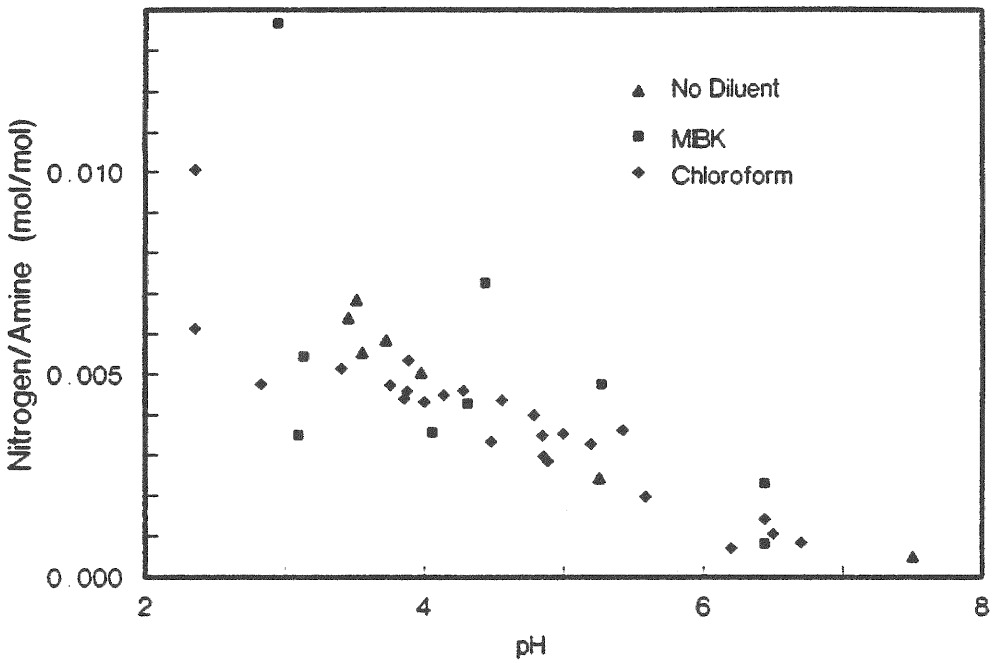


Fig. D-6. Effect of pH on the Normalized Aqueous-Phase Nitrogen Content.

D.4 Washing of the Amine

An attempt was made to wash the amine extractant to determine how much of the impurity could be removed. The amine was washed in a separatory funnel by successive contacting with equal volumes of fresh water. After each contact the phases were separated, and the water wash solutions were analyzed with a Zeiss differential interferometer. The interferometer, which measures the difference in refractive index of the sample water wash and pure water, should give a reading roughly proportional to the concentration of water-soluble material in the water. No attempt was made to calibrate the reading to actual concentrations; rather the method was used to evaluate the extractant/impurity losses during washing qualitatively. Figure D-7 shows the results of 15 water washes of Alamine 336. The amount of water-soluble material decreases sharply with the first few washes, and more slowly with successive washings. In theory, the curve should eventually plateau at the "pure" extractant water solubility, when all the impurity has been washed out. But, this was not achieved in 15 washes.

Kjeldahl analyses of water contacted with an equal volume of as-received Alamine 336, and water contacted with the amine, after it had been washed washed four times with three times its volume of water, gave 0.00131 and 0.0006 mol/L of nitrogen, respectively.

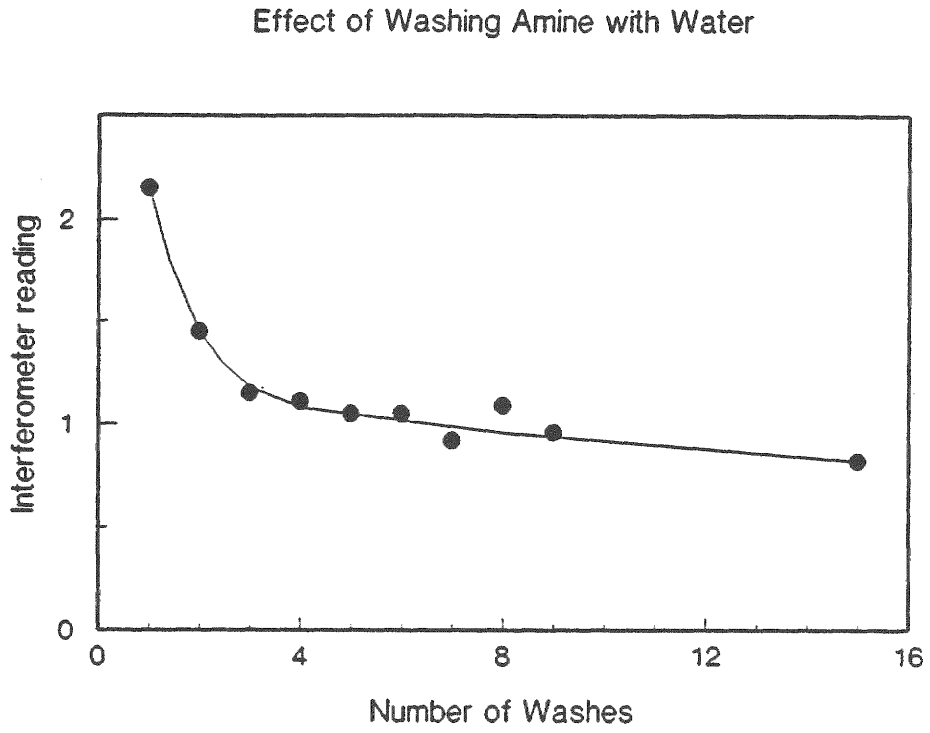


Fig. D-7. Water Washing of the Amine.

REFERENCES

Henkel Corp., RED LINE Technical Bulletin "Alamine 336", Henkel Technical Center, Minneapolis, MN (1984).

Stumm, W. and Morgan, J. J., *Aquatic Chemistry//An Introduction Emphasizing Chemical Equilibria in Natural Waters*, John Wiley & Sons, New York (1981).

Wardell, J.M. and King, C.J., "Solvent Equilibria for Extraction of Carboxylic Acids From Water", *J. Chem. and Eng. Data*, 23(2), 144-148 (1978).

APPENDIX E. PROPERTIES OF COMPOUNDS USED IN THIS WORK

Table E-1
Properties of Compounds Used in This Work

Carboxylic Acids

Acid	Formula	pK_{A1}	pK_{A2}
Acetic (ethanoic)	CH_3-COOH	4.756	
Lactic (2-hydroxypropanoic)	CH_3-HCOH-COOH	3.853	
Malonic (propanedioic)	HOOC-CH_2-COOH	2.826	5.696
Succinic (butanedioic)	HOOC-CH_2-CH_2-COOH	4.207	5.635
Fumaric (*trans*-butenedioic acid)	HOOC-CH=CH-COOH	3.10	4.60
Maleic (*cis*-butenedioic acid)	HOOC-CH=CH-COOH	1.910	6.33

Reference: *Lange's Handbook of Chemistry*, 13th ed.,Dean, J. A., Ed., McGraw-Hill, New York, 5-18 to 5-60 (1985).

Extractant

Alamine 336 (Henkel Corp., Minneapolis, MN)

Molecular Weight: 392 g/mol reported by manufacturer
406 g/mol determined by titration in this work

Density: 0.81 g/ml reported by manufacturer
0.80 g/ml determined in this work

Table E-1 (cont'd)
Properties of Compounds Used in This Work

Diluents

MW = molecular weight
bp = boiling point
ρ = density
$C_{S,aq}$ = solvent solubility in water
$C_{W,org}$ = water solubility in solvent

Compound	MW g/mol	bp °C	ρ g/ml	$C_{S,aq}$ wt%	$C_{W,org}$ mol/L	Ref.
n-Heptane	100.2	98.4	0.684	0.003		S
					0.003	K
Methylene Chloride (Dichloromethane)	84.93	40.5	1.323	1.32		L
					0.145	K
Chloroform (Trichloromethane)	119.4	61.	1.475	0.705	0.059	S
					0.074	K
Methyl Isobutyl Ketone (4-Methyl-2-Pentanone)	100.1	116.	0.804	1.7	0.849	S
					0.776	K
1-Octanol	130.2	195.	0.82	0.03		S
					1.74	K
Nitrobenzene	123.1	211.	1.20			S
					0.166	K
m-Cresol	108.1	203.	1.08			S

S = Schulz, W. W. and Navratil, J. D., *Science and Technology of Tributyl Phosphate*, vol. 1, CRC Press 46-85 (1984).

K = Kojima, I. and Davis, S., *Separ. Sci. Tech.*, 20(2&3), 131-151 (1985).

L = *Lange's Handbook of Chemistry*, 13th ed., Dean, J. A., Ed., McGraw-Hill, New York, (1985).

APPENDIX F. NOMENCLATURE

General

$[A]$	concentration of undissociated acid in the aqueous phase, mol/L
$\{A\}$	activity of undissociated acid in the aqueous phase, mol/L
$[\overline{A}]$	concentration of acid monomer in the organic phase, mol/L
$[\overline{B}]$	concentration of free amine in the organic phase, mol/L
$\{\overline{B}\}$	activity of the free amine in the organic phase, mol/L
$[\overline{A_pB_q}]$	concentration of the (p,q) complex in the organic phase, mol/L
$\{\overline{A_pB_q}\}$	activity of the (p,q) complex in the organic phase, mol/L
$[\overline{A_pB_qD_r}]$	concentration of the (p,q,r) complex in the organic phase, mol/L
$\{\overline{A_pB_qD_r}\}$	activity of the (p,q,r) complex in the organic phase, mol/L
$C_{A,tot}$	total (initial) concentration of acid in the system (mol/L)
$C_{A,aq}$	concentration of acid in the aqueous phase at equilibrium (mol/L)
$C_{A,org}$	concentration of acid in the organic phase at equilibrium (mol/L)
$C_{B,tot}$	total (initial) concentration of amine in the system (mol/L)
$C_{W,org}$	concentration of water in the organic phase at equilibrium (mol/L)
D	distribution ratio = $C_{A,org}/C_{A,aq}$
K_A	acid dissociation constant
K_d	dimerization constant for carboxylic acids in an organic solvent
K_d^*	adjusted dimerization constant = $2P^2K_d$
K_{pq}	apparent stepwise equilibrium constant for association of p acid and q amine molecules
$K_{pq,true}$	thermodynamic stepwise equilibrium constant for association of p acid and q amine molecules

p	stoichiometric coefficient for the number of acid molecules per complex
q	stoichiometric coefficient for the number of amine molecules per complex
r	stoichiometric coefficient for the number of diluent molecules per complex
P	partition coefficient
y_A	activity coefficient of the acid in the aqueous phase
y_B	activity coefficient of the amine in the organic phase
y_{ApBq}	activity coefficient of the (p,q) complex in the organic phase
Z	loading = $C_{A,org}/C_{B,tot}$, adjusted for extraction by the diluent alone
β_{pq}	overall equilibrium constant for association of p acid and q amine molecules
$\beta_{pq,true}$	apparent overall equilibrium constant for association of p acid and q amine molecules
β_{pqr}	overall equilibrium constant for association of p acid, q amine, and r diluent molecules

Chapter 5

$K_{A,org}$	equilibrium constant for the reaction	$\overline{HA} = \overline{H}^+ + \overline{A}^-$
K_B	equilibrium constant for the reaction	$\overline{BH^+} = \overline{B} + H^+$
K_B^*	equilibrium constant for the reaction	$\overline{BH^+} = \overline{B} + \overline{H}^+$
K_P	equilibrium constant for the reaction	$\overline{BH^+} + A^- = \overline{BHA}$
δ	Hildebrand solubility parameter	
a	Shmidt sensitivity coefficient	
b	Shmidt sensitivity coefficient	
DP	Shmidt diluent parameter	
K_o	Shmidt equilibrium constant for standard solute and diluent	
K_o^*	$K_o + b\Delta G$	
ΔG	free energy fo hydration	

Chapter 6

ΔG	free energy of stepwsie (p,q) complex formation
$\overline{H_i}$	partial molar enthalpy of species i
$H_{\text{pure i}}$	enthalpy of pure species i
$\Delta\overline{H_i}$	partial molar excess enthalpy (heat of mixing) of species i
ΔH_{dil}	heat of dilution
ΔH_{fus}	heat of fusion
$\Delta\overline{H}_{\text{soln}}$	partial molar enthalpy of solution
ΔH_{trans}	heat of transfer
ΔH_{pq}	apparent enthalpy of stepwise (p,q) complex formation
$\Delta H_{pq,\text{true}}$	true enthalpy of stepwise (p,q) complex formation
ΔS_{pq}	apparent entropy of stepwise (p,q) complex formation
R	gas constant
T	temperature

Chapter 8

$C_{p,W}$	heat capacity of water, kcal/L
$C_{p,S}$	heat capacity of solvent, kcal/L
E	energy consumption, kcal/hr
L_{min}	minimum reflux in distillation column
S	solvent flow rate, L/hr
S_R	solvent flow rate into regenerator for diluent-swing regeneration, L/hr
S_D	active diluent flow rate leaving top of distillation column, L/hr
W	water flow rate, L/hr
W_E	water flow rate in extractor, L/hr
W_R	water flow rate in regenerator, L/hr
T_E	temperature of extractor, °C

T_R temperature of regenerator for temperature-swing regeneration, °C

T_c temperature of the condensor of distillation column, °C

T_f temperature of feed to the distillation column, °C

T_r temperature of the reboiler of distillation column, °C