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Densities, ultrasonic speeds, refractive indices, excess and partial molar properties of binary mixtures of imidazolium based ionic liquid with pyrrolidin-2-one at temperatures from 298.15 L to 323.15 K

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ABSTRACT

The densities, ρ, speeds of sound, u and refractive indices, n_D of binary mixtures of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [Bmim][NTf_2] and pyrrolidin-2-one, including those of pure liquids, over the entire composition range were measured at temperatures (298.15, 303.15, 308.15, 313.15, 318.15 and 323.15) K and atmospheric pressure. Using the experimental results, the excess molar volume, V^E_m, excess isentropic compressibility, κ^E_s, excess molar isentropic compressibility, $K^E_{s,m}$, excess speed of sound, u^E, deviations in refractive index, $\Delta_\phi n_D$, deviations in molar refraction, ΔR_M have been calculated. The partial molar volume and compressibility, excess partial molar volume and compressibility over the whole composition range; and the partial molar volume and compressibility, and excess partial molar volume and compressibility, of the components at infinite dilution have also been calculated. The excess properties were correlated by the Redlich–Kister polynomial equations. The variations of these parameters with composition and temperature are discussed in terms of intermolecular interactions prevailing in these mixtures. The V^E_m values for these mixtures were also calculated by using Prigogine–Flory–Patterson (PFP) theory and the results are compared with experimental findings.

1. Introduction

The physicochemical studies involving volumetric, acoustic, viscometric and optical properties of room temperature ionic liquids (RTILs) and their mixtures with other organic solvents have attracted considerable research interest in recent years [1–5]. RTILs are a unique class of organic salts comprising entirely of ions and are liquids at room temperature. The interest has grown because of their properties, *viz.*, non-volatility, thermal stability, high polarity, non-flammability, high ionic conductivity and very low vapour pressure, which allows their use as alternatives to volatile organic compounds (VOCs). The most extensively studied class of ionic liquids is based on the imidazolium cation, and these have been effectively used [6–9] in chemical reactions, multiphase bioprocess operation, liquid-liquid separations, batteries, capacitors, fuel cells, electrochemical and optical sensors. They are also environmental benign solvents in view of their recyclability [10] and as potential "green solvents" for electrochemistry, catalysis, solvent extraction, chromatography, biotechnology, material separation, templates for the synthesis of nanomaterials and extractive distillation [11–14]. The systematic studies of thermodynamic and kinetic reactions which are carried out in the presence of ionic liquids are different from those in conventional molecular solvents [15].

Physicochemical properties of pure ionic liquids and their mixtures, such as density, speed of sound, viscosity, heat capacity, activity coefficients at infinite dilution [16–19], liquid-liquid equilibria [20,21], and excess molar volume, V^E_m [22,23] are required for developing reliable predictive models for better understanding of the nature of molecular interactions in liquid mixtures. The thermodynamic properties of mixtures, undergoing specific interactions exhibit significant deviations from ideality due to difference in molecular size, shape and structure [22]. The density and speed of sound values for binary liquid mixtures are useful in elucidating solute-solvent and solute-solute interactions [1–5,24].

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Table 1
Details of chemical source, purification method, purity and analysis method.

Chemical name (CAS number)	Source	Initial mass fraction purity	Purification method	Final mass fraction purity	Analysis method
[Bmim][NTf_2] (174899-83-3)	Iolitech, Germany	>0.995	Used as received	>0.995	NA
Pyrrolidin-2-one (616-45-5)	Sigma-Aldrich, USA	>0.99	Fractional distillation	>0.994	GC[a]

[a] GC = Gas chromatography.

In continuation to our previous studies [25–27] on physico-chemical studies on binary solvents containing ionic liquids and other industrially important organic solvents, here we report the results of our study on binary mixtures of [Bmim][NTf_2] and pyrrolidin-2-one over the entire composition range at different temperatures. [Bmim][NTf_2] is one of the most important and most commonly investigated ionic liquids [28]. Pyrrolidin-2-one [29] is highly polar (dipole moment = 3.91 D at 20 °C) aprotic solvent having low volatility, miscibility with water and organic solvents. It has been chosen because of its wide use in applied chemistry, industry and participation in biological processes [30,31]. Pyrrolidin-2-one is a five member cyclic amide (lactam) possessing high dipole moment due to which the basic structural peptide bond —NH—CO— confers theoretically interesting properties as solvent. It adopts cis conformation (n < 9) [29] and due to the presence of the acid —C═O and basic —NH groups, it is self-associated through hydrogen bonding in pure state [32].

The densities, ρ, speeds of sound, u and refractive indices, n_D of binary mixtures of {[Bmim][NTf_2]} and pyrrolidin-2-one, including those of pure liquids, over the entire composition range were measured at temperatures (298.15, 303.15, 308.15, 313.15, 318.15 and 323.15) K and atmospheric pressure. Using the experimental values, the excess properties, *viz.*, V_m^E, κ_s^E, $K_{s,m}^E$, u^E, $\Delta_\phi n_D$, ΔR_M have been calculated. The partial molar volume, $\overline{V}_{m,1}$ and $\overline{V}_{m,2}$, excess partial molar volume, $\overline{V}_{m,1}^E$ and $\overline{V}_{m,2}^E$ of the components over whole composition range, partial molar volumes, $\overline{V}_{m,1}^\circ$ and $\overline{V}_{m,2}^\circ$, and excess partial molar volume, $\overline{V}_{m,1}^{\circ E}$ and $\overline{V}_{m,2}^{\circ E}$ of the components at infinite dilution; the partial molar compressibility, $\overline{K}_{s,m,1}$ and $\overline{K}_{s,m,2}$, excess partial molar compressibility, $\overline{K}_{s,m,1}^E$ and $\overline{K}_{s,m,2}^E$ over the whole composition range, partial molar compressibility, $\overline{K}_{s,m,1}^\circ$ and $\overline{K}_{s,m,2}^\circ$, excess partial molar compressibility, $\overline{K}_{s,m,1}^{\circ E}$ and $\overline{K}_{s,m,2}^{\circ E}$ of the components at infinite dilution have also been calculated. Values of excess partial volumes of the components at infinite dilution for the mixtures were also calculated using the coefficients obtained from Redlich-Kister equation. The variations of these parameters with composition and temperature have been discussed in terms of intermolecular interactions prevailing in these mixtures. The V_m^E values for these mixtures were calculated by using Prigogine-Flory-Patterson (PFP) theory and the results are compared with experimental findings.

2. Experimental

2.1. Materials

The ionic liquid, 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [Bmim][NTf_2] (Iolitec GmBH, Germany, mass fraction purity > 0.995) used after determination of water content. The water content in IL was determined by using Karl Fischer Titrator (Metrohm, 890 Titrando) [33] and found to be less than 40×10^{-6}. Pyrrolidin-2-one (Sigma Aldrich, India, mass fraction purity >0.99) was purified by vacuum distillation over calcium oxide. Prior to measurements, all the samples were dried for at least 24 h under vacuum (100 kPa) and moderate temperature (beginning from room temperature and increasing gradually to 333 K over a period of 6 h). The final purities and other specifications of the liquids are given in Table 1. The purities of the pure liquids were further ascertained by comparing the values of ρ, u and n_D of pure liquids with the corresponding values available in the literature [28,34–46]. The comparison is given in Table 2 and the agreement between these values is good in general. All the samples were prepared by mass and stored in Amber coloured glass vials (8 mL) with screw caps having PFE septa, and a secure sealed with parafilm to prevent absorption of moisture from the atmosphere. All samples were prepared immediately prior to measurements using an electronic balance (CPA-225D, Sartorius, Germany) precisely within ±0.01 mg. The uncertainty in the mole fraction was estimated to be within $\pm 1 \times 10^{-4}$.

2.2. Apparatus and procedure

The densities and speeds of sound for pure liquids and their binary mixtures were measured by using the digital Density and Sound Analyzer (DSA 5000 M, Anton Parr, Austria) instrument which employs the well-known oscillating U-tube principle (for density measurement); with reproducibility of $\pm 1 \times 10^{-3}$ kg·m^{-3} for density and $\pm 1 \times 10^{-2}$ m·s^{-1} for speed of sound. The densimeter was calibrated with triply-distilled freshly degassed water (ρ = 997.075 kg·m^{-3} at 298.15 K) and with dry air at atmospheric pressure as described earlier [26]. After each measurement the distilled water and anhydrous ethanol were used to clean the vibrating tube. The speed of sound is measured using a propagation time technique and measures the speed of sound at frequency of 3 MHz. The standard uncertainties associated with the measurements for temperature, density and speed of sound were estimated to be within ±0.01 K, ±0.5 kg·m^{-3} and ± 0.5 m·s^{-1}, respectively.

The refractive indices of pure components and binary mixtures were measured using an automatic refractometer Dr. Krenchen Abbemat HP (RXA170 Heavy duty, Anton Paar, Austria) with a temperature controller that keeps the samples at working temperature. For determining refractive index are very expeditious and highly accurate and usually employ very small amount 0.2 mL of sample with light source is LED, with wavelength 589.3 ± 0.1 nm (Sodium D). The apparatus was calibrated by measuring the refractive index of millipore quality water and tetrachloroethylene before each series of measurement. The standard uncertainties in the temperature and refractive index measurements were estimated to be within ±0.02 K and ±0.00005, respectively. A more detailed description of these equipments had been given in our earlier study [27].

3. Results and discussion

The experimental values of ρ, u and n_D for the binary mixtures of [Bmim][NTf_2] with pyrrolidin-2-one as functions of mole fraction, x_1 of [Bmim][NTf_2] and temperature listed in Table 3.

3.1. Excess properties

The values of V_m^E, κ_s^E, u^E, $K_{s,m}^E$, $\Delta_\phi n_D$ and ΔR_M have been calculated by using the following standard relations [47–50]