COMPUTER SIMULATIONS OF AQUEOUS SOLUTIONS AND NANOPARTICLE DISPERSIONS

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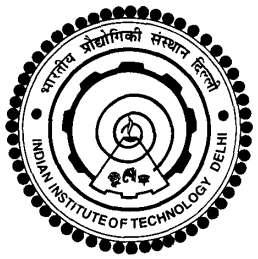

DEPARTMENT OF CHEMISTRY

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COMPUTER SIMULATIONS OF AQUEOUS SOLUTIONS AND NANOPARTICLE DISPERSIONS

by

SAURAV PRASAD

DEPARTMENT OF CHEMISTRY

Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the

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Dedicated To My Parents and
(Late) Prof. Charusita Chakravarty

Certificate

This is to certify that the thesis titled **"COMPUTER SIMULATIONS OF AQUEOUS SOLUTIONS AND NANOPARTICLE DISPERSIONS"** is being submitted by **Mr. Saurav Prasad** to the Department of Chemistry, Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy**. This thesis is a record of bona-fide research work carried out by him under the supervision of (Late) Prof. Charusita Chakravarty from 21 July, 2011 to 29 March, 2016 and subsequently under our guidance. In our opinion, the thesis has reached the standards fulfilling the requirements of the regulations relating to the degree.

The results contained in this thesis have not been submitted to any other university or institute for the award of any degree or diploma.

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Saurav Prasad Date

Abstract

This thesis presents molecular dynamics simulations of two types of complex fluids: liquids with varying degrees of tetrahedrality and nanoparticle dispersions. The relationships between structure, entropy and transport properties are examined for (a) modified hybrid water models, (b) LiCl aqueous solutions in water and modified hybrid waters and (c) bulk water at very high pressures. Simulations of modified hybrid water models provide explanation for thermodynamic scaling observed in RTIL's and hydrogen-bonded systems and also demonstrate that the Rosenfeld scaling does not depend on the degree of configurational energy virial correlation. LiCl appears to be better solvated in liquid with high hydrogen bond strength than SPC/E water, which is in contrast to NaCl solvation as revealed from solvation of constant concentration of LiCl in liquids with varying hydrogen bond strengths. The effects of LiCl concentration on local order, entropy, mobility and their relation with the experimental phase diagram and the glass forming region of aqueous LiCl solutions at 1 atm pressure are examined. The tetrahedral structure of water breaks with increasing LiCl concentration and it is linearly correlated with the pair entropy in the region where the aqueous solution is in contact with ice I_h. The Nernst-Einstein deviation shows pronounced negative deviation in the glass forming region. One-to-one mapping of pressure values of water to the composition values of aqueous LiCl solutions is shown for pair entropy, diffusivity and viscosity. In bulk water, with increase in pressure, orientational disorder increases, whereas in aqueous LiCl solutions with increase in concentration the structure of the liquid shifts from tetrahedral to close-packed structure. The second category of complex liquids studied here are the nanoparticle dispersions of end group functionalized gold nanoparticles in modified hybrid water models and decane solvent. All the pair potentials of mean force between identical nanoparticles show attractive well depths. The well depths and the degree of anisotropy are significantly dependent on the solvent and ligand chemistry.

PERMISSIONS

Permissions have been taken from the respective journals for the publications related to work presented in this thesis.

List of Publications Related to Work Presented in this Thesis

1. **S. Prasad** and C. Chakravarty*, Onset of Simple Liquid Behaviour in Modified Water models, *J. Chem. Phys.*, **140**, 164501 (2014).

2. **S. Prasad*** and C. Chakravarty, Tuning the Tetrahedrality of the Hydrogen-bonded Network of Water: Comparison of the Effects of Pressure and Added Salts, *J. Chem. Phys.*, **144**, 234509 (2016).

3. **S. Prasad**, C. Chakravarty and H. K. Kashyap*, Concentration-dependent Structure and Dynamics of Aqueous LiCl Solutions: A Molecular Dynamics Study, *J. Mol. Liq.*, **225**, 240-250 (2017).

4. **S. Prasad*** and C. Chakravarty, Solvation of LiCl in Model Liquids with High to Low Hydrogen Bond Strengths, *J. Chem. Phys.*, **146**, 184503 (2017).

5. **S. Prasad***, M. Gupta, Hari O. S. Yadav and C. Chakravarty, Gold Nanoparticles Passivated with Functionalized Alkylthiols: Simulations of Solvation in the Infinite Dilution Limit, *Phys. Chem. Chem. Phys.*, (Submitted).

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