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Physicochemical properties of aqueous solution of 1-methylimidazolium acetate ionic liquid at several temperatures

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ABSTRACT

Densities (ρ) and viscosities (η) of 1-methylimidazolium acetate ([Mim]Ac) protic ionic liquid + water mixture were measured at $T =$ (293.15, 298.15, 303.15, 308.15 and 313.15) K under atmospheric pressure. Refractive indices (n_D) and electrical conductivities (κ) of the above-mentioned system over the entire composition range were measured at 298.15 K. Excess molar volumes (V^E), viscosity deviations ($\Delta\eta$) and refractive index deviations (Δn_D) were obtained from the experimental data and fitted to the Redlich–Kister equation with satisfactory results. The results show that V^E values of the system are negative over the whole composition range, whereas $\Delta\eta$ and Δn_D values are positive. Other volumetric properties such as apparent molar volumes ($V_{\phi i}$), partial molar volumes ($\overline{V}_{m,i}$) and excess partial molar volumes ($\overline{V}^E_{m,i}$) of the system were calculated from the density data. The concentration dependence of κ was fitted according to the empirical Casteel–Amis equation. The measured and derived properties were employed to investigate the intermolecular interactions of the system.

1. Introduction

Protic ionic liquids (PILs) produced through the combination of a Brønsted acid and Brønsted base were widely used as catalyst or solvent during chemical process [1–3], biomolecular processes [4,5] and CO_2 capture [6,7] due to their unique properties. The key properties that distinguish PILs from other aprotic ionic liquids (APILs) are the proton transfer from the acid to the base, leading to the presence of proton-donor and -acceptor sites, which can be used to build up a hydrogen-bonded network [8]. To further understand the microstructures and to make better use of PILs, the physicochemical properties of pure PILs and their mixtures with solvents were measured in the last few years [9–18], and such work is still going on.

Recently, certain classes of ionic liquids (ILs) with acetate-based anion have received more and more attention and shown a great potential in absorption of acidic gas [19–23], dissolution of cellulose and biomass [24–27] and extractive distillation [28,29]. Related researches have demonstrated that addition of a solvent significantly influences the physicochemical properties of ILs, and thus affects the application of ILs. For example, the influence mechanism of water as a cosolvent on solubility of cellulose in 1-butyl-3-methylimidazolium acetate ([Bmim]Ac) APILs has been investigated by molecular dynamics simulations and quantum chemistry calculations [27]. The results show that the strong preferential solvation of Ac^- by water can compete with the cellulose-Ac^-interaction in the dissolution process, resulting in decreased cellulose solubility. Therefore, the physicochemical properties of such acetate-based ILs and their mixtures with solvents have also attracted the interest of the researchers [30–34]. For example, Almeida et al. explored the density, viscosity, refractive index and surface tension of five acetate-based ILs including two PILs and three APILs at different temperatures[30]. Fendt et al. presented the viscosities of the binary mixtures of 1-ethyl-3-methylimidazolium acetate ([Emim]Ac) and [Bmim]Ac APILs with water or organic solvents at temperature range from 353.15 to 393.15 K [33].

Despite numerous publications about the properties of acetate-based ILs, the thermophysical properties of protic acetate-based ILs are still poorly characterized especially compared with those of aprotic acetate-based ILs [30–34]. 1-Methylimidazolium acetate ([Mim]Ac) is a protic acetate-based IL and widely used as reaction medium in the Baeyer-Villiger reaction [35] and single electron transfer-living radical polymerization (SET-LRP) [36]. The physicochemical properties and microstructures of pure [Mim]Ac and the mixtures with solvents were investigated by experimental method [37,38], mass spectrum [39], Raman spectroscopy [40] and ab initio quantum mechanical calculations [41]. To better understand the molecular interactions of [Mim]Ac with water, in this work, the physicochemical properties of [Mim]Ac + water mixture, specifically density (ρ), viscosity (η), refractive index (n_D), and electrical conductivity (κ) were measured over the whole concentration range. The excess properties such as V^E, $\Delta\eta$, and refractive index deviations (Δn_D) were calculated and fitted to the Redlich–Kister equation. The concentration dependence of κ was fitted according to the empirical Casteel–Amis equation. Other volumetric properties such as apparent molar volumes ($V_{\phi i}$), partial molar volumes ($\overline{V}_{m,i}$) and excess partial molar volumes ($\overline{V}^E_{m,i}$) of the system were calculated from the density data. The intermolecular interactions and

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structural factors of [Mim]Ac + water system were discussed according to the measured and derived physicochemical properties, and compared with those of [Mim]Ac + alcohols and other aprotic acetate-based ILs + water systems.

2. Experimental

2.1. Chemicals

1-Methylimidazole (99.0%) and acetate acid (99.5%) were AR grade and purchased from Aladdin Reagent Co. Ltd., Shanghai, China. They were used without additional purification. High-purity water obtained from a deionizing system (resistivity, 18 MΩ·cm) was used in the binary systems. [Mim]Ac was synthesized according to our previous literature (see Scheme 1 in supplementary file) [37] and dried under vacuum at 60 °C for at least 24 h before use. The water content in [Mim]Ac determined by Karl Fischer titration (Mettler Toledo DL32, Switzerland) was 200 ppm. The structure of [Mim]Ac was identified by ^{1}H NMR spectroscopy (Bruker 400 NMR, $CDCl_3$, TMS as internal references), which was consistent with our previous work [37]. The total peak integral in ^{1}H NMR spectrum was found to correspond for [Mim]Ac to a nominal purity higher than 99%.

2.2. Apparatus and procedures

The binary mixture of [Mim]Ac with water was prepared by weighing on a Mettler AX-205 analytical balance with a precision of $\pm 1.0 \cdot 10^{-5}$ g, following the procedure reported in a previous work [42]. Taking into account the mass of each component placed into the vial and the balance accuracy, the uncertainty in mole fractions of the binary mixtures was estimated to be less than $1.0 \cdot 10^{-4}$. All of the samples were prepared immediately before the measurement. [Mim]Ac used in the experiment was not recycled and reused.

Densities of [Mim]Ac + water mixture over the entire concentration range were measured with a vibrating-tube densimeter (Anton Paar DMA 5000 M) at temperature range from 293.15 to 313.15 K. Two integrated Pt 100 platinum thermometers (uncertainty: ±0.01 K) together with Peltier elements provide an extremely precise thermostatting of the sample. According to the supplier specifications, the densimeter was calibrated at 298.15 K with high-purity water and dry air. The uncertainty of density measurement was estimated to be $\pm 5.0 \cdot 10^{-5}$ g·cm^{-3}. The values of V^E were deduced from the densities of the pure compounds and mixture using the standard equations with an accuracy greater than $\pm 5.0 \cdot 10^{-4}$ cm^3·mol^{-1}.

Viscosities of [Mim]Ac + water system were measured at temperature range from 293.15 to 313.15 K by an Anton Paar AMVn automated microviscometer having calibrated glass capillaries of different diameters (1.6 mm and 1.8 mm), which was based on the rolling-ball principle [16]. The temperature was controlled by a built-in precise Peltier thermostat within ±0.01 K, and the accuracy of the flow time is ±0.001 s. Each viscosity value of the fluid was reported by averaging three consecutive runs. The uncertainty of the viscosity measurement was less than ±0.001 mPa·s. The values of $\Delta\eta$ for [Mim]Ac + water system were obtained from the viscosity data with an accuracy greater than ±0.005 mPa·s.

The measurement procedures and apparatus of the refractive index of [Mim]Ac + water system were similar to our previous work [17]. An Abbe refractometer produced by Shanghai Precision Scientific Instrument Co., Ltd (Model WAY-2S) with a measuring accuracy of $\pm 1.0 \cdot 10^{-4}$ was employed to measure the refractive index data. The apparatus was calibrated by measuring the refractive index of the high-purity water, and the temperature was controlled by a circulating-water bath with the accuracy of ±0.01 K. The sample was rinsed with acetone and dried with a paper towel. The measurements for each sample were made in triplicate and the average values are reported. The values of Δn_D were deduced from the refractive indices of the pure compounds and mixture using the standard equation with an accuracy greater than $\pm 5.0 \cdot 10^{-4}$.

The electrical conductivities were performed by a Mettler FE30K conductivity meter, which was calibrated with standard liquid provided by the supplier. In the experiment, the sample and the electrode were sealed in a glass cell for measurement. The temperature was controlled by a thermostat with an uncertainty of ±0.01 K. The attaining thermal equilibrium time was 30 min. The uncertainties of the experimental values were estimated to be ±0.5%.

3. Results and discussion

3.1. Densities and volumetric properties of [Mim]Ac + water mixture

Experimental values of the density (ρ) of [Mim]Ac + water mixture at temperature from 293.15 to 313.15 K in steps of 5 K and atmospheric pressure are presented in Table 1 and Fig. 1 (see supplementary file) as a function of mole fraction of [Mim]Ac (x_1) for whole composition range. Fig. 1 shows that ρ values of [Mim]Ac + water mixture increase significantly up to $x_1 \approx 0.25$ at all temperatures studied, and then decrease as the mole fraction of [Mim]Ac increases above ≈0.25. A similar phenomenon has been observed in [Emim]Ac + water mixture by Quijada-Maldonado et al. [43]. According to literature [44], the decrease in ρ values of [Mim]Ac + water mixture with x_1 may be due to a decrease in the ion pair interactions between [Mim]Ac and water. As can be seen from Table 1 and Fig. 1 (see supplementary file), the ρ values of [Mim]Ac + water mixture always decrease with the temperature increasing.

The excess molar volumes (V^E) were calculated to estimate the non-ideality and microstructures of the system using the following equation,

$$V^E = \left(\frac{x_1M_1 + x_2M_2}{\rho}\right) - \left(\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}\right) \quad (1)$$

where x_1 and x_2 are mole fractions of components 1 and 2, ρ_1 and ρ_2 are the densities of pure components 1 and 2, ρ is the density of mixture, and M_1 and M_2 are molecular weights of components 1 and 2. The calculated values of V^E for the above-mentioned mixture are also listed in Table 1. The results of V^E were fitted with following form of Redlich–Kister polynomial equation [44,45]:

$$Y = x_1x_2\sum_{k=0}^{m} A_k(x_1 - x_2)^k \quad (2)$$

where $Y \equiv (V^E, \Delta\eta$ or $\Delta n_D)$, and the coefficients of A_k are adjustable parameters which can be obtained by the least-squares analysis. m is the degree of the polynomial expansion. The correlated results are given in Table 2 (see supplementary file), in which the standard deviation (σ) between the experimental and calculated values is defined by following equation:

$$\sigma = \left[\sum \frac{\left(Y_{exp} - Y_{cal}\right)^2}{n}\right]^{1/2} \quad (3)$$

where n is the number of direct experimental data, Y_{exp} is the experimental value and Y_{cal} is the calculated value from Eq. (2).

The composition dependence of the V^E represents the deviation from ideal behavior of the mixtures, and provides an indication of the interactions between solute and solvent. The V^E values of [Mim]Ac + water mixture versus x_1 at different temperatures are plotted in Fig. 2, which shows negative excess molar volumes over the entire mole fraction range for the system, indicating negative deviations from ideal behavior. This behavior is similar to the binary systems of alkylammonium-based acetate PILs + water mixtures [16,17] and diisopropyl-ethylammonium heptanoate PILs or diisopropyl-ethylammonium octanoate PILs + water

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