

Towards the understanding of the structure and formation of Deep Eutectic Solvents using classical molecular dynamics and fragmentation simulations

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Résumé

Introduction

Since their conception Deep Eutectic Solvents (DES) have been a constant subject of interest for researchers working on tailor-made solvents for various applications including catalysis, biomass conversion and drug delivery. The presence of diverse type of constituent molecules that make up these solvents and a spectrum of non-covalent interactions between these constituents help in designing solvents for particular applications by fine-tuning the functional groups of the molecules. The experiments developed to understand the nature of DES are generally accompanied by a computational study to aid in interpretation of the experimental results. In this thesis, we set out to understand the structure and formation of two types of DES using classical molecular dynamics, quantum mechanical calculations and fragmentation simulations of non-covalent clusters. The first part of this work involved parameterization of non-bonding parameters of GAFF v2.11 forcefield for molecular dynamics simulations of Urea : Choline Chloride (2:1 molar ratio) (named Reline) to accurately represent the thermophysical properties (density, diffusion coefficients and viscosity) and the structure of the solvent relative to the experimental results. The quantum mechanical calculations involving DFT and semi-empirical methods were used in the second part of this work for thermochemical calculations of non-covalent clusters of Reline and Evernic/Usinic acid to corroborate the stability results observed in the soft-ionisation mass spectrometric experiments. Finally a major part of this thesis involves adopting and adapting the algorithm for molecular fragmentation simulations (M₃C) to make the computational study of fragmentation of non-covalent in mass spectrometry computationally tractable. Despite the initial computational bottleneck of the fragmentation simulations, with a combination of semi-empirical methods and density functional approximations methods we are able to finalize a workflow that can be employed in calculating the breaking curves of the chemical systems at the scale of supramolecular assemblies in mass spectrometry on a high-performance computing (HPC) cluster.

Keywords

Deep Eutectic Solvents, Molecular Dynamics, Collision-induced dissociation, Fragmentation, Parametrization

Results and Discussion

Forcefield parametrization for Reline

Since it was demonstrated that the incorporation of empirical charge-scaling can be avoided in molecular dynamic simulations by parametrization of Lennard-Jones(LJ) parameters of GAFF v2.11 forcefield in certain deep eutectic systems, this project started with adopting that approach for Reline system. The additional parametrization required for this specific system is the LJ parameters of Hydrogen and Nitrogen atoms of urea that participate in interactions extensively. After surveying the parameter hyperspace and incorporating the non-linear structure of urea in Reline, we were able to simulate a system with reasonable agreement with experimental density (3.5 % relative error). The structure of the simulated system determined by the radial distribution functions (RDFs) also show reasonable agreement with the experimental RDFs.

Thermochemical calculations of non-covalent clusters

Along with the normal mass-spectra, the other form experimental information of non-covalent clusters available for interpretation of the stability of certain clusters with theoretical calculations is the variation of these cluster-ion intensities at a range of orifice 1 (OR1) voltages.

Two forms of comparison can be made based on the available experimental breaking curves: (i) cross-species comparison and (ii) intra-sample comparison. (i) The cross-species comparison involves comparing the experimental stability of urea-containing clusters and corresponding thiourea-containing clusters. (ii) The intra-sample comparison between different cluster species observed in the same experiment. This is a straight-forward comparison between the fraction of ion intensities of each species at a range of OR1 voltages.

The preliminary approach to understand the stability of certain clusters against the in-source collision-induced dissociation was calculating the interaction energies of these clusters using quantum chemical methods.

Fragmentation simulations of non-covalent clusters

added from the workstation