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THEORETICAL AND EXPERIMENTAL STUDY OF MIXED SOLVENT ELECTROLYTES

Final Report

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P. T. Cummings
UT/ORNL Distinguished Scientist
Department of Chemical Engineering
University of Tennessee
419 Dougherty Engineering Building
Knoxville, TN 37996-2200
and
Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6181

Submitted to:
Dr. F. D. Stevenson
Department of Energy
19901 Germantown Road
Germantown, MD 20874

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1. Introduction

This Report describes research accomplished with support from the one-year research grant, DE-FG05-94ER14421, to the principal investigator (PI), Peter Cummings, at the University of Tennessee. ¹⁻¹⁹

On January 1, 1994, the PI assumed a UT/ORNL Distinguished Scientist position jointly with the Department of Chemical Engineering at the University of Tennessee (UT) in Knoxville, TN, and the Chemical Technology Division at Oak Ridge National Laboratory (ORNL) in Oak Ridge, TN. The Distinguished Scientist position affords many advantages to the Prof. Cummings' DOE-supported research program, such as the opportunity to interact with the experimental program in aqueous solution chemistry in the Chemistry Division of ORNL and access to the massively parallel computing facilities at ORNL and UT. The move from the University of Virginia to UT resulted in considerable disruption to the research program. For example, renovations of computational laboratories at the University of Tennessee were not completed until early March and the experimental laboratory located at ORNL was not fully operational until the early summer. Delays in the delivery of workstations also hindered progress. Despite these difficulties, however, it has been a very productive year accented by high visibility for the research program. Between the start of the grant and August 1, five manuscripts have been submitted for publication acknowledging DOE support from this grant¹⁻⁵. Several more manuscripts will be submitted for publication before the end of 1994, one in the proceedings of the 12th International Conference on the Properties of Water and Steam to be held in Orlando in September, several of the papers to be presented at the 1994 AIChE Annual meeting will be submitted for publication in an ACS Symposium Series volume on supercritical fluids, and the experimental paper by Slusher *et al.* to be presented at the 1994 AIChE Annual meeting will be submitted for publication in a special issue of the Journal of Chemical and Engineering Data. By the end of 1994, eleven papers based on work completed this year will have been presented at conferences during this period⁶⁻¹⁶. One of the conference presentations⁹ was an invited presentation.

In the original proposal for this one year grant, four research objectives were formulated:

1. Perform Gibbs ensemble Monte Carlo (GEMC) simulation of mixed solvent electrolytes, in particular of ethanol/water/NaCl;
2. Perform molecular dynamics simulation of supercritical aqueous solutions, with emphasis on supercritical electrolyte solutions;

3. Perform experimental measurements of phase equilibria in water/alcohol/organic salt mixtures; and
4. Conduct integral equation studies of mixed solvent electrolytes.

Given the constraints imposed by the move from the University of Virginia to the University of Tennessee, progress on these four objectives has been very good. The most progress has been made on objective 2, and as a reflection of this, all of the papers submitted so far this year (up to August, 1994) have related to this subject.

2. Research Accomplishments During Grant Period

2.1. Gibbs Ensemble Monte Carlo Simulation of Mixed Solvent Electrolytes

In previous DOE-supported research²⁰⁻²², we performed GEMC simulations of vapor liquid equilibrium (VLE) in salt free methanol/water and salt-containing methanol/water systems. The agreement with experiment for the salt-free case was very good; for the salt-containing simulations, methanol is salted out (as is observed experimentally) though the simulations tend to overestimate the effect of the salt on the methanol/water VLE. By calculating the structural properties of methanol/water and methanol/water/NaCl at VLE, we were able to confirm that the molecular mechanism for salting out of alcohols from aqueous solution by alkali halides is that the water complexes more easily with the ions than does the alcohol, so that the water forms low volatility, high molecular weight complexes thus lowering the volatility of the water relative to the alcohol. These simulation studies were performed using the SPC model for water²³, the Haughney *et al.* H1 model for methanol-methanol interaction²⁴, the Fumi-Tosi ion-ion potentials^{25,26} and the Chandrasekhar *et al.* model for the ion-water interaction²⁷, with all other interactions being derived by Lorentz-Berthelot combining rules. Thus, there were no adjustable parameters and the GEMC results for methanol/water and methanol/water/NaCl were pure predictions. The remarkable success of this work generated considerable interest, including that of industry, in the use of GEMC for predicting phase equilibria in complex aqueous systems.

Our goal in the current grant period was to perform GEMC studies of ethanol/water and ethanol/water/ NaCl. Difficulties were encountered in obtaining convergence in the GEMC simulations for ethanol/water which suggested inadequacies in the ethanol/ethanol interaction. Rather than pursuing the ethanol-containing systems, we decided to return to the methanol-containing systems to investigate the reasons for the inaccuracy of the methanol/water/NaCl results given that the methanol/water results were in such good agreement with experiment. We reached the conclusion that since the SPC potential for water and the H1 potential for methanol

both underestimate their respective critical points^{28,29}, the good agreement between the methanol/water GEMC simulations and experimental VLE data was to some extent fortuitous and represented a cancellation of two inaccuracies. We are now performing GEMC simulations of water/methanol using the SPCE potential for water³⁰ which produces much better pure water VLE³¹ and the H1 potential for methanol. The next step is to replace the H1 potential for methanol by the modified H1 potential developed by van Leeuwen and Smit²⁹ which reproduces the phase envelope of methanol with a high degree of accuracy. Very preliminary results on the SPCE/H1 GEMC were reported in several conference presentations and invited seminars^{6,17,18}. This work is still in progress.

We regard the use of SPCE and modified H1 as intermediate steps to the adoption of full polarizable potentials in our future aqueous systems work. The inadequacies of non-polarizable models in describing the phase envelope of pure water are, in our opinion, attributable to the high effective dipole moments of these models which, while quite reasonable in low temperature high density liquid states, are inappropriate for low density vapor states. Additional evidence from neutron scattering in supercritical fluids is discussed in the next Section.

2.2. Molecular Simulation and Theory of Supercritical Aqueous Solutions

Part of our research effort this year has involved the extension of our molecular formalism for the description of supercritical mixtures developed with prior DOE support³². In a comment on a paper published by Gude and Teja³³, we pointed out some important relationships between macroscopic thermodynamic quantities and molecular counterparts¹. In particular, the parameter $(\partial P/\partial x_U)_{T,\rho_V}$, where P is the pressure, ρ_V is the density of the pure solvent, T is the absolute temperature and x_U the mole fraction of the solute, which at the solvent critical point is the Krichevskii parameter³⁴, can be related both to integrals of the direct correlation functions as well as to N_{UV}^{ex} , the excess number of solvent molecules around a solute compared to that around a solvent molecule. For a mixture of solvent molecules (labeled V) with infinitely dilute solute labeled U , the latter relationship is given by

$$N_{UV}^{ex} = 4\pi\rho_V \int_0^\infty [g_{UV}(r') - g_{VV}(r')] r'^2 dr' = -\kappa_T \left. \frac{\partial P}{\partial x_U} \right|_{T,\rho_V}^\infty = 1 - \rho_V \bar{v}_U^\infty \quad (1)$$

where $g_{UV}(r)$ and $g_{VV}(r)$ are respectively the solute-solvent and solvent-solvent radial distribution functions, κ_T is the isothermal compressibility of the solvent, $\bar{v}_U^\infty$ is the solute partial molar volume at infinite dilution and the ∞ superscript on the quantity $(\partial P/\partial x_U)_{T,\rho_V}$ indicates the infinite dilution limit of that quantity. The relationship between our molecular solvation formulation (expressed in terms of direct correlation functions and radial distribution functions) and the macroscopic thermodynamics of supercritical mixtures was further explored in

Figure 1. The potential of mean force for NaCl in supercritical water calculated by molecular dynamics simulations at high temperature, low density ($T=800\text{K}$, $\rho=0.083\text{g/cc}$)³⁵, $T=616\text{K}$, $\rho=0.27\text{g/cc}$ ⁴ ($T_r=1.05$ and $\rho_r=1$ for SPC) and ambient conditions ($T=298\text{K}$, $\rho=1.0\text{g/cc}$)³⁶. The first two studies used the SPC model for water^{4,35} while the last study used flexible SPC³⁶.

In the past year⁴, we have calculated the potential of mean force between Na^+ and Cl^- ions at infinite dilution in supercritical water at $T_r=1.05$ and $\rho_r=1$ with the result shown in Figure 1. The simulations are performed by constraining the Na^+-Cl^- distance at various values of separation r , calculating the direct and average solvent induced forces on the ions, and integrating the mean force to obtain the potential of mean force $\Psi(r)$. The radial distribution function at infinite dilution is then related to $\Psi(r)$ by

$$g_{\text{NaCl}}^\infty(r) = \exp\left[-\frac{\Psi(r)}{k_B T}\right] \quad (2)$$

from which can be calculated the equilibrium constant for ionic association,

$$K_a = \frac{\rho_{\text{NaCl}}}{\rho_{\text{Na}^+} \rho_{\text{Cl}^-}} \quad (3)$$

where ρ_{NaCl} , ρ_{Na^+} and ρ_{Cl^-} are, respectively, the densities of associated ion pairs, unassociated Na^+ and unassociated Cl^- ions. At $T_r=1.05$ and $\rho_r=1$, we find from the simulation that

$K_a \approx 8 \times 10^4 \text{ mol/lit}$ in agreement with expectations based on experimental measurements. These theoretical calculations are being carried out in concert with experimental studies by Mesmer and Simonson of the High Temperature Aqueous Chemistry group at Oak Ridge National Laboratory. Also shown in Figure 1 are the potentials of mean force at lower density and higher temperature calculated by Cui and Harris³⁵ and at ambient conditions by Guardia *et al.*³⁶. At the high temperature/low density state, the associated ion pair is favored strongly over the solvent separated ion pair ($\text{Na}^+\text{-Cl}^-$ separated by one solvent molecule) while at ambient conditions the solvent separated ion pair is favored over the associated ion pair. At the supercritical state studied by us, the associated ion pair is favored over the solvent separated ion pair, but to a much lesser extent than that exhibited at high temperature/low density.

Figure 2. Comparison between the experimental and the simulated SPCE and SPCG O—H, $g_{\text{OH}}(r)$, radial distribution functions of water at $T = 573\text{K}$ and $\rho = 0.72\text{gm/cc}$. Note that the neutron scattering (NDIS) results include an intramolecular peak at short range which is not included in the simulation results.

Recently Postorino *et al.*³⁷ reported neutron scattering results for supercritical water. We compared MD simulations of SPC, SPCE and SPCG (the SPC model but with charges rescaled to have the bare dipole moment of water of 1.85D initially proposed by Strauch and Cummings³⁸ for use in the vapor phase of water) to the neutron scattering results at the same state conditions. We found that SPCG was remarkably accurate in reproducing the neutron scattering results (see Figure 2). SPC and SPCE overpredict the amount of structure in supercritical states (SPCE to a

greater extent than SPC) due to the high dipole moments of these two models. The success of effective models like SPC and SPCE for liquid water at ambient condition, coupled with their inaccuracy at supercritical states which is apparently most closely tied to the high effective dipole moment, is further evidence that we need to adopt a polarizable model if we wish to reproduce the properties of liquid water over wide ranges of temperature and density.

2.3. Experimental Measurements of Phase Equilibria

As noted in the Introduction, considerable delays were experienced in setting up the experimental facilities at Oak Ridge National Laboratory (ORNL). As of August, 1994, the experimental facilities have been fully operational for only three months. Nevertheless, some experimental measurements have been taken. The efficiency of the experimental research has been enhanced by the new equipment available at ORNL. The composition analysis of the liquid phase has been simplified considerably with the new Hewlett Packard 5890E gas chromatograph (GC) with computer data acquisition capability. By using a small unpacked section of column at the entrance to the packed column, we have been able to trap salt in the alcohol/water/salt liquid samples and perform GC analysis on the alcohol/water mixture alone. This automatically generates the salt-free composition of the liquid, which previously was calculated by material balance rather than by GC analysis. Reproducible results to within 1% are now obtained for liquid phase compositions as well as for the gas phase compositions which, as in our previous work, are obtained by GC analysis. [Note that the vapor phase contains essentially no salt due to its low volatility.] Experimental measurements this summer have been made on n-propanol/water/tetrapentyl-ammonium bromide VLE to complement our existing measurements with isopropanol.

Considerable effort was expended during the year in setting up the Paar DM58 vibrating tube densimeter, an instrument acquired from another researcher at ORNL. The instrument is now operational and will be used to duplicate density measurements being performed at the University of Virginia under the supervision of Professor John P. O'Connell. The VLE and density measurements will be reported at the 1994 AIChE meeting in San Francisco¹⁴.

2.4 Integral Equation Studies of Electrolyte Solutions

Our goal of applying integral equation approximations to the description of supercritical mixtures, particularly supercritical aqueous solutions of electrolytes, received a significant boost in May with the arrival in the research group of Professor Yuriy Kalyuzhnyi from the Institute for Condensed Matter Physics in Lviv, Ukraine, as a sabbatical visitor for one year. Professor Kalyuzhnyi is an expert in the application of modern integral equation theories, particularly those

that take into account association³⁹⁻⁴¹ which is a key effect in supercritical aqueous electrolytes. In the period May-August, 1994, Professor Kalyuzhnyi and the PI have performed some preliminary calculations which suggest that ion-ion, ion-water and water-water association effects all need to be accounted for in an integral equation theory of supercritical aqueous electrolytes, an effort that is currently underway. Agreement with molecular dynamics simulation is qualitative at this stage in the development of the theory.

3. Publications and Presentations Acknowledging DOE Support

Refereed Papers Submitted During Grant Period:

1. Chialvo, A. A.; Cummings, P. T., Comment on: Near Critical Behavior of Dilute Mixtures. *Molec. Physics* accepted for publication (1994).
2. Chialvo, A. A.; Cummings, P. T., Solvation Thermodynamics of Gas Solubility at Near Critical Conditions. *A.I.Ch.E. Journal* submitted for publication (1994).
3. Chialvo, A. A.; Cummings, P. T., Molecular-based Solvation Formalism for Supercritical Mixtures in Terms of Krichevskii's Parameters. *Int. J. Thermophysics* submitted for publication (1994).
4. Chialvo, A. A.; Cummings, P. T.; Cochran, H. D., Solvation Structure, Hydrogen Bonding, and Ion-Pairing in Dilute Supercritical Aqueous NaCl Mixtures. *Int. J. Thermophysics* submitted for publication (1994).
5. Chialvo, A. A.; Cummings, P. T., Hydrogen bonding in supercritical water. *J. Chem. Phys.* in press (1994).

Conference Presentations:

6. Chialvo, A. A. and Cummings, P. T., "Gibbs Ensemble Monte Carlo Simulation of Vapor-Liquid Equilibrium in Water/Alcohol/NaCl Mixtures," AIChE Spring Meeting, Atlanta, GA, April 17-20, 1994
7. Chialvo, A. A. and Cummings, P. T., "Vapor-Liquid Equilibrium of SF₆: How well do simple models describe it?," AIChE Spring Meeting, Atlanta, April 17-20, 1994.
8. Chialvo, A. A., "Solute Synergism in Dilute Near-Critical Ternary Mixtures," AIChE Spring Meeting, Atlanta, April 17-20, 1994.
9. Cummings, P. T., "Molecular Simulation of Water and Aqueous Solutions," 4th Liblice Conference on Statistical Mechanics of Liquids, Lake Milovy, Czech Republic, June 6-10, 1994. [Invited]

10. Chialvo, A. A. and Cummings, P. T. and Cochran, H. D., "Solvation Structure, Hydrogen Bonding and Ion-Pairing in Dilute Supercritical Aqueous Solutions," 12th International Symposium on Thermophysical Properties, Boulder, CO, June 18-24, 1994.
11. Chialvo, A. A. and Cummings, P. T., "Molecular Based Solvation Formalism for Supercritical Mixtures in Terms of Krichevskii's Parameters," 12th International Symposium on Thermophysical Properties, Boulder, CO, June 18-24, 1994.
12. Chialvo, A. A. and Cummings, P. T. and Cochran, H. D., "Molecular Simulation of Supercritical Aqueous Solutions," 12th International Conference on the Properties of Water and Steam, Orlando, FL, September 12-16, 1994.
13. Chialvo, A. A., Cummings, P. T., Cochran, H. D., Simonson, J. M. and Mesmer, R. E., "Solvation, Hydrogen Bonding, and Ion-Pairing in Supercritical Aqueous Solutions: Simulation and Experiments," Annual Meeting, San Francisco, November 13-18, 1994.
14. Slusher, J. T., Vega, C. A., O'Connell, J. P. and Cummings, P. T. "Vapor-Liquid Equilibrium and Density Measurements of Alkyl Ammonium Bromide/Propanol/Water Systems," Annual Meeting, San Francisco, November 13-18, 1994.
15. Chialvo, A. A. and Cummings, P. T., "How Well Do Current Intermolecular Potential Models Describe the Microstructure and Hydrogen Bonding of Water at Supercritical Conditions?" Annual Meeting, San Francisco, November 13-18, 1994.
16. Chialvo, A. A. and Cummings, P. T., "Molecular Based Approach to Gas Solubility at Near Critical Conditions," Annual Meeting, San Francisco, November 13-18, 1994.

Invited Seminars:

17. Cummings, P. T., "Molecular Simulation of Water and Aqueous Solutions," Applied Thermodynamics Laboratory, Department of Chemical Engineering, Technical University of Delft, May 31, 1994.
18. Cummings, P. T., "Molecular Simulation of Water and Aqueous Solutions," Koninlinje/Shell Research Amsterdam, June 3, 1994.
19. Cummings, P. T., "Molecular Simulation of Water and Aqueous Solutions," Thermophysics Division, National Institute of Science and Technology, Gaithersburg, MD, October 5, 1994.

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