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Molecular interactions of choline based ionic liquids with water at different temperatures: An experimental study

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ABSTRACT

To understand the molecular interactions among the components of aqueous solutions with cholinium based aprotic ionic liquids (AILs), their partial molar properties have been studied. Four cholinium based AILs-namely, cholinium propanoate ([Chl][Pro]), cholinium butanoate ([Chl][But]), cholinium pentanoate ([Chl][Pen]) and cholinium hexanoate ([Chl][Hex]) were synthesized and characterized. Thermodynamic properties of these AILs in water at various temperature (293.15 to 333.15) K and at atmospheric pressure were determined from density and speed of sound measurements. Derived thermodynamic properties and related empirical parameters at infinite dilution were also determined using the Redlich-Mayer type of equation. The studied AILs are observed to interact strongly with water, although the ion-solvent interactions decrease with increase in temperature as well as with increase in concentration.

1. Introduction

Ionic liquids (ILs) are the molten salts with melting point below 100 °C and have unique physicochemical properties such as negligible vapor pressure, wide electrochemical window, high thermal stability, and excellent ability to solubilize organic compounds [1–5]. Consequently, ILs have found several applications in the fields of energy, synthesis, catalysis, extraction, electrochemistry and lubrication [1,4–7]. They are termed as designer solvents as unique combination of cation and anion can lead to the formation of IL with desirable or tunable physicochemical properties [8–9]. Broadly, ILs can be grouped into two categories: namely, protic ionic liquid (PIL) and aprotic ionic liquid (AIL). While the PILs are formed by the proton transfer from a Bronsted acid to a base, AIL are mostly synthesized by non-reversible alkylation followed by metathesis reaction leading to generation of a formal charge center on the heteroatom. AILs can also be synthesized by neutralizing a quaternary base with appropriate acid and removal of water. In either case, the charge on cation appears due to the net addition of R^+ or H^+ to a heteroatom lone pair which is an integral part of the incipient cation [9–11].

Due to the volatility of common volatile organic compounds (VOC), they are considered harmful to environment. The ILs have almost zero vapor pressure, and thus are considered as green solvents since they do not enter into the atmosphere due to vaporization. However all ILs may not always be considered as green [12–13] considering the process involved in their synthesis. The toxicity associated with ILs arises mostly from cationic part; though anionic part also found to influence the overall toxicity. The toxicity can be minimized by synthesizing ILs from carefully selected naturally-derived materials [12,14]. In this regard, the environmentally friendly ILs based on benign cholinium [$NMe_3(CH_2CH_2OH)^+$] cation and suitable anionic moieties have been synthesized [14–15]. Due to their low vapor pressure, ILs do not evaporate and the risk of air pollution is minimum, though owing to their solubility in water, ILs can get released to the environment [16–17]. It is reported that ILs can show considerable toxicity [17]. However, the cholinium based ILs have shown to be less toxic [12,15,18] compared to the conventional imidazolium and pyridinium based ILs, though they are more toxic than common solvents [19]. Furthermore, to minimize the environmental concerns, ILs are often used with other solvents so as to successfully replace the volatile organic compounds (VOC) in applications such as catalysis, synthesis of new materials, separation and electrochemistry [20–21].

The physicochemical studies on effect of common molecular solvents (including water) on ILs can extend the compatibility and usability of ILs having higher melting points, where ILs not necessarily be liquid at room temperature but can be soluble in selected molecular solvent. In addition, the thermodynamic studies of binary mixture (ILs + solvents) will assist in the design of the most appropriate fluid for the specific applications, thus improving the whole production cycle [22–23]. As the presence of water is ubiquitous in ILs either as a solvent or impurity, thereby an understanding of water-IL interaction demands more attention [24–25]. The binary solutions of ILs with other solvents often enhance the performance in dissolving cellulose, electrochemistry, catalysis and CO_2 capturing, [26–29]. Thus physicochemical

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properties of pure and aqueous/nonaqueous binary solutions containing ILs with solvents such as methanol, ethanol, or water are crucial [29,23,30–32] for optimizing IL-solvent mixtures for specific applications. In addition, proper designing and optimization of any industrial instrumentation mostly depends on accurate thermodynamic properties data of pure as well as mixtures of working fluids, for example, in the absorption cooling and/or heating systems [33–34].

Considering these facts, in this work, we have studied the possible interactions occurring in binary solutions composed of cholinium based bio-derived ionic liquids and water experimentally. The density and speed of sound of four aprotic ionic liquids (AILs), viz. cholinium propanoate ([Chl][Pro]), cholinium butanoate ([Chl][But]), cholinium pentanoate ([Chl][Pen]), and cholinium hexanoate ([Chl][Hex]) in water at (293.15, 298.15, 303.15, 308.15, 313.15, 318.15, 323.15, 328.15 and 333.15) K were measured at atmospheric pressure. Several important thermodynamic parameters, such as the apparent molar volume (V_ϕ) and apparent molar isentropic compression ($K_{s,\phi}$) have been calculated from this experimental data. The apparent molar properties were further analysed through the help of well-known Redlich-Mayer equation to gain a better understanding of the interactions between ions and solvents.

2. Experimental

2.1. Materials

The chemicals used in this study along with their purity method have been reported in Table 1. All of the chemicals were used as received without further purifications.

2.2. Synthesis and characterization of PILs

The ionic liquids were synthesized by the neutralization of the base with corresponding acids, similar to the method reported by Petkovic et al. [35]. The corresponding acids in slight excess (1.05:1) were added dropwise into an aqueous solution of choline hydroxide kept in an ice bath (0–5 °C) with constant stirring. After the completion of addition, stirring was continued for 12 h at room temperature (~27 °C) and ambient pressure. Water was partially removed through rotary evaporator and the obtained ionic liquid mixture was thoroughly washed with ethyl acetate several times to remove excess reactants. The obtained ionic liquid were then kept in rotary evaporator to remove solvents and further dried under vacuum at 70 °C for 24 h.

2.2.1. Characterization

The ionic liquids were characterized by ^{1}H and ^{13}C NMR (Bruker Avance spectrometer, 400 MHz) spectroscopy. The details are given below (Fig. S1).

[Chl][Pro]: ^{1}H NMR (DMSO-d_6): δ/ppm = 0.89 (t, 3H); 1.89 (q, 2H); 3.14 (s, 9H); 3.43 (t, 2H); 3.84 (s, 2H); ^{13}C NMR (DMSO-d_6): δ/ppm = 11.21; 30.96; 53.08; 54. 95; 67.30; 177.08

[Chl][But]: ^{1}H NMR (DMSO-d_6): δ/ppm = 0.80 (t, 3H); 1.41 (m, 2H); 1.84 (t, 2H); 3.14 (s, 9H); 3.43 (t, 2H); 3.83 (t, 2H); ^{13}C NMR (DMSO-d_6): δ/ppm = 14.48; 19.66; 40.55; 53.06; 54.93; 67.32; 176.21

[Chl][Pen]: ^{1}H NMR (DMSO-d_6): δ/ppm = 0.82 (t, 3H), 1.21 (m, 2H), 1.38 (m 2H), 1.85 (t, 2H), 3.13 (s, 9H), 3.43 (t, 2H), 3.83 (t, 2H); ^{13}C NMR (DMSO-d_6): δ/ppm = 14.05; 22.48; 28.74; 38.17; 53.07; 54.94; 67.31; 176.41

[Chl][Hex]: ^{1}H NMR (DMSO-d_6): δ/ppm = 0.84 (t, 3H), 1.21 (m, 4H), 1.40 (m, 2H), 1.83 (m, 2H), 3.13 (s, 9H), 3.43 (t, 2H), 3.84 (t, 2H); ^{13}C NMR (DMSO-d_6): δ/ppm = 14.03; 22.19; 26.20; 31.75; 38.48; 53.08; 54.9; 67.34; 176.03

Table 1
Name, Source, CAS number and mass fraction purity of the chemicals used.

Chemical name	Source	CAS number	Mass fraction purity
Choline hydroxide solution	Sigma-Aldrich	123-41-1	46 wt% in H_2O
Propionic acid	Sigma-Aldrich	79-09-4	99%
Butyric acid	Sigma-Aldrich	107-92-6	≥99%
Pentanoic acid	Sigma-Aldrich	109-52-4	≥99%
Hexanoic acid	Sigma-Aldrich	142-62-1	≥99%

2.3. Apparatus and procedure

All the binary solution of AILs in freshly degassed and deionized water were made in the air-tight glass vials on mass basis by taking the exact weight on an analytical balance (Sartorius CPA225D) with a precision of ±0.01 mg. Anton Paar vibrating-tube density and sound velocity meter (DSA 5000M) were used to simultaneously measure the density (ρ) and speed of sound (u) of the binary solutions. The measurements were performed at atmospheric pressure and temperature ranging from T = (293.15 to 328.15) K with 5 K difference. The speed of sound analyzer of the densitometer works at a fixed frequency of 3 MHz. The standard uncertainties in the molality of solutions, density and speed of sound were $u(m) = 6.0 \times 10^{-4}$ mol·kg^{-1}, $u(\rho) = 7 \times 10^{-3}$ kg·m^{-3} and $u(u) = 0.50$ m·s^{-1}, respectively. The water content of the synthesized cholinium based ILs was measured by employing Karl Fischer Titrator (Metrohm Titrino Plus). The water contents (≈1800 ppm) are reported in the Supporting information (Table S1) and have been taken into account in molality calculations. The comparison of density and speed of sound of water at different temperatures with literature values have been reported elsewhere [36].

3. Results and discussion

3.1. Partial molar properties

The structure and properties of binary or ternary solutions can be described by estimating the thermodynamic properties of those solutions as a function of concentration and temperature. Particularly, the apparent molar volume (V_ϕ) and apparent molar isentropic compression ($K_{s,\phi}$) are the key factors in this regard. The apparent molar volume and apparent molar compression of binary solution of AILs in water have been calculated using the following equations and are reported in Tables 2 and 3, respectively.

$$V_\phi = [M/\rho] - [(\rho - \rho_o)/(m \cdot \rho \cdot \rho_o)] \quad (1)$$

$$K_{s,\phi} = (\kappa_s \cdot M/\rho) - [(\kappa_s^o \cdot \rho - \kappa_s \cdot \rho_o)/(m \cdot \rho \cdot \rho_o)] \quad (2)$$

where M and m denotes the molar mass and molality of the ILs; ρ and ρ_o are the densities of binary solutions and water; κ_s and κ_s^o are the isentropic compressibilities of binary solutions and water, respectively. The Newton-Laplace's equation: $\kappa_s = 1/(u^2 \cdot \rho)$ have been used to calculate the isentropic compressibility. The standard uncertainties in V_ϕ and $K_{s,\phi}$ values ranges from (0.06 to 0.15) · 10^6 m^3·mol^{-1}and (0.41 to 0.95) · 10^{-15} m^3·mol^{-1}·Pa^{-1}, for low and high concentration range of AILs, respectively.

Table 2 reports the experimental density (ρ) values of all the binary solutions of AILs in water, which increases with increase in concentration but decreases with rise of temperature (Table 2). On the other hand, the speed of sound for the binary solutions (AILs + water) has been observed to increase with both concentration as well as temperature of the solutions (Table 3). However, the density and speed of sound values of binary solutions are higher for the solutions containing AIL with higher anionic chain length and follows the overall trend: [Chl][Pro] > [Chl][But] > [Chl][Pen] > [Chl][Hex]. This observation can be attributed to more efficient packing of the IL molecules with shorter chains.