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Molecular dynamics investigation of thermo-physical properties and hydrogen-bonds of 1-ethyl-3-methylimidazolium dimethylphosphate-water system

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ABSTRACT

Aqueous solution of ionic liquid 1-ethyl-3-methylimidazolium dimethylphosphate ([Emim][Dmp]) have the potential to become the new working fluids for absorption heat pump. The thermo-physical properties, such as density, self-diffusion coefficient and viscosity of [Emim][Dmp] and its aqueous solution relying strongly on their molecular structures, are investigated at different water mole fractions and at the temperature range from 293.15 K to 373.15 K. The structures of [Emim][Dmp] and water are initially optimized by density functional theory and atomic charges were obtained by CHELPG method. The simulated density for researched systems is quite in agreement with the experimental data. The calculated self-diffusion coefficients of [Emim][Dmp] and water increase rapidly with temperature increase. When water mole fraction is less than 0.6, the self-diffusion coefficients of [Emim][Dmp] and water vary little with water mole fraction and the binary solution is more ionic liquid like because the hydrogen-bonds (H-bonds) between IL and water are stronger than that between water molecules. In this case, water molecules are restricted by IL. However, when water mole fraction is more than 0.8, the self-diffusion coefficients of [Emim][Dmp] and water increase obviously due to the fact that some free water molecules can form H-bonds with themselves rather than IL. The weak H-bonds between H2 in cation and O atoms in anion and strong hydrogen bond between O21 in anion and H34 in water are also found from radial distribution functions (RDFs). The strong interaction between $[Dmp]^-$ and water may also explain why [Emim][Dmp] and water have good solubility and affinity. Moreover, the H-bonds between $[Dmp]^-$ and water become weaker with temperature increase.

1. Introduction

With the rapid growth of global economy, human beings have to face more and more serious environmental and energy issues. The ways to solve these problems are developing and utilizing renewable energy resources, enhancing energy utilization efficiency and so on. Absorption chillers or absorption heat pumps (AHP) are both important energy-saving devices which can be driven by a lot of low-grade thermal energy, such as solar energy and industrial waste heat, so the devices will play an important role in improving energy utilization efficiency, reducing environmental pollution and carbon dioxide emissions. So far, the working pairs commonly used in absorption chillers or AHP are lithium bromide-water (LiBr-H_2O) and ammonia-water (NH_3-H_2O), but they have some disadvantages. LiBr-H_2O has strong corrosive tendency to carbon steel and can crystallize easily when the mass concentration of LiBr is higher than 60%. NH_3-H_2O has strong irritating smell and is highly toxic to human body; moreover, it is flammable and explosive. Therefore, finding new working pairs for absorption chillers or AHP has attracted a lot of researchers [1–5].

Room temperature ionic liquids (RTILs) are salts, which are typically composed of organic cation and inorganic anion, with melting point below 373 K. Because of their negligible vapor pressure, wide liquid range and electrochemical windows, excellent thermal and chemical stability, and tunable physical and chemical properties, they have attracted much attention as a promising environmental friendly solvent in variety of applications such as chemical synthesis [6], catalysis [7] and separation processes [8]. Due to the wide potential applications, their properties have been widely studied [9–19]. In recent years, many researches have reported that some imidazolium-based ILs such as [Emim][Dmp], 1-ethyl-3-methylimidazolium diethylphosphate ([Emim][Dep]) and 1-ethyl-3-methylimidazolium acetate ([Emim][OAc]) have good solubility

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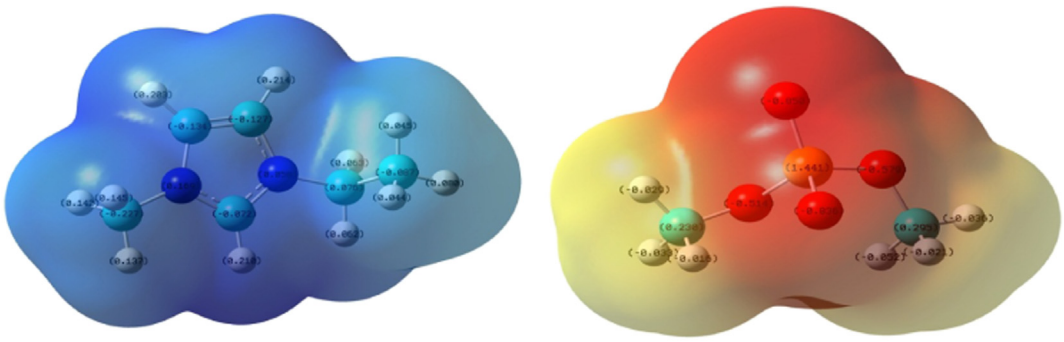

Fig. 1. Atomic charges and electrostatic potential surface of $[Emim]^+$ and $[Dmp]^-$ obtained by CHELPG method.

and affinity to water and have the potential to be used as a new type of absorbent in absorption chiller or AHP [20–27].

Imidazolium-based ILs have been studied extensively both by experiments and computer simulations in recent years. Mitsuhiro et al. [28] measured the electric conductivities and self-diffusion coefficients in dried and water-saturated [BMIM][PF_6] and proposed water-induced acceleration of transport properties in [BMIM][PF_6]. Alessandro et al. [18] used X-ray diffraction to provide the first experimental evidence of the existence of nanoscale segregation in intermediate alkyl chain length RTILs. Many researchers used molecular dynamics simulations to study the thermodynamics properties [29,30], transport properties [31–35], interface properties [35–38] and microstructures [14] of pure

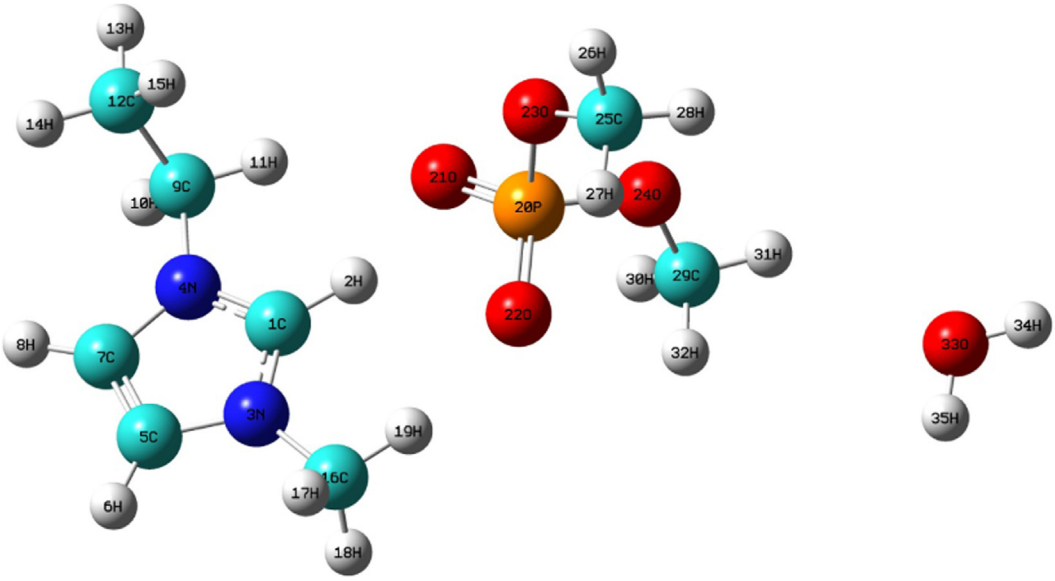

Fig. 2. Chemical structures and atom labels of $[Emim]^+$, $[Dmp]^-$ and water.

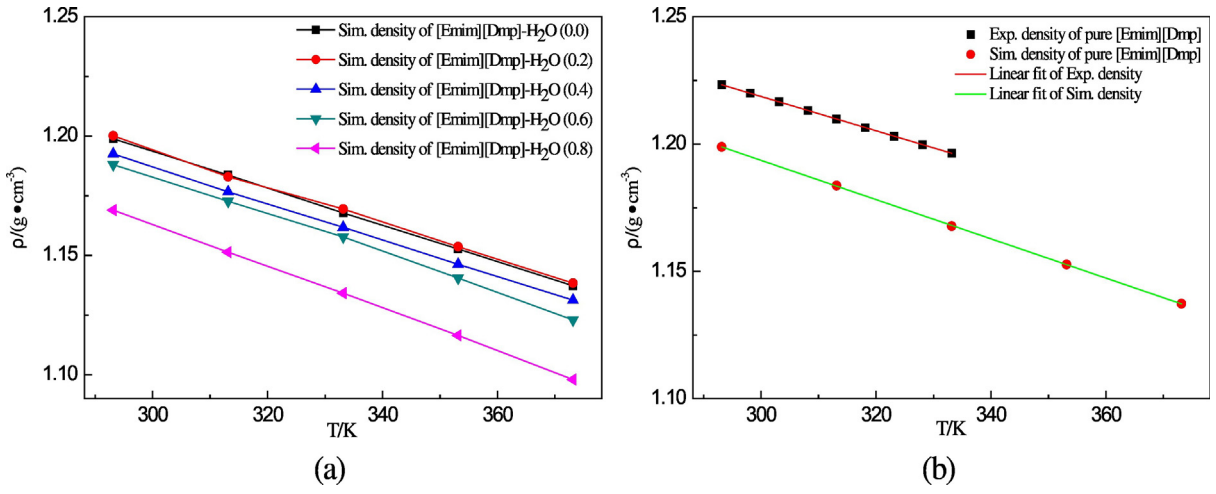

Fig. 3. (a) Variation of simulated density with temperature and water mole fraction; (b) experimental and simulated density.