



Thermophysical properties of two binary aqueous mixtures containing a pyridinium-based ionic liquid



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ABSTRACT

Densities, speeds of sound, refractive indices, surface tensions and kinematic viscosities for (1-propylpyridinium tetrafluoroborate or 1-butylpyridinium tetrafluoroborate + water) mixtures were determined at the temperatures: (293.15, 303.15, 313.15, and 323.15) K and at the pressure of 99.0 kPa. From the experimental data, several excess properties or property deviations have been obtained and correlated. These properties have been discussed taking into account structural and energetic factors; their values seem to indicate that interactions ionic liquids–water are weaker than those operating in the pure compounds.

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1. Introduction

An ionic liquid, IL, is a salt in which, typically, a small anion and a bulky cation with a delocalized charge are weakly coordinated; the compound is a liquid in a wide temperature range. Due to the variety of possible anions and cations, the resulting number of ILs with different chemical–physical properties is very high. These properties can be modulated by adding of different amounts of molecular solvents to the pure ILs. Then, it is possible to design the “perfect IL” depending on the application to perform. Specifically, ILs containing the pyridinium cation are powerful compounds in fuel desulfurization [1,2], good cellulose solvents [3], and effective catalysts in pharmaceutical agents synthesis [4]. However, the high viscosity of the pure ILs can play a detrimental role in some chemical reactions. In such cases it is advisable to use a mixture instead of pure solvent and experimental data of thermophysical properties of mixture are needed.

The bibliographical data concerning to the properties of mixtures containing pyridinium-based ILs are scarce. Regarding the aqueous mixtures, a review of volumetric data of (ILs + water) mixtures has been published in 2015 by Bahadur et al. [5]. On the other hand, there are two papers in the literature including thermophysical properties for the system 1-butylpyridinium tetrafluoroborate + water: Khupse and Kumar [6] measured the dynamic viscosity at $T = 298.15$ K and at atmospheric pressure and Mokhtarani et al. [7] reported densities and dynamic viscosities at temperatures from

(283.15 to 353.15) K and at atmospheric pressure. There are not data for the system 1-propylpyridinium tetrafluoroborate + water.

In this paper, we continue our research [8–12] on the behaviour of the binary mixtures containing a short chain alkanol and 1-propylpyridinium tetrafluoroborate or 1-butylpyridinium tetrafluoroborate with the study of the ILs–water interactions. We report here experimental data of several thermophysical properties for two binary aqueous systems containing 1-propylpyridinium tetrafluoroborate, [ppy][BF₄] or 1-butylpyridinium tetrafluoroborate, [bpy][BF₄]. The determined properties, between $T = 293.15$ K and 323.15 K and at $p = 99.0$ kPa, are: density, speed of sound, refractive index, surface tension and kinematic viscosity, over the whole concentration range. From these data, we calculate the corresponding excess properties and property deviations and we correlate each one using a general equation.

2. Experimental

Table 1 summarizes the information about the ionic liquids employed in this work. In order to eliminate the maximum quantity of water from the ionic liquids, they were dried in vacuum (0.05 kPa) stirring continuously during 24 h before their use, and stored in desiccators. The amount of water present in the ionic liquids was as determined using the Karl Fischer method with an automatic titrator Crison KF 1S-2B, on the other hand, the halide content was checked by ¹⁹F NMR, being the content less than 100×10^{-6} . Mixtures have been made using Milli Pore MilliQ water with resistivity of 18.2 MΩ · cm.

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Table 1
Sample table.

Chemical name	Formula	CAS number	Source	Purification method	Mass fraction purity ^a	Water content/10 ⁻⁶
1-Propylpyridinium tetrafluoroborate	C ₈ H ₁₂ BF ₄ N	239084-00-5	Iolitec	Vacuum treatment	0.98	95
1-Butylpyridinium tetrafluoroborate	C ₉ H ₁₄ BF ₄ N	203389-28-0	Iolitec	Vacuum treatment	0.99	85

^a As stated by the supplier.

Densities, ρ , and speeds of sound, u , of all the samples were measured at the same time using an Anton Paar DSA 5000 densimeter and sound analyzer (operating at around 3 MHz) with temperature control within ± 0.005 K. During density measurement, this apparatus makes an automatic correction based on the viscosity of the sample. Densimeter calibration was made using dry air and ultra-pure water provided by SH Calibration service GmbH. The uncertainties of ρ and u measurements are $1 \times 10^{-3} \text{ g} \cdot \text{cm}^{-3}$ and $1 \text{ m} \cdot \text{s}^{-1}$, respectively.

The refractive indices, n_D , were measured at 589.3 nm sodium wavelength with an automatic refractometer Abbemat-HP DR. Kernchen, that allows to obtain an uncertainty in n_D measurements of 1×10^{-4} , after proper calibration using deionised double-distilled water. Sample temperature during measurement is controlled by a Peltier device in an interval of ± 0.01 K. Simultaneously, an additional Peltier thermostat, controls the internal temperature of the refractometer.

The surface tension, σ , of the pure compounds and their binary mixtures were measured using a Lauda TVT-2 drop volume tensiometer. The temperature was kept constant within ± 0.01 K by means of an external Lauda E-200 thermostat. At least 50 drop volume determinations per sample were performed and the results were averaged. The estimated uncertainty of the surface tension measurements is 1%.

Kinematic viscosities, ν , were measured using different Ubbelohde viscosimeters of appropriate constant together with a Schoot-Geräte AVS-440 automatic measuring unit. A Schoot-Geräte CT 1150/2 thermostat controls the temperature of the samples within ± 0.01 K. The viscosimeter constants, provided by the supplier, were $k = 0.3213 \text{ mm}^2 \cdot \text{s}^{-2}$, $0.0209 \text{ mm}^2 \cdot \text{s}^{-2}$, and $0.00929 \text{ mm}^2 \cdot \text{s}^{-2}$. In order to calculate the kinematic viscosities the time correction due to kinetic energy has been considered. Once density and kinematic viscosity of the samples are known, the dynamic viscosity, η , can be obtained using: $\eta = \rho \cdot \nu$. It has been estimated that the uncertainty in the dynamic viscosity is 8%.

The exact composition of the liquid mixtures was determined by weighing using a Sartorius Semimicro balance CP225-D within $\pm 1 \times 10^{-5} \text{ g}$. This gives an uncertainty in the mole fraction of 1×10^{-4} . All the mixtures were prepared in glass vials just before property measurements to prevent composition modification.

The properties of the pure liquids at the four temperatures taken from previous papers [8–12] or measured in this work are collected in Table 2 along with literature values [7,13,16–19], although for [ppy][BF₄] no literature data were found. For [bpy][BF₄] our experimental values are in agreement with the literature values [7,13]; the biggest deviations are found for viscosity values with an average deviation of 2.8%. On other hand, there are some density and viscosity published values [6,14,15] that present considerable differences with our values, being the average density deviation $0.0037 \text{ g} \cdot \text{cm}^{-3}$ and the average viscosity deviation 46.7%.

3. Results and discussion

The values of all the properties experimentally determined can be found in the [supplementary material](#) along with calculated excess properties and property deviations.

Excess volumes, V^E , were obtained from the density of the mixture, ρ , the mole fraction of the components in the mixture, x_i , and the molar masses, M_i , and densities, ρ_i , of the pure compounds, using the well-known equation:

$$V^E = \sum_i x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i} \right) \quad (1)$$

Under the experimental conditions used ultrasonic absorption is negligible, consequently isentropic compressibility, κ_S , and excess isentropic compressibility, can be obtained using experimental density, ρ , and speed of sound, u , values:

$$\kappa_S = \frac{1}{\rho u^2} \quad (2)$$

$$\text{where: } \kappa_S^E = \kappa_S - \kappa_S^{id} \quad (3)$$

and the ideal isentropic compressibility, is given by the following expression obtained by Benson and Kiyohara [20]:

$$\kappa_S^{id} = \sum_i \phi_i \left[\kappa_{S,i} + \frac{TV_i \alpha_i^2}{C_{p,i}} \right] - T \left(\sum_i x_i V_i \right) \frac{(\sum_i \phi_i \alpha_i)^2}{(\sum_i x_i C_{p,i})} \quad (4)$$

in this equation ϕ_i and x_i are, respectively, the volume fraction and the mole fraction of component i in the mixture, T is the temperature in K and V_i , $\alpha_{p,i}$, $C_{p,i}$ and $\kappa_{S,i}$ are, respectively, the following properties of the pure component i : molar volume, isobaric expansibility molar heat capacity and constant pressure and isentropic compressibility. All the properties used in this equation are gathered in Table 2. Isobaric expansibilities and molar volumes have been obtained using density values measured in our laboratory while literature values [21–23] were used for molar heat capacities.

Reis et al. [24] have obtained an expression to evaluate the refractive index of thermodynamically ideal liquid mixtures. According to this formulation it is possible to calculate the excess refractive indices, n_D^E , of a given liquid mixture using the following equations:

$$n_D^E = n_D - n_D^{id} \quad (5)$$

$$n_D^{id} = \left[\sum_i \phi_i n_i^2 \right]^{1/2} \quad (6)$$

where n_D and $n_{D,i}$ are refractive indices of the mixture and component i , respectively.

The surface tension deviation is a magnitude widely used to describe the variation of the surface tension of a liquid mixture with composition [25,26], surface tension deviations can be calculated by the expression:

$$\Delta\sigma = \sigma - x_1 \sigma_1 - x_2 \sigma_2 \quad (7)$$

where σ is the surface tension of the mixture and x_i and σ_i are the mole fraction and the surface tension of the component i , respectively.

The calculation of viscosity deviation allows description of the viscosimetric behaviour of a liquid mixture with composition [27–29], viscosity deviations can be calculated by using the following equation:

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