Journal of Molecular Liquids 216 (2016) 484–495

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Volumetric, ultrasonic and spectroscopic studies of molecular interactions in binary mixtures of 1-butyl-3-methylimidazolium hexafluorophosphate with 2-propoxyethanol at temperatures from 298.15 to 323.15 K

T. Srinivasa Krishna [a], K.T.S.S. Raju [b], M. Gowrisankar [c], Anil K. Nain [d,*], B. Munibhadrayya [e]

[a] Department of Physics, Vignan Institute of Technology & Science, Hyderabad 508284, Andhra Pradesh, India
[b] Department of Chemistry, Andhra Loyola College, Vijayawada 520008, Andhra Pradesh, India
[c] Department of Chemistry, J.K.C. College, Acharya Nagarjuna University, Guntur 522006, Andhra Pradesh, India
[d] Department of Chemistry, Dyal Singh College, University of Delhi, New Delhi 110 003, India
[e] Department of Physics, Sri Venkateswara College of Engineering, Bangalore 562157, Karnataka, India

ARTICLE INFO

Article history:
Received 6 July 2015
Received in revised form 14 December 2015
Accepted 26 January 2016
Available online xxxx

Keywords:
Density
Ultrasonic speed
Refractive index
1-Butyl-3-methylimidazolium hexafluorophosphate
Molecular interactions

ABSTRACT

The densities, ρ ultrasonic speeds, u and refractive index n_D of the binary mixtures of ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF_6] with 2-propoxyethanol, including those of pure liquids, have been measured over the entire range of composition at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K and atmospheric pressure. The IR spectra of these mixtures have also been recorded at 298.15 K. From the experimental data, excess molar volumes, V_m^E, excess isentropic compressibility, κ_s^E, deviations in ultrasonic speed, Δu, excess molar isentropic compressibility, $K_{s,m}^E$, and deviations in refractive indices, $\Delta_\phi n_D$ were calculated and fitted using the Redlich–Kister equation. The partial molar volumes, $\overline{V}_{m,1}$ and $\overline{V}_{m,2}$, partial molar isentropic compressibilities, $\overline{K}_{s,m,1}$ and $\overline{K}_{s,m,2}$, excess partial molar volumes, $\overline{V}_{m,1}^E$ and $\overline{V}_{m,2}^E$ and excess partial molar isentropic compressibilities, $\overline{K}_{s,m,1}^E$ and $\overline{K}_{s,m,2}^E$ over whole composition range; partial molar volumes, $\overline{V}_{m,1}^\circ$ and $\overline{V}_{m,2}^\circ$, partial molar isentropic compressibilities, $\overline{K}_{s,m,1}^\circ$ and $\overline{K}_{s,m,2}^\circ$, excess partial molar volumes, $\overline{V}_{m,1}^{\circ E}$ and $\overline{V}_{m,2}^{\circ E}$ and excess partial molar isentropic compressibilities, $\overline{K}_{s,m,1}^{\circ E}$ and $\overline{K}_{s,m,2}^{\circ E}$ of the components at infinite dilution have also been calculated. The variations of these parameters with composition and temperature have been discussed in terms of intermolecular interactions prevailing in these mixtures.

1. Introduction

Ionic liquids (ILs) are a group of organic salts, which result from the combination of organic cations and inorganic anions, and they may be liquid at room temperature. The most commonly studied ILs contain the imidazolium cation with varying heteroatom functionality. In this study, we have used the ionic liquid formed by 1-butyl-3-methylimidazolium ion ($BMIM^+$) as cation and hexafluorophosphate ion (PF_6^-) as anion. The addition of a co-solvent can improve the properties of ionic liquids for their effective use in various chemical processes. Among the various physicochemical properties of ILs, density has probably been the most widely studied because of its high significance and experimental accessibility [1–5]. In recent years the mixtures of ILs with other organic solvents have been the focus of many scientific investigations [6–12]. Physicochemical properties of ethylene glycol derivatives in the aqueous or non aqueous solvents have been widely studied [13–19]. However, the refractive index of binary mixtures containing ionic liquids has received considerably little attention [20–23]. The physicochemical properties of mixtures of [BMIM][PF_6] with some organic solvents have been studied by various researchers [24–30]. However, the literature review indicates that the systematic volumetric, acoustic, optical and spectroscopic properties of binary mixtures of [BMIM][PF_6] with 2-propoxyethanol have not been reported earlier. 2-Propoxyethanol (ethylene glycol monopropyl ether) is useful in printing and other specialized coatings applications. Due to its fast evaporation and high solubility in water and active solvency make it ideal, for a variety of cleaning applications such as cleaning fluids, paints, coatings, and inks. In the present work, we will be investigating the molecular interactions of 1-butyl-3-methylimidazolium ion of [BMIM][PF_6] with hydroxyl (−OH) group in 2-propoxyethanol and how these interactions affect the volumetric, acoustic, optical, spectroscopic properties and their derived parameters of [BMIM][PF_6] + 2-propoxyethanol binary mixtures.

* Corresponding author.
E-mail address: ak_nain@yahoo.co.in (A.K. Nain).

http://dx.doi.org/10.1016/j.molliq.2016.01.085
0167-7322/

In the present study, we report the densities, ρ ultrasonic speeds, u and refractive indices, n_D of the binary mixtures of ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF_6] with 2-propoxyethanol, including those of pure liquids, over whole composition range at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K and atmospheric pressure. From the experimental data, various physicochemical parameters, *viz.*, V_m^E, κ_s^E, Δu $K_{s,m}^E$ and $\Delta_\phi n_D$ of the mixtures; $\overline{V}_{m,1}$ and $\overline{V}_{m,2}$, $\overline{K}_{s,m,1}$ and $\overline{K}_{s,m,2}$, $\overline{V}_{m,1}^E$ and $\overline{V}_{m,2}^E$ and $\overline{K}_{s,m,1}^E$ and $\overline{K}_{s,m,2}^E$ over whole composition range; $\overline{V}_{m,1}^\circ$ and $\overline{V}_{m,2}^\circ$; $\overline{K}_{s,m,1}^\circ$ and $\overline{K}_{s,m,2}^\circ$; $\overline{V}_{m,1}^{\circ E}$ and $\overline{V}_{m,2}^{\circ E}$ and $\overline{K}_{s,m,1}^{\circ E}$ and $\overline{K}_{s,m,2}^{\circ E}$ of the components in the mixture at infinite dilution, have been calculated. The variations of these parameters with composition and temperature have been discussed in terms of intermolecular interactions in these mixtures. The IR spectra of these mixtures have also been recorded at 298.15 K and analyzed in terms of intermolecular interactions.

2. Experimental

2.1. Chemicals and preparation of samples

The 1-butyl-3-methylimidazolium hexafluorphosphate [BMIM][PF_6] was procured from Iolitec (Germany); the stated purity of the ionic liquids is >99% with <100 ppm water content and <100 ppm halide ion concentration. Water content of the ionic liquids was estimated by Karl Fischer titration using Karl Fisher coulometer (890 KF Titrando, Metrohm, USA) [31] and found to be within limits specified by the manufacturer. The 2-propoxyethanol was supplied by Sigma Aldrich, India with mass fraction purity >0.99. The source, purity and water content of solvents used in this work are listed in Table 1. All these compounds were used without further purification.

All the samples were prepared in Amber colored glass vials (8 mL) with screw caps having PFE septa, and a secure sealed with parafilm to prevent absorption of moisture from the atmosphere, and was then stirred for more than 30 min to ensure total dissolution of the mixtures. Samples were taken from the vials with a syringe through the PFE septum. The mass of the dry bottle was first determined. The less volatile component (IL) of the mixture was introduced in the bottle and mass was recorded. The other component (2-propoxyethanol) was added and the mass of bottle including two components was determined. All samples were prepared immediately prior to measurements using an electronic balance (CPA-225D, Sartorius, Japan) with a precision of ± 0.01 mg. The uncertainty in the mole fraction was estimated to be within $\pm 1 \cdot 10^{-4}$. In order to avoid water absorption, the ionic liquid was used inside a glove box under argon.

2.2. Equipments and procedures

The densities and ultrasonic speeds of pure liquids and their binary mixtures were measured by using the digital vibrating tube Density and Sound Analyzer (DSA 5000 M, Anton Parr, Austria) with reproducibility of $\pm 1 \cdot 10^{-3}$ kg·m^{-3} for density and $\pm 1 \cdot 10^{-2}$ m·s^{-1} for speed of sound. The densimeter was calibrated with triply-distilled freshly degassed water ($\rho = 997.075$ kg·m^{-3}) and with dry air at atmospheric pressure as described earlier [32]. The standard uncertainties associated with the measurements for temperature, density and speed of sound were estimated to be within ± 0.01 K, $\pm 5 \cdot 10^{-3}$ kg·m^{-3} and $\pm 5 \cdot 10^{-2}$ m·s^{-1}, respectively.

The refractive indices of pure liquids and their binary mixtures were determined using an automatic refractometer Abbemat HP (RXA170, Anton Paar, Austria) with a temperature controller that keeps the samples at working temperature. The apparatus was calibrated by measuring the refractive index of millipore quality water and tetrachloroethylene before each series of measurement. The uncertainties in the temperature and refractive index measurements were estimated to be within ± 0.02 K and $\pm 4 \cdot 10^{-4}$, respectively.

Purity of the liquids was checked by comparing the density, ultrasonic speed and refractive index at the investigated temperatures with their corresponding values available in the literature [5,29,30,33–41]. The comparison is given in Table 2 and the agreement between the experimental and the literature values was found good.

FT-IR measurements of binary liquid mixtures of [BMIM][PF_6] with 2-propoxyethanol at different concentrations were carried out with FT-IR Spectrometer (Alpha FT-IR, Bruker, Germany) with accessory Alpha E by using ATR technique (400–4000) cm^{-1} with 4.0 cm^{-1} resolution to investigate the presence of hydrogen bonding and strength of molecular associations The IR data were analyzed using OPUS 6.5 software.

3. Results

The values of the experimental density, ρ, speed of sound, u, refractive index, n_D, for the binary mixtures of [BMIM][PF_6] with 2-PE as a function of mole fraction, x_1 of [BMIM][PF_6] at different temperatures are given in Table 3.

3.1. Excess properties

The excess molar volume, V_m^E, excess compressibility, κ_s^E, deviations in ultrasonic speed, Δu, excess molar isentropic compressibility, $K_{s,m}^E$ and deviations in refractive index, $\Delta_\phi n_D$ have been calculated using the following equation [42,43]

$$V_m^E = V_m - (x_1 V_{m,1} + x_2 V_{m,2}) \tag{1}$$

$$\kappa_s^E = \kappa_s - \kappa_s^{id} \tag{2}$$

$$\Delta u = u - \left(\rho^{id} k_s^{id}\right)^{-1/2} \tag{3}$$

$$K_{s,m}^E = K_{s,m} - K_{s,m}^{id} \tag{4}$$

$$\Delta_\phi n_D = n_D - \left[\phi_1 n_{D,1} + \phi_2 n_{D,2}\right] \tag{5}$$

where V_m is the molar volume, subscript 1 and 2 refer to [BMIM][PF_6] and 2-propoxyethanol, respectively; κ_s is the isentropic compressibility, $K_{s,m}$ is the molar isentropic compressibility, ϕ_i is the volume fraction, and the superscript 'id' represents ideal mixture. The values of V_m, κ_s, $K_{s,m}$, ρ^{id}, ϕ_i, $\kappa_s^{id}$and $K_{s,m}^{id}$ are calculated using the relations [42,43]

$$V_m = (x_1 V_{m,1} + x_2 V_{m,2})/\rho \tag{6}$$

$$\kappa_s = 1/u^2\rho \tag{7}$$

Table 1
Specification of chemical samples.

Chemical name (CAS number)	Source	Initial mass fraction purity	Purification method	Final mass fraction purity	Analysis method
[BMIM][PF_6] (174501-65-6)	Iolitec, Germany	>0.99	Vacuum Desiccation	>0.995	GC[a]
2-Propoxyethanol (2807-30-9)	Sigma-aldrich, India	>0.99	Fractional distillation	>0.996	GC[a]

[a] Gas chromatography.