MOLECULAR DYNAMICS STUDIES OF COMPLEX SYSTEMS: MOLECULAR CHAINS AND IONIC LIQUIDS

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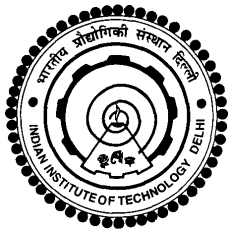

DEPARTMENT OF CHEMISTRY
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MOLECULAR DYNAMICS STUDIES OF COMPLEX SYSTEMS: MOLECULAR CHAINS AND IONIC LIQUIDS

by

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DEPARTMENT OF CHEMISTRY

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Certificate

This is to certify that the thesis titled **"MOLECULAR DYNAMICS STUDIES OF COMPLEX SYSTEMS: MOLECULAR CHAINS AND IONIC LIQUIDS"** is being submitted by **Mr. Gourav Shrivastav** 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 our guidance and supervision. 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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. . . to my beloved family and
(Late) Prof. Charusita Chakravarty

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New Delhi Gourav Shrivastav

Abstract

The work in the thesis encompasses a molecular dynamics study of systems exhibiting wide variety of complexities in context of both fundamental and industrial applications. The main focus is on developing an understanding of thermodynamic and structural aspects of two important classes of non-aqueous complex fluids: (a) molecular chain fluids with primary focus on alkanes and (b) ionic liquids (ILs). Depending on nature of the system, various analyses are used to probe the structure based on nearest neighbour distribution, such as pair correlation function, triplet correlation function, bond order parameter, single chain order parameter, structure function, spatial distribution function and lateral number density. Among thermodynamic properties, free energy, excess entropy, and isothermal compressibility are calculated. In particular, for alkanes, the concepts applicable to simple liquids are further generalized by using the fluctuation's correlation and semi-quantitative relationships between the thermodynamic excess entropy, structure, and dynamics. Thermodynamic integration method is used to obtain thermodynamic excess entropy. For structural estimation of entropy, both pair and triplet entropies are used. It is shown that alkanes exhibit pseudo-simple behaviour, and the structural and dynamic behaviours are dominated by the packing of monomeric units. Hence, homologous series of n-alkanes, with constant number density of monomeric units, can be used to design similar synthetic solvation environment in a broad range of temperature. We then investigate the thermophysical and

rheological properties of mixtures of alkanes with various other hydrocarbons to mimic the composition of gasoline. The outcomes of adding oxygenates, biomass-derived alkyl levulinates and methyl tertiarybutyl ether, are compared in conventional gasoline and proposed reformulated gasoline. It is shown that alkyl levulinates can be utilized for partial as well as complete removal of toxic aromatics in gasoline. We have then extended our study to examine the stress-strain behaviour for semi-crystalline configurations of mesomeric/polymeric alkane chains, with and without covalently bound hydroxyl groups. Since different crystallinity of the sample may affect their stress-strain behaviour, a simple method is proposed to compute the sole effect of added group without affecting the actual distribution of crystalline, interphase, and amorphous content. It is shown that small amount of hydroxyls, e.g. 4 or 8%, does not have significant effect on mechanical properties of polyethylene. In the case of ILs, the microscopic level knowledge of structure is crucial for understanding of structure-quantity relationships. By studying mixtures of butylammonium nitrate (BAN) with primary alcohols, we have demonstrated how the chain length of the added alcohols changes the nanoscale spatial arrangement of BAN IL. For this, two- and three-body correlations of different species of the mixture were examined. Then, using a room-temperature IL, ethylmethylimidazolium tetrafluoroborate [EMIM][BF_4], the thermodynamic aspects of solvophobic effects in the confinements of nanoscale sheets are discussed. To achieve this, the density fluctuation behaviour is monitored to compute the probability of finding number of heavy atoms in a given probe volume which is subsequently used to estimate the associated free energy. Akin to aqueous conditions, the IL studied also manifests solvophobic effects although it is weaker than water. For similar sized solute, the stable vapor phase within the confinement, forms at lower separation in the IL than that for water.

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. **G. Shrivastav**, R. C. Remsing, and H. K. Kashyap, "Capillary evaporation of the ionic liquid [EMIM][BF_4] in nanoscale solvophobic confinement", *J. Chem. Phys.* **148**, 193810 (2018)

2. **G. Shrivastav**, T. S. Khan, M. Agarwal, and M. A. Haider, "Reformulation of gasoline to replace aromatics by biomass-derived alkyl levulinates", *ACS Sustainable Chem. Eng.* **5**, 7118 (2017)

3. **G. Shrivastav**, M. Agarwal, C. Chakravarty, and H. K. Kashyap, "Thermodynamic regimes over which homologous alkane fluids can be treated as simple liquids", *J. Mol. Liq.* **231**, 106 (2017)

4. **G. Shrivastav**, A. Gupta, A. Rastogi, D. Dhabal, and H. K. Kashyap, "Molecular dynamics study of nanoscale organization and hydrogen bonding in binary mixtures of butylammonium nitrate ionic liquid and primary alcohols", *J. Chem. Phys* **146**, 064503 (2017)

5. **G. Shrivastav** and M. Agarwal, "Stress-strain relationships in hydroxyl substituted polyethylene", *J. Phys. Chem. B* **120**, 7598 (2016)

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