Final Report for Period 11/1/2001-10/31/2002

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Molecular Modeling and Simulation of Aqueous Electrolyte Systems

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1. Summary

In this Report, we briefly describe the progress during the final grant period (11/1/2001-10/30/2002) for project DE-FG05-94ER14421. This project was initially funded for the period 1/1/94-12/31/94; a final report on this grant and a continuation proposal were submitted in 1994, and resulted in a grant for the period 3/1/95-2/28/98. A final report on this grant and a continuation proposal were submitted in 2000, and resulted in a grant for the period 3/1/98-2/28/2001, which received a no-cost extension to 10/31/2001. A final report on this grant and a continuation proposal were submitted in 2001, and resulted in a grant for the period 11/1/2001-10/30/2004. However, this grant was terminated in 2002 as a result of the PI, Cummings, moving to Vanderbilt University; a new project, DE-FG02-03ER15385, was initiated to replace DE-FG05-94ER14421.

This report is the final report for project DE-FG05-94ER14421, and covers the final funding period of this grant. Significant progress was made on the main objectives of the research program identified in the proposal.

During the current period, eleven manuscripts were submitted for publication acknowledging DOE support from this grant [see items 1-11 in the Appendix] and ten talks based on work completed that year were presented at conferences. Additionally, on behalf of the Basic Energy Sciences Advisory Committee (BESAC) and the Advanced Scientific Computing Advisory Committee (ASCAC), the principal investigator was involved in organizing and co-authoring the report on a DOE workshop on computational nanoscience. The Appendix contains a list of the papers submitted for publication in refereed journals during the current grant period, as well as conference and seminar presentations. The workshop report is listed under "Other."

2. Report

Our proposal focused on the following research areas:

1. Development of intermolecular potentials for water and aqueous solutions
2. Molecular-based study of polymorphic phase transitions and growth of nanocrystalline aggregates in hydrothermal solutions
3. Molecular simulation of ion-pairing in high-temperature high-pressure electrolyte solutions
4. SAFT equation of state modeling of supercritical aqueous solutions
 - a. Solubility of alkanes in supercritical water
 - b. Ion speciation in ambient and supercritical aqueous solutions

We have made progress in all four areas, details of which we describe below. Before doing so, however, we reflect on some of the significant changes impacting the research program during the past year.

The proposal as submitted included Dr. Clare McCabe as a co-principal investigator. Dr. McCabe became a tenure-track faculty member at the Colorado School of Mines effective January 1, 2002. She continued to be actively involved as co-principal investigator in the research and received funding for her efforts via a subcontract to the Colorado School of Mines.

Another major event during the grant period was the PI being offered and accepting a chaired professorship (the John R. Hall Professorship) at Vanderbilt

University. The physical move to Vanderbilt took place in August, 2002. The student supported on the grant – Jose Rivera –completed his Ph.D. in the Fall of 2002 at the University of Tennessee.

2.1. Development of intermolecular potentials for water and aqueous solutions

Our main achievement related to developing intermolecular potentials for water was to perform quench molecular dynamics (QMD) simulations of water modeled by the pair potential developed within our group (the so-called SCPDP potential) [6]. In QMD, a fluid is directly simulated in the two-phase region, resulting in the simulation cell splitting into a liquid phase and a vapor phase. As a method of computing phase equilibria, QMD is generally less preferable than Gibbs ensemble Monte Carlo (GEMC) unless there is interest in studying the interface – for example, to calculate the interfacial surface tension and/or the width of the interface. For a polarizable model such as ours, it can be advantageous to use QMD rather than GEMC because Monte Carlo is typically not very efficient for polarizable fluids. Milan Predota, formerly in our group, explored and developed a method for making Monte Carlo more efficient. We performed the QMD to compare against his calculations, to have available this alternative route to phase equilibrium and to compare with surface tension and interface thickness data. The QMD results agree well with those obtained using our fast Monte Carlo method.

It is clear from our work and that of many others that sophisticated models are needed to accurately model water over wide ranges of temperature and density. However, recently Ivo Nezbeda, a visitor to our group over the past year, has proposed that much of the phenomena associated with water (and many other polar substances) can largely be explained by the nature of the short-ranged interactions. As evidence for this, Monte Carlo simulations were performed by Milan Predota and Ivo Nezbeda using two simplified models of water to investigate hydration around hydrophobic particles and at hydrophobic surfaces (the limiting case of a hydrophilic particle, in the limit that the radius becomes infinite) [8]. Despite the use of a short-ranged simple model for water, most of the phenomena seen in hydrophobic hydration are observed.

In related work, we carried out Gibbs ensemble simulations on both the full and short-range models of carbon dioxide, acetone, methanol, and water along the vapor-liquid coexistence curve [7]. In addition, we also considered methanol in two homogeneous phases, liquid and supercritical, to determine its structure and thermodynamic properties. We found that the long-range interactions affect all considered properties only marginally and that the short-range system provides a reasonably accurate and reliable zeroth-order approximation. A simple theoretical analysis was developed to estimate the effect of the long-range interactions on the thermodynamic properties both in the homogeneous phase and at phase equilibrium.

2.2. Molecular-based study of polymorphic phase transitions and growth of nanocrystalline aggregates in hydrothermal solutions

During the grant period, we expended a considerable effort in getting this new direction underway. Pavan Naicker, a newly hired post-doc, developed a molecular dynamics simulation of TiO_2 in water using the general molecular dynamics code DLPOLY. The nanoparticles being simulated range from 1nm to 5 nm. We have been investigating

whether structural transitions take place in the nanoparticle, as has been suggested based on experimental measurements. We expect to submit a publication on this subject very shortly.

2.3. Molecular simulation of ion-pairing in high-temperature high-pressure electrolyte solutions

In the area of ion-pairing in high-temperature high-pressure electrolyte solutions, we extended our study of limiting conductance to assess the impact of the charge by considering several artificial ions, Na^{2+} , Cl^{2-} , Na^0 , and Cl^0 in supercritical water over a wide range of density [4]. The results confirm our previous conjecture about the dominant role of the number of hydration water molecules around ions in the higher-density region in explaining the density dependence of the limiting conductance of Na^+ and Cl^- in supercritical water.

We extended our study of ion pairing in infinitely dilute HCl in supercritical water over a wide range of state conditions [5] by determining the potential of mean force for the $\text{H}_3\text{O}^+ - \text{Cl}^-$ pair in aqueous solution by constraint molecular dynamics. The ion-pair association constant is consequently calculated and compared with that obtained from the most accurate recent electrical conductance experiments [Ho, P. C.; Palmer, D. A.; Gruszkiewicz, M. S. *J. Phys. Chem. B* **2001**, *105*, 1260-1266] at corresponding states. Resulting equilibrium constants between contact and solvent-shared ion-pair configurations indicate that more than 97% of configurations are contact ion-pairs.

Figure 1. At left, we compare the molecular-based predicted constant of association with the latest experimental values based on conductance measurements, while at right is the predicted composition dependence of the degree of dissociation at five state conditions. Results are from [4].

2.4. SAFT equation of state modeling of supercritical aqueous solutions

Thus far, we have focused on anomalies of alkane solubility in supercritical water. SAFT-HS, a simplified form of the SAFT equation of state, has been used to compute the solubility of alkanes in near critical water, in particular the water+ octane and water + butane system has been studied to compare with earlier simulations. The agreement between the theory and simulation is very good (Figure 2), particularly in the crossover region, and especially since none of the SAFT-HS parameters were fitted to the simulation results. The main difference between simulation and the SAFT-HS results is that the maximum in the Henrys constant for SAFT-HS is observed at a lower

temperature than seen in the simulations. We also see indication of a re-crossing at higher temperatures.

In both the simulations and SAFT-HS, the crossover in the Henry's law constant (or, equivalently, ΔG_{hyd}) for alkanes in water as a function of carbon number occurs at around 630K. In the previous studies this was interpreted as a crossover in solubility of the alkane in water, assuming that liquid-liquid immiscibility continues to be present at these elevated temperatures. However, the SAFT-HS calculations suggest that both butane-water and octane-water are in the one phase region at these state conditions. Hence, although there is a crossover in ΔG_{hyd} , it may not be appropriate to associate it with changes in solubility of immiscible alkane in the aqueous phase. We are currently investigating the ramifications of the crossover in ΔG_{hyd} in terms of the phase equilibria of water-alkane systems.

Figure 2. Prediction of Henry's law constant for butane (blue) and octane (red) from SAFT-HS. Solid symbols are simulation results of Yezdimer et al.

Results of this work were presented at conferences [18,21] and will form the basis of a journal publication..

2.5. Other research supported by the grant

During the grant period, several other research directions have been explored.

Yurij Kalyuzhnyi, a frequent visitor and consultant to the PI's research group, and Clare McCabe performed combined theoretical and simulation studies of model chain fluids [3,11]. This lays the groundwork for future work on polyelectrolytes, which we expect to study in the future.

Soon-Chool Kim, a sabbatical visitor, performed density functional studies of

adsorption into slit pores of nitrogen and a model colloid-polymer system [1,2]. We expect to perform simulations of fluids in nanopores in the future, and the theoretical work of Professor Kim will be a useful addition to this work.

In a series of simulations, we studied the stability of methane hydrates [9,10]. This is an extension of our simulations of water with polar, non-polar and ionic solutes, with the difference is that in this case the simulations are performed at high pressure and low temperature. We found interesting differences between the stability of carbon dioxide and methane hydrates. However, by simulation we were only able to probe one part of the overall cycle for solubilization of a gas molecules into a hydrate. To determine the overall relative stability of carbon dioxide and methane hydrates requires additional calculations.

**APPENDIX: Publications and Presentations Acknowledging DOE Support,
11/1/2001-10/30/2002**

Refereed Papers Submitted During Current Grant Period, 11/1/2001-10/30/2002:

1. Kim, S.C. and P.T. Cummings, *Adsorption properties of a colloid-polymer mixture confined in a slit pore*. Physical Review E, 2001. **64**04(4): p. art. no.-041507.
2. Kim, S.C. and P.T. Cummings, *Adsorption isotherm of a Lennard-Jones nitrogen in a carbon slit-like pore*. Molecular Physics, 2001. **99**(13): p. 1099-1105.
3. Kalyuzhnyi, Y.V. and P.T. Cummings, *Multicomponent mixture of charged hard-sphere chain molecules in the polymer mean-spherical approximation*. Journal of Chemical Physics, 2001. **115**(1): p. 540-551. Erratum: *ibid*, 2002. **116**(19): p. 8637-8637.
4. Lee, S.H. and P.T. Cummings, *Molecular dynamics simulation of limiting conductance for Na^{2+} , Cl^{2-} , Na^0 , and Cl^0 in supercritical water*. Molecular Simulation, 2001. **27**(4): p. 199-213.
5. Chialvo, A.A., P.C. Ho, D.A. Palmer, M.S. Gruszkiewicz, P.T. Cummings and J.M. Simonson, *$\text{H}_3\text{O}^+/\text{Cl}^-$ association in high-temperature aqueous solutions over a wide range of state conditions. A direct comparison between simulation and electrical conductance experiment*. Journal of Physical Chemistry B, 2002. **106**(8): p. 2041-2046.
6. Rivera, J.L., M. Predota, A.A. Chialvo and P.T. Cummings, *Vapor-liquid equilibrium simulations of the SCPDP model of water*. Chemical Physics Letters, 2002. **357**(3-4): p. 189-194.
7. Kettler, M., I. Nezbeda, A.A. Chialvo and P.T. Cummings, *Effect of the range of interactions on the properties of fluids. Phase equilibria in pure carbon dioxide, acetone, methanol, and water*. Journal of Physical Chemistry B, 2002. **106**(30): p. 7537-7546.
8. Predota, M., I. Nezbeda and P.T. Cummings, *Hydrophobic hydration at the level of primitive models. II: Large solutes and water restructuring*. Molecular Physics, 2002. **100**(14): p. 2189-2200.
9. Chialvo, A.A., M. Houssa and P.T. Cummings, *Molecular Dynamics Study of the Structure and Thermophysical Properties of Model sI Clathrate Hydrates*. J. Phys. Chem. B, 2002. **106**: p. 442 -451.
10. Yezdimer, E., P.T. Cummings and A.A. Chialvo, *Determination of the Gibbs free energy of gas replacement in sI clathrate hydrates by molecular simulation*. J. Phys. Chem. B, 2002. **106**: p. 7982-7987.
11. McCabe, C., Y.V. Kalyuzhnyi and P.T. Cummings, *Thermodynamic properties of freely-jointed hard-sphere multi-Yukawa chain fluids: theory and simulation*. Fluid Phase Equilibria, 2002. **194-197**: p. 185-196.

Conference Presentations:

12. Cummings, P. T. and Chialvo, A. A., "Molecular modeling and simulation of supercritical water and aqueous solutions," 27th International Conference on Solution Chemistry, Vaals, Netherlands, August 26-31, 2001 [Invited]

13. Predota, M., Nezbeda, I., and Cummings, P. T., "Hydrophobic Hydration at the level of Primitive Models," American Institute of Chemical Engineers Annual Meeting, Reno, NV, November 3-9, 2001 [Contributed]
14. Yezdimer, E. M., Chialvo, A. A., and Cummings, P. T., "Simulating the Henry's Law Constant for Aqueous Hydrocarbons in the Near Critical Region," American Institute of Chemical Engineers Annual Meeting, Reno, NV, November 3-9, 2001 [Contributed]
15. Nezbeda, I., Chialvo, A. A., and Cummings, P. T., "Effect of the Range of Interactions on the Properties of Fluids, Equilibria of CO₂, Acetone, Methanol, and Water," American Institute of Chemical Engineers Annual Meeting, Reno, NV, November 3-9, 2002 [Contributed]
16. Rivera-Rojas, J. L., Milan Predota, M., Chialvo, A. A., and Cummings, P. T., "Vapor-Liquid Equilibrium Simulations for the SCPDP Model of Water," American Institute of Chemical Engineers Annual Meeting, Reno, NV, November 3-9, 2003 [Contributed]
17. Chialvo, A. A., Yezdimer, E. M., and Cummings, P. T., "Structure and Thermophysical Properties of Model sI clathrate Hydrates by Molecular Simulation," American Institute of Chemical Engineers Annual Meeting, Reno, NV, November 3-9, 2009 [Contributed]
18. Cummings, P. T., "Molecular Simulation of Supercritical Fluids and Mixtures: Supercritical Aqueous Systems and Reverse Micelles in Supercritical Carbon Dioxide," 8th International Meeting of the International Society for the Advancement of Supercritical Fluids, Bordeaux, France, April 14-17, 2002 [Invited - Plenary]
19. Cummings, P. T., "Using Molecular Simulation to Directly Model Real Systems: Utility and Limitations," 6th Liblice Conference on Statistical Mechanics of Liquids , Spindleruv Mlyn, Czech Republic, June 9-14, 2002 [Invited - plenary]
20. Clare McCabe, Yuriy Kalyuzhnyi and Peter T. Cummings, "Thermodynamic Properties of Freely Jointed Hard-Sphere Multi-Yukawa Chain Fluids: Theory and Simulation," 6th Liblice Conference on Statistical Mechanics of Liquids , Spindleruv Mlyn, Czech Republic, June 9-14, 2002 [Contributed]
21. McCabe, C., Galindo, A. and Cummings, P. T., "Anomalies in the Solubility of Alkanes in Near Critical Water," 16th European Conference on Thermophysical Properties, Imperial College, London, September 1-4, 2002 [Contributed]

Invited Seminars:

22. Cummings, P. T., "Molecular Modeling, Simulation, and Visualization of Complex Molecular Systems," Computational Materials Science Seminar Series, Oak Ridge National Laboratory, Oak Ridge, TN, October 11, 2001
23. Cummings, P. T., "Molecular Modeling, Simulation, and Visualization of Complex Molecular Systems," Department of Chemical Engineering, Colorado State University, Fort Collins, CO, October 17, 2001

Other:

1. McCurdy, C.W., E. Stechel, P.T. Cummings, B. Hendrickson and D. Keyes, *Theory and Modeling in Nanoscience: Report of the May 10–11, 2002, Workshop Conducted by the Basic Energy Sciences and Advanced Scientific Computing Advisory Committees to the Office of Science, Department of Energy*. 2002.