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THEORETICAL AND EXPERIMENTAL STUDY OF MIXED SOLVENT ELECTROLYTES

Final Report

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DEPARTMENT OF CHEMICAL ENGINEERING

SCHOOL OF
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UNIVERSITY OF VIRGINIA
School of Engineering and Applied Science

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A Final Report
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THEORETICAL AND EXPERIMENTAL STUDY OF MIXED SOLVENT ELECTROLYTES

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FINAL REPORT

DOE Grant DE-FG05-88ER13943

Theoretical and Experimental Study of Mixed Solvent Electrolytes

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1 Introduction

The DOE grant DE-FG05-88ER13943 supported research on the thermophysical properties of aqueous electrolyte solutions at the University of Virginia for the period 7/1/88-12/31/91. In the original proposal, four goals were formulated:

1. Fundamental modeling of mixed solvent electrolytes using numerically solved integral equation approximation theories

2. Evaluation of intermolecular pair potential models by computer simulation of selected systems for comparison with experiment and the numerical integral equation studies

3. Development of fundamentally based correlations for the thermodynamic properties of mixed solvent electrolyte solutions using analytically solvable statistical mechanical models

4. Extension of experimental database on mixed solvent electrolytes by performing vapor-liquid equilibrium measurements on selected systems

Progress on these four goals has been mixed, and our view of the relative importance of and the ease of achieving these four goals has evolved during the course of the program. Goals 1 and 3, for example, have proved to be much more difficult than originally anticipated and our attempts to achieve these goals through the dissertation research of graduate students have been only partially successful to date. We have pursued goal 4 to the extent permitted by the availability of students to perform experiments. Goal 2 has evolved and expanded to become the major emphasis of the research program to date. When the proposal was written in 1987, the Gibbs ensemble technique which permits direct molecular simulation of phase equilibria was still under development. We used the support of the grant to become familiar with this new technique and to apply it to mixed solvent electrolytes. Another factor in the evolution of the program was the addition of John O'Connell as co-principal investigator at the beginning of 1990 after John joined the faculty at the University of Virginia. John brought with him a strong background in applied statistical thermodynamics. He is the leading proponent and developer of fluctuation solution theory, a statistical mechanics based method for analyzing and predicting the thermodynamic properties of mixtures. Thus the program expanded its domain of interest to include mixed electrolytes (aqueous solutions of mixtures of salts) and electrolyte solutions at elevated temperature and pressure. The final element in the evolution of the program was the initiation of an interaction by Peter Cummings with researchers at Oak Ridge National Laboratory. This collaboration with Dr. H. D. Cochran of the Chemical Technology Division and and Drs. J. M. Simonson and R. E. Mesmer of the Aqueous Chemistry Group resulted in the first molecular simulation of supercritical aqueous solutions with both charged and uncharged solutes present at infinite dilution. The technological importance of supercritical aqueous systems and the relative ease with which such systems can be modeled (many of the difficulties experienced in theoretical studies at ambient conditions-high dielectric constant, very long rotational relaxation times-are ameliorated at supercritical conditions) has resulted in the study of these systems being incorporated into the research program.

Thus, the goals of the research program have evolved into the following:

1. Molecular simulation of phase equilibria in aqueous and mixed solvent electrolyte solutions

2. Molecular simulation of solvation and structure in supercritical aqueous systems

3. Extension of experimental database on mixed solvent electrolytes

4. Analysis of the thermodynamic properties of mixed solvent electrolyte solutions and mixed electrolyte solutions using fluctuation solution theory

5. Development of analytic expressions for thermodynamic properties of mixed solvent electrolyte solutions using analytically solved integral equation approximations

6. Fundamental modeling of mixed solvent electrolytes using numerically solved integral equation approximation theories

We report and evaluate our progress during the period of the grant in light of these six goals in detail in the section below.

2 Research Achievements During Grant Period

2.1 Molecular Simulation of Phase Equilibria in Electrolyte Solutions

At the start of the grant period, a new simulation methodology, the Gibbs ensemble Monte Carlo (GEMC) method, was introduced by Panagiotopoulos[1]. GEMC permits the direct molecular simulation of vapor–liquid phase equilibrium. We developed a GEMC simulation code and successfully tested it on a model for simple fluids, the two–Yukawa hard core fluid[2]. In a collaboration with de Pablo and Prausnitz at Berkeley, we then applied the GEMC method to the simple point charge (SPC) model of water developed by Berendsen *et al.*[3]. The aim was to compute the vapor–liquid phase envelope, shown in Figure 1, and critical point[4]. The long range forces were handled using the Ewald sum method[5–7]. The use of the Ewald sum removed significant system size dependences that had been observed by de Pablo and Prausnitz [8] in an earlier simulation of vapor–liquid equilibrium of another model for water, TIP4P. The critical point parameters obtained are a critical temperature T_c = 587 K and a critical density ρ_c = 0.27 gm/cc which is in only moderate agreement with the experimental values of T_c = 647.3 K and ρ_c = 0.32 gm/cc. Strauch and Cummings[9] suggested a simple modification of SPC which followed from recognizing that the dipole moment of the SPC water molecule, 2.24D, is an effective dipole moment that attempts to take into account the permanent, gas phase dipole moment of 1.8D plus contributions from polarizability. Strauch and Cummings suggested using the physically more correct gas phase dipole moment for water molecules in the vapor phase. The resulting vapor and liquid phase densities are in better agreement with experiment, shown also in Figure 1, and the estimated critical temperature (606 K) is closer to experiment.

The next step was to apply the GEMC simulation techniqu to mixed solvent electrolyte solutions[10, 11]. Our initial work has focused on methanol/water/NaCl. In view of the good representation SPC provides of the dielectric constant of water at ambient conditions, we used the SPC model for the water–water interaction. The methanol–methanol potential was the H1 potential of Haughney *et al.*[12]. Since SPC and H1 are both site–site LJ and charge–charge potentials, the methanol–water potential was constructed with no adjustable parameters by using the usual Coulombic formula for charge interactions and the Berthelot rules for the LJ parameters

$$\sigma_{ij} = (\sigma_i + \sigma_j)/2, \quad \epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2} \tag{1}$$

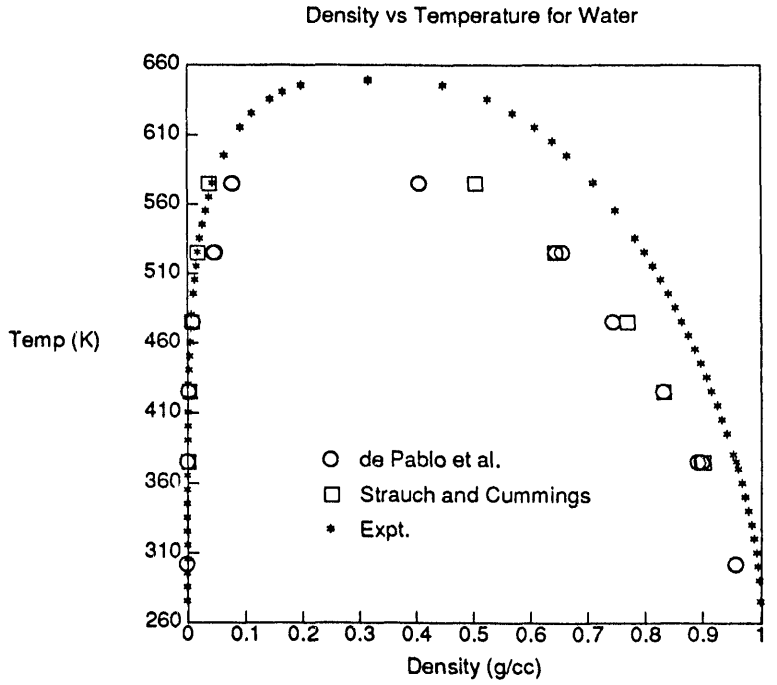

Figure 1: Gibbs ensemble Monte Carlo simulation results for SPC water with the same dipole moment in each phase (○, de Pablo *et al.*[4]) and with different dipole moments in each phase (□, Strauch and Cummings[9]) compared with experimental data.

For the ion–ion potentials for the Na^+–Na^+, Na^+–Cl^- and Cl^-–Cl^- interactions, we adopted the interionic potentials of Fumi and Tosi[13, 14] which are fitted to solid state properties of the alkali halides. The ion–water potentials were taken from Chandrasekhar *et al.*[15] and are fitted to *ab initio* calculations of ion–water interaction surfaces. The ion–water potentials are LJ plus charge–charge interactions. From the Berthelot mixing rules for the methanol–water interaction, one can infer the ion–methanol potential without any adjustable parameters. Thus, the simulations were performed with no adjustable parameters in the potentials.

Strauch and Cummings[10, 11] report the results of water/NaCl, water/methanol and water/methanol/NaCl simulations in detail. Here we focus only on the water/methanol and water/methanol/NaCl simulations. In Figure 2, the GEMC results for vapor liquid equilibrium in salt free methanol/water and salt-containing methanol water systems is shown in the form of a $y - x$ plot. The agreement with experiment for the salt-free case is very good; for the salt-containing simulations, methanol is salted out (as is observed experimentally) though the simulations tend to lead to a higher salting coefficient k_s[10, 11] than is observed in experiment[16].

It is clear that our goal of applying molecular simulation techniques to the study of phase equilibria in electrolyte systems has been a outstanding success to date and stands as one of the

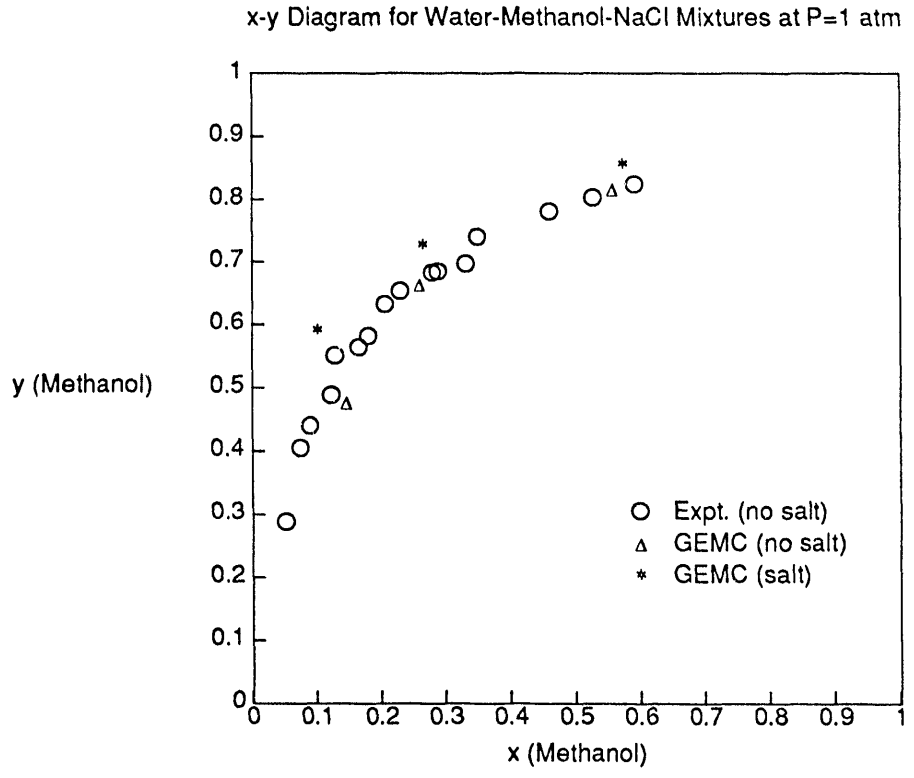

Figure 2: GEMC simulation results for vapor–liquid equilibrium in water/methanol/NaCl. Experimental results with no salt (○), GEMC with no salt (Δ) and GEMC with salt mole fraction of 0.017.

major achievements of our research program over the past few years. We expect to pursue this effort even more vigorously in the future.

2.2 Molecular Simulation of Solvation and Structure in Supercritical Aqueous Systems

Our simulation of the vapor–liquid phase envelope of SPC water was the first molecular simulation to yield with reasonable statistical certainty the phase envelope and critical point of a molecular model for water. Knowing the critical point of SPC water made it possible for us to study and compare the solvation of Na^+ and Cl^- ions, a nonpolar solute (argon) and a polar solute (methanol) in supercritical (SC) water ($T_r = T/T_c = 1.05$, $\rho_r = \rho/\rho_c = 1.0$) and at high density and temperature ($T_r = 1, \rho_r = 1.5$)[17, 18]. The simulations were performed at infinite dilution with a single solute molecule surrounded by 215 or 255 solvent water molecules. The system size was chosen to be considerably larger than the correlation length for water at each of the state points studied. Some studies were performed with 863 water molecules to check that there was no significant system size effects.

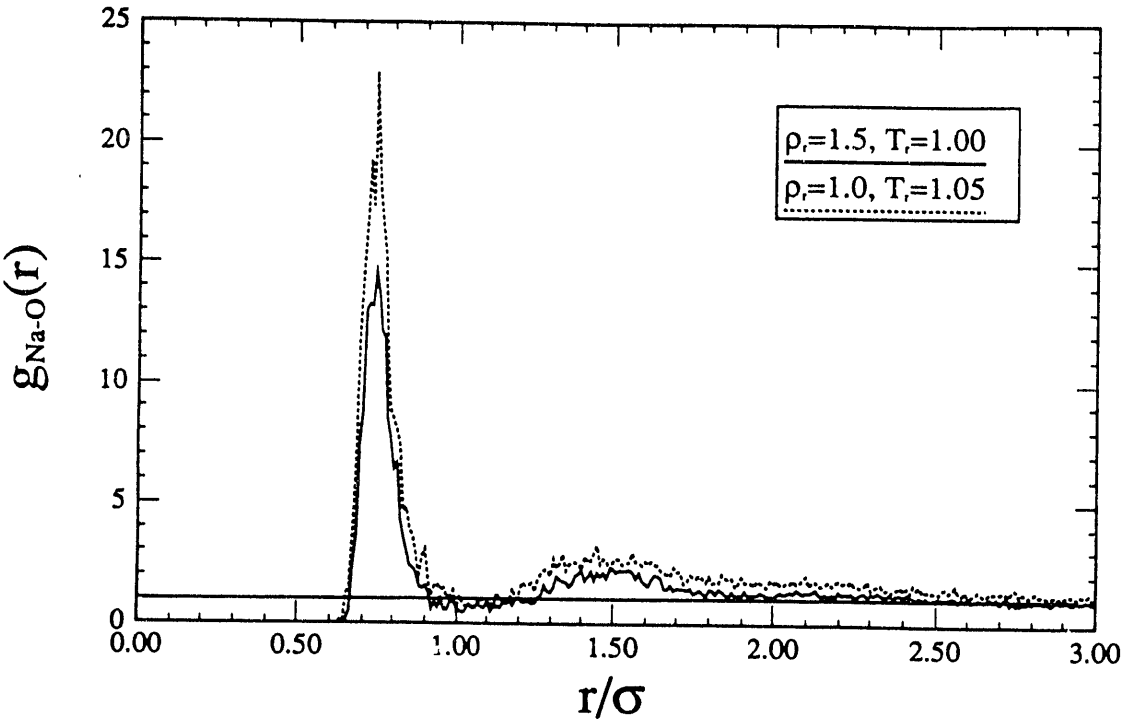

Figure 3: Sodium–water radial distribution functions $g_{NaO}(r)$ for Na^+ in SPC water calculated by MD[17]. The center of the water molecule is taken to be the center of the oxygen (O) atom.

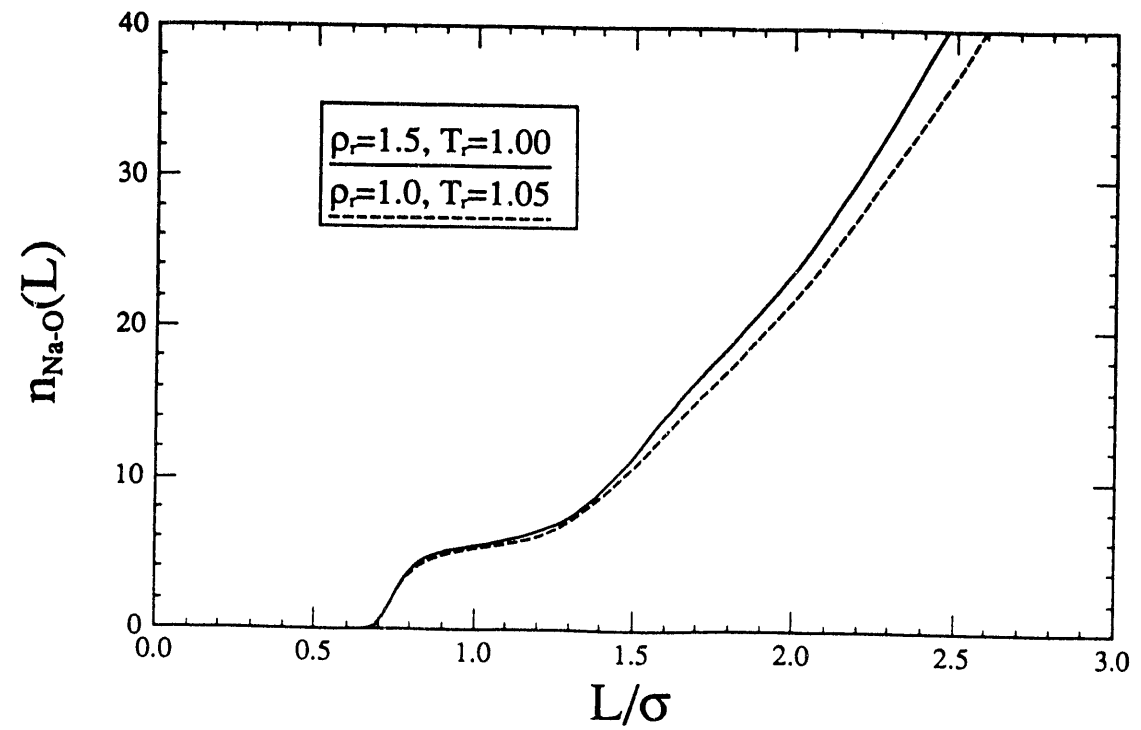

Figure 4: Number of water molecules $n_{NaO}(L)$ located with a sphere of diameter L around an Na^+ in SPC water calculated by MD[17].

	ρ_r	T_r	ϵ	U_{conf} (kcal/mole)	U_{total} (kcal/mole)	P (bar)
SPC	1.0	1.05	14.7±10%	-4.83±0.09	-3.39±0.09	220±30
Expt	1.0	1.05	9.6	-4.64	...	234.7
SPC	1.5	1.0	8.8±10%	-3.83±0.09	-2.39±0.09	270±30
Expt	1.5	1.0	5.1	-3.52	...	310

Table 1: Thermodynamic properties and dielectric constant of SPC water calculated by molecular dynamics and compared with experiment

ρ_r	T_r	Solute	n_{NN}
Ambient		Na^+	4.3
1.0	1.05	Na^+	6.5
1.5	1.0	Na^+	10.0
Ambient		Cl^-	11.7
1.0	1.05	Cl^-	6.5
1.5	1.0	Cl^-	10.5

Table 2: Number of nearest neighbors n_{NN} around infinitely dilute ions at ambient and supercritical states.

We first note that, as indicated in Table 1, the thermodynamic properties (pressure P and internal energy U) and dielectric constant ϵ of the pure SC water at the two state points are in good agreement with experiment, particularly considering that the SPC potential is fitted to ambient thermodynamic and structural properties. As an example of the results obtained, consider Figures 3 and 4 which contain, respectively, the Na^+–water radial distribution function (rdf) and the number of water molecules within a sphere of diameter L surrounding the ion. The peak in the rdf in Figure 3 indicates that the water molecules are strongly attracted into a short ranged solvation shell around the ion. Despite the low densities involved (less than half that at ambient conditions), the number of water molecules in the solvation shell is similar to that at ambient conditions. In Table 2, we give the number of nearest neighbors around each solute ions at the state points considered.

We also investigated the extent to which hydrogen bonding was altered by the presence of an ionic or neutral solute at SC conditions[9]. Consider Figure 5 in which the number of hydrogen bonds per water molecule is shown as a function of distance from the center of the solute molecule for the two state points studied. The higher density state point has a higher number of hydrogen bonds per molecule (about 1.1) than does the lower density state point (about 0.8). The remarkable feature of these result is that the solute does not appear to affect the hydrogen bonding to any significant degree. We attribute this to the fact that at these high temperatures there is not very much hydrogen bonding taking place between water molecules in the bulk. These simulations have provided the first significant insight into the nature of solvation of water molecules around ionic, non–polar and polar solutes at SC conditions.

It is evident from our discussion here that our goal of studying the solvation of ionic, nonpolar

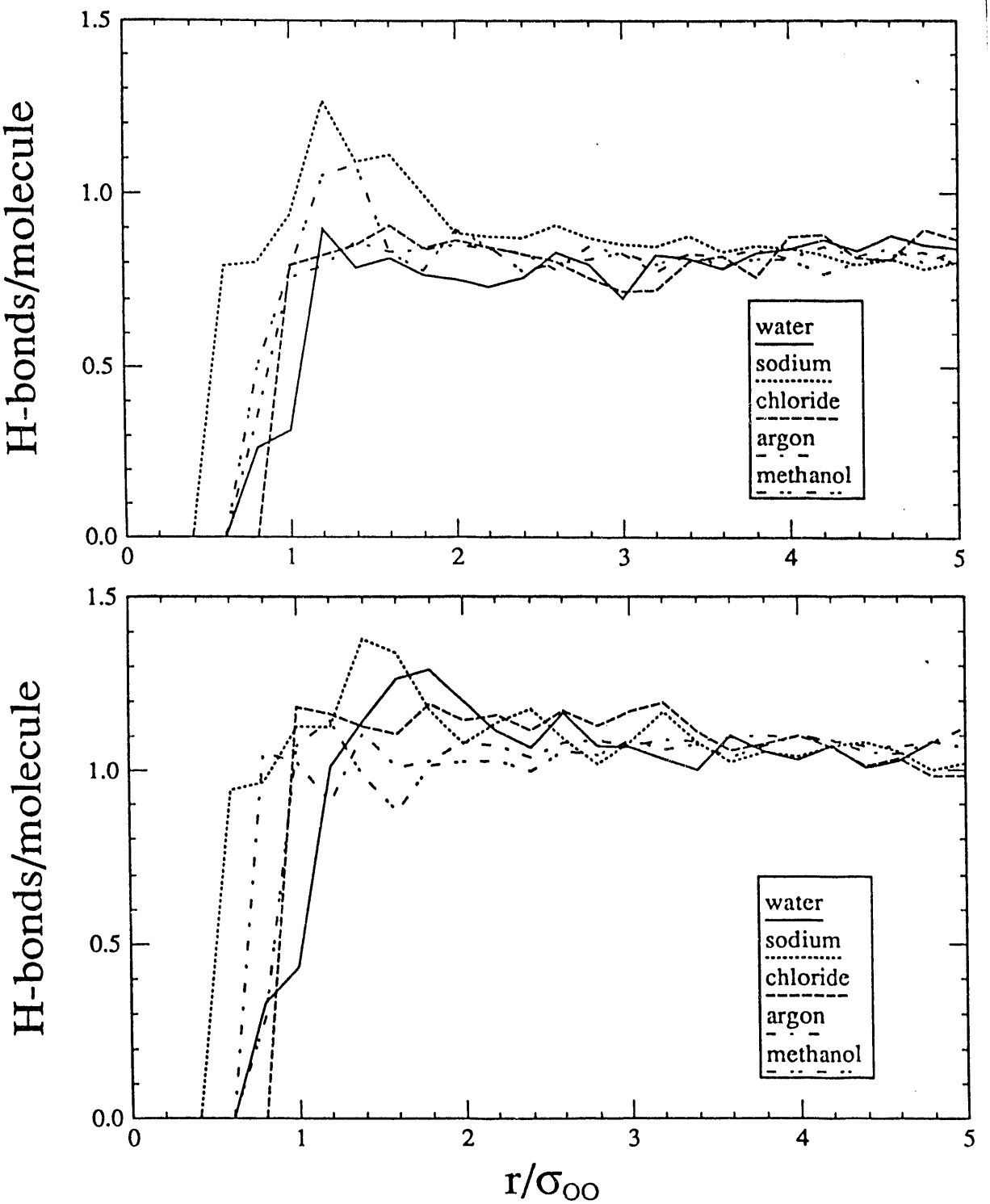

Figure 5: Number of hydrogen bonds per molecule as a function of distance from the center of a solute molecule. Top: $T_r = 1.05$, $\rho_r = 1.0$; bottom: $T_r = 1$, $\rho_r = 1.5$. The solid curve for water is calculated for pure water.

and polar solutes by water at high temperatures and pressures using molecular dynamics has been achieved and has resulted in hitherto unsuspected new insights into solvation in these systems. We expect to continue this work in future DOE-sponsored research.

2.3 Extension of Experimental Database on Mixed Solvent Electrolytes

The development of theories of the salt effect demands vapor-liquid equilibrium data over the whole range of salt concentration (salt free to saturation) in order for there to be a meaningful comparison of theory and experiment. In order to develop a collection of vapor-liquid equilibrium data on mixed solvent systems spanning the full salt concentration range, experimental measurements have been performed in the Department of Chemical Engineering at the University of Virginia for several years under the direction of Randall L. Perry (now with DuPont) and the author[16]. The specific systems studied to date are H_2O-KCl-methanol, H_2O-KBr-methanol, H_2O-NaCl-methanol, H_2O-NaBr-methanol, H_2O-KBr-1-propanol, H_2O-NaCl-1-propanol, H_2O-NaBr-1-propanol and H_2O-NaBr-2-propanol. The choice of systems is designed to isolate the effect of specific cations and anions (as in the methanol series of experiments) and the contribution of methyl and methylene groups in the alcohol.

The apparatus used in our experimental program is a modified Othmer still. Alcohol and water concentrations are measured using a thermal conductivity detector in a Hewlett-Packard HP 5890A gas chromatograph with autoinjector. Salt concentrations can be obtained by overall material balance. The analytical procedures are described in in detail in our paper[16]. During the course of the DOE supported research, we have performed measurements on isopropanol/water/tetramethyl ammonium bromide (TMAB) and isopropanol/water/tetrabutyl ammonium bromide (TBAB)[19] using a modified Boublík-Benson still[20, 21]. These results suggested that at low concentrations of isopropanol, the alcohol is salted in while at high concentrations it is salted out; TMAB is salted out for all isopropanol concentrations. The TBAB result is intriguing but we have been unable to confirm these results using the more reliable Othmer still. We plan to do this as part of the research proposed for the next three years.

In addition, we are in the process of measuring densities of the pure and mixed solvent systems for which vapor-liquid equilibria exist. This will be valuable in testing fluctuation solution theory results as well as provide direct input into the Born-Oppenheimer modeling. The apparatus is a Sodev (Canada) vibrating tube densimeter which is generally capable of attaining 1 ppm accuracy.

Our progress on the experimental program has been less than anticipated largely because of difficulties in staffing the experiment with graduate students. In the last few months, after a hiatus of over a year, we have been able to interest two M.S. students in performing experimental measurements. Hopefully, the apparatuses and experimental procedures can be put on a firm footing by these two students to permit future measurements to be performed by chemical engineering seniors as senior thesis research.

2.4 Fluctuation Solution Theory

Progress has been made on several aspects of the development and application of fluctuation solution theory to multicomponent solutions, especially electrolytes. This includes 1) a paper in press of extended tabulations of correlation function integrals from experiment, 2) an explanatory paper being submitted on the distinctions among sets of thermodynamic variables which make a difference in relating theory, modeling and experiment of dilute liquid solution properties, and 3) a modeling

paper in preparation utilizing the consequences of this thermodynamic analysis for the properties of aqueous electrolytes. Some elements of these findings have also been reported in a review article[22] and three presentations made at international conferences.

The statistical mechanics of fluctuations in solutions from Kirkwood and Buff[23] leads to relationships for the concentration derivatives of chemical potentials in terms of $[\underline{H}]_{\alpha\beta}$, the set of integrals of the total correlation function (TCFI)

$$\rho \frac{\partial \mu_\alpha / RT}{\partial \rho_\beta}\bigg|_{T,\rho_{\gamma\neq\beta}} = [(\underline{X} + \underline{X}\underline{H}\underline{X})^{-1}]_{\alpha\beta} \tag{2}$$

where $\underline{X}$ = diagonal mole fraction matrix and

$$(\underline{H})_{\alpha\beta} = \rho \int (g_{\alpha\beta} - 1) d\vec{r} \tag{3}$$

with $g_{\alpha\beta}$ = radial distribution function between α and β.

These relations are somewhat simpler in terms of $[\underline{C}]_{\alpha\beta}$, the set of direct correlation function integrals (DCFI)[24].

$$\rho \frac{\partial \mu_\alpha / RT}{\partial \rho_\beta}\bigg|_{T,\rho_{\gamma\neq\beta}} = [\underline{X}^{-1} - \underline{C}]_{\alpha\beta} \tag{4}$$

or, in terms of the activity coefficient,

$$N \frac{\partial ln \gamma_\alpha}{\partial N_\beta}\bigg|_{T,V,N_{\gamma\neq\beta}} = (1 - C_{\alpha\beta}) \tag{5}$$

where

$$C_{\alpha\beta} = \rho \int c_{\alpha\beta} d\vec{r} \tag{6}$$

with $c_{\alpha\beta}$ the direct correlation function of Ornstein & Zernike. Also, the concentration derivative of the pressure is

$$\frac{\partial P/RT}{\partial \rho_\alpha}\bigg|_{T,\rho_{\beta\neq\alpha}} = \frac{\overline{V}_\alpha}{\kappa_T RT} \tag{7}$$

$$= \sum_\beta x_\beta (1 - C_{\alpha\beta}) \tag{8}$$

where the concentrations are ρ_α, the density is $\rho(T, P, x_2)$, the partial molar volumes are $\overline{V}_2(T, x_2)$ and the isothermal compressibility is $\kappa_T(T, x_2)$.

With a model for the $[\underline{C}]_{\alpha\beta}$, the activity coefficient and pressure derivatives can be integrated from a pure component reference state to find the density and activity coefficients of solutions[22]. These equations are slightly modified[25, 26] for "reactive components" such as salts, where the solution actually contains species such as ions, but the analysis is the same. The goal of our research is to develop the level of understanding needed to establish models for the $[\underline{C}]_{\alpha\beta}$ which can be used to predict the desired properties for all kinds of solutions, especially electrolytes.

In binary systems, there are 3 DCFI at each state point which can be found from experimental data.

$$1 - C_{11} = \frac{\overline{V}_1^2}{\rho \kappa_T RT} + \frac{x_2^2}{x_1} \frac{\partial \ln \gamma_2}{\partial x_2}\bigg|_T \tag{9}$$

$$1 - C_{12} = \frac{\overline{V}_1 \overline{V}_2}{\rho \kappa_T RT} - x_2 \frac{\partial \ln \gamma_2}{\partial x_2}\bigg|_T \tag{10}$$

$$1 - C_{22} = \frac{\overline{V}_2^2}{\rho \kappa_T RT} + \frac{\partial \ln \gamma_2}{\partial x_2}\bigg|_T \tag{11}$$

For electrolytes the salt-ion stoichiometric coefficients are involved and the activity coefficient derivatives are usually taken with respect to molality.

Comparison of experimental values of the DCFI with those from theories and models for equations of state and excess Gibbs energies can be a useful and demanding test because the data contain in a sensitive way both density and chemical potential information. We have completed a very careful evaluation of vapor-liquid equilibria, excess volumes and mixture compressibilities for 26 diverse binary nonelectrolyte mixtures at a variety of temperatures in order to establish a data base of values for this purpose. The solution types included pairs of nearly ideal, azeotropic, solvating, aqueous and very different globular and chain-like molecules. The article[27] contains equations which any researcher can use to reproduce the information and many tables of detailed results are also available from the authors on floppy disks. Figure 6 shows the variations of the various DCFI in the chloroform–acetone system. Note that the $1 - C_{12}$ value is sometimes close to the average of $1 - C_{11}$ and $1 - C_{22}$ but the variations are complex, especially at the composition limits.

Besides making the data readily available for use by others in their modeling work, the analysis demonstrated the sensitivity of the results to empirical expressions, especially for strongly nonideal systems which may be close to immiscibility. In such cases, only the most careful fitting of current models gave reliably the observed single phase behavior. For example, the popular NRTL model often gave erroneous multiple liquids. On the other hand, though it cannot yield multiple phases, the Wilson equation gave exceptionally sharp, and probably unrealistic, variations of the DCFI at low concentrations in some systems. Thus, this type of analysis might be a useful consistency test for data and correlations. Finally, we also found how the balance between the volumetric (first terms of equations 9 to 11) and the chemical thermodynamic (second terms) influences appear in this variety of systems. The results show the variety of challenges that mixtures make to the current goal of developing practical equations of state — especially their mixing and combining rules for parameters — for predicting phase and volumetric behavior.

Similar treatment of aqueous electrolyte solutions yields considerably different behavior for the $C_{\alpha\beta}$ from that of nonelectrolytes. In addition to uncertainties in the data, especially volumetric information close to saturation, similar sensitivities are found, making accurate results difficult to obtain. It is likely that we will need to develop an similar data bank for aqueous electrolytes so that experimentalists and modelers can test their work.

During the past few years, we have examined a number of approaches to modeling aqueous electrolytes which tried to take advantage of basic theories for correlation functions. While quite successful[22] for gas solubilities and liquid compressibilities of nonelectrolytes, except for correlating partial molar volumes of salts at infinite dilution over wide ranges of temperature and pressure[28], this approach did not generally lead to high accuracy when using the additivity of ionic contributions

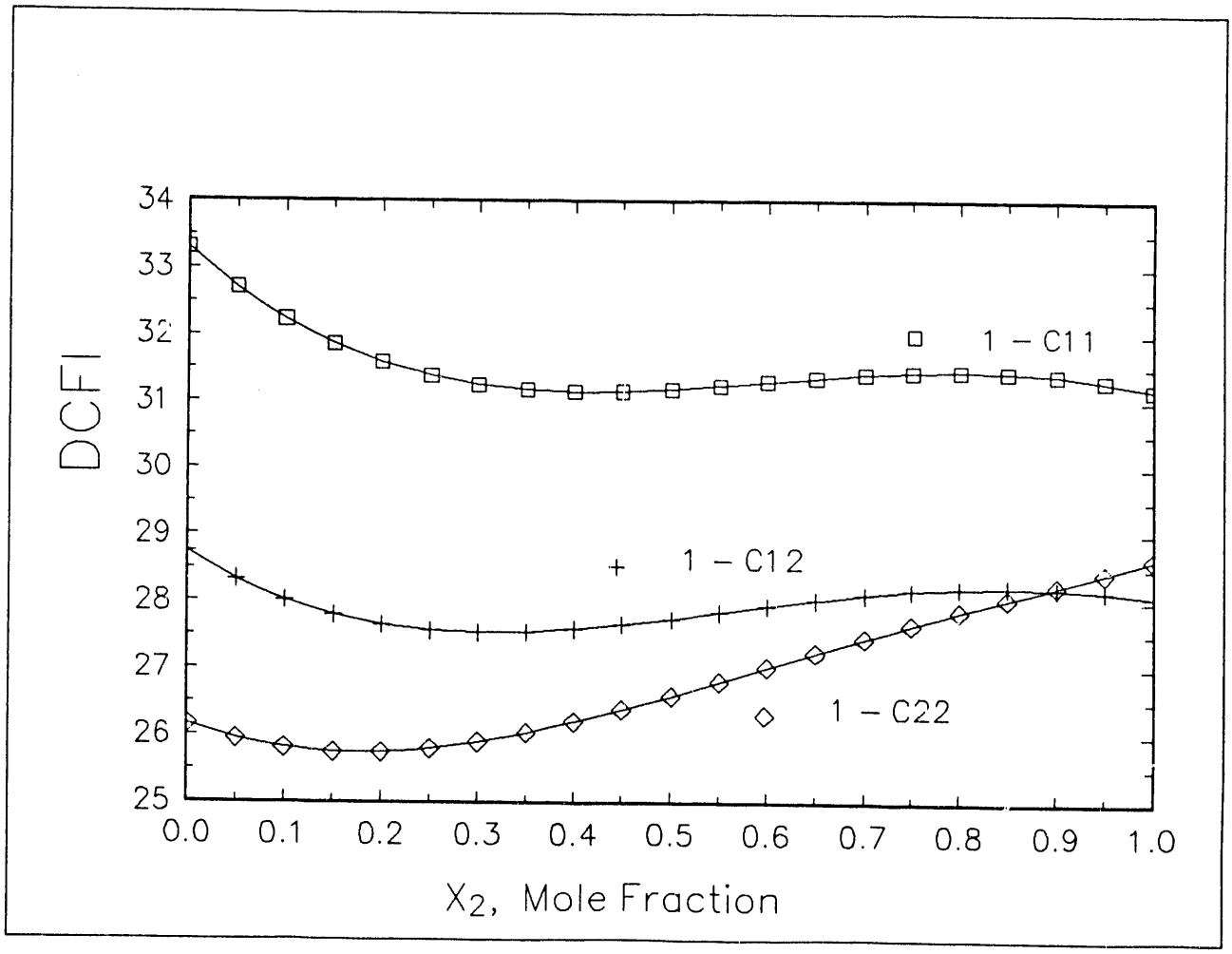

Figure 6: Direct Correlation Function Integrals for Chloroform(1)–Acetone at 25 °C.

that the formalism demands. In the past year, a reexamination of the thermodynamics of such systems with our methodology has exposed more fully an extremely subtle aspect of the relations between theory, experiment and thermodynamics that caused this failure. This effect has been touched on from time to time in the literature[29, 30], but generally not been taken into account. We have recognized that it especially affects a variety of physicochemical liquid solutions such as electrolytes, polymers, and two-phase aqueous extraction for biologicals[31].

The optimal way to express the intricacies of the situation is still being worked out, but its features are as follows. There are a variety of experimental measurements that characterize the behavior of solutes in solvents. These include vapor-liquid and liquid-liquid phase distributions, isopiestic equilibria (where several multisolute samples are equilibrated at the same solvent chemical potential via vapor phase transfer of solvent to adjust the sample compositions), osmotic pressures and chemical reaction equilibria such as electrode potentials. In most cases, the data recorded and the properties varied are the temperature, pressure and molality. It is known that thermodynamics is only concerned about how many independent variables are necessary to characterize the state of a system, not which ones. Thus, density, chemical potential, molarity and other quantities are equally suitable to use, though not usually as convenient in the laboratory. Finally, molecular theory often leads to novel sets of "natural" variables when combining them in different ways to simplify relationships among them and to lead to effective models. An example is the continuous dielectric surrounding the ions of the Debye-Hückel theory for electrolytes. The solvent is characterized by the value of its chemical potential when pure even as solute is added to the system. Such a process is realized in the laboratory by the osmotic pressure measurement, but is not obtained in vapor pressure or freezing point lowering experiments. The issue we have addressed is how to derive general, explicit connections between the various experiments as well as to demonstrate the ways in which theories should be implemented for the most desirable cases. It appears that fluctuation solution theory contains a particularly useful way to do this because it explicitly lists the thermodynamic quantities both varied and kept constant as a part of its derivatives as well as provides completely general connections among them.

The analyses which give the most general basis for categorizing these differences are embodied in the Kirkwood-Buff (KB) treatment with variables of $T, V, \underline{N}$, the Lewis-Randall (LR) variables of $T, P, \underline{N}$ and the McMillan-Mayer (MM) set of $T, V, \underline{N}_s, \underline{\mu}_S$ where $\underline{N}_s$ is the set of solute amounts and $\underline{\mu}_S$ is the list of solvent chemical potentials. The most immediate application of this new understanding is to the use of osmotic virial expansions for liquid properties. In particular, experimental phase equilibrium data are often correlated with LR coefficients because these are the most convenient. However, the values which arise from theory (MM) for predictions at other conditions, e.g. for polymers of different molecular weights without new parameters or with true ionic additivity (KB) for salts. Though there have been some treatments in previous literature[29, 30] to connect the various osmotic coefficients, fluctuation solution theory gives a particularly simple but general way to relate and interconvert the osmotic virial coefficients. Thus we have been able to list the rigorous, general connections among the derivatives for the first time. This analysis is the subject of a paper now being submitted for publication[31]. It describes the situations in which the differences can and cannot be ignored and what is needed to effectively use theory. We intend to help experimentalists understand the most effective way to analyze their data and to guide modelers to the distinctions they must make among the various theories they use and the various cases they will treat.

There are a number of important extensions of this analysis to conditions well beyond the ambient aqueous single or double solute cases presently treated. These include the vapor-liquid

critical region of the solvent and the mixed solvent case. Previous work[32] had made a contribution to correcting errors made in the mixed solvent electrolyte phase equilibria. However, our current formulation allows for a much more general approach. Connecting our analysis with the current description of critical point divergences in terms of paths to the critical point explicitly shows that while KB quantities are only weakly divergent (of no practical importance), the MM and LR quantities have strong divergences. The difference appears in the correction terms from KB since they involve the compressibility of the solution. This revelation suggests new lines of critical region modeling via correlation functions that can complement the simplifying features of simulation in the critical region as discussed in Section 2.2.

Finally, the new thermodynamic insights direct the way in which fluctuation solution theory should be used to model the properties of aqueous electrolytes. Proper data analysis demonstrates several interesting effects. In particular, the activity coefficient derivatives for the LR and MM variables are fairly close to each other for 1–1 aqueous salts while the ionically additive KB derivatives are quite different. Figure 7 shows the different activity coefficient derivatives for KCl evaluated from the data. The LR(EXP) function is for the actual data; the others have the divergent DHLL behavior removed. In addition to the LR, MM, and KB functions, the extended Debye–Hückel expression (DHEXP) is included. Note that all but the KB functions are close together. For salts of higher solubility, such as for Li^+, the difference is much larger at higher concentrations. Note also the differences in range and variation from those in Figure 8 for the nonelectrolyte mixture chloroform(1)–acetone where no electrostatic effects are present and the whole range of composition can be observed. Still the MM values are much closer to the LR values than are those for KB variables.

Thus, the relative success of workers over many years assuming that Debye–Hückel Theory gives an excess Gibbs energy (LR rather than the rigorous MM) may be due in large part to a near–cancellation of terms in single solvents (the mixed solvent case is much different), but no proper ionic treatments (KB) can be achieved via this strategy. In our own work, comparisons with data with theory had not been correct because the conversion terms were not fully taken into account. Current examination of the set of 9 salts from 6 ions (Na^+, Li^+, K^+, Cl^-, Br^-, NO_3^+) at ambient conditions indicates that ionic additivity can be achieved up to saturation when the proper connections are made. Figure 9 and Figure 10 show how the DCFI for solvent–solvent ($1-C_{11}$) and salt–solvent ($1-C_{12}$) pairs of various salts(2) in water(1) behave over their ranges of solubility at 25 °C. These seem to be able to be correlated well by ionically additive osmotic virial coefficients. (The unusual variations of LiCl and LiCl are probably due to experimental error.)

We have accumulated data for a large number of systems that can be analyzed this way as well as be correlated. This work is proceeding rapidly and will be described in a manuscript in preparation.

2.5 Analytically Solved Integral Equation Approximation Theories

We have pursued the goal of applying integral equation techniques to modeling mixed solvent electrolytes, but have not been completely successful. For molecular fluid mixtures (i.e., mixtures containing species which are non–spherical), the Ornstein–Zernike (OZ) equation is[33]

$$h_{ij}(\vec{r}_{12}\vec{\omega}_1\vec{\omega}_2) = c_{ij}(\vec{r}_{12}\vec{\omega}_1\vec{\omega}_2) + \sum_{k=1}^{m} \frac{\rho_k}{\Omega} \int c_{ik}(\vec{r}_{13}\vec{\omega}_1\vec{\omega}_3) h_{kj}(\vec{r}_{32}\vec{\omega}_3\vec{\omega}_2) d\vec{r}_3 d\vec{\omega}_3 \qquad (12)$$

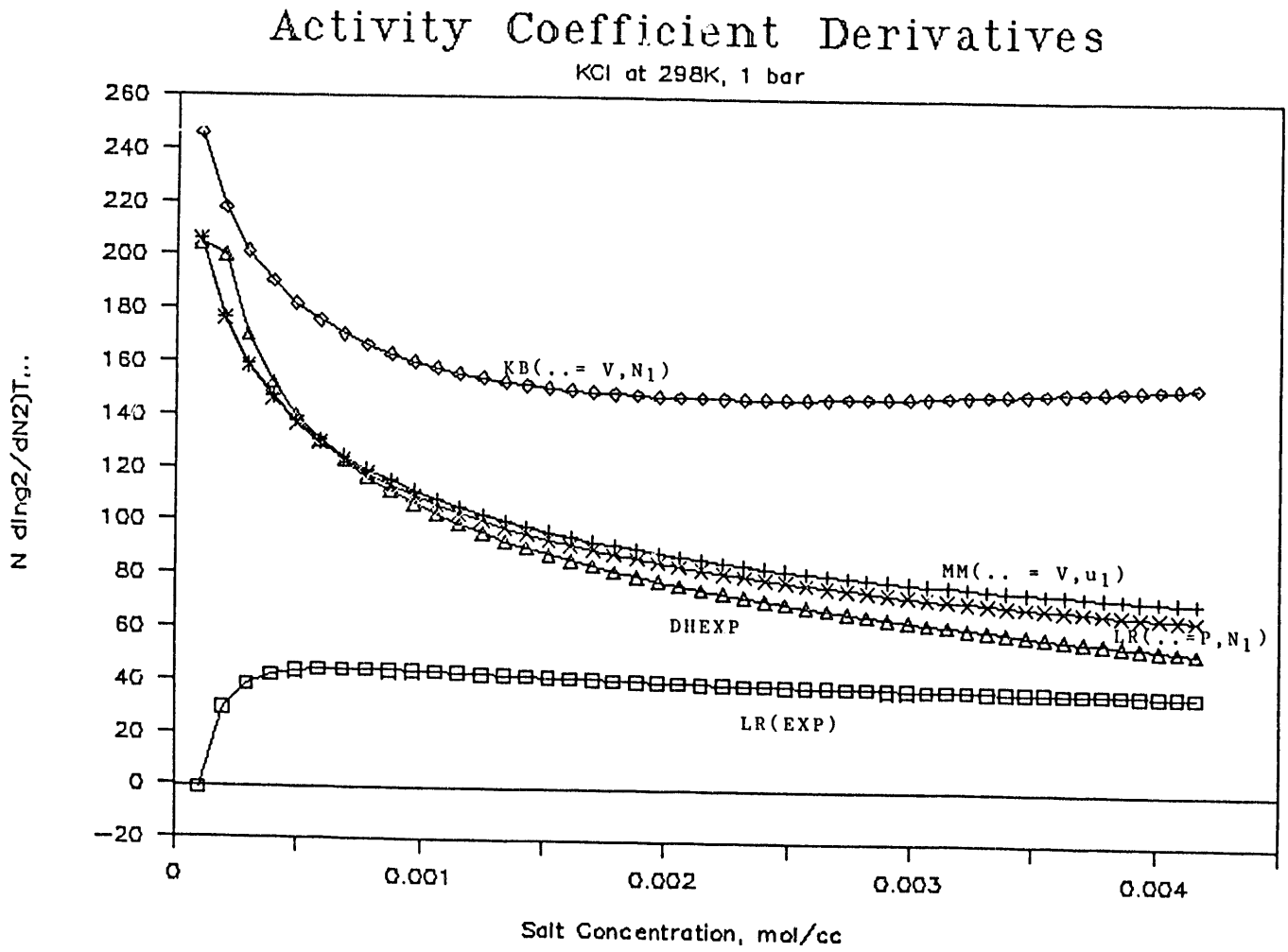

Figure 7: Various activity coefficient derivatives for KCl(2) in water at 25 °C.

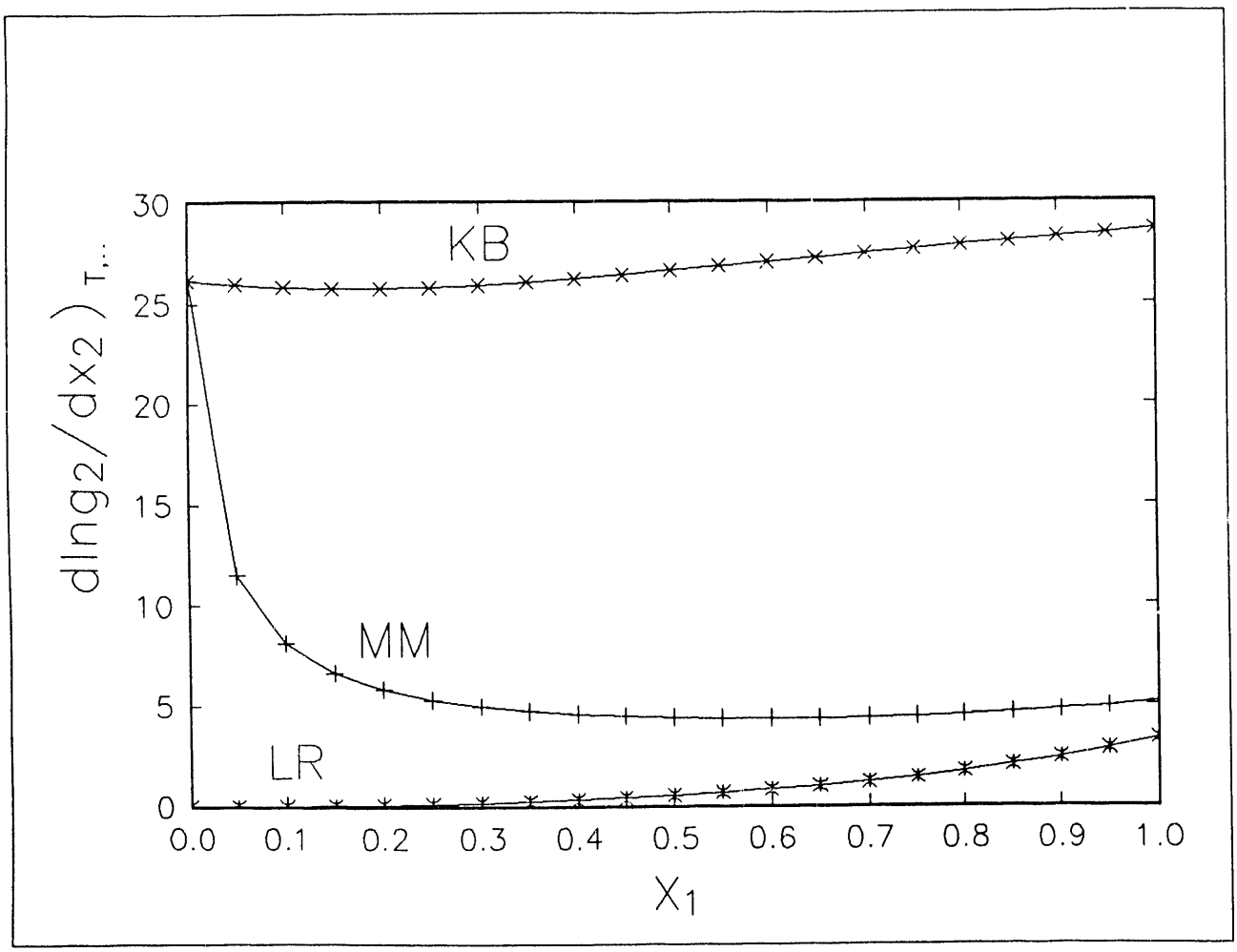

Figure 8: Various activity coefficient derivatives for Chloroform (1) with Acetone at 25 °C.

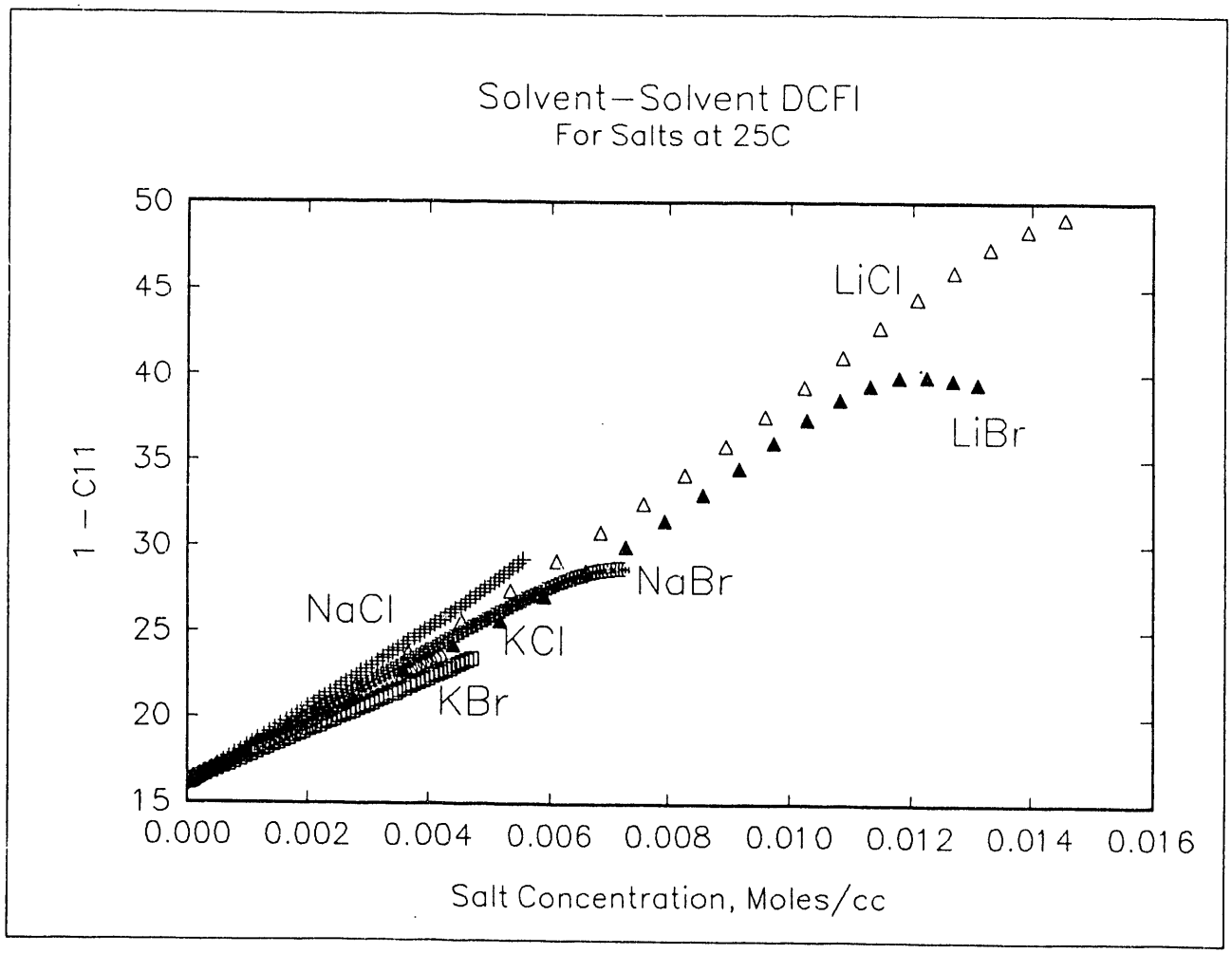

Figure 9: Solvent–solvent DCFI for various 1–1 salts in water at 25 °C.

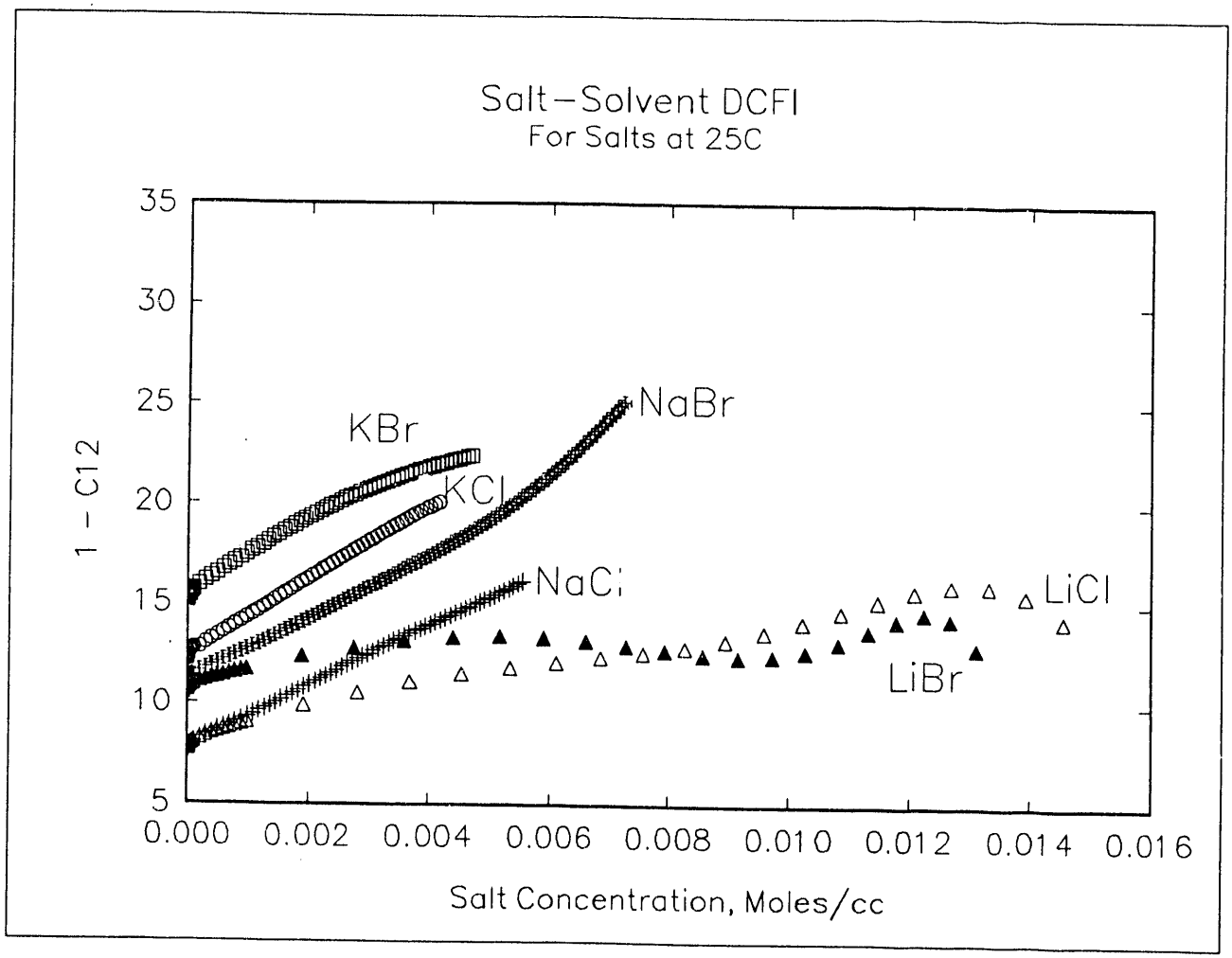

Figure 10: Salt–solvent DCFI for various 1–1 salts in water at 25 °C.

where $\vec{r}_{ij}$ is the vector joining the centers of mass of molecule i and j, $\vec{\omega}_i$ denotes the set of angles specifying the orientation of molecule i and $\Omega = \int d\omega = 4\pi$ for linear molecules, $8\pi^2$ for nonlinear molecules. The solution of the OZ equation requires the use of the invariant expansion method for expanding the OZ equation and the closure approximation in terms of a set of rotational invariants. For any function $f(\vec{r}_{12}\vec{\omega}_1\vec{\omega}_2)$, the invariant expansion of f is given by

$$f(\vec{r}_{12}\vec{\omega}_1\vec{\omega}_2) = \sum_{\ell_1\ell_2\ell} \sum_{n_1 n_2} f(\ell_1\ell_2\ell; n_1 n_2; r_{12}) \psi^{\ell_1\ell_2\ell}_{n_1 n_2}(\vec{\omega}_1\vec{\omega}_2\vec{\omega}) \tag{13}$$

where $f(\ell_1\ell_2\ell; n_1 n_2; r_{12})$ is a expansion coefficient, $\psi^{\ell_1\ell_2\ell}_{n_1 n_2}(\vec{\omega}_1\vec{\omega}_2\vec{\omega})$ is a rotational invariant and $\vec{\omega}$ describes the orientation of $\vec{r}_{12}$ in space. The technical details of the invariant expansion and expressions for $f(\ell_1\ell_2\ell; n_1 n_2; r_{12})$ are given elsewhere[33, 34]. Expanding h, g, c and u in the OZ equation and the closure approximation in terms of rotational invariants yields a set of coupled integral and algebraic equations for the expansion coefficients.

Our focus has been a simple model of mixed solvent electrolyte solutions to provide the starting point for analytic expressions for solution properties. For a nonelectrolyte–water–salt system, Strauch[10] solved the mean spherical approximation analytically for a four component mixture composed of two dipolar hard sphere species and two ionic species, *viz*

$$\begin{aligned}
u_{ij}(\vec{r}_{12}\vec{\omega}_1\vec{\omega}_2) &= \infty && r < \sigma_{ij} \\
&= u_{ij}^{DD} + u_{ij}^{DQ} + u_{ij}^{QQ} && r > \sigma_{ij} \\
& && ij = 11, 12, 22 \\
u_{ij}(\vec{r}_{12}\vec{\omega}_1\vec{\omega}_2) &= \infty && r < \sigma_{ij} \\
&= u_{ij}^{CC} && r > \sigma_{ij} \\
& && ij = 33, 34, 44 \\
u_{ij}(\vec{r}_{12}\vec{\omega}_1\vec{\omega}_2) &= \infty && r < \sigma_{ij} \\
&= u_{ij}^{CD} + u_{ij}^{CQ} && r > \sigma_{ij} \\
& && ij = 13, 14, 23, 24
\end{aligned} \tag{14}$$

In these equations, the superscripts C, D and Q refer to charge, dipole and quadrupole respectively. Strauch used a generalization of the method of Blum[35–37] based on the technique of Baxter[38, 39] and Wertheim[40] for factorizing the OZ equation into sets of simplified one dimensional integral equations for the expansion coefficients of the correlation functions. The analysis has been brought to the point where its completion requires the numerical solution of a set of coupled nonlinear algebraic equations. We propose to pursue this during the next grant period (1992–1994).

With DOE support, we have solved analytically the MSA for a simple model of water that includes short ranged, directional forces that mimic the hydrogen bond forces in real water[41]. Professor Blum expects this model to be implemented numerically in the near future (private communication, 1991).

Thus, we have made significant progress toward the goal of developing an equation of state for mixed solvent electrolytes based on the analytic solution of the MSA for a mixture of dipolar and ionic species. Bringing the goal to fruition will require additional effort and expertise. We are investigating the possibility of involving Professor Blum and his graduate students in the research as one means for completing the goal in a timely fashion.

2.6 Numerically Solved Integral Equation Approximation Theories

We have taken the first steps toward the goal of solving the OZ equation for alcohol–water–salt mixtures subject to the full hypernetted chain (HNC) approximation for molecular species

$$c_{ij}(\vec{r}_{12}\vec{\omega}_1\vec{\omega}_2) = g_{ij}(\vec{r}_{12}\vec{\omega}_1\vec{\omega}_2) - 1 - \ln g_{ij}(\vec{r}_{12}\vec{\omega}_1\vec{\omega}_2) - \frac{u_{ij}(\vec{r}_{12}\vec{\omega}_1\vec{\omega}_2)}{k_B T} \tag{15}$$

The HNC has been shown to be the most accurate integral equation approximation for systems with long–range forces[42–45]. The numerical solution of the OZ equation requires the use of the invariant expansion method for expanding the OZ equation and the closure approximation in terms of a set of rotational invariants. The logarithmic term in the HNC approximation can be handled using Patey's technique[46, 47]. In order to satisfactorily represent the intermolecular potentials for the non–spherical species and to adequately approximate the correlation functions, a large number of terms is required in the invariant expansion. With DOE support, we have reached the point where we have a satisfactory program working for solving the HNC for a pure Stockmayer fluid—i.e., a fluid whose molecules interact by a potential composed of LJ and dipole–dipole interactions.

This relatively small degree of progress was achieved only by several years effort by two Ph.D. students. It is clear that achieving the goal of solving the OZ equation with HNC closure for realistic models of alcohol–water–salt mixtures is much more difficult than originally anticipated and can probably only be achieved by a collaborative effort with other senior researchers. In addition, the evolution of the GEMC technique as a viable means for studying phase equilibria directly has lessened the need for achievement of this goal and resulted in it being assigned a lower priority in our research.

3 Publications Supported by Grant

The support of the grant has resulted in the following publications:

1. Blum, L., Cummings, P. T. and Bratko, D., "A General Solution of the Molecular Ornstein–Zernike Equation for Spheres with Anisotropic Surface Adhesion and Electric Multipoles," *J. Chem. Phys.* **92** (1990) 3741–3747.

2. Rudisill, E. N. and Cummings, P. T., "Gibbs Ensemble Simulation of Phase Equilibrium in the Hard Core Two–Yukawa Fluid Model for the Lennard–Jones Fluid," *Molec. Phys.* **68** (1989) 629–635.

3. de Pablo, J. J., Prausnitz, J. M., Strauch, H. J. and Cummings, P. T., "Molecular Simulation of Water Along the Liquid–Vapor Coexistence Curve from 25°C to the Critical Point," *J. Chem. Phys.*, **93** (1991) 7355–7359.

4. Cummings, P. T., Cochran, H. D., Simonson, J. M., Mesmer, R. E. and Karaborni, S., "Simulation of Supercritical Water and of Supercritical Aqueous Solutions," *J. Chem. Phys.* **94** (1991) 5606–5621.

5. Cochran, H. D., Cummings, P. T. and Karaborni, S., "Solvation in Supercritical Water," *Fluid Phase Equil., accepted for publication (1991).*

6. Strauch, H. J. and Cummings, P. T., "Comment on: Molecular Simulation of Water Along the Liquid-Vapor Coexistence Curve from 25°C to the Critical Point," *J. Chem. Phys., submitted for publication (1991).*

7. Beil, N. B., Strauch, H. J., Karaborni, S. and Cummings, P. T., "Molecular Simulation of the Dielectric Constant of SPC Water," *Molec. Phys., in preparation (1991).*

8. Strauch, H. J. and Cummings, P. T., "Gibbs Ensemble Simulation of Phase Equilibria in Mixed Solvent Electrolytes Systems," *Fluid Phase Equil., in preparation (1991).*

9. O'Connell, J. P., "Thermodynamic Properties of Mixtures from Fluctuation Solution Theory," in *Fluctuation Theory of Mixtures*, ed. by E. Matteoli and G. A. Mansoori, Taylor and Francis, 1990, p 45.

10. O'Connell, J. P., "Thermodynamic Properties of Fluids from Fluctuation Solution Theory," *Journal of High Pressure-High Temperature, in press (1991).*

11. Wooley, R. J. and O'Connell, J. P., "A Database of Fluctuation Thermodynamic Properties and Molecular Correlation Integrals for a Variety of Binary Liquids," *Fluid Phase Equil., in press (1991).*

12. Cabezas, Jr., H., and O'Connell, J. P. , "Some Uses and Misuses of Dilute Solution Thermodynamic Models," *Ind. Eng. Chem. Res., in preparation.*

Conference presentations describing research supported by the grant include:

1. O'Connell, J. P., "Thermodynamic Properties of Fluids from Fluctuation Solution Theory," invited lecture, 12th European Conference on Thermophysical Properties, Vienna, Austria, September, 1990.

2. Cabezas, Jr., H., K. A. Marshall and J. P. O'Connell, " "Fluctuation Solution Theory Model for Aqueous Strong Electrolytes," American Institute of Chemical Engineers Annual Meeting, Chicago, IL, November, 1990.

3. Strauch, H. J. and Cummings, P. T., "Theoretical Approaches to Phase Equilibria in Mixed Solvent Electrolyte Solutions," American Institute of Chemical Engineers Annual Meeting, Chicago, November 11-16, 1990.

4. Cochran, H. D., Cummings, P. T. and Karaborni, S., "Solvation in Supercritical Water," 2nd International Symposium on Supercritical Fluids, May 20-21, 1991.

5. Cochran, H. D., Cummings, P. T., and Karaborni, S., "Structure and Properties of Supercritical Water," 11th Symposium on Thermophysical Properties, June 23-23, 1991.

6. O'Connell, J. P., "Thermodynamic Properties of Aqueous Strong Electrolytes from Fluctuation Solution Theory," 11th Symposium on Thermophysical Properties, June 23-23, 1991.

7. Strauch, H. J. and Cummings, P. T., "Gibbs Ensemble Simulation of Vapor-Liquid Equilibrium in Water/NaCl and Water/Methanol Mixtures," American Institute of Chemical Engineers Annual Meeting, Los Angeles, November 17-22, 1991.

The grant supported the thesis research of four graduate students at the University of Virginia:

1. Osborne, L. R., "Experimental Measurement of Phase Equilibrium in Mixed Solvent Electrolytes," M.S.Ch.E. thesis, University of Virginia, 1989.

2. Beil, N. B., "Molecular Dynamics Simulation of the Dielectric Properties of Water," M.S.Ch.E. thesis, University of Virginia, 1990.

3. Strauch, H. J., "Towards a Statistical Mechanical Theory of Mixed Solvent Electrolyte Solutions, " Ph.D. (Ch.E.) thesis, University of Virginia, 1991.

4. Liu, H., "Salting Effects on Vapor–Liquid Equilibria," M.S.Ch.E. thesis, University of Virginia, 1991.

Literature Cited

[1] A. Z. Panagiotopoulos. *Molec. Phys.*, 61:813, 1987.

[2] E. N. Rudisill and P. T. Cummings. *Molec. Phys.*, 68:629, 1989.

[3] H. J. C. Berendsen, J. P. M. Postma, W. F. von Gunsteren, and J. Hermans. Interaction models for water in relation to protein hydration. In B. Pullman, editor, *Intermolecular Forces*, page 331. Reidel, Dordrecht, 1981.

[4] J. J. de Pablo, J. M. Prausnitz, H. J. Strauch, and P. T. Cummings. *J. Chem. Phys.*, 93:7355, 1991.

[5] S. W. de Leeuw, J. W. Perram, and E. R. Smith. *Proc. Royal Soc. London*, A373:27, 1980.

[6] S. W. de Leeuw, J. W. Perram, and E. R. Smith. *Proc. Royal Soc. London*, A373:57, 1980.

[7] S. W. de Leeuw, J. W. Perram, and E. R. Smith. *Proc. Royal Soc. London*, A388:177, 1983.

[8] J.J. de Pablo and J. M. Prausnitz. *Fluid Phase Equil.*, 53:177, 1989.

[9] H. J. Strauch and P. T. Cummings. *J. Chem. Phys.*, 1991. Submitted for publication.

[10] H. J. Strauch. *Towards a Statistical Mechanical Theory of Mixed Solvent Electrolyte Solutions.* PhD thesis, University of Virginia, 1991. unpublished.

[11] H. J. Strauch and P. T. Cummings. *Fluid Phase Equil.*, 1991. In preparation.

[12] M. Haughney, M. Ferrario, and I. R. McDonald. *Mol. Phys.*, 58:849, 1986.

[13] F. G. Fumi and M. P. Tosi. *J. Phys. Chem. Solids*, 25:31, 1964.

[14] M. P. Tosi and F. G. Fumi. *J. Phys. Chem. Solids*, 25:45, 1964.

[15] J. Chandrasekhar, D. C. Spellmeyer, and W. L. Jorgensen. *J. Am. Chem. Soc.*, 106:903, 1984.

[16] J. C. Morrison, J. F.and Baker, H. C. Meredith, K. E. Newman, T. D. Walter, R. L. Massie, J. D.and Perry, and P. T. Cummings. *J. Chem. Eng. Data*, 35:395, 1990.

[17] P. T. Cummings, H. D. Cochran, J. M. Simonson, R. E. Mesmer, and S. Karaborni. *J. Chem. Phys.*, 94:5606, 1991.

[18] H. D. Cochran, P. T. Cummings, and S. Karaborni. *Fluid Phase Equil.*, 1991. Accepted for publication.

[19] L. R. Osborne. Phase Equilibria of Mixed Solvent Electrolytes. Master's thesis, University of Virginia, 1989. unpublished.

[20] T. Boublík and G. C. Benson. *Can. J. Chem.*, 47:539, 1969.

[21] H. C. Meredith, III. Experimental Measurement of Vapor–Liquid Equilibrium in Mixed Solvent Electrolytes. Master's thesis, University of Virginia, 1987. unpublished.

[22] J. P. O'Connell. Thermodynamic properties of mixtures from fluctuation theory. In E. Matteoli and G. A. Mansoori, editors, *Fluctuation Theory of Mixtures*, Advances in Thermodynamics, Volume 2. Taylor and Francis, New York, 1990.

[23] J. G. Kirkwood and F. P. Buff. *J. Chem. Phys.*, 19:774, 1951.

[24] J. P. O'Connell. *Molec. Phys.*, 20:27, 1971.

[25] R. L. Perry and J. P. O'Connell. *Mol. Phys.*, 52:137, 1984.

[26] R. L. Perry, H. Cabezas, Jr., and J. P. O'Connell. *Molec. Phys.*, 63:189, 19.

[27] R. J. Wooley and J. P. O'Connell. *Fluid Phase Equil.*, 1991. In press.

[28] W.-R. Cooney, Jr. and J. P. O'Connell. *Chem. Eng. Comm.*, 56:341, 1987.

[29] H. L. Friedman. *J. Soln. Chem.*, 1:387, 413, 419, 1972.

[30] B. A. Pailthorpe, D. J. Mitchell, and B. W. Ninham. *J. Chem. Soc. Faraday Trans.*, 80:115, 1985.

[31] H. Cabezas, Jr. and J. P. O'Connell. Uses and misuses of thermodynamic models for dilute liquid solutions. In preparation, 1991.

[32] M. J. E. de M. Cardoso and J. P. O'Connell. *Fluid Phase Equil.*, 33:315, 1987.

[33] C. G. Gray and K. E. Gubbins. *Theory of Molecular Fluids.* Oxford University Press, 1985.

[34] P. T. Cummings, J. Ram, R. Barker, C. G. Gray, and M. S. Wertheim. *Molec. Phys.*, 48:1177, 1983.

[35] L. Blum. *J. Chem. Phys.*, 57:1862, 1972.

[36] L. Blum and A. J. Torruella. *J. Chem. Phys.*, 56:303, 1972.

[37] L. Blum. *J. Chem. Phys.*, 58:3295, 1973.

[38] R. J. Baxter. *Aust. J. Phys.*, 21:563, 1968.

[39] R. J. Baxter. *J. Chem. Phys.*, 52:4559, 1970.

[40] M. S. Wertheim. *J. Math. Phys.*, 5:643, 1964.

[41] L. Blum, P. T. Cummings, and D. Bratko. *J. Chem. Phys.*, 92:3741, 1990.

[42] H. L. Friedman. *Ann. Rev. Phys. Chem.*, 12:171, 1961.

[43] H. L. Friedman. Computed thermodynamic properties and distribution functions for simple models of ionic fluids. In J. O'M. Bockris, editor, *Modern Aspects of Electrochemistry*, chapter 1. Plenum Press, 1971.

[44] H. L. Friedman. *Ann. Rev. Phys. Chem.*, 32:179, 1981.

[45] B. Hafskjold and G. Stell. The equilibrium statistical mechanics of simple ionic liquids. In E. W. Montroll and J. L. Lebowitz, editors, *The Liquid State of Matter: Fluids, Simple and Complex*. North-Holland, Amsterdam, 1982.

[46] J. S. Perkyns, P. H. Fries, and G. N. Patey. *Molec. Phys.*, 57:529, 1986.

[47] J. S. Perkyns, P. G. Kusalik, and G. N. Patey. *Chem. Phys. Letts.*, 129:258, 1986.

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