DOE/ER/13777--T1

DE92 008725

PREDICTION OF THERMODYNAMIC PROPERTIES OF COAL DERIVATIVES

Final Technical Report
for Grant Period
September 1, 1987 to February 28, 1991

Marc D. Donohue

Department of Chemical Engineering
The Johns Hopkins University
Baltimore, Maryland 21218

September 1990

Prepared for

CHEMICAL SCIENCES DIVISION
OFFICE OF BASIC ENERGY SCIENCES
THE U.S. DEPARTMENT OF ENERGY
AGREEMENT NO. DE-FG02-87ER13777

ABSTRACT

The purpose of this research program is to understand the relationship between macroscopic thermodynamic properties and the various types of intermolecular forces. Since coal-derived liquids contain a wide variety of compounds, a theory capable of successfully predicting the thermophysical properties for coal processes must take into account the molecular shapes and all significant intermolecular forces: dispersion forces, anisotropic forces due to dipoles and quadrupoles, as well as Lewis acid-base interactions. We have developed the Acid-Base-Perturbed-Anisotropic-Chain Theory (ABPACT), a comprehensive theory that is capable of predicting the thermophysical properties for many systems where these different intermolecular forces are present.

The ABPACT can treat non-polar compounds, polar compounds and compounds that associate through Lewis acid-base interactions. In addition to our theoretical work, we have used computer simulations to evaluate (and in some cases correct) the assumptions made in this theory. We also have conducted experiments to help us better understand the interplay of different kinds of interactions in multicomponent mixtures.

In continuing this research program, we seek to further improve our understanding of the effects of molecular shape and intermolecular forces on the thermophysical properties of coal-derived liquids. We propose to develop a site-site interaction model that can be used to predict the properties of a large number of compounds and their mixtures from a knowledge of the constituent sites only. We also intend to develop a multiple association site model to treat compounds with several association sites and polymers with repeating units that have association sites. We hope that the computer simulations and experiments we have planned will help us improve the theory sufficiently that the molecular parameters used in the model can be related to independently determinable molecular properties so they will not need to be regressed using experimental data.

TABLE OF CONTENTS

DISCLAIMER

INTRODUCTION

Coal-derived liquids include aliphatic and aromatic hydrocarbons, alcohols, amines, carboxylic acids as well as inorganic compounds such as hydrogen sulfide and sulfur dioxide. These compounds vary greatly in molecular size and shape. They also interact with different types of intermolecular forces. For example, the aliphatic hydrocarbons are non-polar, but aromatic hydrocarbons all have a quadrupole moment due to the π-electrons above and below the rings. Furthermore, functional groups containing oxygen, nitrogen, and sulfur have dipolar character and often can associate with other functional groups through Lewis acid-base forces. Consequently, such fluids cannot be described adequately for design purposes by the traditional, empirical correlations that were developed for petroleum-derived liquids.

The purpose of this research program is to understand the relationship between macroscopic thermodynamic properties and molecular size and the various types of intermolecular forces. This is necessary to describe the properties of coal-derived fluids, and also in a number of other situations including supercritical extraction, polymer processing, and control of hazardous wastes.

Over the course of this research program, we have tried to build an equation of state that is capable of describing the properties of multicomponent mixtures that contain species that differ greatly in size and in the nature of their intermolecular forces. We chose the Perturbed-Hard-Chain Theory (PHCT) (Beret and Prausnitz, 1975; Donohue and Prausnitz, 1978) as the basis for this model because PHCT has been able to correlate the properties of a wide variety of species found in petroleum and because it is applicable to large as well as small molecules. PHCT was the first (and for many years, the only) equation of state that could treat molecules of any size.

In previous contract periods, we systematically extended PHCT to treat polar molecules and hydrogen-bonding molecules. We developed the Perturbed-Anisotropic-Chain Theory (PACT) (Vimalchand and Donohue, 1986) to treat anisotropic (polar) molecules and the Associated-Perturbed-Anisotropic-Chain Theory (APACT) (Ikonomou and Donohue, 1986; 1988) to treat molecules that hydrogen bond.

Our work during this contract period has been concerned with three issues. The first has been to develop a more fundamental understanding of how associating and long-chain molecules behave so that the assumptions that were used in the development of the perturbation chain theories could be corrected or improved. Second, we have tried to relate the parameters needed for the calculations of macroscopic properties directly to measurable molecular properties such as polarizability, dipole moment and bond lengths so that we can minimize the need for fitted parameters. Finally, we have tried to develop a better understanding of the behavior of multicomponent mixtures, particularly mixtures where molecules associate. The importance of the above three issues will be described in the context of our work on theory, computer simulations and experiments.

Research Accomplishments

Our efforts of the previous contract period are discussed in detail in the following sections. Below we present what we believe are the most significant aspects of that work.

- We have evaluated the assumptions made in the Perturbed-Hard-Chain Theory using computer simulations. We have determined that the partitioning between the attractive and repulsive terms in PHCT is better than in other equations of state including Flory, Sanchez-Lacombe and Chain of Rotators. This is discussed later in this Report and in "Comparison of Equations of State for Chain Molecules" by Vimalchand and Donohue (1989).
- We have developed a site-site interaction theory to describe the thermodynamics of solutions containing polar and non-polar compounds. The theory is discussed later in this

Report and in "Thermodynamics of Short Chain Polar Compounds" by Walsh *et al.*, (1990).

- We have developed a general equation of state for multicomponent mixtures where the species associate through Lewis acid-base interactions. The theory is discussed later in this Report and in "Thermodynamics of Lewis Acid-Base Mixtures" by Economou *et al.*, (1990).
- We have shown that the 'chemical' theory of association used in APACT is identical in its composition dependence to Wertheim's equation which is based on a perturbation theory approach. We also have shown that these two theories have the same density dependence if one relaxes one of the original simplifying assumptions made in APACT. This result is discussed later in this Report and in "A Simple Equation of State for Nonspherical and Associating Molecules" by Elliott *et al.*, (1990).
- We have used a first-order perturbation theory to predict the large negative partial molar volumes for infinitely dilute mixtures near their critical point. It had been claimed by several authors that clustering of solvent molecules around the solute was the cause of these large negative partial molar volumes. We have shown that the cause for the large negative partial molar volumes is the change in the compressibility near the critical point, and that clustering has only secondary effects. This is discussed in "Mean Field Theory Calculations of Thermodynamic Properties in Supercritical Fluids" by Economou and Donohue (1990).
- We have measured phase equilibria of aromatic hydrocarbons in supercritical fluids. The results are presented in "High-Pressure Binary Phase Equilibria of Aromatic Hydrocarbons with CO_2 and C_2H_6" by Kim *et al.*, (1989).
- We have measured infinite dilution activity coefficients for aromatic compounds in aqueous solutions. The results and their implications are discussed later in this Report and in "Measurement of Infinite Dilution Activity Coefficients Using High Performance Liquid Chromatography" by Economou *et al.*, (1990).

- We have developed a sophisticated numerical technique to analyze the infra-red spectra obtained for associating mixtures. This will be used in the characterization of acid and base probes. This is discussed later in this Report and will be discussed in "Analysis of FTIR Spectroscopic Data: The Voigt Profile" by Walsh *et al.*, (1990) and in "The Use of Acid-Base Probes in FTIR Spectroscopy" by Walsh *et al.*, (1990).
- We have used FTIR spectroscopy to measure hydrogen bonding of polymers in mixed solvent solutions. This work will be presented at the AIChE meeting in November 1990 and will be discussed in a paper in preparation entitled "Molecular Thermodynamics of Polymer Solutions that Hydrogen Bond" by Economou and Donohue.

Theory

In order to make accurate predictions of thermodynamic properties of fluid mixtures a theory must take into account the differences in molecular size and shape as well as differences in intermolecular forces. In the most general case, the theory needs to take into account non-polar and polar interactions as well as chemical association due to hydrogen-bonding and Lewis acid-base reactions. Morris, Vimalchand and Donohue (1987) developed the Perturbed-Soft-Chain Theory (PSCT) based on the Perturbed-Hard-Chain Theory (PHCT) by using a 'soft' Lennard-Jones potential instead of a 'hard' square-well potential. Anisotropic interactions due to the presence of dipolar and quadrupolar forces were added in the Perturbed-Anisotropic-Chain Theory (PACT) and then this equation was generalized to take into account hydrogen-bonding by incorporating an association equilibrium model.

Recent theoretical work has been concerned with three issues: generalizing the association terms in APACT to treat mixtures where different species have different types of Lewis acid-base properties, developing a rigorous site-site perturbation theory that is free of the assumptions made in the traditional van der Waals approach, and trying to systematically determine parameters for a large number of compounds so that they can be correlated to measurable molecular properties.

The Associated-Perturbed-Anisotropic-Chain Theory was developed to treat hydrogen-bonding molecules. The original theory could treat linear associating species like the alcohols and dimerizing species like acetic acid as well as mixtures of these compounds with 'diluents' such as alkanes. However, other types of complexes can form and this leads to very different behavior. The classic example is a mixture of acetone and chloroform. Neither acetone nor chloroform will hydrogen bond by themselves, but they will hydrogen bond with each other to form dimers; each also will hydrogen bond with an alcohol and with chains of associated alcohol molecules. For binary mixtures, there are four different kinds of behavior that can occur. These can be represented schematically as shown in Figure 1. The three figures show the different association species that are present in a binary mixture. The first figure is for the system where both components I and J are amphoteric (both acidic and basic such as an alcohol). This system can have an infinite number of association species. However, the distribution of the species is such that the larger species are present in very dilute concentrations. The second figure is for the system where component I is amphoteric and the component J is either acidic or basic but not amphoteric. The association species have either no J or a J molecule at one end. The third figure is for the system where one component is acidic and the other is basic. There is only one associated species and a total of three species in the mixture.

Multicomponent mixtures can be very complicated because one must take into consideration all of the possible associated species that form among the Lewis acids, Lewis bases and amphoteric molecules that are present. In modelling such systems, one must have mathematical expressions that describe the composition dependence for all the different types of association that can occur. Some simple examples of this are shown in Figure 2. In this figure, n_T is the 'total' number of moles present and n_0 is the number of moles that would be present if there was no association. For the first case, where

a		J					
		0	1	2	3	…	j
	0		I_0J_1	I_0J_2	I_0J_3	…	I_0J_j
	1	I_1J_0	I_1J_1	I_1J_2	I_1J_3	…	I_1J_j
	2	I_2J_0	I_2J_1	I_2J_2	I_2J_3	…	I_2J_j
I	3	I_3J_0	I_3J_1	I_3J_2	I_3J_3	…	I_3J_j
	⋮	⋮	⋮	⋮	⋮		⋮
	i	I_iJ_0	I_iJ_1	I_iJ_2	I_iJ_3	…	I_iJ_j

b		J	
		0	1
	0		I_0J_1
	1	I_1J_0	I_1J_1
	2	I_2J_0	I_2J_1
I	3	I_3J_0	I_3J_1
	⋮	⋮	⋮
	i	I_iJ_0	I_iJ_1

c		J	
		0	1
I	0		I_0J_1
	1	I_1J_0	I_1J_1

Figure 1. Association species present in a binary system containing (a) two amphoteric components, (b) one amphoteric and one acidic or basic component, and (c) one acidic and one basic component.

both components are amphoteric, association is always present and the different association constants for the two components cause n_T/n_0 to be different in the two pure component limits, but the variation with composition is nearly linear between the two pure component limits. For the second case, where one component is amphoteric and the other is acidic, the limit for the pure acidic component shows no association as association can occur only between an acidic site and a basic site. Identical behavior is observed for a system of an amphoteric compound and a base. In the third case, where one component is acidic and the other is basic the pure component limits show no association for both components, but there are cross associations to form dimers.

We have made a first attempt to derive general expressions which will represent the behavior of multicomponent mixtures of molecules that exhibit acidic and/or basic properties. This new model, which we call the Acid-Base-Perturbed-Anisotropic-Chain Theory (ABPACT) (Economou *et al.*, 1990) shows good agreement with experimental data for mixtures containing two or more associating species. For example, Figure 3 shows the comparison between the prediction of the phase behavior for the Methanol-Chloroform system at 1 atm and the experimental data of Gmehling and Onken (1981). Figure 4 shows the comparison between the prediction of the phase behavior of Ethanol-Acetone system at 1 atm and the experimental data of Gmehling and Onken (1981). From these two figures it can be seen than for systems containing compounds that are Lewis acids (chloroform) or bases (acetone) or amphoteric (ethanol), the theory predicts the phase behavior with reasonable accuracy. In Figure 5 it can be seen that the ABPACT predicts the phase behavior for the n-Butanol-Chloroform system at 1 atm better than the Peng-Robinson equation. This system is similar to the ethanol-chloroform system in that ethanol is amphoteric and chloroform is a Lewis acid. The derivation of this equation and a discussion of its applicability and limitations is given by Economou *et al.*, (1990).

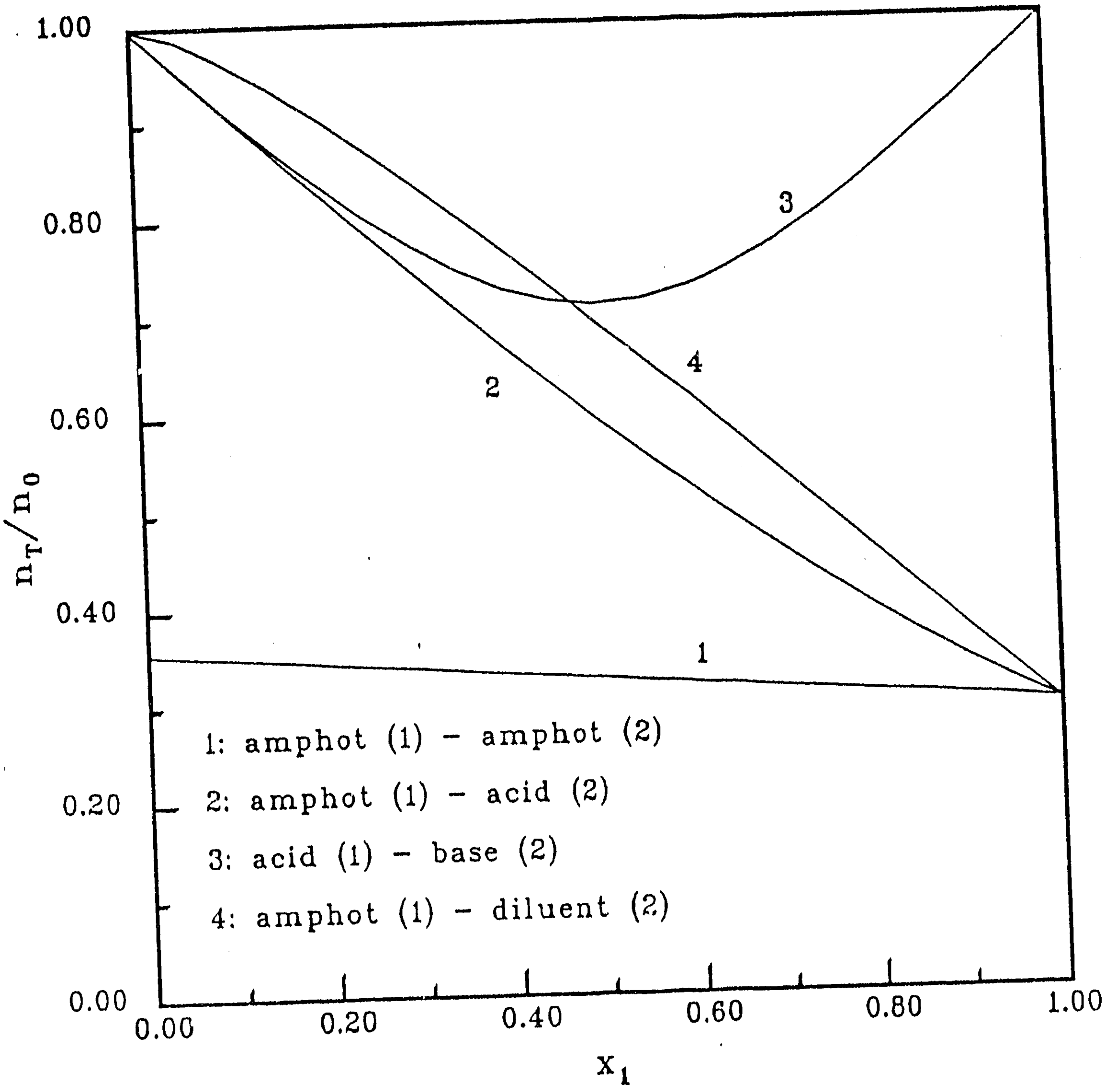


Figure 2. Composition dependence of the various kinds of association.

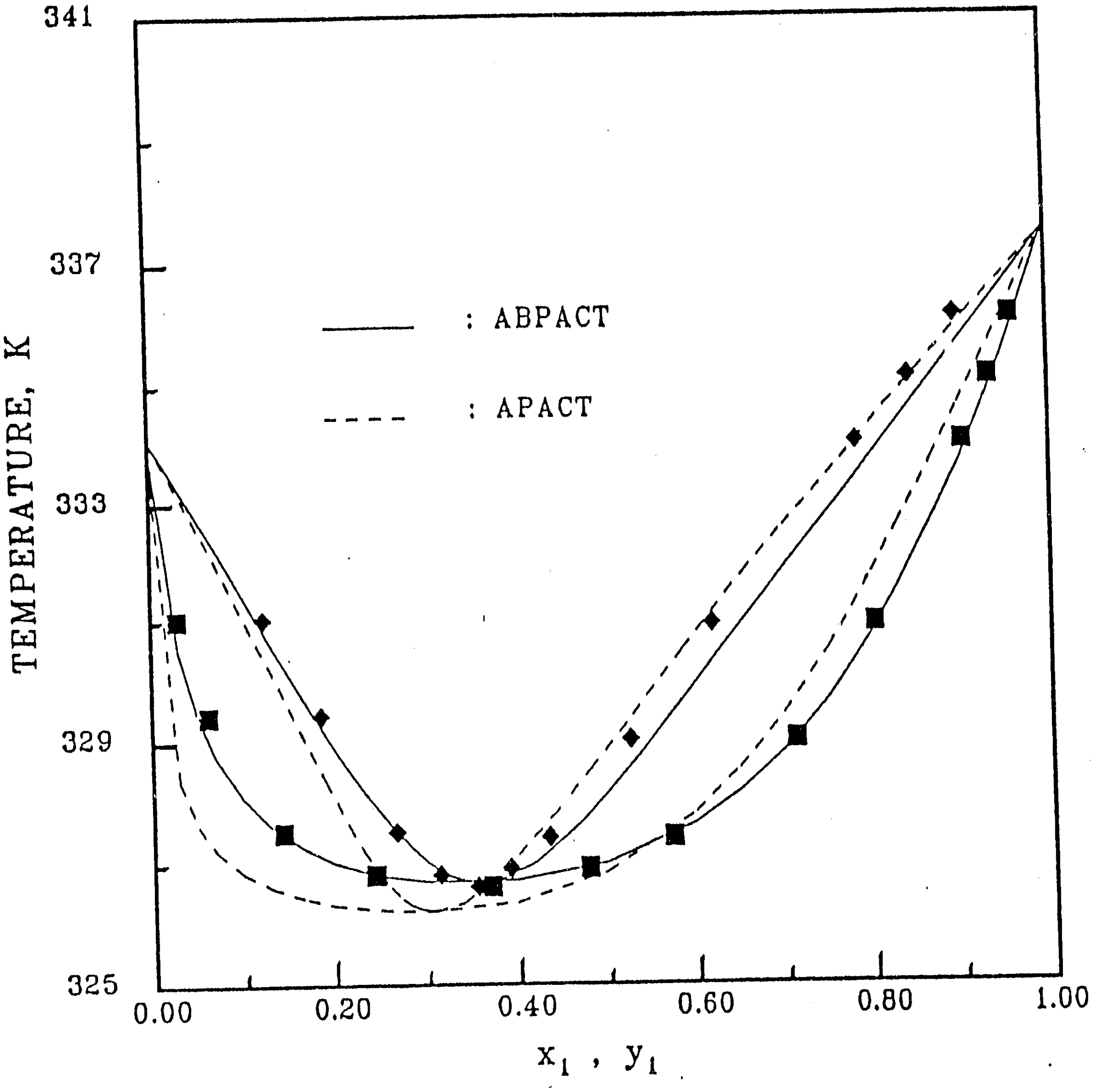


Figure 3. Comparison of experimental VLE data with predictions using APACT and ABPACT for Methanol(1)-Chloroform(2) at 1 atm. Experimental data are from Gmehling and Onken (1981).

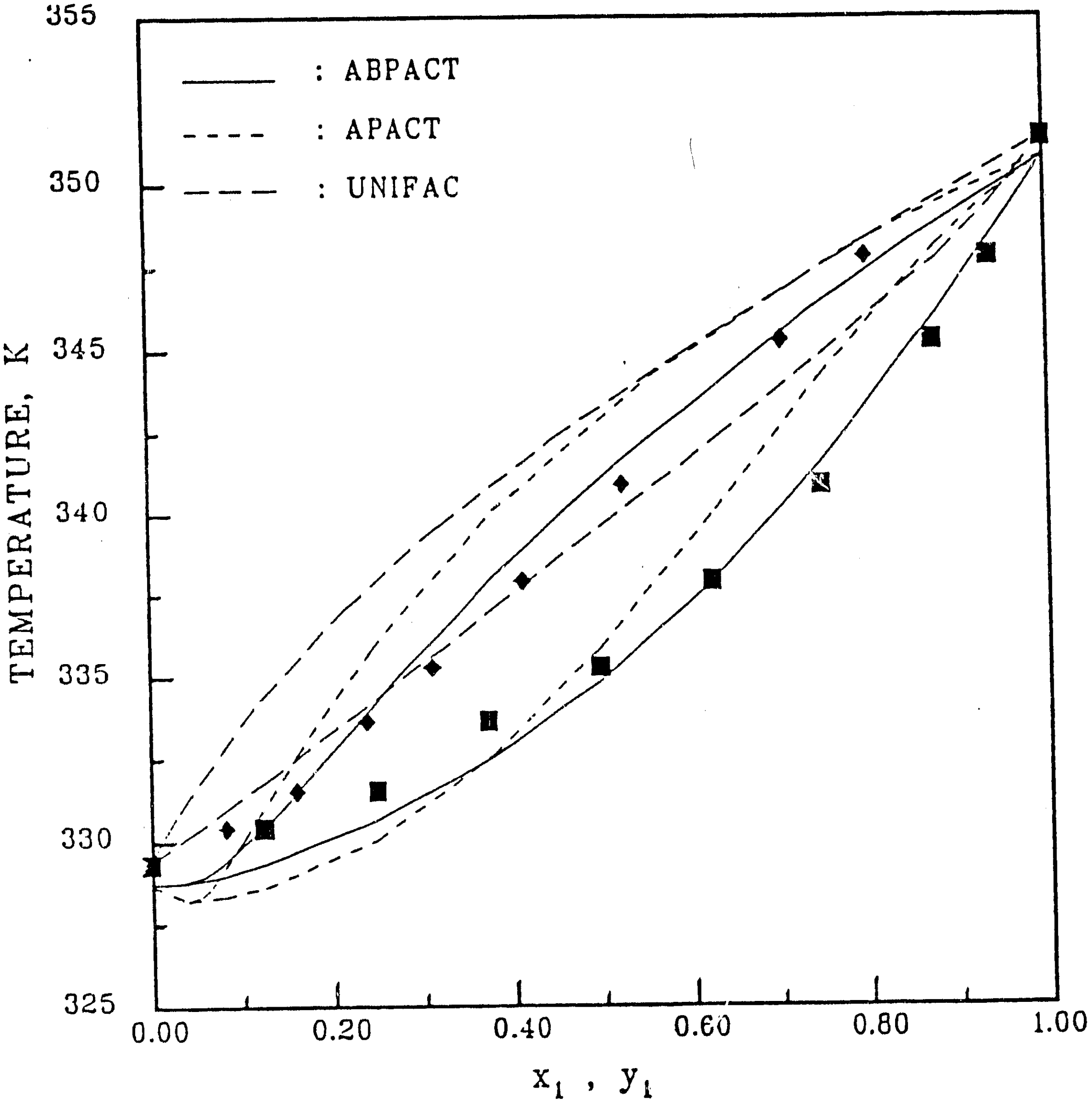


Figure 4. Comparison of experimental VLE data with predictions using APACT, ABPACT and UNIFAC for Ethanol(1)-Acetone(2) at 1 atm. Experimental data are from Gmehling and Onken (1981).

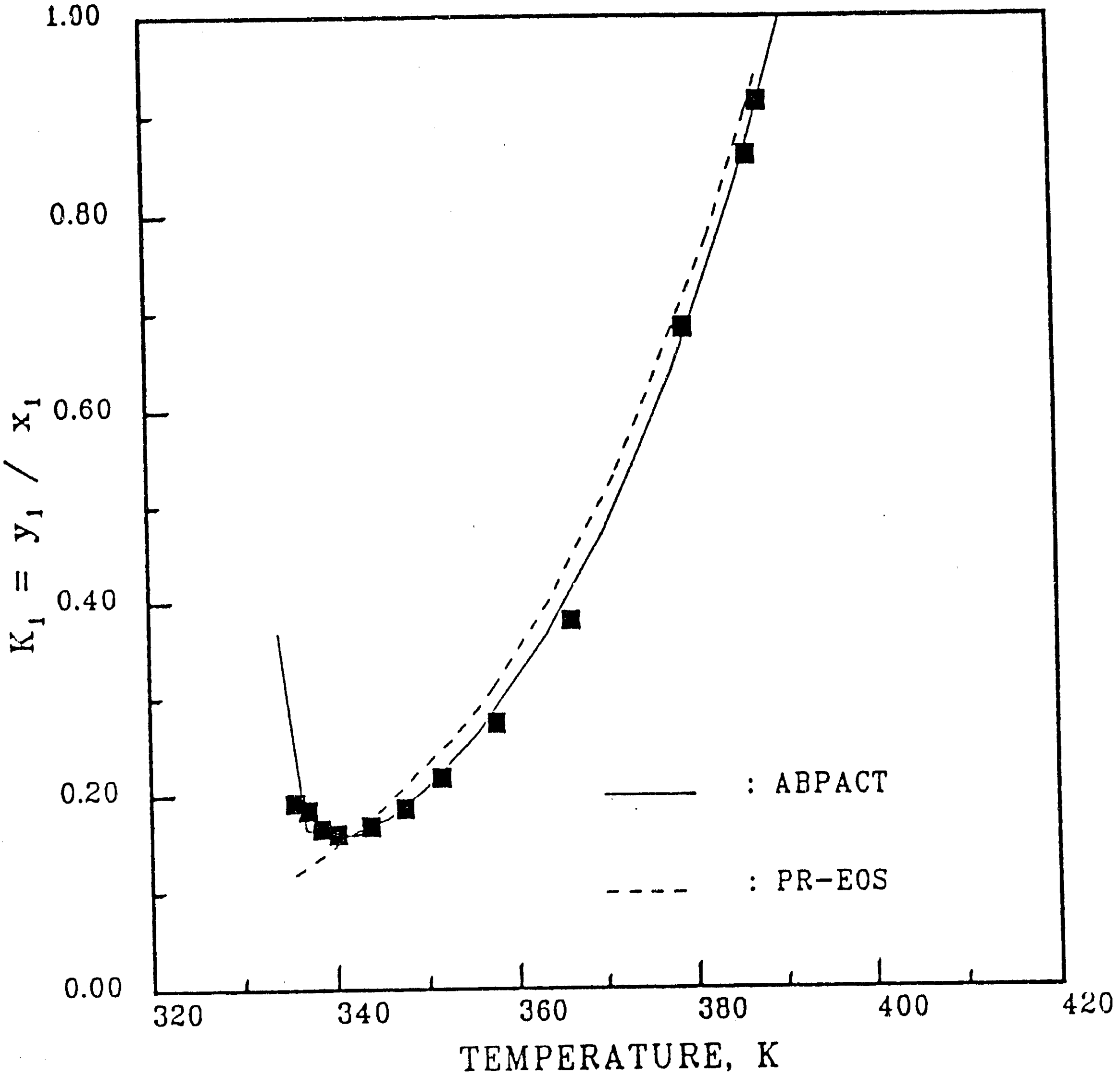


Figure 5. Comparison of experimental VLE data with predictions using ABPACT and Peng-Robinson EOS for n-Butanol(1)-Chloroform(2). Experimental data are from Kogan (1966).

In conjunction with our efforts to derive general multicomponent expressions for the effect of Lewis acid-base interactions, we have been working to understand the similarities and differences between our treatment of association and that of Wertheim (1984). Our treatment of association relies on the framework of chemical equilibria. While this framework is thermodynamically rigorous, its application involves a number of assumptions. Wertheim's approach to treat association relies on the framework of perturbation theory; this framework also is rigorous but relies on quite different assumptions. However, these two approaches should give the same result if the two derivations can be carried out (at least to the extent the different formalisms allow) using the same assumptions in each approach.

The derivation that we have used is based on the chemical equilibria formalism. In this treatment, a pure fluid that associates is treated as a multicomponent mixture of all the species present (monomers, dimers, etc.). Heidemann and Prausnitz (1976) showed that the equations for chemical equilibria could be solved analytically and imbedded into the equation of state once assumptions are made regarding mixing rules used in the equation of state and the variation of the equation of state parameters with the size of the species.

In the Wertheim derivation, association is modelled as short-ranged directional attractions. Though these theories are quite different in their approach, for the cases that we have been able to study to date, we find the two approaches give essentially the same answer when they are compared for the same types of systems. Jackson *et al.*, (1988) have compared the Wertheim approach with Monte Carlo simulations of spheres with a single associating site. Figure 6 shows the mole fraction of monomer for a dimerizing species as a function of density. The lines are predictions using the approaches of Wertheim (1984), Elliott *et al.*, (1990) and APACT. The Elliott *et al.* equation was derived from APACT but corrected one of the original simplifying assumptions. One sees that the results of Elliott *et al.*, agree almost perfectly with Wertheim's perturbation theory results and with the Monte Carlo data of Jackson *et al.*, (1988). This clearly shows the equivalence of these two quite different approaches for dimerizing species. We also have been able to show the equivalence of the two theories for systems that form linear associated species (chains). We presently are working to determine if these theories are equivalent for all bonding schemes.

The third aspect of the theory we have considered is the treatment of large molecules that can be considered to be made up of sites. In this site-site interaction approach, molecules are considered to be made up of sites that interact with each other and with sites on other molecules. A site is either an atom or a group of atoms that can be characterized by its potential function. These sites are identified by their physical properties (size, polarizability, dipole or quadrupole moment, and acid-base properties) and their positions with respect to other sites on the same molecule. One advantage in using this approach is that the sites come within site dimensions of each other and that the physical characteristics of a site are not smeared over the whole molecule. In a molecular interaction approach the molecules come within molecular dimensions of each other and the molecule has net properties which are the contributions of all the sites that make up the molecule. The physical picture resulting from the site-site interaction approach and a molecule-molecule interaction approach are contrasted in Figure 7.

An advantage of the site-site interaction approach is that it is applicable to multicomponent mixtures without using any additional mixing rules or parameters, and therefore a wide variety of compounds and mixtures can be treated. Figures 8 to 10 show comparisons between the predictions using the site-site perturbation theory (SSPT) and experimental data for several systems. Details of the derivation and application of the SSPT are given by Walsh *et al.*, (1990).

The fourth aspect of our theoretical work is concerned with determining molecular and site parameters so that the theory can be applied to a wider variety of systems. In

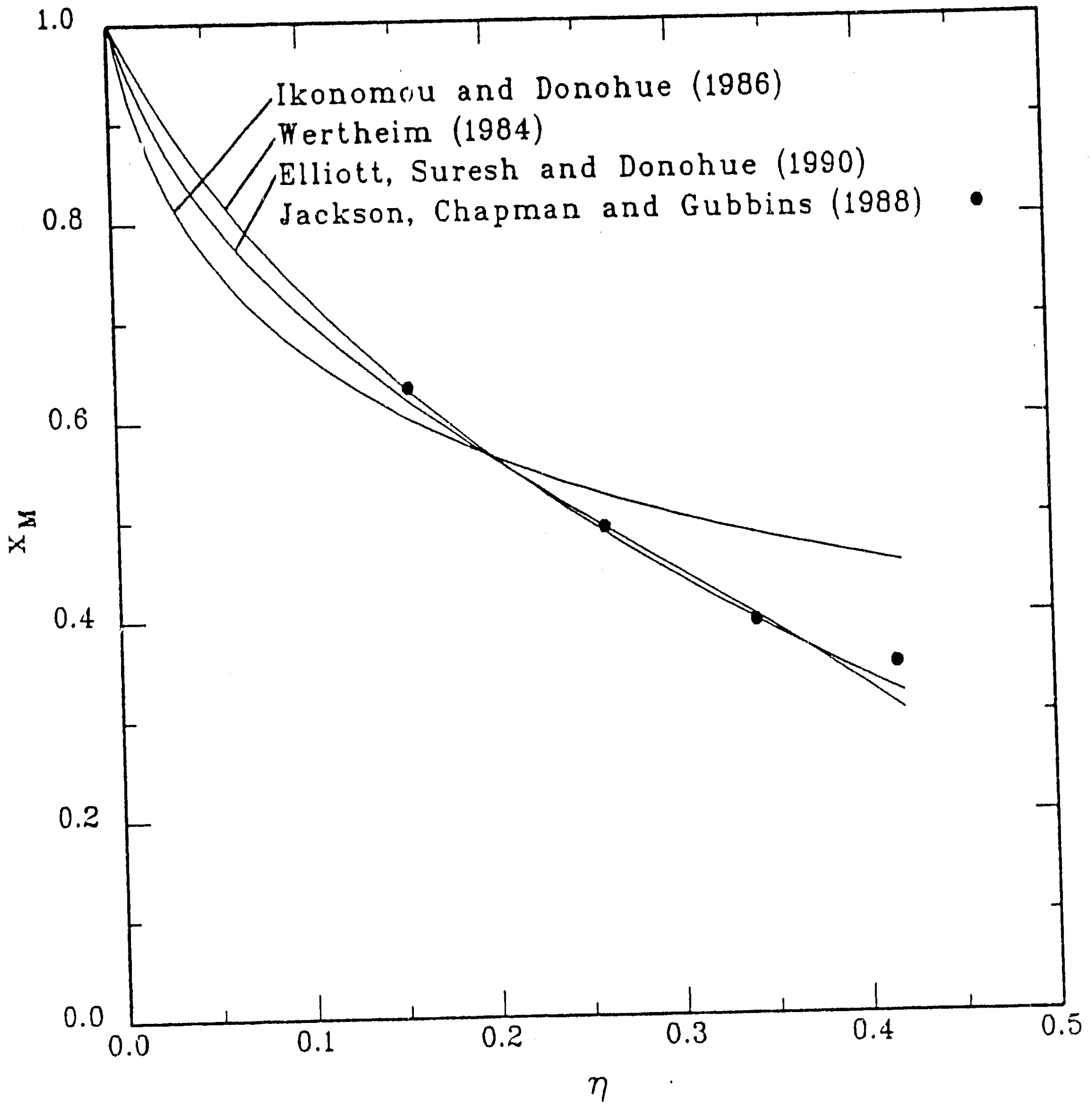


Figure 6. Mole fraction of monomer for a dimerizing species. The simulation data of Jackson *et al.*, (1988) are compared with predictions using the theory of Wertheim (1984) and of Elliott *et al.*, (1990) and APACT (Ikonomou and Donohue, 1986).

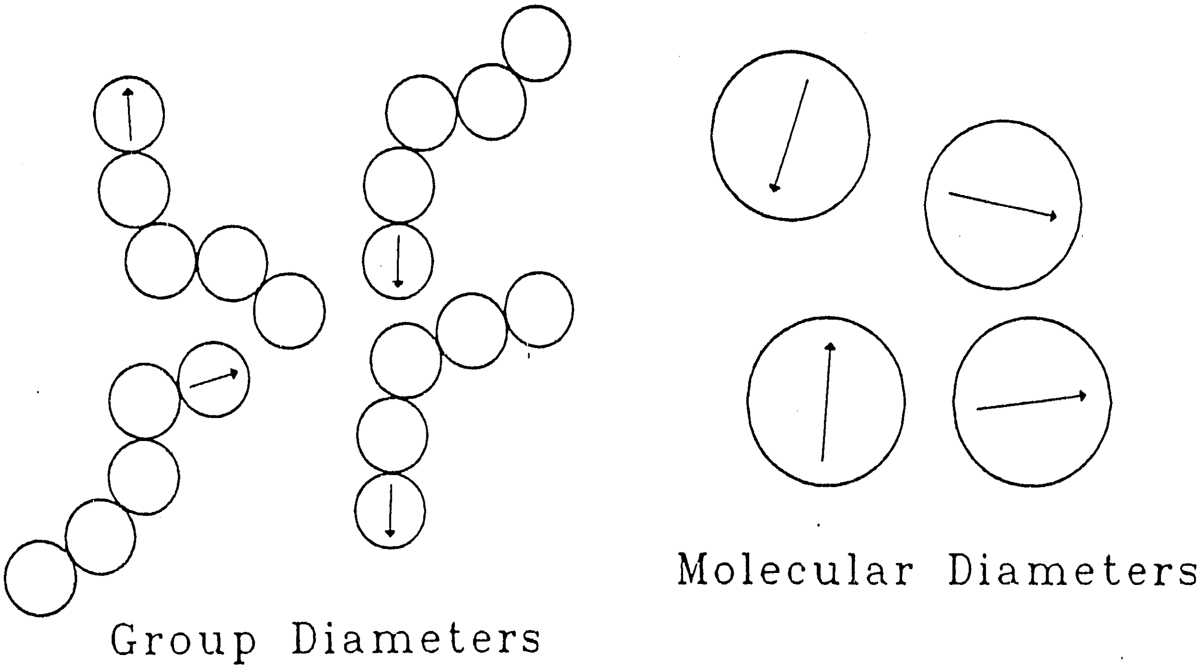
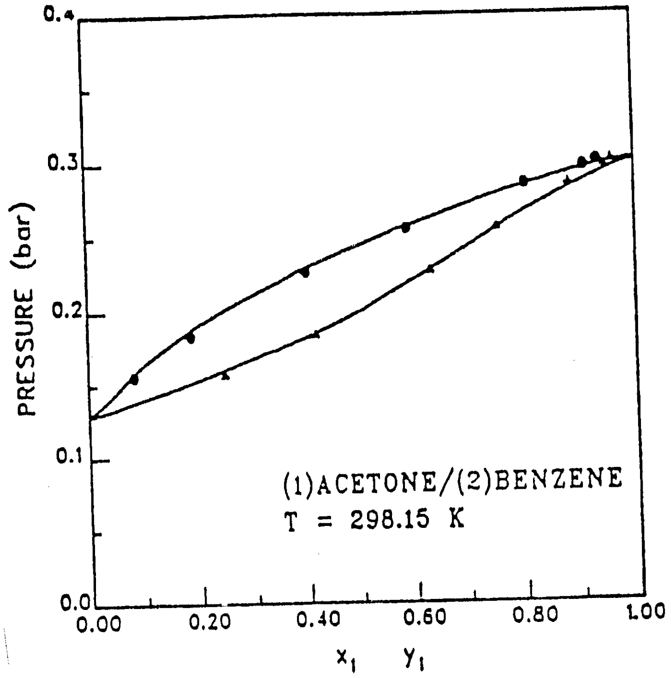


Figure 7. The physical pictures resulting from site-site interaction versus molecule-molecule interaction approaches. Both pictures are for a multifunctional compound such a chloro-butane. As shown the molecule-molecule interaction approach is unrealistic.



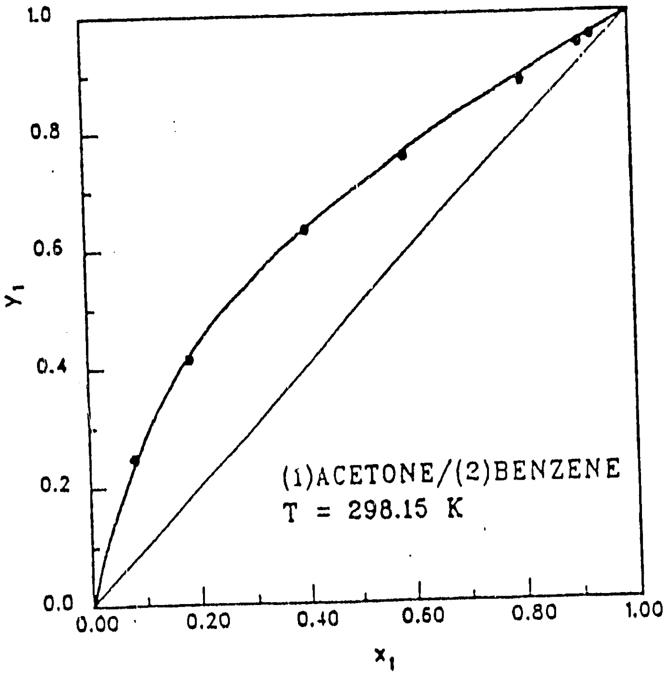


Figure 8. Comparison of experimental VLE data with predictions using the site-site interaction PACT for Acetone(1)-Benzene(2). Experimental data are from Tasic *et al.*, (1978). In these calculations, acetone is treated as having three sites (two CH_3 sites and one $C = O$ site) and benzene is treated as having six (aromatic CH) sites. These sites interact with dispersion forces, induction forces ($C = O$, aromatic CH), dipolar forces ($C = O$), and quadrupolar forces (aromatic CH).

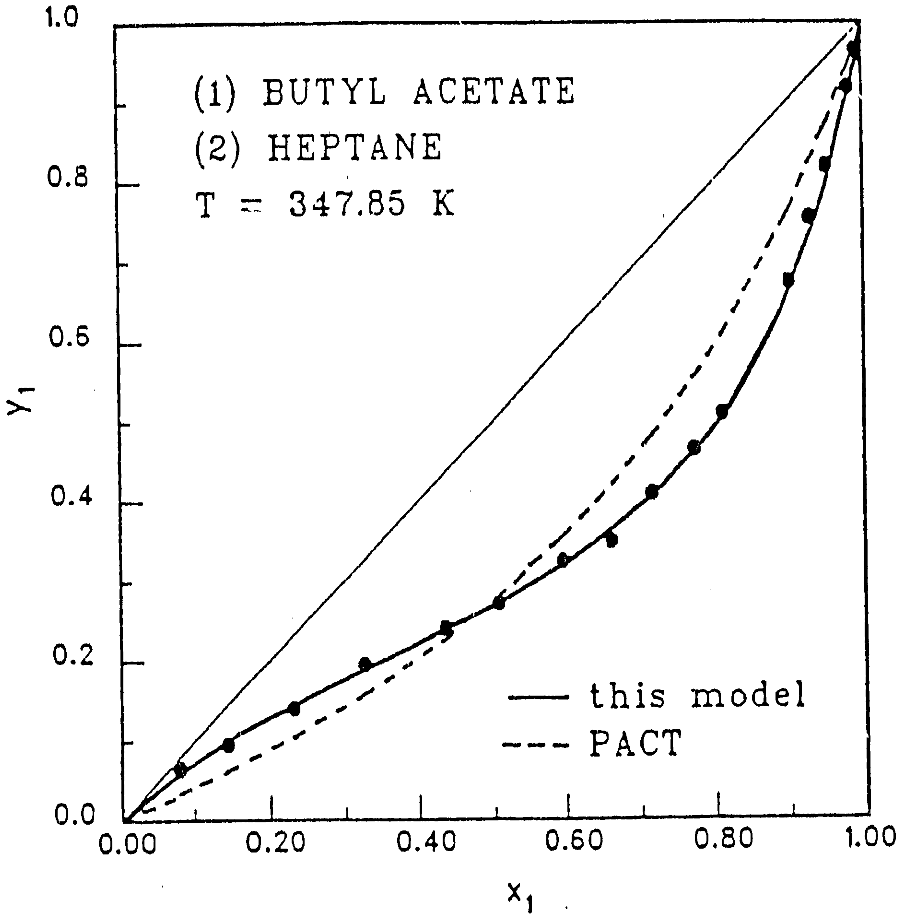


Figure 9. Comparison of experimental VLE data with predictions using the site-site interaction PACT and the original PACT for Butyl Acetate(1)-Heptane(2). Experimental data are from Scheller *et al.*, (1969). In these calculations, butyl acetate is treated as having six sites (two CH_3 sites, three CH_2 sites and one $O-C=O$ site) and heptane is treated as having seven sites (two CH_3 sites and five CH_2 sites). These sites interact with dispersion forces, induction forces ($O-C=O$) and dipolar forces ($O-C=O$).

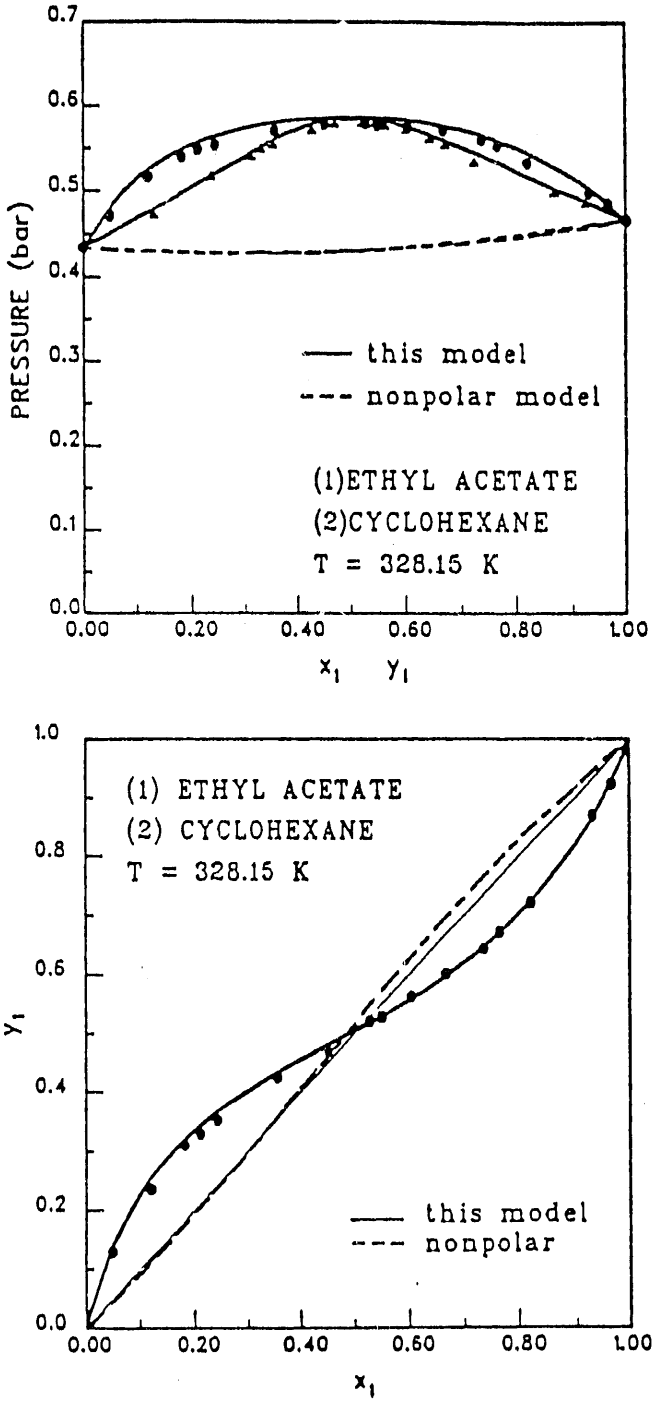


Figure 10. Comparison of experimental VLE data with predictions using the site interaction PACT and a non-polar model for Ethyl Acetate(1)-Cyclohexane(2). Experimental data are from Ohta and Nagata (1980). In these calculations, ethyl acetate is treated as having four sites (two CH_3 sites, one CH_2 site and one $O-C=O$ site) and cyclohexane is treated as having six CH_2 sites. These sites interact with dispersion forces, induction forces ($O-C=O$) and dipolar forces ($O-C=O$).

this effort, we are both correlating parameters that have been determined by regressing macroscopic thermodynamic properties (vapor pressure, liquid density and second virial coefficients) and determining parameters directly from physical properties of the molecule (molecular size, polarizability, dipole moment, quadrupole moment etc.).

Dickman and Hall (1986) have given a prescription in their Generalized Flory (GF) theory for calculating the parameter 'c' from the excluded volume of the chain molecule. Honnell and Hall (1989) developed the Generalized Flory-Dimer (GFD) theory that gives better agreement with simulation results than the GF theory. By fitting the GFD results with the GF theory, values for the parameter 'c' can be obtained directly from molecular shape. The values of the parameter 'c' obtained using this method as a function of carbon-number for n-alkanes are shown in Figure 11. Results of our computer simulations (which are discussed later) suggest that the PHCT would be improved if the GFD values are used rather than treating it as an adjustable parameter.

Jin *et al.*, (1986) correlated the parameters 'c', 'q', and 'v^*' with carbon number for a number of hydrocarbons. A group contribution method was developed and molecular parameters can be calculated from the constituent groups on the molecule. Vimalchand *et al.*, (1988) correlated equation of state parameters for associating molecules with bondi volumes. Parameters for a number of compounds, including aliphatic hydrocarbons, quadrupolar and dipolar compounds and associating compounds were correlated. The parameters 'c' and 'q' are well correlated with each other and also correlate well with bondi volume, as is 'v^*', for the different homologous series studied. For alcohols, that associate to form linear species, it was found that the standard enthalpy of association was independent of the carbon number, and that the standard entropy of mixing decreased with increasing carbon number and then levels off. This would be expected as the enthalpy depends only on the associating sites but the entropy depends on the partition function of the entire molecule.

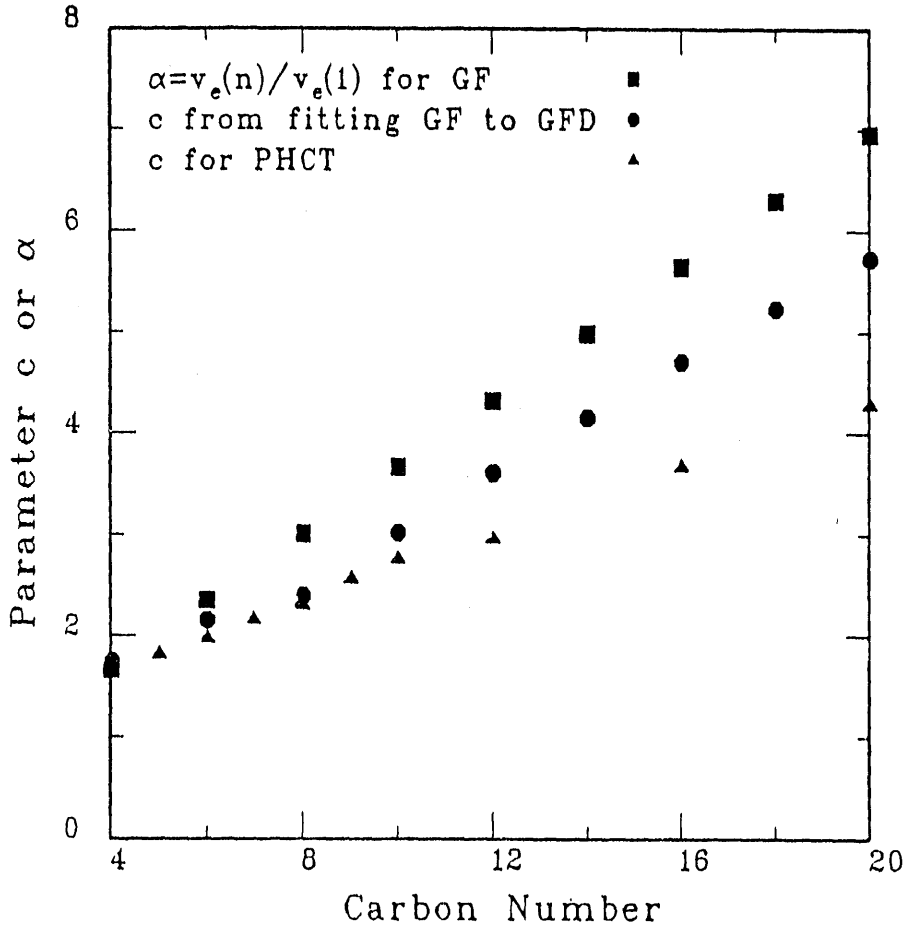


Figure 11. The parameter 'c' as a function of carbon-number for n-alkanes obtained by fitting the GF (Dickman and Hall, 1986) theory to the GFD (Honnell and Hall, 1989) theory.

In the SSPT, repulsive, dispersion, induction, and polar interactions are calculated from site-site potential functions and site-site pair correlation functions. Each site is characterized by its size, polarizability, and moments (dipole and quadrupole). In our work to date, the dipole moment, quadrupole moment and polarizability have been obtained from the literature and the parameters corresponding to the sites size, excluded volume and interaction volume have been regressed from pure-component vapor pressure and density data. Values for these parameters for n-alkanes and ketones are shown in Figure 12. These parameters show excellent correlation with carbon number for each homologous series studied and from this the parameters for the groups that make up these molecules such as, CH_3, CH_2, CH, C, $C = O$, CH_2Cl, $O = C - O$ etc., are obtained. Properties of a large number of pure components and mixtures can be calculated using these group parameters.

Figure 13 shows the variation in the contributions to the total attractive energy for the ketones. As expected, one sees that the polar contribution is approximately constant (actually it decreases somewhat because the dipole moment is not a constant), the induction forces go up linearly with carbon number, and the dispersion forces increase quadratically.

Though it should be obvious from the discussion above and from the papers cited, that we have made considerable progress in correcting the deficiencies in the PHCT-based equations, we are not yet able to make *a priori* predictions of phase behavior. However, we believe we will be able to develop a model which has only one adjustable parameter per site. The work of Hall and coworkers has shown how the parameter 'c' can be determined from molecular size and geometry. Our own work on the site-site perturbation theory will allow us to calculate the parameter 'q' directly from the molecular shape as well. This leaves only one parameter to be determined from macroscopic data. Jin and Donohue (1990) have demonstrated for ionic systems that these equations can give accurate results with only one adjustable parameter. In continuing this work, we intend to apply this one-parameter approach to coal-related compounds.

Computer Simulations

Though there is a great deal of accurate experimental data for small molecules (i.e. molecules with molecular weights less than 200) and there also is considerable data for polymeric molecules, relatively little is known about the molecules of intermediate size that are found in fossil fuels. As a consequence of this, it is difficult to assess the accuracy or even the validity of models developed for coal-derived fluids. Therefore, computer simulations, which can be used to systematically test the various contributions to the equation of state, are an important tool in developing an understanding of the behavior of complex molecules.

Systematic comparisons of various classes of equations of state show that there is relatively little difference in the accuracy of different models that have the same number of adjustable parameters when fitting pure-component properties. However, there are significant differences in the accuracy of the models when they are applied to mixture calculations - especially when the calculations are made without additional adjustable parameters. The primary reason for this difference in accuracy for pure-component and mixture calculations is not due to differences in the mixing rules that are used, but rather is due to the way various equations balance molecular attractions against molecular repulsions. Since the mixing rules are different in the attractive and repulsive terms, if the balancing or partitioning is not done correctly, then mixture calculations will be in error even if pure-component results are quite accurate. Vimalchand and Donohue (1989) have compared the attractive and repulsive terms for several equations of state for chain molecules. In the comparisons, Monte Carlo data of Dickman and Hall (1986) and our own molecular dynamics data were used. In Figure 14 we show the comparison between the theory and the simulations for the attractive and hard-chain terms for

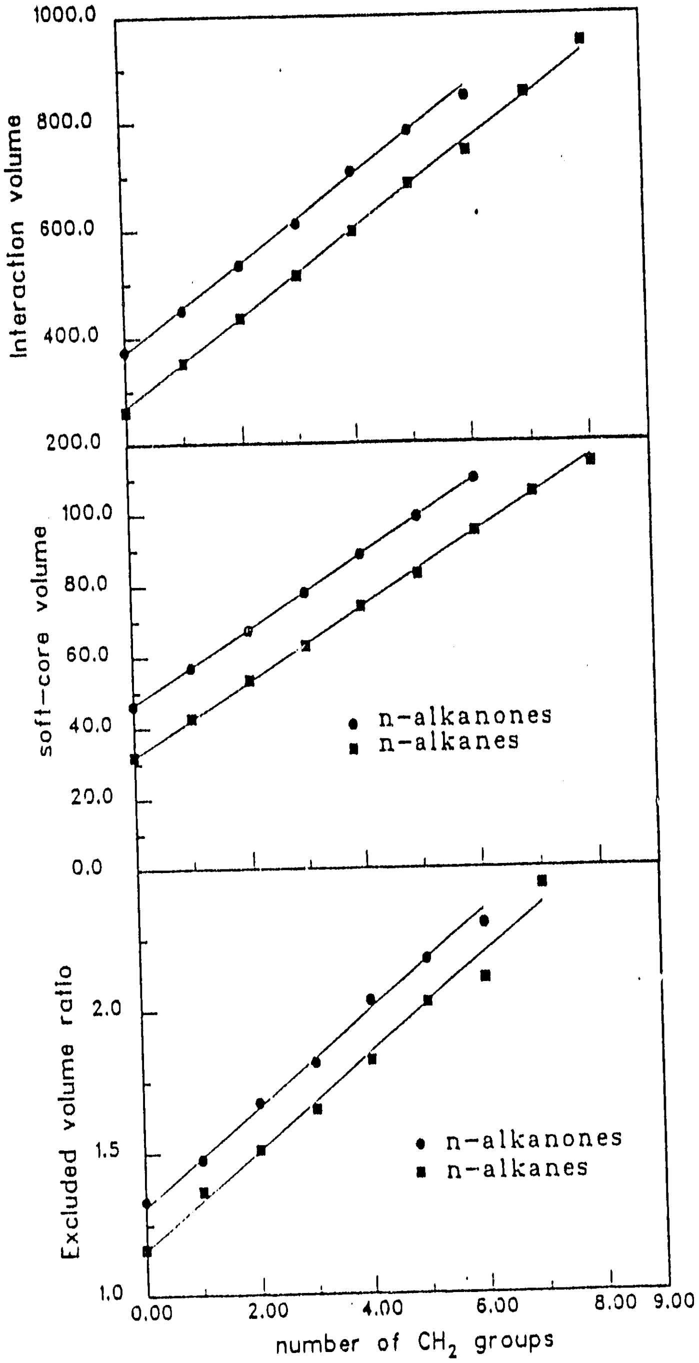


Figure 12. Molecular parameters versus number of methylene groups for the alkanes and ketones. The straight and parallel lines indicate that the parameters realistically reflect the structure of these compounds.

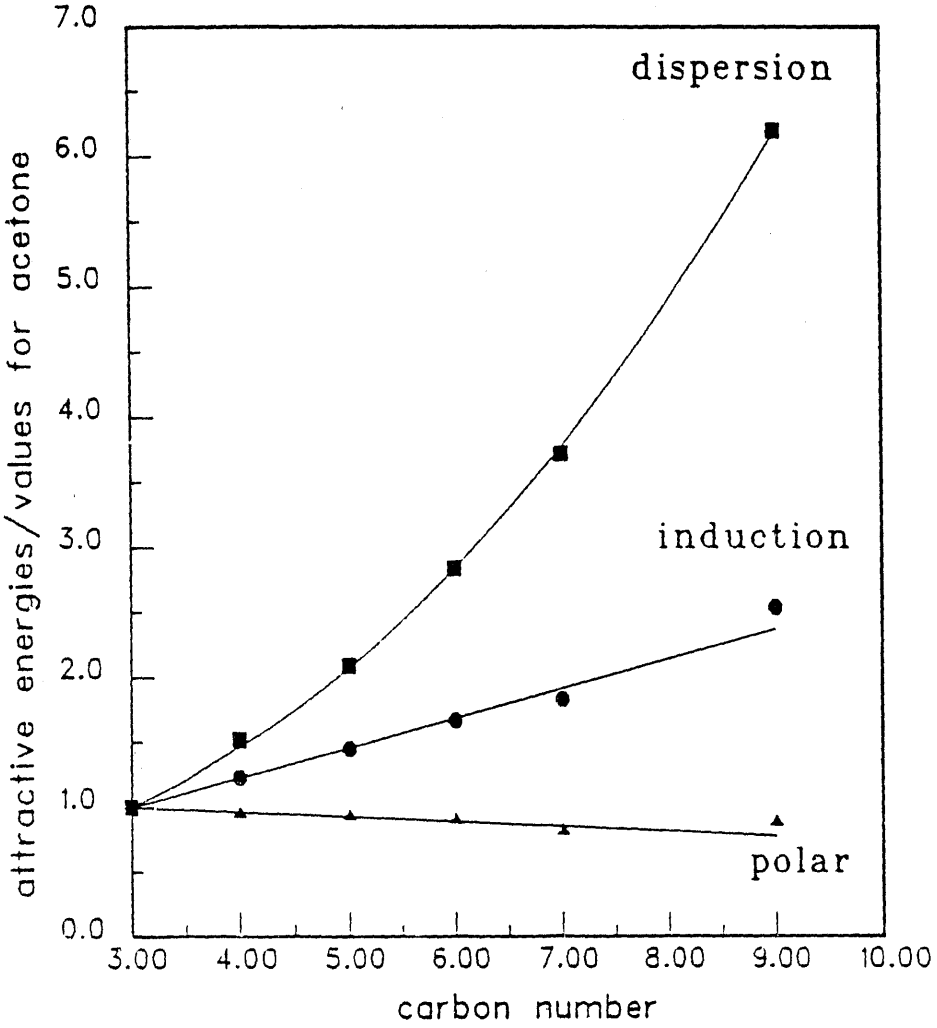


Figure 13. The attractive energies for polar, induction, and dispersion interactions are shown here as a function of carbon number for ketones relative to those for acetone. The change in these energies reflects the change in the number of polar, induction, and dispersion interactions per molecule.

n-butane. Theoretical predictions using PSCT, Flory, Sanchez-Lacombe and Chain of Rotators are shown. Though all the equations fit the PVT data reasonably well, it can be seen that the contribution to the compressibility factor from the various theories are quite different.

In Figure 15 we show a comparison between theory and simulations for the attractive (Z^{att}) and hard-chain ($1 + Z^{rep}$) terms for n-octane. The simulations were performed with 8-mers made of fused Lennard-Jones spheres. Results from simulations using 8-mers made of fused hard spheres (Z^{HC}) are also shown. Theoretical predictions using PSCT and GFD model developed by Honnell and Hall (1989) are shown. It can be seen that the contributions from the theory compare reasonably well with the simulation data. By improving the accuracy of the individual terms through computer simulations, it will be possible to develop even better models for the behavior of large and complex molecules. Although this will not improve calculations for pure components, this will improve mixture calculations considerably.

In our simulations, we have used the Molecular Dynamics algorithms developed by Lee, Haile and co-workers (1988) and our own Monte Carlo algorithms. The simulations are performed using chains made up of overlapping spherical segments interacting with each other with a Lennard-Jones potential or a Hard-Sphere potential. The chains also are modelled as having bond-vibration, bond-bending and bond-rotation potentials. In the Monte Carlo Simulations, the standard metropolis algorithm with periodic boundary conditions is used to sample the randomly generated configurations. As discussed below, these algorithms have been used to generate the results shown in Figures 17 to 19.

While Figures 14 and 15 show that PHCT does a reasonable job of partitioning the equation of state into its attractive and repulsive terms, there are small systematic deviations for larger molecules. As mentioned previously, we have derived a new site-site perturbation theory for chain molecules that removes all the *ad hoc* assumptions in the PHCT-based equations. In the SSPT, the parameter 'q' is the ratio of the interaction

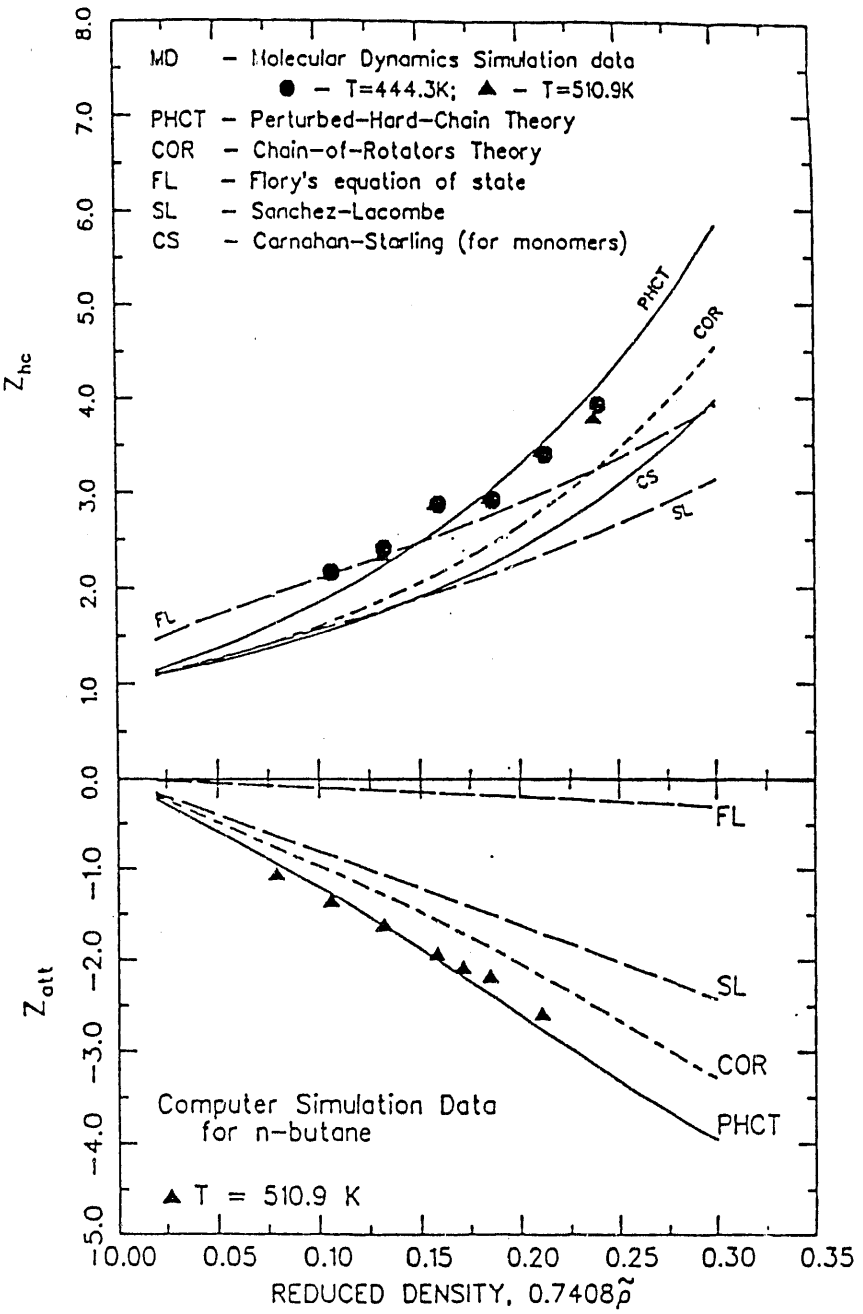


Figure 14. The partitioning of the compressibility into the attractive and repulsive parts for 4-mers. The results shown for PSCT, Flory, Sanchez-Lacombe and Chain of Rotators are for n-Butane.

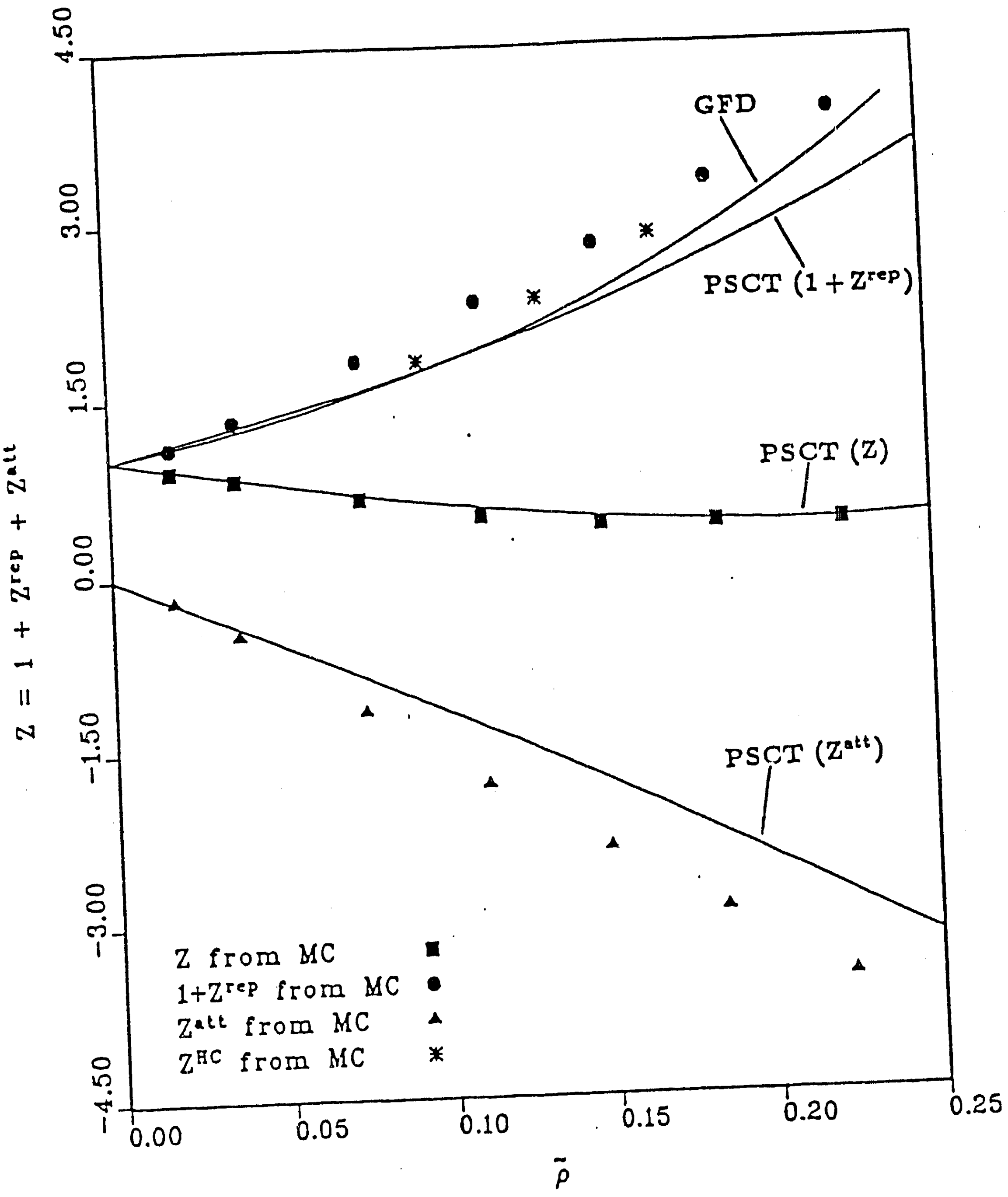


Figure 15. The partitioning of the compressibility into the attractive and repulsive parts for 8-mers. The results shown for PSCT are for n-octane.

volume for the pair of sites under consideration to that for some reference pair of sites. In PHCT this parameter was assumed to be independent of density and temperature, and a pair of hard spheres was used as the reference pair. The interaction volume is the integral of the product of the inter-molecular site-site pair correlation function and the site-site pair interaction potential.

$$I_{\alpha\beta} = \int \bar{u}_{\alpha\beta} g_{\alpha\beta} \bar{r} d\bar{r}$$

where $\bar{u}$ is the dimensionless pair interaction potential, g is pair correlation function and α and β are the pair of sites in consideration. The concept of the 'interaction volume' is illustrated in Figure 16. The pair correlation function $g(r)$ gives the probability of finding a given pair of molecules or sites at a distance r, but does not give any information on the relative orientation of the molecules or their internal configurations. Thus, the pair correlation function reflects the presence of covalently bonded neighboring sites by the existence of a correlation hole. Figure 17 shows the three inter-molecular pair correlation functions for 4-mers, which are made up of two kinds of sites, end and internal, and Figure 18 shows the corresponding integrands appearing in the interaction volume. As expected the correlation hole is smallest for the end-end pair and largest for the internal-internal pair. This is because the end sites have only one neighbor excluding some of the volume for closest approach and the internal sites have two such neighbors. By calculating the pair correlation functions for different sites from the simulations, the assumption about the density independence of the parameter q has been evaluated.

Recently we have made calculations from Monte Carlo simulations for the interaction volume for monomers, 4-mers and 8-mers as a function of density. From these calculations it can be seen that the interaction volume of an n-mer does not scale in a density independent manner with respect to that of monomers. In Figure 19, the interaction volume for monomers is linear over the entire range of density, but the integrals

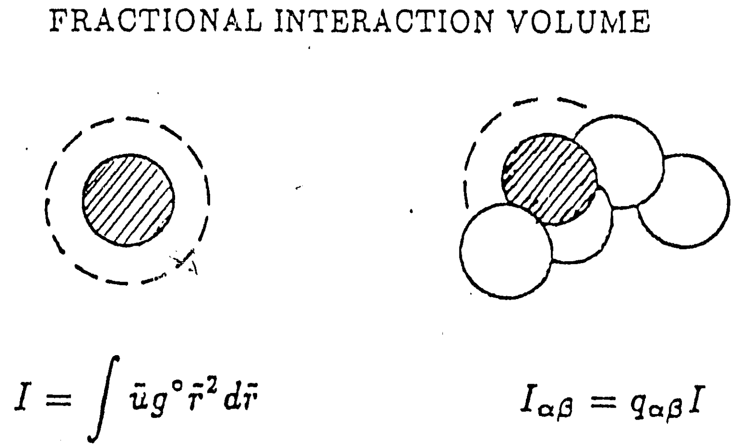


Figure 16. The physical interpretation of the difference between the interaction volume of a small spherical molecule and that of a site on a multifunctional molecule. The interaction volume of a site on a chain molecule is smaller than that of the spherical molecule because the site has covalently bonded neighbors that exclude a portion of the interaction volume.

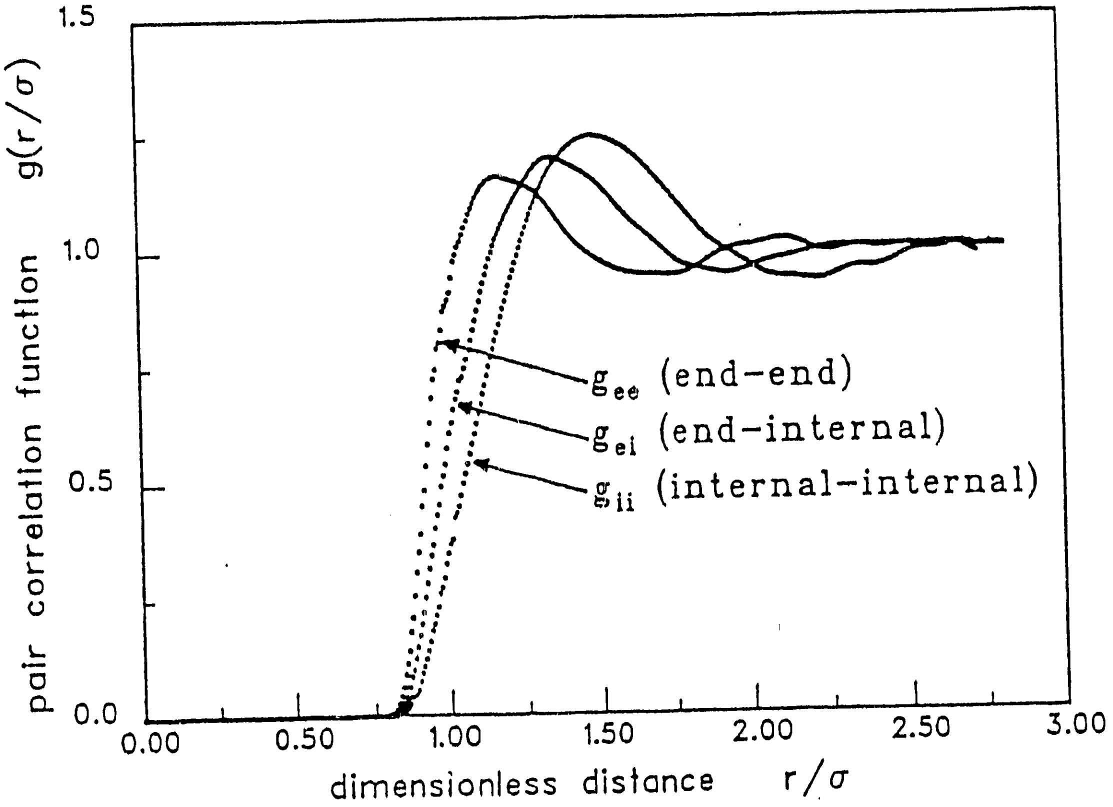


Figure 17. The site-site pair correlation functions for 4-mers. The results were obtained from molecular dynamics simulations of 4-mers.

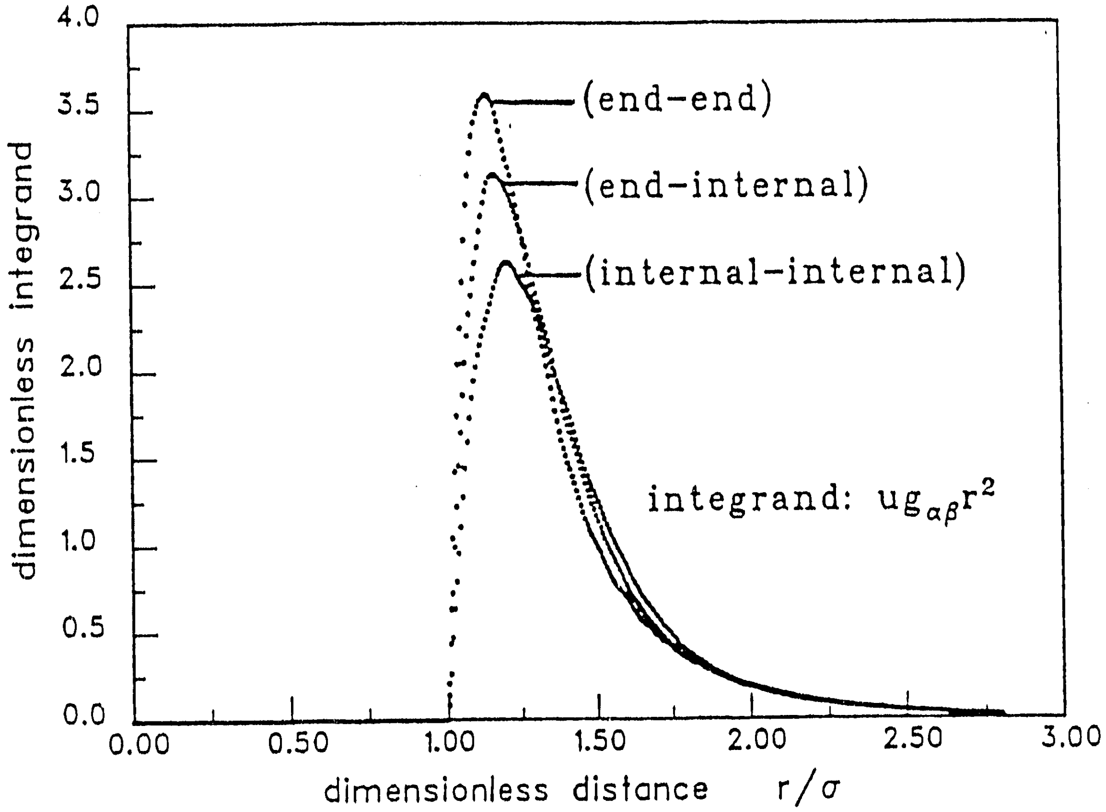


Figure 18. The site-site integrands used in calculating the interaction volume. The results are from molecular dynamics simulations of 4-mers.

for the chain molecules show a distinctly non-linear behavior at low densities. This non-linear behavior has been incorporated into the equation of state and there is a slight improvement in the theory's ability to correlate both vapor and liquid density data. (As mentioned previously, there seldom is much difference in the ability of different equations that have the same number of parameters to correlate pure-component properties). However, correlating the density dependence of the interaction volume does improve the correlation of the molecular parameters with chain length (Figure 20). This should enable us to make better predictions of molecular parameters and therefore macroscopic properties for larger molecules for which there is no experimental data.

Experiments

While most of our work on this research project is theoretical or computational, certain questions only can be answered through laboratory experiments. As discussed above, we have derived equations to describe complex systems, but there is relatively little data that can be used to make definitive tests of the model. We have been using chromatography and spectroscopy to study the effects of hydrogen bonding. Most of our experiments are near infinite dilution in at least one of the species because this allows us to probe specific interactions.

We have measured the retention times of solutes in solvent mixtures using High Performance Liquid Chromatography (HPLC) in a reverse phase packed column with C_{18} as the stationery phase. The solvents (mobile phase) used were aqueous solutions of methanol, ethanol, i-propanol and acetonitrile and the solutes used were benzene, toluene, p-xylene, and cumene. From this data, the ratio of infinite dilution activity coefficients, for a particular solute in two different solvents can be determined. Using this in conjunction with data from Gas Liquid Chromatography, the activity coefficients can be calculated. The results obtained compare well with the activity coefficients obtained

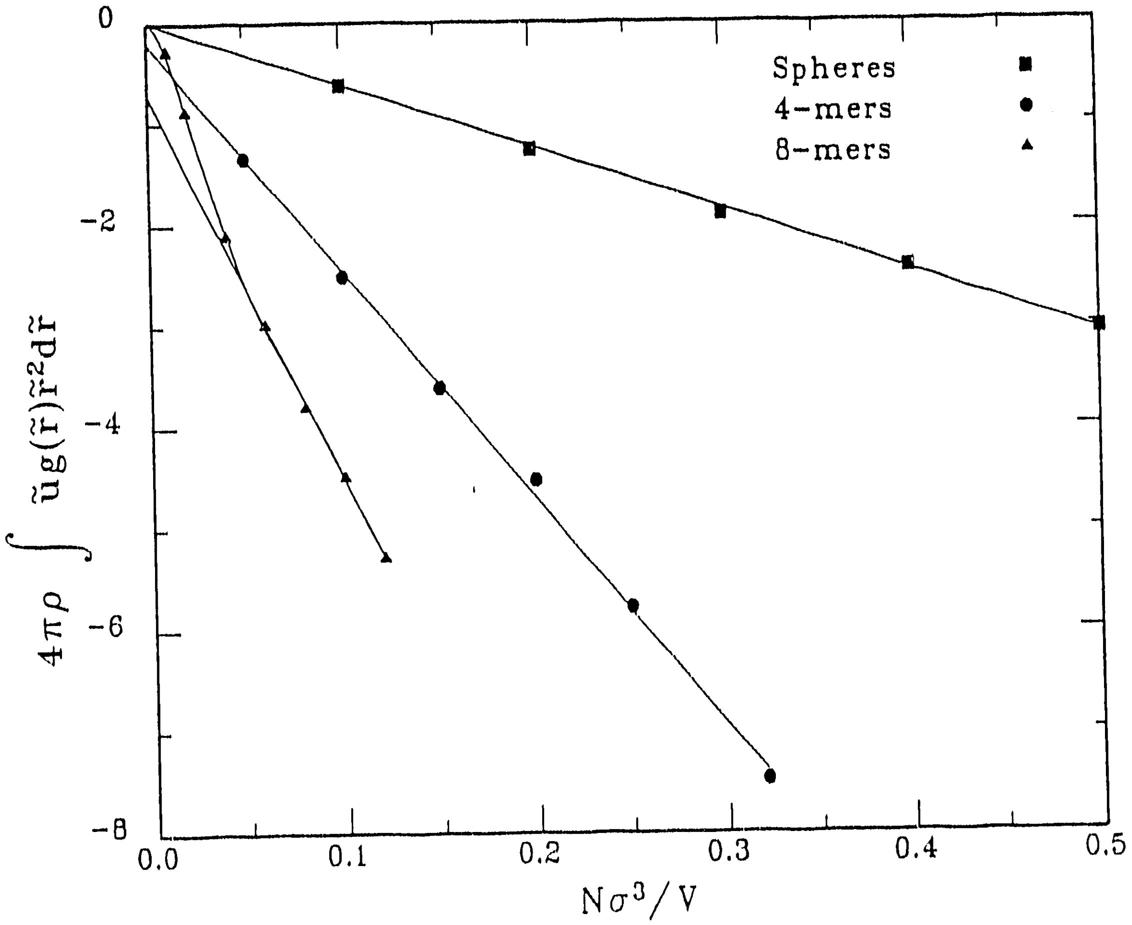


Figure 19. The interaction volume for monomers, 4-mers and 8-mers calculated from Monte Carlo simulations.

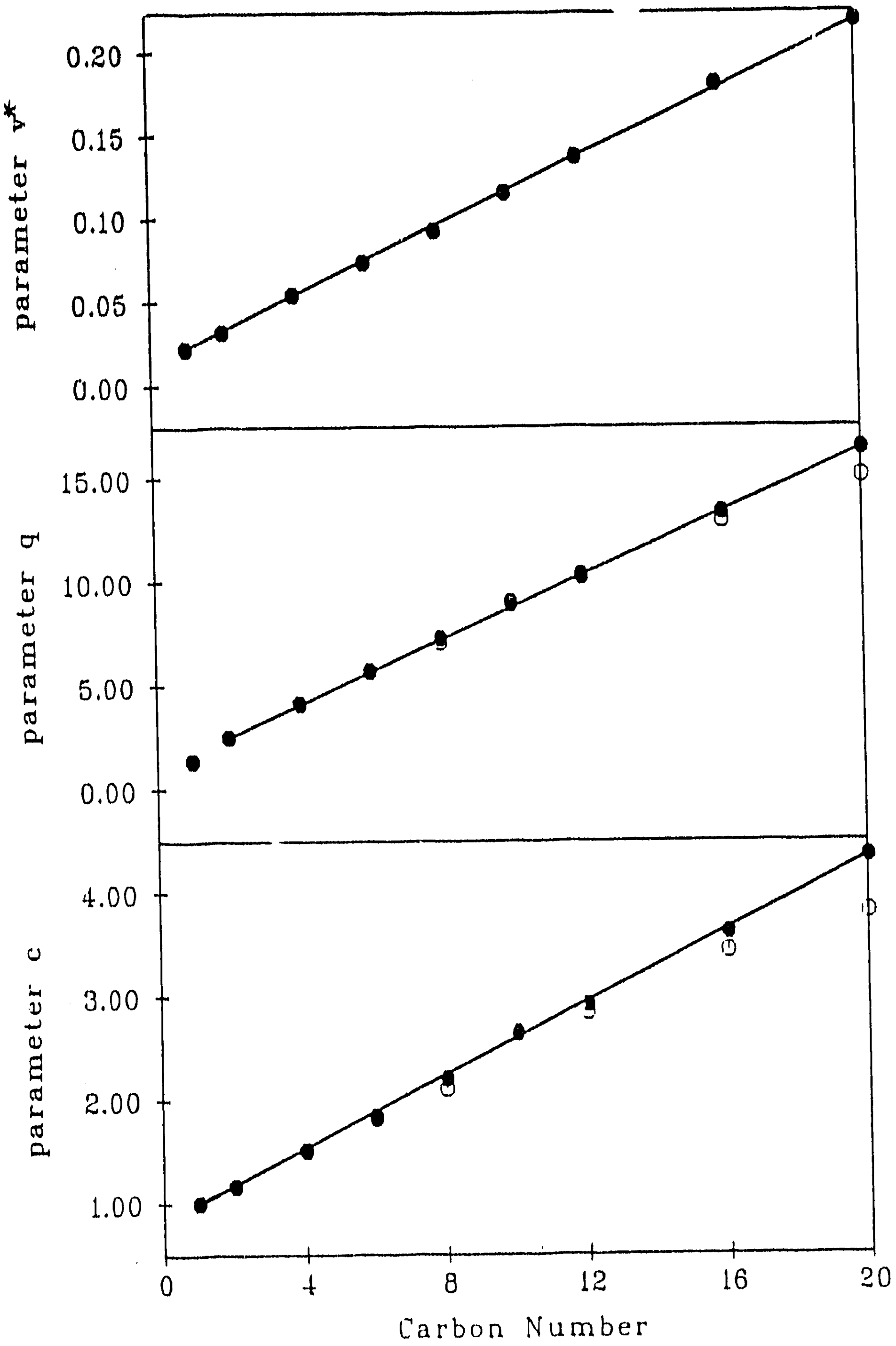


Figure 20. Molecular parameters for n-alkanes used in PHCT calculated from regression of experimental data using an improved density dependence for the interaction volume determined from Monte Carlo simulations. The open symbols are the original parameters.

by Sanemasa *et al.*, (1982). The results were also compared with predictions from different models including UNIFAC, NRTL and APACT. Some of these results are shown in Figures 21 and 22. The strong hydrogen-bonding interactions between water and the organic cosolvents makes these systems quite complex to model and there is considerable variation between the predictions of the various equations. More details of the experimental procedure and the derivation of the theoretical equations are given by Economou *et al.*, (1990).

We also have used Fourier Transform Infra-Red (FTIR) Spectroscopy to study the extent of hydrogen-bonding in liquid mixtures. We have studied systems in which acid-base (hydrogen bonding) interactions between solute, solvent and cosolvent (entrainer) are prevalent. Three types of mixtures are being studied. Type 1 mixtures contain a solute dissolved in an inert solvent with a cosolvent at low concentrations. Type 2 mixtures contain the cosolvent in higher concentrations so that it self-associates. Type 3 mixtures contain a non-inert solvent instead of an inert one as above. The classifications are such that using Type 1 mixtures solute-cosolvent interactions can be studied, using Type 2 mixtures cosolvent-cosolvent interactions can be studied, and using Type 3 mixtures solvent-cosolvent interactions can be studied. The three types of mixtures are schematically illustrated in Figure 23. The spectra obtained for these mixtures exhibit either Lorentzian or a combination of Lorentzian and Gaussian behavior. Lorentzian behavior is observed for systems where one of the association species is prevalent, and Gaussian behavior is observed where there is a distribution in the relative quantities of all the association species. The spectra also exhibit overlapping peaks for the monomeric and associated species. A new data analysis technique was developed to resolve the overlapping peaks that occur in such mixtures. A profile modelling technique also was developed for peaks that observe Gaussian or Lorentzian behavior. A schematic of the numerical peak resolving and data regression technique is shown in Figure 24. The extent of hydrogen-bonding measured using the FTIR technique is compared with the predictions

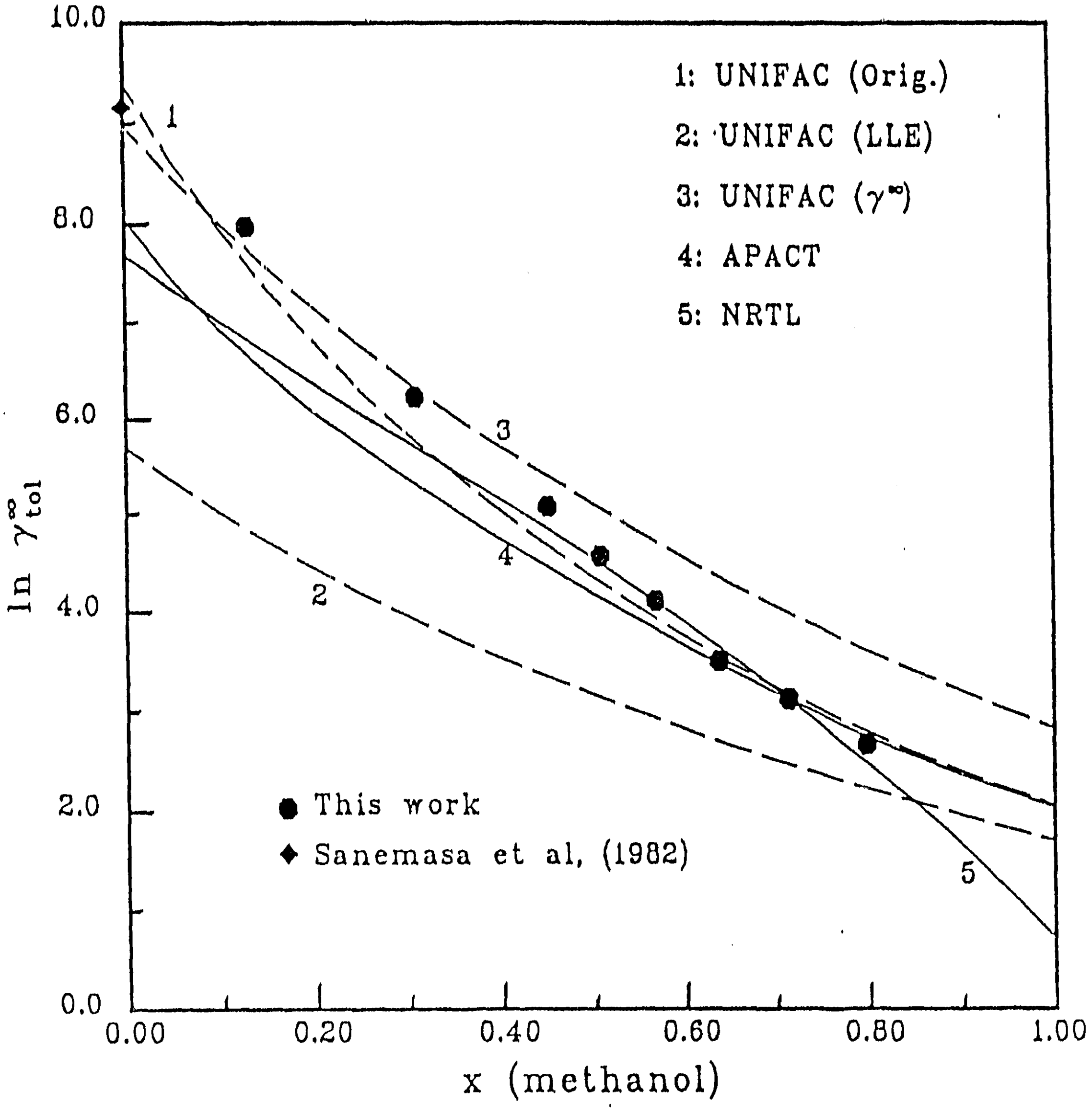


Figure 21. Experimental and predicted values using UNIFAC, APACT and NRTL for $\gamma^\infty_{toluene}$ for methanol-water mixture. The mobile phase is methanol-water and the solute is toluene.

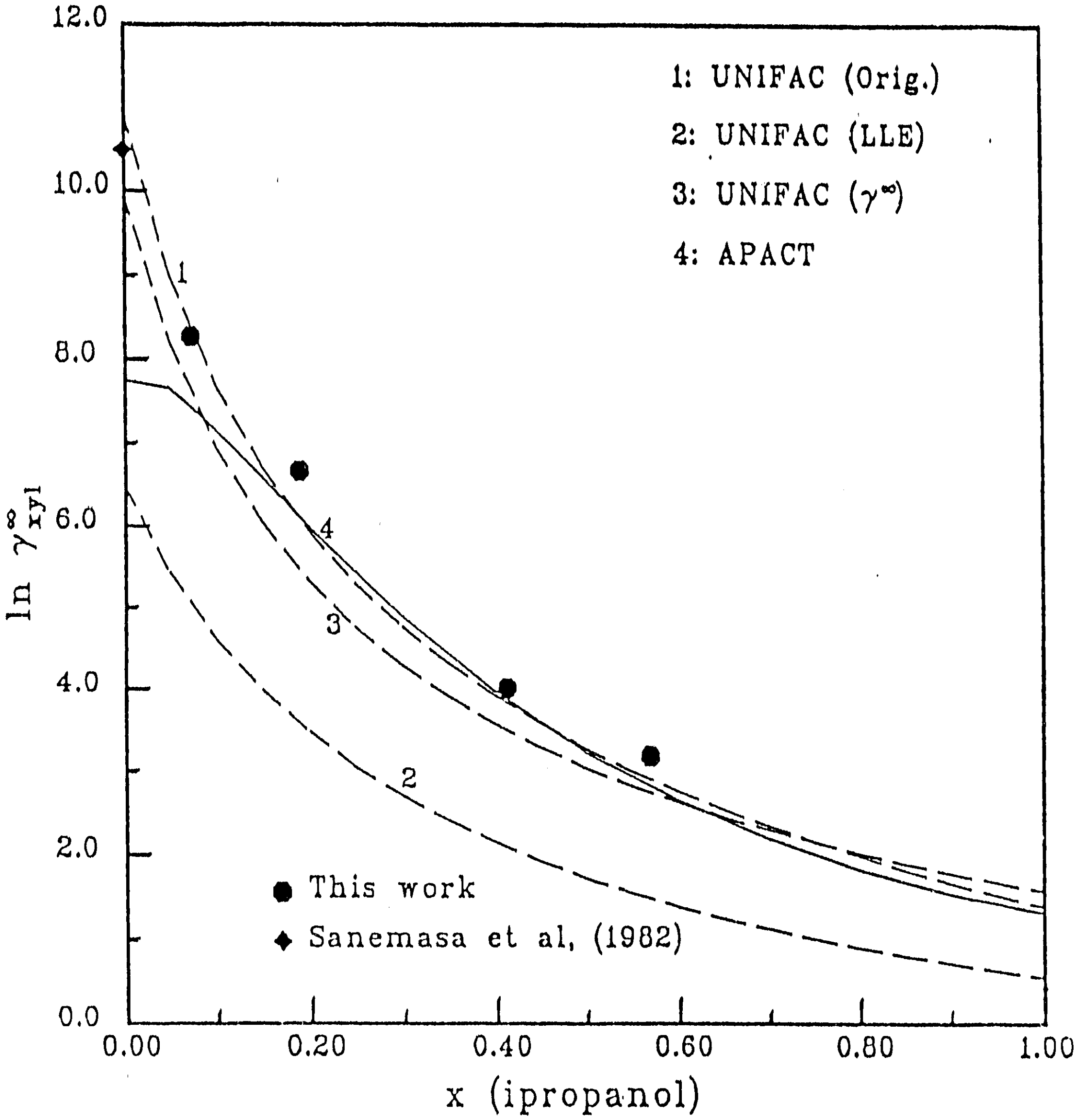


Figure 22. Experimental and predicted results using UNIFAC and APACT for $\gamma^{\infty}_{p-xylene}$ for i-propanol-water mixture. The mobile phase is i-propanol-water and the solute is p-xylene.

of APACT in Figures 25 to 27 for types 1 to 3 respectively. In the calculations using APACT the parameters were determined from the best fit to the experimental data.

We also are using probes to study cosolvent (entrainer) effects in supercritical fluids. The use of probes is well established in other spectroscopic fields including UV, Raman, and visible and it is the basis for solvatochromic characterization of compounds. However, very little work has been done with probes in the infra-red because of the difficulties associated with resolving the highly overlapped peaks. Our spectral analysis technique, which allows us to characterize the Lorentzian and Gaussian components of the absorbance, enables us to characterize the interactions of acid and base probes with a variety of compounds.

To spectroscopically characterize a probe it is necessary to determine what spectral characteristics are due to dispersion, polar, and Lewis acid/base interactions. To do this a boot-strapping procedure, involving a systematic variation in the concentration and complexity of the solvent to be analyzed, is used. The procedure is started by analyzing the spectra of a small amount of the probe in an inert solvent such as cyclohexane, followed by analyzing a series of mixtures containing the inert solvent and the sample solvent to be characterized. The spectra obtained should show a gradual change in features such as area, shape, position and width in going from the pure cyclohexane to the pure sample solvent. This gradual transition is extremely useful in the analysis and interpretation of the spectra. This work will be described in a paper entitled "The use of Acid-Base Probes in FTIR Spectroscopy" that is in preparation for *J. Org. Chem.*

Finally, we have begun to study hydrogen bonding in polymer systems. In Figure 28, we show spectra for the system tetrahydrofuran (THF), methanol, Polyvinyl methyl ketone (PVMK) as a function of the methanol concentration. Analyzing this data, we have determined the fraction of PVMK that is hydrogen bonded; this is shown in Figure 29 along with predictions of the behavior from ABPACT. This work is described in our

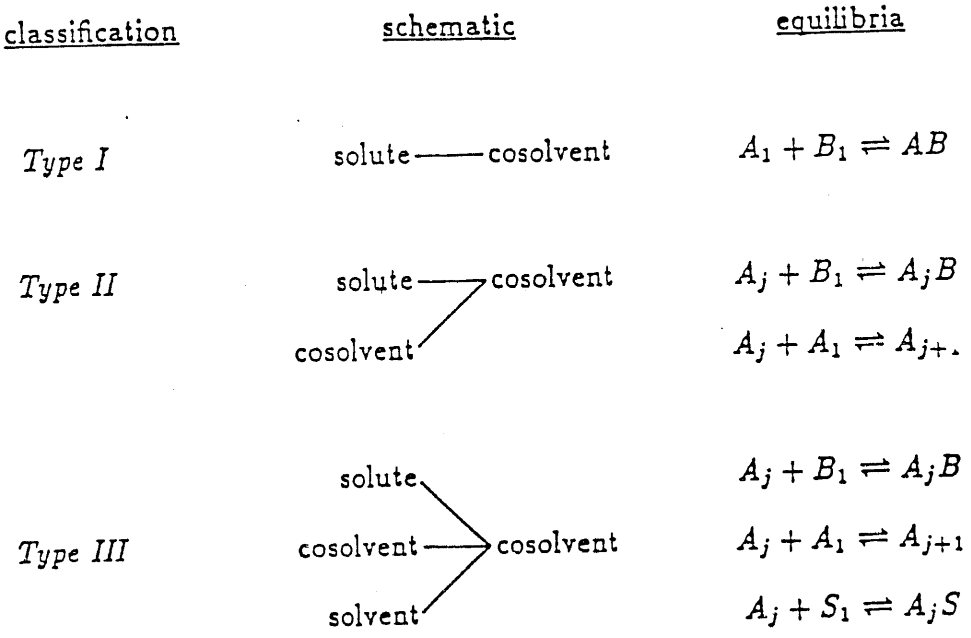


Figure 23. The types of hydrogen bonding competition studied using FTIR with the chemical equilibrium used to model them.

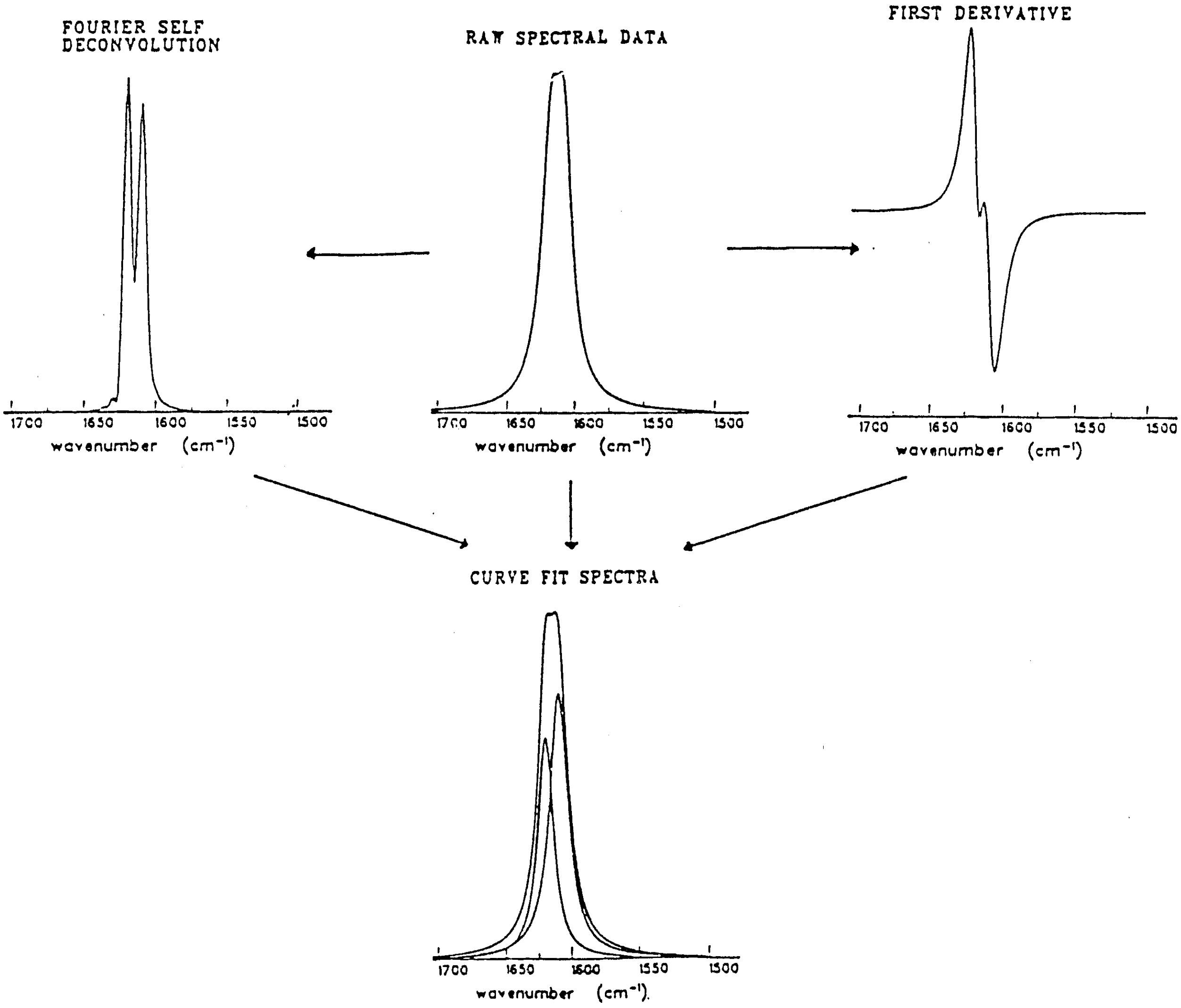
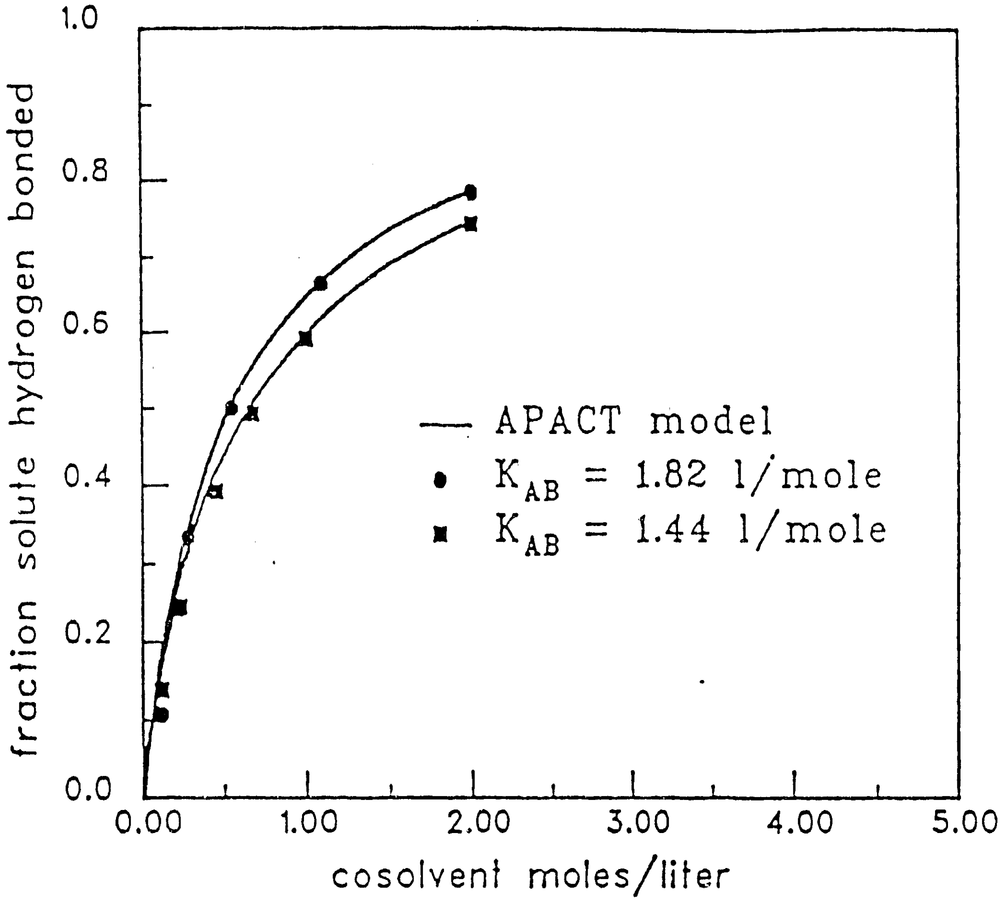
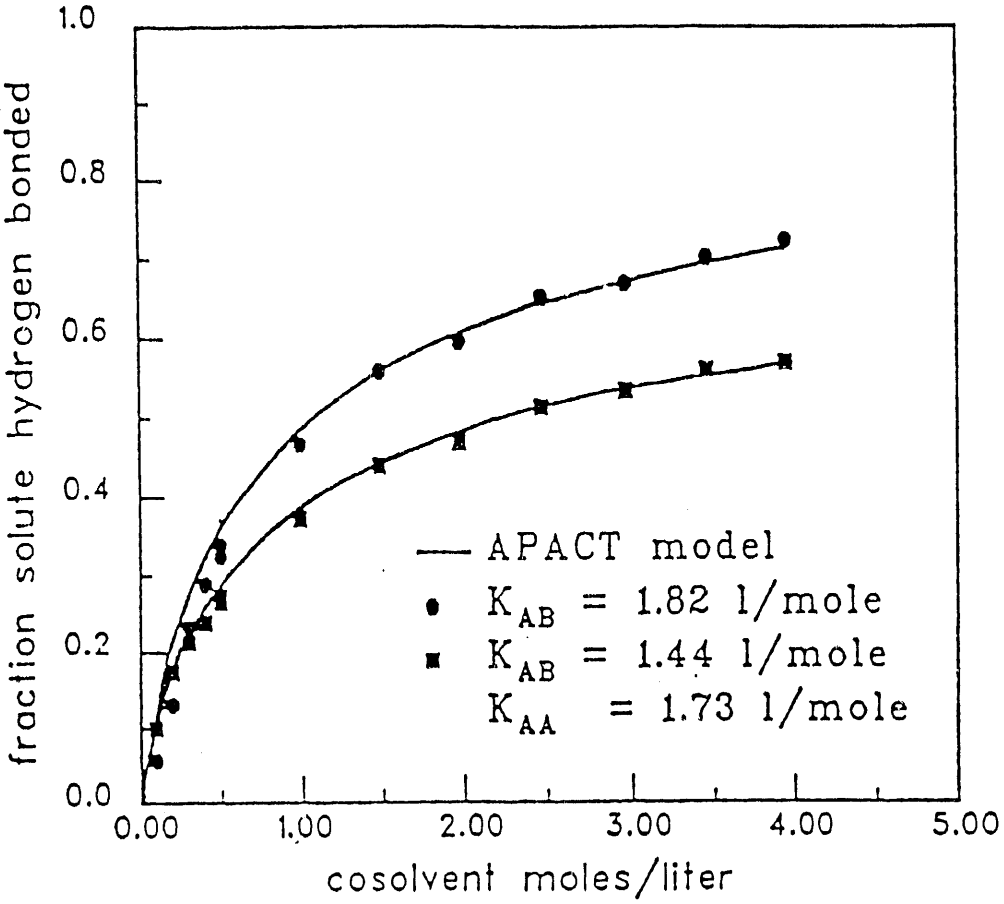


Figure 24. Schematic diagram of the spectral analysis technique used to determine the areas of the monomeric and hydrogen bonded peaks. Nonlinear least squares regression is applied to both the spectral data and the Fourier self-deconvoluted spectral data. The spectrum shown here is that is that of the carbonyl peak of acetone in a mixture of acetone in a mixture of acetone/CCl_4/methanol. The spectrum shows a monomeric and a hydrogen bonded peak.



TYPE I: solute — cosolvent

Figure 25. Solvation in type I mixtures (noncompetitive solvation) Results for two different ketone solutes are shown (acetone and methyl ethyl ketone). The solvent is CCl_4, and the cosolvent is methanol. The concentration of the solute (ketone) was held constant. Results of the APACT model are shown as solid lines. A simplified analysis following the method originally used by Becker (1961) is used. In Becker's analysis, the solvation equilibrium constant is determined from the slope of the line through the data.



TYPE II: solute / cosolvent ⟶ cosolvent

Figure 26. Solvation in type II mixtures (competition with cosolvent self-association). The fraction of the solute that is hydrogen bonded to the cosolvent is plotted as a function of cosolvent concentration. Results for two different ketone solutes are shown (acetone and methyl ethyl ketone). The solvent is CCl_4, and the cosolvent is methanol. The concentration of the solute (ketone) was held constant. Results of the APACT model are shown as solid lines.

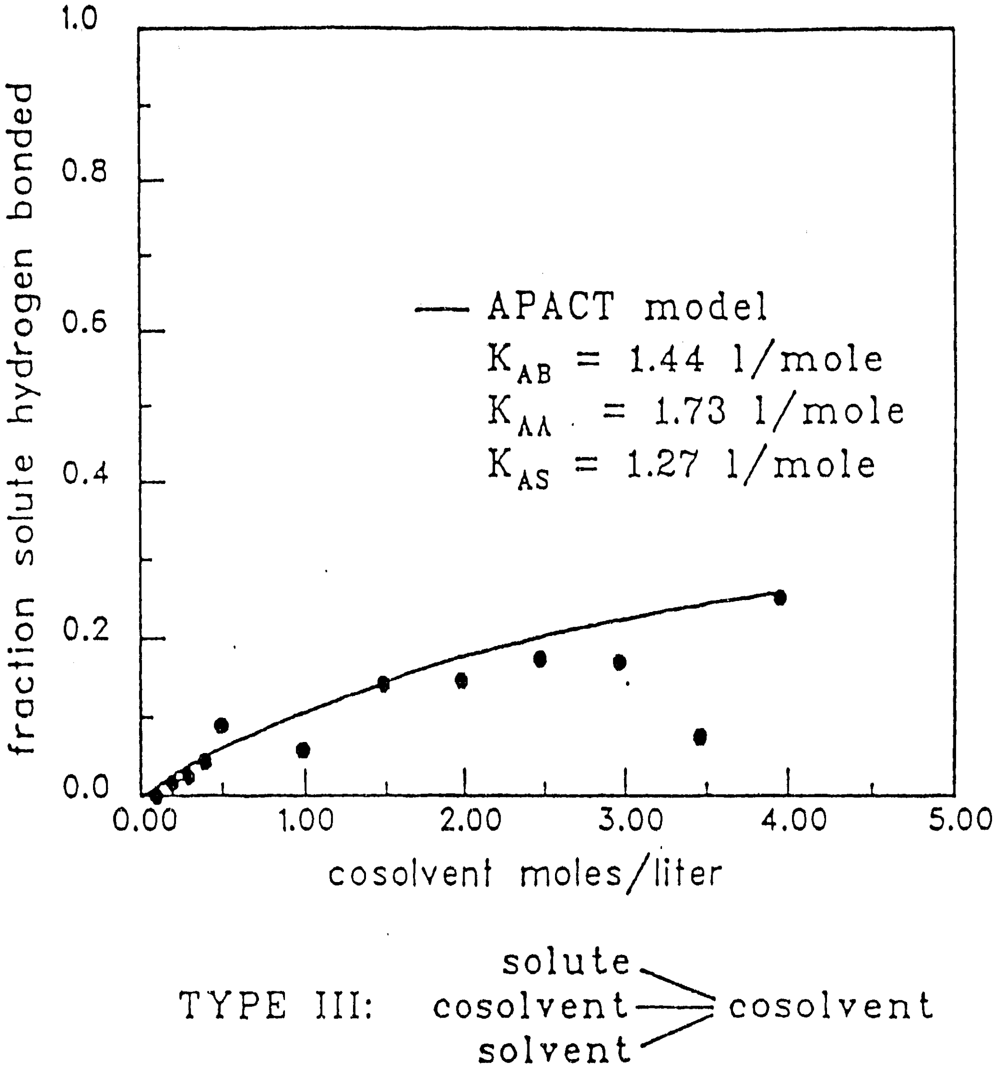


Figure 27. Solvation in type III mixtures (competition with solvent and cosolvent self-association). Only one solute (MEK) was studied. Results of the APACT model are shown as the solid line.

research proposal and in a forthcoming paper entitled "Molecular Thermodynamics of Polymer Solutions that Hydrogen Bond" by Economou and Donohue (1990).

Literature Cited

Becker, E.D., "Infra Red Studies of Hydrogen Bonding in Alcohol-Base Systems," *Spectrochim. Acta*, **17**, 436 (1961).

Beret, S., and J.M. Prausnitz, "Perturbed Hard-Chain Theory: An Equation of State for Fluids Containing Small or Large Molecules," *AIChE J.*, **21**, 1123 (1975).

Dickman, R., and C.K. Hall, "Equation of State for Chain Molecules: Continuous-Space Analogy of Flory Theory," *J. Chem. Phys.*, **85**, 4108 (1986).

Donohue, M.D., and J.M. Prausnitz, "Perturbed Hard Chain Theory for Fluid Mixtures: Thermodynamic Properties for Mixtures in Natural Gas and Petroleum Technology," *AIChE J.*, **24**, 849 (1978).

Economou, I.G., G.D. Ikonomou, P. Vimalchand, and M.D. Donohue, "Thermodynamics of Lewis Acid-Base Mixtures," accepted for publication in *AIChE J.* (1990).

Economou, I.G., P. Vimalchand, and M.D. Donohue, "Measurement of Infinite Dilution Activity Coefficients Using High Performance Liquid Chromatography," submitted to *J. Chromatography* (1990).

Elliott, J.R., S.J. Suresh, and M.D. Donohue, "A Simple Equation of State for Non-spherical and Associating Molecules," *Ind. Eng. Chem. Res.*, **29**, 1476 (1990).

Gmehling, J.D., and U. Onken, Vapor-Liquid Equilibrium Data Collection, DECHEMA, Frankfurt (1981).

Heidemann, R.A., and J.M. Prausnitz, "A Van der Waals-Type Equation of State for Fluids with Associating Molecules," *Proc. Natl. Acad. Sci. U.S.A.*, **73**, 1773 (1976).

Honnell, K.G., and C.K. Hall, "A New Equation of State for Athermal Chains," *J. Chem. Phys.*, **90**, 1841 (1989).

Ikonomou, G.D., and M.D. Donohue, "Thermodynamics of Hydrogen Bonded Molecules: The Associated-Perturbed-Anisotropic-Chain Theory," *AIChE J.*, **32**, 1716 (1986).

Ikonomou, G.D., and M.D. Donohue, "Extension of the Associated-Perturbed-Anisotropic-Chain Theory to Mixtures with More Than One Associating Component," *Fluid Phase Equil.*, **39**, 129 (1988).

Jackson, G., W.G. Chapman, and K.E. Gubbins, "Phase Equilibria of Associating Fluids: Spherical Molecules with Multiple Bonding Sites," *Mol. Phys.*, **65**, 1 (1988).

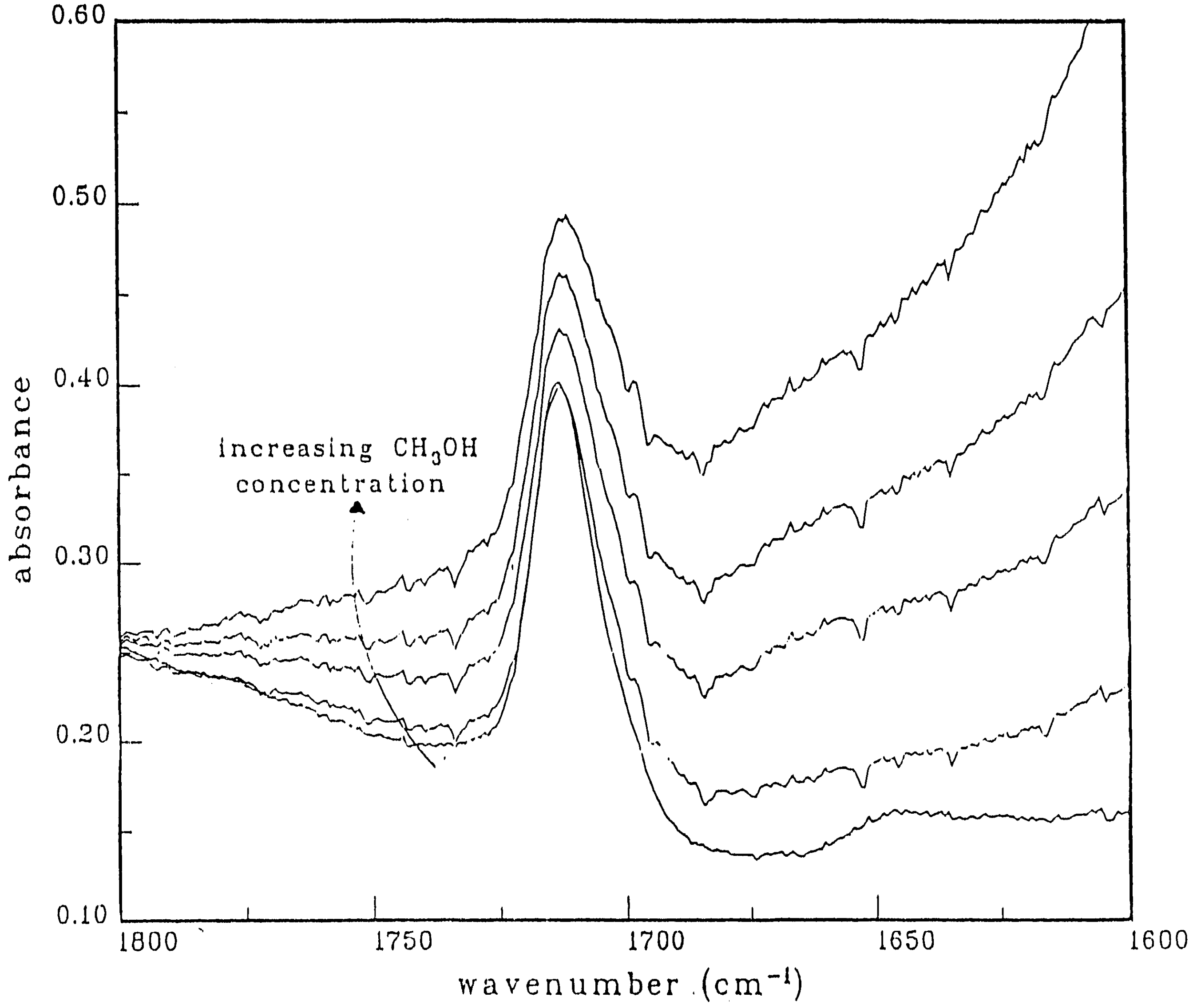


Figure 28. Infra-red spectra for the system tetrahydrofuran (THF), methanol, Polyvinyl methyl ketone (PVMK).

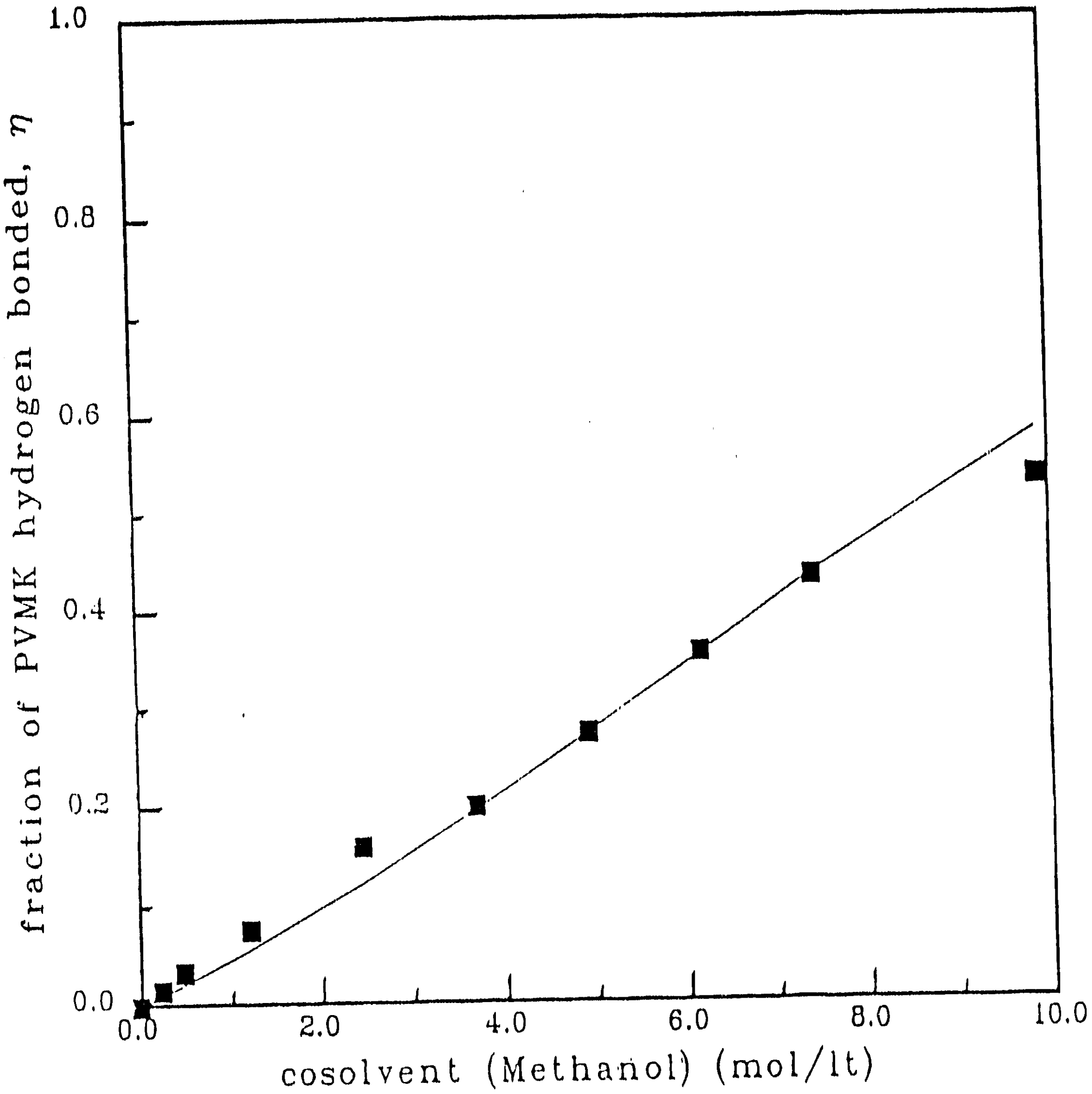


Figure 29. Fraction of PVMK that is hydrogen bonded in the system tetrahydrofuran (THF), methanol, Polyvinyl methyl ketone (PVMK) as a function of methanol concentration obtained by analyzing the InfraOred spectra for this system.

Jin, G., J.M. Walsh, and M.D. Donohue, "A Group-Contribution Correlation for Predicting Thermodynamic Properties with the Perturbed-Soft-Chain Theory," *Fluid Phase Equil.*, **31**, 123 (1986).

Jin, G., and M.D. Donohue, "An Equation of State for Electrolyte Solutions. III. Aqueous Solutions Containing Multiple Salts," accepted for publication in *Ind. Eng. Chem. Res.*, (1990).

Kogan, V.B., Ravnovesie Mazhdu Zhidkost'iu Parom, Izdatelstvo Nauka, Moscow (1966).

Lee, L.L., Molecular Thermodynamics of Non-Ideal Fluids, Butterworths, Boston (1988).

Morris, W.O., P. Vimalchand, and M.D. Donohue, "The Perturbed-Soft-Chain Theory: An Equation of State Based on the Lennard-Jones Potential," *Fluid Phase Equil.*, **32**, 103 (1987).

Ohta, T., and I. Nagata, "Thermodynamic Properties of Four Ester-Hydrocarbon Mixtures," *J. Chem. Eng. Data.*, **25**, 283 (1980).

Sanemasa, I., M. Araki, T. Deguchi, H. Nagai, "Solubility Measurements of Benzene and the Alkyl Benzenes in Water by Making Use of Solute Vapor," *Bull. Chem. Soc. Japan*, **55**, 1054 (1982).

Scheller, W.A., A.R. Torres-Soto, and K.J. Daphthary, "Isothermal Vapor-Liquid Equilibrium Data for the Heptane-Butyl Acetate System at 74.7 °C and 100.0 °C," *J. Chem. Eng. Data.*, **14**, 17 (1969).

Schweizer, K.S., and J.G. Curro, "Equation of State for Polymer Melts: General Formulation of a Microscopic Integral Equation Theory," *J. Chem. Phys.*, **89**, 3342 (1988).

Tasic, A., B. Djordjevic, D. Grozdanic, N. Afgan, and D. Malic, "Vapor-Liquid Equilibria of the Systems Acetone-Benzene, Benzene-Cyclohexane and Acetone-Cyclohexane at 25 °C," *Chem. Eng. Sci.*, **33**, 189 (1978).

Vimalchand, P., M.D. Donohue, and I. Celmins, "Thermodynamics of Multipolar Compounds: The Perturbed-Anisotropic-Chain Theory," *ACS Symp. Ser., Equations of State: Theories and Applications*, 300, 297 (1986).

Vimalchand, P., G.D. Ikonomou, and M.D. Donohue, "Correlation of Equation of State Parameters for the Associated-Perturbed-Anisotropic-Chain Theory," *Fluid Phase Equil.*, **43**, 121 (1988).

Vimalchand, P., and M.D. Donohue, "Comparison of Equations of State for Chain Molecules," *J. Phys. Chem.*, **93**, 4355 (1989).

Walsh, J.M., G. Jin, and M.D. Donohue, "Thermodynamics of Short Chain Polar Compounds," accepted for publication in *Fluid Phase Equil.* (1990).

Wertheim, M.S., "Fluids with Highly Directional Attractive Forces. II: Thermodynamic Perturbation Theory and Integral Equations," *J. Stat. Phys.*, **35**, 35 (1984).

Publications Resulting from this Research Program During the Previous Contract Period

Donohue, M.D., D.M. Shah, K.G. Connally, and V.R. Venkatachalam, "Henry's Constants for C_5 to C_9 Hydrocarbons in C_{10} and Larger Hydrocarbons," *Ind. Eng. Chem. Fundam.*, **24**, 241 (1985).

Vimalchand, P., and M.D. Donohue, "Thermodynamics of Quadrupolar Molecules: The Perturbed-Anisotropic-Chain Theory," *Ind. Eng. Chem. Fundam.*, **24**, 246 (1985).

Morris, W.O., and M.D. Donohue, "Vapor-Liquid Equilibria in Mixtures Containing Carbon Dioxide, Toluene and 1-Methylnaphthalene," *J. Chem. Eng. Data*, **30**, 259 (1985).

Donohue, M.D., P. Vimalchand, and G.D. Ikonomou, "Phase Equilibrium Predictions for Polar and Hydrogen Bonding Mixtures," *Fluid Phase Equil.*, **30**, 307 (1986).

Jin, G., J.M. Walsh, and M.D. Donohue, "A Group-Contribution Correlation for Predicting Thermodynamic Properties with the Perturbed-Soft-Chain Theory," *Fluid Phase Equil.*, **31**, 123 (1986).

Kim, C-H, P. Vimalchand, and M.D. Donohue, "Vapor-Liquid Equilibria for Binary Mixtures of Carbon Dioxide with Benzene, Toluene and p-Xylene," *Fluid Phase Equil.*, **31**, 299 (1986).

Vimalchand, P., M.D. Donohue, and I. Celmins, "Thermodynamics of Multipolar Compounds: The Perturbed-Anisotropic-Chain Theory," *ACS Symp. Ser., Equations of State: Theories and Applications*, **300**, 297 (1986).

Ikonomou, G.D., and M.D. Donohue, "Thermodynamics of Hydrogen Bonded Molecules: The Associated-Perturbed-Anisotropic-Chain Theory," *AIChE J.*, **32**, 1716 (1986).

Kim, C-H, P. Vimalchand, M.D. Donohue and S.I. Sandler, "Local Composition Model for Chainlike Molecules: A New Simplified Version of the Perturbed-Hard-Chain Theory," *AIChE J.*, **32**, 1726 (1986).

Vimalchand, P., I. Celmins, and M.D. Donohue, "VLE Calculation for Mixtures Containing Multipolar Compounds Using the Perturbed-Anisotropic-Chain Theory," *AIChE J.*, **32**, 1735 (1986).

Morris, W.O., P. Vimalchand, and M.D. Donohue, "The Perturbed-Soft-Chain Theory: An Equation of State Based on the Lennard-Jones Potential," *Fluid Phase Equil.*, **32**, 103 (1987).

Donohue, M.D., and P. Vimalchand, "Recent Improvements in the Perturbed-Hard-Chain Equation," *66th Annual GPA Proceedings* (1987).

Ikonomou, G.D., and M.D. Donohue, "COMPACT: A Simple Equation of State for Associated Molecules," *Fluid Phase Equil.*, **33**, 61 (1987).

Walsh, J.M., G.D. Ikonomou, and M.D. Donohue, "Supercritical Phase Behavior: The Entrainer Effect," *Fluid Phase Equil.*, **33**, 295 (1987).

Publications Resulting from this Research Program During the Current Contract Period

Ikonomou, G.D., and M.D. Donohue, "Extension of the Associated-Perturbed-Anisotropic-Chain Theory to Mixtures with More Than One Associating Component," *Fluid Phase Equil.*, **39**, 129 (1988).

Donohue, M.D., and P. Vimalchand, "The Perturbed-Hard-Chain Theory: Extensions and Applications," *Fluid Phase Equil.*, **40**, 185 (1988).

Vimalchand, P., G.D. Ikonomou, and M.D. Donohue, "Correlation of Equation of State Parameters for the Associated-Perturbed-Anisotropic-Chain Theory," *Fluid Phase Equil.*, **43**, 121 (1988).

Kim, C-H, A.B. Clark, P. Vimalchand, and M.D. Donohue, "High-Pressure Binary Phase Equilibria of Aromatic Hydrocarbons with CO_2 and C_2H_6," *J. Chem. Eng. Data*, **34**, 391 (1989).

Vimalchand, P., and M.D. Donohue, "Comparison of Equations of State for Chain Molecules," *J. Phys. Chem.*, **93**, 4355 (1989).

Walsh, J.M., G. Jin, and M.D. Donohue, "Thermodynamics of Short Chain Polar Compounds," accepted for publication in *Fluid Phase Equil.* (1990).

Economou, I.G., G.D. Ikonomou, P. Vimalchand, and M.D. Donohue, "Thermodynamics of Lewis Acid-Base Mixtures," accepted for publication in *AIChE J.* (1990).

Economou, I.G., and M.D. Donohue, "Mean Field Theory Calculations of Thermodynamic Properties in Supercritical Fluids," accepted for publication in *AIChE J.* (1990).

Economou, I.G., P. Vimalchand, and M.D. Donohue, "Measurement of Infinite Dilution Activity Coefficients Using High Performance Liquid Chromatography," submitted to *J. Chromatography* (1990).

Papers to be Submitted Before the End of the Current Contract Period

Walsh, J.M., A. Thomas, and M.D. Donohue, "A Parameterization of the Configurational Energy for Short-Chain Molecules," in preparation for *Chem. Eng. Sci.*

Vimalchand, P., and M.D. Donohue, "An Improved SPHCT Equation of State," in preparation for *Fluid Phase Equil.*

Walsh, J.M., J.T. Reilly, M.L. Greenfield, and M.D. Donohue, "Analysis of FTIR Spectroscopic Data: The Voigt Profile," in preparation for *Spectrochim. Acta.*

Walsh, J.M., J.T. Reilly, M.L. Greenfield, M.A. McHugh, and M.D. Donohue, "The use of Acid-Base probes in FTIR Spectroscopy," in preparation for *J. Org. Chem.*

Kim, C-H., A.B. Clark, J.T. Reilly, P. Vimalchand, and M.D. Donohue, "The Extraction of Model Coal Compounds from 1-Methylnaphthalene mixtures: The entrainer-cosolvent effect," in preparation for *J. Chem. Eng. Data.*

Conforti, R.M., P. Vimalchand, T.A. Barbari, and M.D. Donohue, "A New Lattice Model for Gas Sorption in Glassy Polymers," in preparation for *Macromol.*

Economou, I.G., and M.D. Donohue, "Molecular Thermodynamics of Polymer Solutions that Hydrogen Bond," in preparation for *AIChE J.*

END

DATE
FILMED

4/10/92