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MOLECULAR DYNAMICS SIMULATIONS OF THE EFFECTS OF SALTS ON THE AGGREGATION PROPERTIES OF BENZENE IN WATER

Final Report

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DISCLAIMER

NOTICE

The aim of this award is to study the effects of different salts on the solubility of benzene in water. Molecular dynamics simulations are being used to determine the nature of the interactions between benzene and different anions and cations at the atomic level in an attempt to understand the relationship between association with, and exclusion from, the solute and how this affects the solubility of the solute. A clear understanding of these effects would provide the opportunity to design solutions with particular solubility characteristics.

The specific aims of the project were:

1. To provide an atomic level description of the interactions between benzene, water and ions in solution.

2. To determine the degree of association between two benzene molecules in aqueous and salt solutions.

3. To investigate the structure and dynamics of the interface between benzene and water or salt solution.

The Award was also intended to foster collaborations between EPSCoR States and DOE National Labs. We have been working with Dr. Tjerk P. Straatsma who is a member of the Computational Chemistry Group at PNNL. Since starting this project the two of us have also been part of a successful MSCF CGCA proposal for supercomputer time on the IBM SP machine at PNNL (Computational Studies in Molecular Geochemistry and Biogeochemistry - Andrew Felmy, Team Leader). Dr. Straatsma has been involved with the development of the NWChem computational chemistry package. Dr. Straatsma has provided valuable assistance in the development of the current research from both technical and theoretical aspects. I visited PNNL twice this year, once to visit with Dr. Straatsma, and then to attend the NWChem Users Meeting, resulting in two presentations of the research funded by this grant. Further interaction with Dr. Straatsma has resulted in a computer time grant submission which has been partially funded (Biomolecular Simulation of Base Excision Repair and Protein Signaling - Tjerk P. Straatsma, Team Leader). Dr. Straatsma is currently including our Kirkwood-Buff approach in the analysis tools for NWChem, and will visit the campus at Kansas State in the near future.

Following our studies of the solubility changes observed for simple nonpolar solutes in different cosolvent solutions we have been investigating the use of Kirkwood-Buff (KB) theory to describe the change in solubility (chemical potential) of solutes in terms of the distributions (rdfs) between the various species in the system.(J. Phys. Chem. B, (2001) 105:11513-11522). Our initial calculations strongly suggested that rdfs obtained from NpT molecular dynamics simulations can be used to determine thermodynamic properties of these solutions, via KB theory, which were not previously easily accessible to simulation (from thermodynamic integration for example). The method provides high precision thermodynamic data which can analyzed in terms of perturbations to the cosolvent and water structure in the various solvation

shells surrounding the solute (J. Chem. Phys. (2001), 114, 426-435). We have now shown that the combined use of KB theory and computer simulations is a new and important extension of current techniques for the theoretical determination of solution thermodynamics (J. Phys. Chem. B (2001), 105, 11513-11522).

This has finally provided a direct route to one of the major aspects of the project (Aim 1), i.e. a description of salt effects in terms of specific and nonspecific interactions of the different salt cations and anions with the solute. We are continuing our simulations of a single benzene in different cosolvent solutions in an attempt to quantitatively rationalize the effects of salts/cosolvents on the properties of benzene (Aim 1). However, in our latest studies we have discovered that the common force fields in use for studying biological systems perform poorly in describing the experimentally observed degree of cosolvent and solvent association with solutes in solution (J. Chem. Phys., (2001) 115:5521-5530; J. Chem. Phys., (2003) 118:5901-5910). Hence, we have pursued the development of new force fields which more accurately describe the real solution thermodynamics (J. Chem. Phys. (2003) 118:10663-10670; J. Phys. Chem. B (2003) 107:3891-3898).

A realistic force field for NaCl will be submitted for publication shortly. It is only now that we can study the effects of salt on the properties of benzene in solution with any degree of confidence. This type of approach also provides a route to other salt force fields which are difficult to parameterize due to inability to compare the simulation results with enough relevant experimental data.