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Water-Enhanced Solubility of Carboxylic Acids in Organic Solvents and Its Applications to Extraction Processes

John N. Starr* and C.J. King
*(Ph.D. Thesis)

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John N. Starr* and C. Judson King
(*Ph.D. Thesis)

Department of Chemical Engineering
University of California

and

Enery and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

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MASTER

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WATER-ENHANCED SOLUBILITY OF CARBOXYLIC ACIDS IN ORGANIC SOLVENTS AND ITS APPLICATIONS TO EXTRACTION PROCESSES

by

John Nelson Starr

ABSTRACT

The solubilities of carboxylic acids in certain organic solvents increase remarkably with an increasing amount of water in the organic phase. This phenomenon leads to a novel extract regeneration process in which the co-extracted water is selectively removed from an extract, and the carboxylic acid precipitates. This approach is potentially advantageous compared to other regeneration processes because it removes a minor component of the extract in order to achieve a large recovery of acid from the extract.

Carboxylic acids of interest include adipic acid, fumaric acid, and succinic acid because of their low to moderate solubilities in organic solvents. Solvents were screened for an increase in acid solubility with increased water concentration in the organic phase. Most Lewis-base solvents were found to exhibit this increased solubility phenomena. Solvents that have a carbonyl functional group showed a very large increase in acid solubility.

The solid - liquid and liquid - liquid equilibria for adipic acid, fumaric acid, and succinic acid in cyclohexanone and methylcyclohexanone at 25°C and 45°C were measured. These results show that the solubility of fumaric acid in cyclohexanone increased over 800% upon the addition of water. The liquid - liquid equilibria showed that 3 to 4 moles of water are co-extracted per mole of acid transferred into the organic phase. A chemical complexation model was used to interpret the liquid - liquid equilibria.

Batch precipitation experiments were performed to determine vapor - liquid equilibria, as measured by an average separation factor between the water and the ketone solvent. The presence of the acid lowered the separation factor compared to the binary

solvent - water mixture, but the separation factor is still high enough to be of practical use. The batch precipitation experiments displayed high acid recoveries. For instance, 88% of the acid precipitated by evaporating only 31 wt% of the initial solution in one case.

Process design calculations show that for a given extract composition, a minimum amount of energy is consumed per mole of acid recovered when 90-95% of the water initially in the extract has been vaporized. Higher acid concentrations in the extract reduced the amount of energy required per mole of acid recovered.

C. Judson King

Professor and Provost
University of California
Berkeley, California

To Lori

I am glad to give my love to you,
I know you feel the way I do.

J. Lynne, R. Orbison, T. Petty

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CHAPTER 1. INTRODUCTION

Economical and efficient recovery of carboxylic acids from dilute aqueous solution is important in the chemical processing industry and for environmental control. Adipic acid and citric acid are examples of carboxylic acids that are made on a large scale and must be recovered from aqueous solution. Adipic acid is separated from other acids in aqueous solution in its manufacture from cyclohexane. Citric acid is recovered from a complex fermentation broth. These are just two specific examples of types of feed streams of interest -- fermentation broths and industrial process streams.

Carboxylic acids are hydrophilic and tend to favor an aqueous phase. Most have low volatility. The solutions from which they must be recovered are often dilute and complex. Therefore, innovative and energy-efficient regeneration methods are needed in order to recover carboxylic acids economically.

1.1 Possible Separation Methods

1.1.1 Distillation

Volatile carboxylic acids, such as acetic acid and propionic acid, can be removed from water by distillation. The distillation of water from acetic acid is very energy intensive because their separation factor is near one; propionic acid and water form a low boiling azeotrope. Distillation is not a viable separation method for nonvolatile carboxylic acids because of the cost of evaporating large amounts of water for a small amount of product and the lack of separation of the acid from other non-volatile species.

1.1.2 Calcium Salt Precipitation

Calcium salt precipitation is the conventional separation process used to recover low-volatility carboxylic acids from aqueous solution. Citric acid, a commodity chemical made by fermentation, is recovered this way on a large scale (1). The calcium citrate process consists of adding calcium hydroxide to the fermentation broth, and precipitating out calcium citrate. A sulfuric acid solution is added to protonate the acid, and insoluble calcium sulfate is filtered out of solution. The citric acid solution then goes through a number of final purification steps to reach the purity needed. The calcium precipitation process generates over a ton of calcium sulfate for every ton of citric acid produced. The disposal of this calcium sulfate is a major drawback to this process.

1.1.3 Adsorption

Adsorption of the acid onto a solid polymeric adsorbent or activated carbon is a viable recovery method for many carboxylic acids. Kawabata, et al. (2) studied the adsorption of adipic acid, citric acid, and eleven other carboxylic acids on to a cross-linked poly(4-vinylpyridine). They recovered the acid by leaching with a polar organic solvent such as methanol. Chanda, et al. (3) studied the adsorption of low molecular weight, mono-carboxylic acids onto polybenzimidazole. Kuo, et al. (4) investigated the adsorption of acetic acid onto activated carbon and other adsorbents.

Adsorption is especially efficient at low solute concentrations (< 5 wt%) in the feed because the adsorbents have limited capacity and typically have favorable isotherms at low concentrations. Adsorption processes should not contaminate the feed stream, which may provide an advantage over solvent extraction. Possible regeneration techniques for removing low-volatility carboxylic acids from the adsorbent include solvent leaching, leaching with a high pH aqueous solution, and displacing the acid with a volatile, stronger acid, and then boiling off the displacer acid.

1.1.4 Ion Exchange

Ion exchange resins useful in the recovery of carboxylic acids have a cation immobilized on a polymeric backbone with a free anion such as Cl^- or OH^-. The carboxylic acid anion is exchanged for the free anion. The recovery of the acid depends upon how well the acid competes for the cationic sites compared with the other anions in solution. Garcia and King (5) studied the recovery of acetic acid using weak-base ion-exchange resins, which may act more like adsorbents. Tung (6) is studying the recovery of succinic acid with weak-base ion-exchange resins.

Liquid ion exchangers of possible interest for the recovery of carboxylic acids have strongly hydrophobic positive ions, such as methyl trioctyl amine, paired with hydrophilic negative ions, such as chloride. The carboxylic acid anion then exchanges with the chloride ion as it distributes into the organic phase.

Ion exchange resins or liquids can be regenerated by displacing the carboxylic acid with another anion. This regeneration technique consumes chemicals, and recovers the carboxylic acid as a salt instead of in the protonated form.

1.1.5 Membrane Processes

Membrane separation processes can be efficient concentrators. An appropriate reverse osmosis membrane could selectively pass water to concentrate the acid. "Water splitting" electrodialysis membrane processes would be useful when the pH of the feed stream to the extractor is higher than the pK_a of the acid, i.e. the acid is dissociated. This process converts the salt of an acid, such as sodium fumarate, into its protonated form by splitting water into hydroxyl ion and a proton. An electric field is used to drive species across anion specific and cation specific membranes to form an acid, fumaric acid, and a base, sodium hydroxide. This process is still in development, with the stability of the membrane, especially to alkaline conditions, being the limiting factor (7).

In each of these membrane processes, another process, such as evaporative crystallization or extraction, would probably be needed in order to recover the acid fully from the concentrated aqueous stream.

1.2 Solvent Extraction

Solvent (or liquid-liquid) extraction is the separation process under study in this work.

In solvent extraction, the aqueous feed is contacted with an immiscible organic solvent. The carboxylic acid and any other species in the feed stream, including water, distribute between the aqueous phase and the organic phase according to the laws of thermodynamic equilibrium. The two phases are allowed to coalesce, and the acid-laden organic phase, the extract, is separated from the aqueous phase. Then the extract needs regeneration, which involves removing the carboxylic acid to allow the solvent to be recycled.

Often in solvent extraction, an extractant is mixed with a solvent to form the organic phase fed to the extractor. This extractant is a chemical compound that changes the distribution of the solute of interest such that the organic phase is favored. In many cases the extractant and the solute form a complex in the organic phase, and this complexation is what increases the distribution of the solute in to the organic phase. The complexation should be reversible for the solute to be recovered and the solvent to be recycled. For extracting carboxylic acids, basic organic compounds, such as tertiary amines and phosphine oxides, have been found to be effective (8).

A drawback of solvent extraction can be loss of solvent to the raffinate. If the raffinate is to be discharged as waste, a solvent recovery system may have to be used in order for the effluent to meet present environmental standards. For many fermentation systems, the raffinate will be recycled back to the fermenter. In extractive fermentation, the problem becomes the toxicity of the solvent to the organism. Research has been done on various methods to protect the micro-organisms from the toxic effects of organic solvents (9). If the toxicity of the solvent becomes a major problem, a solvent recovery system will be needed. A substantial loss of the solvent is a cost burden.

Solvent selection is one of the most important decisions in the development of a solvent extraction process. Factors to be considered include (10):

(1) Distribution ratio of the solute -- The distribution ratio, D, is defined as the concentration of the solute in the organic phase divided by the concentration of the solute in the aqueous

phase. The value of the distribution ratio has a direct relationship with the solvent to feed ratio needed for a specific separation. The greater the distribution ratio the smaller the solvent to feed ratio.

(2) Selectivity for the solute -- The distribution ratio is a measure of how a specific substance distributes between phases; selectivity is a comparison of how two different substances distribute between phases. The selectivity of the solvent for the solute over water is an important factor for a process recovering a solute from an aqueous stream. The selectivity for the carboxylic acid of interest over other components, e.g., in a fermentation broth or waste stream, is also a factor to be considered.

(3) Regenerability -- The solute must be separated from the organic phase in order to regenerate the solvent for recycle to the extractor. The choice of solvent will affect the choice of the method of regeneration as well as the ease of regeneration. Since regeneration of the solvent is typically the energy-intensive portion of a solvent extraction process, solvent regenerability is an important factor in determining operating costs and the overall economic feasibility of the process.

(4) Chemical Stability -- The solvent should not react irreversibly with any component in the feed stream during the extraction or regeneration. For carboxylic acids, their reactions with alcohols to form esters and with ammonia and primary and secondary amines to form amides is the biggest concern.

(5) Phase Stability -- The solvent should separate easily from the aqueous phase. This requirement sets limits on the density of the solvent compared to that of water, since most phase separations are driven by gravity. The solvent should not become miscible with water at the highest possible solute concentration, and should not form a stable emulsion.

(6) Water Solubility -- The losses of the solvent into the raffinate greatly depend upon the solubility of the solvent in water. The lower the solvent solubility, the lower the costs of replacing the solvent or the smaller amount of solvent that needs to be recovered.

(7) Price and Availability -- The solvent should be inexpensive to keep solvent inventory costs low, and available from reliable suppliers.

(8) Environmental Soundness -- The solvent should be nontoxic to humans, noncorrosive, and nonflammable. The solvent should not cause serious contamination to the streams it contacts.

(9) Viscosity -- The solvent should have a low enough viscosity to be pumped easily.

There is no perfect solvent whose physical properties and extraction characteristics will be optimum for every factor listed above. Compromises between solvents have to be made with the most important factors for a cost-effective separation process providing guidelines to the proper solvent selection. In some cases, a mixture of solvents of an extractant with a specific solvent will be the optimum choice.

Carboxylic acids interact with each other and water through hydrogen bonds. These strong interactions cause the acid to have a low activity coefficient in the water, making it difficult for the solvent to extract the acid. In order for the organic phase to compete effectively for the acid, the solvent should have the ability to hydrogen bond.

The pH of the aqueous stream fed to the solvent extractor is an important operating parameter. The concentration of the un-ionized acid usually provides the driving force for the distribution of the acid into the organic phase. A feed stream pH below the pK_a's of the acid is favorable since the acid will mainly be un-ionized.

1.3 Regeneration Methods for Solvent Extraction

After the forward extraction of the acid into the solvent, the acid must be removed from the extract to allow solvent recycling and full recovery of the acid.

Three of the regeneration processes described in this section are swing processes, meaning that the extract is contacted with an aqueous stream in the regenerator, and the carboxylic acid is back extracted into the aqueous phase. The operating conditions between the forward extractor and the regenerator must differ in some way such that the equilibrium distribution of the acid between the two phases is changed. The forward extraction operating conditions are chosen such that the organic phase is favored; the regenerator operating conditions are chosen such that the transfer of the acid into the aqueous phase is favored. In these processes, the organic solvent swings between the two different operating conditions.

1.3.1 Distillation

Volatile acids can be distilled from the solvent. Acetic acid is distilled from ethyl acetate or similar solvents in a solvent extraction process to separate acetic acid from water by solvent extraction. For nonvolatile carboxylic acids, straight distillation of the solvent is usually not an economical regeneration method.

Ratchford, et al. (11) investigated the recovery of lactic acid by solvent extraction. A regeneration technique was considered in which the chloroform - lactic acid - tertiary amine extract was steam distilled to evaporate the chloroform and amine. However, amines that had good extraction characteristics had low volatility. and an ammonium lactate salt was formed in the aqueous solution. Amines that are volatile enough to be steam distilled have poor extraction characteristics.

1.3.2 pH Swing

A pH swing process takes advantage of the fact that carboxylic acids distribute almost entirely into a high-pH aqueous phase. Therefore, contacting the extract with a calcium hydroxide aqueous solution will partition nearly all the carboxylic acid into the aqueous phase. The aqueous phase from this back extraction will, in general, have a greater acid concentration than in the original feed to the forward extraction. However, the acid has been converted to its calcium salt. The addition of sulfuric acid will protonate the acid, but this acid addition forms a calcium sulfate waste stream. The consumption of base and acid is also a disadvantage of the pH swing process.

Poole and King (12) have studied an alternative pH-swing process. In their process, the carboxylic acid is regenerated by back extraction into an aqueous phase with a volatile base, such as trimethylamine. The back extract is then heated and concentrated by evaporation as necessary to volatilize the trimethylamine. This process has a potential advantage over the conventional pH-swing process described above, in that the trimethylamine can be recycled and there is no consumption of chemicals.

1.3.3 Temperature Swing

The distribution of carboxylic acids between water and organic solvents depends upon temperature. Therefore, a separation process in which the acid is extracted at one temperature and regenerated by back extraction into water at another temperature is possible. The forward extraction is at low temperature, where the distribution into the organic phase is favored. The regeneration is at a higher temperature, where the transfer of the acid into the aqueous phase is favored. A flowsheet of a temperature swing process is shown in Figure 1.1.

Baniel, et al. (13) described the extraction of citric acid at low temperature, e.g. (20°C), and the back extraction into water at high temperature, e.g. (60-80°C). A mixed solvent phase consisting of a solvent and either a tertiary or secondary amine was used. The solvents varied widely from aromatic and aliphatic hydrocarbons to nitrobenzene to alcohols to mixtures of the solvents mentioned.

Tamada and King (14) studied the extraction of succinic acid at different temperatures using an organic phase consisting of methylisobutylketone or chloroform, and Alamine 336, a mixture of tertiary amines made by Henkel Corp. The succinic acid concentration in the aqueous stream exiting the regenerator was calculated to be at least four times greater than the concentration of succinic acid in the feed stream for a methylisobutylketone:Alamine 336 mixture as solvent. (15)

1.3.4 Solvent Swing

The distribution of carboxylic acids greatly depends upon the nature of the solvent.

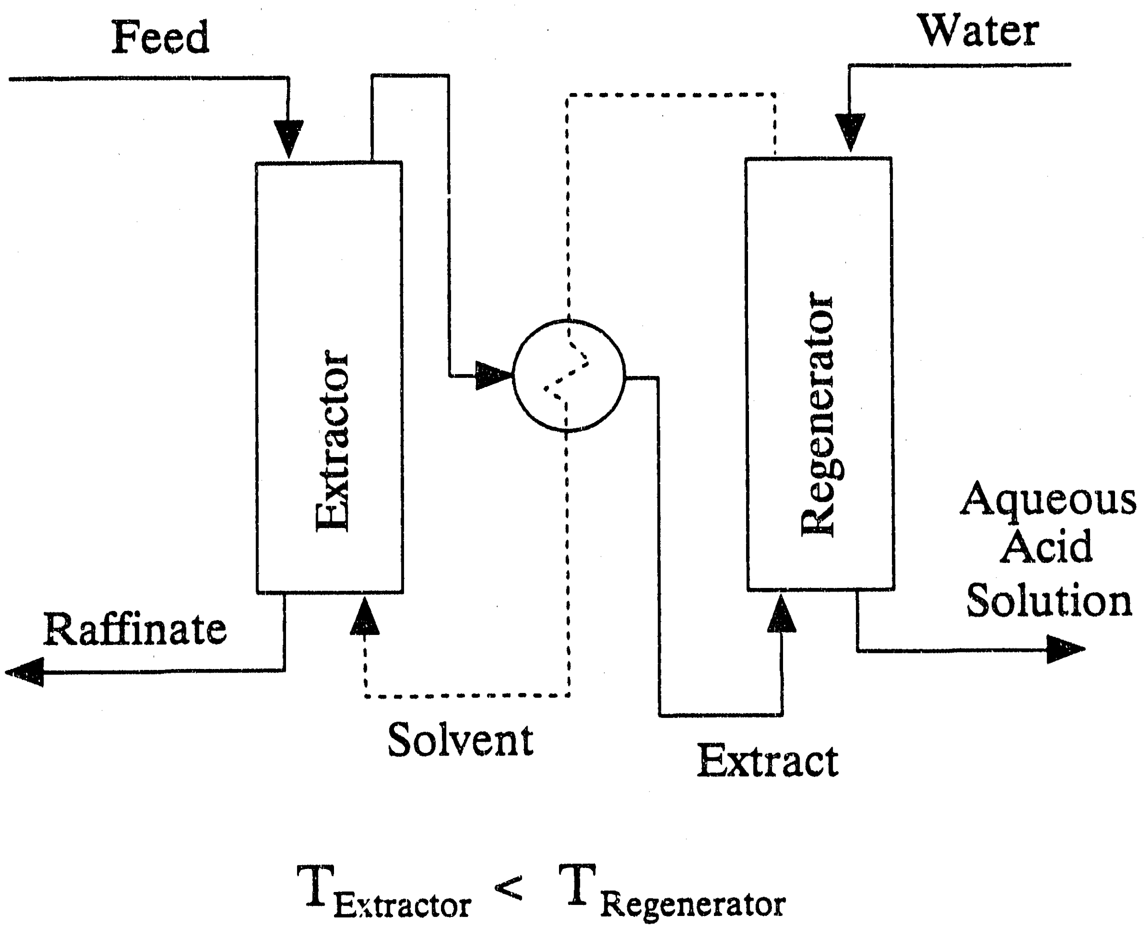

Figure 1.1 Temperature swing process flowsheet

In a solvent swing process, the composition of the solvent changes between the extraction and regeneration. The composition change is made to alter the distribution of the acid such that the aqueous phase is more favored for the solvent composition used in the regenerator. Since the solvent composition is changing, at least two different organic compounds make up the solvent fed to the extractor. Two of the components in the solvent are designated as active and inactive. The active component of the solvent is defined as the component of the solvent that promotes the extraction of the acid into the organic phase. The inactive component of the solvent is defined as the component of the solvent that depresses the extraction of the acid. The active solvent can be separated by distillation from the extract before the extract enters the regenerator, and added back into the mixture before the forward extraction. A flowsheet of a solvent swing process with a volatile active solvent is shown in Figure 1.2. Alternatively, the inactive solvent can be separated from the stream exiting the regenerator, and added back to the extract before it enters the regenerator. A flowsheet of a solvent swing process with a more volatile inactive solvent is shown in Figure 1.3. The temperature and solvent swing processes can be combined to give an even greater concentrating power in the regeneration step.

Baniel, et al. (13) investigated the effect of solvent composition on the distribution of citric acid between water and mixtures of aromatic and aliphatic hydrocarbons, nitrobenzene, and alcohols with varying amounts of an amine extractant. As an example, a nitrobenzene and tridecylamine solvent mixture extracted over 90% of the citric acid fed to the extractor at room temperature, but only 13% of the acid could be removed with water at 60°C. After adding a low-boiling hydrocarbon fraction to the mixture, 75% of the citric acid was recovered.

Tamada and King (14) investigated a solvent swing process for the recovery of succinic acid. The distribution of the acid in an organic phase of Alamine 336 with different volume ratios of chloroform to heptane was determined. Tamada (15) determined that a

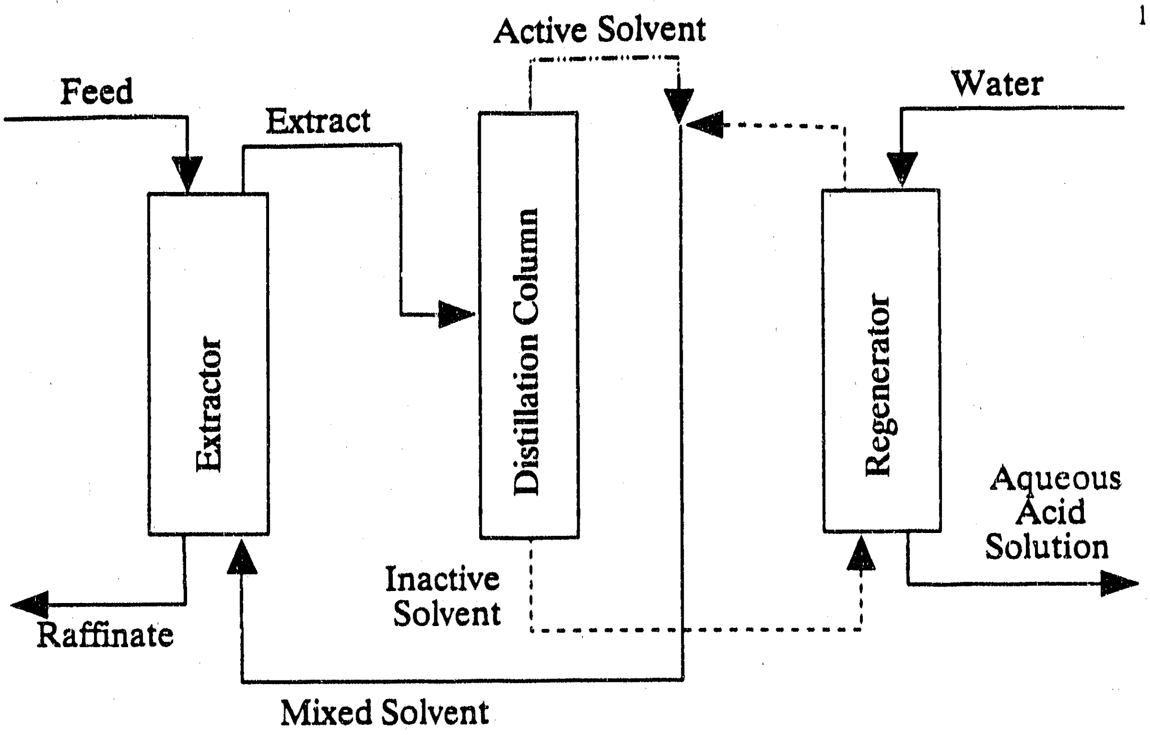

Figure 1.2 Diluent swing process flowsheet with the active solvent more volatile than the inactive solvent.

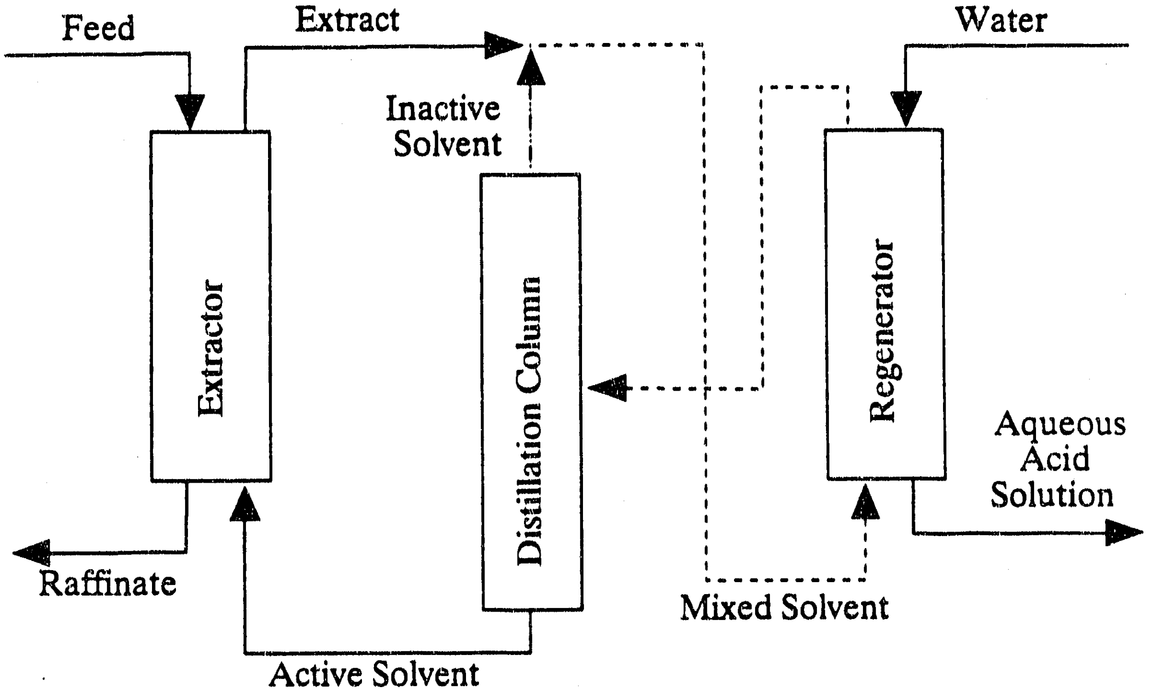

Figure 1.3 Diluent swing process flowsheet with the inactive solvent more volatile than the active solvent.

solvent swing process had more concentrating power than a temperature swing process when the succinic acid concentration in the feed was less than 0.15 mole per liter.

1.3.5 Displacement of the Acid by a Volatile Acid

Ruckl, et al. (16) investigated a displacement regeneration method for citric acid. A solvent consisting of isodecanol, alkanes, and tertiary amines was contacted with an aqueous citric acid stream. The resulting extract was contacted with an aqueous solution of acetic acid, and the acetic acid displaced the citric acid in the organic phase. An aqueous citric acid stream was produced, and the acetic acid was distilled out of the extract for reuse.

1.3.6 Precipitation by Solvent Removal

Evaporation of the solvent to induce the precipitation or crystallization of the acid is feasible for nonvolatile carboxylic acids with limited solubility in organic solvents. This process does not separate the carboxylic acids from other low-boiling compounds that have been extracted along with the acid.

1.4 Precipitation of the Acid by the Removal of Co-Extracted Water

The solubilities of carboxylic acids in certain organic solvents increase remarkably with an increasing amount of water present in the organic phase. As shown in Chapter 2, even small amounts of water, 1-2 wt. percent, can increase the solubilities of carboxylic acids several fold in some solvents. In these systems, removal of the water can cause precipitation of the acid. This fact leads to a regeneration process in which the co-extracted water is removed selectively from an extract, and the acid precipitates. A flowsheet of this process is shown in Figure 1.4. This regeneration method is investigated in detail in this work and currently pending patent approval (17).

This method is advantageous compared to precipitation by solvent evaporation because it removes only a minor component from the extract in order to achieve a large recovery of the acid from the extract. Also, low-boiling impurities will probably not

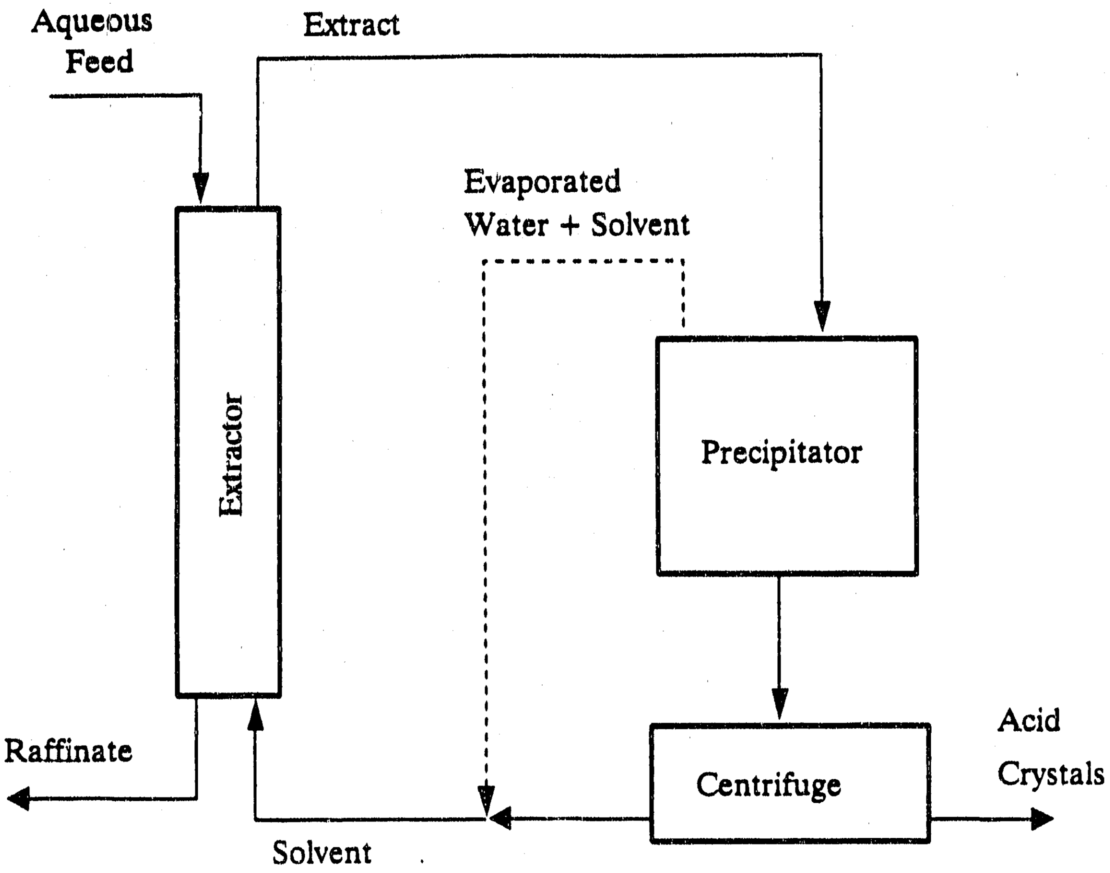

Figure 1.4 Flowsheet for precipitation of the acid by the removal of co-extracted water

precipitate because of their low concentrations in the extract.

For this method to be efficient, carboxylic acids of with low to moderate solubilities in organic solvents are necessary, and the solubility of the carboxylic acid in the organic solvent has to increase sharply with an increase in the concentration of water in the organic solvent. These requirements enables the regeneration method to provide a high single-pass recovery of the acid.

1.5 Acids of Interest

Three of the acids that fit this description of low to moderate solubility in certain organic solvents and a markedly increasing solubility in those solvents with an increase in water concentration in the solvent are fumaric acid, succinic acid and adipic acid. Some of their properties of interest are shown in Table 1.1. They are all similar in that they all have two carboxylic acid functional groups, low volatility, and low to moderate water solubility. Fumaric acid and succinic acid are candidates to be made by fermentation in the future. Adipic acid is the raw material for the manufacture of Nylon 66.

1.5.1 Fumaric Acid

Fumaric acid is currently produced by the catalytic isomerization of maleic acid (18). Maleic anhydride is the usual source of the maleic acid, and is made by the vapor-phase oxidation of benzene, butane, and/or butylene. Fumaric acid production was about 32 million pounds per year in 1989, and it is mainly used as a food acidulant and in polyester resins (19).

Fumaric acid was made by fermentation in the past until using an oil-based feedstock became more economical. Rhodes, et al. (20) found that *Rhizopus arrhizus* and other similar fungi have the ability to produce large quantities of fumaric acid by fermentation. Yields of 0.62 g fumaric acid per g sugar fermented are typical with fumaric acid consisting of

Table 1.1 Physical Properties of Dicarboxylic Acids

Acid	M.W.	Molecular Formula	pK_1[a] 25°C	pK_2[a] 25°C	Water Solubility[b] (Mol/L) 25°C
Fumaric Acid trans-Butenedioic	116.07	$HO_2CCH{=}CHCO_2H$	3.03	4.44	0.054
Succinic Acid Butanedioic	118.09	$HO_2CCH_2CH_2CO_2H$	4.16	5.61	0.65
Adipic Acid Hexanedioic	146.14	$HO_2C(CH_2)_4CO_2H$	4.43	5.41	0.098

(a) *CRC Handbook of Chemistry and Physics*, 65th ed., Weast, R. C., Ed. 1984
(b) *The Merck Index*, 10th ed., Windholz, M., Ed. 1983

approximately 80% of the total acid produced. Waksman (21) suggests running the fumaric acid fermentation at pH 5 to 6.5, but also mentions that *Rhizopus nigricans* has the capacity to produce fumaric acid at pH as low as 2.4. Ling and Ng (22) have developed a method of fermenting sugars to fumaric acid by controlling the amount of oxygen dissolved in the broth.

1.5.2 Succinic Acid

Succinic acid is produced by the catalytic hydrogenation of maleic acid or maleic anhydride (23). A large amount of succinic acid is made as a by-product in the production of adipic acid. Succinic acid has many uses in plastics, detergents, and food industries (24).

Succinic acid is formed during fermentation of sugars by many microorganisms. *Anaerobiospirillum succiniciproducens* produces succinic acid with high yields and concentration (25).

1.5.3 Adipic Acid

Adipic acid is produced by nitric acid oxidation of cyclohexanol/cyclohexanone mixtures (26). This mixed feed is produced from the air oxidation of cyclohexane. Adipic acid is then crystallized from the nitric acid aqueous solution. Virtually all adipic acid is used to make nylon 66 fibers and resin. Adipic acid is made in large quantities; in 1985, consumption was 1.5 billion pounds (27).

Succinic acid and glutaric acid are by-products in the nitric acid oxidation and must be removed to meet the strict purity requirements for polymer grade adipic acid. There has been a large effort in the industrial community towards recovering the adipic acid and removing the succinic acid and glutaric acid by-products using solvent extraction. This mixed acid feed stream is the mother liquor from the first crystallization of the adipic acid. Danly and Witesell (28) show that fractional extraction with an saturated, unsubstituted alcohol solvent is capable of separating the adipic acid from the other two acids with the adipic acid being in the organic phase. Konno (29) describes a similar fractional extraction distillation process in which the solvent is cyclohexanone and/or cyclohexanol. This mixed solvent showed a selectivity of 3.36 for adipic acid over succinic acid.

Adipic acid can also be made from succinic acid through 1,4-butanediol. Mabry, et al. (30) employed a palladium/rhenium-on-carbon catalyst to produce 1,4-butanediol from succinic acid, fumaric acid, and other similar compounds. The 1,4-butanediol is reacted with acetic acid to form 1,4-butanediol diacetate. Dake, et al. (31) studied the carbonylation of 1,4-butanediol diacetate to adipic acid.

1.6 Overview of Dissertation

Chapter 2 discusses water-enhanced solubility of solutes and systems that show this phenomena with the use of three-phase diagrams. The solubilities of the three carboxylic acids in organic solvents with varying amounts of water are reported.

Chapter 3 reports the solid - liquid equilibria for fumaric acid, succinic acid, and adipic acid in cyclohexanone and methylcyclohexanone with varying amounts of water at

25°C and 45°C.

Chapter 4 reports the liquid - liquid equilibria for fumaric acid, succinic acid, and adipic acid in cyclohexanone and methylcyclohexanone with varying amounts of acid at 25°and 45°C. Thermodynamic parameters of the transfer of the acid into the organic phase are reported and discussed.

Chapter 5 discusses the chemical interactions in the organic phase in terms of IR and NMR spectroscopy. Different thermodynamic models are used to describe the acid and water behavior in the organic phase.

Chapter 6 reports the results of a number of batch precipitation experiments performed to demonstrate the process and provide information on vapor - liquid equilibrium.

Chapter 7 discusses results of process design calculations and the energy required for the precipitation of the acid from the extract.

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CHAPTER 2. ENHANCED SOLUBILITIES OF SOLUTES IN ORGANIC SOLVENTS

The solubilities of some solutes in organic solvents increase with increasing amounts of water in the solvent. This chapter discusses this phenomenon in terms of ternary phase diagrams and the systems found in the literature that show this effect. It also reports solubilities of carboxylic acids in various organic solvents.

2.1 Ternary Phase Diagrams

A ternary phase diagram for a system having a partially miscible liquid pair is shown in Figure 2.1. Each corner of the triangle represents a pure component. In this case, the solute is a liquid and fully miscible with water and the solvent. Water and the solvent dissolve in each other only slightly and are only partially miscible over a range of concentrations. The solute distributes between the two phases, and tie lines connect phase compositions that are in equilibrium with each other. The plait point is the point on the phase envelope where the concentrations of the two equilibrium phases become identical. As the concentration of the solute increases, the water and solvent become more nearly miscible until the mixture forms a single phase.

Figure 2.2 shows a ternary phase diagram for a solid solute that has high solubility in both water and the solvent. The solubility of the solid is great enough so that the solid - liquid equilibrium line lies above the phase envelope. The solid - liquid equilibrium line is shown as a linear function of the binary solubilities of the solute. A straight solid - liquid line is characteristic of the binary solute - water and solute - solvent interactions being the most important. In this case, the solute solubility in the solvent is greater than that in water, and the solubility of the solute decreases with increasing water in the organic phase.

Figure 2.3 shows a ternary phase diagram for a solid solute that has lower solubility in the water and solvent. The solid - liquid equilibrium line crosses the phase envelope, and

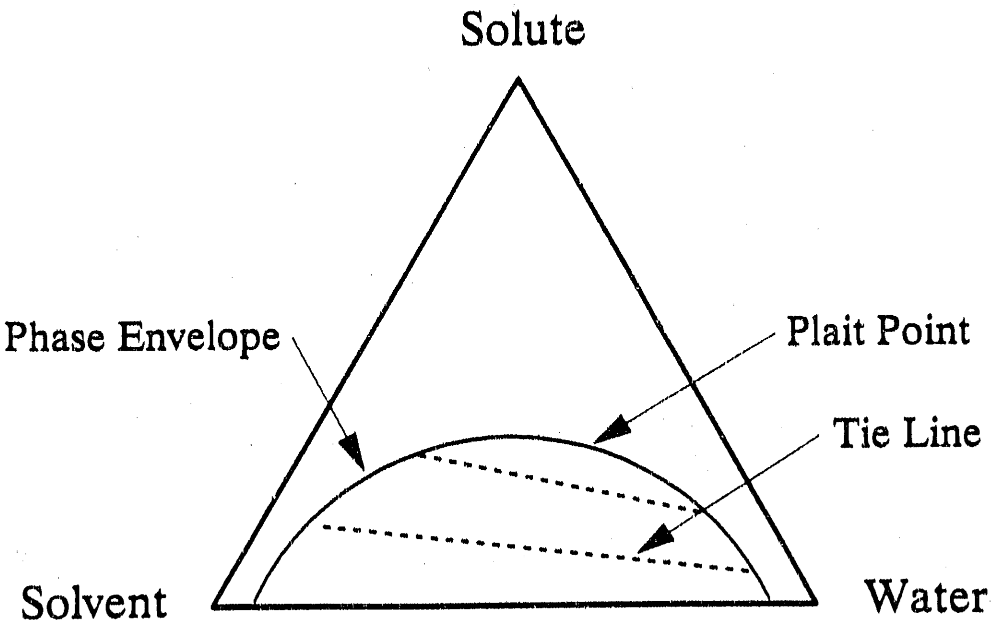

Figure 2.1 Ternary phase diagram for liquid solute that is miscible with both the solvent and water.

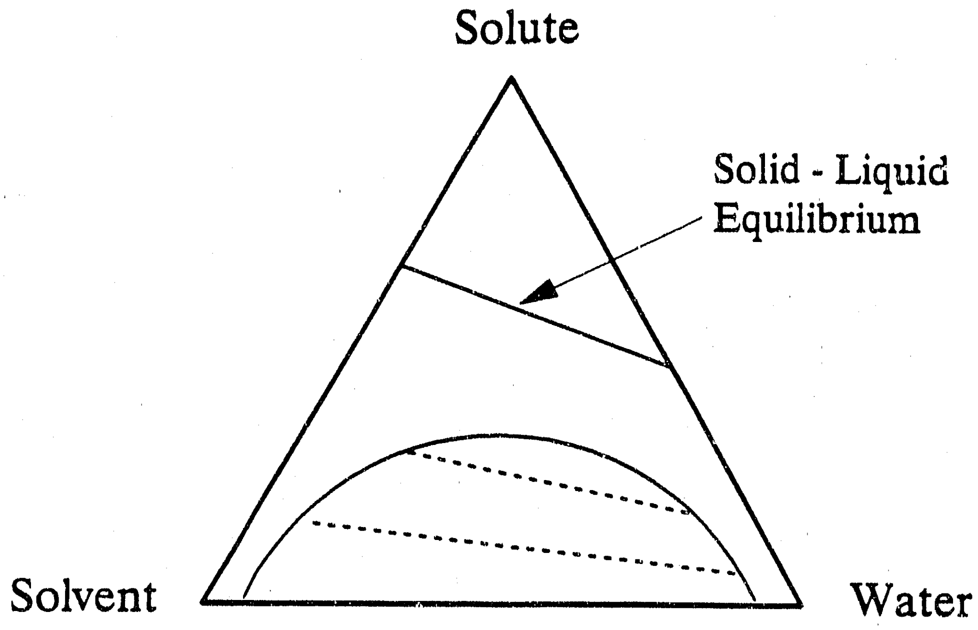

Figure 2.2 Ternary phase diagram with high solubility of the solute in each liquid phase.

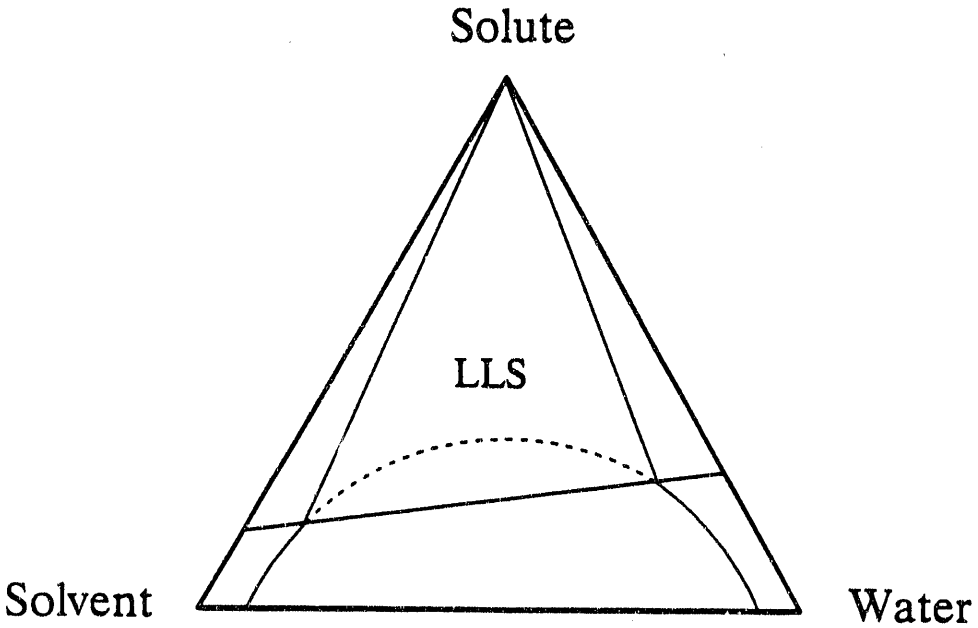

Figure 2.3 Ternary phase diagram with low solubility of the solute in each liquid phase. The solid - liquid equilibrium line crosses the phase envelope.

forms an area of liquid - liquid - solid (LLS) equilibrium. In this case, the solute solubility is greater in water than that in the solvent, and the solubility of the solute increases with increasing water concentration.

In a precipitation process, the lower the solute solubility in the mother liquor, the higher the equilibrium recovery of the solute from the process given a fixed feed concentration. Therefore, ternary systems where the solute exhibits a low solubility in an organic solvent present the most promise for recovery by precipitation.

There are many solutes that show low solubilities in organic solvents, and high solubility in water. However, the combination of high solubility in water and low solubility in the solvent typically gives very low distribution coefficients into the organic phase. The low distribution coefficients cause the solvent-to-feed ratio to be high and make the overall separation method of extraction followed by precipitation from the extract less economical.

The solubilities of carboxylic acids in water and solvents increase as the temperature increases. Also, the phase envelope generally becomes narrower and lower as the temperature increases. Combined, these two phenomena cause the solid - liquid equilibrium line to move away from the liquid - liquid phase envelope. Figure 2.4 shows the effect of temperature on the tertiary phase diagram. The intermediate temperature shown is the lowest temperature where the solid - liquid equilibrium line is in contact with the phase envelope. The last point of contact is the plait point.

2.2 Maximum Solubility of Solutes in Mixed Solvents

The solid - liquid equilibrium lines in the phase diagrams discussed above are idealized in that the solubility of compounds in mixed solvents typically cannot be described as a linear function of the pure component solubility. Depending upon the system, the solubility of a compound in a mixed solvent could reach a maximum or a minimum. Dehn

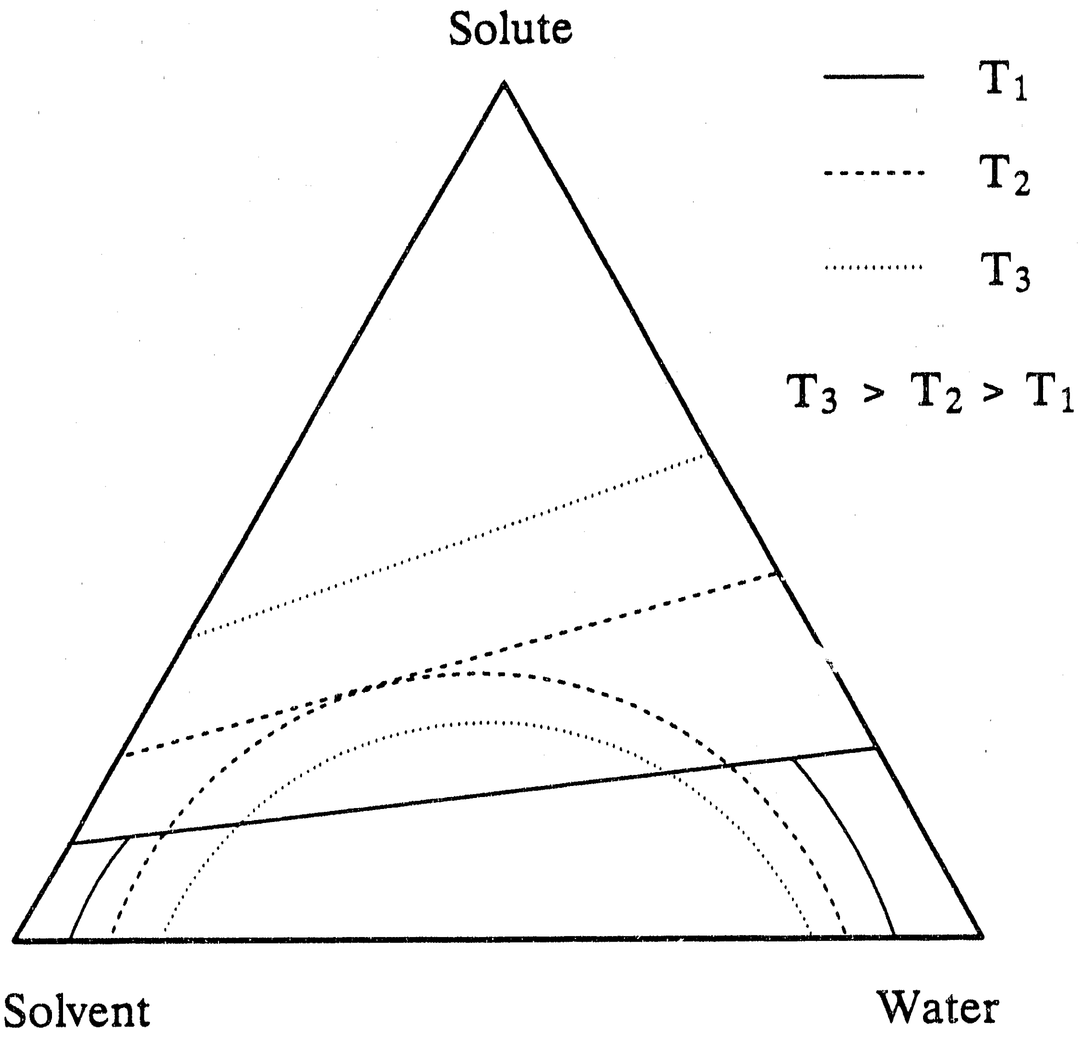

Figure 2.4 Ternary phase diagram showing equilibrium at three temperatures. The phase envelope and solid - liquid equilibrium line move away from each other as the temperature increases.

(1) studied the solubilities of 85 compounds in water, pyridine, and a 50/50 mixture of water and pyridine. Three compounds, all sugars, showed a minimum solubility in the water - pyridine mixture. Sixteen compounds had a maximum solubility in the mixture. Those sixteen compounds were similar in that each had an oxygen, nitrogen , or sulfur atom in its atomic structure.

Pyridine is a water-miscible liquid, therefore, it could not be used for a solvent extraction system. But certainly, the idea that a solute can be more soluble in a mixture of an organic solvent and water than in the pure organic solvent can be generalized to water immiscible solvents. The water concentration in the immiscible organic solvent is limited by the formation of an aqueous phase. A ternary system where the two liquids are immiscible and the solute has a maximum solubility in a mixture of the solvents is shown in Figure 2.5.

Forbes and Coolidge (2) fully investigated the water - diethyl ether - succinic acid system between 15 and 25°C. The solubilities of succinic acid in anhydrous ether and in water-saturated ether at 25°C were found to be 0.487 and 1.689 weight percent, respectively. This is an increase in solubility of over 200% upon the addition of only 1.66 weight percent water. The solubility of succinic acid in ether-saturated water at 25°C was found to be 8.76 weight percent, as opposed to 7.67 weight percent in pure water. Furthermore, the solubility of water in the ether increased with the presence of the succinic acid. The solubility of water in ether at 25°C was 1.19 weight percent, but the solubility of water in ether saturated with succinic acid was increased to 1.66 weight percent. The solubility of succinic acid is low, and the solid - liquid equilibrium line crosses the phase envelope. A ternary phase diagram of a system with solubility characteristics similar to the water - succinic acid - diethyl ether system is shown in Figure 2.6.

In Figure 2.6, a tie line joins the two points which are the intersections of the phase envelope and the solid - liquid equilibrium line. At the intersection points, three phases -- solid solute, an organic liquid phase, and an aqueous liquid phase -- are in equilibrium with each other. This point is defined as the triple point.

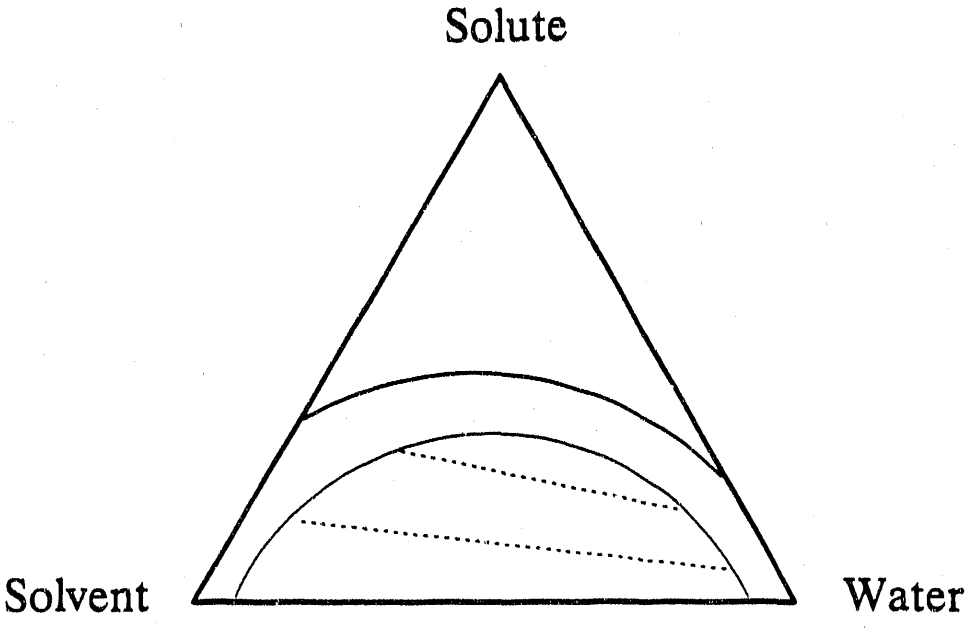

Figure 2.5 Ternary phase diagram with a maximum solubility of the solute in a mixture of the liquids.

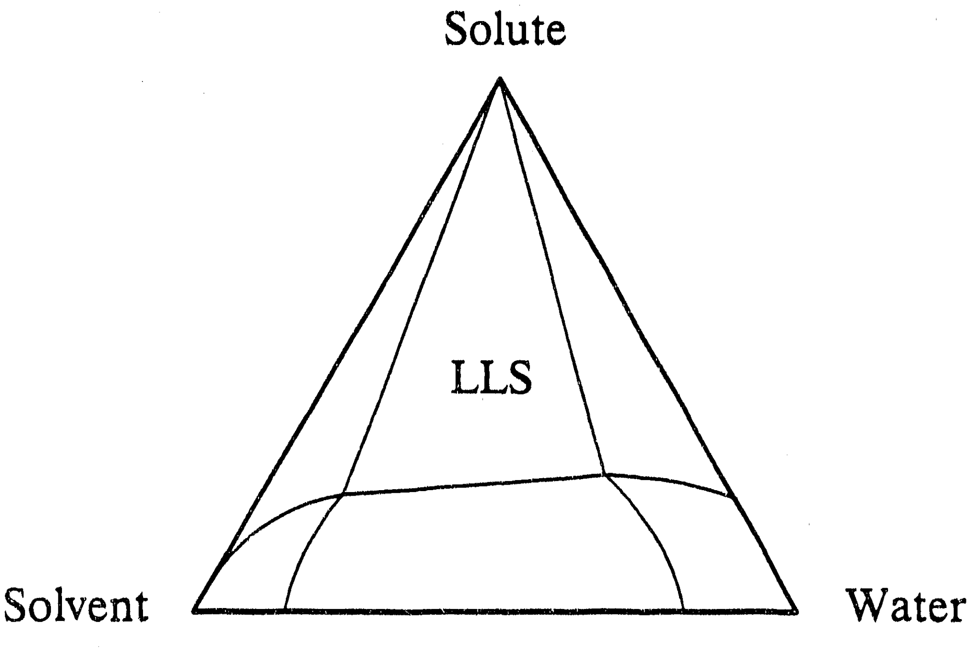

Figure 2.6 Ternary phase diagram with solid - liquid equilibrium line crossing phase envelope. Solute shows increased solubility in mixtures.

Table 2.1 reports water - solute - solvent systems which show maximum solute solubilities in mixtures of water and the solvent. The ratio of the solute solubility in a mixture of water and organic solvent to that in the anhydrous organic solvent is given, and labeled $S_{hydrated}/S_{anhydrous}$. Ethanol, 1-propanol, 2-propanol, 1-butanol, acetone, and dioxane are miscible with water. These systems are especially favorable for an extract regeneration process where the water is selectively removed in order to precipitate the solute. Systems where the solute solubility is highest in pure water, similar to Figure 2.3, are also candidates for this regeneration process since the solute concentration in the organic phase does increase with water concentration in the solvent. However, as the solute solubility in the water increases relative to the solvent, the solute distribution between the two phases may become very unfavorable.

2.3 Phase Equilibrium

For all phases in equilibrium, the chemical potentials of each component must be equal in both phases. Equation 2.1 is a mathematical statement of equilibrium for component i in phases α and β.

$$\mu_i^{\alpha} = \mu_i^{\beta} \tag{2.1}$$

An equivalent statement, Equation 2.2, is that the activities of each component must be equal.

$$a_i^{\alpha} = a_i^{\beta} \tag{2.2}$$

The activity of a component in a solution can be written as the product of its mole fraction and activity coefficient, as shown in Equation 2.3.

Table 2.1 Water - Solute - Solvent systems which show a maximum solute solubility in a mixture of the water and solvent.

	Solute	Solvent	$S_{hydrated}/S_{anhydrous}$	Reference
Water	Succinic Acid	Acetone	5.4	2
Water	Succinic Acid	Cyclopentanone	6.59	3
Water	Succinic Acid	Di-n-ethyl Ether	3.57	4
Water	Succinic Acid	Dioxane	1.28	5
Water	Succinic Acid	1-Butanol	3.18	6
Water	Succinic Acid	1-Propanol	3.1	2
Water	Adipic Acid	Ethanol	1.5	2
Water	Adipic Acid	Acetone	4.5	2
Aqueous Salt Solution	Thioacetic Acid	2-Butanone	2.77	5
Water	Picric Acid	Ethanol	1.72	6
Water	Picric Acid	1-Propanol	3.30	6
Water	Picric Acid	2-Propanol	1.54	6
Water	5-methyl hydantoin	Ethanol	5.30	7
Water	5-ethyl hydantoin	Ethanol	2.76	7
Water	5-isobutyl hydantoin	Ethanol	1.62	7
Water	2-methanamido butanoic acid	Ethanol	1.95	7
Water	2-methanamido-4-methyl valeric acid	Ethanol	1.20	7
Water	Oxalic acid	Trioctylamine + Benzene	N.A.	8
Water	Oxalic acid	Trioctylamine + Carbon tetrachloride	N.A.	8
Water	2,5-Xylenol	Diisobutyl Ketone	1.08	9
Water	Acetanilide	Ethanol	1.15	10

N.A. - Values of the concentrations were not available from the reference.

$$a_i^\alpha = x_i^\alpha \gamma_i^\alpha \tag{2.3}$$

Substituting Equation 2.3 into Equation 2.2 gives Equation 2.4, which is the relevant equation for the distribution of a solute between two phases.

$$x_i^\alpha \gamma_i^\alpha = x_i^\beta \gamma_i^\beta \tag{2.4}$$

The activity coefficient is a function of the composition of the phase of interest, with many different forms of this relationship being proposed. The activity of a solid solute is normally defined as 1.

Increasing solubility of a solute in an organic solvent with increasing concentration of water in the solvent can be defined in terms of mole fractions and activity coefficients. The relevant equation, Equation 2.5, compares the hydrated organic solution to the anhydrous organic solution, recognizing that both are in equilibrium with solid solute and therefore with one another.

$$\frac{x_{i,\text{hydrated}}^{\text{org}}}{x_{i,\text{anhydrous}}^{\text{org}}} = \frac{\gamma_{i,\text{anhydrous}}^{\text{org}}}{\gamma_{i,\text{hydrated}}^{\text{org}}} > 1 \tag{2.5}$$

From Equation 2.5, the presence of the water in the organic phase must depress the activity coefficient of the solute. The ternary system therefore shows negative deviations from ideality.

Many theories have been developed to describe or predict the activity coefficient of a component given the composition of the solution. Scatchard-Hildebrand regular solution theory predicts that the solubility of a solute will be a maximum in a solvent when the solubility parameter of the solvent equals the solubility parameter of the solute. Therefore, mixing a solvent having a solubility parameter greater than that of the solute and a solvent having a solubility parameter less than that of the solute in the correct proportion will maximize solute solubility. Regular solution theory is limited to nonpolar liquids and solids. Snyder (13) expanded regular solution theory to more polar solutions by proposing partial solubility parameters that take into account dipole - dipole interactions and proton-donor and proton-acceptor strength.

The UNIFAC equation and NRTL equation are other methods to compute the activity coefficient of a component from the composition of the solution. Both equations are able to predict activity coefficients in multicomponent solutions using only binary parameters and to describe miscibility gaps. Both are applicable to polar solutions. The NRTL equation has another parameter, α_{12}, that is related to the "nonrandomness" of the solution. A typical value for α_{12} is 0.3 (14). Prausnitz, et al. note that it is difficult to predict accurately both the activity coefficients at the miscibility limit and in the miscible region (14).

The three-suffix Margules equation has a ternary parameter, besides the binary parameters, and that may be helpful in describing the liquid - liquid and solid - liquid equilibria under study. The complex nature of the systems considered in this work make them difficult to model.

2.4 Experimental Investigations of Enhanced Solubility

The solubilities of dicarboxylic acids in anhydrous organic solvents and organic solvents in equilibrium with water were determined. The solubility of an acid in an organic solvent that is in equilibrium with water is the acid concentration at the triple point as discussed in regards to Figure 2.6. All the systems studied have ternary phase diagrams similar to Figure 2.6 where the solid - liquid equilibrium line intersects with the phase envelope, unless described otherwise. Details of the experimental procedure can be found in Appendix B.

The solvents examined were chosen to be representative of different classes of solvents, such as ketones and ethers. Other solvents were chosen to determine the effect that the placement of the functional group of interest has on the solubility of the carboxylic acid. The solvents chosen have the ability to hydrogen bond, except for heptane which was chosen as a representative aliphatic solvent.

Mixed solvents were investigated. A few of the solvents were chosen to be combined with Alamine 336 (Henkel Corp.), a mixture of tertiary amines with 8 - 10 carbon atoms per aliphatic chain. As discussed earlier, an amine can be used as an extractant to increase the distribution coefficient of the acid. Trioctyl phosphine oxide, also an extractant, is a solid at room temperature and was dissolved in heptane. Table 2.2 shows the results of experiments measuring solubilities of fumaric acid.

The solubility of fumaric acid increased greatly with an increase in the water content of the organic phase for both methylisobutylketone (MIBK) and n-butyl acetate. Smaller increases in the solubility of fumaric acid with increasing water content were found for di-n-butyl ether, 1-octanol, toluene with 0.0612 M Alamine 336, tritolyl phosphate, and MIBK with 0.064 M Alamine 336. In general, Lewis-base solvents showed increased fumaric acid solubility with increased water content.

The solubility of fumaric acid did not change with water concentration in chloroform. The solubilities of fumaric acid in chloroform, heptane, and toluene are very low and difficult to measure accurately for both the anhydrous and hydrated systems. The solubility of fumaric acid decreased with increasing water concentration in chloroform with 0.0612 M Alamine 336, tributyl phosphate, and heptane with 6.85 weight percent trioctylphosphine oxide. Three phases were formed in the water - fumaric acid - Alamine 336 system, and those results are not reported.

Two factors guided the choice of a solvent which would be likely to be among the more attractive for this precipitation process. The first is the ratio of the solute solubility in

Table 2.2 Fumaric acid solubility in different solvents at 25°C. The water concentration was not determined for the fumaric acid - MIBK and fumaric acid - MIBK - Alamine 336 systems.

Solvent	Acid Solubility (mol/L)	Water Concentration (mol/L)	$S_{hydrated}/S_{anhydrous}$
n-Butyl Acetate	0.0069 0.0393	0.034 0.700	5.70
Chloroform	0.0004 0.0004	0.004 0.077	1.0
Chloroform with 0.0612M Alamine 336	0.0603 0.0586	0.089 0.094	0.97
Di-n-butyl Ether	0.0022 0.0036	0.011 0.083	1.64
1-Octanol	0.0614 0.0899 0.0962	0.066 1.54 2.24	1.56
n-Heptane	0.0001	0.005	--
Toluene with 0.0612M Alamine 336	0.043 0.047	0.026 0.051	1.1
Tri-n-butyl Phosphate	0.848 0.759	0.156 2.76	0.89
Heptane with 6.85 wt% Tri-n-octyl Phosphine Oxide	0.0566 0.0552	0.017 0.032	0.97
Tritolyl Phosphate	0.0175 0.0291	0.145 0.340	1.66
Methylisobutylketone	0.0161 0.091	Anhydrous 2 Phase	5.65
Methylisobutylketone with 0.064M Alamine 336	0.115 0.193	Anhydrous 2 Phase	1.68

hydrated solvent to that in anhydrous solvent. This ratio is an indicator of the achievable recovery of the acid by precipitation when all of the water in the extract is removed. This ratio is shown in the fourth column of Table 2.2. The other factor is the absolute solubility of the carboxylic acid in the hydrated solvent. This is a measure of the capacity of the solvent and the distribution ratio of the acid between phases. Based upon the ratio of the solubilities, MIBK and butyl acetate were the solvents that merited further study. However, the solubility of fumaric acid in MIBK is over twice that in butyl acetate. Based on these findings, methylisobutylketone and other ketones were studied further.

The solubility of fumaric acid in the anhydrous MIBK - Alamine 336 mixture is 0.099 moles/L greater than that in the anhydrous MIBK. So, each mole of tertiary amine in solution raises the solubility of the fumaric acid by approximately 1.5 moles of acid. Possible causes for the overloading of the amine are discussed by Tamada, et al. (15) and in Appendix A.

The difference in the fumaric acid solubility between the anhydrous MIBK and hydrated MIBK is 0.075 M; the difference between anhydrous MIBK - Alamine 336 and hydrated MIBK - Alamine 336 is 0.078 M. The presence of the tertiary amine does not significantly affect the role of water in increasing the fumaric acid solubility. Since the solubility of fumaric acid is higher in the amine system, the factor of increase due to the presence of water is less.

2.4.2 Acid Solubilities in Heptanone Isomers

The solubilities of fumaric acid, succinic acid, and adipic acid were determined in anhydrous and hydrated MIBK, 2-heptanone, 3-heptanone, and 4-heptanone, and are shown in Table 2.3. The solubilities of the acids in the different heptanone isomers were determined to find the effect of the position of carbonyl group, i.e. the stereochemistry, on the acid solubility and the change in acid solubility with water content.

Although the water concentrations were not measured for the fumaric acid - MIBK and succinic acid - MIBK systems, they can be estimated from the water concentrations in

Table 2.3 Solubilities of fumaric acid, succinic acid, and adipic acid in methylisobutylketone and isomers of heptanone at 25°C. The water concentration was not determined in the fumaric acid - MIBK and succinic acid - MIBK systems.

Solvent	Acid	Acid Solubility (mol/L)	Water Concentration (mol/L)	$S_{hydrated}/S_{anhydrous}$
Methylisobutylketone	Fumaric Acid	0.0161 0.091	Anhydrous 2 Phase	5.65
2-Heptanone	Fumaric Acid	0.0120 0.0625	0.0 0.81	5.21
3-Heptanone	Fumaric Acid	0.0076 0.0286	0.0 0.52	3.76
4-Heptanone	Fumaric Acid	0.00623 0.0255	0.0 0.47	4.09
Methylisobutylketone	Succinic Acid	0.030 0.150	Anhydrous 2 Phase	5.00
2-Heptanone	Succinic Acid	0.0231 0.0944	0.0 0.88	4.09
3-Heptanone	Succinic Acid	0.0147 0.0391	0.0 0.57	2.66
4-Heptanone	Succinic Acid	0.0108 0.0348	0.0 0.50	3.22
Methylisobutylketone	Adipic Acid	0.0488 0.166	0.18 1.29	3.40
2-Heptanone	Adipic Acid	0.0271 0.109	0.0 0.87	4.02
3-Heptanone	Adipic Acid	0.0150 0.0474	0.0 0.54	3.16
4-Heptanone	Adipic Acid	0.0118 0.0420	0.0 0.48	3.56

the adipic acid - MIBK system, based on the observation that the water concentrations in the heptanone series did not vary greatly from acid to acid.

There were very distinct solubility trends among solvents. For all three acids, the acid solubilities in the anhydrous solvents decreased in the order MIBK > 2-heptanone > 3-heptanone > 4-heptanone. The hydrated solvents showed the same order of acid solubility. The lowest ratio of acid solubility in the hydrated solvent to that in the anhydrous solvent was in 3-heptanone for all three acids. Fumaric acid and succinic acid showed the highest ratio of acid solubilities in MIBK as compared with the other solvents; for adipic acid, the highest ratio occurred in 2-heptanone. The solvents with the carbonyl carbon in the 2 position showed the highest solubilities and the greatest solubility increase with the addition of water.

The relative results for the different acids varied for different solvents. Adipic acid always showed the highest solubility; fumaric acid showed the lowest solubility. However, fumaric acid always had the largest ratio of acid solubilities between hydrated and anhydrous conditions. Adipic acid had the lowest ratio of acid solubilities for the solvents with the carbonyl in the 2 position; succinic acid displayed the lowest ratio of acid solubilities in 3-heptanone and 4-heptanone.

From these data, it was determined that ketones that had a carbonyl group that was not sterically hindered would demonstrate the greatest increase in acid solubility in organic solvents with increasing water concentration. Cyclohexanone was an obvious choice for further screening of solvents. The mutual solubility for water and cyclohexanone is much higher than for any of the other solvents discussed so far. Based on reducing solvent losses to the raffinate and reducing the amount of water vaporized in the regeneration step, methylcyclohexanone and acetophenone (methylbenzylketone) were also screened.

2.4.2 Acid Solubilities in Cyclic Ketones

Table 2.4 displays the solubilities of the three acids of interest in cyclohexanone, methylcyclohexanone, and acetophenone. The ratio of the acid solubilities in the hydrated

Table 2.4 Solubilities of fumaric acid, succinic acid, and adipic acid in cyclohexanone, methylcyclohexanone, and acetophenone at 25°C. The water concentration was not determined for the acetophenone - acid systems.

Solvent	Acid	Acid Solubility (mol/L)	Water Concentration (mol/L)	$S_{hydrated}/S_{anhydrous}$
Cyclohexanone	Fumaric Acid	0.053 0.456	0.0 4.75	8.60
Methylcyclohexanone	Fumaric Acid	0.0392 0.295	0.0 2.68	7.53
Acetophenone	Fumaric Acid	0.0114 0.0634	Anhydrous 2 Phase	5.54
Cyclohexanone	Succinic Acid	0.136 1.04	0.0 8.32	7.65
Methylcyclohexanone	Succinic Acid	0.083 0.519	0.0 3.44	6.25
Acetophenone	Succinic Acid	0.035 0.161	Anhydrous 2 Phase	4.6
Cyclohexanone	Adipic Acid	0.163 1.06	0.0 7.38	6.50
Methylcyclohexanone	Adipic Acid	0.102 0.607	0.0 3.23	5.95
Acetophenone	Adipic Acid	0.0382 0.196	Anhydrous 2 Phase	5.13

cyclic ketones to those in the anhydrous state significantly increased in comparison with the other ketones studied. Cyclohexanone exhibits the highest solubilities and the highest ratio of acid solubilities, as well as water concentrations twice those for the methylcyclohexanone system. Methylcyclohexanone demonstrated fairly high solubilities and an increase in acid solubility second only to cyclohexanone. Acetophenone gave acid solubilities and ratios of acid solubilities that were similar to the other ketones with the carbonyl in the 2 position.

As with the other ketone solvents, adipic acid had the highest solubility, and fumaric acid had the lowest solubility and the largest ratio of acid solubilities.

The solubilities of the acids are highly dependent upon the temperature of the system. The acid solubilities in anhydrous and hydrated cyclohexanone and methylcyclohexanone at 45°C were determined, and the results are shown in Table 2.5. Not surprisingly, the acid solubilities in the anhydrous and hydrated solvents increased with an increase in temperature.

The most unusual finding was that the solid - liquid equilibrium line did not intersect the phase envelope for the adipic acid - cyclohexanone and succinic acid - cyclohexanone systems at 45°C. This phenomena of the solid - liquid equilibrium line rising above the phase envelope with increasing temperature was described in Figure 2.4. All the other systems discussed so far have been similar to Figure 2.6, where the solid - liquid equilibrium line intersects with phase envelope.

Since the triple point does not exist for the adipic acid - cyclohexanone and succinic acid - cyclohexanone systems, the acid solubility in a mixture that was approximately 50/50 water/cyclohexanone by volume was determined. This mixture has a water concentration of approximately 21.5 M.

For the other four systems studied, the ratio of the acid solubility in the hydrated solvent to that in the anhydrous solvent decreased with increasing temperature. The differences in solubility among acids did not change at the higher temperature.

Clearly, cyclohexanone and methylcyclohexanone show promise for an extract

Table 2.5 Solubilities of fumaric acid, succinic acid, and adipic acid in cyclohexanone and methylcyclohexanone at 45°C.

Solvent	Acid	Acid Solubility (mol/L)	Water Concentration (mol/L)	$S_{hydrated}/S_{anhydrous}$
Cyclohexanone	Fumaric Acid	0.0850 0.624	0.0 5.64	7.34
Methylcyclohexanone	Fumaric Acid	0.0620 0.419	0.0 3.02	6.76
Cyclohexanone	Succinic Acid	0.226 2.114	0.0 21.9*	9.35
Methylcyclohexanone	Succinic Acid	0.141 0.930	0.0 4.31	6.60
Cyclohexanone	Adipic Acid	0.290 1.76	0.0 21.6*	6.07
Methylcyclohexanone	Adipic Acid	0.195 1.04	0.0 4.70	5.33

* - Not in equilibrium with an aqueous phase (see text)

regeneration process where the acid is precipitated by selective removal of the co-extracted water. From this limited amount of data, it was not possible to define clearly which of the two solvents might give the most economical process since cyclohexanone had a greater capacity and theoretical yield, but required twice as much water to be removed.

Another important consideration in the solvent selection is the distribution of the acid between the aqueous and organic phases. As reported in Chapter 4, the distribution ratios of the acids into the cyclohexanone and methylcyclohexanone are favorable for an extraction process. In an effort to determine the practicality of the regeneration method, experiments were performed in order to describe the solid - liquid and the liquid - liquid equilibrium characteristics more fully for fumaric acid, succinic acid, and adipic acid in cyclohexanone and methylcyclohexanone.

2.5 Summary

Fumaric acid solubilities in hydrated and anhydrous organic solvents were measured. Ketone solvents showed a large increase in acid solubility upon the addition of water. The steric availability of the carbonyl group is important as shown by acid solubilities in heptanone isomers. Acid solubilities in cyclohexanone increased greatly with an increased water content.

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CHAPTER 3. SOLID - LIQUID EQUILIBRIUM

Results of solid - liquid equilibrium experiments for fumaric acid, succinic acid, and adipic acid in cyclohexanone and methylcyclohexanone with varying water content are presented in this chapter. Simple curve-fitting models are used to describe the data. The solubilities of the acids in the water-solvent mixture were measured as described in Appendix B.

3.1 Acid Dissolution Equilibrium Time

The time for the solid - liquid systems to come to equilibrium through the dissolution of the carboxylic acid was surprisingly long. Experiments were carried out with a solid acid phase present, and changes were made such that more acid should dissolve. The original acid concentration, C_o, was measured at a given water concentration in the cyclohexanone, and then a small amount of water was added to the cyclohexanone - acid system. The acid concentration was measured over time until it reached a steady state value, C_f. Figure 3.1 shows the acid concentration over time. Notice that the systems did not reach equilibrium until after eight days. The acid concentration jumps to approximately 74% of its final value after only one day, then slowly increases to its final value. For the solid - liquid equilibrium data reported here, the systems were left at least ten days at the temperature of interest before being analyzed for the acid and water content.

3.2 Equilibrium Concentrations

Figures 3.2-13 show the solid - liquid equilibrium data at 25°C and 45°C. These figures can be considered to be the solvent corner of the ternary phase diagram with the axes at 90°, instead of 60°. The ternary phase diagrams and the figures have the water concentration on the x-axis, however the equations below are written with the acid

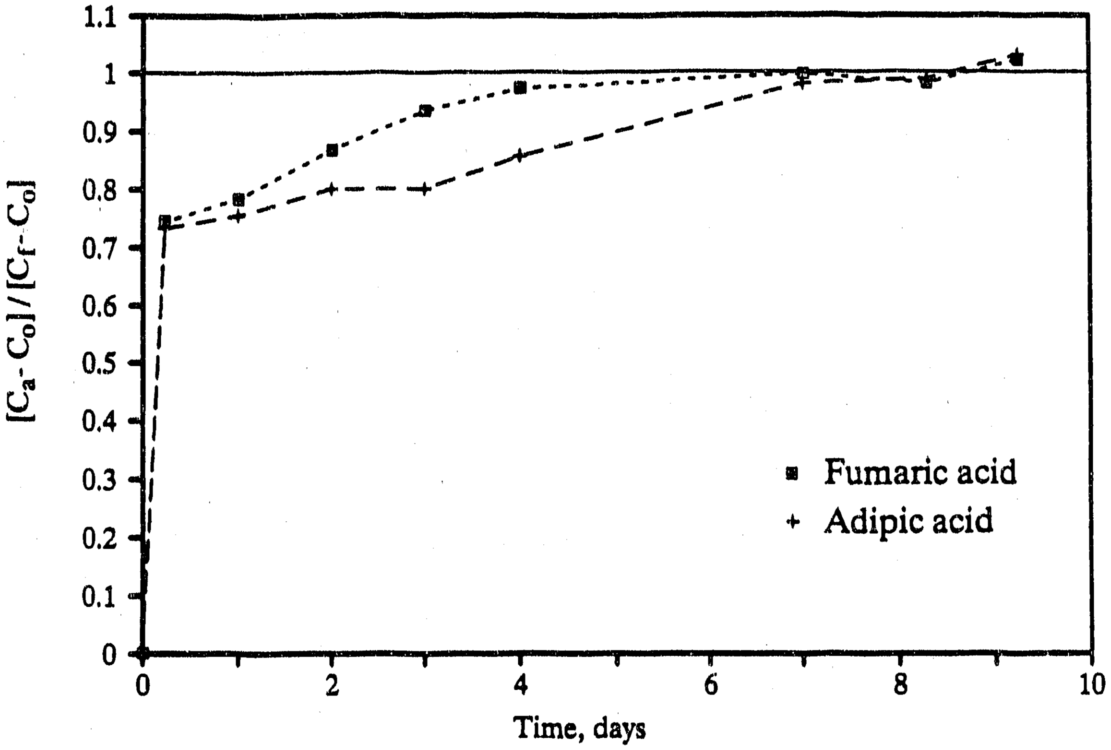

Figure 3.1 Equilibration time for dissolving fumaric acid and adipic acid in cyclohexanone at 25 C.

$C_{o,\text{ fumaric acid}}$ = 0.25 mol/L
$C_{f,\text{ fumaric acid}}$ = 0.43 mol/L

$C_{o,\text{ adipic acid}}$ = 0.74 mol/L
$C_{f,\text{ adipic acid}}$ = 1.21 mol/L

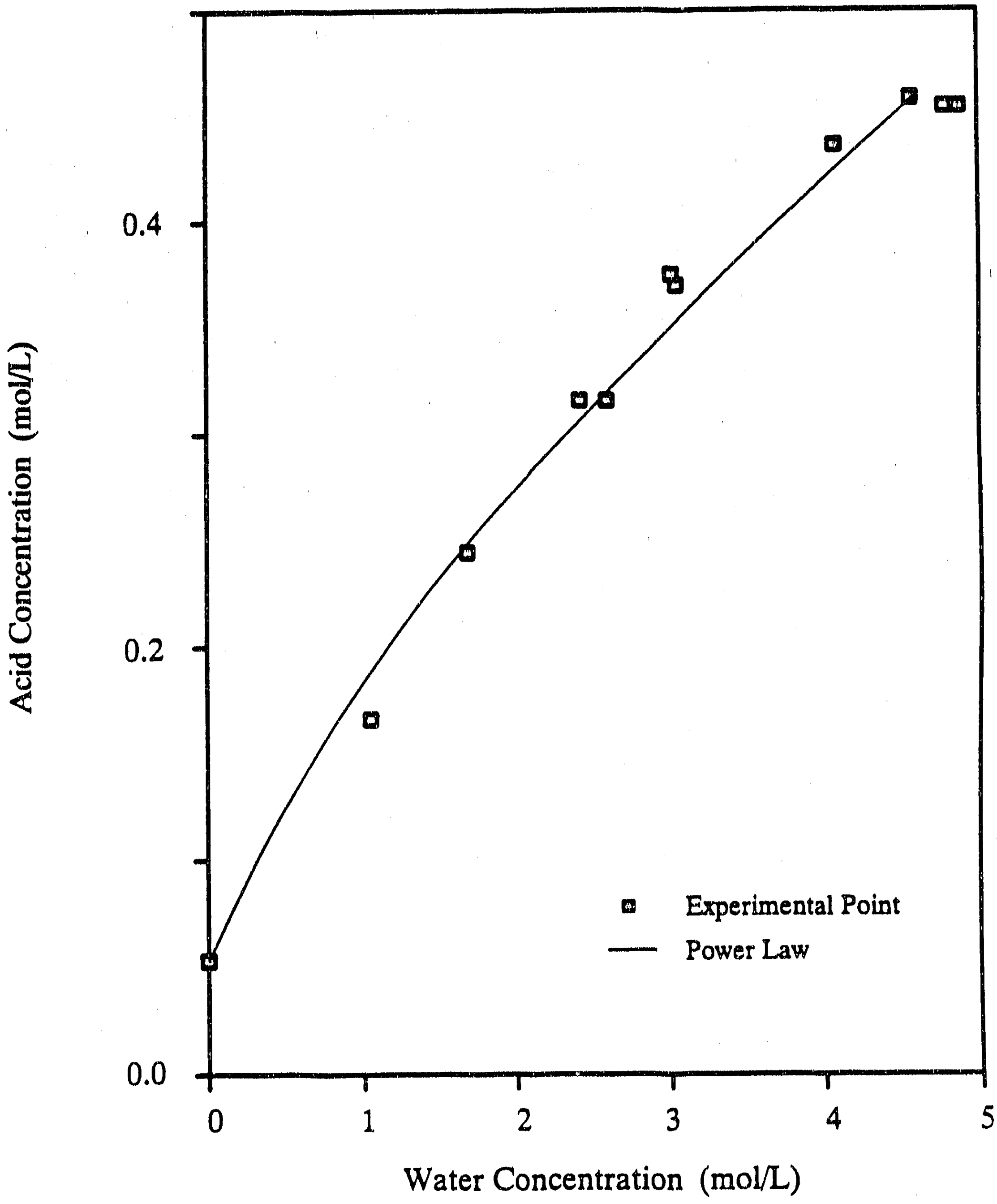

Figure 3.2 Fumaric acid - cyclohexanone - water solid - liquid equilibrium at 25 C with best fit curve.

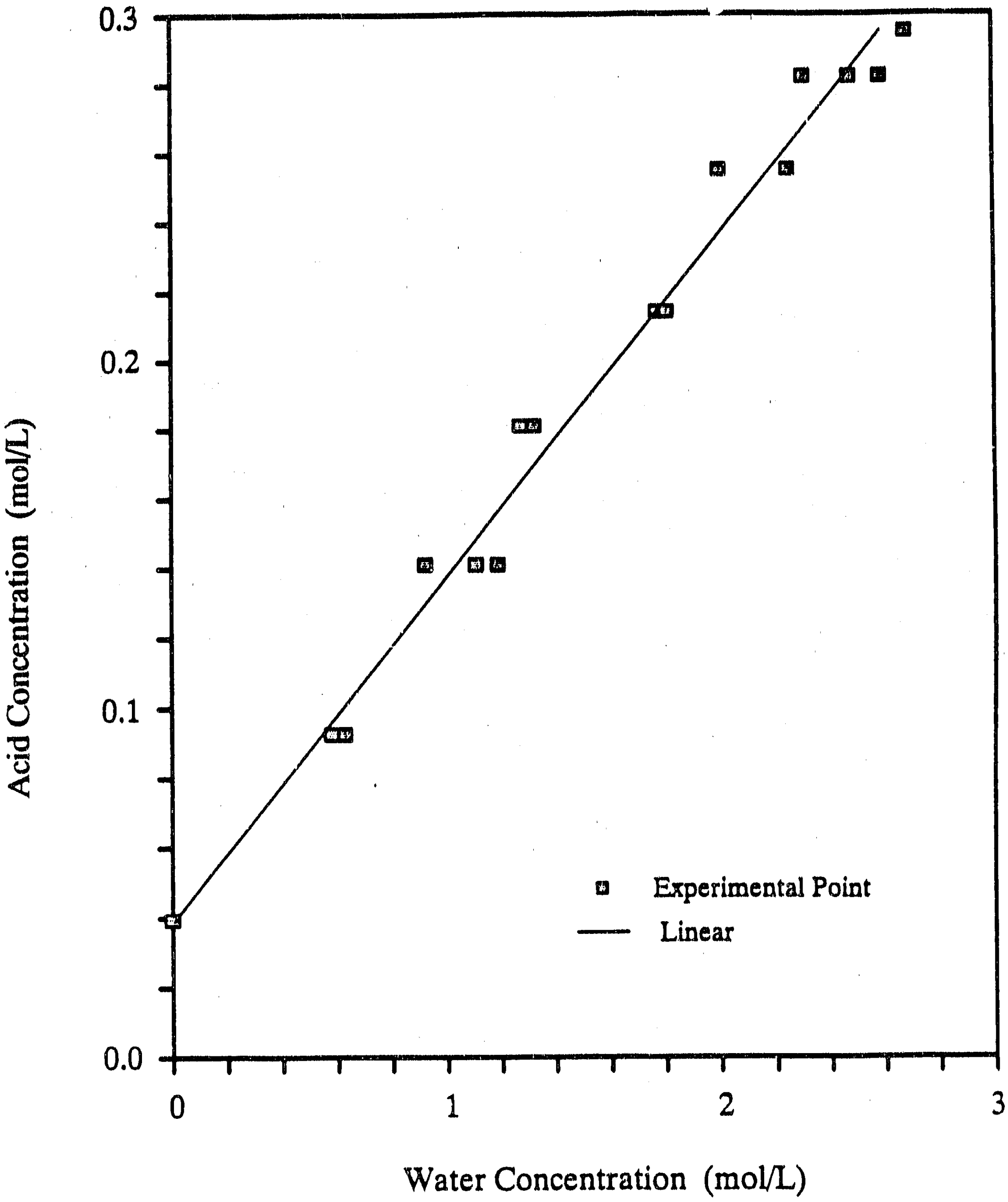

Figure 3.3 Fumaric acid - methylcyclohexanone - water solid - liquid equilibrium at 25 C with best fit curve.

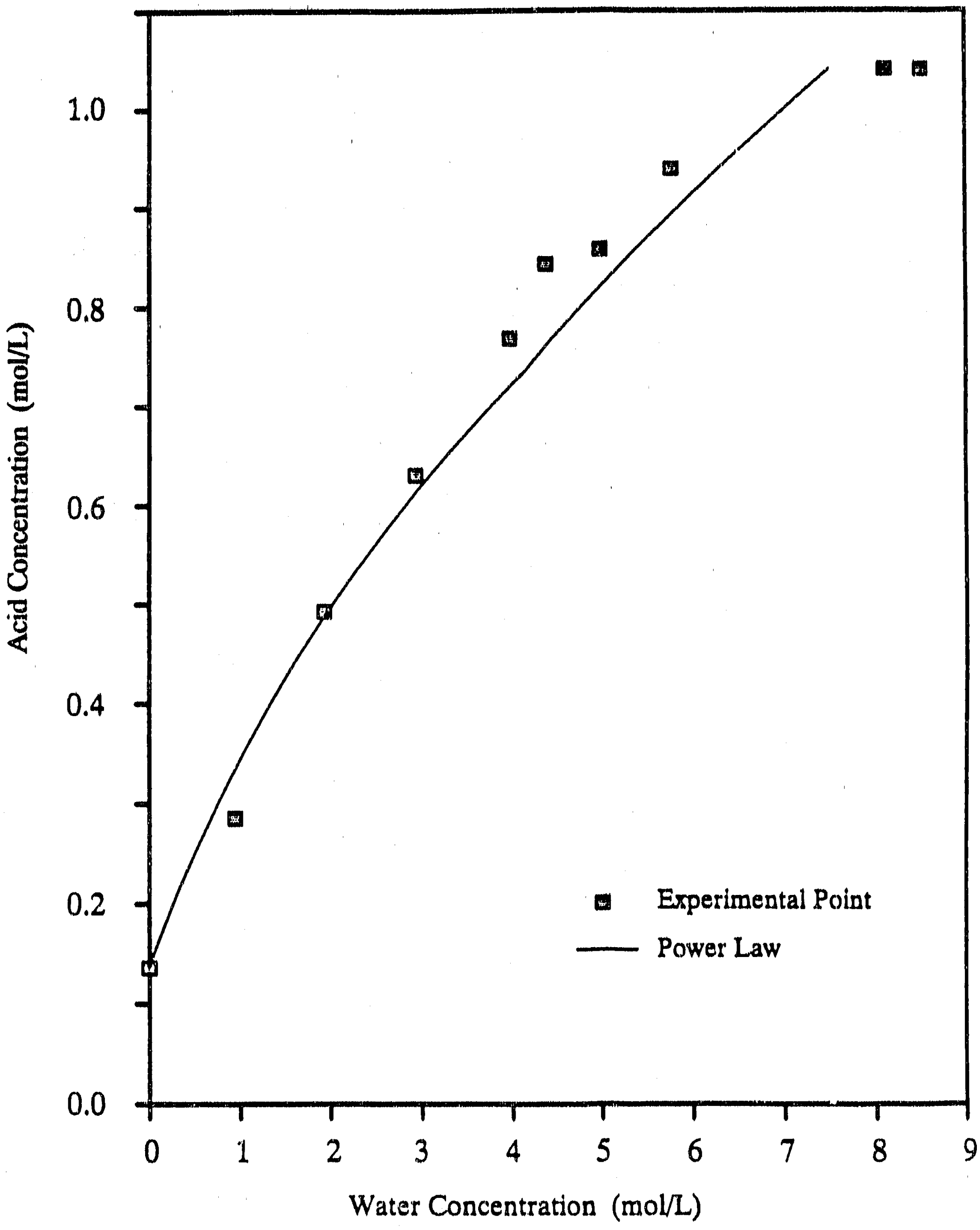

Figure 3.4 Succinic acid - cyclohexanone - water solid - liquid equilibrium at 25 C with best fit curve.

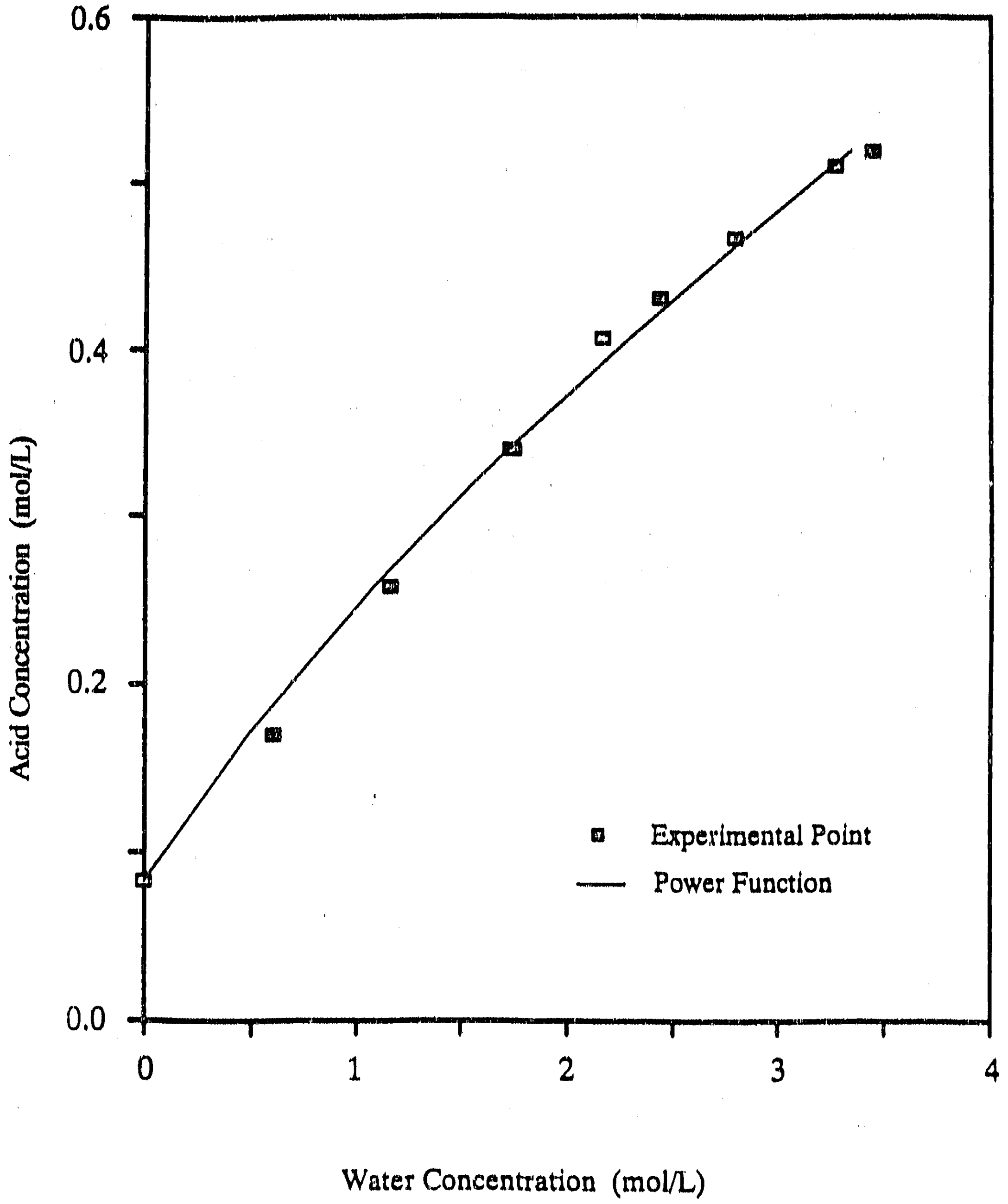

Figure 3.5 Succinic acid - methylcyclohexanone - water solid - liquid equilibrium at 25 C with best fit curve.

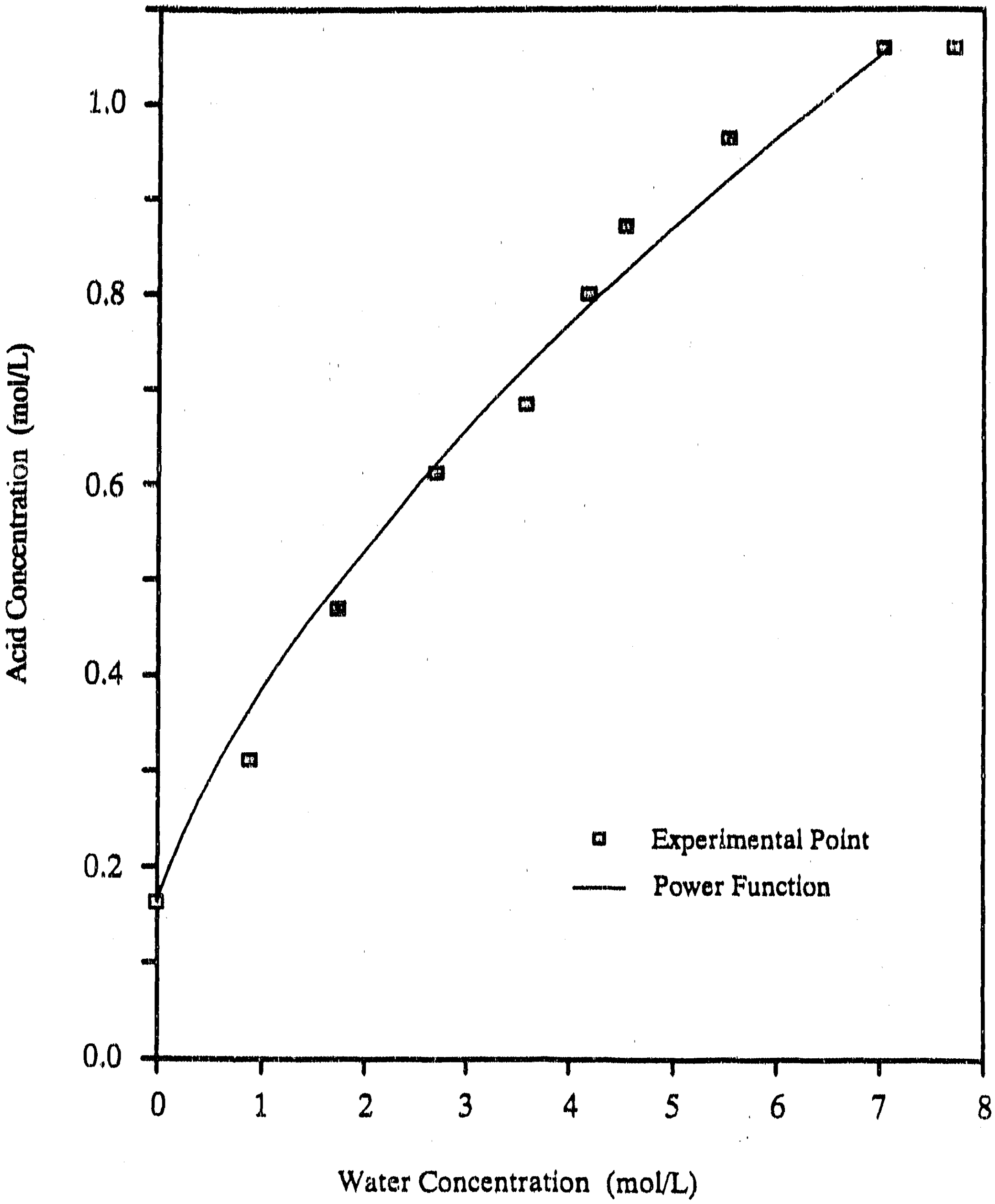

Figure 3.6 Adipic acid - cyclohexanone - water solid - liquid equilibrium at 25 C with best fit curve.

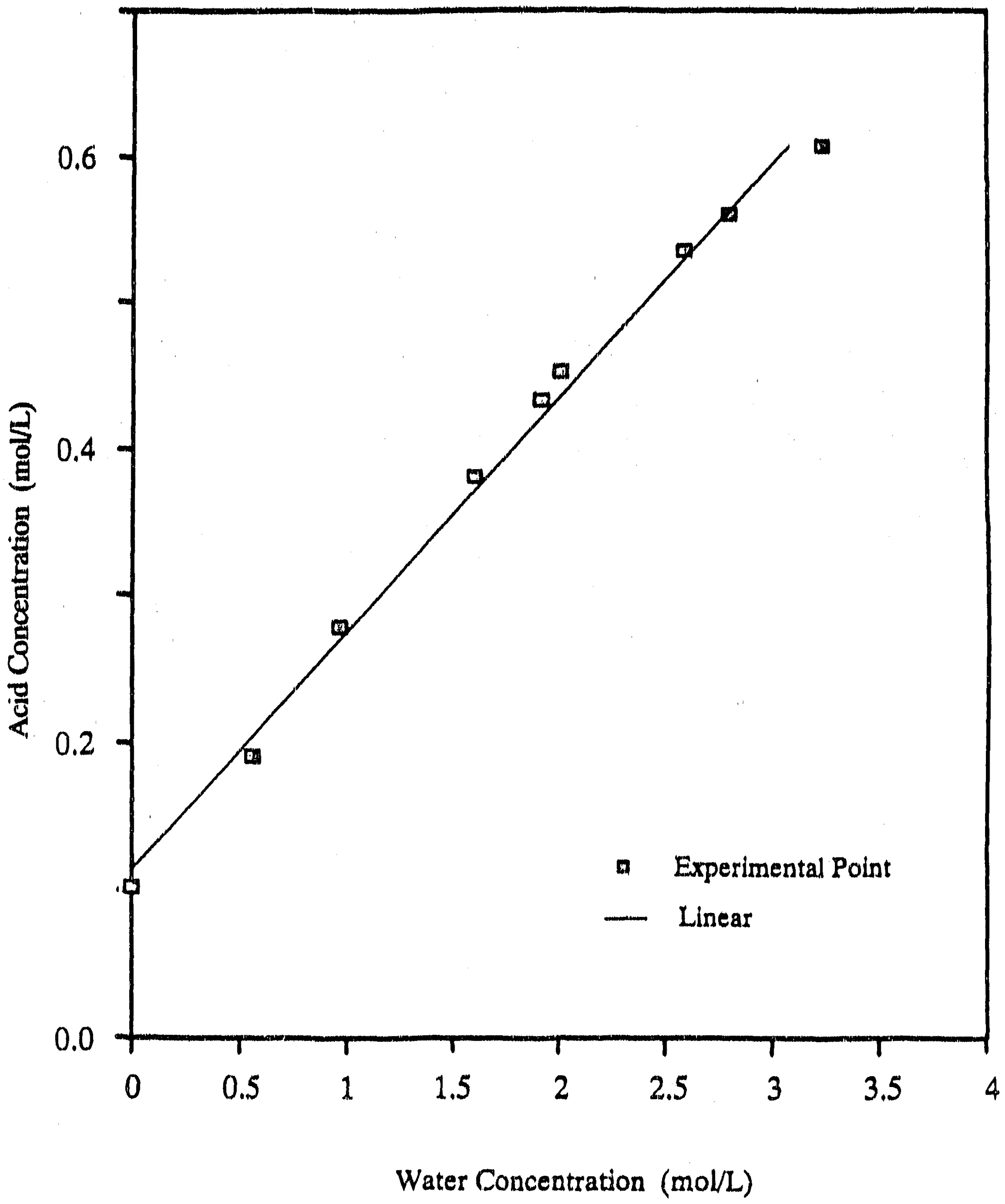

Figure 3.7 Adipic acid - methylcyclohexanone - water solid - liquid equilibrium at 25 C with best fit curve.

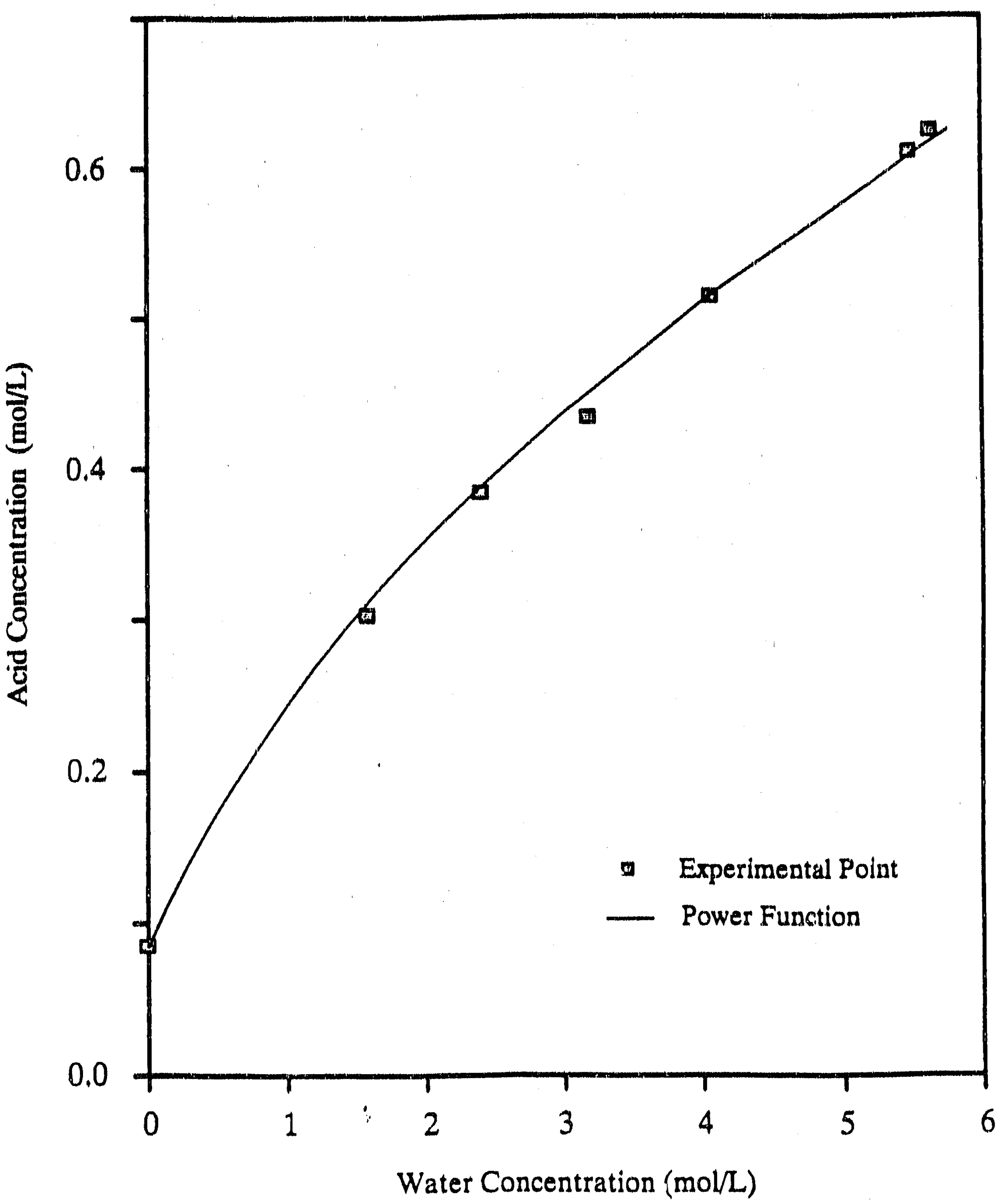

Figure 3.8 Fumaric acid - cyclohexanone - water solid - liquid equilibrium at 45 C with best fit curve.

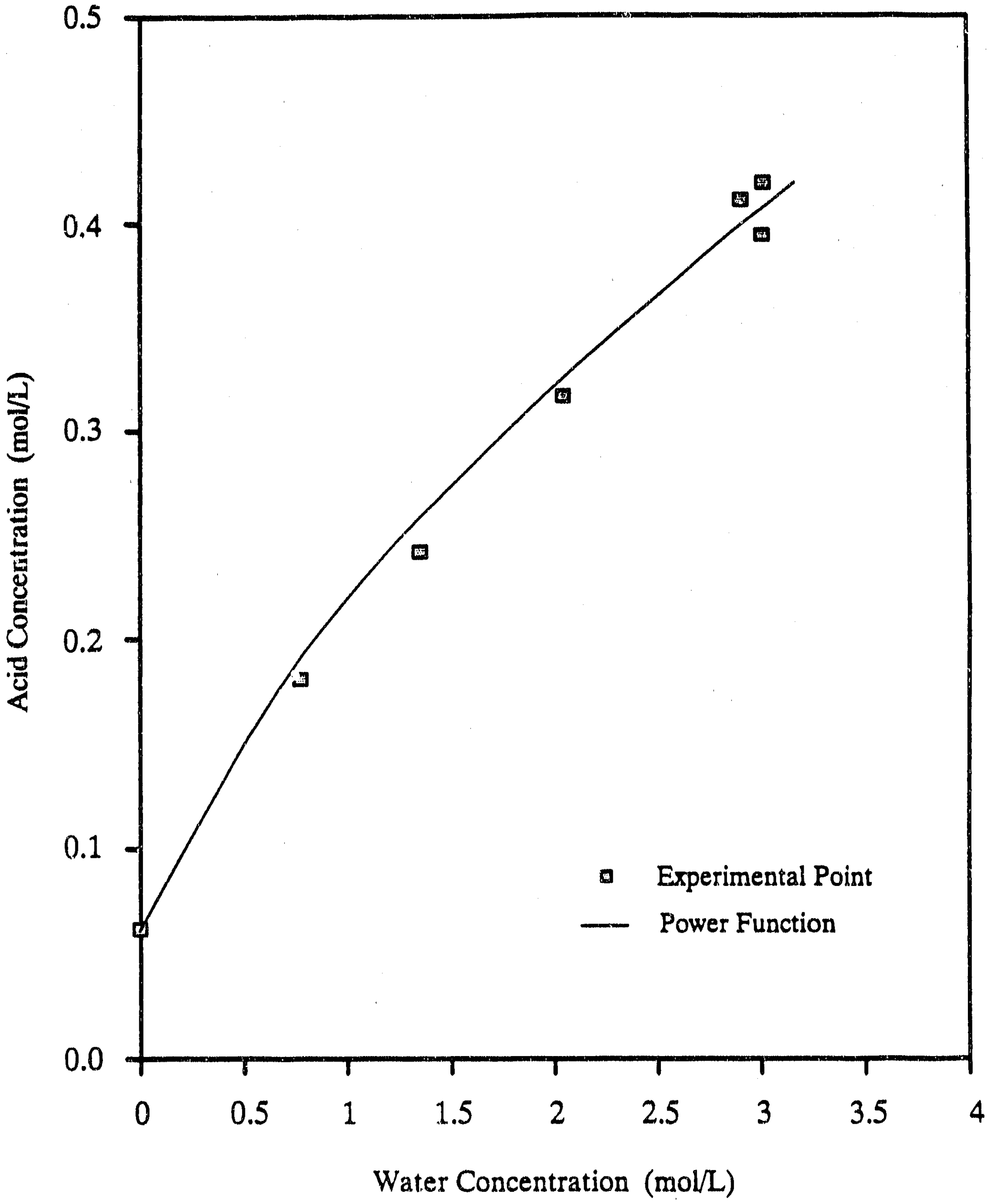

Figure 3.9 Fumaric acid - methylcyclohexanone - water solid - liquid equilibrium at 45 C with best fit curve.

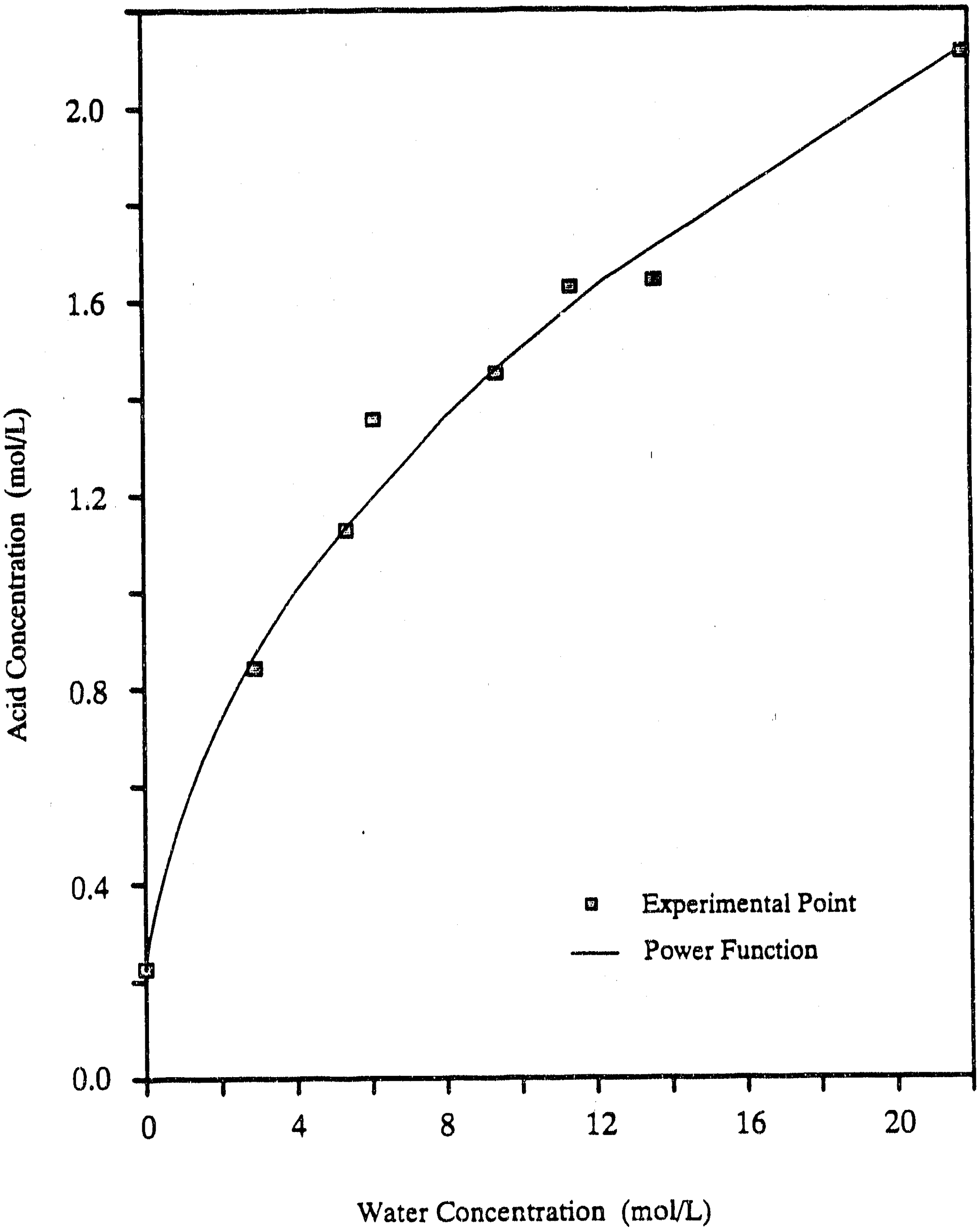

Figure 3.10 Succinic acid - cyclohexanone - water solid - liquid equilibrium at 45 C with best fit curve.

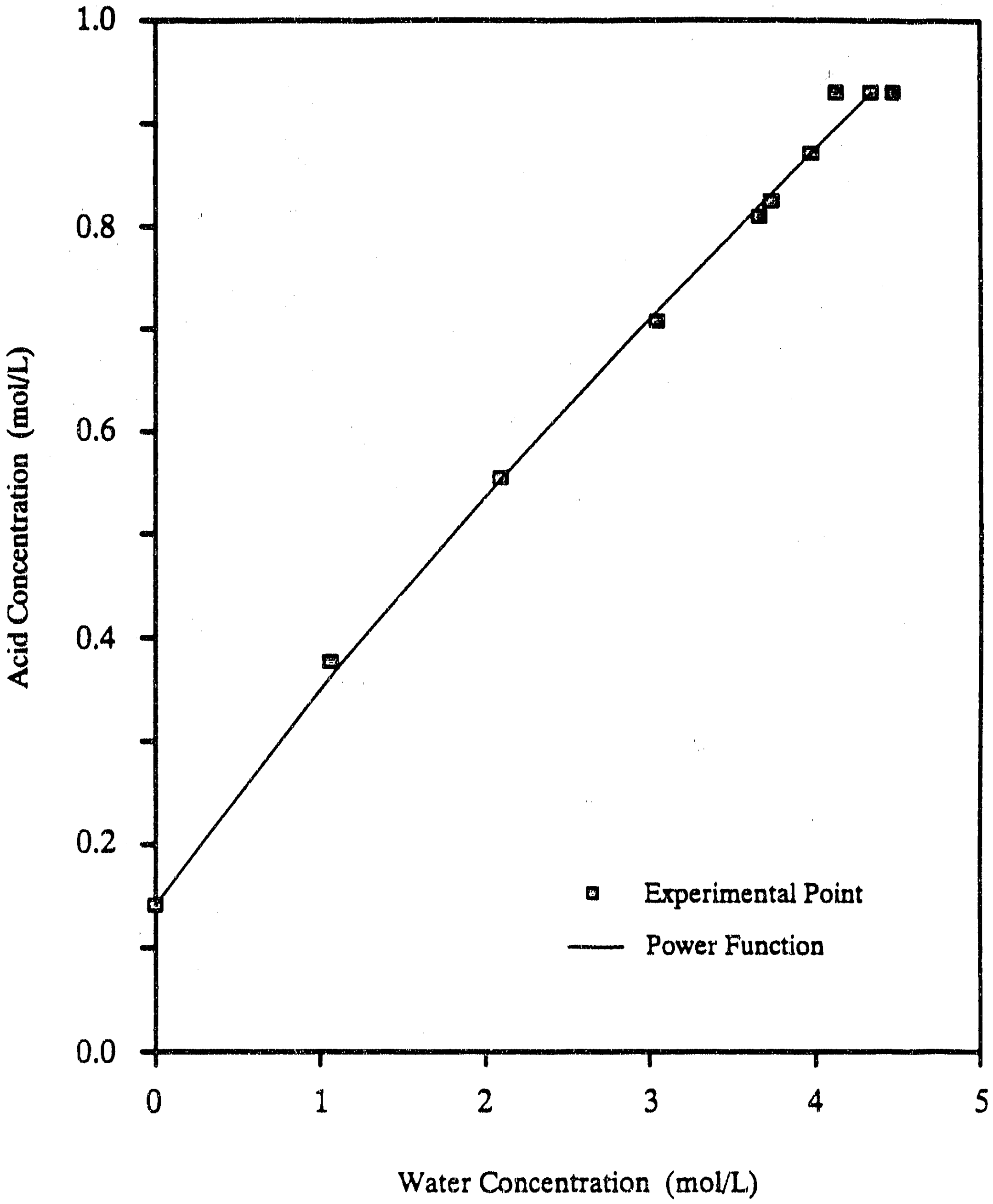

Figure 3.11 Succinic acid - methylcyclohexanone - water solid - liquid equilibrium at 45 C with best fit curve

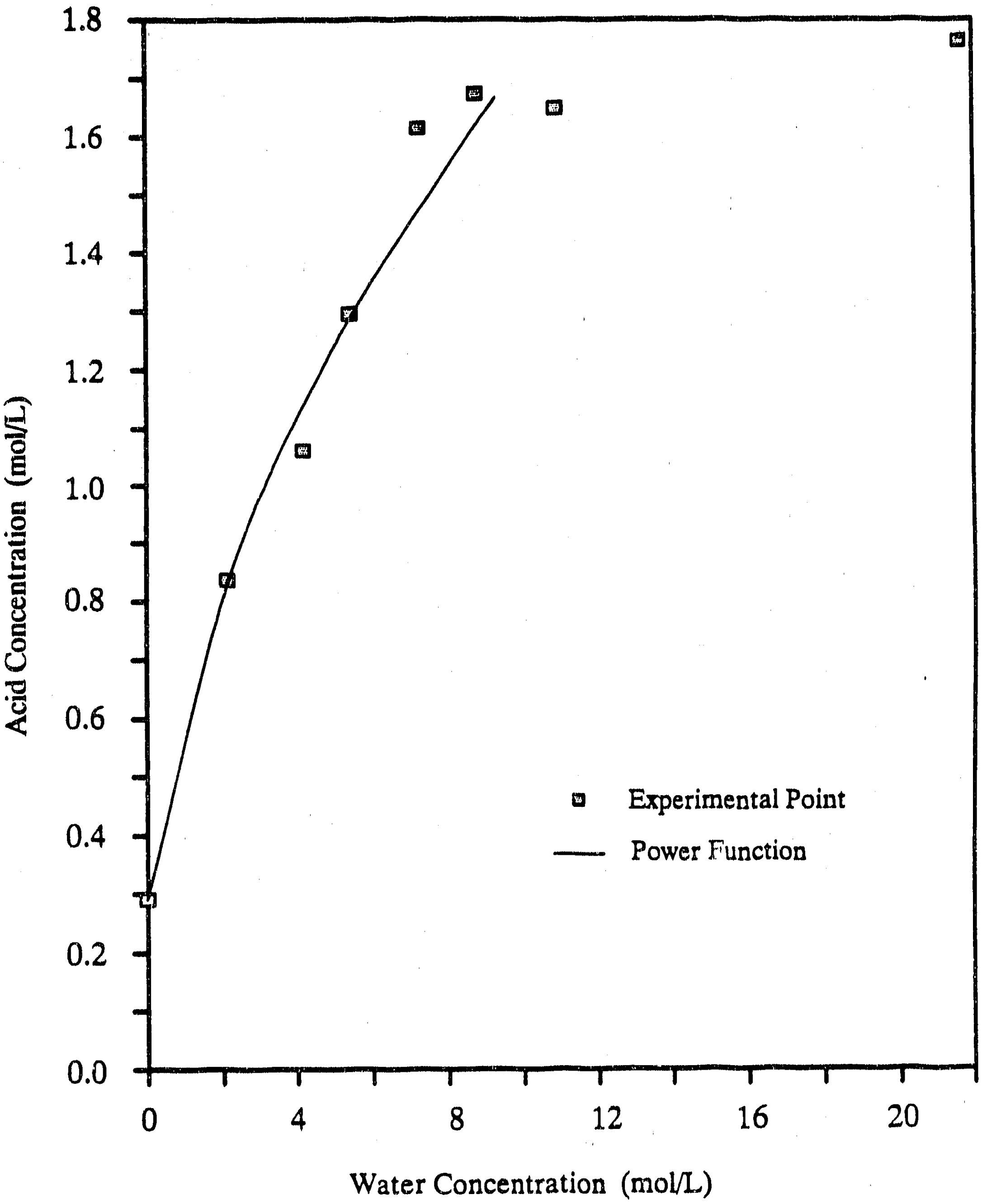

Figure 3.12 Adipic acid - cyclohexanone - water solid - liquid equilibrium at 45 C with best fit curve.

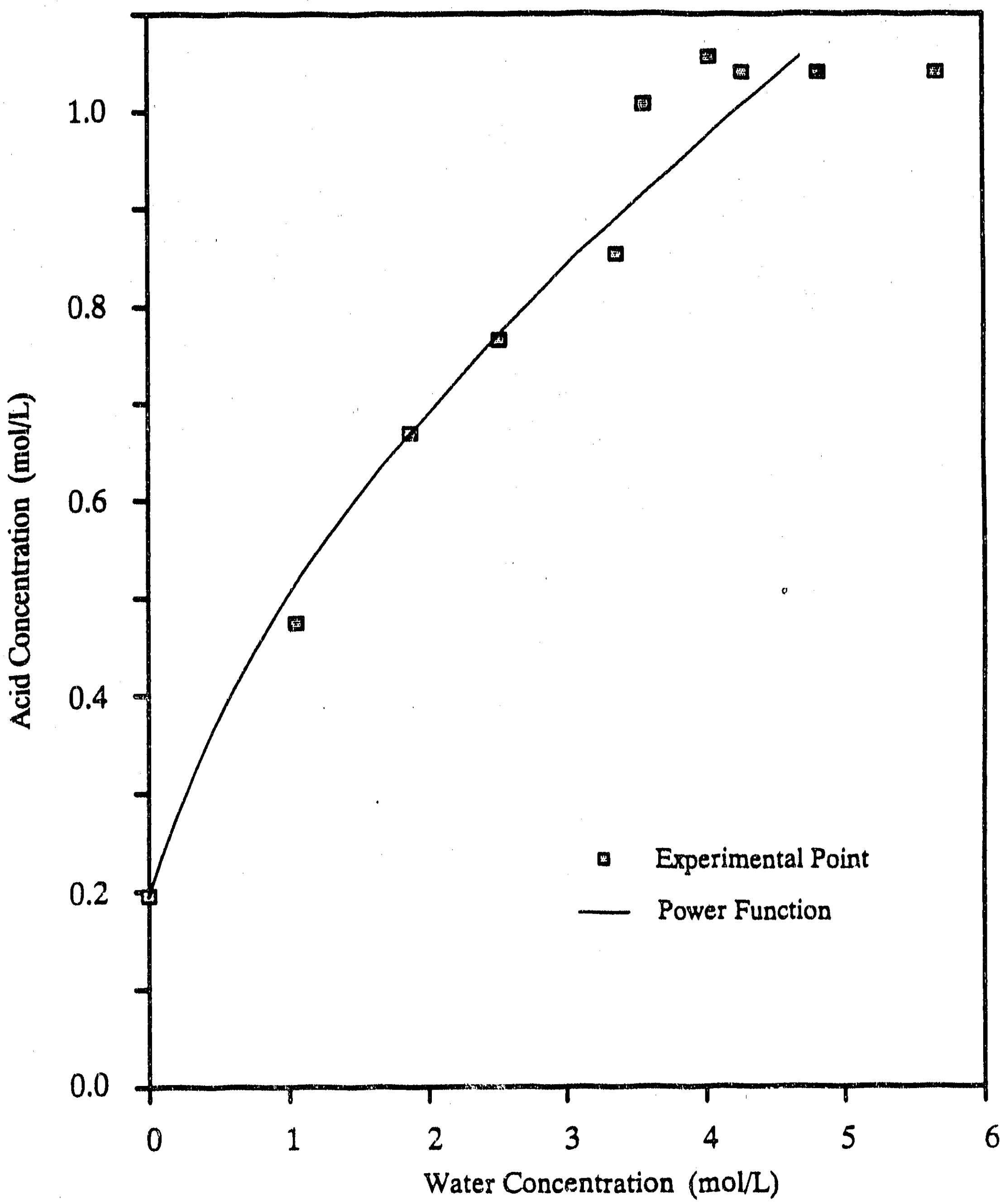

Figure 3.13 Adipic acid - methylcyclohexanone - water solid - liquid equilibrium at 45 C with best fit curve.

concentration as the x value. Some samples had repeated analyses of the water concentration giving multiple data points for a given acid concentration. Data points taken at the highest acid concentration are at the triple point, except for the adipic acid - cyclohexanone and succinic acid - cyclohexanone systems at 45°C. As mentioned in Chapter 2, the solid - liquid equilibrium curve has risen above the phase envelope and the triple point does not exist for these systems at that temperature.

Linear and power law equations relating the acid solubility to the water content in the mixed solvent were tested. Linear regression was used to determine the value of the constants, and the correlation coefficient value, r^2, from the regression determined which equation fit the data better. For the power law equation, a linear regression analysis of the data plotted on log - log coordinates gave an estimate of the exponent.

The linear and power law equations, Equations 3.2 and 3.3, are shown below.

$$C_w = \alpha\, C_a + \beta \tag{3.1}$$

$$C_w = \alpha\, C_a^{\beta} + \gamma \tag{3.2}$$

The power law equation has three constants to be determined, while the linear equation has only two. Since the data were felt not to be sufficient to justify calculating three parameters, γ was chosen such that the curve passed through the data point taken under anhydrous conditions. The resulting equation, Equation 3.3, was used for all remaining calculations.

$$C_w = \alpha\, (C_a^{\beta} - C_{a\ \mathrm{anhydrous}}^{\beta}) \tag{3.3}$$

The linear equation fit the fumaric acid - methylcyclohexanone - water and adipic acid - methylcyclohexanone - water at 25°C systems better. On the other hand, the power law equation, Equation 3.2, fit the rest of the systems better. From the ternary phase diagrams in Chapter 2, some curvature of the solid - liquid equilibrium line can be expected. The probable reason that the linear equation works well for describing the fumaric acid - methylcyclohexanone and adipic acid - methylcyclohexanone data is that the water and acid concentrations are not high enough to enter the range of significant curvature. The rest of the data, which do correspond to relatively large water and acid concentrations, can best be described by a relationship that is non-linear. For the adipic acid - cyclohexanone - water system at 45°C, the data point taken at the highest water concentration was not used in the regression analysis. Table 3.1 and Table 3.2 give the values of α and β calculated for the systems studied at 25°C and 45°C, respectively.

Each of the best fit curves has a positive slope showing an increase in acid solubility with an increase in water concentration. The value of the slope as written in the equations is the change in water concentration divided by the change in the acid concentration. Since both concentrations are in units of moles per liter, the slope of the line can be interpreted as the number of water molecules per molecule of acid entering the organic phase.

For systems described by a linear equation, the water per incremental acid is a constant over all concentrations of acid and water. For systems described by the power law equation, the water per additional acid depends upon the acid concentration. Taking the derivatives of Equation 3.1 and Equation 3.3 with respect to the acid concentration gives the formulas for finding the value of the number of waters per incremental acid entering the organic phase. These formulas are shown in Equation 3.4 for the linear equation and Equation 3.5 for the power law equation.

$$\frac{\partial C_w}{\partial C_a} = \alpha \tag{3.4}$$

$$\frac{\partial C_w}{\partial C_a} = \alpha \beta C_a^{\beta-1} \tag{3.5}$$

Equation 3.5 shows that the amount of water per acid incrementally entering the

Table 3.1 Values for solid - liquid equilibrium linear regression constants at 25°C

System	Equation	α	β
Fumaric Acid-Cyclohexanone	Power Law	15.4	1.5
Fumaric Acid - Methylcyclohexanone	Linear	10.1	-0.38
Succinic Acid - Cyclohexanone	Power Law	7.3	1.64
Succinic Acid - Methylcyclohexanone	Power Law	9.1	1.4
Adipic Acid - Cyclohexanone	Power Law	6.7	1.69
Adipic Acid - Methylcyclohexanone	Linear	6.2	-0.71

Table 3.2 Values for solid - liquid equilibrium linear regression constants at 45°C

System	Equation	α	β
Fumaric Acid-Cyclohexanone	Power Law	13.6	1.75
Fumaric Acid - Methylcyclohexanone	Power Law	14.0	1.66
Succinic Acid - Cyclohexanone	Power Law	4.1	2.22
Succinic Acid - Methylcyclohexanone	Power Law	5.3	1.2
Adipic Acid - Cyclohexanone	Power Law	3.4	2.02
Adipic Acid - Methylcyclohexanone	Power Law	4.4	1.85

organic phase increases as the acid concentration increases, as long as $\beta > 1$. This is advantageous to the regeneration process in which the water is selectively removed in order to precipitate the acid. This is because there is the greatest decrease in acid solubility at low water concentrations, where the process will probably be operated.

Table 3.3 and Table 3.4 show the values of the slopes, the incremental water per incremental acid at very low water concentrations, along with the acid solubility at anhydrous conditions for the systems studied at 25°C and 45°C, respectively. The two systems that were best described by a linear equation showed the highest values of the slope. Since the slope for the linear equation is an average over the entire acid concentration range, and the other systems show an increasing amount of water per acid entering the organic phase with an increase in the acid concentration, the linear equation may overestimate the water required to solvate the acid at low water concentrations in the organic phase.

In every system studied, the amount of water needed to solubilize an acid into the organic phase was greater at 25° than at 45°C. At 25°C, the methylcyclohexanone systems required more water per acid than the cyclohexanone systems. At 45°C, there was not a significant difference in the amount of water needed per acid between the two solvents.

For a given solvent at a given temperature, fumaric acid requires the most water to enter the organic phase, except for the cases of methylcyclohexanone at 45°C where succinic acid had the highest slope value.

The amount of water needed to solubilize the acid into the organic phase at low water concentrations gives insight to the nature of the water - acid interactions. The fact that the amount of water needed to solubilize the acid into the organic phase is on the order of the number of hydrogen-bonding sites on the acid is evidence for specific hydrogen bonding between the acid and water.

The fact that fumaric acid requires more water than the other two acids is probably related to the fact that fumaric acid cannot form intramolecular hydrogen bonds because the carboxylic acid functional groups are located *trans* across the double bond. On the other

Table 3.3 Water per acid values for systems at 25°C at anhydrous conditions

System	Equation	$S_{anhydrous}$ (mol/L)	$\left.\frac{\partial C_w}{\partial C_a}\right\|_{w=0}$
Fumaric Acid-Cyclohexanone	Power Law	0.053	5.3
Fumaric Acid - Methylcyclohexanone	Linear	0.039	10.1
Succinic Acid - Cyclohexanone	Power Law	0.136	3.3
Succinic Acid - Methylcyclohexanone	Power Law	0.083	4.7
Adipic Acid - Cyclohexanone	Power Law	0.163	3.2
Adipic Acid - Methylcyclohexanone	Linear	0.102	6.2

Table 3.4 Water per acid values for systems at 45°C at anhydrous conditions

System	Equation	$S_{anhydrous}$ (mole/L)	$\left.\frac{\partial C_w}{\partial C_a}\right\|_{w=0}$
Fumaric Acid-Cyclohexanone	Power Law	0.085	3.8
Fumaric Acid - Methylcyclohexanone	Power Law	0.062	3.6
Succinic Acid - Cyclohexanone	Power Law	0.226	1.5
Succinic Acid - Methylcyclohexanone	Power Law	0.141	4.3
Adipic Acid - Cyclohexanone	Power Law	0.290	2.0
Adipic Acid - Methylcyclohexanone	Power Law	0.195	2.1

hand, both succinic acid and adipic acid can form intramolecular hydrogen bonds. If the number of water needed to solubilize the acid is related to satisfying the acids hydrogen bonding sites, then fumaric acid, which cannot intramolecular hydrogen bond, should require more water per acid.

3.3 Effect of Temperature

The solubility of the acid increases as the temperature increases. Equation 3.6 shows how the solubility of a solid in a liquid depends on the temperature, with m as the molarity of the acid in the liquid solution expressed in moles per kilogram.

$$\frac{d \ln m}{dT} = \frac{\Delta H_{solution}}{RT^2} \tag{3.6}$$

Integrating Equation 3.6 and with the knowledge that RT ln m = ΔG = ΔH - TΔS, gives Equation 3.7, which is used to calculate the enthalpy and entropy of solution for the acid from the solubility of the acid at two temperatures.

$$\ln m = \frac{-\Delta H_{solution}}{RT} + \frac{\Delta S_{solution}}{R} \tag{3.7}$$

The dependence of the enthalpy and entropy of solution on the composition of the organic phase was determined. For a given water concentration in the organic phase, the acid molalities at 25°C and 45°C were calculated by interpolation of the data. Knowing ln m at two temperatures allows the calculation of the enthalpy and entropy of solution. While the acid concentration analysis is reproducible generally to ±1%, caution should be taken in extending and interpreting the enthalpy and entropy results because only two temperatures were used to calculate the values. Once ΔH and ΔS are calculated, the change in free energy,

Table 3.5 Enthalpy, entropy, and free energy of solution for three acids in cyclohexanone with varying amounts of water.

(a) Fumaric Acid

C_w (mol/L)	ΔH (kcal/mol)	ΔS (cal/mol·K)	ΔG at 25°C (kcal/mol)	ΔG at 45°C (kcal/mol)
0.0	4.6	9.8	1.7	1.5
0.5	3.6	7.8	1.3	1.1
1.0	3.3	7.4	1.1	0.91
2.0	2.3	5.3	0.75	0.64
3.0	1.6	3.5	0.58	0.51
4.0	1.8	4.5	0.48	0.40
4.5	2.0	5.1	0.46	0.35

(b) Succinic Acid

C_w (mol/L)	ΔH (kcal/mol)	ΔS (cal/mol·K)	ΔG at 25°C (kcal/mol)	ΔG at 45°C (kcal/mol)
0.0	4.8	12.2	1.2	0.91
1.5	2.8	7.7	0.52	0.37
3.0	2.7	8.3	0.25	0.08
4.5	1.8	5.6	0.08	-0.03
6.0	3.1	10.3	0.02	-0.19
7.5	3.0	10.2	-0.02	0.22

(c) Adipic Acid

C_w (mol/L)	ΔH (kcal/mol)	ΔS (cal/mol·K)	ΔG at 25°C (kcal/mol)	ΔG at 45°C (kcal/mol)
0.0	5.4	14.5	1.1	0.76
1.0	4.5	13.1	0.63	0.37
2.0	4.2	12.7	0.38	0.12
3.0	3.5	11.0	0.25	0.03
4.0	2.8	9.0	0.14	-0.04
5.0	2.6	8.5	0.04	-0.13
6.0	3.1	10.4	-0.01	-0.22
7.0	3.6	12.2	-0.05	-0.29

Table 3.6 Enthalpy, entropy, and free energy of solution for three acids in methylcyclohexanone with varying amounts of water.

(a) Fumaric Acid

C_w (mol/L)	ΔH (kcal/mol)	ΔS (cal/mol·K)	ΔG at 25°C (kcal/mol)	ΔG at 45°C (kcal/mol)
0.0	4.4	8.5	1.9	1.7
0.5	4.9	11.7	1.4	1.2
1.0	3.6	8.5	1.1	0.95
1.5	2.8	6.3	0.93	0.80
2.0	2.6	6.0	0.80	0.68
2.5	2.3	5.4	0.71	0.60

(b) Succinic Acid

C_w (mol/L)	ΔH (kcal/mol)	ΔS (cal/mol·K)	ΔG at 25°C (kcal/mol)	ΔG at 45°C (kcal/mol)
0.0	5.0	11.9	1.4	1.2
0.5	4.5	11.6	1.1	0.82
1.0	4.1	11.2	0.82	0.59
1.5	3.6	10.0	0.65	0.45
2.0	3.3	9.3	0.53	0.34
2.5	3.4	9.8	0.45	0.26
3.0	3.6	10.8	0.40	0.18

(c) Adipic Acid

C_w (mol/L)	ΔH (kcal/mol)	ΔS (cal/mol·K)	ΔG at 25°C (kcal/mol)	ΔG at 45°C (kcal/mol)
0.0	6.1	16.1	1.3	0.98
0.5	5.6	15.6	0.96	0.65
1.0	4.6	13.1	0.70	0.44
1.5	4.4	13.0	0.55	0.29
2.0	4.0	12.1	0.42	0.18
2.5	3.6	11.1	0.34	0.12
3.0	3.3	10.1	0.28	0.08

ΔG, can be calculated at each temperature. Tables 3.5 and 3.6 report the calculated values of the enthalpy, entropy, and free energy of solution for the acid in cyclohexanone and methylcyclohexanone.

The enthalpy of solution is the sum of the change in enthalpy associated with breaking up the crystal structure of the acid and the change in enthalpy associated with dissolving the acid into the solvent. The change in enthalpy associated with break up of the acid crystal is constant, and any variation in the calculated value must be related to the change in the solvent composition. A similar argument can be made that variations of the change in entropy and free energy are due to differences in the solvent composition.

For all systems studied, the changes in the enthalpy and entropy upon dissolution are positive, indicating that solvating the solid acid is an non-ordering, endothermic process. The crystal structures of the acids studied are very stable; the high melting points of the compounds are evidence of the stability. Fumaric acid sublimes at 200°C; succinic acid and adipic acid melt at 186°C and 152°C, respectively (1). The stability and periodic structure of the solid phase accounts for the endothermic, non-ordering nature of the dissolving process.

For the acids in cyclohexanone and methylcyclohexanone, the value of the free energy and enthalpy of solution in anhydrous solvent decreases in the order adipic acid > succinic acid > fumaric acid. This order is inversely proportional to the melting point of the acid. Therefore, the stability of the solid phase is an important factor in determining the value of the free energy and enthalpy of solution. The value of the change in entropy in anhydrous solvent decreases in the same order. This is not surprising since adipic acid has two additional $-CH_2-$ groups that should increase the entropy over that of succinic acid when dissolved. The relatively rigid structure of fumaric acid gives it lower values of change in entropy than for succinic acid.

As the water concentration increases in the organic phase, the changes in enthalpy and entropy upon dissolution decrease. The presence of the water causes the solvation of the acid to become more exothermic and ordering. This phenomena is consistent with water and ketone arranging around the acid in a hydrogen bonding network.

For the three cyclohexanone systems and the succinic acid - methylcyclohexanone system, the enthalpy and entropy of solution are a minimum at an intermediate water concentration. This suggests that a second phenomenon is important at higher water concentrations, causing the solvation of the acid to be more endothermic and non-ordering. A possible explanation is that the water concentration is high enough that the hydrogen bonding becomes less specific for the carboxylic acid.

The free energies of solution were calculated for all systems from the changes in enthalpy and entropy. Surprisingly, the change in free energy did not go through a minimum value at an intermediate water concentration, even though the changes in enthalpy and entropy did. At low water and acid concentrations, the changes in enthalpy, ΔH are decreasing faster than the changes in the product of entropy and temperature, $T\Delta S$, which causes the change in free energy to decrease. For the systems which show minimum values for the changes in enthalpy and entropy, $T\Delta S$ increases faster than ΔH at higher water concentrations, so as to continue the trend of a decreasing change in free energy.

For a given acid and solvent, the changes in free energy decreased as the temperature increased. This follows since the change in enthalpy is endothermic and determines the dependence of the free energy on temperature.

3.4 Summary

Experiments were performed to determine solid - liquid equilibria for fumaric acid, succinic acid, and adipic acid in cyclohexanone and methylcyclohexanone with varying amounts of water. The data can be described by linear or power law equations. From an analysis of the slopes of the data, two to ten waters are needed to solubilize a dicarboxylic acid at low concentrations in the organic phase. In most cases, the amount of water needed to solubilize the acid increases as the acid concentration increases. Changes in enthalpy and entropy of solution of the acid provide evidence for strong hydrogen bonding in the organic phase.

REFERENCES

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CHAPTER 4. LIQUID - LIQUID EQUILIBRIUM

Experiments were performed to determine the distribution of fumaric acid, succinic acid, and adipic acid between water and two solvents -- cyclohexanone and methylcyclohexanone -- at two temperatures. The water and acid concentrations in the organic phase were determined. Linear or power law equations were able to describe the data. Values for the change in enthalpy and entropy upon transfer were calculated. The liquid - liquid equilibria were measured as described in Appendix B.

4.1 Acid Distribution

Figures 3.1-3 show the distribution of fumaric acid, succinic acid, and adipic acid from water into cyclohexanone and methylcyclohexanone at 25°C and 45°C. The distribution ratio on a concentration basis, D, for the data point at the highest acid concentration is also reported. For the three acids in both solvents, an increase in temperature decreases the amount of acid extracted into the organic phase. For a given acid at a given temperature, cyclohexanone extracted more acid than did methylcyclohexanone. The differences among the acids were great with the amount of acid extracted decreasing in the order fumaric acid > adipic acid > succinic acid for a solvent at a specific temperature.

The partition coefficient, P, is different from the distribution ratio in that the distribution ratio is the ratio of the total acid concentration in the organic phase to the total acid concentration in the aqueous phase. The partition coefficient is the ratio of the monomer acid concentration in the organic phase divided by the concentration of undissociated acid in the aqueous phase. The acid monomer concentration in the organic phase will equal the total acid concentration in the organic phase if dimerization or other aggregation of the acid is not significant. The partition coefficient is especially useful for prediction of distribution of the carboxylic acid when the pH of the aqueous phase has been adjusted by the addition of an

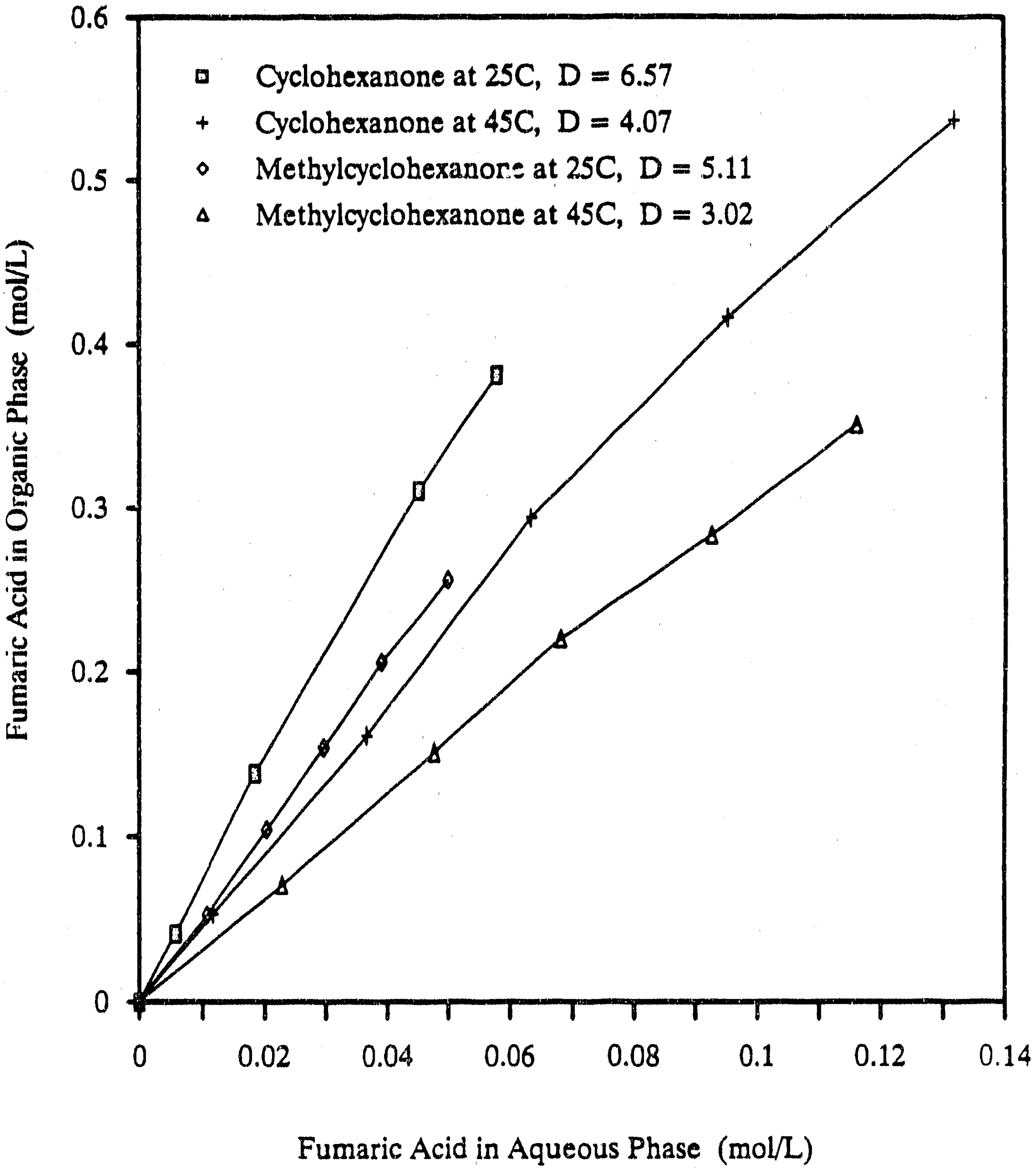

Figure 4.1 Fumaric acid distribution between the aqueous and organic phases in two different solvents at two temperatures

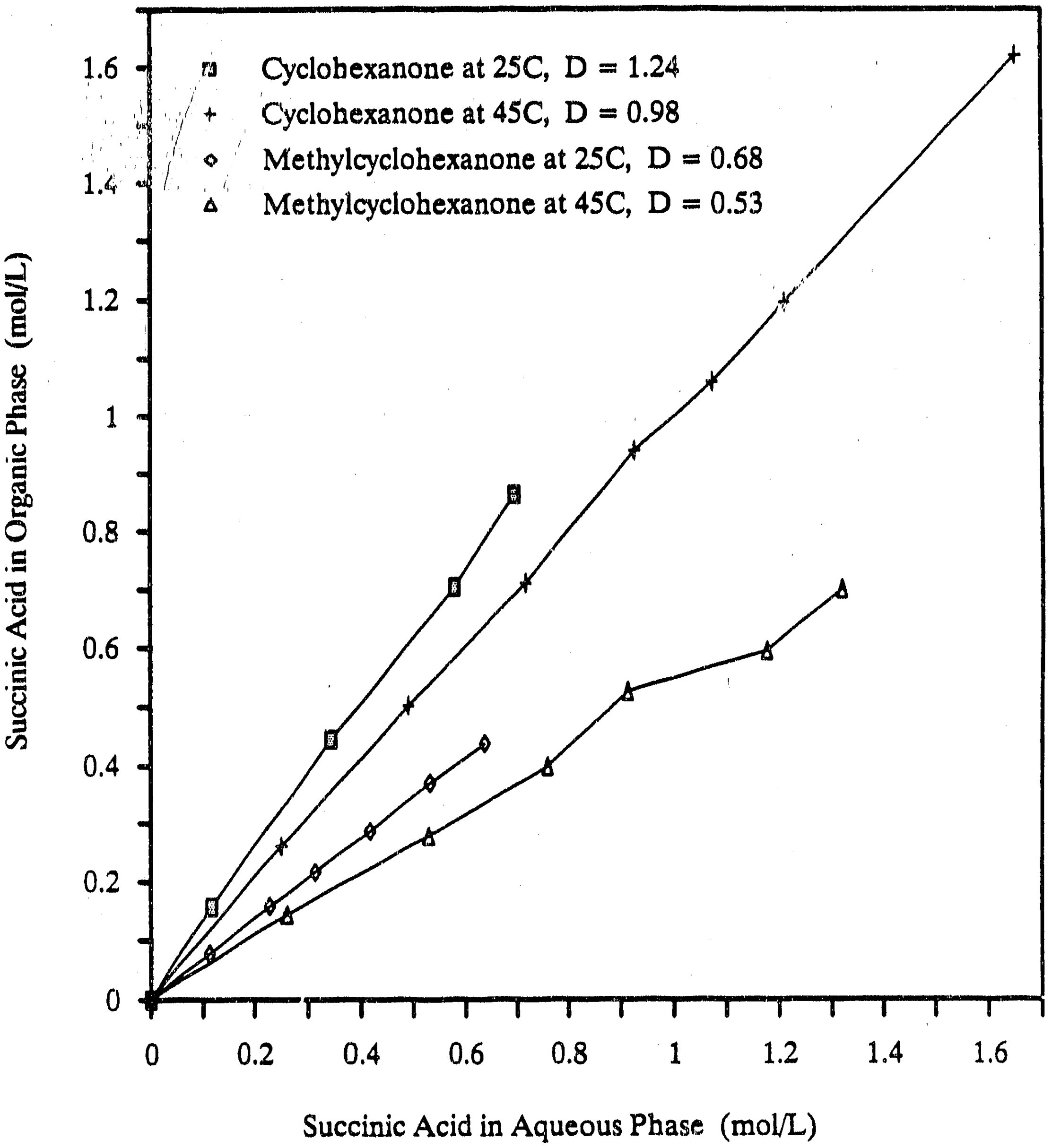

Figure 4.2 Succinic acid distribution between aqueous and organic phases in two different solvents at two temperatures.

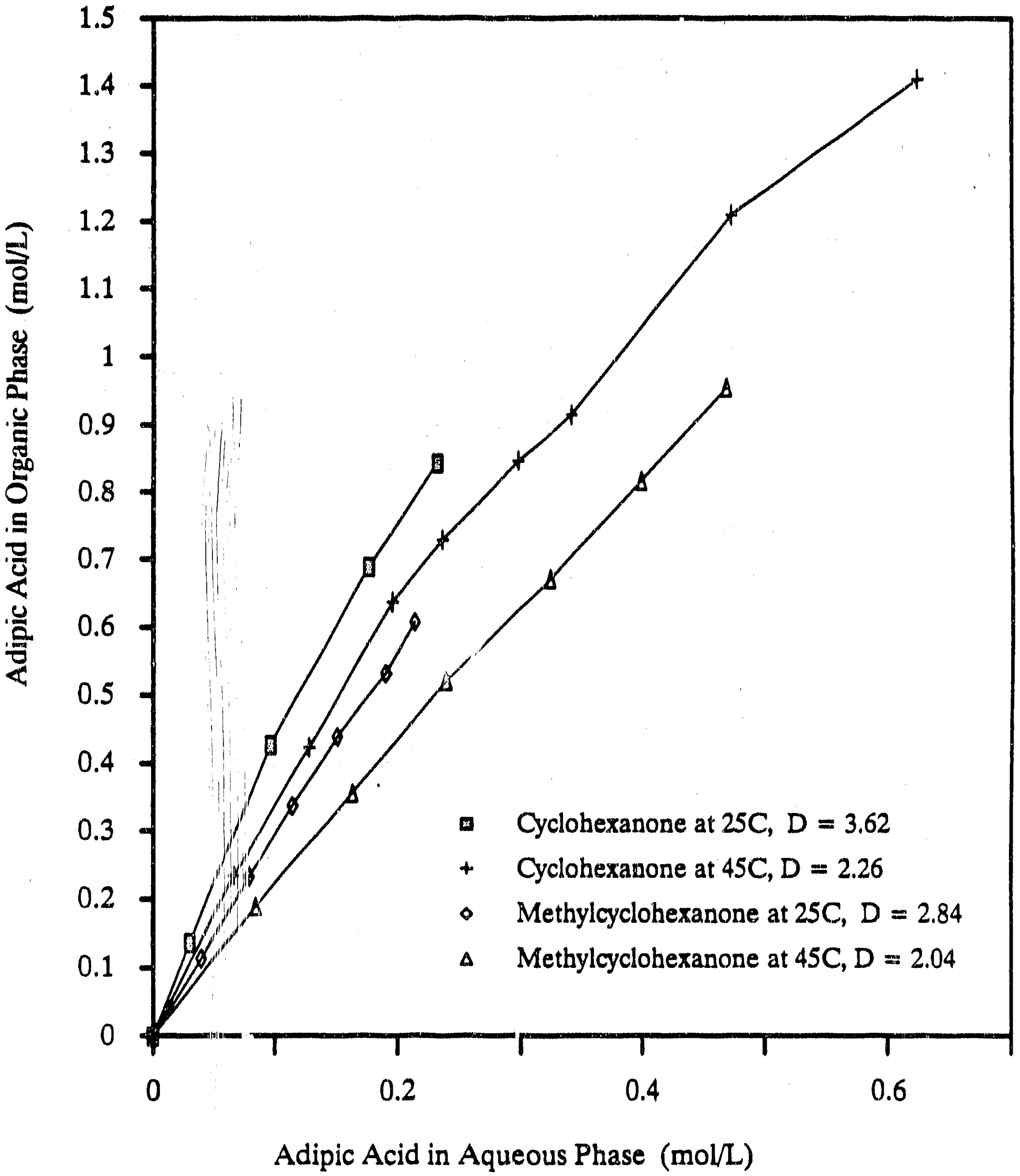

Figure 4.3 Adipic acid distribution between aqueous and organic phases in two different solvents ata two temperatures.

acid, such as H_3PO_4, or base, such as NaOH.

To calculate the partition coefficient, the concentration of undissociated acid in the aqueous phase must be calculated first. The pH and total acid concentration in the aqueous phase are measured. The total acid concentration is the sum of the concentrations of the acid in its various possible ionic states, as shown in Equation 4.1. The brackets in Equation 4.1 denote concentrations.

$$C_{a,aq} = [H_2A]_{aq} + [HA^-]_{aq} + [A^=]_{aq} \tag{4.1}$$

Substituting in the dissociation equations for the acid, one can solve for the undissociated acid concentration, $[H_2A]$, as shown in Equation 4.2, where K_{a1} and K_{a2} are the first and second dissociation constants, respectively, for the dicarboxylic acid, and $[H^+]$ is the proton concentration. The values for K_{a1} and K_{a2} were taken from Das, et al. (1) for fumaric acid, Dash and Mishra (2) for succinic acid, and Dash and Nayak (3) for adipic acid. Table 4.1 reports the pK_{a1} and pK_{a2} values used. In each of these references, the pK_a values of the carboxylic acid were determined over a range of temperature. In general the values used are slightly above the values published in the *CRC Handbook of Chemistry and Physics* (65th ed.).

$$[H_2A]_{aq} = \frac{C_{a,aq}}{1 + \dfrac{K_{a1}}{[H^+]} + \dfrac{K_{a1}\,K_{a2}}{[H^+]^2}} \tag{4.2}$$

With the value of the undissociated acid concentration calculated, the value of the partition coefficient and the importance of the dimerization of acid in the organic phase can be determined. The distribution ratio of the acid increases with increasing acid concentration

Table 4.1 Dissociation constants, pK_{a1} and pK_{a2}, for fumaric acid, succinic acid, and adipic acid at 25°C and 45°C.

Acid	Temp. (°C)	pK_{a1}	pK_{a2}	Reference
Fumaric Acid	25	3.10	4.64	1
Fumaric Acid	45	2.94	4.71	1
Succinic Acid	25	4.22	5.66	2
Succinic Acid	45	4.18	5.68	2
Adipic Acid	25	4.42	5.97	3
Adipic Acid	45	4.37	6.17	3

Table 4.2 Partition coefficients and dimerization constants for fumaric acid, succinic acid, and adipic acid in cyclohexanone and methylcyclohexanone at 25°C and 45°C.

Acid	Solvent	Temp.	Partition Coefficient	Dimerization Constant
Fumaric Acid	Cyclohexanone	25	10.2 ±0.2	-0.28 ±0.03
		45	5.5 ±0.2	-0.16 ±0.03
	Methylcyclohexanone	25	6.27 ±0.05	-0.15 ±0.02
		45	3.67 ±0.06	-0.16 ±0.03
Succinic Acid	Cyclohexanone	25	1.41 ±0.03	-0.07 ±0.02
		45	1.05 ±0.02	-0.02 ±0.01
	Methylcyclohexanone	25	0.71 ±0.01	-0.03 ±0.01
		45	0.56 ±0.03	-0.04 ±0.05
Adipic Acid	Cyclohexanone	25	4.97 ±0.08	-0.11 ±0.01
		45	3.68 ±0.10	-0.09 ±0.01
	Methylcyclohexanone	25	3.05 ±0.06	-0.05 ±0.02
		45	2.33 ±0.03	-0.06 ±0.01

Values are ± the standard error

when dimerization of the acid in organic phase is significant. Eq. 4.3 shows the total acid concentration in the organic phase as the sum of the monomer and dimer acid concentrations.

$$C_{a,org} = [H_2A]_{org} + 2\,[(H_2A)_2]_{org} \tag{4.3}$$

The extent of dimerization is measured by the value of K_d, the dimerization constant, as shown in Equation 4.4.

$$K_d = \frac{[(H_2A)_2]_{org}}{[H_2A]^2_{org}} \tag{4.4}$$

Substituting Equation 4.4 and the definition of the partition coefficient into Equation 4.3 gives Equation 4.5, the relevant equation for determining the partition coefficient and dimerization constant from experimentally determined variables.

$$C_{a,org} = P\,[H_2A]_{aq} + 2\,P^2\,K_d\,[H_2A]^2_{aq} \tag{4.5}$$

The two constants, P and K_d, are determined by linear regression of the undissociated aqueous acid concentration, $[H_2A]_{aq}$, and the ratio of the total organic acid concentration to the undissociated aqueous acid concentration, $C_{a,org}/[H_2A]_{aq}$. The results are shown in Table 4.2. The value of the dimerization constant was calculated to be negative for all systems studied, demonstrating that dimerization of the dicarboxylic acids in cyclohexanone and methylcyclohexanone is not significant.

Because dimerization is not significant in these systems, the partition coefficient reported here is for the acid at very low acid concentrations. For all of the systems, the partition coefficient decreases slightly with increasing acid concentrations. The decrease in partition coefficient is not surprising considering the amount of water that is in the organic phase. Many of the systems have a partition coefficient greater than 1.0, indicating that the organic phase is favored. So when the water concentration in the organic phase increases, making it more like the aqueous phase, the partition coefficient decreases towards 1.0. For the two systems that exhibit partition coefficients less than or equal to 1.0, the partition coefficient is nearly independent of the acid concentration, as shown by the values of the dimerization constant being close to zero. This explanation is also supported by the fact that the dimerization constants with the largest absolute value, indicating the largest changes in the partition coefficient, are for the systems with the greatest values of the partition coefficient, i.e. fumaric acid in cyclohexanone.

The effects on the values of the partition coefficient caused by changing the acid, solvent, or temperature are similar to the trends of the distribution ratio described above. An increase in temperature decreases the partition coefficient for the three acids in both solvents. For a given acid at a given temperature, cyclohexanone exhibits higher partition coefficients than methylcyclohexanone. Partition coefficients among the carboxylic acids decrease in the order fumaric acid > adipic acid > succinic acid for a solvent at a specific temperature.

The partition coefficients for the acids in cyclohexanone are higher than those found in many other solvents. Tamada and King (4) determined the partition coefficient for succinic acid in methylisobutylketone to be 0.19 at 25°C, and the partition coefficient decreased as the temperature increased. Kertes and King (5) compiled partition coefficients for carboxylic acids. The highest partition coefficient they report for succinic acid is 1.20 for the succinic acid - n-butanol system, and the highest for fumaric acid is 4.60 for the fumaric acid - isobutanol system. Marvel and Richards (6) report the distribution ratios for fumaric acid, succinic acid and adipic acid in cyclohexanone at 26°C to be 3.45, 1.10, and 3.12, respectively. These values were calculated from batch experiments with an initial acid concentration in the aqueous phase of 0.16 wt%. The distribution ratios determined in this work are greater than the those reported by Marvel and Richards, especially for fumaric acid.

This discrepancy could be due to their failure to subtract out the acid initially present in the ketone as an impurity, which can be significant at low acid concentrations. Marvel and Richards (6) also report that n-butanol exhibits distribution ratios slightly greater than cyclohexanone for succinic acid and adipic acid.

4.2 Organic Phase Equilibrium Concentrations

Figures 4.4-15 report the measured acid and water equilibrium concentrations for fumaric acid, succinic acid, and adipic acid in cyclohexanone and methylcyclohexanone at 25°C and 45°C. The solid - liquid equilibrium data from Chapter 3 are shown as well. A linear equation, Equation 4.6, describes the relationship between the acid concentration and the water concentration in the organic phase for the liquid - liquid equilibrium data, except for the adipic acid - cyclohexanone and succinic acid - cyclohexanone systems at 45°C. As mentioned before, these are the two systems in which the solid - liquid equilibrium relationship does not cross with the phase envelope. These two systems are described by a power law equation, Equation 4.7, with the equation being forced through the measured water solubility at zero acid concentration in order for the power law equation to have only two parameters.

$$C_w = \lambda C_a + \mu \tag{4.6}$$

$$C_w - C_w(0) = \lambda C_a^{\mu} \tag{4.7}$$

Tables 4.3 and 4.4 give the values and standard error of λ and μ calculated by linear regression for the systems studied at 25° and 45°C, respectively. Note that for systems described by the linear equation, μ is really an estimate of the solubility of water in solvent, and should, in principle, be equal for all three acids in a given solvent at a given temperature.

The experimentally determined solubility of water in cyclohexanone was 2.96 moles/L

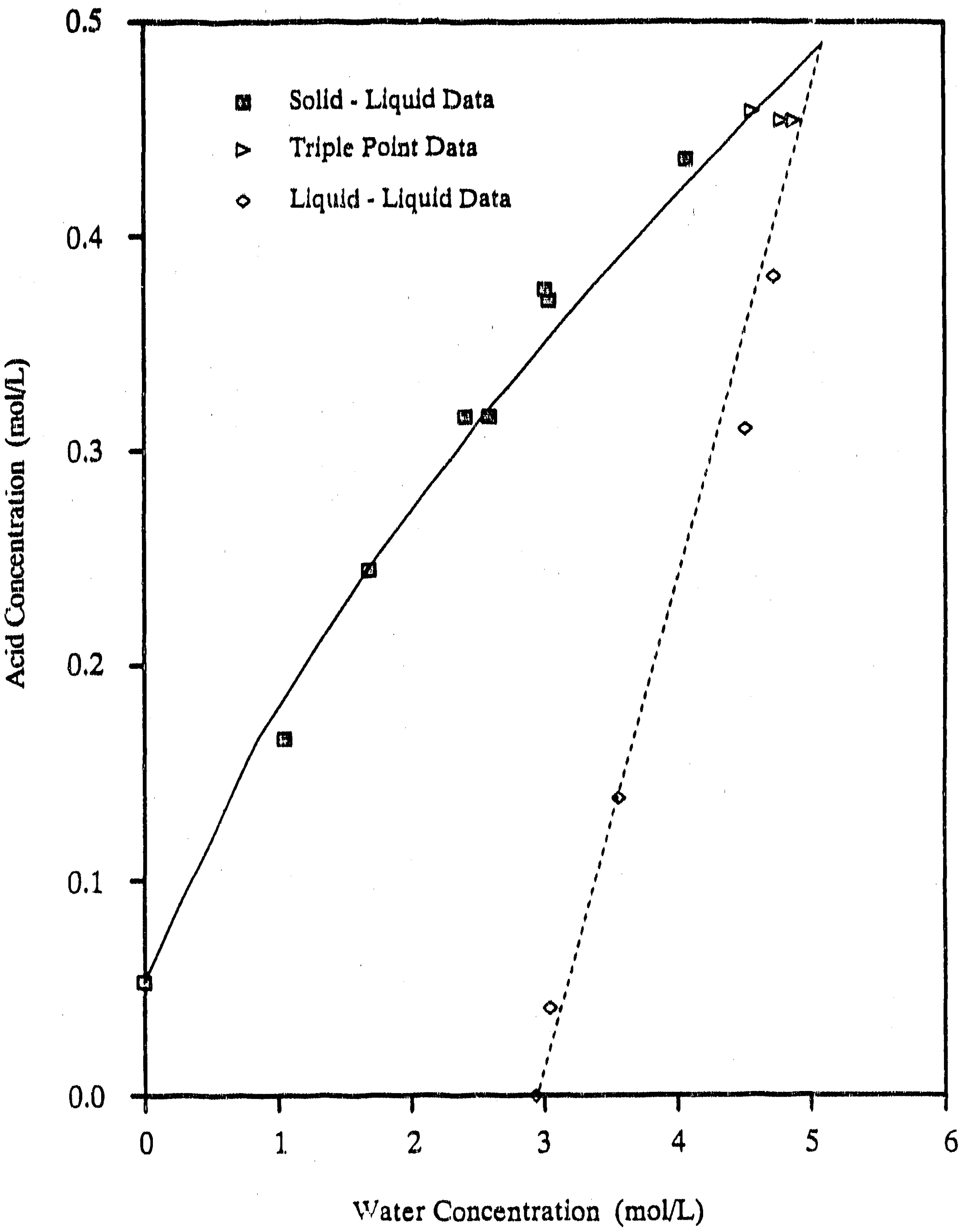

Figure 4.4 Fumaric acid - cyclohexanone - water liquid - liquid and solid - liquid equilibria at 25 C.

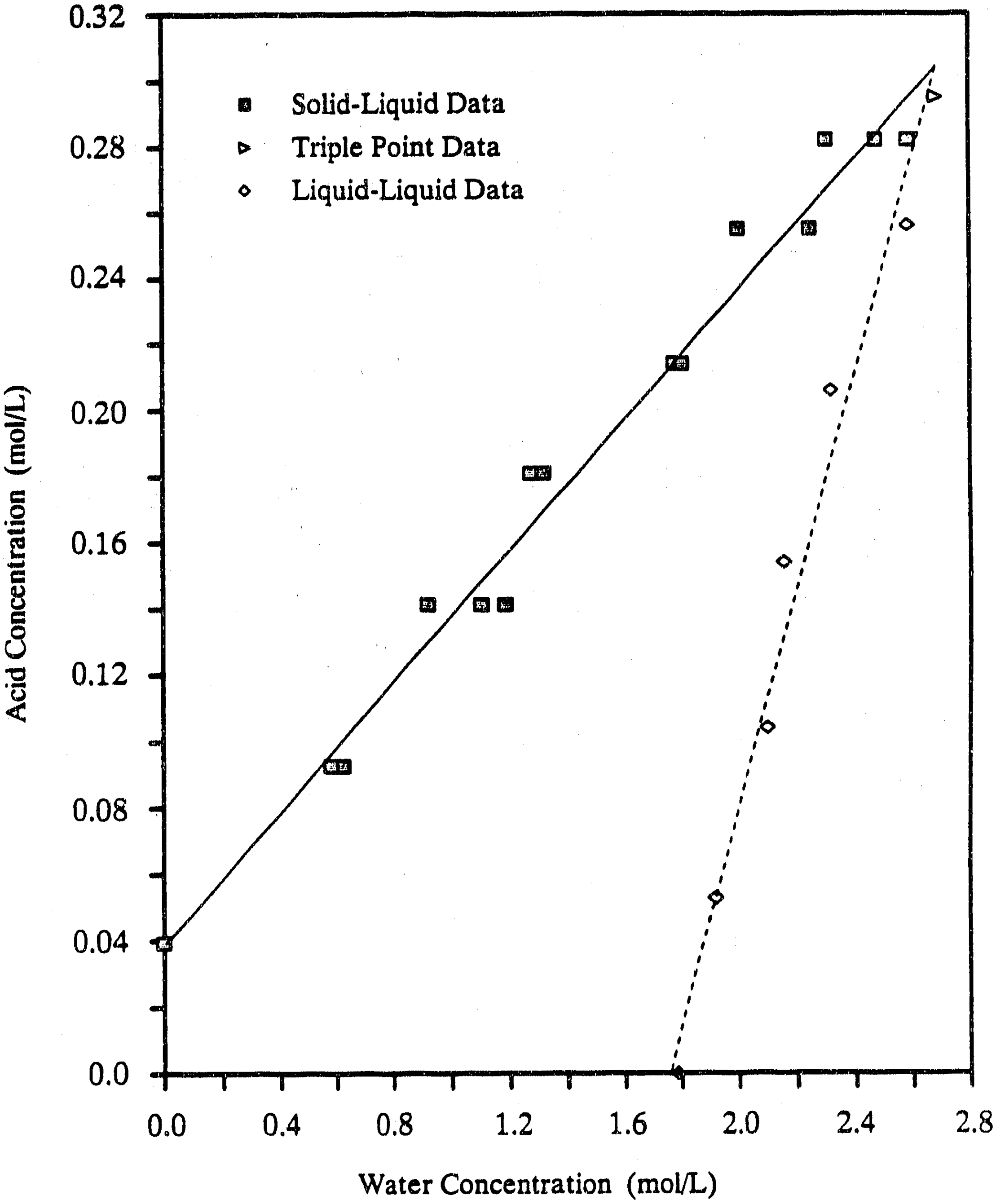

Figure 4-5 Fumaric acid - methylcyclohexanone - water liquid - liquid and solid - liquid equilibria at 25 C.

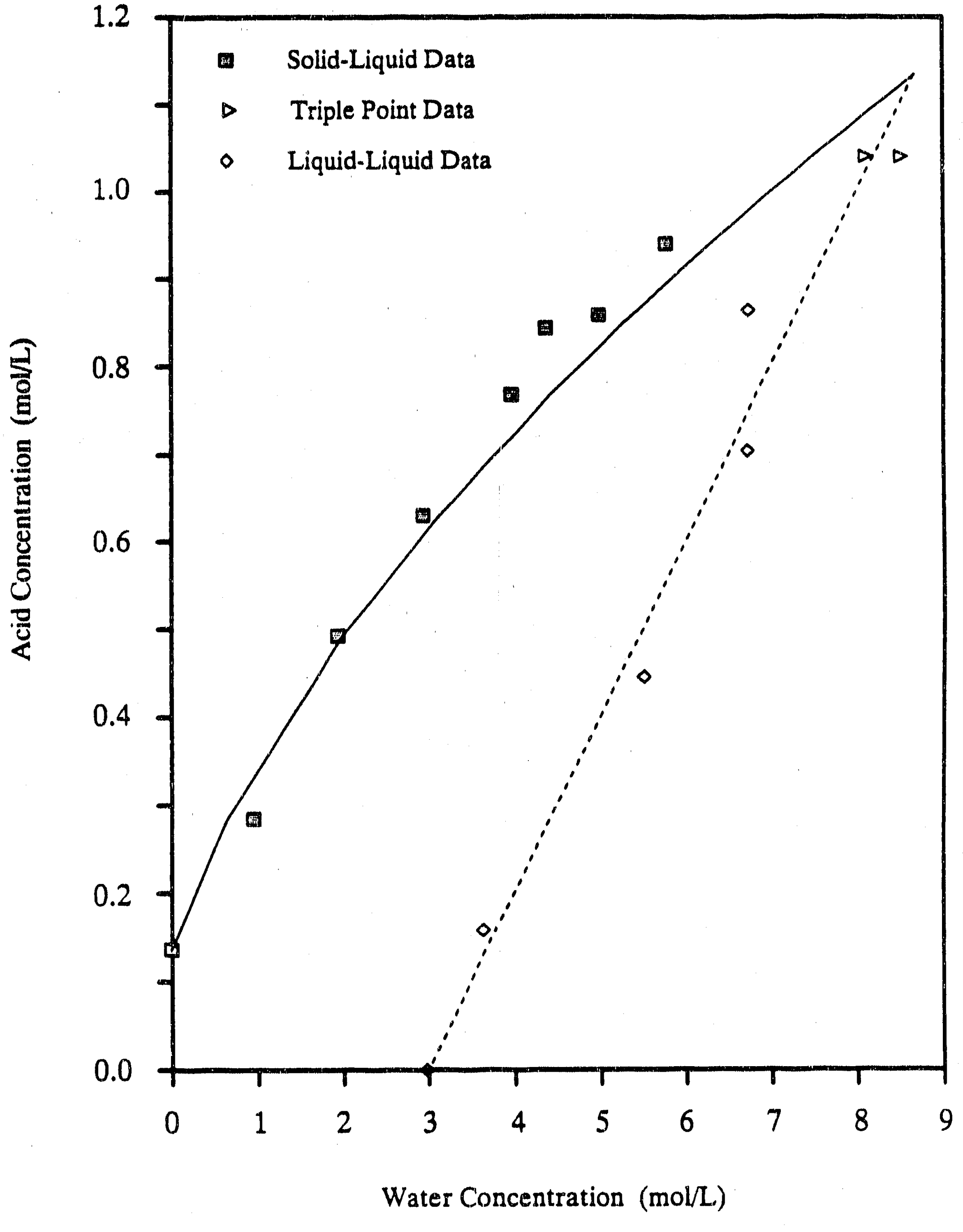

Figure 4.6 Succinic acid - cyclohexanone - water liquid - liquid and solid - liquid equilibria at 25 C.

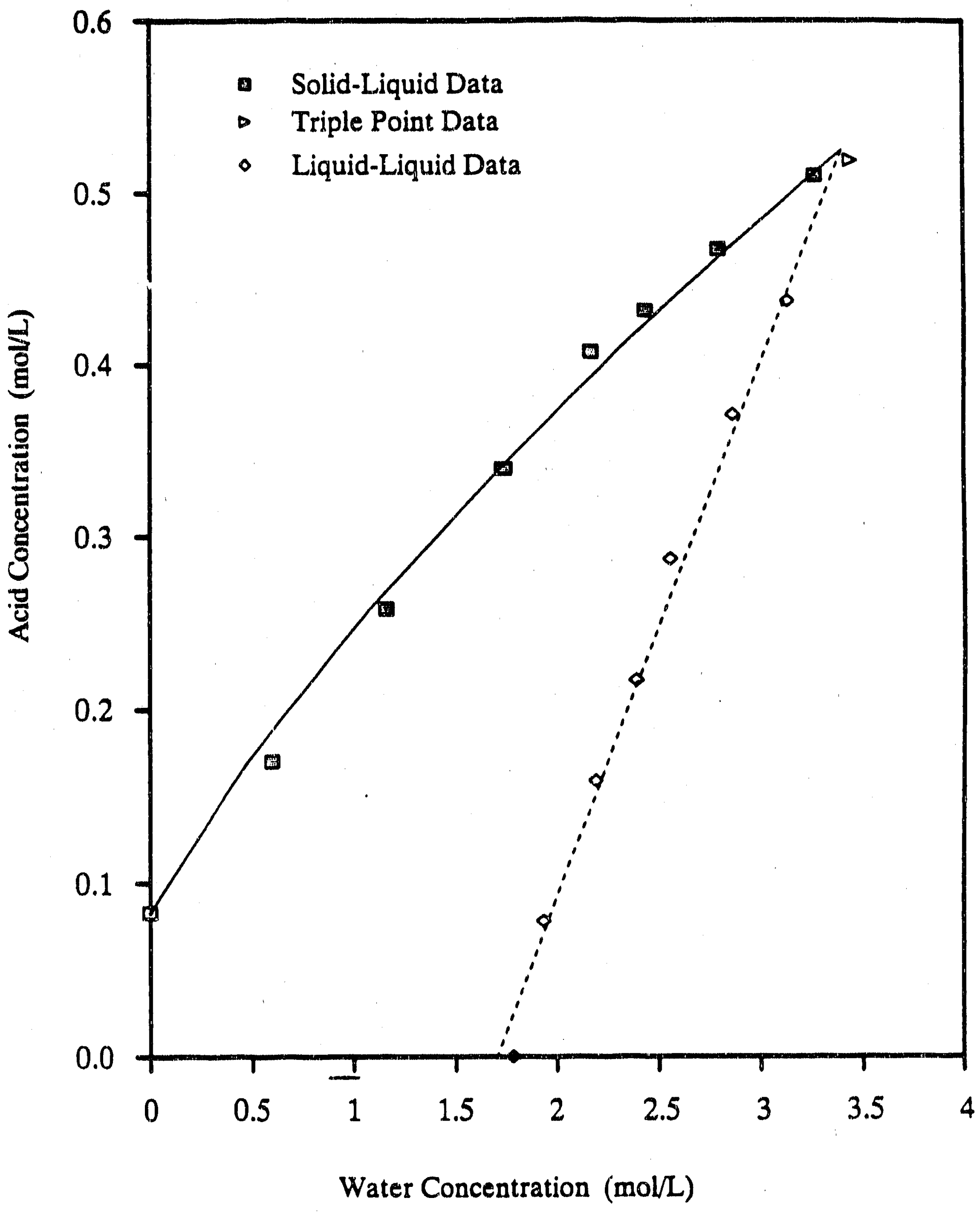

Figure 4.7 Succinic acid - methylcyclohexanone - water liquid - liquid and solid - liquid equilibria at 25 C.

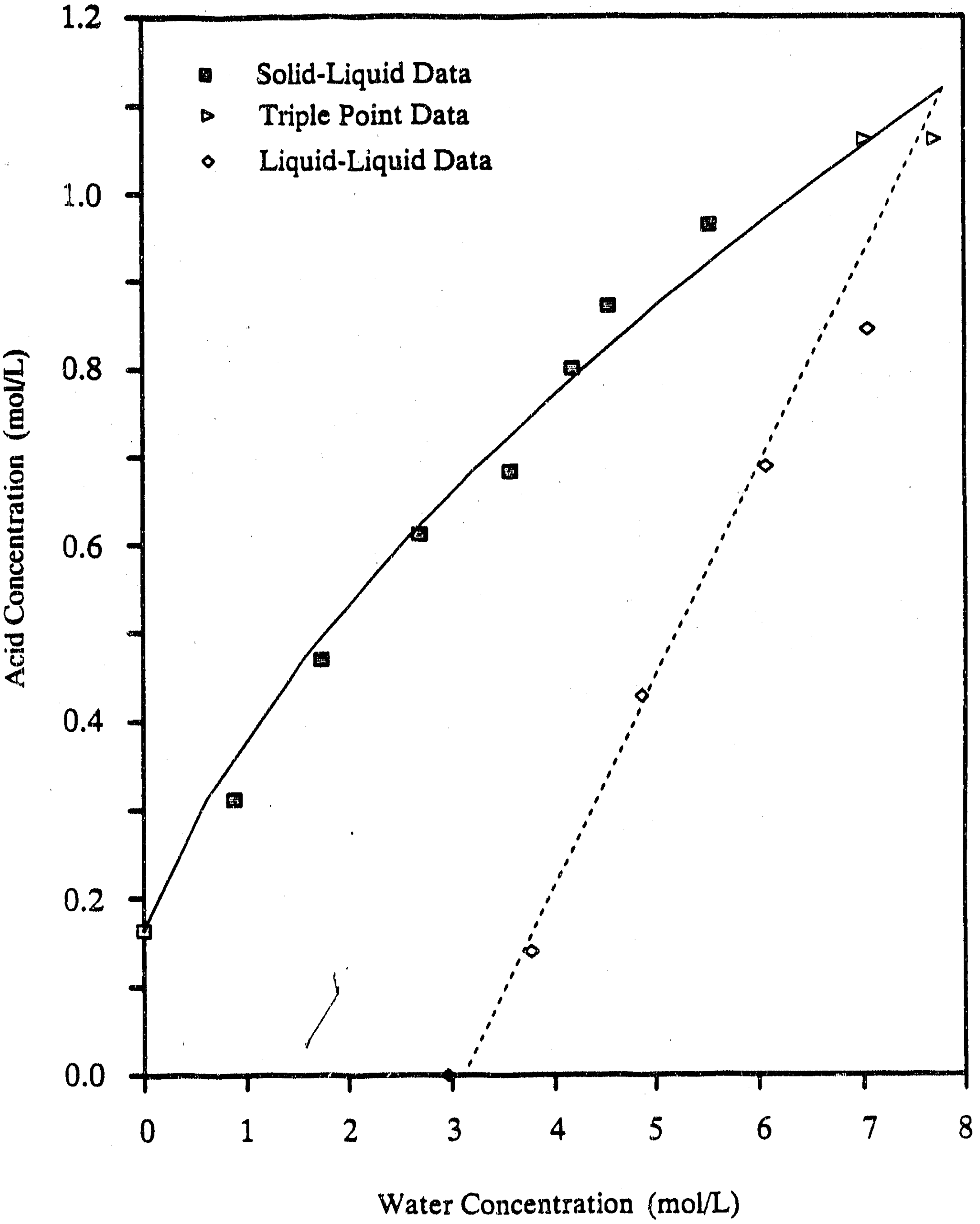

Figure 4.8 Adipic acid - cyclohexanone - water liquid - liquid and solid - liquid equilibria at 25 C.

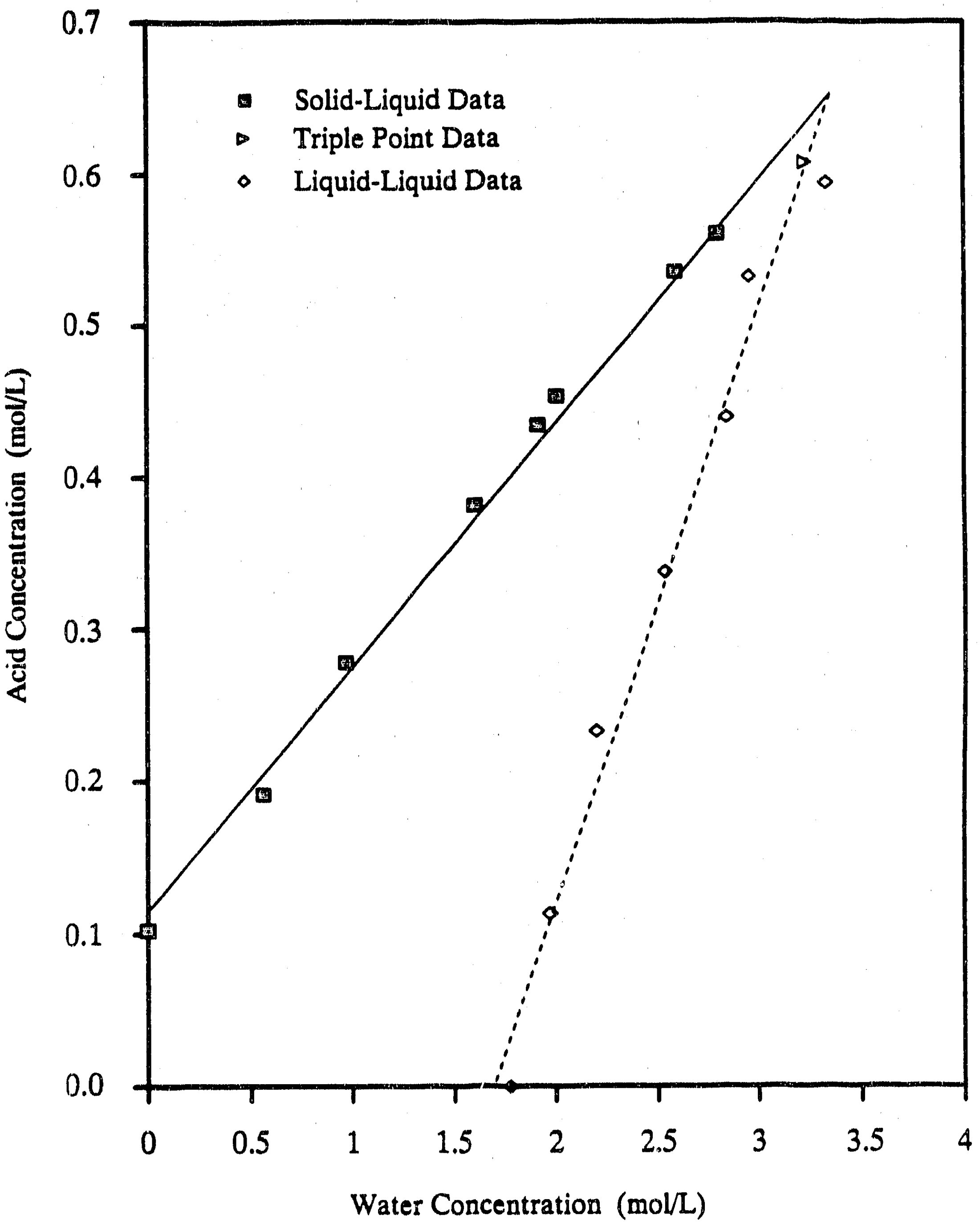

Figure 4.9 Adipic acid - methylcyclohexanone - water liquid - liquid and solid - liquid equilibria at 25 C.

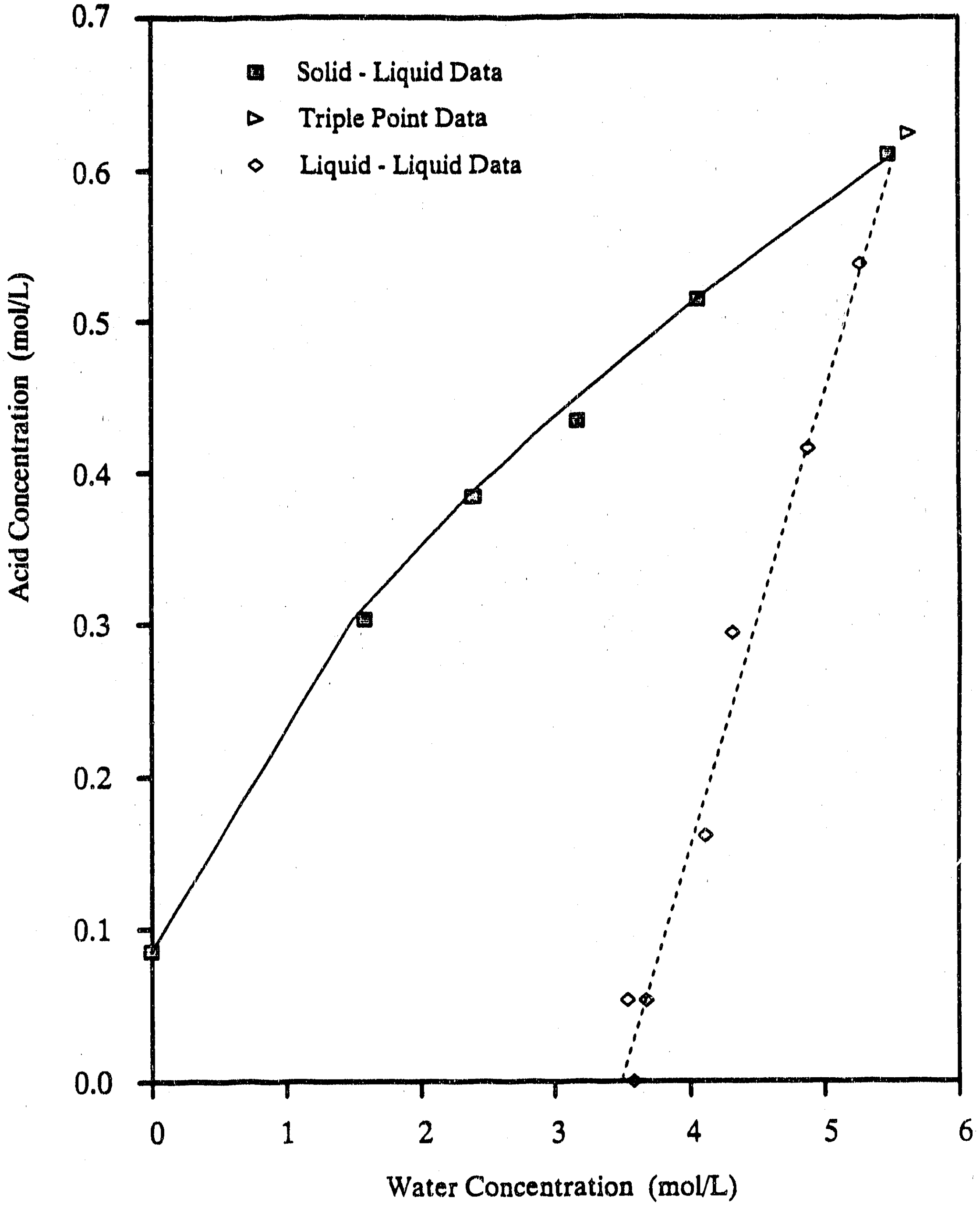

Figure 4.10 Fumaric acid - cyclohexanone - water liquid - liquid and solid - liquid equilibria at 45 C.

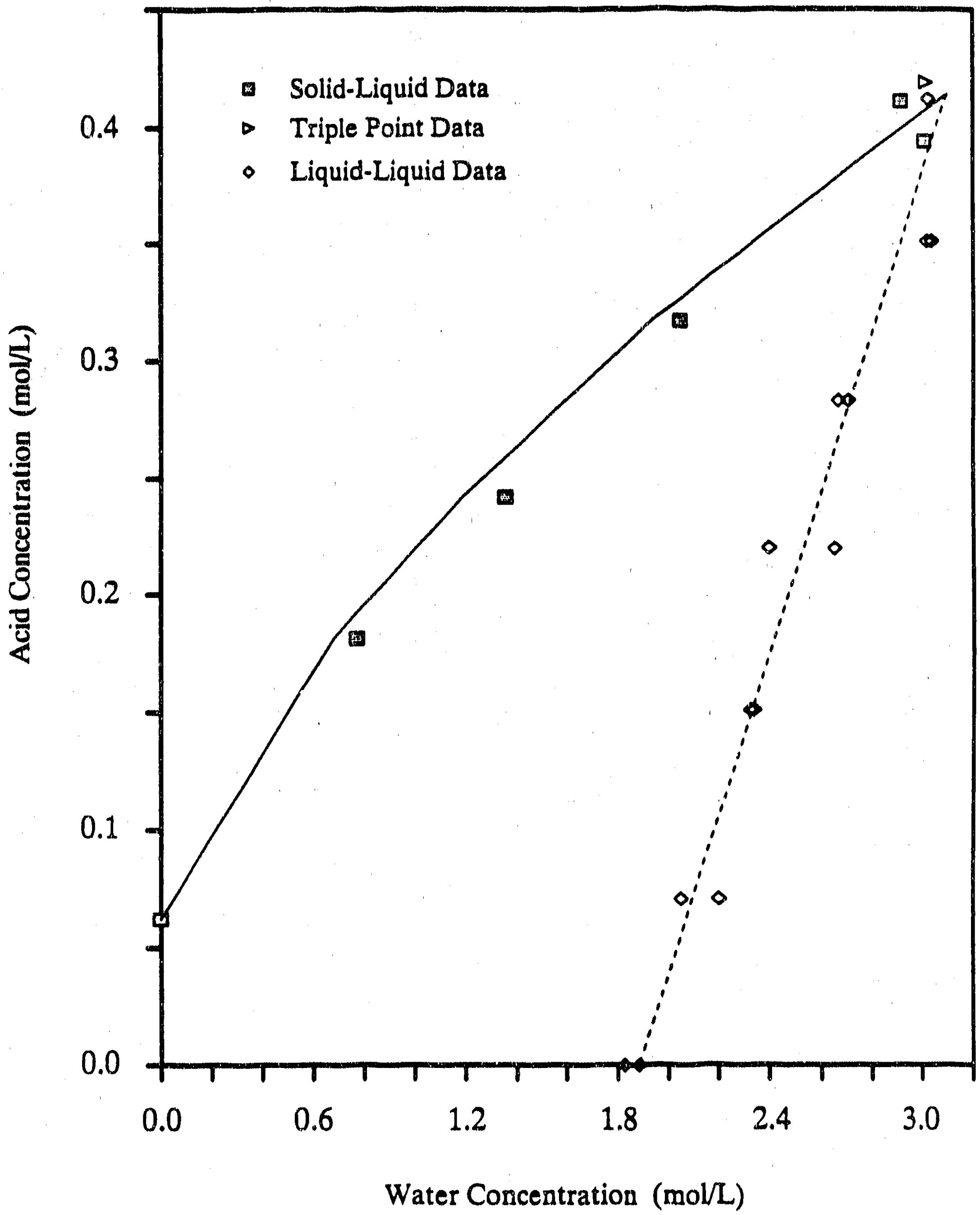

Figure 4.11 Fumaric acid - methylcyclohexanone - water liquid - liquid and solid - liquid equilibria at 45 C.

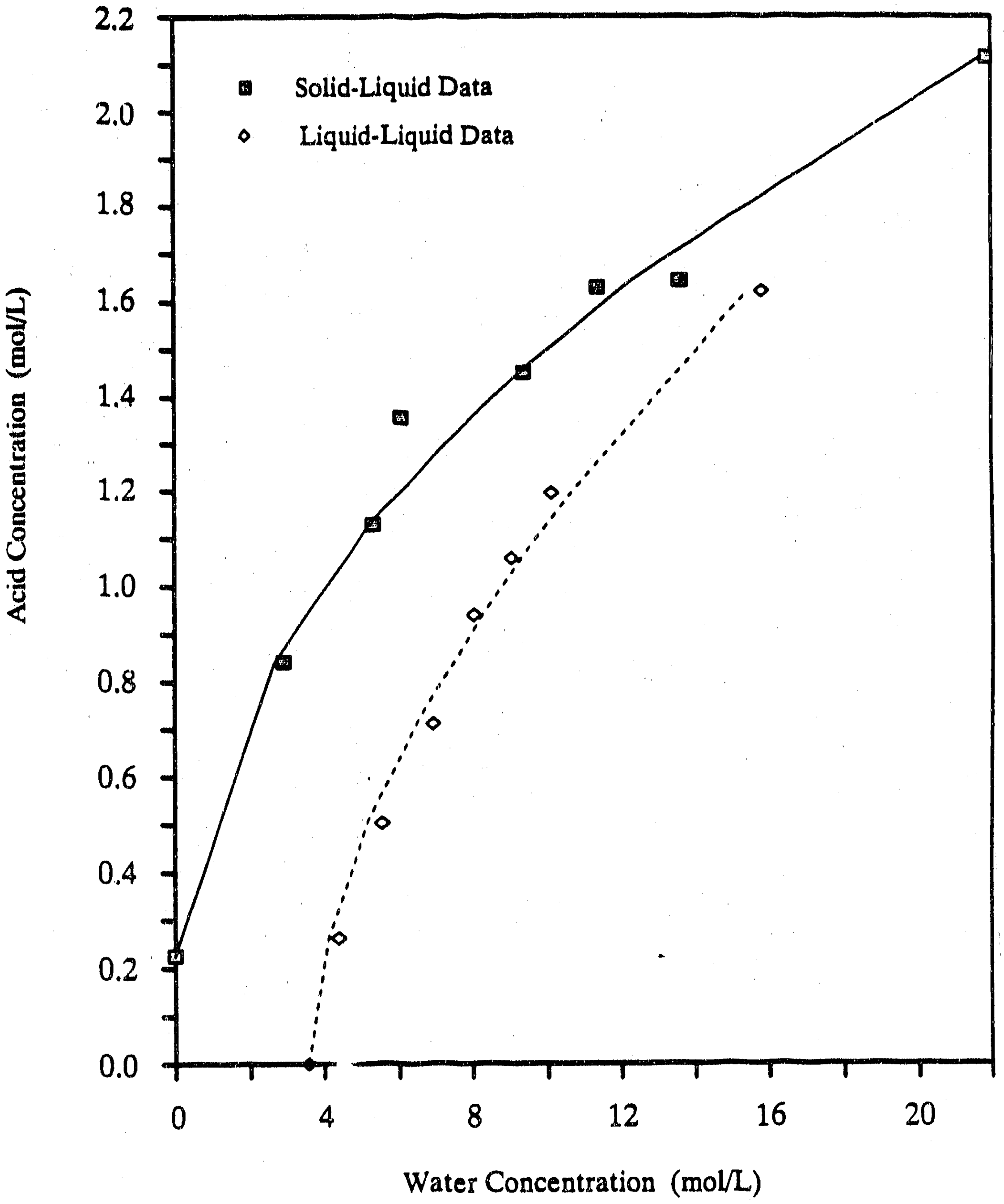

Figure 4.12 Succinic acid - cyclohexanone - water liquid - liquid and solid - liquid equilibria at 45 C.

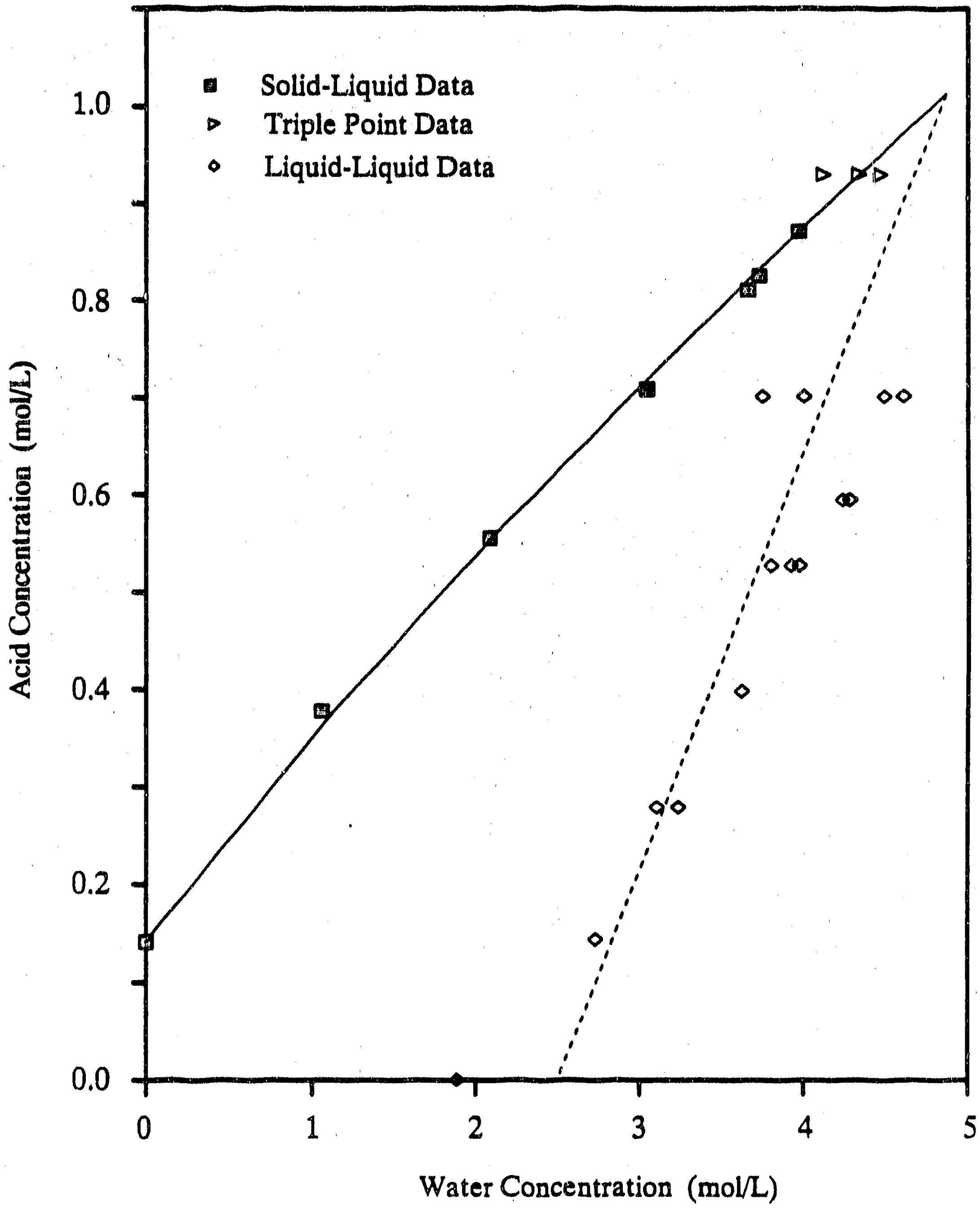

Figure 4.13 Succinic acid - methylcyclohexanone - water liquid - liquid and solid - liquid equilibria at 45 C.

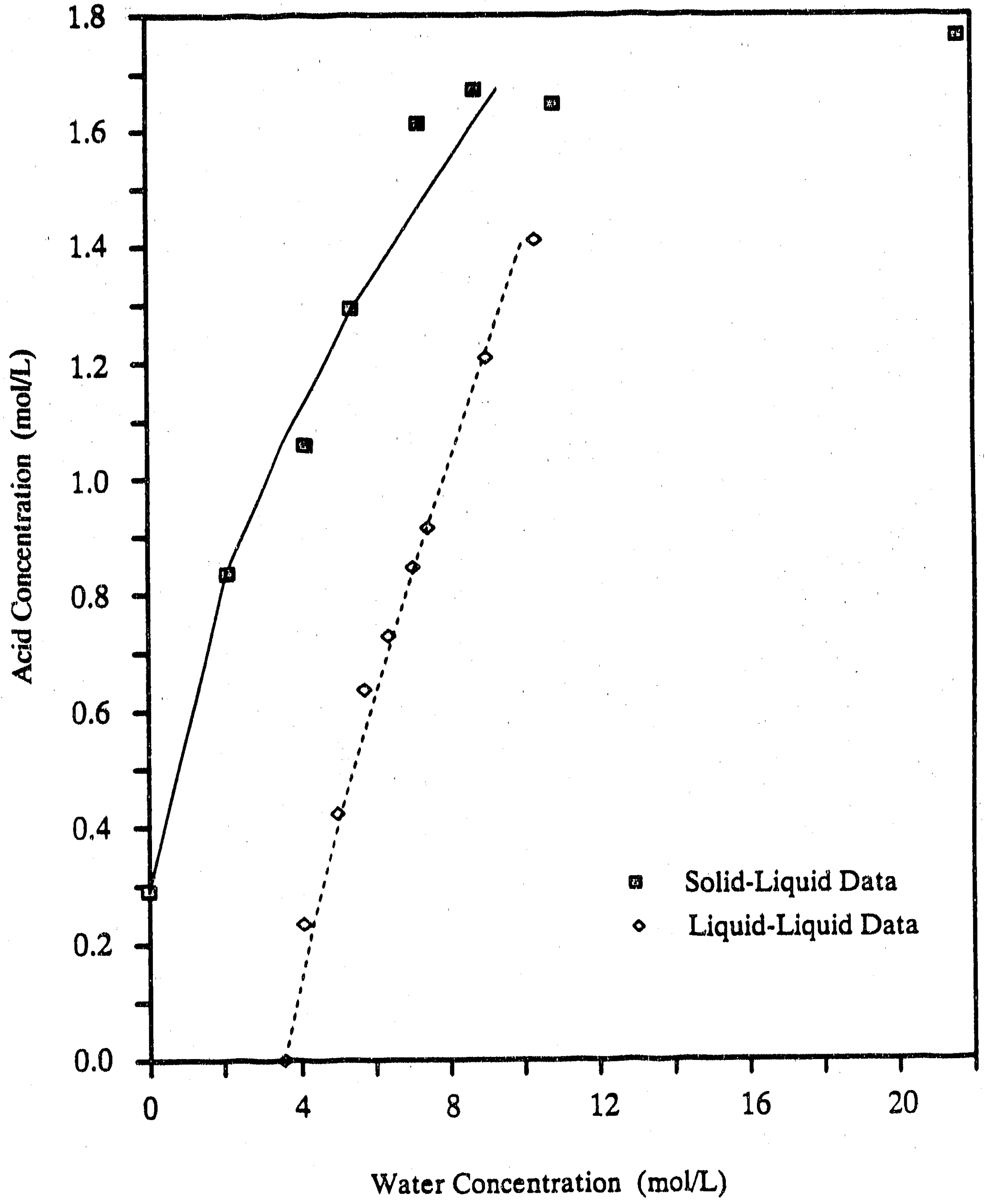

Figure 4.14 Adipic acid - cyclohexanone - water liquid - liquid and solid - liquid equilibria at 45 C.

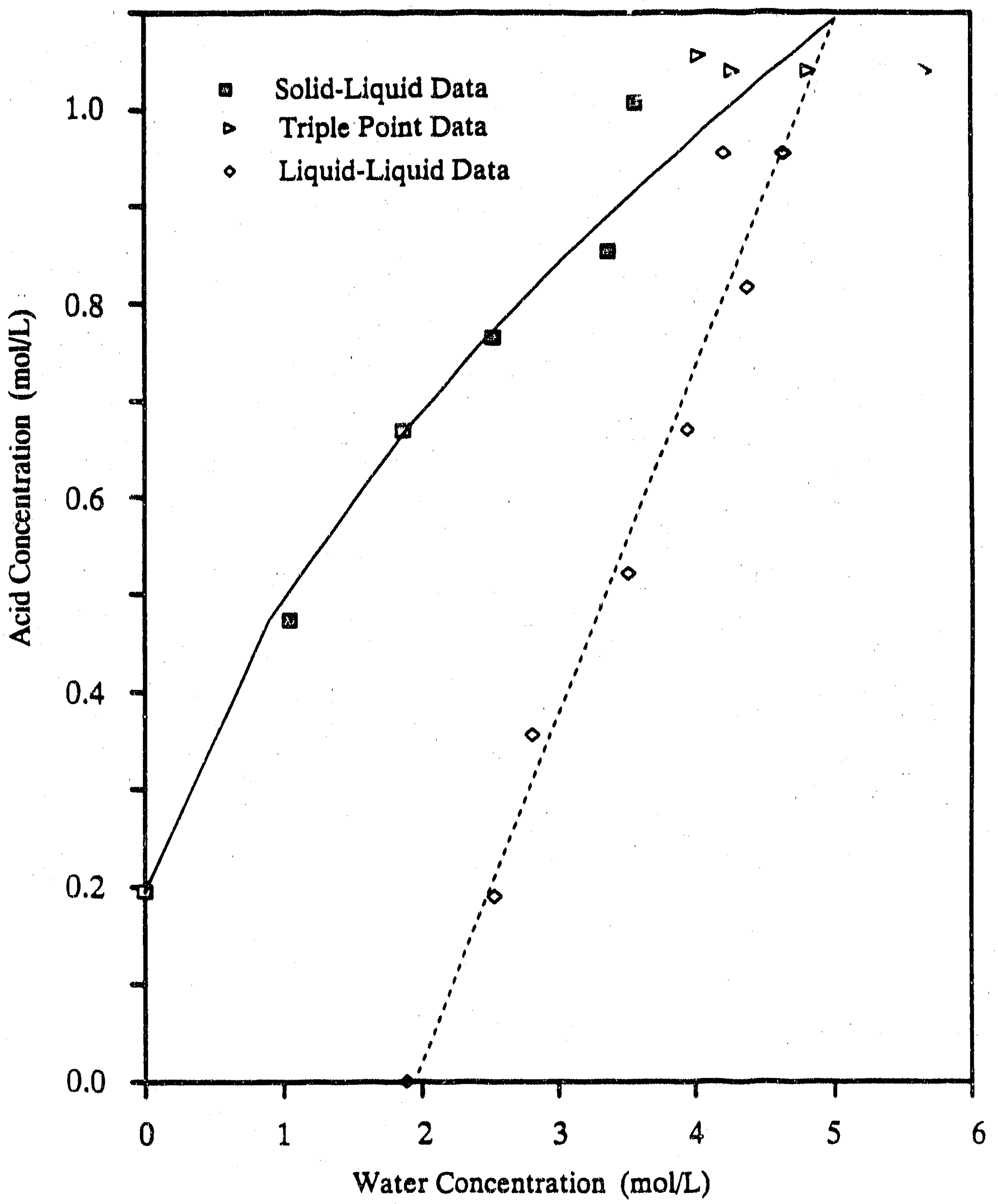

Figure 4.15 Adipic acid - methylcyclohexanone - water liquid - liquid and solid - liquid equilibria at 45 C.

and 3.58 moles/L at 25°C and 45°C, respectively. This compares favorably with the values of 3.14 moles/L and 3.56 moles/L reported by Sorensen and Arlt (8). The solubility of water in methylcyclohexanone was determined to be 1.78 moles/L and 1.88 moles/L at 25°C and 45°C. The 25°C value is greater than the value of 0.72 moles/L reported Sorensen and Arlt (8).

The data taken at the triple point at 45°C tend to show more scatter than most of the other data because of the difficulties of taking a sample from a water saturated solution at an elevated temperature. The intersection point of the liquid - liquid and solid -liquid equilibrium curves is very sensitive to the slope of the liquid - liquid equilibrium line. Perhaps using a weighted linear regression analysis with the triple points weighted more heavily would give an intersection point closer to the experimental triple point for some of the systems. That analysis was not done in this work.

Each of the lines or curves in Figures 4.4-15 has a positive slope showing an increase in the water concentration with an increase in the acid concentration in the organic phase. The value of the slope of the line is the incremental moles of water entering the organic phase per mole of incremental acid. For a given acid at a given temperature, the value of the slope is greater in cyclohexanone than in methylcyclohexanone. The slopes are greater at 25°C than at 45°C for a given acid in a given solvent, except for the adipic acid - methylcyclohexanone system.

Figures 4.16-19 show the liquid - liquid equilibrium data for all three acids in either cyclohexanone or methylcyclohexanone at 25°C or 45°C. Especially at low acid concentrations, it appears that a single linear relationship describes the acid and water concentrations for all three acids. The lines shown in these figures are discussed in the next few paragraphs.

The hypothesis that $\lambda_{\text{fumaric, 25°C}} = \lambda_{\text{succinic, 25°C}} = \lambda_{\text{adipic, 25°C}}$ was checked by an analysis of variance test using a 95% confidence level. Details of this statistical method can be found in Edwards (9). The 25°C data in each solvent show that there is no evidence to

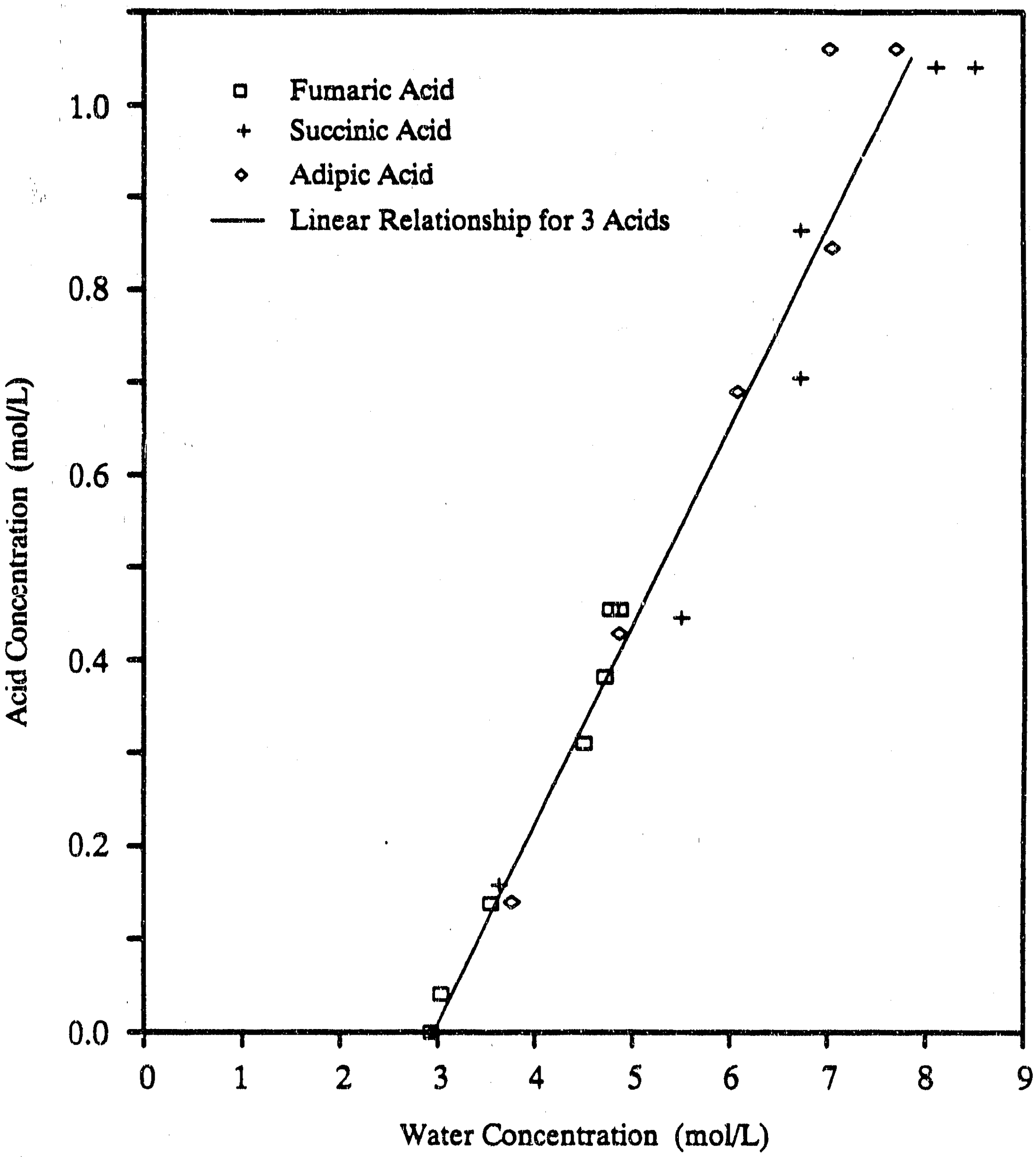

Figure 4.16 Liquid - liquid equilibrium of fumaric acid, succinic acid, and adipic acid in cyclohexanone at 25 C with best fit line.

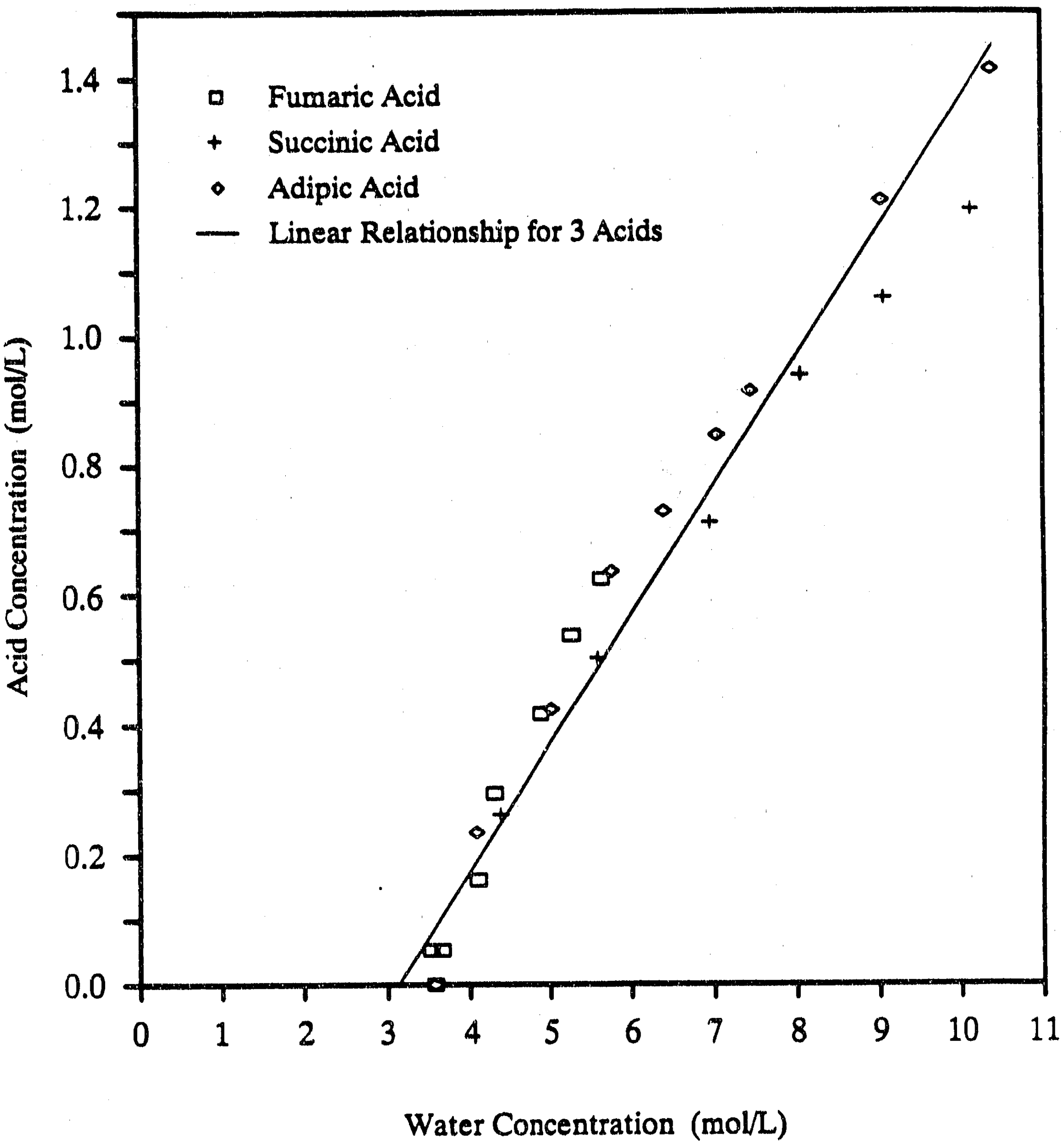

Figure 4.17 Liquid - liquid equilibrium of fumaric acid, succinic acid, and adipic acid in cyclohexanone at 45 C with best fit line.

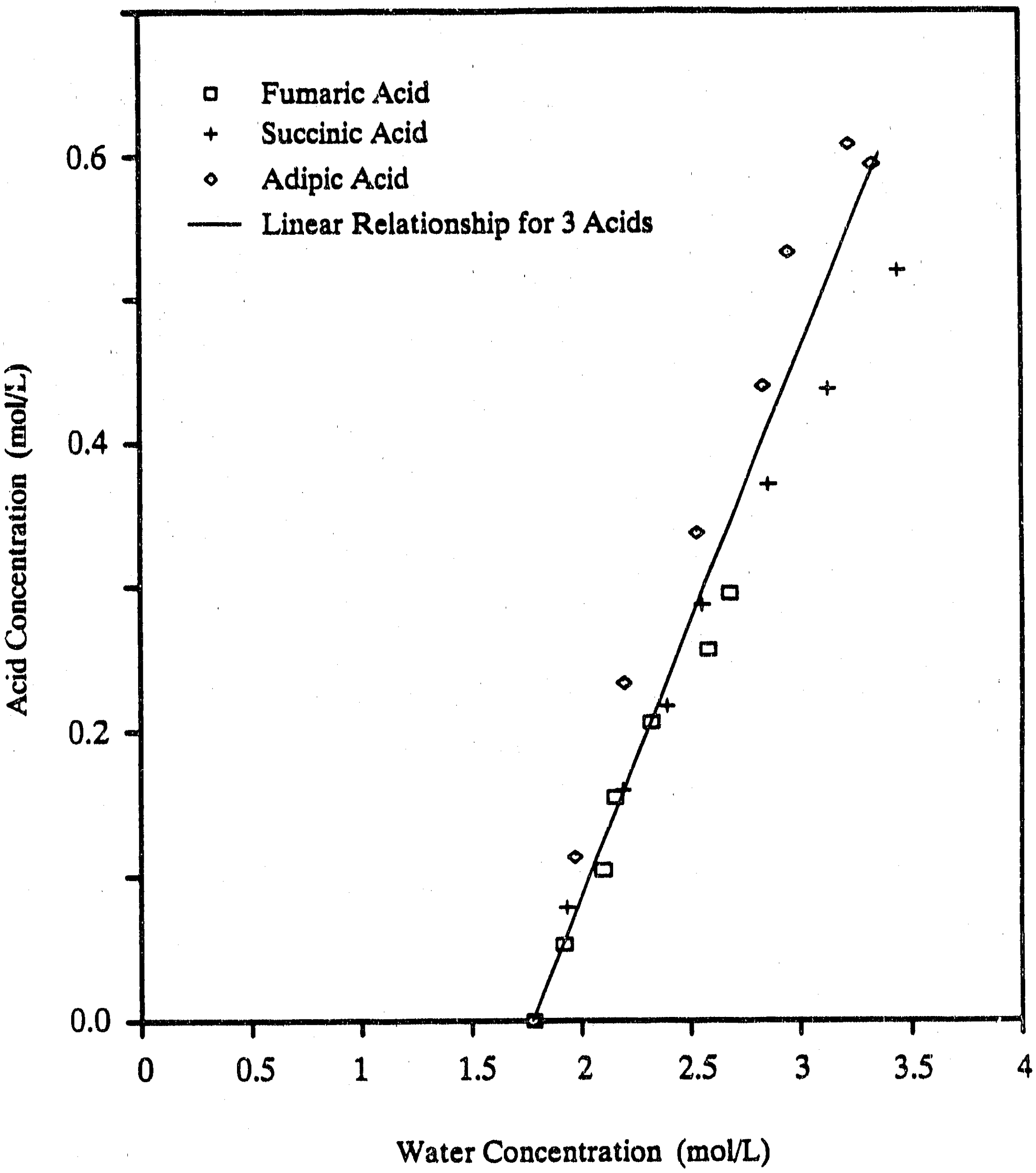

Figure 4.18 Liquid - liquid equilibrium of fumaric acid, succinic acid, and adipic acid in methylcyclohexanone at 25 C with best fit line.

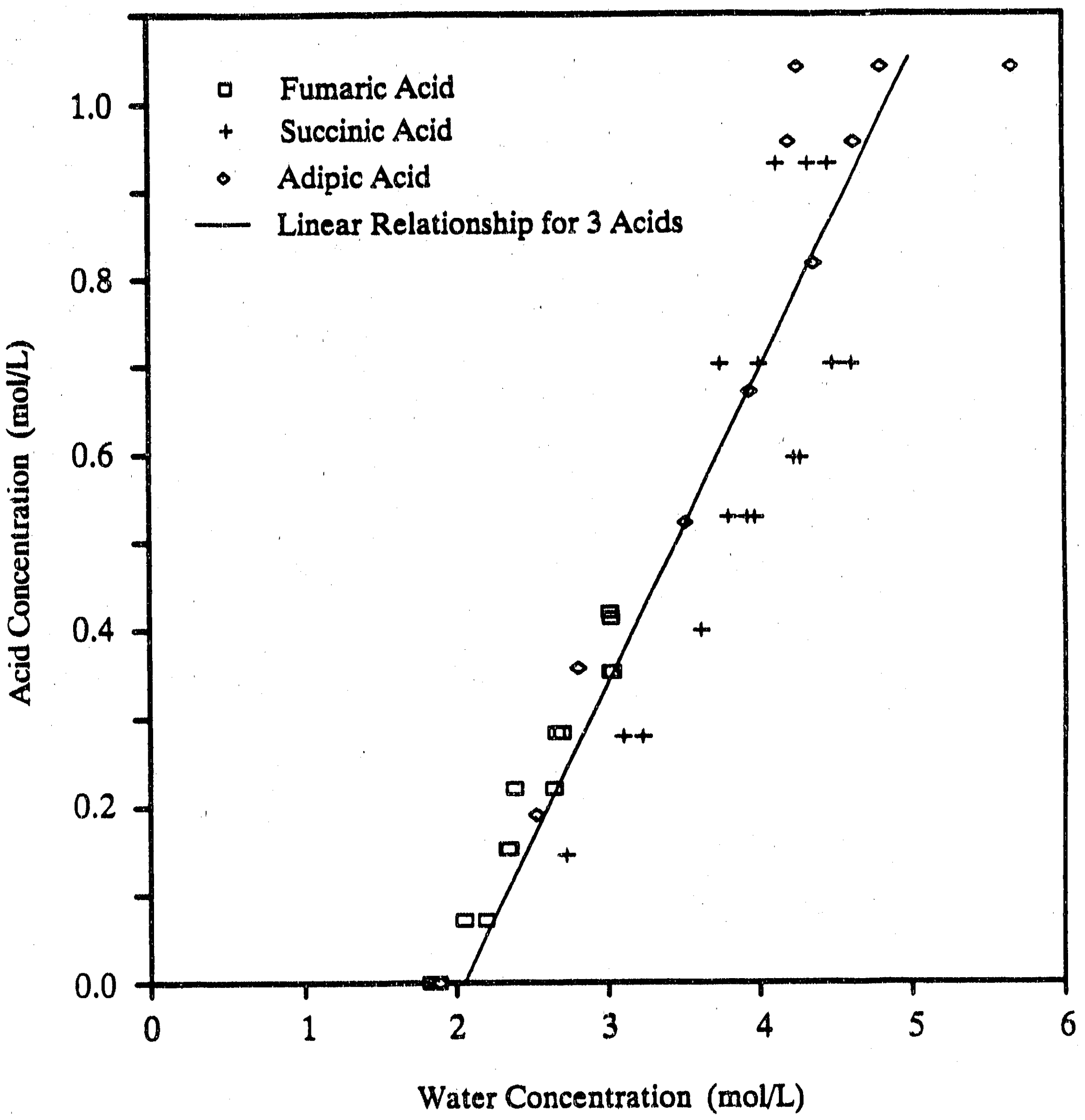

Figure 4.19 Liquid - liquid equilibrium of fumaric acid, succinic acid, and adipic acid in methylcyclohexanone at 45 C with best fit line.

Table 4.3 Values for liquid - liquid equilibrium regression parameters at 25°C with the standard error of the values.

System	Equation	λ	μ
Fumaric Acid-Cyclohexanone	Linear	4.39 ±0.28	2.95 ±0.13
Fumaric Acid - Methylcyclohexanone	Linear	3.05 ±0.20	1.76 ±0.052
Succinic Acid - Cyclohexanone	Linear	5.00 ±0.33	3.00 ±0.34
Succinic Acid - Methylcyclohexanone	Linear	3.23 ±0.12	1.70 ±0.054
Adipic Acid - Cyclohexanone	Linear	4.19 ±0.30	3.18 ±0.32
Adipic Acid - Methylcyclohexanone	Linear	2.54 ±0.14	1.70 ±0.083

Table 4.4 Values for liquid - liquid equilibrium regression parameters at 45°C with standard error of the values.

System	Equation	λ	μ
Fumaric Acid-Cyclohexanone	Linear	3.36 ±0.16	3.48 ±0.10
Fumaric Acid - Methylcyclohexanone	Linear	2.63 ±0.22	2.00 ±0.13
Succinic Acid - Cyclohexanone	Power Law	5.24 ±0.12	1.7
Succinic Acid - Methylcyclohexanone	Linear	2.33 ±0.32	2.50 ±0.34
Adipic Acid - Cyclohexanone	Power Law	4.30 ±0.04	1.3
Adipic Acid - Methylcyclohexanone	Linear	2.81 ±0.29	1.95 ±0.35

reject the hypothesis. A single slope for each solvent, calculated from the 25°C data, can describe the relationship between the acid concentration and the water concentration for the three acids.

The cyclohexanone data at 45°C were better described by the curved power law equation, rather than a linear equation. A consequence of the power law equation is that the incremental moles of water entering the organic phase per incremental mole of acid increases as the acid concentration increases, and the slope goes to zero as the acid concentration goes to zero. For the purpose of the analysis of variance test, a linear equation was used to describe the data for all three acids. For the succinic acid - cyclohexanone system at 45°C, the data point at the highest acid concentration was not used in the linear regression. The analysis of variance test showed that the cyclohexanone data at 45°C could not reject the hypothesis that the same line describes all three acids. The line shown is calculated by linear regression of the data points with acid concentrations below 1.5 moles/L for the three acids.

The analysis of variance test on the acid - methylcyclohexanone data at 45° showed that the hypothesis is rejected; the slopes are significantly different from each other when tested at the 95% confidence level.

The succinic acid - methylcyclohexanone data at 45°C gave higher water concentrations at a given acid concentration than for the other two acids in methylcyclohexanone, except at high acid concentrations. The succinic acid data at low acid concentrations show a slope similar to those for the other two acids, but the intercept on the water concentration axis is much greater than the experimental data point. It is possible that this increased water concentrations are due to an experimental error, and not an actual increase in the water content. The pattern of the data caused the line describing the data to have a value of μ much larger than that for the other two acids. As mentioned earlier, μ is a measure of the water solubility in the solvent and should be equal for all three acids.

Next, the acid - methylcyclohexanone data taken at a single acid concentration with multiple water concentration analyses were averaged such that a single averaged water concentration corresponded to each acid concentration. Using the new averaged data points, the analysis of variance test can not reject the hypothesis that the lines are the same for all acids.

This averaging procedure changes two factors for the analysis of variance test. The degrees of freedom have decreased, which increases the critical value for the variance test. Also, the standard error of the slope typically decreases when the slope is calculated from the average of the points, and not the points themselves. The two factors affect the analysis of variance test in opposite ways. The increased critical variance value makes it harder for the hypothesis to be rejected. On the other hand, the lower standard error of the slope makes it easier for the hypothesis to be rejected. The line shown on Figure 4.19 is calculated from the linear regression of the average water concentrations at the various acid concentrations for the three acids. The values of the slopes and intercepts which describe the relationships between the acid and water concentrations for the three acids in both solvents at the two temperatures are reported in Table 4.5.

The conclusion that a single line can describe the relationship between the molar acid and water concentrations in the organic phase for the three acids is potentially useful. Following that conclusion, these results can be extrapolated to other dicarboxylic acids, such as glutaric acid, maleic acid, and malonic acid, that have molecular structures similar to those of the three acids investigated here.

The hypothesis that $\lambda_{acid,\ 25^{\circ}C} = \lambda_{acid,\ 45^{\circ}C}$ for each solvent can also be checked by a significance test. Interestingly enough, for cyclohexanone and methylcyclohexanone, the significance test could not reject with 95% confidence the hypothesis that the slopes of the liquid -liquid equilibrium line at different temperatures have the same value. The values of the slopes for cyclohexanone and methylcyclohexanone were calculated by linear regression using Equation 4.8 with $C_w(0,T)$ being the water concentration for $C_a = 0$ at temperature T.

Table 4.5 Values for the liquid - liquid equilibrium linear regression parameters and standard error determined for both solvents at two temperatures. The single linear equation describes the behavior of the three acids as described in the analysis of variance test.

Solvent	Temp. (°C)	λ	μ	Remarks
Cyclohexanone	25	4.67 ±0.19	2.97 ±0.33	
Cyclohexanone	45	5.03 ±0.21	3.14 ±0.43	$C_a < 1.5$ mol/L
Methylcyclohexanone	25	2.65 ±0.14	1.78 ±0.13	
Methylcyclohexanone	45	2.81 ±0.16	2.06 ±0.24	C_w averaged

$$C_w - C_w(0,T) = \lambda\, C_a(T) + \mu \tag{4.8}$$

The values of the slopes calculated were 4.85 ± 0.15 and 2.89 ± 0.12 for cyclohexanone and methylcyclohexanone, respectively. However, from the ternary phase diagrams shown in Figure 2.4, the number of waters entering the organic phase per acid should increase as the temperature increases. In other words, as the temperature increases, the slope of the phase envelope becomes shallower.

The differences between the values of the slope at 25°C and 45°C can be estimated by means of a significance test with 95% confidence levels. Equation 4.9 is used to calculate the difference between the value of the two slopes with Λ as the calculated difference between the two slopes, s_z as the standard error of the slope at temperature z, and t as the value taken from the t distribution for a 95% confidence level and the correct degrees of freedom.

$$\lambda_{45^\circ C} - \lambda_{25^\circ C} = \Lambda \pm t\sqrt{(s_{25^\circ C})^2 + (s_{45^\circ C})^2} \tag{4.9}$$

The differences in the values of the slopes between the two temperatures are shown below.

Cyclohexanone	$\lambda_{45^\circ C} - \lambda_{25^\circ C} = 0.36 \pm 0.57$
Methylcyclohexanone	$\lambda_{45^\circ C} - \lambda_{25^\circ C} = 0.24 \pm 0.43$

Note that the difference includes zero, which is another way of stating the previous finding that the hypothesis that the slopes are equal cannot be rejected.

4.3 Effect of Temperature on Liquid - Liquid Equilibrium

The solubilities of water in both cyclohexanone and methylcyclohexanone increase with an increase in temperature. As discussed above, the amount of water entering the organic phase per acid at 45°C is equal to or greater than that at 25°C.

4.3.1 Enthalpy and Entropy of Acid Transfer

Table 4.2 shows that the partition coefficients for the extraction of the acid into the organic phase at low acid concentrations decrease with an increase in temperature. Equation 4.10 shows the relationship between the free energy of phase transfer and temperature (10).

$$\frac{d(\Delta G/RT)}{dT} = \frac{-\Delta H_{transfer}}{RT^2} \qquad (4.10)$$

Integrating Equation 4.10 with the recognition that $\Delta G = \Delta H - T\Delta S = -RT \ln P$, gives Equation 4.11, the equation to calculate the change in enthalpy and entropy for the transfer of the acid from the aqueous phase to the organic phase. It has been assumed that the enthalpy of transfer is constant over the temperature range.

$$\ln P = \frac{-\Delta H_{transfer}}{RT} + \frac{\Delta S_{transfer}}{R} \qquad (4.11)$$

Table 4.6 reports the values of the changes in enthalpy and entropy for fumaric acid in three ketone solvents and for succinic acid and adipic acid in two ketone solvents, computed from the data at 25°C and 45°C.

The enthalpy and entropy for acid transfer include the effects of the accompanying water. All of the changes in enthalpy are negative, indicating that the transfer of the acid into the organic phase is exothermic. All of the changes of entropy are negative, indicating that the transfer of the acid into the organic phase from the aqueous phase orders the system overall. The exothermic and ordering nature of the transfer of the acid into the organic phase provides clear evidence for strong hydrogen bonding in the organic phase. The values of enthalpies of transfer are about -5 kcal/mole or more, and the values of the entropy of transfer are -15 cal/mole K or more. Joesten and Schaad (7) list enthalpies and entropies of

Table 4.6 Enthalpy, entropy, and free energy of transfer of acids from the aqueous phase to the organic phase.

Acid	Solvent	$\Delta H_{transfer}$ (kcal/mol)	$\Delta S_{transfer}$ (cal/mol·K)	$\Delta G_{transfer}$ (kcal/mol)
Fumaric Acid	Cyclohexanone	-5.8	-14.9	-1.4
Fumaric Acid	Methylcyclohexanone	-5.1	-13.3	-1.1
Fumaric Acid	Methylisobutylketone	-3.4	-9.8	-0.48
Succinic Acid	Cyclohexanone	-2.7	-8.5	-0.17
Succinic Acid	Methylcyclohexanone	-2.3	-8.4	+0.20
Adipic Acid	Cyclohexanone	-2.8	-6.4	-0.89
Adipic Acid	Methylcyclohexanone	-2.5	-6.3	-0.62

Table 4.7 Values of the parameters and the standard errors for the relationship between the water distribution between the organic and aqueous phases and the acid concentration in cyclohexanone and methylcyclohexanone.

Solvent	σ $(mol/L)^{-1}$	τ
Cyclohexanone	0.092 ± 0.003	-0.005 ± 0.008
Methylcyclohexanone	0.052 ± 0.002	0.002 ± 0.006

hydrogen bonding, and most of the values are on the order of -5 kcal/mole and -10 cal / mole K. Therefore, the enthalpies and entropies of transfer are comparable to the formation of a single hydrogen bond.

4.3.2 Enthalpy and Entropy of Water Transfer

The liquid - liquid equilibrium data show that there is a strong relationship between the acid and water concentrations in the organic phase. The transfers of the acid and water into the organic phase are coupled. The enthalpy and entropy changes associated with the transfer of the water from the organic phase to the aqueous phase were calculated. Again these values include the effects of the acid accompanying the water into the organic phase.

First, the distribution coefficient of the water needed to be determined. It was established earlier by the analysis of variance test that the hypothesis that the slopes of the curves describing the acid - water equilibrium among the different acids at 25°C and 45°C are equal cannot be rejected. Therefore, a linear equation, Eq. 4-12, was used to describe the relationship between the water distribution and the acid concentration in each solvent. The values of σ and τ and their standard error are reported in Table 4.7 for each solvent.

$$\frac{C_{w,org}}{C_{w,aq}} - \frac{C_{w,org}(0,T)}{C_{w,aq}(0,T)} = \sigma\, C_{a,org} + \tau \qquad (4.12)$$

$C_{w,org}(0,T)$ and $C_{w,aq}(0,T)$ are the concentrations of water in moles per liter at zero acid concentration and T°C in the organic and aqueous phases, respectively. To calculate the moles per liter of water in aqueous phase, the concentration of acid and solvent in the aqueous phase must be known or estimated. The acid concentration was measured by titration, and the experimental results are reported in Appendix C.

The solvent concentration in the aqueous phase was measured by gas chromatography using a thermal conductivity detector. The amount of cyclohexanone in the aqueous phase increased with an increase in acid concentration; the amount of methylcyclohexanone in the aqueous phase stayed constant. The increase in cyclohexanone concentration is an example of the acid reducing the immiscibility of water and cyclohexanone.

The values of the solubilities of cyclohexanone and methylcyclohexanone in water at 25°C are 0.950 mole/L and 0.115 mole/L , respectively, as reported by Sorensen and Arlt (8). The cyclohexanone solubility in water at 45°C was reported by Sorensen and Arlt to be 0.78 moles/L, which is a decrease from that reported at 25°C. The thermal conductivity detector output, which is typically proportional to the weight percent of the compounds in the mixture, gave another estimate of the solubilities of the solvents in water. The experimentally determined values of the solvent solubility in water at 25°C were 0.59 moles/L and 0.17 moles/L for cyclohexanone and methylcyclohexanone, respectively, as measured by the thermal conductivity detector.

A linear equation was used to describe the increase in the cyclohexanone solubility in water with an increase in the aqueous acid concentration. Equations 4.13 and 4.14 are the equations used for the two temperatures.

$$\text{At } 25^\circ\text{C} \qquad C_{\text{cyclohexanone, aq}} = 0.86\ C_{\text{acid, aq}} + 0.95 \qquad (4.13)$$

$$\text{At } 45^\circ\text{C} \qquad C_{\text{cyclohexanone, aq}} = 0.71\ C_{\text{acid, aq}} + 0.78 \qquad (4.14)$$

The water distribution was calculated using both estimates. The value of the water distribution was very insensitive to the amount of solvent present in the aqueous phase, and the two estimates of the solvent solubility gave nearly identical results. The literature values of the solvent solubility in water were used in the final calculations with 0.10 moles/L being used for the solubility of methylcyclohexanone in water at 45°C in lieu of a literature value.

The enthalpy and entropy changes of water transfer depend upon the composition of the organic phase. Therefore, the water distribution was calculated using Equation 4.12 over a wide range of acid concentrations at the two temperatures. Thus, the enthalpies and entropies of water transfer can be calculated at given acid and water concentrations in the organic phase. Tables 4.8 and 4.9 report these results for cyclohexanone and methylcyclohexanone, respectively.

As noted above, the transfer of acid into the organic phase causes a transfer of water into the organic phase, i.e. the transfers of the two species are coupled. Therefore, the change in enthalpy and entropy for acid transfer and the change in enthalpy and entropy for water transfer, all of which are calculated from the equilibrium acid and water concentrations, are not independent of each other.

The trends in the values of the changes in enthalpy and entropy can be explained by hypothesizing a hydrogen bonding network in the organic phase. Caution should be used in extrapolating these results and arguments since the data were taken at only two temperatures.

4.3.3 Acid Transfer Discussion

The change in enthalpy for acid transfer can be interpreted as the sum of the enthalpy associated with removing the acid and the associated water from the aqueous phase and the enthalpy associated with adding the acid and that water to the organic phase. The exothermic nature of this process can be attributed to the exothermic nature of removing the acid and water from the aqueous phase, or the exothermic nature of adding the acid and water to the organic phase, or a combination of both. The same reasoning can be applied to the change in entropy of acid transfer. The ordering nature of the acid and water transfers into the organic phase can be attributed to the order caused by removing the acid and water from the aqueous phase, or the order caused by adding the acid and water to the organic phase, or a combination of both.

For fumaric acid in the three solvents, the changes in free energy and enthalpy of acid transfer decrease in the order cyclohexanone > methylcyclohexanone > methylisobutylketone. This is the same order as that of the ratios of the acid solubilities in the hydrated solvent to

Table 4.8 Enthalpy, entropy, and free energy of water transfer into cyclohexanone which has varying amounts of acid and water.

$C_{acid, org}$ (mol/L)	$\Delta H_{transfer}$ (kcal/mol)	$\Delta S_{transfer}$ (cal/mol·K)	$\Delta G_{transfer}$ at 25°C (kcal/mol)
0.0	0.96	0.23	0.89
0.1	0.82	-0.07	0.84
0.2	0.72	-0.27	0.80
0.3	0.64	-0.41	0.76
0.4	0.58	-0.52	0.74
0.5	0.52	-0.59	0.70
0.6	0.48	-0.65	0.67
0.7	0.44	-0.69	0.65
0.8	0.41	-0.72	0.62
0.9	0.38	-0.74	0.60
1.0	0.36	-0.75	0.58

Table 4.9 Enthalpy, entropy, and free energy of water transfer into methylcyclohexanone which has varying amounts of acid and water.

$C_{acid, org}$ (mol/L)	$\Delta H_{transfer}$ (kcal/mol)	$\Delta S_{transfer}$ (cal/mol·K)	$\Delta G_{transfer}$ at 25°C (kcal/mol)
0.0	0.23	-2.60	1.0
0.1	0.20	-2.56	0.96
0.2	0.18	-2.52	0.93
0.3	0.16	-2.47	0.90
0.4	0.15	-2.42	0.87
0.5	0.13	-2.37	0.84
0.6	0.12	-2.32	0.81
0.7	0.11	-2.28	0.79

those in the anhydrous solvent. This correspondence between the change in free energy, which can be calculated from liquid - liquid equilibrium data, and the increase in acid solubility with increasing water concentrations in the organic phase, which is taken from solid - liquid equilibria, may provide a connection between the two equilibria measured in this work. It also provides a possible method of expanding on this work by screening solvents for this enhanced solubility effect by calculating the free energy and enthalpy of acid transfer. This could be valuable since liquid - liquid data are generally plentiful in the literature, while data on the solubility of acids in organic solvents are much scarcer.

The same trend in the change in free energy and enthalpy of acid transfer is found for succinic acid and adipic acid, with the cyclohexanone value being greater than the methylcyclohexanone value. Tamada and King (4) report the enthalpy change of acid transfer for the succinic acid - methylisobutylketone system as -1.7 kcal/mole, following the same trend as found for fumaric acid. From this information, one would expect that the increase in succinic acid solubility with increasing water concentration in methylisobutylketone would not be as great as found for succinic acid in cyclohexanone or methylcyclohexanone. The probable reason behind the trend of the solvents for the increase in acid solubility and the enthalpy change of acid transfer is the order of availability of the oxygen atom of the carbonyl group to hydrogen bond with the acid and water.

The free energies and enthalpies of transfer show the same dependence among solvents for all three acids. The value of the free energy of transfer is dominated by the value of the enthalpy of transfer. The contribution of the entropy of transfer to the value of the free energy of transfer is small because the entropy effects from transferring a species from one liquid phase to another liquid are generally small.

For a given solvent, the free energies and enthalpies of acid transfer decrease in the order succinic acid > adipic acid > fumaric acid. The free energy and enthalpy of acid transfer can be correlated with the ability of the acid to form intramolecular hydrogen bonds.

However, the order of the values of the enthalpy of transfer cannot be related to the number of acid-water interactions since the slope analysis discussed earlier shows that the three carboxylic acids co-extract the same amount of water per mole of acid.

The differences in the enthalpy of transfer between the three acids could be explained by solvent interactions with the hydrated acid. Fumaric acid, with its rigid structure, may give carbonyl groups of the solvent the most opportunity to interact with the acid and its waters of hydration. Succinic acid and adipic acid, with their ability to self-associate and to "flop", may be less available for hydrogen bonding to the carbonyl group. This is not to say that the acid-water interactions do not add to the overall exothermic nature of the acid transfer, only that the differences in the value of the enthalpy of acid transfer between acids is related to solvent - hydrated acid interactions.

For a given acid, cyclohexanone exhibited values of the entropy of acid transfer equal to or less than those for methylcyclohexanone, meaning that the acid transfer into cyclohexanone is more ordering than the transfer into methylcyclohexanone. This could be caused by the greater amount of water entering the organic phase per acid for cyclohexanone than that in methylcyclohexanone. If this water is structured, it would account for the greater value of the entropy of transfer.

For fumaric acid, methylisobutylketone shows a lower value of the entropy of transfer than those for the other two solvents. However, Tamada and King (4) report a entropy of transfer value of -8.7 cal/mole·°K for the succinic acid - methylisobutylketone system, which is a higher value than found in the present work for cyclohexanone or methylcyclohexanone. For a given solvent, the absolute values of the entropy of acid transfer decreased in the order fumaric acid > succinic acid > adipic acid. This order could be interpreted in terms of the structural rigidity of the acid and its ability to self-associate. The trend of the values of the entropy of acid transfer could be caused by the ketone solvent arranging itself around the acid and its water of hydration, and the tendency for the ketone to arrange itself around the acid is related to the rigidity of the acid and ability of the acid to self-associate.

4.3.4 Water Transfer Discussion

The free energies and enthalpies of water transfer are greater than zero for both solvents at all acid concentrations. The interesting result from the change in enthalpy calculation is that as the acid concentration increases, the value of the enthalpy of transfer decreases, i.e., the transfer becomes less endothermic. At very low acid concentrations, the water mainly interacts with the basic ketone and other water molecules. As the acid concentration increases, the water can interact with the acidic hydrogen providing a more exothermic interaction.

The changes in the entropies of water transfer exhibit opposite behaviors with increasing acid concentration in the two solvents. As the acid concentration increases, the change in entropy decreases in cyclohexanone, but increases slightly in methylcyclohexanone. The hypothesis of a strong hydrogen bonding network in the organic phase would suggest that the water transfer would be more ordering at higher acid concentrations, following the trend shown by cyclohexanone. The increase in the change in entropy as the acid concentration increases in methylcyclohexanone may be related to the fact that the system moves towards the plait point as the acid concentration increases, and the change in entropy goes to zero as the plait point is reached. So there are possibly two competing phenomena, the ordering due to hydrogen bonding and the disordering related to the lowering immiscibility of the phases, that effect the value of the change in entropy as the acid concentration increases. The first one seems to dominate in cyclohexanone, and the second one dominates in methylcyclohexanone. The fact that the absolute values of the entropy of water transfer are much greater for methylcyclohexanone than for cyclohexanone may be the reason for the lowering immiscibility phenomenon to dominate in methylcyclohexanone.

The changes in the values of the enthalpies and entropies of water transfer are small compared to the enthalpy and entropy associated with the formation of a hydrogen bond. However, there are approximately three to five moles of water entering the organic phase per mole of acid, amplifying the changes in the values.

4.4 Summary and Conclusions

In conclusion, the liquid - liquid equilibria of fumaric acid, succinic acid, and adipic acid in cyclohexanone and methylcyclohexanone were studied. The acid distribution between the phases favored the organic phase except for the succinic acid - methylcyclohexanone system. Evidence for strong hydrogen bonding between all three components of the organic phase includes: (1) the incremental moles of water per incremental mole of acid entering the organic phase (on the order of 4, the number of hydrogen bonding sites on a dicarboxylic acid), (2) the trends in values of the enthalpy and entropy of acid transfer among the different acids and solvents, and (3) the decreasing values of the enthalpy of water transfer as the acid concentration increases in the organic phase.

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CHAPTER 5. CHEMICAL INTERACTIONS IN THE ORGANIC PHASE

This chapter discusses two possible hypotheses that would describe the interactions of the carboxylic acid, water, and ketone in the organic phase. Molecular scale evidence for hydrogen bonding in carboxylic acid, water, and ketone mixtures from the literature is discussed. Thermodynamic modeling of the system with the NRTL equation and three-suffix Margules equation failed to describe the system. A chemical complexation model that proposed a single acid:water:solvent complex fit the data well.

5.1. Possible Explanations of Thermodynamic Behavior in Organic Phase

5.1.1. Reverse Micelle Formation

Reverse micelles are thermodynamically stable aggregates of high water content in an organic phase with amphiphilic molecules at the boundary of the water-rich micelle and the solvent-rich bulk phase. Kress, et al. (1) studied the extraction of copper from aqueous solution into an organic phase consisting of trioctylamine, 2-ethyl hexanoic acid, and toluene. The water concentration in the organic phase increased linearly with the copper concentration in the organic phase, similar to the ketone - carboxylic acid - water systems discussed in Chapter 4. Through water uptake measurements and vapor pressure osmometry, they concluded that the systems formed reverse micelles. Water uptake and vapor pressure osmometry are secondary evidence for the formation of reverse micelles because they are measuring the effects that the reverse micelles have on the solution, and not the presence of the reverse micelles. The formation of reverse micelles should be confirmed by other more direct techniques.

The possibility of formation of reverse micelles was considered for the carboxylic acid - ketone - water system, given the fact that the water concentrations in the organic phase increased linearly with amount of solute extracted, as in the systems studied by Kress, et al. (1).

Dynamic light scattering is a technique for measuring the size of reverse micelles or other particles in solution. Solutions of varying concentrations of fumaric acid and water in cyclohexanone were examined by dynamic light scattering. There was no evidence of reverse micelle formation or any inhomogeneous "structure" down to a resolution of 50Å.

5.1.2. Hydrogen Bonding

Strong hydrogen bonding among all three species - carboxylic acid, ketone, and water -- could also explain the results of the equilibrium experiments. Experimental results provide a great deal of evidence for the formation of hydrogen bonds between all three compounds in solution.

This evidence includes the observation that the incremental moles of water needed to dissolve an incremental mole of dicarboxylic acid at low water concentrations is on the order of the number of hydrogen bonding sites on a dicarboxylic acid. The enthalpy and entropy of solution of the acids becomes more exothermic and ordering as the water concentration increases for solid - liquid equilibria. The liquid - liquid equilibria data show that the enthalpy and entropy of acid transfer into the organic phase are exothermic and ordering. Also, the incremental number of moles of water entering the organic phase per mole of acid is on the order of the number of hydrogen bonding sites on the acid. The enthalpy of water transfer becomes more exothermic as the acid concentration in the organic phase increases.

5.2. Molecular Scale Evidence for Hydrogen Bonding

There are a number of different techniques that investigators have used in the past to obtain qualitative and quantitative information about hydrogen bonding in liquid solutions. These techniques include infrared (IR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy.

5.2.1. Infrared Spectroscopy

IR spectroscopy measures the electromagnetic energy absorbed by molecules as they are excited to a higher vibrational energy. Certain bonds have characteristic frequencies in which they absorb energy. The O-H bond strongly absorbs at 3620-3640 cm^{-1} in a free state and 3250-3450 cm^{-1} in an associated or hydrogen bonded state. The C=O bond has a characteristic absorption at 1715 cm^{-1} (2).

Water in the samples for IR spectroscopy can be very troublesome for two reasons. One is that water attacks the cell windows typically used, and special materials of construction for the cell must be used. The other, more difficult problem is that the O-H bond of water strongly adsorbs over much of the IR spectrum. Very low water concentrations are required to produce reliable results using typical IR spectroscopy procedures. Meaningful spectra from samples with high water content are measured using a number of experimental techniques including short-path-length cells, dual-beam spectrometers, or attenuated total reflectance spectroscopy (3). Raman spectroscopy is also a possible technique for aqueous solutions since water gives only a weak Raman spectrum (4).

Schriver and Corset (5) studied the molecular interactions of water, thiocyanic acid, and methylisobutylketone. The spectra were interpreted through the formation of a 1:1:2 thiocyanic acid:water:methylisobutylketone complex in a excess of methylisobutylketone. The oxygen of the water is hydrogen bonded to the acidic proton, and the two carbonyl groups are hydrogen bonded to the hydrogens of the water. The work of Schriver and Corset provides evidence that similar ternary complexes could be formed in the organic phases of the systems under study in this work.

Mohr, et al. (6) used infrared spectroscopy to examine the association of water with bases, such as acetone, in carbon tetrachloride. At low base concentrations, they explained their results by the formation of a single hydrogen bond between the water and base. At high base concentrations, their results showed the formation of a 1:2 water:base species with a basic molecule hydrogen bonded to each hydrogen of water. Their conclusions about water-Lewis base interactions in solution are in agreement with the conclusions of Shriver and Corset (5).

5.2.2. Nuclear Magnetic Resonance Spectroscopy

The nuclei of atoms have two energy states in the presence of a magnetic field. In NMR, electromagnetic energy is absorbed by the nucleus of an atom in a transition from the lower energy state to the higher energy state. The exact wavelength of energy absorbed depends upon the electron density surrounding the atom of interest. The greater the electron density the more the atom is shielded from the applied magnetic field. As the electron density or shielding decreases, the frequency at which the nucleus absorbs energy will increase. Absorption peaks at high frequency are considered to be downfield from those at lower frequencies. The formation of hydrogen bonds changes the electron shielding of the nuclei and shifts the absorption peaks. Nuclei of interest for our purposes include H^1, C^{13}, and O^{17}.

5.2.2.1 H^1 NMR

The H^1 NMR spectra of carboxylic acids with water is complicated by proton exchange. The time scale for proton exchange at room temperature is much faster than the time scale associated with an NMR experiment, and the acidic proton will give a peak for a time-averaged environment.

Davis and Pitzer (7) studied the hydrogen bonding of acetic acid, benzoic acid and formic acid in benzene and carbon tetrachloride by H^1 NMR. They reported that the peak associated with the acidic hydrogen shifted downfield as the concentration of the acid in the solvent increased. For a given acid concentration, the acidic hydrogen peak moved upfield as the temperature was increased. They explained their observations by proposing an equilibrium between the a monomer and dimer form of the acid in solution, and calculated an equilibrium constant between the monomer and dimer and peak shifts as a functions of temperature.

Muller and Rose (8) studied the proton spectra of acetic acid in acetone, acetic anhydride, and 1,4-dioxane with varying amounts of water. The acetic acid - acetone system, which would be most similar to the systems under investigation in this work, showed trends very similar to those found by Davis and Pitzer (7), with the peak shifting downfield with increasing acid concentration at a given temperature and decreasing temperature at a given acid concentration. As the water concentration increases in the acetic acid-acetic anhydride system, the original sharp peak broadens, then moves upfield corresponding to hydration breaking up self-association. These results show evidence for specific hydrogen bonding between carboxylic acid and carbonyl functional groups, and that water can alter this acid - ketone bonding.

5.2.2.2 C^{13} NMR

Studying hydrogen bonding through C^{13} NMR is advantageous over H^1 NMR because there is not the added complexity of proton exchange. However, C^{13} NMR measures the electronic changes of a carbon atom that is one or two bonds away from the hydrogen bond.

The C^{13} shifts for the carboxyl group of acetic acid were determined in water, acetone, chloroform, and cyclohexane by Maciel and Traficante (9). Pure acetic acid is dimerized and possibly polymerized, but an increase in hydrogen bonding to the carboxyl oxygen or by the acidic proton should lead to a downfield shift. The results show very different behavior between acetone and water as solvents. For acetic acid in acetone, the peak shifted downfield as the acetic acid concentration decreased until it reached an asymptotic limit at low concentrations of acetic acid. The results are explained by the dissociation of the acetic acid dimers and polymers by acetone, and the nearly 1:1 complex between acetic acid and acetone at lower acid concentrations. Water is both a base and an acid, unlike acetone which is only basic. Water can fully replace any hydrogen bonds disrupted as the acetic acid dimers and polymer dissociate. For the water - acetic acid system, the peak shifts downfield with decreasing acid concentration until a maximum shift occurs at approximately 1:2 volume ratio of acetic acid to water, then the peak slowly shifts upfield as the acid concentration decreases. The peak position at low acetic acid concentrations is close to the peak position of pure acetic acid. Also at low acetic acid concentrations, the peak shifts are very similar to those found for the acetic acid - cyclohexane system. This can be explained by acetic acid dimers in cyclohexane being fully hydrogen bonded and the water forming hydrogen bonds to the two sites on acetic acid.

The results of Maciel and Traficante (9) reveal that acid - water and acid - acid hydrogen bonds have similar characteristics, and that acidic proton - ketone hydrogen bonds are favorable as shown by the large downfield shift of the acid - ketone complex.

5.2.2.3 O^{17} NMR

Studying hydrogen bonding effects by O^{17} provides many advantages because O^{17} does not exchange with other oxygen and it directly participates in hydrogen bonding. Also, since the isotopically-enriched material must be used, the effects of hydrogen bonding for only water, acid, or ketone can be distinguished.

Reuben (10) investigated the effect of solvents on O^{17} chemical shifts with enriched water, acetic acid, or acetone in a number of solvents. The O^{17} chemical shifts of water in acetic acid and acetone moved upfield as the concentration of water decreased, with the shift associated with acetone being much larger than that for acetic acid. Reuben explains the results by the formation of acetone - water complexes at low water concentrations and by the water being only slightly less hydrogen bonded in acetic acid than in pure water. This explanation is in agreement with the explanation of C^{13} chemical shifts by Maciel and Traficante (9) discussed earlier.

Reuben (10) also studied the O^{17} chemical shifts of acetic acid in acetone and water, as well as other solvents. The chemical shifts moved upfield in acetone as the acetic acid concentration decreased, which is consistent with acetone disrupting the acetic acid dimer. The chemical shifts of acetic acid in water at different pH were determined. At low pH, the chemical shift was similar to that found for pure acetic acid. At high pH, acetic acid has been ionized, and the chemical shift has moved upfield.

Reuben (10) also investigated the O^{17} chemical shifts of acetone in water. The chemical shift moves downfield as the acetone concentration decreases, which is consistent with hydrogen bonding.

The results from NMR experiments that have the same functional groups as the systems studied in this work fully support the hypothesis that a strong hydrogen bonding network among all three species in the organic phase is responsible for the large increase in the solubilities of the acids with increasing water concentration (solid -liquid equilibrium), and the increasing solubility of water in the organic phase with increasing acid concentration (liquid - liquid equilibrium).

5.3 Thermodynamic Modeling

5.3.1 Physical Models

There are a number of thermodynamic equations to calculate the activity coefficients of the components in a mixture as a function of the composition of the mixture. The non-random, two-liquid (NRTL) equation is one such method to calculate the activity coefficients as a function of composition. Prausnitz, et al. (11) report this equation, and suggest that it can describe strongly nonideal and partially immiscible mixtures. However, only binary parameters are used to predict multicomponent equilibria with the NRTL equation. The NRTL equation for a multi-component mixture is Equation 5.1.

$$\ln \gamma_i = \frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{m} G_{li} x_l} + \sum_{j=1}^{m} \frac{x_j G_{ij}}{\sum_{l=1}^{m} G_{lj} x_l} \left\{ \tau_{ij} - \frac{\sum_{r=1}^{m} x_r \tau_{rj} G_{rj}}{\sum_{l=1}^{m} G_{lj} x_l} \right\} \qquad (5.1)$$

The parameters for the NRTL equation, G_{ij} and τ_{ij}, are calculated from g_{ij} and α, which are parameters characteristic of the i-j interaction energy, and the nonrandomness of the mixture, respectively. Equations 5.2 and 5.3 show the relevant equations to calculate G_{ij} and τ_{ij}. Prausnitz, et al. (11) suggest a value of 0.3 for the α parameter.

$$\tau_{ij} = (g_{ij} - g_{jj})/RT \tag{5.2}$$

$$G_{ij} = \exp(-\alpha\ \tau_{ij}) \tag{5.3}$$

The NRTL parameters were calculated to fit the experimental data measured in this work for $\alpha = 0.2$ and $\alpha = 0.3$. The values were calculated from the solubility of the acid in water (12) or the pure solvent (this work) and the mutual solubility of the two liquids (13). Table 5.1 lists the values of the NRTL parameters. All of the data were converted to mole fractions, and the activity coefficients for all components in the aqueous and organic phase were calculated.

The equilibrium relationship for a component distributed between two phases was given in Chapter 2 as Equation 2.4. This equation can be rearranged to give Equation 5.4 for the ith component in the mixture. The left side of Equation 5.4 is calculated from experimental data; the right side of Equation 5.4 is calculated from the NRTL equation.

$$\frac{x_{i,aq}}{x_{i,org}} = \frac{\gamma_{i,org}}{\gamma_{i,aq}} \tag{5.4}$$

Table 5.2 reports values of the ratio of the mole fractions (the left hand side of Eq. 5.4) and the ratio of the activity coefficients (the right hand side of Eq. 5.4) for the fumaric acid - cyclohexanone - water liquid - liquid equilibria at 25°C and $\alpha = 0.3$. The NRTL model correctly predicts the behavior of the solution if the two values are approximately equal. The table shows that the NRTL equation does a reasonable job of predicting the distribution of cyclohexanone and water between the aqueous and organic phases, but it cannot predict the

Table 5.1 NRTL equation parameters for cyclohexanone (1) - water (2) - fumaric acid (3) at 25°C for $\alpha = 0.2$ and $\alpha = 0.3$.

Parameter	$\alpha = 0.2$	$\alpha = 0.3$
τ_{12}	-0.03	0.755
τ_{21}	4.12	3.56
τ_{13}	17.4	12.8
τ_{31}	-4.07	-2.27
τ_{23}	20.4	14.8
τ_{32}	-4.57	-2.62
G_{12}	1.01	0.80
G_{21}	0.44	0.34
G_{13}	0.03	0.022
G_{31}	2.26	1.98
G_{23}	0.017	0.012
G_{32}	2.49	2.20

Table 5.2 Ratio of mole fraction in aqueous phase to that in the organic phase and the ratio of the activity coefficient in the organic phase to that in the aqueous phase for all three components of the fumaric acid - cyclohexanone - water system at 25°C. The activity coefficients are calculated from the NRTL equation with $\alpha = 0.3$.

$C_{acid,org}$ (M)	$\frac{x_{sol,org}}{x_{sol,aq}}$	$\frac{\gamma_{sol,aq}}{\gamma_{sol,org}}$	$\frac{x_{water,org}}{x_{water,aq}}$	$\frac{\gamma_{water,aq}}{\gamma_{water,org}}$	$\frac{x_{acid,org}}{x_{acid,aq}}$	$\frac{\gamma_{acid,aq}}{\gamma_{acid,org}}$
0.0	44.5	41.8	0.243	0.222		
0.041	43.6	40.9	0.251	0.228	30.7	205
0.138	40.8	37.6	0.284	0.246	31.6	8280
0.310	36.3	32.5	0.338	0.278	28.1	44200
0.381	35.0	31.0	0.350	0.287	26.5	44290
0.458	33.9	29.8	0.358	0.295	26.7	42410

distribution of the acid. The equation predicts that the acid should be almost entirely in the organic phase. The NRTL equation results for $\alpha = 0.2$ are not shown because the agreement with the experimental data for $\alpha = 0.3$ was better than for $\alpha = 0.2$.

The main reason for the failure of the NRTL model to predict the acid distribution is that it uses only binary parameters in a system which has strong ternary interactions. Because of the greatly increased solubility of fumaric acid in the hydrated organic phase, the NRTL equation is also being extrapolated to acid concentrations much greater than expected from binary data. The solubility of fumaric acid in anhydrous cyclohexanone at 25°C is 0.053 moles/liter. There are only two data points taken and shown in Table 5.2 that have a fumaric acid concentration below 0.053 moles/liter.

The three-suffix Margules equation is another equation of state that can be used to predict the distribution of components between two phases, and is shown in Equation 5.5 (11). Wohl's expansion has a parameter, Q_{123}, that accounts for ternary interactions. When the ternary parameter is set equal to zero, the expansion reduces to the two-suffix Margules equation. The fact that this equation could account for ternary interactions made it of interest for modeling the fumaric acid - cyclohexanone - water system.

$$\begin{aligned}\ln \gamma_1 = {} & A_{12}x_2^2(1-2x_1) + 2A_{13}x_1x_2(1-x_1) + A_{13}x_3^2(1-2x_1) + 2A_{31}x_1x_3(1-x_1) - 2A_{32}x_2^2x_3 \\ & + [\tfrac{1}{2}(A_{12} + A_{21} + A_{13} + A_{23} + A_{32}) - Q_{123}](x_2x_3 - 2x_1x_2x_3) \qquad (5.5)\end{aligned}$$

The binary parameters were calculated from acid solubility data and mutual liquid solubility data similar to what was done for the NRTL equation. Table 5.3 reports the binary parameters for the Margules equation. The ternary parameter was then chosen on the basis of the match of the prediction with the experimental data.

The ternary parameter, Q_{123}, was chosen to be -345.2, such that the three-suffix Margules equation correctly predicted the fumaric acid distribution at the triple point of the system. However, with this value, the Margules equation predicted that virtually no acid

Table 5.3 Three-suffix Margules equation parameters for cyclohexanone (1) - water (2) - fumaric acid (3) system at 25°C.

A_{12}	3.90
A_{21}	0.85
A_{13}	-468.
A_{31}	8.18
A_{23}	-1048
A_{32}	8.98
Q_{123}	-345.2

Table 5.4 Ratio of mole fraction in aqueous phase to that in the organic phase and the ratio of the activity coefficient in the organic phase to that in the aqueous phase for all three components of the fumaric acid - cyclohexanone - water system at 25°C. Activity coefficients are calculated from the three-suffix Margules equation.

$C_{acid,org}$ (M)	$\frac{x_{sol,org}}{x_{sol,aq}}$	$\frac{\gamma_{sol,aq}}{\gamma_{sol,org}}$	$\frac{x_{water,org}}{x_{water,aq}}$	$\frac{\gamma_{water,aq}}{\gamma_{water,org}}$	$\frac{x_{acid,org}}{x_{acid,aq}}$	$\frac{\gamma_{acid,aq}}{\gamma_{acid,org}}$
0.0	44.5	41.0	0.243	0.26		
0.041	43.6	32.6	0.251	0.45	30.7	3.6×10^{-7}
0.138	40.8	18.7	0.284	1.10	31.6	8.9×10^{-6}
0.310	36.3	7.1	0.338	2.03	28.1	0.016
0.381	35.0	4.63	0.350	2.40	26.5	0.57
0.458	33.9	2.98	0.358	2.80	26.7	26.7

would be found in the organic phase at low acid concentrations as reported in Table 5.4. Also, the equation predicted a physical impossibility in that at high acid concentrations, all of the ratios of the mole fractions in the organic phase to those in the aqueous phase were greater than one. In other words, the mole fraction of each component in the organic phase is predicted to be greater than that in the aqueous phase. Obviously, this cannot be true.

Other values of the ternary parameter were examined. The data point at 0.041 moles/liter could be predicted with a value of -235.6. However, using this value of the ternary parameter, the acid distribution at high acid concentrations was predicted very poorly. The Margules equation is very sensitive to changes in the value of the ternary parameter, as shown by the fact that a change from -345.2 to -235.6 shifted the distribution of the acid by seven magnitudes of order.

The thermodynamic models using binary parameters discussed and used in this work were unable to predict qualitatively the fumaric acid distribution between cyclohexanone and water at 25°C. Modeling the systems of adipic acid or succinic acid in cyclohexanone or methylcyclohexanone was not attempted.

5.3.2 Chemical Models

Another model used to describe solution behavior is based on "chemical" interactions. Chemical theories of liquid solutions account for nonideal solutions by proposing that monomer species in the solution form complexes characterized by equilibrium constants. If the mole fractions of the all species, both monomer and complexes, were known, solution behavior could be predicted. The chemical theories work well when the specific interactions between molecules, such as acid:base interactions, are dominant over dispersion interactions. A disadvantage to chemical-based models is that the choice of which complexes are formed is somewhat arbitrary unless there is an independent evidence, such as NMR or IR spectroscopy, for the existence of a complex.

Models based on chemical theory were used to model the carboxylic acid - ketone - water systems. There is certainly evidence for strong hydrogen bonding between the three species in the mixture as discussed earlier.

Christian and co-workers have studied molecular complexes of water in the vapor phase and organic solvents (14,15,16,17,18,19). Using chemical complexation models with water and solute partitioning data, Van Duyne, et al. (15) found that benzoic acid partitioning from water into benzene could be fit by 1:1, 1:2, and 2:1 acid:water complexes. Wood, et al. (17) reported that 1:2 and 2:1 acid:water complexes could successfully fit benzoic acid partitioning into diphenylmethane from water. Christian, et al. (19) described vapor pressure data for the triflouroacetic acid - water system by using a acid dimer and 1:2 acid:water complex.

In all these studies, the formation of 1:2 acid:water complex is needed to model the data, and this complex, as proposed by Christian, et al. (19), is shown in Figure 5.1. The cyclic nature of the complex leaves two hydrogen atoms available for the formation of hydrogen bonds, either to another water or a basic solvent. If two ketone molecules are associated with the 1:2 acid:water complex, the a 1:2:2 acid:water:ketone complex should fit the data well. The 1:2:2 complex is attractive because the work of Shriver and Corset (5), and Mohr, et al. (6) provide evidence for strong water - ketone interactions. Because the acids studied in this work are *di*carboxylic acids, 1:4:4 acid:water:ketone complexes may be useful in fitting the data.

Johnson, et al. (16) studied the binary water - cyclohexanone system using a vapor pressure technique, and found that a monomer and trimer species of water fit the data best. Johnson proposed that the trimer of water was cyclic, leaving three hydrogens available for hydrogen bonding with cyclohexanone.

The model used was based on a single acid:water:ketone complex in the organic solvent. The complexation constant, β_{pqr}, characterizes a reaction of *p* undissociated acid

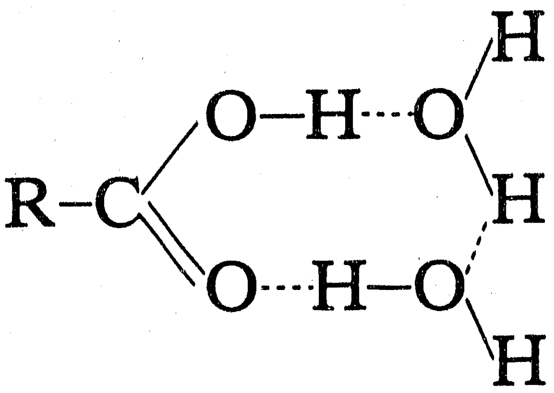

Figure 5.1 Cyclic arrangement of 1:2 acid:water complex

molecules in the aqueous phase, A, *q* water molecules in the organic phase, W, and *r* ketone molecules in the organic phase, K, and is defined in Equation 5.6. The overbar indicates an organic-phase species, and the brackets indicate the species activity.

$$pA + q\overline{W} + r\overline{K} = \overline{A_pW_qK_r} \qquad \beta_{pqr,true} = \frac{\overline{\{A_pW_qK_r\}}}{\{A\}^p\{\overline{W}\}^q\{\overline{K}\}^r} \tag{5.6}$$

The species activity was not measured, but for practical purposes, the activity of the species was assumed to be proportional to the concentration of the species. The constants of proportionality are then incorporated into a new equilibrium constant, $\beta_{pqr,apparent}$. This new equilibrium constant is defined in Equation 5.7, with the square brackets indicating the molar concentration of each species.

$$\beta_{pqr,apparent} = \frac{\overline{[A_pW_qK_r]}}{[A]^p[\overline{W}]^q[\overline{K}]^r} \tag{5.7}$$

From the liquid - liquid equilibria data, it was found that an acid co-extracted approximately four water molecules into cyclohexanone and approximately three water molecules into methylcyclohexanone. Therefore, the molecules of water per complex, *q*, will have a value of 4 or 3, depending upon the solvent. The acid distribution showed no evidence for dimerization of the acid in the organic phase (Chapter 4). Thus, the molecules of acid in the complex, *p*, will always be 1. The molecules of solvent per complex, *r*, was varied to see which one complex gave the best fit to the experimental data.

Another assumption in the model presented is that every acid in the organic phase is complexed. This is supported by the fact that the presence of the second aqueous phase in the liquid - liquid equilibria provides a large driving force for the hydration of the acid in the organic phase. Also, the ratio of water molecules to acid molecules in the organic phase is large due to the low solubility of carboxylic acids and the relatively high natural solubility of water in the solvents.

The total concentration of water in the organic phase is the sum of the monomeric water and the complexed water, as written in Equation 5.8. Similar species balances for the ketone solvent and acid are written in Equations 5.9-10, respectively.

$$C_{\text{water, total, org}} = [\overline{W}] + q\overline{[A_pW_qK_r]} \tag{5.8}$$

$$C_{\text{ketone,total,org}} = [\overline{K}] + r\overline{[A_pW_qK_r]} \tag{5.9}$$

$$C_{\text{acid,total,org}} = p\overline{[A_pW_qK_r]} \tag{5.10}$$

In this model, the total concentration of water in the organic phase, a measured quantity, was predicted from the model with the value of the complexation constant, β_{pqr}, and the moles of solvent per complex varied such that the error between the experimental and predicted water concentration is minimized. The predicted total water concentration was calculated in the following manner. The values of the molecules of solvent per complex and the complexation constant were chosen. Equation 5.7 was solved for the complex concentration and substituted into Equations 5.9 and 5.10. The concentrations of the water monomer, [W], and solvent monomer, [K], were calculated from these two equations. The predicted water concentration was calculated using Equation 5.8. The error, E, was calculated as shown in Equation 5.11, with the sum being over all data points for a acid - solvent system.

$$E = \Sigma \left| \log \frac{\overline{C}_{\text{water, predicted}}}{\overline{C}_{\text{water, experiment}}} \right| \tag{5.11}$$

This form of the error assumes that the relative error of the data is constant over the concentrations of acid and water measured. The value of the equilibrium constant is varied such that the error is minimized for a given complex. Then a different complex is proposed, and the whole process is repeated. The standard deviation of the model, σ, is defined in Equation 5.12, where n is the number of data points.

$$\sigma = \frac{E}{\sqrt{n - 1}} \tag{5.12}$$

Table 5.5 reports the complexation constant, the value of the complexation constant associated with the minimum error, and the standard deviation for all twelve systems. Figures 5.2 and 5.3 show the experimental data and the predicted water concentration curve for the fumaric acid - cyclohexanone system at two temperatures. The values of the standard deviation for these system are low, and there is a good fit between the predicted and experimental water concentrations. Nine of the twelve systems studied have values of the standard deviation less than 0.03, and the predicted curve will fit about as well as shown in Figure 5.3.

Figures 5.4 and 5.5 show the experimental data and predicted water concentrations for the succinic acid - cyclohexanone and succinic - methylcyclohexanone systems at 45°C. These two systems show the highest value of the standard deviation for a given solvent. Figure 5.4 shows that the fit of the model is good except for the data point at the highest acid concentration. Model fits to the data excluding the data point at the high acid concentration fit the well with a standard deviation in the range of the rest of the data. Figure 5.5 shows that there is no systematic deviation of the predicted curve from the experimental data, and the model fits fairly well considering the scatter in the data.

The number of ketone molecules in the complex was varied in the model in order to find the minimum error. In general, all the chosen values of the number of ketone molecules per complex fit the experimental data well at intermediate acid concentrations. The ability of a model to fit the experimental data at the lowest and highest acid concentrations was the determining factor as to which postulated complex gave the lowest error.

Table 5.5 Best-fit complexation constants, their values, and the standard deviation associated with the fit for fumaric acid, succinic acid, and adipic acid in cyclohexanone or methylcyclohexanone at 25°C or 45°C.

Fumaric Acid Cyclohexanone 25°C $\beta_{144} = 0.0000212$ $\sigma = 0.012$	Fumaric Acid Methylcyclohexanone 25°C $\beta_{132} = 0.0184$ $\sigma = 0.021$
Fumaric Acid Cyclohexanone 45°C $\beta_{140} = 0.0434$ $\sigma = 0.025$	Fumaric Acid Methylcyclohexanone 45°C $\beta_{131} = 0.0716$ $\sigma = 0.016$
Succinic Acid Cyclohexanone 25°C $\beta_{143} = 0.0000267$ $\sigma = 0.048$	Succinic Acid Methylcyclohexanone 25°C $\beta_{130} = 0.833$ $\sigma = 0.015$
Succinic Acid Cyclohexanone 45°C $\beta_{142} = 0.0000866$ $\sigma = 0.072$	Succinic Acid Methylcyclohexanone 45°C $\beta_{130} = 0.388$ $\sigma = 0.033$
Adipic Acid Cyclohexanone 25°C $\beta_{142} = 0.000682$ $\sigma = 0.022$	Adipic Acid Methylcyclohexanone 25°C $\beta_{130} = 0.0186$ $\sigma = 0.030$
Adipic Acid Cyclohexanone 45°C $\beta_{142} = 0.000524$ $\sigma = 0.024$	Adipic Acid Methylcyclohexanone 45°C $\beta_{130} = 0.0457$ $\sigma = 0.028$

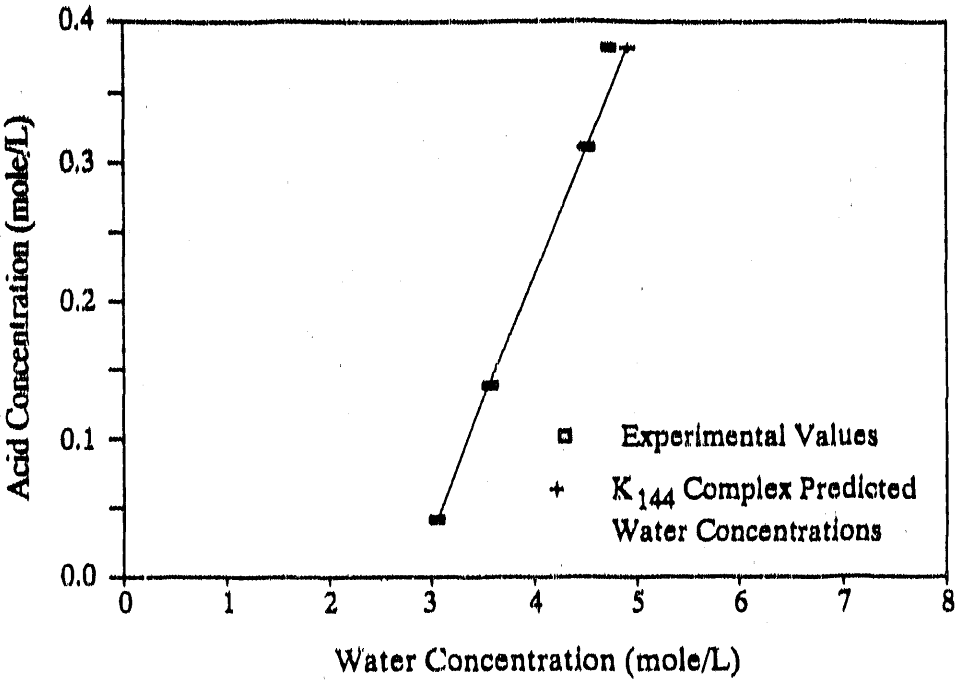

Figure 5.2 Fumaric acid - cyclohexanone liquid - liquid equilibrium at 25C with predicted water concentration from complexation model.

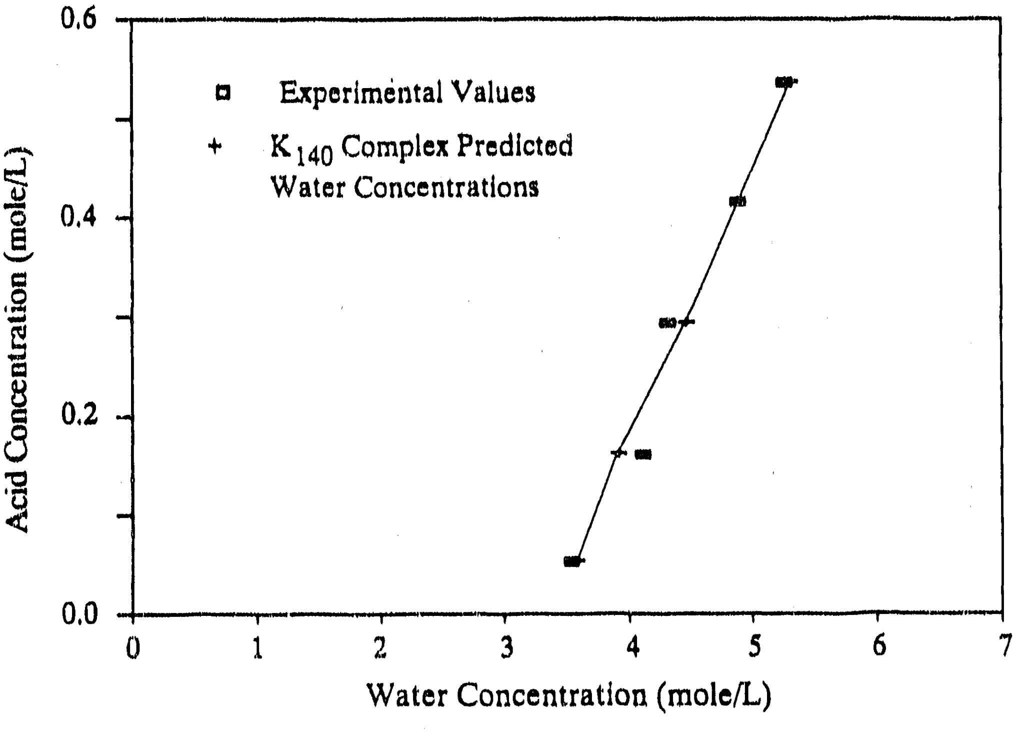

Figure 5.3 Fumaric acid - cyclohexanone liquid - liquid equilibrium at 45C with predicted water concentration from complexation model.

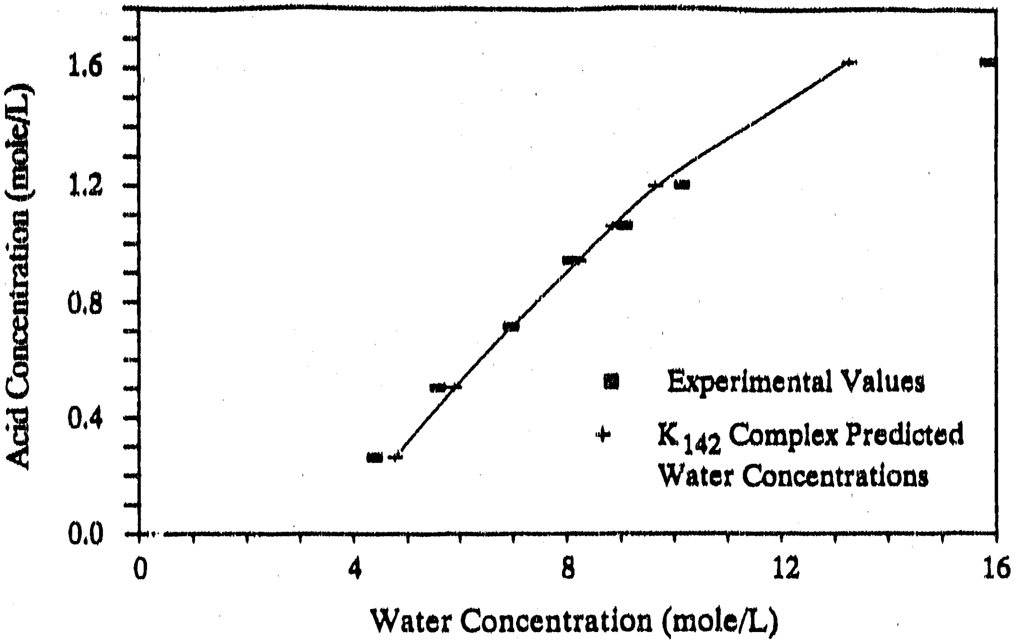

Figure 5.4 Succinic acid - cyclohexanone liquid - liquid equilibrium at 45C with predicted water concentration from complexation model.

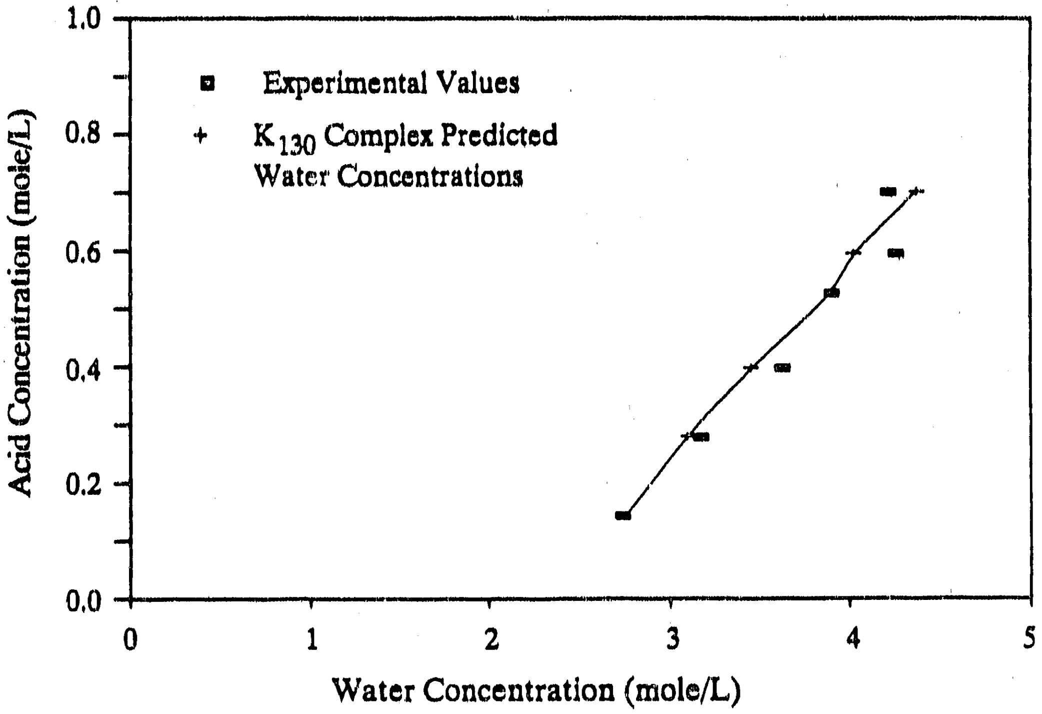

Figure 5.5 Succinic acid - methylcyclohexanone liquid - liquid equilibrium at 45C with predicted water concentration from complexation model.

The number of solvent molecules in the complex varies from zero to four depending upon the system. For a given acid at a given temperature, the number of solvent molecules in the complex is generally greater for cyclohexanone than for methylcyclohexanone. The number of solvent molecules per complex at 45°C is less than or equal to those at 25°C. For both cyclohexanone and methylcyclohexanone, the complex with the greatest number of solvent molecules is the fumaric acid - solvent system at 25°C.

The number of solvent molecules per acid complex is in general agreement with the explanations for the trends in the enthalpy and entropy of acid transfer data reported in Chapter 4. The higher enthalpy of acid transfer in cyclohexanone than that in methylcyclohexanone could be related to the results of the complexation model showing that an acid in cyclohexanone interacts with more water and solvent molecules than in methylcyclohexanone. Fumaric acid exhibits the greatest enthalpy of acid transfer among the three acids which could be related to fumaric acid showing the greatest number of solvent molecules in the complexation.

The idea that the large increase in the solubility of the acid is due to strong hydrogen bonding between a hydrated acid and the ketone can possibly explain some of the solubility data reported in Chapter 2. Table 2.2 reported the solubilities of fumaric acid in a number of anhydrous and hydrated organic solvents. In general, Lewis-base solvents showed an increase in fumaric acid solubility with an increased water concentration in the organic phase. However, tributyl phosphate and trioctyl phosphine oxide actually showed a decrease in fumaric acid solubility when the water concentration in the organic phase increased. Also, it was found that the presence of a tertiary amine did not significantly enhance the effect of the increased acid solubility with increasing water content. A possible explanation of this behavior is that the strongly basic phosphoryl and amine functional groups break up this hydrated acid structure. Of course, tritolyl phosphate does show an increase in acid solubility with an increased water content. This may be due to the steric hinderance of the phosphoryl group by the large phenyl groups attached to the phosphate atom.

5.4 Summary and Conclusions

Experimental results give evidence for the formation of hydrogen bonds among all three components of the ketone - carboxylic acid - water systems. Past research on these and related systems using molecular probes, such as IR spectroscopy and NMR, provides evidence for strong hydrogen bonding as well. The NRTL equation and the three-suffix Margules equation could not adequately describe the behavior of the three component systems. A model based on acid:water:ketone complexation described the liquid - liquid equilibria well. The number of ketone molecules in the complex can rationalize the differences in the values of the enthalpy of acid transfer.

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CHAPTER 6. BATCH PRECIPITATION EXPERIMENTS

Results of batch precipitation experiments with fumaric acid, succinic acid, and adipic acid in cyclohexanone and methylcyclohexanone are presented in this chapter. These experiments confirmed directly that removing the water from the extract causes the precipitation of the acid. Also, an average separation factor between water and the solvent was calculated to give information on the vapor - liquid equilibrium of the solutions. The concentrations of acid and water in the final solutions from the precipitation experiments were measured and are compared to the solid - liquid equilibria reported in Chapter 3.

6.1 Introduction

In order to precipitate the dicarboxylic acid from the extract, water must be removed. There are a number of methods to accomplish this goal including evaporation of the water, permeation through water-selective membranes, and adsorption on to molecular sieve. Since most crystallizers work on the principle of increasing the solute concentration by evaporating the solvent, vaporizing the ketone - water - acid mixture was explored in this work. The other two methods have a possible disadvantage in that a second solid phase is introduced in order to provide the separation. The solid acid crystals may adhere to the membrane or molecular sieve causing reduced flux or poor hydrodynamics.

Experiments to simulate a batch crystallizer were performed. A single phase mixture of the ketone solvent, dicarboxylic acid, and water was placed into a flask under vacuum, and the solution was evaporated at low temperature (45°C). A nearly anhydrous mixture of ketone, solvent, and acid was evaporated as well. The weight percent of the solution evaporated and the percent recovery of the acid were the measured variables. Experimental details can be found in Appendix B.

The purpose of these experiments was to determine the liquid - vapor equilibrium, as measured by an average separation factor, α, between water and the ketone solvent. The separation factor was calculated from Equation 6.1, which is taken from King (1). This equation describes batch distillation, where an initial solution of L_o moles and composition of $x_{i,o}$ and $x_{j,o}$ has a product stream removed continuously until L moles of the original solution remain with a composition x_i and x_j. The mole fractions are calculated on a acid-free basis.

$$\ln \frac{L}{L_o} = \frac{1}{\alpha_{ij} - 1} \ln \frac{x_i \; x_{j,o}}{x_{i,o} \; x_j} + \ln \frac{x_{j,o}}{x_j} \qquad (6.1)$$

The vapor - liquid equilibria determine the amount of solvent that is evaporated along with the water. From this information, the energy requirements for evaporating the water and solvent can be calculated. The energy costs are an important factor in the operating costs of the extraction process.

The precipitation of an acid from a solution occurs when the concentration of the acid exceeds the saturation concentration. The difference between the acid concentration of the supersaturated solution and the equilibrium acid concentration is the driving force for precipitation. Solutions in which precipitation is occurring are, by definition, not at equilibrium.

It was not the purpose of these experiments to determine how operating variables of the crystallization process affect the particle size distribution or growth rate. Kibler (2) patented a fumaric acid crystallization process that gives a relatively low content of fine crystals. Mullin and Whiting (3) and Qui and Rasmuson (4) have studied the effects of operating parameters on the growth of succinic acid crystals in aqueous solution. David, et al. (5), have proposed a kinetic model for the crystallization of adipic acid.

Most of the work that has been done on the crystallization of these three acids has been for crystallization from an aqueous phase. Davey, Mullin, and Whiting (6) examined succinic acid crystals grown from water and isopropanol. Succinic acid crystals formed from aqueous solution are plates, while the crystals from isopropanol are needle-like. Their study shows that the solvent can have an important effect upon the growth rate of the crystal, and the particular crystal faces on which that growth occurs. Crystallizing dicarboxylic acids from a ketone - water mixture may produce growth rates significantly different from those found in an aqueous solution. This phenomenon was not studied in this work.

All three acids form monoclinic crystals (7). In the crystal structure, all three acids form hydrogen bonds between the carboxylic acid functional groups (8,9,10), as shown in Figure 6.1. The average distance between oxygen atoms in the hydrogen bond is 2.65Å. The crystals are stabilized by the hydrogen bonding between atoms.

6.2 Experimental Results

6.2.1 Evaporation of Solvents and Water

Experiments were performed with both solvents in which a binary mixture of the solvent and water was vaporized. These experiments give a base case with which to compare the results of the experiments when the acid is present. Table 6.1 gives the results of the batch vaporization experiments for a cyclohexanone - water mixture and a methylcyclohexanone - water mixture. The value of the separation factor between water and the solvent is much higher for methylcyclohexanone than for cyclohexanone.

Table 6.2 displays the separation factor between cyclohexanone and water as calculated from vapor - liquid equilibrium data reported by Gmehling, et al. (11). The separation factor decreases as the mole fraction of water in the solution increases. The average value of the separation factor determined in this work seems to be in general agreement with the literature values considering the trend in the separation factor with water content and that the mole fraction of water decreased from 0.225 to 0.172 during the

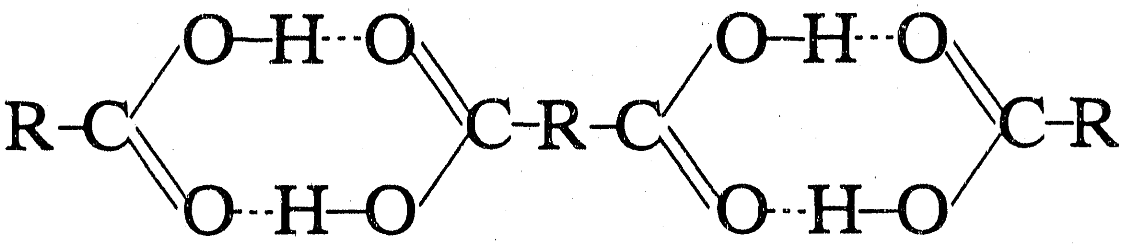

Figure 6.1 Arrangement of carboxylate functional groups in crystal structure of fumaric acid, succinic acid, and adipic acid.

Table 6.1 Results from cyclohexanone - water and methylcyclohexanone - water evaporation process.

	Cyclohexanone	Methylcyclohexanone
Initial Water Mole Fraction	0.225	0.192
Final Water Mole Fraction	0.172	0.082
Weight Percent Evaporated	3.35%	3.67%
Temperature (°C)	45	45
Average Separation Factor	18.6	69.9

Table 6.2 Separation factors between water and cyclohexanone at 50°C at varying water concentrations. Data reported by Gmehling, et al. (11).

Mole Fraction of Water	Separation Factor
0.076	34.8
0.140	27.4
0.192	23.5

evaporation step.

6.2.2 Cyclic Ketone - Dicarboxylic Acid - Water Batch Precipitation

Table 6.3 reports the measured and calculated parameters of the batch precipitation experiments for adipic acid, succinic acid, and fumaric acid in cyclohexanone. Table 6.4 reports these same parameters for succinic acid and fumaric acid in methylcyclohexanone.

For both cyclohexanone and methylcyclohexanone, two precipitation experiments were performed with fumaric acid. The second experiment was performed to determine how much the calculated separation factor varied with the amount of solution evaporated. Note that the mole fraction of water on an acid-free basis is quite large for a few of the initial solutions, however, these mole fractions convert to less than 23 weight percent water.

The acid recoveries achievable by removing a large portion of the water are remarkable. For the fumaric acid - cyclohexanone system, 87.8% of the acid was recovered by evaporating only 31 wt% of the solution. The adipic acid - cyclohexanone system exhibits similar results with a 79% acid recovery with only 30% of the solution evaporated. Methylcyclohexanone displays even better results with 78% of fumaric acid recovered with the removal of 15 wt% of the original solution. The batch precipitation results demonstrate the advantage of this process -- high acid recoveries by the removal of a minor component in the extract.

For both the cyclohexanone and methylcyclohexanone precipitation experiments, the calculated values of separation factor were smaller than that calculated from the solvent - water binary evaporation experiment. This is not surprising considering that the presence of the acid in the organic phase should lower the activity coefficient of the water. The lowering of the water activity coefficient with increasing acid content is displayed in the liquid - liquid equilibria data (Chapter 4). The water concentration in the organic phase increased with an increase in the acid concentration. The product of the mole fraction and activity coefficient

Table 6.3 Measured and calculated values from the dicarboxylic acid - cyclohexanone - water precipitation experiments.

	Adipic Acid	Succinic Acid	Fumaric Acid	Fumaric Acid
Initial Water Mole Fraction	0.530	0.615	0.363	0.363
Initial Acid Concentration (mole/L)	1.12	1.32	0.485	0.485
Weight Percent Evaporated	29.9	24.9	30.7	13.3
Final Water Mole Fraction	0.067	0.414	0.078	0.179
Final Acid Concentration (mole/L)	0.420	1.26	0.11	0.378
Acid Recovery	79.3	37.6	87.8	37.4%
Acid Mass Balance Error	-1.6%	-5.3%	-2.7%	-3.4%
Temperature (°C)	45	45	45	45
Average Separation Factor	11.0	4.6	7.1	11.2

Table 6.4 Measured and calculated values from the dicarboxylic acid - methylcyclohexanone - water precipitation experiments.

	Succinic Acid	Fumaric Acid	Fumaric Acid
Initial Water Mole Fraction	0.365	0.270	0.270
Initial Acid Concentration (mole/L)	0.783	0.356	0.356
Weight Percent Evaporated	7.77	14.8	5.92
Final Water Mole Fraction	0.213	0.003	0.129
Final Acid Concentration (mole/L)	0.545	0.103	0.238
Acid Recovery	45.2	78.4	42.0
Acid Mass Balance Error	-7.2%	-2.4%	+4.3%
Temperature (°C)	45	45	45
Average Separation Factor	15.2	(44)	29.7

equals the activity. If the mole fraction of water increases, the activity coefficient must decrease if the activity stays constant. Assuming the activity of the water is constant does not cause significant error considering that the organic phase is in equilibrium with an aqueous phase. The reduced activity coefficient of water causes a decrease in the vapor pressure of water which leads to a smaller value of the separation factor.

The presence of succinic acid in the cyclohexanone or methylcyclohexanone caused the value of the separation factor to decrease by the greatest amount. For cyclohexanone, the value of the separation factor decreased the smallest amount for systems with adipic acid present. This is based on comparing the single adipic acid - cyclohexanone system with the fumaric acid - cyclohexanone systems that had approximately the same amount of mass going overhead (30%).

For the fumaric acid - cyclohexanone system, two precipitation experiments were performed with the same initial solution. Different amounts of solvent and water were evaporated. The values of the separation factor determined from these two experiments show that the separation factor decreased as the amount of material evaporated increased.

Similar trends are seen when the experiments with methylcyclohexanone, water, and acid are compared with the methylcyclohexanone - water system with no acid. The value of the separation factor decreased more for the succinic acid - methylcyclohexanone system than for the fumaric acid - methylcyclohexanone systems.

Two precipitation experiments were performed on the fumaric acid - methylcyclohexanone - water system. The value of the separation factor was greater for the system which had the greater amount of material evaporated, in contrast to the fumaric acid - cyclohexanone system. However, the value of the separation factor for the experiment in which 14.8 weight percent was evaporated has a large margin of error. The value of the separation factor depends greatly on the final mole fraction of water in the methylcyclohexanone. The first experiment listed shows that the mole fraction of water in the final solution was reduced to 0.003. This value is an estimate since the amount of water in the methylcyclohexanone was below the detection limit of the thermal conductivity detector used for the water analysis. This estimate was made determining that the water "peak" from the final precipitation solution was considerably smaller than the water peak from a mixture of water and methylcyclohexanone with a water mole fraction of 0.006.

A batch precipitation experiment was not performed for the adipic acid - methylcyclohexanone system because cyclohexanone should be the solvent of choice for an extraction process recovering adipic acid. This is because cyclohexanone is one of the intermediates in the manufacture of adipic acid, and the mother liquor from the solid - liquid separator is easily recycled back into the manufacturing process.

6.3 Precipitation and Solid - Liquid Equilibria

If the solution being evaporated is at equilibrium with the solid acid phase, the concentrations of water and carboxylic acid in the final solution should be characterized by the solid - liquid equilibria reported in Chapter 3. However, the final carboxylic acid concentration may be greater than the equilibrium concentration for the determined water concentration, by the amount of the driving force needed for the precipitation. Figures 6.2-6 show the solid - liquid equilibria (Chapter 3), liquid - liquid equilibria (Chapter 4), and the concentrations of water and acid measured in the final precipitation solution.

The compositions of the final precipitation solutions agree well with the solid - liquid equilibria as shown in Figures 6.2-6. In Figure 6.2, the concentration of fumaric acid in cyclohexanone is near the equilibrium concentration for one of the precipitation experiments, but for the experiment that showed a greater amount of material evaporated the final fumaric acid concentration appears to be somewhat below the equilibrium concentration. The rest of the compositions of the final precipitation solutions are very near or slightly above the solid - liquid - equilibrium line. It is not known why the fumaric acid - cyclohexanone system falls

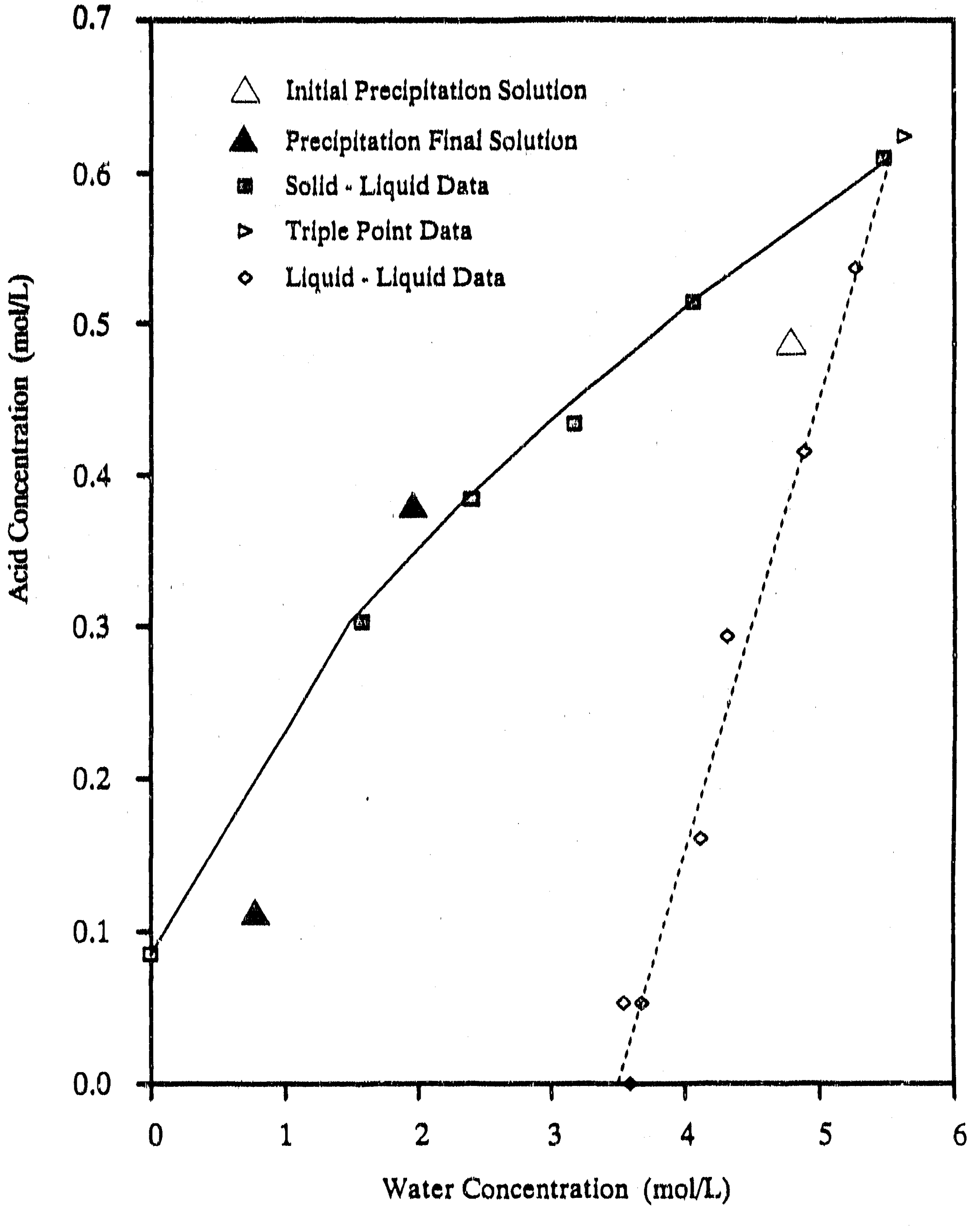

Figure 6.2 Fumaric acid - cyclohexanone - water liquid - liquid and solid - liquid equilibria at 45 C with points marking acid amd water concentrations of solutions from precipitation experiments.

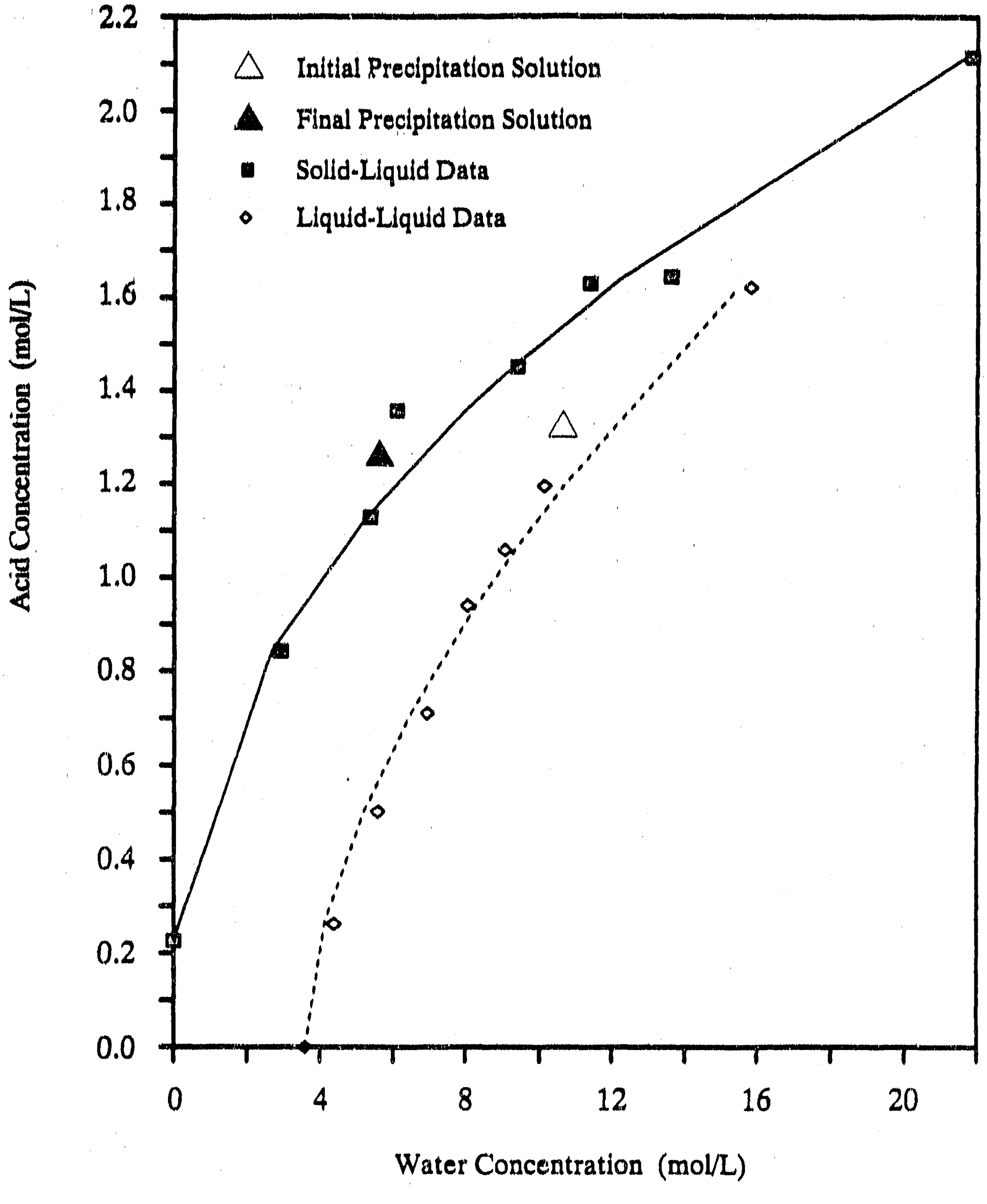

Figure 6.3 Succinic acid - cyclohexanone - water liquid - liquid and solid - liquid equilibria at 45 C with points marking acid and water concentrations of solutions from precipitation experiments.

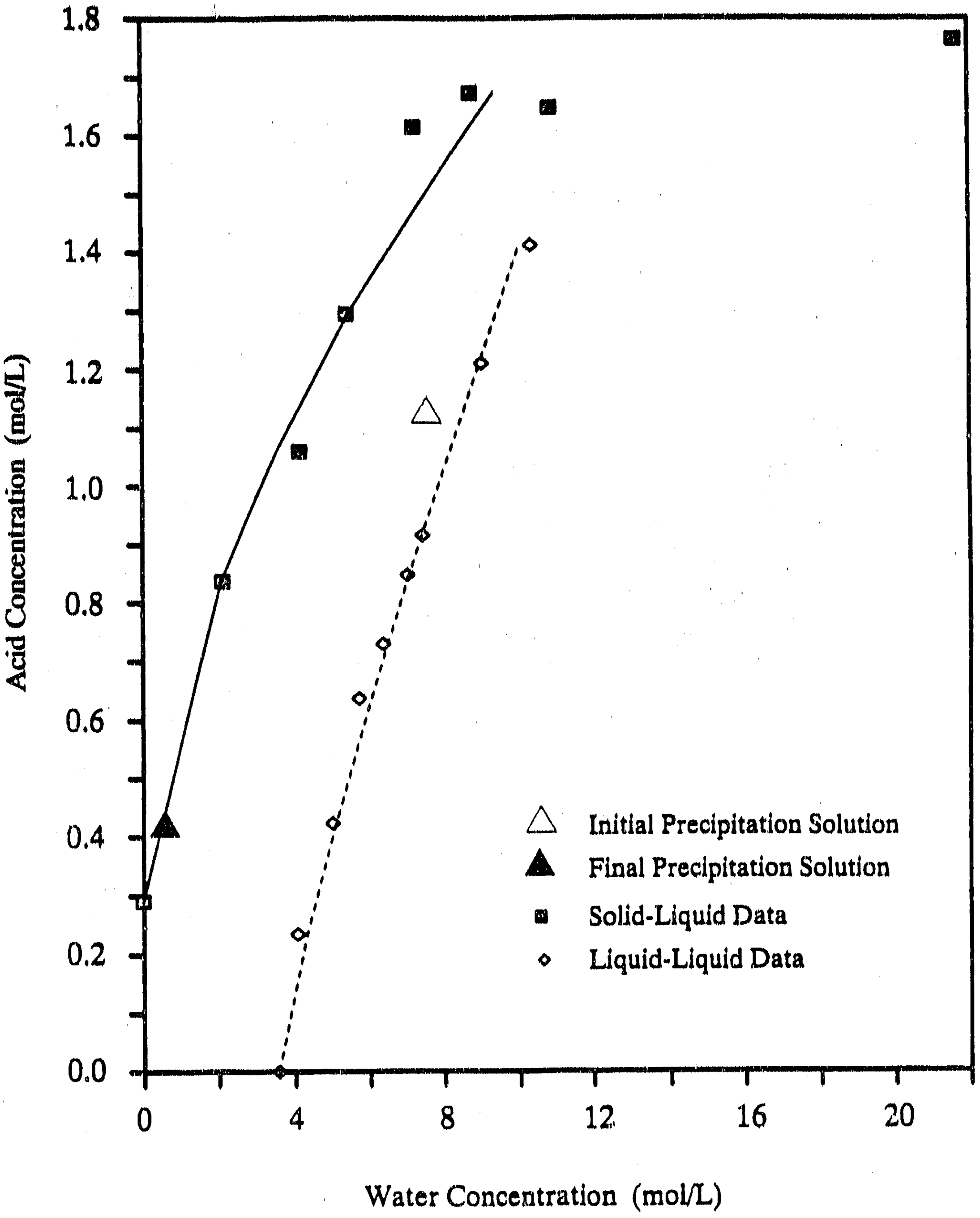

Figure 6.4 Adipic acid - cyclohexanone - water liquid - liquid and solid - liquid equilibria at 45 C with points marking acid and water concentrations of solutions from precipitation experiments.

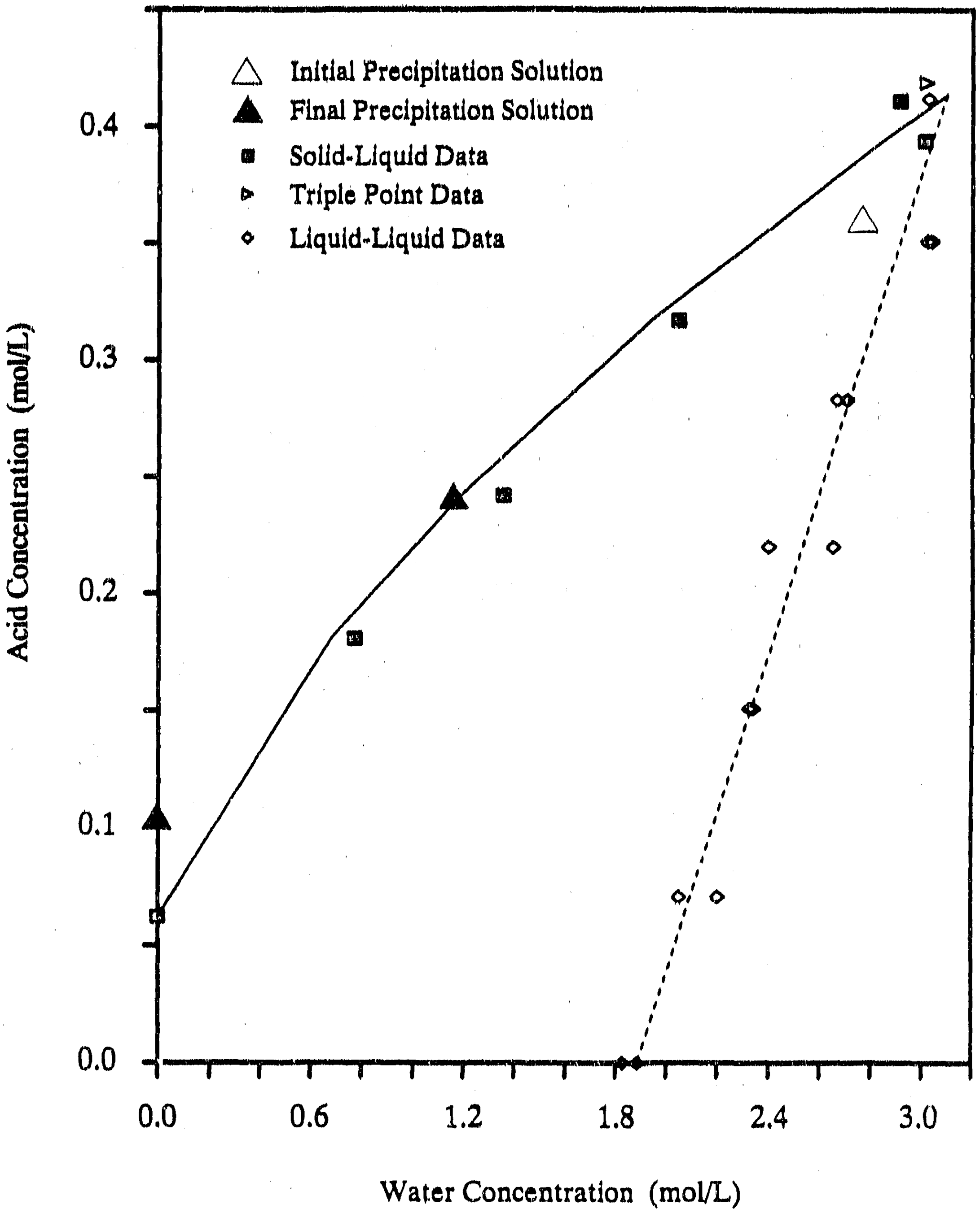

Figure 6.5 Fumaric acid - methylcyclohexanone - water liquid - liquid and solid - liquid equilibria at 45 C with points marking acid and water concentrations of solutions from precipitation experiments.

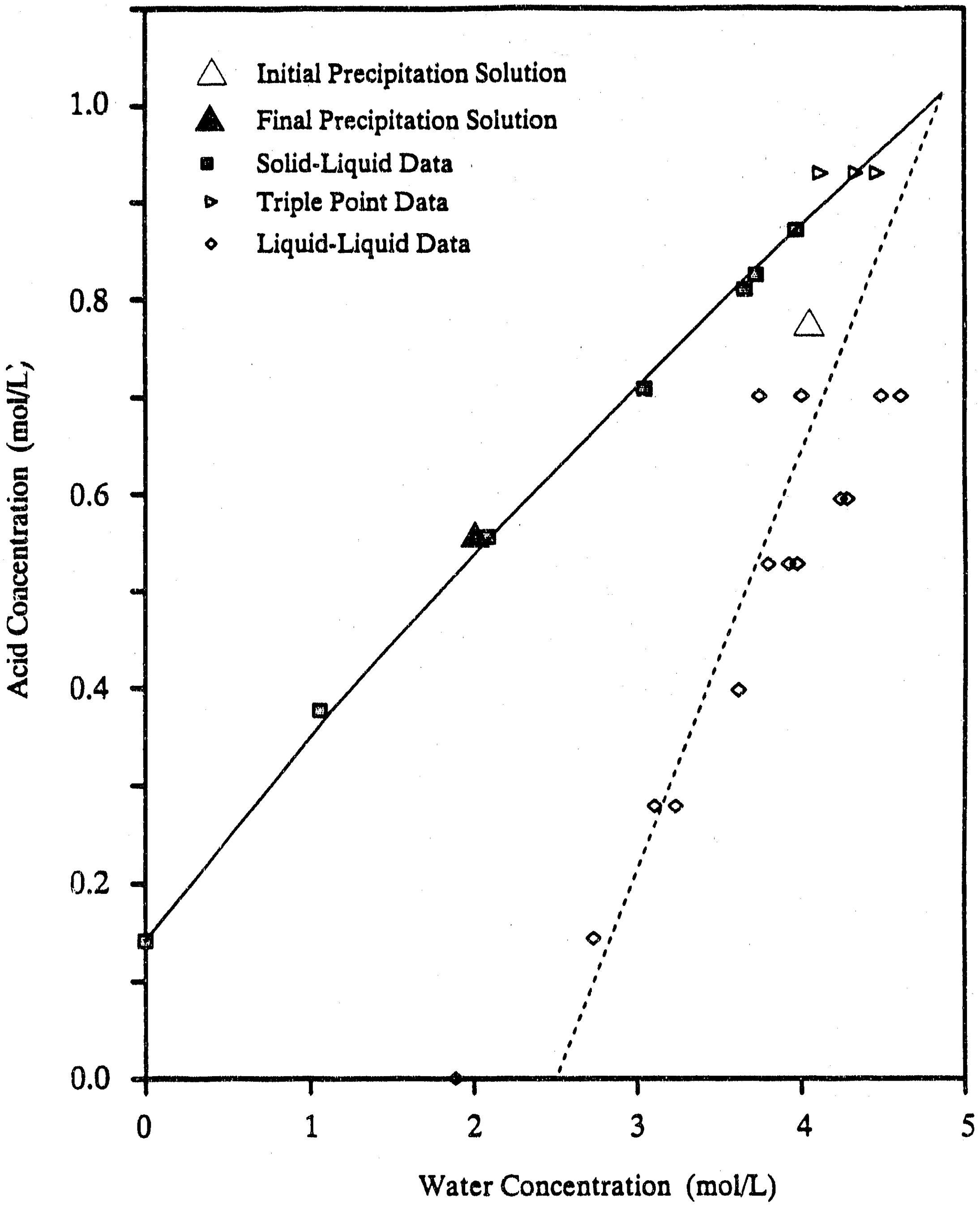

Figure 6.6 Succinic acid - methylcyclohexanone - water liquid - liquid and solid - liquid equilibria at 45 C with points marking acid and water concentrations of solutions from precipitation experiments.

below the solid -liquid equilibrium line.

The acid and water concentrations of the solutions initially placed in the evaporation process are also shown in Figures 6.2-6. The initial solutions were in contact with an aqueous phase prior to the evaporation process, and should be characterized by the liquid -liquid equilibria discussed in Chapter 4. However, all initial solutions exhibited water concentrations that were slightly lower than the equilibrium water concentration.

6.4 Hydrated and Anhydrous Solutions

Nearly anhydrous and fully hydrated mixtures of fumaric acid and methylisobutylketone (MIBK) were evaporated under reduced pressure. MIBK was used in these experiments because cyclic ketones had not been identified as solvents that would emphasize the effect of increasing acid solubility with increasing water concentration. MIBK has a greater vapor pressure than cyclohexanone or methylcyclohexanone, and therefore, the separation factor between water and MIBK is smaller than for the cyclic ketones.

For the nearly anhydrous solution, it was expected that the amount of acid precipitated would be proportional to the amount of solvent removed once the acid had reached its solubility limit. For the hydrated solution, it was expected that the mixture would follow the solid - liquid equilibrium which is a function of both the water and acid concentrations in the MIBK. This equilibrium was not measured in this work.

Table 6.5 reports the experimental results for the hydrated and anhydrous MIBK precipitation experiments with fumaric acid. The initial acid concentration in the hydrated MIBK was much larger than that in the nearly anhydrous MIBK. This reflects the effect of increased acid solubility with increasing water concentration in ketone solvents. However, the percent saturation, the initial acid concentration divided by the acid concentration at saturation, is approximately the same for both the nearly anhydrous and hydrated samples. The final acid concentrations in the hydrated systems decreased significantly upon

Table 6.5 Measured and calculated values from the nearly anhydrous and hydrated methylisobutylketone - fumaric acid precipitation experiments.

	Anhydrous	Hydrated	Hydrated
Initial Acid Concentration (moles/liter)	0.0158	0.0874	0.0874
Initial Acid Saturation	98 %	96 %	96 %
Initial Water Concentration	0.06 wt%	2.1 wt%	2.1 wt%
Weight Percent Evaporated	18.1	14.2	26.6
Final Acid Concentration (moles/liter)	0.0181	0.0576	0.0482
Final Water Concentration	0.30 wt%	0.95 wt%	0.76 wt%
Percent Acid Recovery	1.6 %	39.1 %	46.8 %
Acid Mass Balance Error	4.5	4.7	13.1
Average Separation Factor	---	6.7	4.5

evaporation, while the acid concentration in the nearly anhydrous system increased. This may be due to the water concentration in the nearly anhydrous systems increasing and raising the solubility of the acid. It is not understood why the water concentration in the nearly anhydrous sample increased after the evaporation step.

The difference in the acid recovery between the hydrated MIBK - fumaric acid system and the anhydrous MIBK - fumaric acid system confirms that the removal of the water is the dominating factor in the precipitation of the acid. Also, as seen in the fumaric acid - cyclohexanone system, the apparent separation factor decreased with an increase in the total amount of mass evaporated.

6.5 Summary and Conclusions

Batch precipitation experiments displayed that high acid recoveries could be achieved by stripping the water. The separation factors between water and the solvent were lower than those for the binary water - solvent systems, but still high enough to be of practical use. The separation factors for the methylcyclohexanone - carboxylic acid - water systems were much greater than for the cyclohexanone - carboxylic acid - water systems. The presence of succinic acid in the solution depressed the value of the separation factor more than the presence of the other two acids. The initial and final solutions of the precipitation experiments are well described by the liquid - liquid and solid - liquid equilibria reported in Chapters 3 and 4.

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CHAPTER 7. REGENERATION PROCESS DESIGN CONSIDERATIONS

The energy requirements and other process design considerations are discussed for a regeneration process which precipitates the acid by removal of the co-extracted water. A flowsheet of such process is shown in Figure 1.4. The performance of the regeneration process proposed in this work is compared to a base case in which all the water and solvent are evaporated. The phase compositions of the process streams were calculated from the solid - liquid and liquid - liquid equilibria measured in this work. Flash vaporization calculations were used to describe the evaporation of the water and solvent. The energy required per acid recovered from the extract reaches a minimum value at an intermediate value of the percent water evaporated. A two stage process reduces the amount of energy required per acid recovered over that for a single stage process.

7.1 Introduction

In this process, the water is removed until the acid concentration in the organic phase exceeds the equilibrium acid concentration. At this point, the acid precipitates, and as the water concentration is lowered further, more acid is precipitated. Figure 7.1 shows the important liquid phase compositions of the precipitation process on a solid - liquid and liquid - liquid equilibrium diagram similar to those reported in Chapter 4.

The fumaric acid - methylcyclohexanone and adipic acid - cyclohexanone systems were chosen to be studied in the process design portion of this work. The adipic acid - cyclohexanone system was chosen because of the industrial importance of adipic acid manufacture, and the fact that cyclohexanone is an intermediate in the manufacture of adipic acid. The fumaric acid - methylcyclohexanone system was chosen to contrast with the high acid and water concentrations found in the adipic acid - cyclohexanone system.

The two systems studied exhibit a wide range of thermodynamic behavior. The

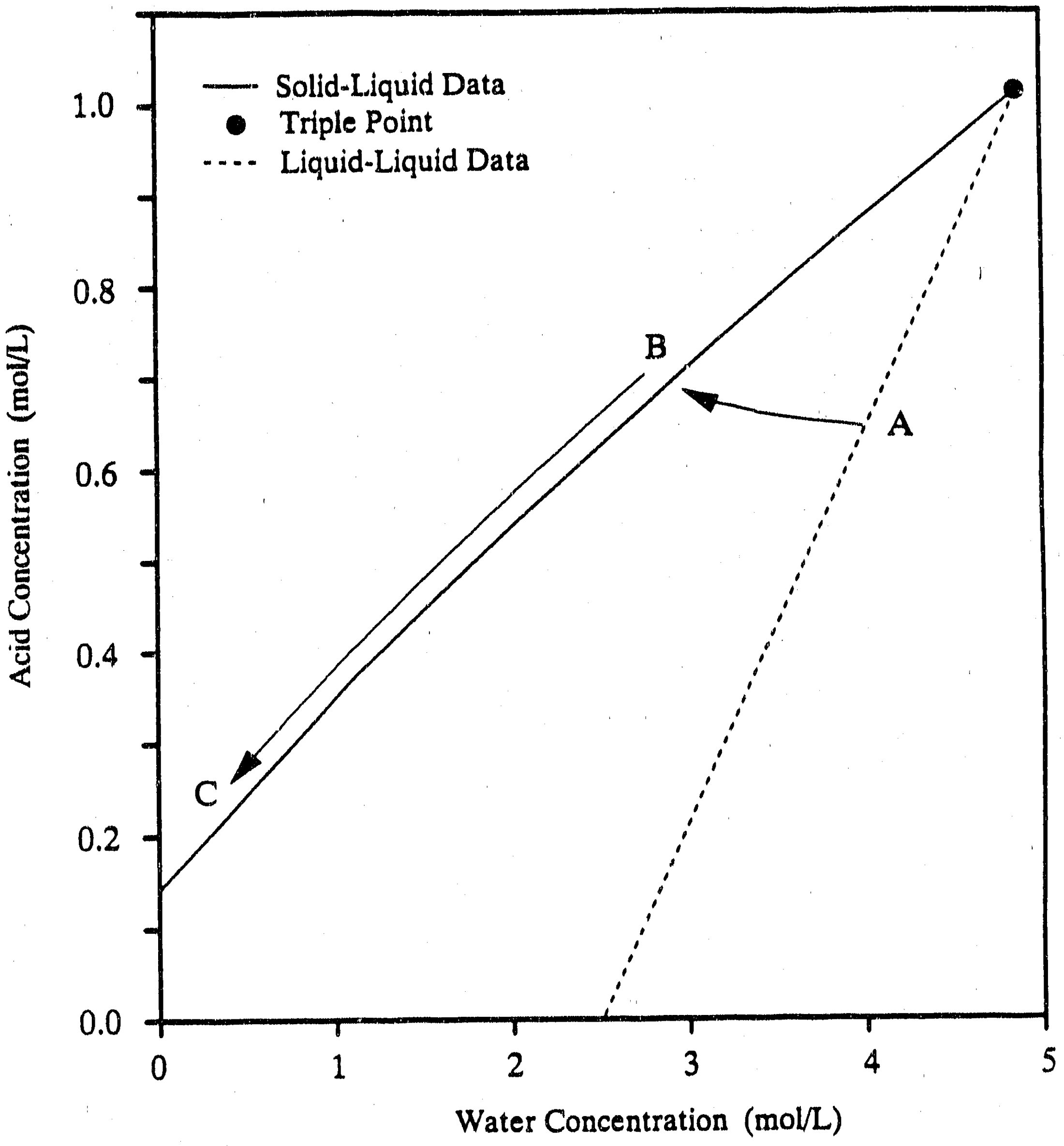

Figure 7.1 Solid - liquid and liquid - liquid equilibrium showing the organic phase compositions as water is removed.

A -- Composition of extract entering precipitator
B -- Composition at which precipitation thermodymamically possible
C -- Composition of liquid exiting precipitator

solubility of adipic acid in hydrated cyclohexanone is three times greater than the solubility of fumaric acid in hydrated methylcyclohexanone. There is three times the amount of water in the adipic acid - cyclohexanone system than in the fumaric acid - methylcyclohexanone system. The separation factor for the fumaric acid - methylcyclohexanone system is about four times larger than that for the adipic acid - cyclohexanone system.

7.2 Process Configurations Studied

A single stage crystallizer in which all the water and solvent is evaporated and the acid precipitates was one of the two processing schemes studied. The other was a two-stage system in which the water and solvent are evaporated in the first stage, but the amount of liquid evaporated is not great enough for the acid to reach its solubility limit. In the second stage, more water and solvent are evaporated and the acid is precipitated.

7.3 Design Basis and Calculations

The design was based on a 1 liter/minute flow of the extract to the evaporation/precipitation process. This is a low flowrate, but the results and conclusions from the calculations are independent of the exact flowrate. The temperature of the extraction was 25°C for the fumaric acid - methylcyclohexanone system and 45°C for the adipic acid - cyclohexanone system. The temperature of the precipitation step was 45°C for both systems.

A number of simplifying assumptions were made for calculating the mass balances and energy requirements and are listed below.

1. Infinite stages in extraction column -- this allows the exiting streams to be in equilibrium with the entering streams.
2. No solvent losses in the raffinate.
3. All the acid is in an undissociated form.
4. Constant separation factor (relative volatility) between water and solvent.

5. The acid is nonvolatile.

6. Liquid solution exiting precipitator is in equilibrium with solid acid.

An initial acid concentration in the aqueous phase was chosen. The acid concentration in the organic phase in equilibrium with the aqueous phase was calculated using Equation 4.5 with parameter values from Table 4.2. The water concentration in the organic phase was calculated from Equation 4.6 or 4.7 with parameter values from Table 4.3 or 4.4. Knowing the density of each stream, the molar flows of each component were calculated.

A flash vaporization calculation was used to describe the evaporation of water and solvent. King (1) discusses algebraic methods for solving flash vaporization processes depending upon which operating parameters of the system are specified. When the temperature and split for a single component are chosen, the relevant equation for determining the mass balance is Equation 7.1 with f_i and v_i being the moles of component i in the feed and vapor, respectively.

$$\frac{f_j}{v_j} = \alpha_{ij}\left(\frac{f_i}{v_i} - 1\right) + 1 \tag{7.1}$$

The moles and mass of water and solvent are then calculated for the liquid and vapor phases. The energy required for vaporization was calculated from the product of the enthalpy of vaporization and the mass of vapor produced for both components. Knowing the density and the mass of the liquid leaving the precipitator, the volume of solution is determined, and the water concentration in moles/liter can be determined. Using the inverse of Equation 3.2 and parameter values in Table 3.2, the equilibrium concentration of the acid in the liquid is calculated. The amount of acid precipitated is the difference between the moles fed to the precipitator and the moles of acid in the liquid leaving the precipitator. The addition of the acid to the liquid has given the liquid exiting the precipitator a greater mass than had been estimated from the solvent and water alone. Therefore, a new volume of liquid is calculated and the calculations are iterated until the mass balance on the acid is satisfied to 0.01 percent.

For the two stage process, the calculations were essentially identical except that two flash calculations were required. The liquid from the first stage was the feed into the second stage. The amount of water vaporized in the first stage was chosen to be about 95% of the amount of water needed to saturate the solution with respect to the acid.

The composition of the organic stream recycled back to the extractor is the sum of the liquid from the precipitator and the vapor condensed from the precipitator. In other words, the composition is determined from the amount and composition of the extract entering the precipitator, minus the acid that precipitated. The aqueous stream in equilibrium with this organic liquid entering the extractor was calculated, and a mass balance over the extractor completed the calculations.

7.4 Design Results

7.4.1 Results for Single Stage and Two Stage Processes

The amount of water vaporized was varied from 80 to 100% in the calculations. Equation 7.1 shows that if 100% of the water is evaporated, 100% of the solvent will be evaporated as well. The results from the 100% evaporation case are used for a comparison to other values of percent water vaporized. The 100% water evaporation case is a good base case because the energy requirements are constant for a given initial extract composition, for either the single stage or two stage processes.

Figure 7.2 reports the mass balance over the extraction and a single stage precipitation process for the fumaric acid - methylcyclohexanone system with 0.040 moles/L in the aqueous feed and 95% of the water evaporated. Note that more acid is in the extract than is feed into the aqueous feed because of the large amounts of acid entering the extraction column in the organic phase.

Figure 7.3 reports the percent acid recovered, weight % evaporated, relative energy use and relative energy per acid recovered for the fumaric acid - methylcyclohexanone system

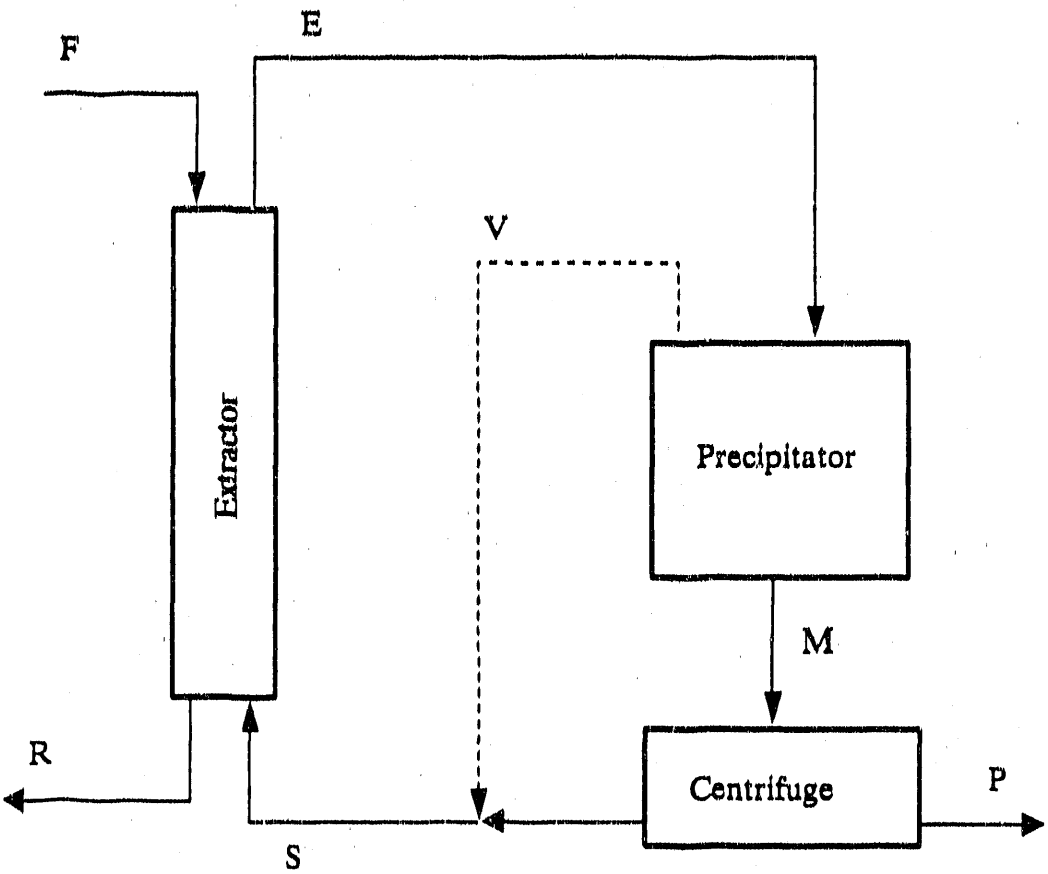

Figure 7.2 Mass balance for fumaric acid - methylcyclohexanone precipitation process with a single stage and 95% of the water in the extract evaporated and 0.040 mole/liter fumaric acid in the aqueous phase.

	F	E	M	V	P	S	R
Methylcyclohexanone	0.0	863.6	585.5	278.1	0.0	863.6	0.0
Water	5586.	44.43	2.215	42.21	0.0	44.43	5568.
Fumaric Acid	26.06	26.93	7.893	0.0	19.04	7.893	7.196
Density (g/ml)	1.0	0.935	0.914	---	---	0.91	1.0

All values in grams/minute. Based on 1 liter/minute flow of extract (E).

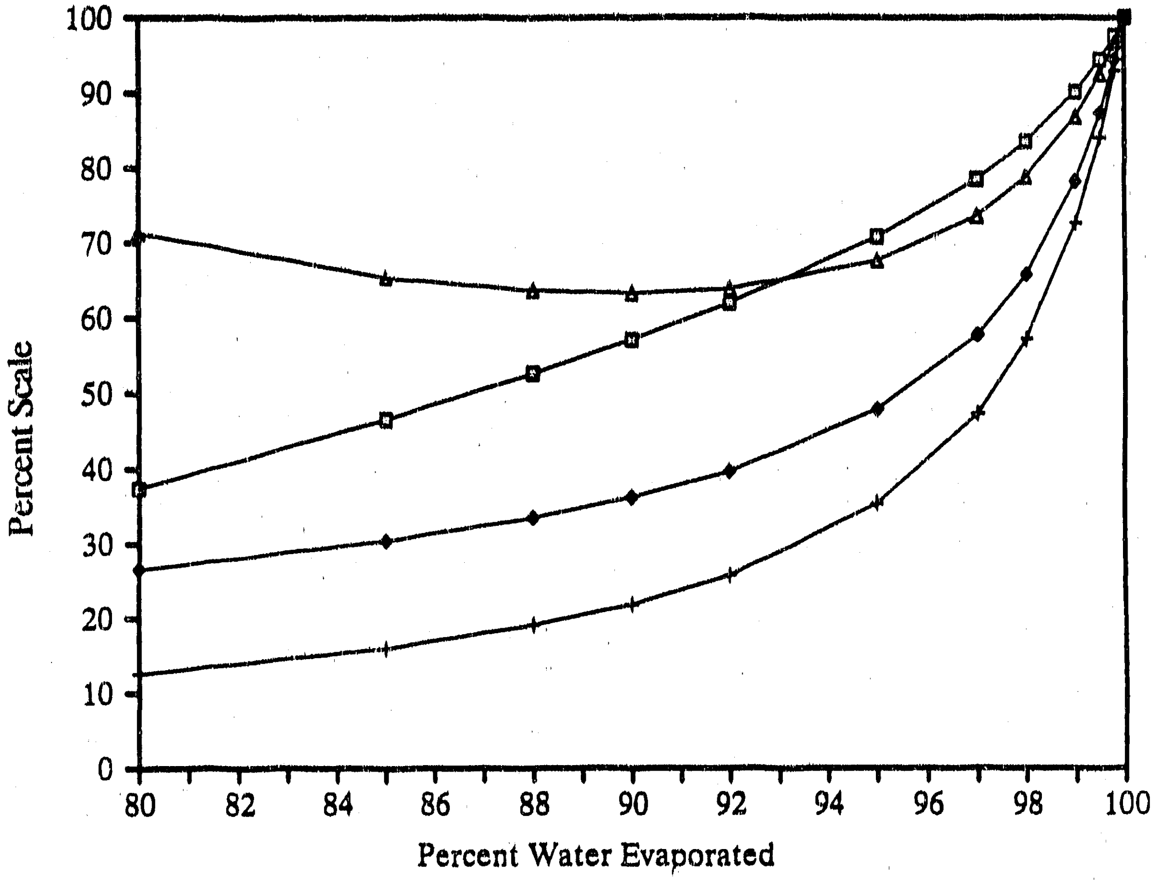

Figure 7.3 Percent acid recovery, weight percent evaporated, relative energy required, and relative energy required per acid recovered for the fumaric acid - methylcyclohexanone system for a single stage crystallizer. Fumaric acid concentration in the aqueous phase was 0.040 mole/L.

□	% Acid Recovery	+	Weight % Evaporated
◇	Relative Energy	△	Relative Energy/Acid

in a single stage precipitator. The aqueous acid concentration for these cases was 0.04 mole/L. The energy use and energy per acid have been normalized by the energy use and energy per acid values from the case where 100% of the water was vaporized. As expected, as the amount of water vaporized decreases, the acid recovery, the weight percent evaporated, and total energy required decrease.

Figure 7.3 shows that the acid recovered and the total relative energy required decreased with a decrease in the amount of water vaporized. However, a better measure of the energy efficiency of the process is the amount of energy required per acid recovered. The energy per acid recovered compensates for the different degrees of recovery of the acid. Figure 7.3 shows that the relative energy required per acid recovered has a broad minimum value at 90% of the water vaporized. In this range, the energy required per acid recovered is about 63% of the value for full evaporation.

The minimum value of the energy per acid recovered results from two different phenomena. First, Figure 7.1 shows that some water must be evaporated before any acid is precipitated. Therefore, the first acid precipitated has a very high value for the energy per acid recovered. But as more and more acid is recovered, the average amount of energy required per acid recovered decreases. Second, Figure 7.3 shows that the weight percent evaporated increases rapidly as the percent of water evaporated goes to 100%. Therefore, the energy required per acid recovered increases when nearly all the water is removed because the amount of solvent vaporized increases rapidly.

Figure 7.4 reports the percent acid recovery, weight percent evaporated, relative energy required, and relative energy required per acid recovered for the fumaric acid - methylcyclohexanone system for a two stage precipitation process. Note that the energy required per acid recovered shows a minimum at 55% of the energy per acid required to recover all the acid in this process configuration.

Figure 7.5 shows the percent acid recovered and the relative energy per acid recovered

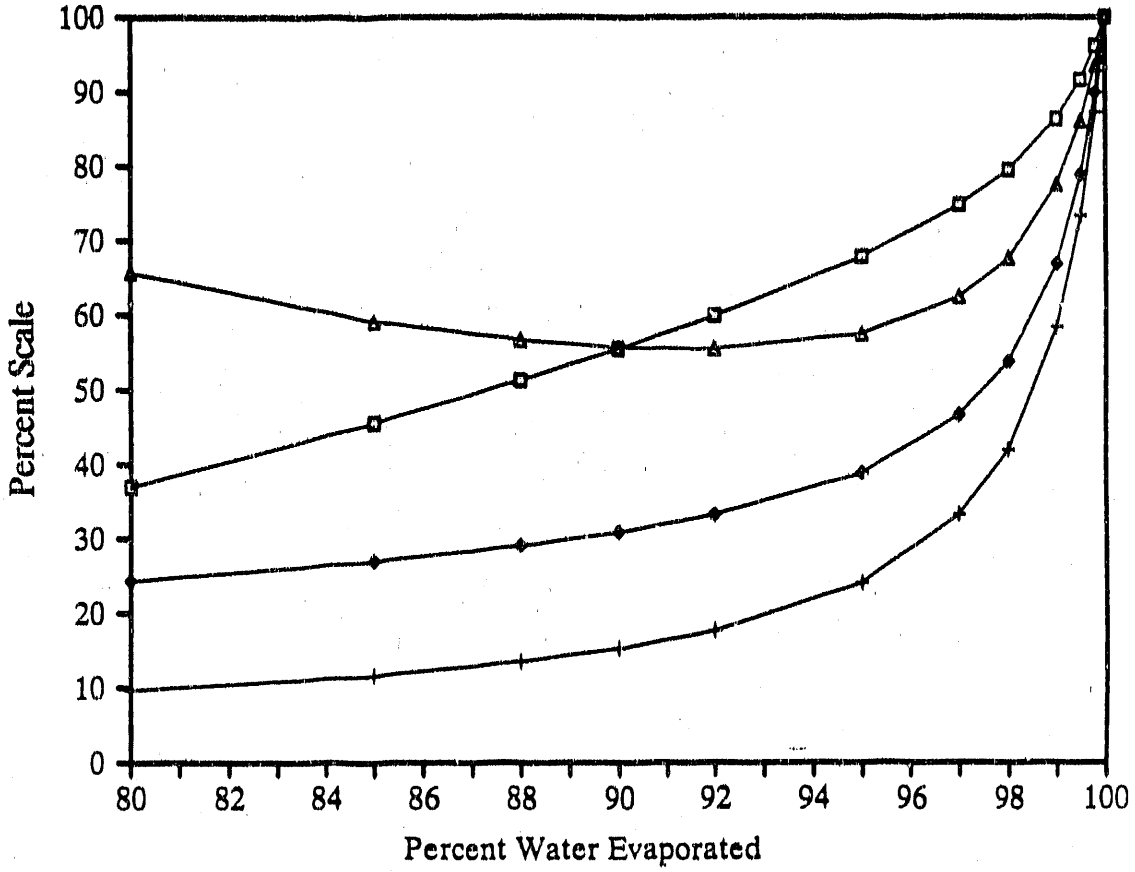

Figure 7.4 Percent acid recovery, weight percent evaporated, relative energy required, and relative energy required per acid recovered for the fumaric acid - methylcyclohexanone system for a two stage crystallizer. Fumaric acid concentration in the aqueous phase was 0.040 mole/L.

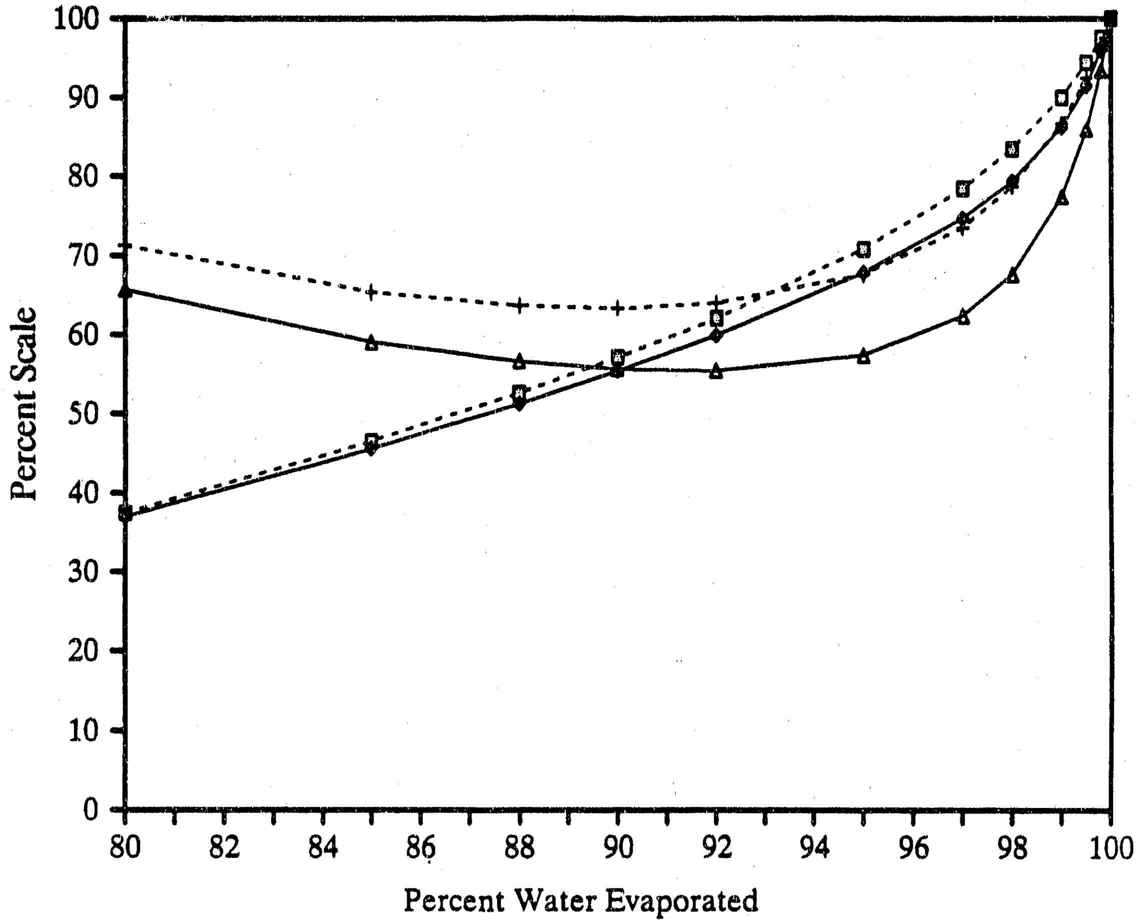

Figure 7.5 Percent acid recovery and relative energy required per acid recovered for the fumaric acid - methylcyclohexanone system for both a single stage and two stage crystallizer at 45C. Fumaric acid concentration in the aqueous phase was 0.040 mole/L.

for the fumaric acid - methylcyclohexanone systems for both the single stage and two stage precipitation processes. The energy required per acid recovered for the two stage process is lower than for the single stage process. This is because less solvent is evaporated in the two stage process than in the single stage process.

Additional stages would lower the energy requirements even further, but would also raise the capital costs of the process. Any process with more than two stages should probably be carried out as the stripping section of a distillation column with the crystallizer as the bottom stage.

Figure 7.6 reports the mass balance over the extraction and a single stage precipitation process for the adipic acid - cyclohexanone system with 0.50 moles acid/L in the aqueous feed and 95% of the water evaporated. Figure 7.7 shows the percent acid recovery, weight percent evaporated, relative energy required, and relative energy per acid recovered for the adipic acid - cyclohexanone system in a two stage process configuration. The adipic acid - cyclohexanone system shows similar trends with increasing amounts of water vaporized. The energy required per acid recovered reaches a minimum of 96% of the energy per acid for the base case of 100% water evaporation.

Figure 7.8 shows the percent acid recovery and relative energy required per acid recovered for the adipic acid - cyclohexanone system in the single stage and two stage process configurations. The energy per acid recovered for the single stage process is nearly horizontal from 95% to 100% of the water evaporated, and increases for lower percentage evaporation of water. In this case, there is no energy advantage to precipitation caused by preferential removal of water. The lower value of the separation factor for this system requires that a higher proportion of cyclohexanone be evaporated in order to achieve a certain water removal compared to methylcyclohexanone systems. The shallow minimum value in the energy per acid recovered for the two stage process shows the importance of staging when the value of the separation factor is low.

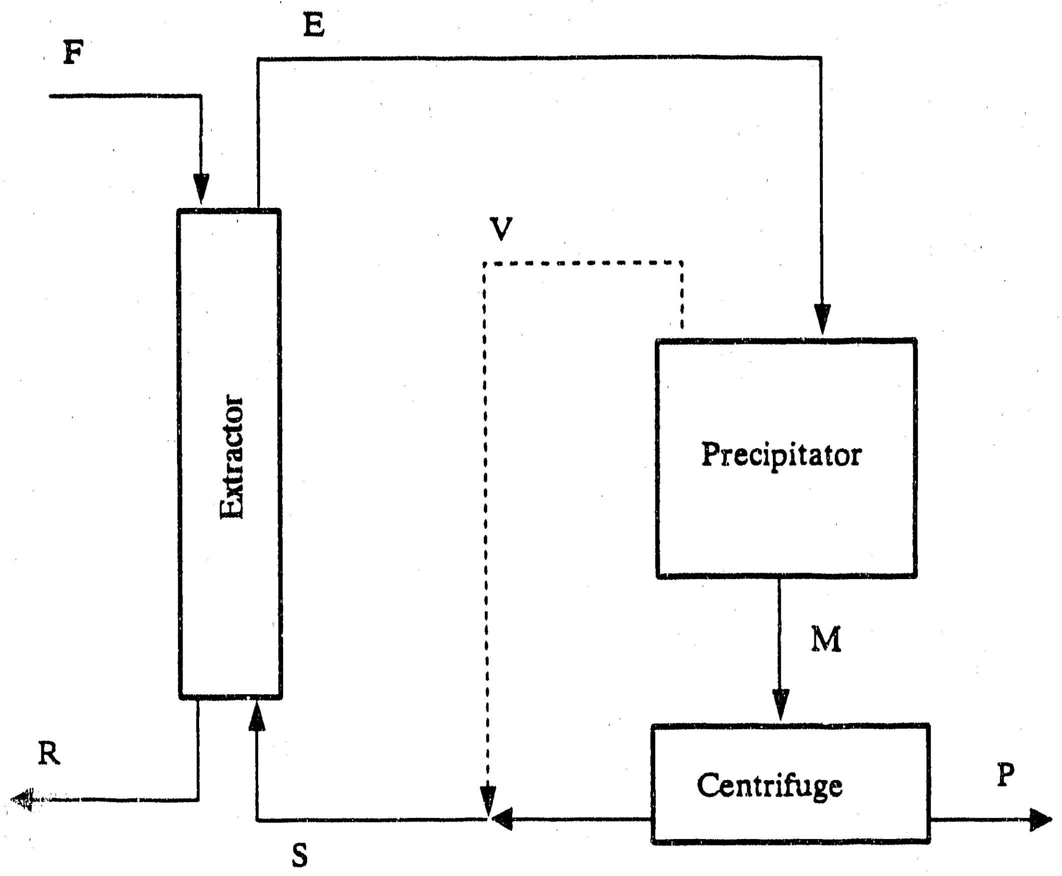

Figure 7.6 Mass balance for adipic acid - cyclohexanone precipitation process with a single stage and 95% of the water in the extract evaporated and 0.50 mole/liter adipic acid in the aqueous feed.

	F	E	M	V	P	S	R
Cyclohexanone	0.0	630.5	231.2	399.3	0.0	630.5	0.0
Water	2183.	159.7	7.99	151.7	0.0	159.7	2183.
Adipic Acid	172.1	179.7	30.2	0.0	149.5	30.2	22.6
Density (g/ml)	1.0	0.97	0.97	---	---	0.97	1.0

All values in grams/minute. Based on 1 liter/minute flow of extract (E).

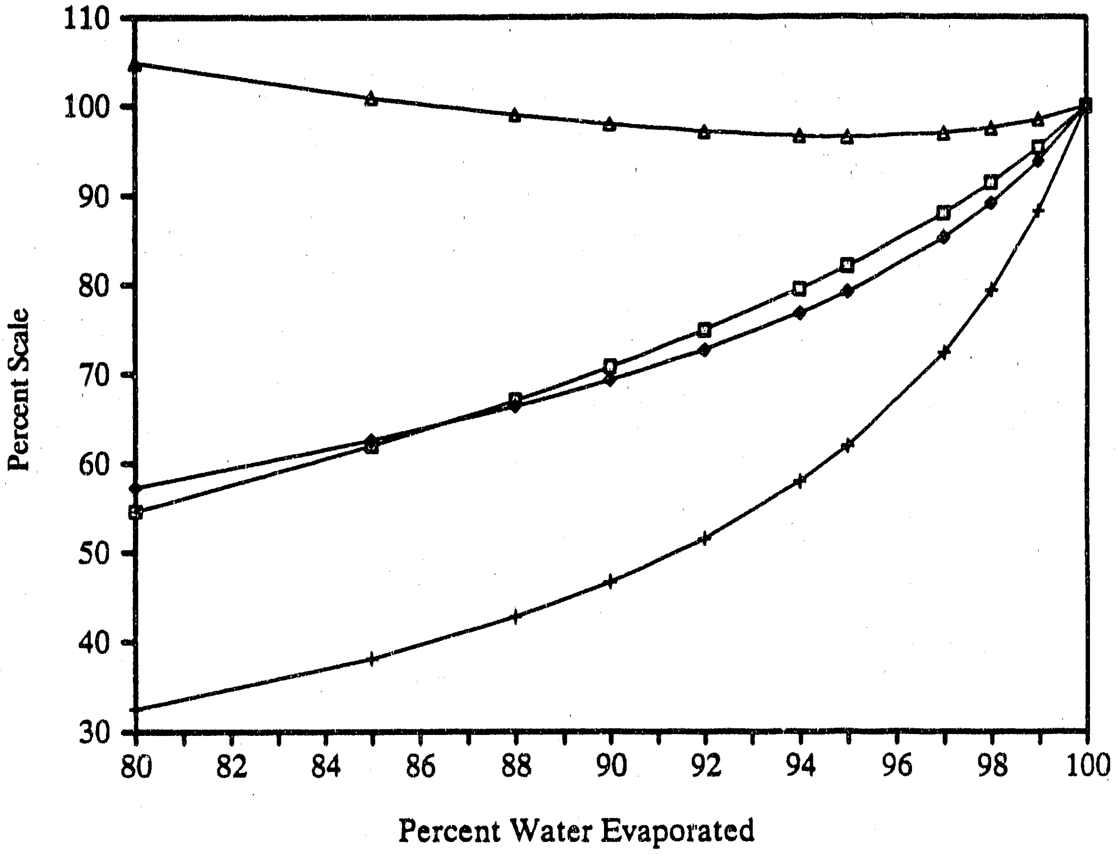

Figure 7.7 Percent acid recovery, weight percent evaporated, relative energy required, and relative energy per acid recovered for the adipic acid - cyclohexanone system for a two stage process with 0.50 mole/L adipic acid in the aqueous feed.

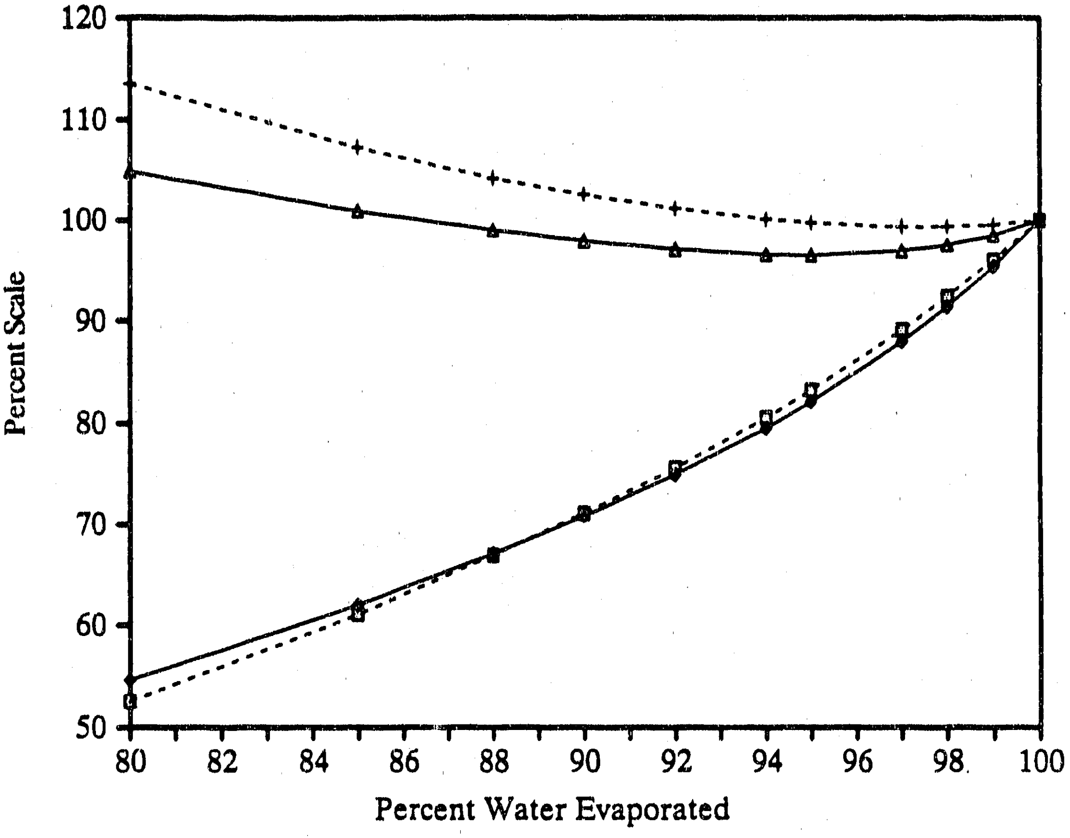

Figure 7.8 Percent acid recovery and relative energy required per acid recovered for the adipic acid - cyclohexanone systems with single stage and two stage evaporation processes. The adipic acid concentration in the aqueous feed was 0.50 mole/L.

The adipic acid - cyclohexanone system does not show a deep minimum value of the energy required per acid recovered is because of the high value of the enthalpy of vaporization for water compared to that for cyclohexanone, the high water content in the extract, and the low value of the separation factor. For the full evaporation case, evaporating the water accounts for 62% of the total energy requirements. In contrast, the energy required to evaporate the all the water in the fumaric acid - methylcyclohexanone system is only 25% of the total energy required for full evaporation of solvent and water. These figures set the minimum energy required to reach a specific percent water evaporated. The low value of the separation factor dictates that considerable amounts of cyclohexanone are evaporated at intermediate values of the percent water evaporated.

The adipic acid - cyclohexanone precipitation process calculations demonstrate that high values of the separation factor and low initial water content in the extract are important for minimizing energy requirements per acid recovered. Both these factors lead to using methylcyclohexanone or some other high molecular weight ketone solvent for the recovery of the acids considered here. If cyclohexanone must be used, multistage distillation should certainly be considered a strong candidate for water removal.

7.4.2 Results for Varying the Aqueous Acid Concentration in Feed

Figure 7.9 reports the energy required per mole of acid recovered for three different aqueous acid concentrations in the feed to the extractor for the fumaric acid - methylcyclohexanone system with a two stage process. The values of the energy required per mole of acid in Figure 7.9 were calculated by dividing the energy required for the evaporation process by the moles of acid recovered, and thus, fully account for the different degrees and amounts of acid recovered.

As shown in Figure 7.9, as the acid concentration increases, the energy required per mole of acid recovered decreases for a given percent water evaporated. All three acid

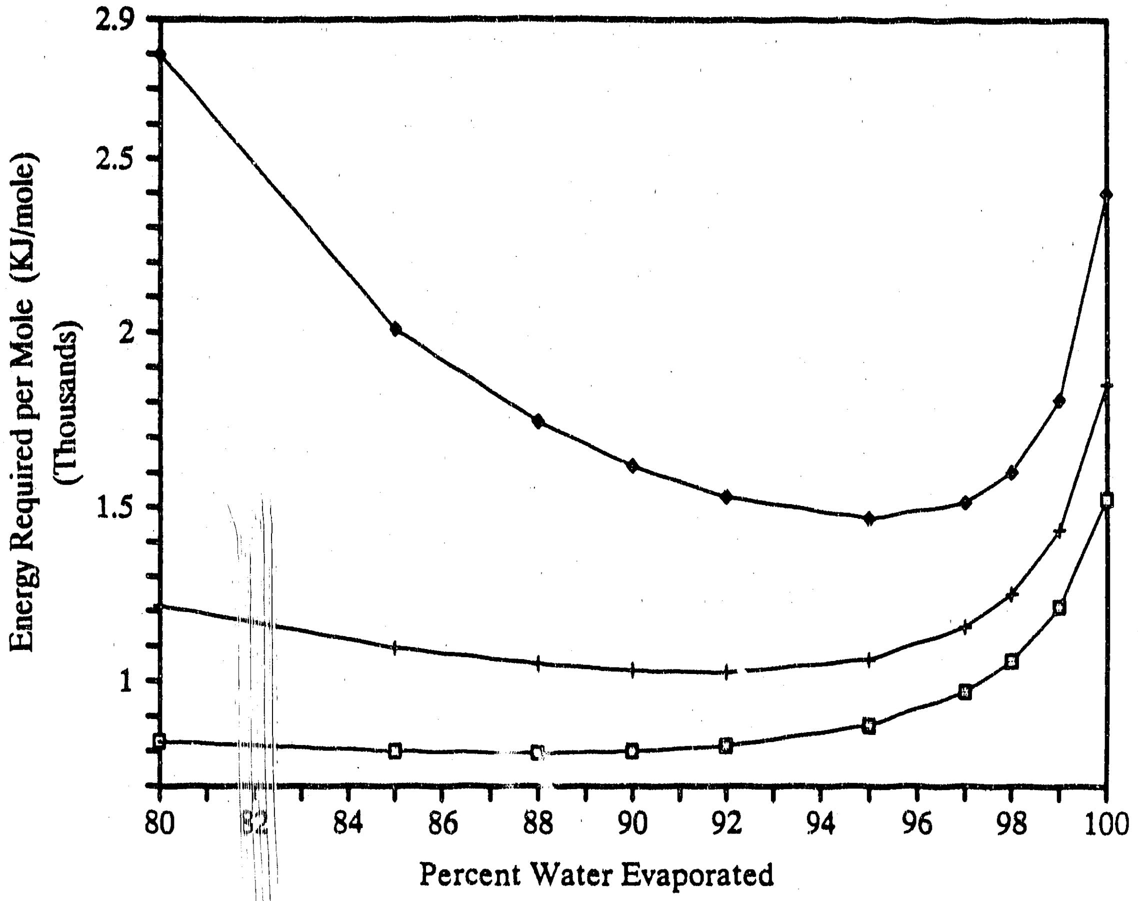

Figure 7.9 Energy required per mole of acid recovered for three different acid concentrations in the aqueous feed for the fumaric acid - methylcyclohexanone system with a two stage process.

- ◇ 0.030M Fumaric Acid in Aqueous Phase
- \+ 0.040M Fumaric Acid in Aqueous Phase
- ◻ 0.050M Fumaric Acid in Aqueous Phase

concentrations show a minimum value of the energy required per mole of acid recovered at an intermediate value of percent water evaporated. At the highest acid concentration in the aqueous phase, 0.050 mole/liter, the energy required per mole of acid shows a broad minimum from 85% to 90% of the water evaporated.

For the highest acid concentration, the energy required per mole of acid recovered slowly increases as the amount of water evaporated decreases. Remember that this increasing energy requirement per acid was because a large amount of energy had to be expended before any acid precipitated. However, due to the thermodynamic behavior of the fumaric acid - methylcyclohexanone system, as the acid concentration in the extract increases, the liquid - liquid and solid - liquid equilibrium lines get closer together. Less water needs to be evaporated before the acid starts to precipitate. Therefore, the energy required per mole of acid remains near the minimum value at low water evaporation rates because little energy was used to achieve acid saturation. If an extract with the composition of the triple point (0.136 moles/L fumaric acid in aqueous phase at 45°C, or 0.0522 moles/L fumaric acid in aqueous feed at 25°C) was fed to the evaporation process, the acid would exceed the equilibrium acid concentration as soon as any water was removed.

Figure 7.10 reports the energy required per mole of acid recovered for the adipic acid - cyclohexanone system with varying amounts of adipic acid in the aqueous feed. All three curves show a minimum energy per mole of acid at an intermediate value of percent water evaporated. In contrast to the fumaric acid - methylcyclohexanone system, the energy required per mole of acid increases as the percent water evaporated decreases for the adipic acid - cyclohexanone system. This is a consequence of the thermodynamic behavior of the adipic acid - cyclohexanone system at 45°C. Figure 4.14 shows that for this system, a triple point composition does not exist. Therefore, some water will always have to be removed before the acid concentration exceeds the equilibrium acid concentration.

The amount of energy required per mole of acid recovered for the adipic acid -

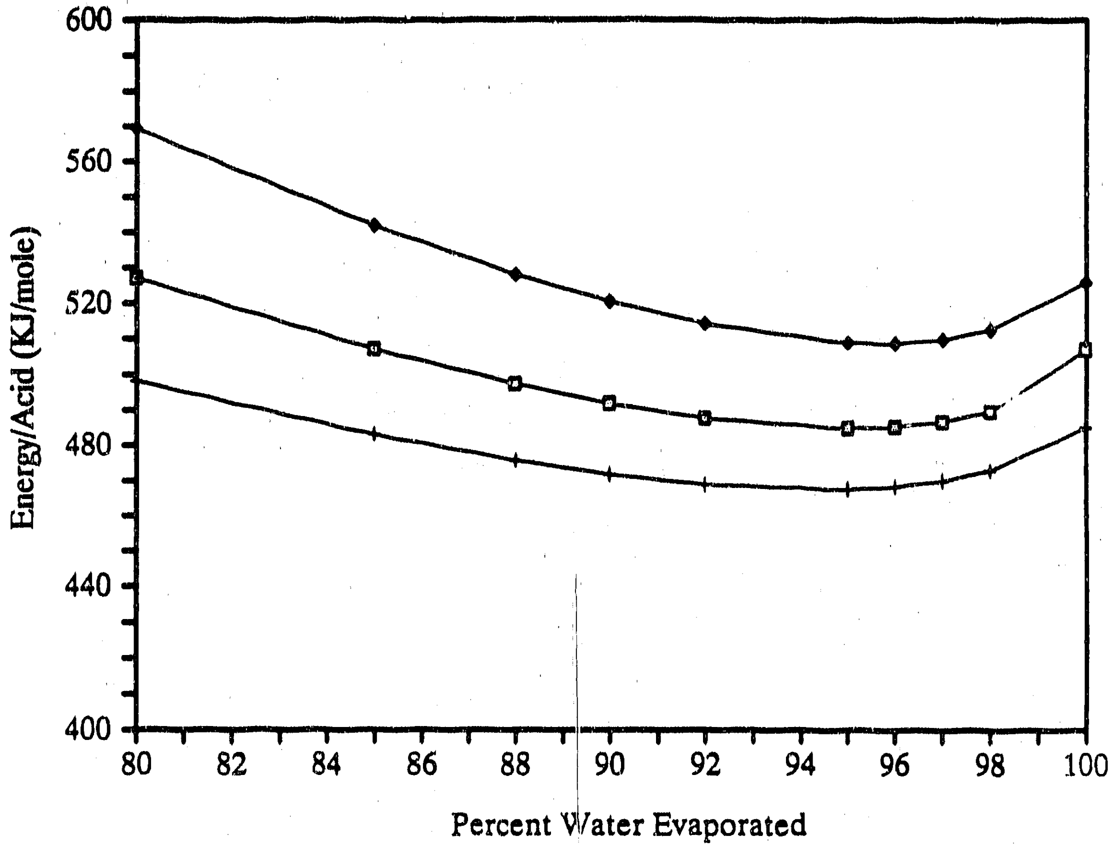

Figure 7.10 Energy required per mole of acid recovered for three different acid concentrations in the aqueous feed for the adipic acid - cyclohexanone system with a two stage evaporation process.

◇ 0.45 mole/L Adipic Acid in the Aqueous Feed

▣ 0.55 mole/L Adipic Acid in the Aqueous Feed

\+ 0.50 mole/L Adipic Acid in the Aqueous Feed cyclohexanone system is much lower than for the fumaric acid - methylcyclohexanone system (430 KJ/mole vs. 800 KJ/mole). This may be surprising considering that the initial water concentration in the extract is much larger than for methylcyclohexanone, and the total energy required is larger for the cyclohexanone system. However, the concentration of adipic acid in cyclohexanone was much greater than the concentration of fumaric acid in methylcyclohexanone. Therefore, the total energy required is being divided by a much larger number of moles of acid recovered, thus lowering the energy required per mole of acid recovered.

7.5 Temperature and Pressure Considerations

The calculations shown were for the precipitation step at 45°C. At this temperature, the process will have to be run at reduced pressures. Running processes under vacuum is expensive and raising the temperature of the process would reduce or eliminate the costs associated with the generating a vacuum. However, an increase in temperature generally decreases the separation factor between water and solvent. This results in an increased energy requirement for the precipitation process since more solvent will be evaporated. The decrease in the costs associated with the reduced pressure are balanced by the increased cost of evaporating more solvent. The compensating effects should produce an optimum temperature for the precipitation process. However, determining this optimum temperature was not attempted.

Another possible advantage of a multi-stage process is that the stages can be run at different temperatures. The first stages could be run at a higher temperature than the precipitator giving a greater acid solubility for a given water concentration. This means more water can be removed in the early stages which should be economical in general. The precipitator is then run at a low temperature which gives high acid recoveries due to the lowered acid solubility and a higher separation factor when it is needed most -- at low water concentrations.

7.6 Acid Recovery in the Extraction Process

Running the process at the percent water evaporated associated with the minimum energy required per acid recovered may not be the most economical process. Other factors, such as capital costs, need to be considered. In addition, the acid that is not recovered in the precipitation process will be recycled back into the extractor. The concentration of the acid in the recycle stream sets the acid recovery in the extractor. If the raffinate is not recycled back to a reactor or fermenter, achieving high acid recovery in the extractor may be critical to reduce product losses. More likely, the raffinate is recycled, and then a larger extraction column and reactor will be needed in order to hold the additional acid that is being recycled around the system. Therefore, the optimum evaporation rate may be greater than the evaporation rate associated with the lowest energy requirement per acid. Fortunately, the acid concentration in the recycle is lowered in two different ways when the total mass evaporated increases. First, higher acid recoveries are possible due to the lowered water concentration in the organic phase and the reduced volume of the liquid phase. Also, the acid in the recycle is diluted further when the increased amount of condensed vapor is added back to the liquid leaving the precipitator.

7.7 Conclusions

The energy required per acid recovered has a minimum value for an intermediate value of the percent of water evaporated. A two stage process gives lower energy requirements than a single stage process for the same amount of water evaporated. Systems with a low value of the separation factor between water and the solvent benefit more from multi-stage processes. The energy required per mole of acid recovered decreases as the acid concentration in the feed increases. For systems in which a triple point exists, the value of the energy required per mole of acid recovered is nearly constant up to 95% of the water evaporated when the extract composition is near the triple point.

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APPENDIX A. TEMPERATURE AND DILUENT SWING PROCESSES

In Chapter 1, temperature and diluent swing processes were discussed as possible regeneration methods for carboxylic acid extracts. This appendix examines these two swing processes for the recovery of fumaric acid.

The organic phase in these experiments consisted of an extractant, Alamine 336, and a diluent, typically methylisobutylketone (MIBK). For the diluent swing process, mixtures of Alamine 336, MIBK and n-heptane were used. Alamine 336, is an aliphatic tertiary amine with aliphatic chains of 8 - 10 carbon atoms (Henkel Corp.).

Tamada, et al. (1-3) studied the effects of solvent and temperature on the complexation of dicarboxylic acids with Alamine 336. Complexation constants for the acid - amine complex were calculated from liquid - liquid equilibrium data. The authors also used IR spectroscopy to examine self-association and hydrogen bonding among succinic acid, fumaric acid, and maleic acid. The work described in this appendix extends the work of Tamada to the extraction and recovery of fumaric acid.

A.1 Complexation Model

The distribution of fumaric acid between water and organic phase was described using a "chemical" model. A series of stoichiometric complexation reactions are proposed to describe the extraction data. A complexation reaction of p acid molecules, A, and q amine molecules, B, is shown in Equation A.1, with its corresponding equilibrium constant, $\beta_{pq,true}$. The braces indicate the species activities, and the overbar indicates an organic-phase species.

$$pA + q\overline{B} = \overline{A_pB_q} \qquad \beta_{pq,true} = \frac{(\overline{A_pB_q})}{(A)^p(\overline{B})^q} \qquad (A.1)$$

The species activity was not measured, but for practical applications, the activity of the species was assumed to be proportional to the concentration of the species. The constants of proportionality are then incorporated into the equilibrium constant. The new apparent equilibrium constant is written in Equation A.2, with the square brackets indicating the molar concentrations of each species. The concentration of undissociated acid in the aqueous phase, [A], is the relevant acid concentration.

$$\beta_{pq} = \frac{[\overline{A_pB_q}]}{[A]^p[\overline{B}]^q} \tag{A.2}$$

The equilibrium constants for the overall reaction can be rewritten to characterize the stepwise addition reaction, as shown in Equation A.3. The stepwise equilibrium constant, K_{pq}, is the ratio of the overall equilibrium constants, $\beta_{pq}/\beta_{p-1,q}$, and K_{11} equals β_{11}.

$$A + \overline{A_{p-1}B_q} = \overline{A_pB_q} \qquad K_{pq} = \frac{[\overline{A_pB_q}]}{[A][\overline{A_{p-1}B_q}]} \tag{A.3}$$

The loading of the extractant, Z, is the total moles of acid in the organic phase per mole of amine in the organic phase. Overloading, loading greater than unity, indicates that complexes with multiple acids per amine have formed.

The characteristic curves for these systems plot the loading as a function of the logarithm of the undissociated acid concentration in the aqueous phase, Z vs. log [A]. For systems with only one amine per complex, the loading does not depend on the amine concentration. If there are complexes with more than one amine, the loading increases with amine concentration at low acid concentrations.

The values of the equilibrium constants are determined to achieve the best fit of the data. Various sets of complexes are proposed and the values of the equilibrium constants are calculated by minimizing the error between the experimental data points and the model prediction.

A.2 Liquid - Liquid Equilibrium

The experimental data points and the model prediction for the fumaric acid - MIBK - Alamine 336 system at 25°C, 50°C, and 75°C are shown in Figures A.1-3, with varying amine concentrations. The derived values of the overall equilibrium constants for each complex at 25°C, 50°C, and 75°C are reported in Tables A.1, A.2, and A.3, respectively.

Figures A.1-3 show the experimental data points and the curves calculated from the complexation models. The calculated curves show good agreement with the experimental data. At 25°C, there is a definite trend that the loading of the amine is greater at higher amine concentrations for a given undissociated acid concentration in the aqueous phase. This trend can be described by the inclusion of complexes that have multiple amines per complex.

At 25°C, three different complexes were needed in order to describe the data satisfactorily. Both a 2:2 acid:amine complex and a 1:2 acid:amine complex are needed to describe the dependence of the loading on the amine concentration. A 2:1 acid:amine complex is needed to describe the data at loadings greater than unity. The existence of a 1:2 acid:amine complex is rationalized by each amine interacting with one of the carboxylate groups of the dicarboxylic acid. The 2:2 acid:amine complex is probably due to two 1:1 acid:amine complexes forming dimers through an interaction with carboxylate groups that are not interacting with the amine. The 2:1 acid:amine complex is explained by the formation of a hydrogen bond between a carboxylate group and a 1:1 acid:amine complex. The carboxyl group of the second acid forms a hydrogen bond to the conjugated CO of the carboxylate group of the first acid that is interacting with the amine. Figure A.4 shows the molecular arrangement associated with a 2:1 acid:amine complex. Tamada and King (2) discuss overloading and the evidence for the existence of 2:1 acid:amine complexes for experiments performed by the authors as well as other researchers.

Tamada and King (2) examined fumaric acid and Alamine 336 mixtures in chloroform

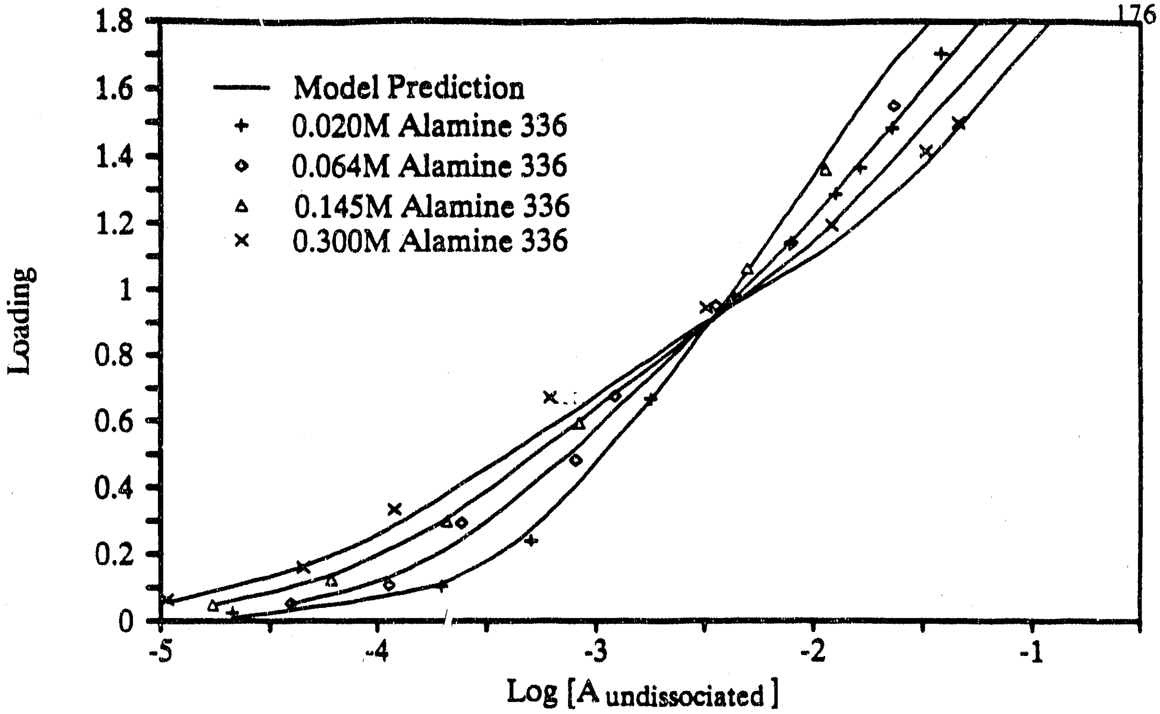

Figure A.1 Fumaric acid extraction into MIBK and varying amounts of Alamine 336 at 25C. The loading is the moles of acid extracted per mole of Alamine 336.

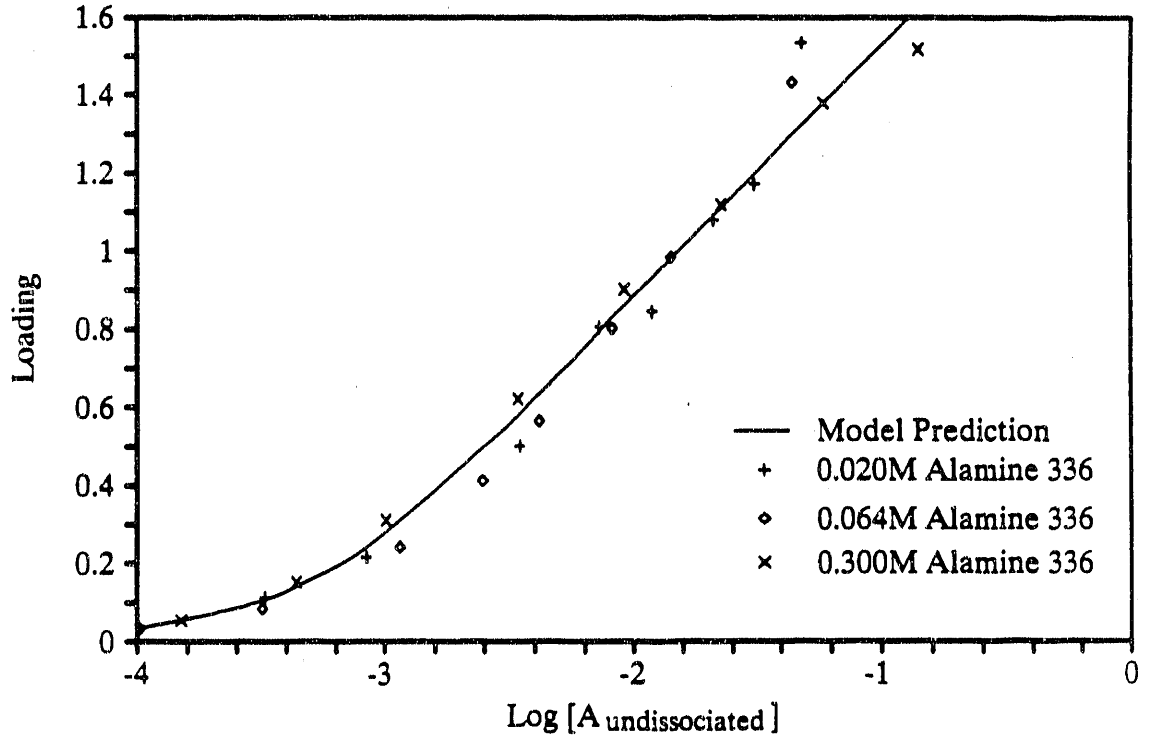

Figure A.2 Fumaric acid extraction into MIBK and varying amounts of Alamine 336 at 50C.

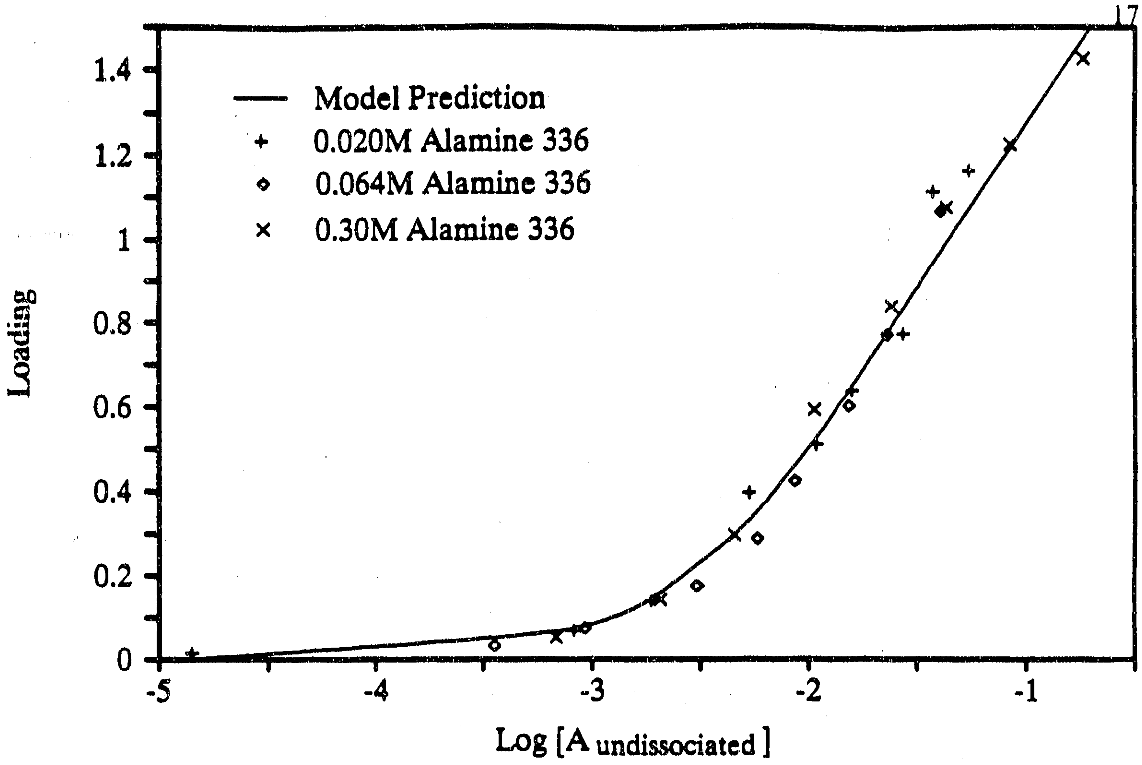

Figure A.3 Fumaric acid extraction into MIBK and varying amounts of Alamine 336 at 75C.

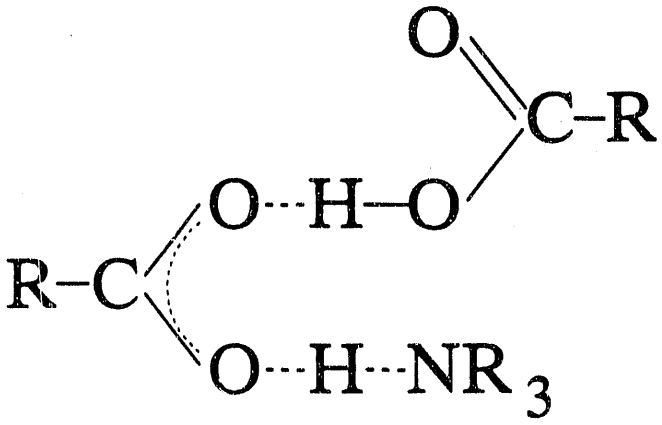

Figure A.4 The formation of a hydrogen bond between the -OH of the second acid to the conjugated CO of the complexed acid explains the overloading phenomena found experimentally in methylisobutylketone.

Table A.1 Overall equilibrium constants for the extraction of fumaric acid into a mixture of MIBK with varying amine concentrations at 25°C.

log β_{12}	4.34 $(L/mole)^2$
log β_{22}	7.52 $(L/mole)^3$
log β_{21}	4.82 $(L/mole)^2$

Table A.2 Overall equilibrium constants for the extraction of fumaric acid into a mixture of MIBK with varying amounts of amine concentrations at 50°C.

log β_{11}	2.54 (L/mole)
log β_{21}	3.63 $(L/mole)^2$

Table A.3 Overall equilibrium constants for the extraction of fumaric acid into a mixture of MIBK with varying amounts of amine concentrations at 75°C.

log β_{11}	1.92 (L/mole)
log β_{21}	2.70 $(L/mole)^2$

Table A.4 Overall equilibrium constants for the extraction of fumaric acid into a organic phase of 0.064 mole/L Alamine 336 in a mixture of 50\50 volume percent MIBK and heptane at 25°C.

log β_{11}	1.85 (L/mole)
log β_{21}	3.01 $(L/mole)^2$

by IR spectroscopy. They interpreted their results through the formation of 1:2 acid:amine and 2:2 acid:amine complexes. Due to its ability to interact with the conjugated CO of the carboxylate group of the complexed acid, chloroform, when used as a solvent, does not show any overloading tendencies (1).

At 50°C and 75°C, the loading of the amine is independent of the amine concentration, unlike the data at 25°C. The data can be fit with by proposing a 1:1 acid: amine complex and a 2:1 acid:amine complex. Both systems show strong overloading of the amine. Increasing the temperature causes a decrease in the value of the complexation constant for a given complex.

The extraction of fumaric acid into a mixture of Alamine 336, MIBK, and heptane was determined. Methylisobutylketone is an "active" diluent because the carbonyl functional group interacts with the acid:amine complex and provides an environment favorable to the formation of acid/:amine complexes. This is evident by the strong overloading of the amine. Heptane is an "inert" diluent because it provides an inert hydrocarbon environment for the complexes. As the ratio of MIBK to heptane changes for a specific alamine 336 concentration, the amount of fumaric acid extracted will change as well. This is the basis for the diluent swing process discussed in Chapter 1.

Table A.4 reports the overall equilibrium constants and Figure A.5 shows the experimental data and the line calculated from the complexation model for 0.064 mole/L Alamine 336 in a 50/50 volume percent mixture of MIBK and heptane at 25°C. The values of the complexation constants decreased when heptane was added to the diluent.

A.3 Extract Regeneration Process

Figure A.6 shows a McCabe-Thiele diagram for a generic extraction process with regeneration by back-extraction. The equilibrium lines are determined through liquid - liquid equilibrium experiments, comparable to the ones performed in this work. The

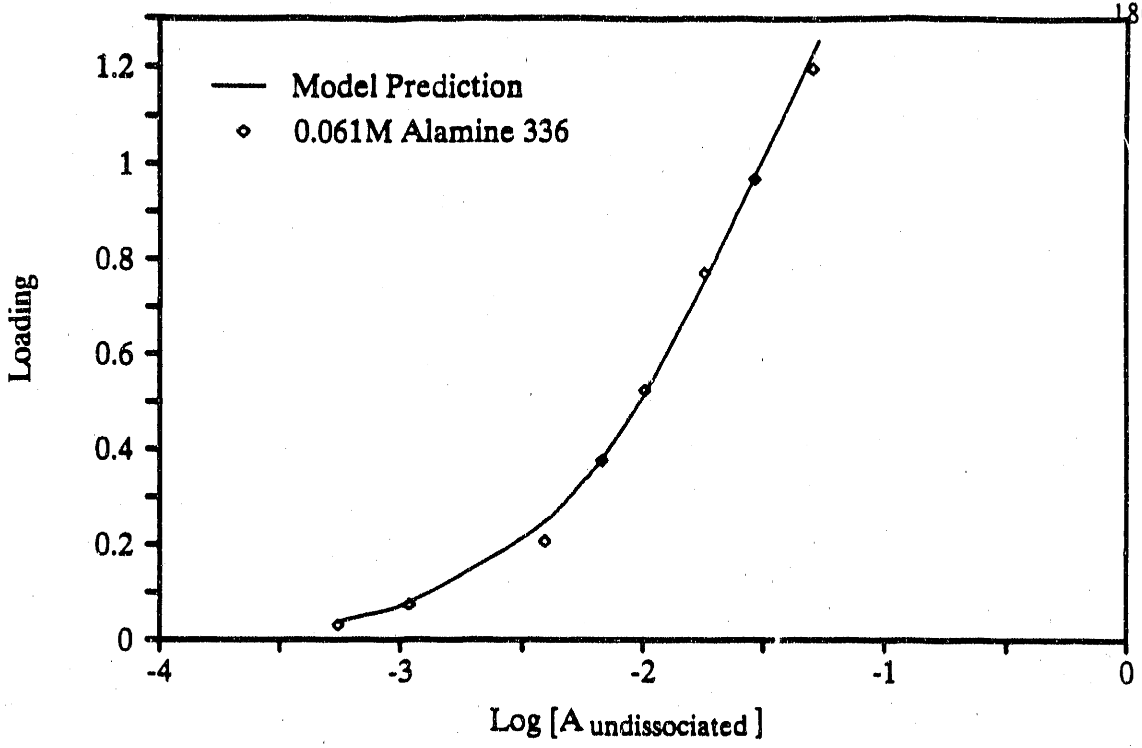

Figure A.5 Fumaric acid extraction into 0.061 mole/L Alamine 336 in 50/50 (v/v) MIBK/heptane at 25C.

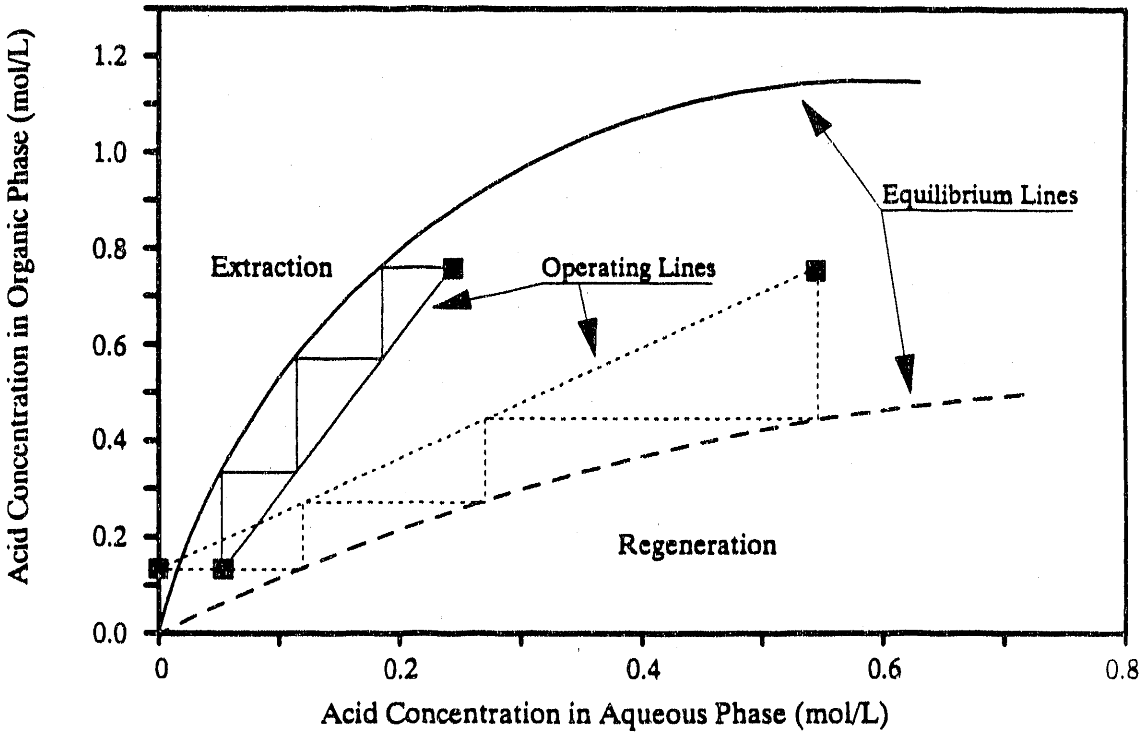

Figure A.6 McCabe-Thiele diagram for a multi-stage extraction process with regeneration by back-extraction into water.

operating line is determined by operating conditions, and its slope is equal to the ratio of the water to solvent flow rate. For extraction, the operating line has to be below the equilibrium line, and for back-extraction, the operating line has to be above the equilibrium line. In order to recover the solute at a reasonable product concentration, the equilibrium line for the regeneration must be below the equilibrium line for the extraction. The greater the difference between the two equilibrium lines, the greater the potential concentrating power of the extraction process.

Figure A.7 shows the equilibrium distribution of fumaric acid between water and a mixture of 0.064 mole/L Alamine 336 in MIBK at three different temperatures. The concentration of fumaric acid extracted into the organic phase decreases as the temperature increases for a given acid concentration in the aqueous phase. The change in the equilibrium distribution is the basis for the temperature swing regeneration process discussed in Chapter 1.

Figure A.8 reports the equilibrium distribution of fumaric acid between water and two different organic solutions. One solution is 0.064 mole/L Alamine 336 in MIBK, the other is 0.064 mole/L Alamine 336 in a 50/50 volume percent mixture of MIBK and heptane. The fumaric acid extracted decreases as heptane is added to the diluent while keeping the concentration of the extractant the same. This figure shows that the fumaric acid extraction into an organic phase is dependent upon the composition of the diluent, and a diluent swing process is an alternative regeneration process. Note that Figure A.7 does not show the equilibrium lines needed design a diluent swing process since the equilibrium lines shown are for the same Alamine 336 concentration. A true diluent swing process would have different Alamine 336 concentrations between the extractor and regenerator since the composition of the diluent is being changed between the extractor and regenerator.

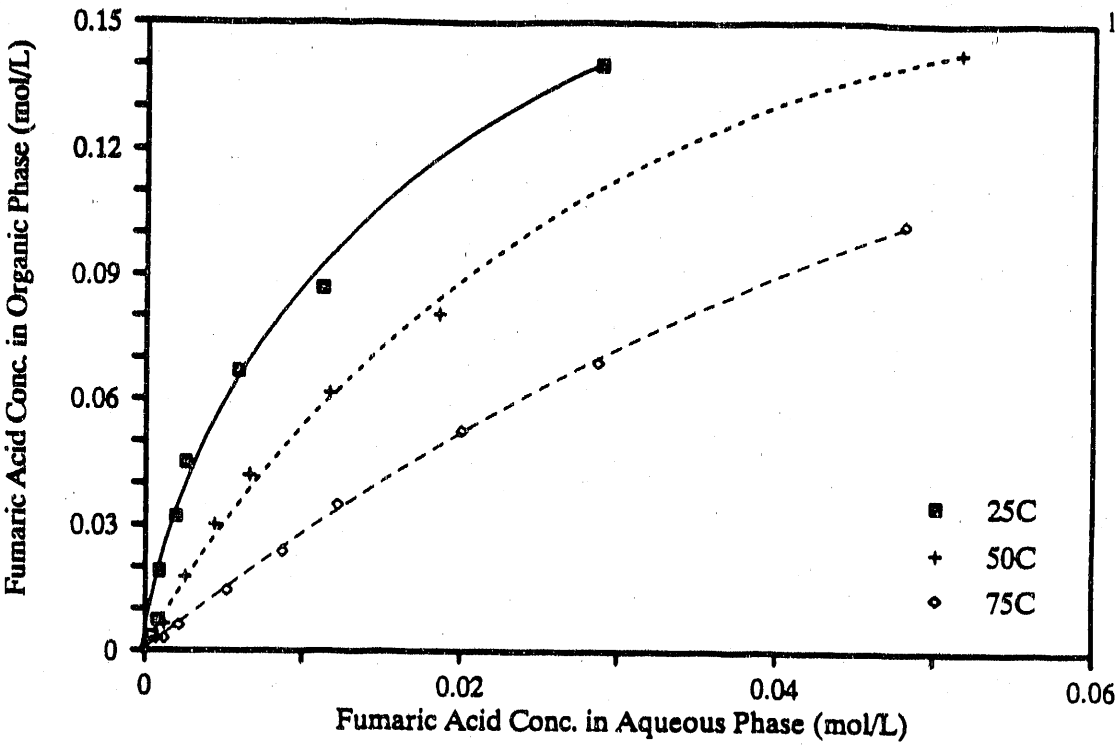

Figure A.7 Fumaric acid distribution into 0.064M Alamine 336 and MIBK at three temperatures.

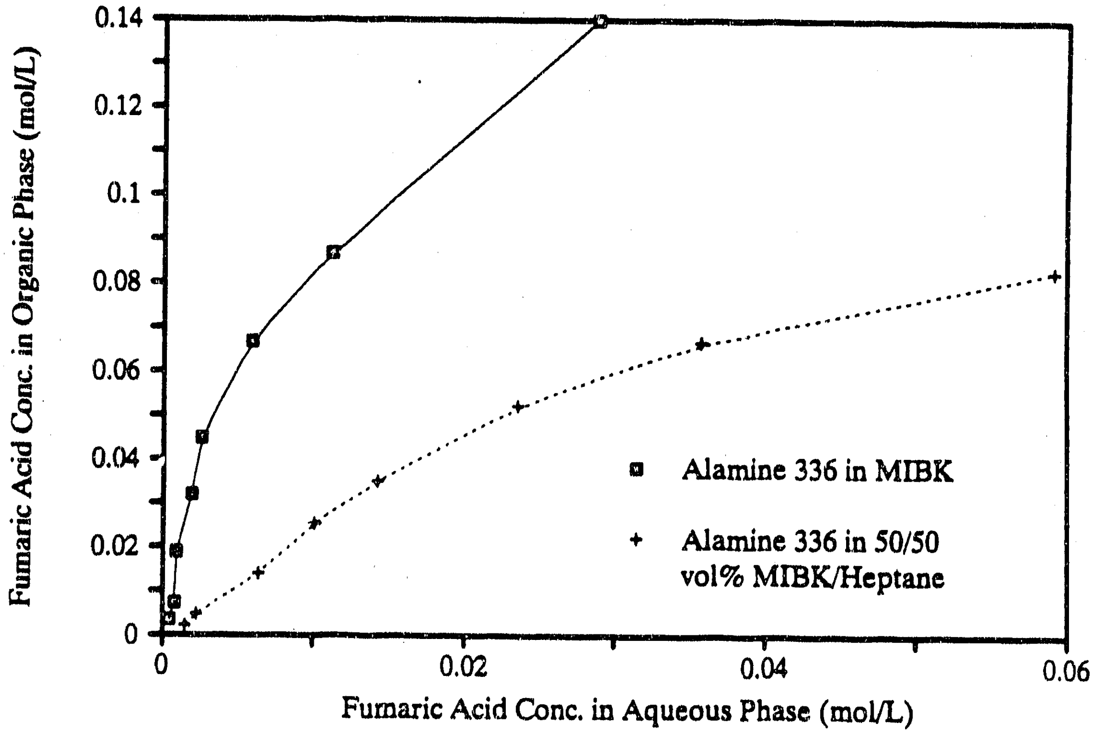

Figure A.8 Fumaric acid distribution into two diluents each having an Alamine 336 concentration of 0.064 moles/L.

A.4 Precipitation of Acid from an Acid - Amine - Solvent System

Combining the high distribution ratio exhibited by solvent - amine solutions in the extraction of carboxylic acids with the precipitation of the acid through the removal of co-extracted water looks attractive. In Chapter 2, it was shown that a methylisobutylketone - Alamine 336 mixture does show increased acid solubility with an increased water concentration in the organic phase. However, the anhydrous solubility of fumaric acid was relative high compared to fumaric acid solubility in the hydrated solution and the theoretical acid recovery by selective removal of the water was much lower than for the pure cyclic ketone solvents.

There is another more subtle reason not to use amine - solvent mixtures in the process for acid precipitation from an extract by removal of the co-extracted water process. Equation A.2 shows the equilibrium relationship between the concentrations of aqueous acid, amine, and acid:amine complex.

$$\beta_{pq} = \frac{[\overline{A_pB_q}]}{[A]^p[\overline{B}]^q} \tag{A.2}$$

If the half the solvent is evaporated, the concentrations of the acid and amine in the organic phase double. Consequently, the concentration of the acid:amine complex must quadruple in order for the equilibrium relationship to be satisfied for a 1:1 acid:amine complex. The evaporation of the water and solvent drives the formation of acid:amine complexes and limits the increase in the concentration of the uncomplexed acid. Since the complexed acid will not precipitate or would precipitate as an amine:acid salt, acid recovery is hampered.

A.5 Conclusions

The results reported here demonstrate that fumaric acid is strongly extracted by amine-solvent mixtures, and that the distribution of fumaric acid is affected by the temperature and the nature of the solvent. Temperature swing and diluent swing regeneration processes take advantage of this changing distribution ratio in order to recovery fumaric acid from aqueous solution. These processes are alternatives to the regeneration process discussed in the main body of this work. Temperature swing and diluent swing processes produce a concentrated acid solution and require that the acid be precipitated in a later process step. The advantage of regeneration by precipitation over these two regeneration methods is that it produces the acid in a solid form.

REFERENCES

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3. Tamada, J. A.; King, C. J. *Ind. Eng. Chem. Res.*, 1990, *29, 1333*

APPENDIX B. EXPERIMENTAL PROCEDURES

B.1 Materials

Chemical	Manufacturer	Purity
Fumaric Acid	Aldrich Chemical Co.	99%
Succinic Acid	Fluka Chemical Corp.	>99.5%
Adipic Acid	Aldrich Chemical Co.	99+%
Cyclohexanone	Fluka Chemical Corp.	>99.5%
Methylcyclohexanone	Fluka Chemical Corp.	mix of isomers
Methylisobutylketone	Aldrich Chemical Co.	99.7%
Alamine 336	Henkel Corp.	mix of amines
2-Heptanone	Fluka Chemical Corp.	>98%
3-Heptanone	Fluka Chemical Corp.	>97%
4-Heptanone	Fluka Chemical Corp.	>98%
Acetophenone	Fluka Chemical Corp.	99.%
n-Butyl Acetate	Aldrich Chemical Co.	+99%
Chloroform	Fisher Scientific	~99% (0.75% EtOH)
Di-n-butyl ether	Aldrich Chemical Co.	+99%
n-Heptane	J.T. Baker Chemical Co.	99.7%
1-Octanol	Aldrich Chemical Co.	99%
Methanol	Burdick & Jackson	
Toluene	Fisher Scientific	
Tri-n-butyl Phosphate	Alfa Products	
Tritolyl Phosphate	Matheson, Coleman, Bell	Technical
Tri-n-octyl Phosphine Oxide	Eastman Kodak Co.	
Karl-Fischer Reagent	GFS Chemicals, Inc.	

The water used in all experiments was distilled water passed through a Milli-Q water purification system (Millipore).

B.2 Solid - Liquid Equilibrium

Measured volumes of solvent and water were added to a flask. The carboxylic acid of interest was added in excess. If all the acid dissolved, more was added to the flask. Molecular sieve (4Å, Davison Chemical) was added to flasks when the acid solubility in an anhydrous solvent was determined. Chloroform was washed twice with water in a 1:1 volume ratio to remove ethanol, which is used as a stabilizer. Methylisobutylketone was washed with water in order to remove acidic impurities. Flasks were held at constant temperature in either a Fisher-Scientific Versa-Bath S or Labline Orbit water shaker baths. The density of the organic phase was measured by weighing out one milliliter of solution.

Organic phase acid concentrations were measured by back extraction of the acid into 0.1, 0.01, or 0.001 mole/liter NaOH. The resulting basic solution was back titrated with 0.1, 0.01, or 0.001 mole/liter HCl using a phenolphthalein indicator. The acid concentration in the organic phase was found by difference. Multiple analyses were done over a time span of days to make sure the solutions were at equilibrium, and the standard deviations of multiple analyses were typically 1% of the average value. The NaOH and HCl concentrations were chosen to give approximately the same relative precision for low concentrations as for high concentrations.

The acid concentration in butyl acetate was determined by HPLC since highly basic solutions catalyze the hydrolysis of esters. A C_{18} Radial-Pak Bondapak column (Waters) was contained in a radial compression module (Waters, RCM-100). A 60:40 (v/v) methanol: water mixture was used as the mobile phase. A Perkin-Elmer Series 10 pump, Waters Model 440 absorbance detector at 254 nm, and Hewlett-Packard 3390A integrator were used.

Organic phase water concentrations were determined by Karl Fischer titration with a Quintel model MS-1 automatic titrator. Ketone solvents interfere with the Karl Fischer reaction, and the water concentration in ketone solvents was therefore determined by gas chromatography. A Varian Model 3700 gas chromatograph with a thermal conductivity detector, and a 2 m x 3.17 mm stainless steel column packed with Poropak PS (Waters) at 160°C were used. Helium was the carrier gas. An external standard was used to compensate for any day to day variations in the performance of the gas chromatograph. The external standard was a cyclohexanone - water or methylcyclohexanone - water mixture that was analyzed when the calibration curve was determined and each day that water was analyzed in that particular solvent. The water concentrations in the samples analyzed on a given day were multiplied by the ratio of the water concentration in the external standard for the calibration to that on the day of analysis.

B.3 Liquid - Liquid Equilibrium

Measured volumes of solvent and water, typically 25 ml of each, were pipetted into flasks. Varying amounts of solid acid were added to the flasks, and the flasks were held at constant temperature in either of the water baths mentioned above. A blank run, in which the solvent and water equilibrated with no acid, was performed, and the acid concentration determined in the blank sample was subtracted from the value determined for the samples with added acid.

Acid concentrations in the aqueous phase were determined by titration with NaOH with a phenolphthalein indicator. The aqueous pH was measured with a Orion 601A pH meter and a Orion Ross electrode.

The acid and water concentrations in the organic phase were determined back titration into a basic solution and gas chromatography, the same method as in the solid - liquid equilibrium experiments.

B.4 Batch Precipitation Experiments

One hundred milliliters of an organic solution of known composition was pipetted into a three-neck flask. Acid and water concentrations in the organic phase were determined as previously discussed. The flask was placed in a 45°C ± 0.2° C water bath under reduced pressure of 400-500 mm Hg with nitrogen sparging to evaporate the liquid. The three-neck flask was magnetically stirred. After the evaporation step, the flask was weighed, and the amount of vapor lost was measured by difference. Then, the solution was filtered. The filter paper and the three-neck flask, which still had residual crystal solids were dried in a vacuum oven overnight. The recovery of the acid was determined by mass difference of the filter paper and the three-neck flask used for the evaporation. The density of the final precipitation solution was measured by weighing out one milliliter of the final precipitation solution.

APPENDIX C. EXPERIMENTAL DATA

C.1 Liquid - Liquid and Solid - Liquid Equilibrium Data

Results of equilibria experiments are listed in Table C.1. The experimentally measured quantities are listed below.

W_{acid} = mass of acid added to system (g)

$C_{acid,org}$ = equilibrium organic-phase acid concentration (mole/L)

$C_{acid,aq}$ = equilibrium aqueous-phase acid concentration (mole/L)

$C_{water,org}$ = equilibrium organic-phase water concentration (mole/L)

$W_{water,org}$ = equilibrium organic-phase water weight percent (wt%)

ρ = density of organic phase (g/ml)

pH = $-\log(H^+)$

(*** denotes that the data point was taken at the triple point of the solution)

C.2 Batch Precipitation Data

Results from the batch precipitation experiments are listed in Table C.2. The measured variables listed are self-explanatory.

Table C.1 Liquid - liquid and solid - liquid equilibrium experimental data

Fumaric Acid - Cyclohexanone
Temperature = 25°C

W_{acid}	$C_{acid,org}$	$C_{acid,aq}$	$C_{water,org}$	$W_{water,org}$	ρ	pH
0.0	0.0	0.0	2.94	5.45	0.97	4.35
0.1349	0.041	0.006	3.05	5.68	0.97	2.75
0.4520	0.138	0.019	3.57	6.73	0.97	2.46
1.0667	0.310	0.045	4.52	8.61	0.98	2.18
1.3455	0.381	0.058	4.73	9.09	0.98	2.13
***	0.454		4.79	9.29	0.98	
***	0.454		4.88	9.47	0.98	
***	0.458		4.57	8.88	0.98	
	0.436		4.08	7.90	0.98	
	0.375		3.02	5.86	0.97	
	0.370		3.05	5.92	0.97	
	0.316		2.60	5.02	0.97	
	0.316		2.42	4.67	0.97	
	0.244		1.69	3.27	0.96	
	0.166		1.05	2.02	0.96	
	0.053		0.0	0.0	0.96	

Fumaric Acid - Cyclohexanone
Temperature = 45°C

W_{acid}	$C_{acid,org}$	$C_{acid,aq}$	$C_{water,org}$	$W_{water,org}$	ρ	pH
0.0	0.0	0.0	3.59	6.96	0.93	4.29
0.1559	0.0531	0.0118	3.54	6.89	0.93	2.32
0.1559	0.0531	0.0118	3.67	7.15	0.93	2.32
0.4832	0.161	0.0368	4.12	8.06	0.94	2.06
0.8568	0.294	0.0637	4.32	8.55	0.94	1.90
1.2028	0.416	0.0952	4.89	9.82	0.94	1.81
0.6547	0.537	0.132	5.27	10.71	0.95	1.77
***	0.624		5.64	11.54	0.95	
	0.610		5.48	11.20	0.95	
	0.514		4.07	8.22	0.95	
	0.434		3.17	6.36	0.95	
	0.384		2.41	4.80	0.95	
	0.384		2.40	4.79	0.95	
	0.303		1.58	3.13	0.94	
	0.085		0.0	0.0	0.94	

Succinic Acid - Cyclohexanone
Temperature = 25°C

W_{acid}	$C_{acid,org}$	$C_{acid,aq}$	$C_{water,org}$	$W_{water,org}$	ρ	pH
0.0	0.0	0.0	2.99	5.54	0.97	4.5
0.8409	0.158	0.116	3.65	6.91	0.97	2.58
2.5111	0.445	0.346	5.51	10.81	0.97	2.34
4.1856	0.704	0.579	6.74	13.52	0.98	2.20
5.0185	0.863	0.696	6.75	13.83	0.98	2.16
***	1.04		8.12	17.05	0.98	
***	1.04		8.52	17.89	0.98	
	0.939		5.78	11.97	0.98	
	0.858		4.99	10.35	0.97	
	0.843		4.39	9.07	0.97	
	0.768		3.98	8.15	0.97	
	0.63		2.95	5.92	0.97	
	0.492		1.94	3.88	0.96	
	0.285		0.95	1.85	0.96	
	0.136		0.0	0.0	0.96	

Succinic Acid - Cyclohexanone
Temperature = 45°C

W_{acid}	$C_{acid,org}$	$C_{acid,aq}$	$C_{water,org}$	$W_{water,org}$	ρ	pH
0.0	0.0	0.0	3.58	6.96	0.93	4.35
0.2348	0.262	0.25	4.39	8.65	0.94	2.16
2.4622	0.502	0.492	5.59	11.11	0.96	1.99
3.6899	0.711	0.717	6.97	14.19	0.97	1.87
4.9219	0.939	0.928	8.06	16.86	0.97	1.82
5.7385	1.058	1.074	9.07	18.94	0.99	1.75
6.5601	1.195	1.211	10.15	21.22	1.00	1.70
8.9977	1.62	1.653	15.84	34.4	1.02	1.57
	2.114		21.87	49.8	1.04	
	1.642		13.63	30.82	0.99	
	1.628		11.41	25.84	0.99	
	1.45		9.43	20.87	0.98	
	1.356		6.11	13.36	0.98	
	1.128		5.38	11.44	0.98	
	0.842		2.92	6.05	0.97	
	0.226		0.0	0.0	0.96	

Adipic Acid - Cyclohexanone
Temperature = 25°C

W_{acid}	$C_{acid,org}$	$C_{acid,aq}$	$C_{water,org}$	$W_{water,org}$	ρ	pH
0.0	0.0	0.0	2.96	5.50	0.97	4.46
0.6196	0.136	0.0299	3.78	7.16	0.97	3.06
1.9957	0.428	0.0964	4.87	9.66	0.97	2.79
3.5757	0.688	0.177	6.09	12.46	0.98	2.70
4.6458	0.844	0.233	7.06	14.83	0.98	2.63
***	1.06		7.71	16.83	0.98	
***	1.06		7.04	15.35	0.98	
	0.964		5.54	11.88	0.98	
	0.872		4.54	9.70	0.97	
	0.800		4.19	8.84	0.97	
	0.684		3.58	7.42	0.97	
	0.612		2.70	5.52	0.97	
	0.470		1.74	3.52	0.96	
	0.312		0.89	1.75	0.96	
	0.163		0.0	0.0	0.96	

Adipic Acid - Cyclohexanone
Temperature = 45°C

W_{acid}	$C_{acid,org}$	$C_{acid,aq}$	$C_{water,org}$	$W_{water,org}$	ρ	pH
0.0	0.0	0.0	3.58	6.96	0.93	
0.9024	0.234	0.659	4.10	8.20	0.93	2.69
1.7715	0.423	0.128	5.03	10.31	0.94	2.54
2.6833	0.636	0.196	5.76	12.04	0.95	2.44
3.2594	0.728	0.237	6.40	13.42	0.96	2.39
3.8702	0.846	0.298	7.06	15.08	0.97	2.34
4.4730	0.914	0.342	7.46	16.12	0.99	2.32
6.0307	1.209	0.473	9.05	20.03	1.00	2.16
7.5049	1.411	0.623	10.40	23.43	1.00	2.13
	1.763		21.65	49.8	1.04	
	1.647		10.91	26.10	0.99	
	1.672		8.79	21.13	0.99	
	1.614		7.27	17.31	0.99	
	1.294		5.46	12.35	0.98	
	1.060		4.19	9.14	0.98	
	0.836		2.14	4.53	0.97	
	0.290		0.0	0.0	0.96	

Fumaric Acid - Methlycyclohexanone

Temperature = 25°C

W_{acid}	$C_{acid,org}$	$C_{acid,aq}$	$C_{water,org}$	$W_{water,org}$	ρ	pH
0.0	0.0	0.0	1.78	3.51	0.92	3.53
0.1424	0.0527	0.0108	1.92	3.75	0.93	2.52
0.2805	0.104	0.0204	2.10	4.12	0.93	2.37
0.4201	0.154	0.0297	2.16	4.24	0.93	2.27
0.5633	0.206	0.0392	2.32	4.59	0.93	2.21
0.7007	0.256	0.0501	2.59	5.14	0.94	2.15
***	0.295		2.68	5.34	0.94	
	0.282		2.31	4.59	0.94	
	0.282		2.48	4.93	0.94	
	0.282		2.59	5.15	0.94	
	0.255		2.00	3.98	0.94	
	0.255		2.25	4.48	0.94	
	0.214		1.81	3.59	0.93	
	0.214		1.78	3.53	0.93	
	0.181		1.28	2.53	0.93	
	0.181		1.33	2.63	0.93	
	0.141		1.19	2.35	0.93	
	0.141		1.11	2.20	0.93	
	0.141		0.92	1.83	0.93	
	0.0925		0.58	1.15	0.93	
	0.0925		0.62	1.23	0.93	
	0.0925		0.63	1.24	0.93	
	0.0392		0.0	0.0	0.92	

Fumaric Acid - Methlycyclohexanone

Temperature = 45°C

W_{acid}	$C_{acid,org}$	$C_{acid,aq}$	$C_{water,org}$	$W_{water,org}$	ρ	pH
0.0	0.0	0.0	1.83	3.69	0.89	3.40
0.0	0.0	0.0	1.89	3.82	0.89	3.40
0.2232	0.070	0.0229	2.05	4.17	0.89	2.12
0.2232	0.070	0.0229	2.20	4.48	0.89	2.12
0.4403	0.151	0.0478	2.32	4.77	0.90	1.93
0.4403	0.151	0.0478	2.34	4.80	0.90	1.93
0.6679	0.220	0.0682	2.40	4.92	0.90	1.85
0.6679	0.220	0.0682	2.66	5.45	0.90	1.85
0.8819	0.283	0.0926	2.71	5.60	0.90	1.77
0.8819	0.283	0.0926	2.67	5.51	0.90	1.77
1.1062	0.351	0.116	3.04	6.33	0.91	1.70
1.1062	0.351	0.116	3.02	6.29	0.91	1.70
***	0.419		3.02	6.27	0.92	
	0.412		3.03	6.28	0.92	
	0.411		2.92	6.05	0.92	
	0.394		3.01	6.24	0.92	
	0.317		2.05	4.20	0.92	
	0.242		1.36	2.76	0.91	
	0.181		0.77	1.56	0.91	
	0.0		0.0	0.0	0.91	

Succinic Acid - Methlycyclohexanone
Temperature = 25°C

W_{acid}	$C_{acid,org}$	$C_{acid,aq}$	$C_{water,org}$	$W_{water,org}$	ρ	pH
0.0	0.0	0.0	1.78	3.51	0.91	3.53
0.4568	0.0783	0.112	1.94	3.82	0.92	2.55
0.9120	0.159	0.229	2.19	4.35	0.93	2.39
1.3034	0.217	0.315	2.40	4.77	0.93	2.30
1.7034	0.287	0.418	2.56	5.13	0.93	2.24
2.2004	0.371	0.532	2.87	5.76	0.94	2.17
2.6064	0.437	0.639	3.13	6.30	0.95	2.13
***	0.519		3.44	6.96	0.95	
	0.510		3.27	6.60	0.95	
	0.467		2.80	5.65	0.95	
	0.431		2.44	4.96	0.94	
	0.407		2.17	4.43	0.93	
	0.340		1.75	3.55	0.92	
	0.340		1.73	3.53	0.92	
	0.258		1.16	2.35	0.92	
	0.170		0.61	1.21	0.92	
	0.083		0.0	0.0	0.92	

Succinic Acid - Methlycyclohexanone
Temperature = 45°C

W_{acid}	$C_{acid,org}$	$C_{acid,aq}$	$C_{water,org}$	$W_{water,org}$	ρ	pH
0.0	0.0	0.0	1.89	3.82	0.89	
0.9552	0.144	0.260	2.73	5.46	0.92	2.10
1.9020	0.279	0.530	3.24	6.52	0.93	1.91
1.9020	0.279	0.530	3.11	6.26	0.93	1.91
2.8556	0.398	0.760	3.62	7.38	0.93	1.80
3.8026	0.527	0.760	3.98	8.19	0.94	1.80
3.8026	0.527	0.915	3.81	7.83	0.94	1.74
3.8026	0.527	0.915	3.93	8.09	0.94	1.74
4.7531	0.595	1.176	4.28	8.86	0.94	1.66
4.7531	0.595	1.176	4.24	8.77	0.94	1.66
5.7084	0.701	1.320	4.01	8.37	0.94	1.62
5.7084	0.701	1.320	3.76	7.84	0.94	1.62
5.7084	0.701	1.320	4.50	9.38	0.94	1.62
5.7084	0.701	1.320	4.61	9.63	0.94	1.62
***	0.93		4.13	8.84	0.95	
***	0.93		4.34	9.30	0.95	
***	0.93		4.47	9.58	0.95	
	0.871		3.98	8.57	0.94	
	0.825		3.74	8.02	0.94	
	0.810		3.66	7.87	0.93	
	0.708		3.05	6.84	0.93	
	0.555		2.10	4.38	0.93	
	0.377		1.07	2.18	0.92	
	0.141		0.0	0.0	0.92	

Adipic Acid - Methlycyclohexanone
Temperature = 25°C

W_{acid}	$C_{acid,org}$	$C_{acid,aq}$	$C_{water,org}$	$W_{water,org}$	ρ	pH
0.0	0.0	0.0	1.78	3.51	0.91	
0.4434	0.113	0.0400	1.97	3.96	0.91	2.92
0.9110	0.233	0.0782	2.20	4.49	0.92	2.78
1.3593	0.337	0.115	2.54	5.26	0.92	2.70
1.8096	0.439	0.151	2.84	5.96	0.92	2.64
2.2715	0.532	0.191	2.96	6.28	0.92	2.60
2.7234	0.593	0.214	3.34	7.15	0.93	2.65
***	0.607		3.23	6.94	0.93	
	0.560		2.80	5.96	0.93	
	0.535		2.59	5.50	0.93	
	0.453		2.01	4.24	0.92	
	0.434		1.92	4.03	0.92	
	0.381		1.61	3.35	0.92	
	0.278		0.97	2.00	0.92	
	0.190		0.56	1.14	0.92	
	0.102		0.0	0.0	0.91	

Adipic Acid - Methlycyclohexanone
Temperature = 45°C

W_{acid}	$C_{acid,org}$	$C_{acid,aq}$	$C_{water,org}$	$W_{water,org}$	ρ	pH
0.0	0.0	0.0	1.89	3.82	0.89	
0.8192	0.190	0.084	2.54	5.25	0.89	2.53
1.6386	0.356	0.164	2.82	5.95	0.90	2.40
2.4557	0.521	0.240	3.52	7.59	0.91	2.31
3.2837	0.670	0.324	3.95	8.69	0.92	2.24
4.1028	0.816	0.399	4.38	9.85	0.92	2.21
4.9222	0.955	0.469	4.21	9.70	0.92	2.16
4.9222	0.955	0.469	4.64	10.70	0.92	
4.9222	0.955	0.469	4.63	10.67	0.92	
***	1.040		4.82	11.26	0.92	
***	1.040		5.67	13.23	0.92	
***	1.040		4.27	9.98	0.92	
***	1.056		4.04	9.46	0.92	
	1.007		3.57	8.33	0.92	
	0.853		3.37	7.66	0.92	
	0.765		2.53	5.66	0.92	
	0.669		1.88	4.14	0.92	
	0.474		1.06	2.25	0.91	
	0.195		0.0	0.0	0.91	

Table C.2 Precipitation experimental data

Fumaric Acid - Cyclohexanone I

Tare	240.41	g
Sample Volume	100	ml
Tare + Sample	335.48	g
Initial Acid Concentration	0.485	mole/L
Initial Water Weight Fraction	0.0947	
Initial Water Concentration	4.70	mole/L
Tare + Sample after Evaporation	306.27	g
Final Acid Concentration	0.110	mole/L
Final Water Weight Fraction	0.0153	
Final Water Concentration	0.90	mole/L
Tare + Crystals after Drying	243.62	g
Filter Paper Tare	0.4921	g
Filter Paper + Crystals	2.2268	g
Density of Final Solution	0.932	g/ml

Fumaric Acid - Cyclohexanone II

Tare	227.45	g
Sample Volume	100	ml
Tare + Sample	322.52	g
Initial Acid Concentration	0.485	mole/L
Initial Water Weight Fraction	0.0947	
Initial Water Concentration	4.70	mole/L
Tare + Sample after Evaporation	309.89	g
Final Acid Concentration	0.378	mole/L
Final Water Weight Fraction	0.0385	
Final Water Concentration	2.16	mole/L
Tare + Crystals after Drying	228.31	g
Filter Paper Tare	0.4961	g
Filter Paper + Crystals	1.7408	g
Density of Final Solution	0.948	g/ml

Succinic Acid - Cyclohexanone

Tare	255.97	g
Sample Volume	100	ml
Tare + Sample	355.21	g
Initial Acid Concentration	1.320	mole/L
Initial Water Weight Fraction	0.2265	
Initial Water Concentration	10.52	mole/L
Tare + Sample after Evaporation	330.48	g
Final Acid Concentration	1.26	mole/L
Final Water Weight Fraction	0.1148	
Final Water Concentration	5.64	mole/L
Tare + Crystals after Drying	256.63	g
Filter Paper Tare	0.5065	g
Filter Paper + Crystals	5.7065	g
Density of Final Solution	0.968	g/ml

Adipic Acid - Cyclohexanone

Tare	203.32	g
Sample Volume	100	ml
Tare + Sample	300.91	g
Initial Acid Concentration	1.12	mole/L
Initial Water Weight Fraction	0.1716	
Initial Water Concentration	7.74	mole/L
Tare + Sample after Evaporation	305.58	g
Final Acid Concentration	0.420	mole/L
Final Water Weight Fraction	0.013	
Final Water Concentration	0.73	mole/L
Tare + Crystals after Drying	215.29	g
Filter Paper Tare	0.2226	g
Filter Paper + Crystals	1.2339	g
Density of Final Solution	0.931	g/ml

Fumaric Acid - Methylcyclohexanone I

Tare	226.54	g
Sample Volume	100	l
Tare + Sample	318.47	g
Initial Acid Concentration	0.356	mole/L
Initial Water Weight Fraction	0.0562	
Initial Water Concentration	2.74	mole/L
Tare + Sample after Evaporation	304.89	g
Final Acid Concentration	0.103	mole/L
Final Water Weight Fraction	0.0005	*estimate*
Final Water Concentration	0.03	mole/L
Tare + Crystals after Drying	229.37	g
Filter Paper Tare	0.4872	g
Filter Paper + Crystals	0.5872	g
Density of Final Solution	0.907	g/ml

Fumaric Acid - Methylcyclohexanone II

Tare	226.92	g
Sample Volume	100	ml
Tare + Sample	318.79	g
Initial Acid Concentration	0.356	mole/L
Initial Water Weight Fraction	0.0562	
Initial Water Concentration	2.74	mole/L
Tare + Sample after Evaporation	313.35	g
Final Acid Concentration	0.238	mole/L
Final Water Weight Fraction	0.0233	
Final Water Concentration	1.39	mole/L
Tare + Crystals after Drying	227.53	g
Filter Paper Tare	0.5103	g
Filter Paper + Crystals	1.6080	g
Density of Final Solution	0.91	g/ml

Succinic Acid - Methylcyclohexanone

Tare	237.47	g
Sample Volume	100	ml
Tare + Sample	331.47	g
Initial Acid Concentration	0.783	mole/L
Initial Water Weight Fraction	0.0846	
Initial Water Concentration	3.98	mole/L
Tare + Sample after Evaporation	324.17	g
Final Acid Concentration	0.546	mole/L
Final Water Weight Fraction	0.0417	
Final Water Concentration	2.35	mole/L
Tare + Crystals after Drying	237.54	g
Filter Paper Tare	0.5029	g
Filter Paper + Crystals	4.0010	g
Density of Final Solution	0.927	g/ml

Cyclohexanone - Water Binary System

Tare	236.67	g
Tare + Sample	312.79	g
Initial Water Weight Fraction	0.0507	
Tare + Sample after Evaporation	310.24	g
Final Water Weight Fraction	0.0366	

Methlycyclohexanone - Water Binary System

Tare	227.37	g
Tare + Sample	303.83	g
Initial Water Weight Fraction	0.0368	
Tare + Sample after Evaporation	301.03	g
Final Water Weight Fraction	0.0142	

Fumaric Acid - Methylisobutylketone I

Tare	41.875	g
Sample Volume	20	l
Tare + Sample	58.066	g
Initial Acid Concentration	0.0874	mole/L
Initial Water Weight Fraction	0.0210	
Initial Water Concentration	0.93	mole/L
Tare + Sample after Evaporation	55.768	g
Final Acid Concentration	0.0576	mole/L
Final Water Weight Fraction	0.00949	
Final Water Concentration	0.42	mole/L
Tare + Crystals after Drying	41.893	g
Filter Paper Tare	0.2349	g
Filter Paper + Crystals	0..2959	g
Density of Final Solution	0.81	g/ml *estimate*

Fumaric Acid - Methylisobutylketone II

Tare	38.976	g
Sample Volume	20	ml
Tare + Sample	55,130	g
Initial Acid Concentration	0.0874	mole/L
Initial Water Weight Fraction	0.0210	
Initial Water Concentration	0.93	mole/L
Tare + Sample after Evaporation	50.84	g
Final Acid Concentration	0.0482	mole/L
Final Water Weight Fraction	0.0076	
Final Water Concentration	0.34	mole/L
Tare + Crystals after Drying	38.991	g
Filter Paper Tare	0.2369	g
Filter Paper + Crystals	0.3170	g
Density of Final Solution	0.81	g/ml *estimate*

APPENDIX D

Nomenclature

a_i^α	Activity of component i in phase α
A_{12}	Parameter for three-suffix Margules equation (Chapter 5)
$C_{a,z}$	Concentration of acid in phase z (moles/L)
$C_{w,z}$	Concentration of water in phase z (moles/L)
D	Distribution Ratio
f_i	Moles of component i in feed (Chapter 7)
g_{ij}	Parameter for NRTL equation (Chapter 5)
G_{ij}	Parameter for NRTL equation (Chapter 5)
G	Gibbs Free Energy
H	Enthalpy
$H_{solution}$	Enthalpy of solution (Chapter 3)
$H_{transfer}$	Enthalpy of transfer (Chapter 4)
K_a	Dissociation constant for acid
K_d	Dimerization constant for acid in organic solvent
K_{pq}	Stepwise equilibrium constant for p:q acid:amine complex (Appendix A)
L	Moles of liquid in batch distillation (Chapter 6)
m	molarity (moles/kg)
P	Partition Coefficient
Q_{123}	Ternary parameter for three-suffix Margules equation (Chapter 5)
R	Gas Constant
s	Standard error (Chapter 4)
S	Solubility of solute in solvent (moles/L) (Chapter 2)
S	Entropy
$S_{solution}$	Entropy of solution (Chapter 3)

$S_{transfer}$	Entropy of transfer
t	critical variance value from t distribution (Chapter 4)
T	Temperature
v_i	Moles of component i in vapor (Chapter 7)
x_i^α	Mole fraction of component i in phase α

$[H_2A]$	Concentration of undissociated dicarboxylic acid
$[HA^-]$	Concentration of bicarboxylate acid ion
$[A^=]$	Concentration of carboxylate ion
$[(H_2A)_2]$	Concentration of dicarboxylic acid dimer
$[A]$	Concentration of undissociated dicarboxylic acid (moles/L) (Chapter 5)
$[W]$	Concentration of water in the organic phase (moles/L) (Chapter 5)
$[K]$	Concentration of ketone solvent (moles/L) (Chapter 5)
$[A_pW_qK_r]$	Concentration of p:q:r acid:water:ketone complex
$\{J\}$	Activity of species J

α	Slope of solid - liquid equilibrium curves (Chapter 3)
α	Nonrandomness parameter of NRTL equation (Chapter 5)
α_{ij}	Separation factor between components i and j
β	Exponent or intercept of solid - liquid equilibrium curves (Chapter 3)
β_{pqr}	Equilibrium constant for p:q:r acid:water:ketone complex (Chapter 5)
$\beta_{pq,true}$	Overall equilibrium constant for p:q acid:amine complex (Appendix A)
γ_i^α	Activity coefficient of component i in phase α
Δ	Change in a variable between two states
λ	Slope of liquid - liquid equilibrium curves (Chapter 4)
Λ	Difference between the values of two slopes
μ_i^α	Chemical potential of component i in phase α

μ	Exponent or intercept of liquid - liquid equilibrium curves (Chapter 4)
σ	Slope of water distribution curve (Chapter 4)
τ_{ij}	Parameter for NRTL equation (Chapter 5)
τ	Intercept of water distribution curve

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