Molecular Dynamics Simulations of Pseudo-Binary Mixtures of Ethaline with Water or Methanol

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Deep eutectic solvents (DESs) are promising alternative media for chemical reactions, liquid-liquid extraction, separation and gas capture applications [1]. The "type III" DESs, mixtures of choline chloride (ChCl) with a hydrogen bond donor molecule, e.g. urea, ethylene glycol or glycerol, have garnered particular interest in the past decade due to their facile preparation, low toxicity, environmental compatibility and low cost; being partly ionic, they share favorable properties with the ionic liquids (ILs), specifically low vapor pressure compared to conventional organic solvents, but also some major drawbacks, most important of which is high viscosity under ambient conditions.

The addition of controlled amounts of molecular solvents to these DESs, e.g., water, alcohols, or aprotic organic solvents, has been shown to effectively reduce their viscosity while maintaining favorable DES characteristics. However, understanding the intermolecular interactions and liquid structure of the resulting highly complex "pseudo-binary" mixtures - since the DES is itself a mixture - remains challenging and a field of active study.

The excess thermodynamic properties of DES/cosolvent mixtures, which reflect changes in intermolecular interactions and molecular arrangements, exhibit interesting variations as a function of mixture composition, indicating nonideal mixing behavior [2]. Interestingly, the excess molar enthalpies (or mixing enthalpies, H^E) of the DES "ethaline" (ChCl/ethylene glycol mixture in a 1:2 molar ratio) with either water or methanol have been found to be of opposite sign: large negative values for aqueous mixtures, and small positive values for methanol mixtures [3]. While both cosolvents reduce the viscosity of ethaline, the H^E sign difference indicates that their effects on the intermolecular interactions in the DES are different.

We have performed classical Molecular Dynamics (MD) computer simulations of ethaline/water and methanol mixtures to rationalize the experimental H^E sign difference [4]. The simulations reproduce, for the first time, the experimental H^E signs and essential trends for these mixtures. Structural analyses show that water interacts strongly with the DES anion, Cl^-, forming hydrogen-bonded bridged structures between neighboring Cl^- anions; it is also able to form hydrogen bonds with other DES components and with itself, all of which is consistent with a large negative H^E. Methanol also forms ionic hydrogen bonds with Cl^-, but is unable to support the hydrogen bonded network that characterizes the pure ethaline DES, which explains the small positive H^E of these mixtures.

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