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Dynamics and Structure of Ionic Solutions and Polar Fluids

Jayendran C. Rasaiah

Principal Investigator; University of Maine, Orono, rasaiah@maine.edu

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Final Report for Period: 07/1997 - 02/2000**Submitted on:** 05/01/2002**Principal Investigator:** Rasaiah, Jayendran C.**Award ID:** 9610288**Organization:** University of Maine**Title:**

Dynamics and Structure of Ionic Solutions and Polar Fluids

Project Participants**Senior Personnel****Name:** Rasaiah, Jayendran**Worked for more than 160 Hours:** Yes**Contribution to Project:****Post-doc****Name:** Noworyta, Jerzey**Worked for more than 160 Hours:** Yes**Contribution to Project:****Graduate Student****Name:** Koneshan, Sivapathasundar**Worked for more than 160 Hours:** Yes**Contribution to Project:****Name:** Lynch, Joshua**Worked for more than 160 Hours:** Yes**Contribution to Project:****Undergraduate Student****Name:** Montague, Steve**Worked for more than 160 Hours:** Yes**Contribution to Project:****Other Participant****Research Experience for Undergraduates****Organizational Partners****Other Collaborators or Contacts**

Professor Ruth Lynden-Bell, Queens University, Belfast, U.K.

Dr. Girija Dubey, Hunter College, New York, NY

Activities and Findings**Research and Education Activities:**

1. Major research and educational activities.

The major research carried out during the period of this grant used computer simulation and theoretical analysis to understand experimental data on ion and uncharged solute transport in aqueous solution, the phase behavior of polar fluids and the elastic properties of DNA. The specific problems studied were

- (a) the mobility and friction of ions and uncharged solutes in water at room temperature
- (b) correlation of solute friction with the entropy and dynamics of solvation
- (c) the effect of chain formation in inhibiting phase transitions of polar fluids
- (d) the elasticity of single molecule DNA with CTG.CAG triplet repeat sequences

Two graduate students (J. Lynch and S. Koneshan) and a postdoctoral fellow (Dr. J.P. Noworyta) received training under this project. We also collaborated with Professor Ruth Lynden-Bell of Queens University Belfast U.K. on the first two projects and Dr. G. Dubey of Hunter College N.Y. on the third.

Findings: (See PDF version submitted by PI at the end of the report)

Training and Development:

The following students were trained with the resources provided by this grant:

- (a) Joshua Lynch - graduate student (masters candidate) in Physics
- (b) S. Koneshan - graduate student (doctoral candidate) in Chemistry
- (c) Jerzey P. Noworyta (Ph.D Utah) - post doctoral fellow
- (d) Steve Montague - undergraduate.

The principal investigator wrote an invited article (~100 pages) on, 'The Statistical Mechanics of Strongly Interacting Systems; Solids and Liquids', for the Encyclopedia of Chemical Physics and Physical Chemistry', Editors J. H. Moore and N. D. Spencer, Institute of Physics, Bristol, England. The article was accepted for publication.

Graduate Thesis (completed or in progress during grant period)

Joshua K. Lynch, 'Molecular Dynamics Simulation of CTG.CAG Triplet Repeat Sequences in DNA', MS Thesis (Physics), University of Maine 1999 (completed)

S. Koneshan, 'Simulation Studies of Ion Mobility', doctoral candidate in Chemistry

Outreach Activities:

Journal Publications

R Lynden-Bell and J. C. Rasaiah, "From Hydrophobic to Hydrophilic Behavior: a Simulation Study of Solvation Entropy and Free Energy of Simple Solutes.", Journal of Chemical Physics, p. 1981, vol. 107, (1997). Published

S. Koneshan, J. C. Rasaiah, R. Lynden-Bell and S. H. Lee, "Solvent Structure, Dynamics and Ion Mobility in Aqueous Solutions at 25 degrees C", Journal of Physical Chemistry, p. 4193, vol. 102, (1998). Published

S. Koneshan, R. Lynden-Bell and J. C. Rasaiah, "Friction coefficients of Ions in Aqueous Solution at 25 degrees C", Journal of the American Chemical Society, p. 12041, vol. 120, (1998). Published

J. C. Phillips, J. C. Rasaiah and J. B. Hubbard, "Anomalous Size Dependence of Relaxation Processes", Physical Review Letters, p. 5453, vol. 80, (1998). Published

J. C. Rasaiah, J. P. Noworyta and S. Koneshan, "Structure of Aqueous solutions of Ions and Neutral Solutes at Infinite Dilution at a Supercritical Temperature of 683K", Journal of the American Chemical Society, p. 11182, vol. 122, (2000). Published

Books or Other One-time Publications**Web/Internet Site****Other Specific Products****Contributions****Contributions within Discipline:**

A basic assumption of solution chemistry is that ion transport in an aqueous medium is modulated by frictional forces: -namely hydrodynamic and dielectric friction. Hydrodynamic friction is what drags a swimmer or a sail boat from reaching its target or destination quickly and is determined by the size and shape of the moving entity and the smoothness of the interface it and its surrounding water. Dielectric friction is observed when the moving solute is charged and the solvent is polar when it is polarized by the ion but not in step with its motion. These are classic problems in physical chemistry that have been studied long ago by Max Born and more recently by Robert Zwanzig and also Lars Onsager and Joseph Hubbard.

Our computer simulation studies show that there are additional factors to be considered in aqueous solutions due to the peculiar nature of liquid water forms hydrogen-bonded cages around an uncharged solute. These cages are partially broken down when a large solute is charged and completely broken down if the charged ion is small. These two extremes are characterized as hydrophobic and hydrophilic solvation and provide an additional factor that needs to be considered in understanding how ions move in aqueous solution. We are currently extending this work, with support from the NSF, to understand how this behavior is changed at high temperatures (supercritical water) and in confined spaces (ion channels and nanotubes). Our work is of relevance to all branches of chemistry since many industrial and laboratory reactions are carried out in an aqueous environment.

Contributions to Other Disciplines:

Our research involved the heavy use of computers and the development of new methods to calculate the solvation free energy and entropy as a function of solute charge and size in a single simulation. This involved the use of an extended lagrangian in our simulations treating the solute charge and size as dynamical variables. This is an important contribution which should have wide in the general area of computational biology as well as chemistry.

Contributions to Human Resource Development:

The grant provided training for a postdoctoral fellow and students, at all levels Graduate students S. Koneshan and J. Lynch and an undergraduate(Steve Montague) were members of the group during the whole period of the grant. A post doctoral fellow, Dr. J. Piotr Noworyta, joined the group in July 1, 1998 after his Ph.D. (Univ. of Utah) on density functional theory and Monte Carlo simulations of hard spheres near a wall. He developed expertise very rapidly in molecular dynamics simulations of ionic solutions and alkane thiol membranes and was a major asset to the group. Mr. J. Lynch received his Masters degree in Physics in August 1999, and S. Koneshan, continued his doctoral studies in Chemistry. A new doctoral student, Ms Arpana Waghe, joined the group in the fall of 1999 and another graduate student from the Physics (S.Vaitheeswaran) joined us in December 1999.

The theoretical and computational research of the PI's group attracted several visitors (Prof. R. Lynden-Bell, Dr. Girija Dubey and Dr. Alenka Luzar) and has influenced instruction in physical chemistry at the University of Maine.

Contributions to Resources for Research and Education:

A course on Computer Simulation Methods (CHY 573), inspired and motivated by our research, was recently introduced by the PI, in the graduate/undergraduate curriculum. Graduate students from Physics, Chemistry, Biochemistry and Chemical Engineering have taken the course in recent years and found it extremely useful in their research. Two undergraduates (Craig Bossie and Jason Hallet) who took the course in the spring of 1998 were admitted to doctoral programs in physical chemistry and chemical engineering respectively at Cornell and M.I.T.

Contributions Beyond Science and Engineering:**Categories for which nothing is reported:**

Organizational Partners

Activities and Findings: Any Outreach Activities

Any Book

Any Web/Internet Site

Any Product

Contributions: To Any Beyond Science and Engineering

Major findings resulting from these activities.

(a) Ion transport plays an important role in solution chemistry. Our research was directed towards understanding the characteristic trends shown by ion mobilities at infinite dilution in aqueous solutions at room temperature (25°C), and the relative importance of hydrodynamic and dielectric contributions to the friction coefficient of an ion.

Mr. S. Koneshan, a graduate student in our group, carried out molecular dynamics simulations, using the SPC/E model for water and related solute-water potentials. His results showed the same trends in ion mobility with respect to size and charge type observed in real experiments. In particular, the simulations reproduced the distinct maxima in the mobilities of cations and anions as a function of the ion size seen in experimental data. The lateral shift in the curves for the negative ions with respect to positive ions was traced to the asymmetric charge distribution of the water molecule.

We also studied the diffusion of uncharged solutes, identical in every respect to the ions except that they had zero charge and the mobility of a fictitious I^+ , differing from I^- only in the sign of the charge. This provided useful comparisons of changes in solvent structure and dynamics around an ion on neutralization or charge reversal. We found that the diffusion coefficients of the cations Li^+ , Na^+ and K^+ and of the anion F^- increase on discharge, whereas Cl^- , Br^- and I^- , had larger diffusion coefficients than the corresponding uncharged solutes. Subsequent studies (see below) showed that this unusual behavior is correlated with changes in the entropy of solvation and with the residence times of water in the first hydration shells.

To our knowledge, we are the first to link ion mobility with the entropy of solvation at a molecular level. Our work also revealed the limitations in accepted theories of ion mobility based on a continuum or molecular models for the solvent. We also initiated a study of ion mobility in supercritical water with Dr. J.P. Noworyta when he joined the group as a postdoctoral fellow towards the end of the grant period.

(b) Together with Professor Ruth-Lynden-Bell, the PI developed a novel simulation technique to calculate the thermodynamics of ion solvation in which the charges and the sizes of the ions are treated as dynamical variables using an extended Lagrangian or Hamiltonian. The technique enabled us to shuttle between hydrophilic and hydrophobic solvation in a single long simulation while probing the thermodynamics of solvation as continuous functions of the charge and size. The free energies and entropies of solution obtained agreed well with the experimental results at 25°C for typical monovalent ions. Keeping the solute size constant, we found that entropy of solvation (fig 1) passes through a minimum near zero charge corresponding to cage formation. The water molecules forming the cage are held together by h-bonds (hydrophobic solvation) and the initial increase in entropy on charging the neutral solute reflects the breakup of the cage. Further increase in the charge promotes electrostatic (hydrophilic) ion solvation which decreases the entropy beyond the maximum in the solvation entropy. The asymmetry in the entropy-charge curves arises from the asymmetric charge distribution of the solvating water molecules. This paper has attracted much interest in the scientific community judging from the number of reprint requests.

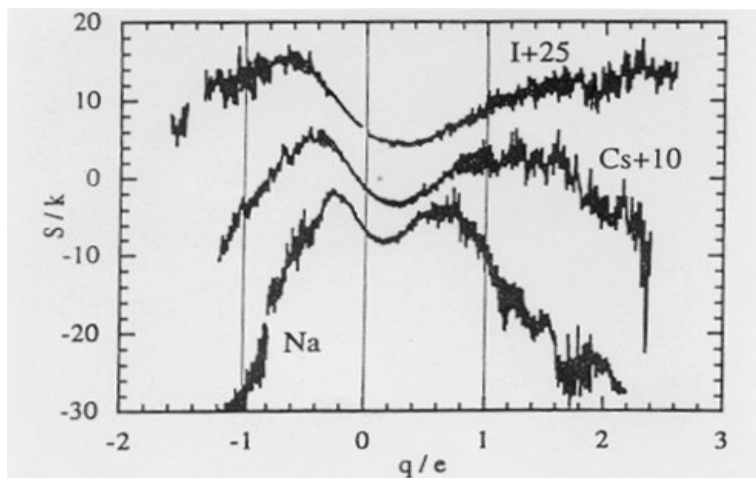


Fig.1. Variation in the solvation entropy of a solute as a function of the charge for three different I, Cs and Na each of constant size. The curves for I and Cs are shifted by the amounts shown.

(c) Phase Transitions of Polar Fluids

We continued our Gibbs ensemble simulations of polar fluids with particular reference to the effect of dipolar chain formation on the liquid-gas phase separation. Interest in this problem began with the observation of chains and ferroelectric behavior in simulations of dipolar hard spheres inhibiting a liquid-gas phase transition. Studies in collaboration with Dr. Dubey of Hunter College, in which Gibbs ensemble simulations of a polar fluid embedded with point dipoles and quadrupoles were carried out to investigate whether a liquid-vapor phase transition occurs when dispersive forces are absent (i.e. $\lambda = 0$) or small. The reduced dipole moments μ^* and quadrupole moments Q^* ranged 0.25 to 2.00 and a liquid-gas phase transition does indeed occur provided there is a finite quadrupole moment. Chain formation was observed in **both** the liquid and gas phases, depending on the number density and strength of the dipolar interaction.

(d) Entropic Elasticity of DNA

Many biological processes involve the coiling and unwinding of DNA in which the molecule bends and stretches like a coiled spring. The elasticity of individual single molecules of double stranded DNA was measured recently by several groups using optical tweezers or mechanical devices to stretch the molecule. Joshua Lynch, a physics graduate student in our group, carried out molecular dynamics simulations of single molecules of double stranded B-DNA containing the triplet (CTG)₃ in one of the strands :



In this duplex the bases (reading from 5' to 3') Cytosine(C), Thymine (T) and Guanine (G) are repeated three times on one strand and a complementary triplet sequence CAG is repeated an equal number of times on the other strand. A control system of the same length but with a random permutation of the bases was also studied under identical conditions. The control was the duplex

5'...G T G C G C T C T 3'
3'...C A C G C G A G A 3'

There are no trinucleotide repeats in the second sequence. Water and ions were explicitly represented at an atomic level in our simulations.

The elastic modulus of each DNA duplex strand was calculated by monitoring the displacement vector \mathbf{r} joining terminal phosphorus at the 5' end and the oxygen of the OH group at the opposite 3' end. Assuming Hooke's law for small deviations from equilibrium, the equipartition theorem implies that the elastic modulus $k_r = kT/\langle\Delta r^2\rangle$ where $\langle\Delta r^2\rangle$ is the time average of the mean square fluctuation in \mathbf{r} . The simulations⁵ gave elastic moduli of 1.63 and 5.38×10^{-20} J/nm² respectively for the CTG and GAC in the first duplex suggesting that the CTG triplet strand is significantly more elastic than its complement (GAC). The control duplex DNA was similar, with the GTG strand more elastic (0.85×10^{-20} J/nm²) than its complement (5.53×10^{-20} J/nm²). Since the fluctuations in \mathbf{r} arise from random forces of the solvent, the calculated modulus corresponds to the entropic elasticity. Although the entropic elasticities of the two sequences taken together as a whole are not very different, the intrinsic elasticity at higher stress, which we plan to investigate, are expected to be different.