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Understanding ion-ion and ion-solvent interactions in aqueous solutions of NMP based protic ionic liquids through partial molar properties and DFT calculations

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ABSTRACT

The precise and accurate thermophysical properties determination of ionic liquid (IL)-solvent binary system is needed for understanding the molecular interactions occurring between these components. The nature of ion-ion and ion-solvent interactions can be studied either experimentally on the basis of apparent and partial molar properties and corresponding infinite dilution properties or by computational studies. In this regard, we have measured the thermodynamic properties of binary aqueous solutions containing newly synthesized *N*-methylpyrrolidone based protic ionic liquids (PILs) in the temperature range (288.15–328.15) K and at ambient pressure. Experimentally measured density and speed of sound data have been used to calculate the infinite dilution partial molar properties and the corresponding empirical parameters through the Redlich-Mayer type of equation. It is observed that the studied PILs interacts strongly with water, however the ion-solvent interactions decreases with increase in anionic chain length and increase in temperature. Observed intra-ionic and inter-ionic interactions in studied aqueous ionic liquid mixtures were also supported by Density Functional Theory (DFT) calculations.

1. Introduction

Ionic liquids (ILs) have received increasing attention for their potential scientific and industrial applications [1–3]. Because of their unique physicochemical properties such as wide electrochemical window, negligible vapor pressures, high thermal stability, broad liquid temperature ranges, and specific solvent abilities, ILs are being employed as 'designer solvent' for targeted application [2,4–6].

ILs can be classified as protic ionic liquid (PIL) and aprotic ionic liquid (AIL), the former involves the proton transfer between a Bronsted acid and a base, whereas the latter is obtained from non-reversible alkylation of the heteroatom thus inducing a formal charge center on the cation. The unitary charge is created on cation by the net addition of R^+ or H^+ to a heteroatom lone pair and this heteroatom is an integral part of the incipient cation [7,8]. Most of the research work have been focused on AIL but recently PILs have gain increasing attention [9–11] due to interesting physical properties [12,13]. Since, PILs participate in strong hydrogen bonding, which become advantageous for applications such as utilizing PILs for protein stabilization, fuel cell, etc. [14,15]. Among PILs [16–19], the new class of ILs based on *N*-methylpyrrolidone (NMP) containing organic anionic moiety have been recently synthesized and studied so as to overcome limitations such as toxicity, high viscosity and cost associated with other PILs [20,21].

Water as a solvent or as an impurity is ubiquitous within ILs, so studies on the water-IL interaction have gained extensive interest [22,23]. The IL-solvent (including water) combinations have shown better performance in CO_2 capturing, cellulose dissolution, electrochemistry and catalysis [24–27]. Results suggests the involvement of both anionic and cationic part of IL in modulating the IL-water interactions [22,23]. However, most of the studies are conducted on imidazolium based AILs or ammonium based PILs [22,28–32]. Recently [33–35] ILs have also been introduced as new absorbents so as to overcome problems such as thermal instability, high volatility and low system performance shown by organic working fluids in absorption cooling systems. The absolute water

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miscibility, lowering of partial pressure of water as compared to aqueous LiBr solution and absence of crystal formation are crucial absorbent features for optimizing the coefficient of performance (COP) for IL containing working pair [36].

So, the thermodynamic properties of pure and aqueous/nonaqueous ILs solutions with various molecular solvents (water, methanol, ethanol etc.) needed [19,37,38] to be studied for optimizing the suitable IL-solvent combination for targeted applications. For instance, accurate thermodynamic properties of pure and mixture fluids are necessary for the suitable design and optimization of the absorption cooling and/or heating systems [33].

In this regard, we have studied the interactions occurring between pyrolidinium based protic ionic liquids and water employing experimental and computational techniques. The density and speed of sound of three protic ionic liquid (PIL), viz. *N*-methyl-2-pyrrolidonium formate [NMP][For], *N*-methyl-2-pyrrolidonium propionate [NMP][Pro] and *N*-methyl-2-pyrrolidonium pentanoate [NMP][Pen] in water at (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, 318.15, 323.15 and 328.15) K and at atmospheric pressure have been measured. These experimental data were used to calculate apparent molar volume, V_ϕ, and apparent molar isentropic compression, $K_{s,\phi}$. The density functional level of theory (DFT) was also employed to understand the nature of inter- and intra-molecular interactions occurring between ions of PIL with water at different temperatures.

2. Experimental

2.1. Materials

The provenance of the chemicals used along with their purity and purification method have been mentioned in Table 1. All the chemicals were used as such without further purifications.

2.2. Synthesis and characterization of PILs

The *N*-methylpyrrolidone based PILs namely *N*-methyl-2-pyrrolidonium formate {[NMP][For]}, *N*-methyl-2-pyrrolidonium propionate {[NMP][Pro]} and *N*-methyl-2-pyrrolidonium pentanoate {[NMP][Pen]} have been synthesized by exothermic neutralization of base (*N*-methylpyrrolidone) with acid (formic or propionic or pentanoic acid) in a double neck round bottom flask at a temperature below 5 °C. Detailed synthesis procedure has been reported elsewhere [21]. The synthesized PILs were dried under high vaccum at 313.15 K for 24 h to remove moisture and any unreacted material. Analab Karl Fischer Titrator (Micro Aqua Cal 100) was employed for the determination of water content present in synthesized PILs. The water content was found to be ≈ 2500 ppm. The water content in the PILs were considered for molality correction of the stock solutions (Water + PILs). Millipore quality freshly degassed water was used for making all the binary solutions.

The PILs were characterized by using ^{1}H NMR, ^{13}C NMR (Bruker Avance 500 MHz) and FTIR (JASCO FT/IR- 4100) spectroscopic techniques.

[NMP][For]: (500 MHz, $CDCl_3$, δppm) d-2.32 (m, 4H), 2.93 (s, 3H) 3.34 (t, 2H) 6–8(broad NH^+ and $HCOO^-$)
[NMP][Pro]: d-1.10 (t, 3H), 2.01 (m, 2H), 2.29 (m, 2H), 2.37 (t, 2H), 2.83 (s, 3H), 3.42 (t, 2H), 6.1(broad NH^+).
[NMP][Pen]: d-0.88 (t, 3H), 1.32(m, 2H), 1.56(m, 2H), 1.99(m, 2H), 2.29(m, 2H), 2.38(q, 2H) 2.82(s, 3H), 3.36(t, 2H) (no broad peak for NH^+).

IR Analysis: The absorption band appeared in the range of 1600 cm^{-1} is for characteristic carbonyl, *ν*(C=O) stretching and *ν*(N-H) plane bending vibrations and 3600–2600 cm^{-1} confirmed the characteristic ammonium peak, *ν*(N-H) and *ν*(O-H) stretching vibration.

2.3. Apparatus and procedure

The solutions of PILs in water were made on mass basis in air-tight glass vials using analytical balance (Sartorius CPA225D) having a precision of ±0.01 mg. Both density, *ρ* and speed of sound, *u* of the solutions were measured simultaneously by using vibrating-tube digital density and speed of sound analyzer (Anton Paar, DSA 5000M) at T = (288.15–328.15) K with 5 K difference and at atmospheric pressure. The speed of sound analyzer works at a fixed frequency of 3 MHz. The standard uncertainties in the molality of solutions, density and speed of sound were $u(m) = 1 \times 10^{-5}$ mol kg^{-1}, $u(\rho) = 0.01$ $kg \cdot m^{-3}$ and $u(u) = 0.50$ m s^{-1}, respectively.

2.4. Computational studies

To investigate intra-ionic and inter-ionic interactions taking place between ions of PILs and water we used density functional level of theory (DFT). The initial structure of PIL in gas phase and solvent was optimised by employing CAM-B3LYP functional in conjugation with 6311G++ (2d, 2p) basis set [39,40]. These optimised geometries from gas phase calculations were used as input for re-optimisation in water (implicit solvent model) using IEFPCM model to address the electrostatic behaviour of water in terms continuous medium [41]. To confirm optimization to a minimum on potential energy curve, a frequency calculation was done at the same level of theory. In order to address deep inside in the solvent behaviour we formulated different solvent models by adding water molecules around IL water systems (explicit solvent model). All these calculations were carried by using Gaussian computational package [42]. The interaction energies for each isolated PIL, were corrected with the basis set superposition error (BSSE) using the

Table 1
The provenance, CAS number and mass fraction purity of chemicals used.

Chemical name	Source	CAS number	Mass fraction purity
N-methylpyrrolidone	Sigma-Aldrich	872-50-4	>0.99[a]
Formic acid	Sigma-Aldrich	64-18-6	>0.99[a]
Propionic acid	Sigma-Aldrich	79-09-4	>0.99[a]
Pentanoic acid	Sigma-Aldrich	109-52-4	>0.99[a]
N-methyl-2-pyrrolidonium formate	Synthesized in lab	–	>0.98[b]
N-methyl-2-pyrrolidonium propionate	Synthesized in lab	–	>0.98[b]
N-methyl-2-pyrrolidonium pentanoate	Synthesized in lab	–	>0.98[b]

[a] The chemicals were used as such without further purification.
[b] The synthesized protic ionic liquids were dried at 313.15 K for 24 h and stored under nitrogen atmosphere. The purity was checked by ^{1}H and ^{13}C NMR spectroscopic techniques.