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Thermophysical Characterization of TFSI Based Ionic Liquid and Lithium Salt Mixtures †

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Abstract: The ionic liquids (ILs) doped with metal salts have become a real alternative as electrolytes for batteries, but the right choice of these compounds for reaching the adequate properties and performance is still a challenge, and strategies are therefore needed for achieving it. The thermophysical properties of IL 1-butyl-1-methylpyrrolidinium bis[(trifluoromethyl)sulfonyl]imide ([bmpyr] [TFSI]) and its mixture with bis-(trifluoromethane)-sulfonimide lithium salt (from 0.1 m to saturation level) were determined in this work. These properties are density (ϱ), speed of sound (U), and corresponding derived magnitudes, such as the bulk modulus and the thermal coefficient, as well as electrical conductivity (σ) against temperature. Density shows a linear decreasing dependence with temperature and a clear increase with the addition of salt, whereas the thermal expansion coefficient increases with temperature and salt addition. Speed of sound decreases with both temperature and salt concentration, and the adiabatic compressibility calculated by means of the well-known Laplace equation increases, as expected, with temperature in all the studied cases, although a small variation with concentration was observed. Electrical conductivity increases with temperature following the Vogel–Fulcher–Tammann (VFT) equation and decreases with the addition of salt.

Keywords: ionic liquids; density; speed of sound; electrical conductivity

1. Introduction

In the global economy, pollution problems and climate change are demanding a renewal of actual technologies and energy sources. In this sense, Ionic Liquids (ILs) can provide very interesting opportunities, which is why they have earned the name Green solvents for many different applications [1]. Due to the high amount of different possible combinations of cations and anions, even with the possibility of an ad hoc design, it could be possible to obtain the ideal IL for a specific application.

In this work, density, speed of sound and electrical conductivity of the ionic liquid 1-butyl-1-methylpyrrolidinium bis[(trifluoromethyl)sulfonyl]imide ([bmpyr] [TFSI]) and its mixtures with bis-

(trifluoromethane)-sulfonimide lithium salt (from 0.1 m to saturation level) have been measured directly over a temperature range, using an Anton Paar DSA 5000 and a Crison Basic 30.

Adiabatic bulk modulus (K_S) and thermal expansion coefficient (α_p) can be obtained using the density and speed of sound. Low values of adiabatic bulk modulus imply good low-temperature fluidity [2,3]. The adiabatic bulk modulus can be used as a predictive parameter for the pressure-viscosity coefficient [2]. The coefficient of thermal expansion (α_p) leads to useful information on the dependence of the volumetric properties with temperature and pressure.

Electrical conductivity (σ) can be a very important parameter depending on the final application of the studied compound. In this case, good electrical conductivity is crucial for its future implementation as a battery electrolyte.

2. Materials and Methods

2.1. Products

The chemical used in this study is commercially available and supplied by IoLiTec; 1-butyl-1-methylpyrrolidinium-bis-[(trifluoromethyl)-sulfonyl]-imide ([bmpyr] [TFSI]) with a molar mass of M_w = 422.41 g·moL^{-1} and chemical purity of 99%. This IL was used as supplied, i.e., the typical dried procedure for ILs under high vacuum was not necessary because the water content of the supplied [bmpyr] [TFSI] was lower than 150 ppm. Lithium bis-[(trifluoromethyl)-sulfonyl]-imide ([Li] [TFSI]) is commercially available and was supplied by Merck with a molar mass of M_w = 287.09 g·moL^{-1} and chemical purity of 99.9%.

Saturated solutions were reached by mixing both components by using an ultrasound bath for 24 to 48 h, and by increasing the molality in 0.5 moL kg^{-1} intervals until the saturation point at room temperature [4].

2.2. Apparatus

The amount of water was measured by using a Karl Fisher titrator (Mettler Toledo C20), whose expanded uncertainty was 0.1 ppm.

Density and speed of sound were measured by using a vibrating densimeter Anton Paar DSA 5000. Adiabatic bulk modulus (K_S) or adiabatic compressibility (k_s) can be calculated from the following expression [2]:

$$K_s = \rho \cdot u^2 = \frac{1}{k_s} \quad (1)$$

The coefficient of thermal expansion (α_p) is related to the variation of the density with temperature [5]:

$$\alpha_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P, \quad (2)$$

Measurements were performed at different temperature ranges, depending on the thermal transitions, which were also determined (not included in this work). The widest temperature range was performed for pure IL and the mixture 0.1 m (278 to 333) K at 995 hPa (according to the day's pressure), with a range of 5 K, with the exception of the 1.5 m mixture whose measurements started at 298 K due to its melting point being close to room temperature. The expanded uncertainty for the speed of sound was 10^{-2} m·s^{-1}, and for density, measurements were 10^{-6} g·cm^{-3}.

Electrical conductivity (σ) was measured by using a conductimeter Crison Basic 30 at the following temperature ranges: 278, 288, 298, 308 and 323 K; heating from 298 to 323 K, cooling until 278 K, and heating again to 288 K. The resolution was better than 1% of the measured value (with a minimum resolution of 2 × 10^{-6} mS·cm^{-1}).

3. Results and Discussion

Figure 1 shows the densities of the pure IL, the lowest (0.1 m) and highest (1.5 m) mixture concentration samples are shown as a function of temperature. As expected, density increases with salt concentration. Density values for pure IL are in very good concordance with the findings of other authors [6,7].

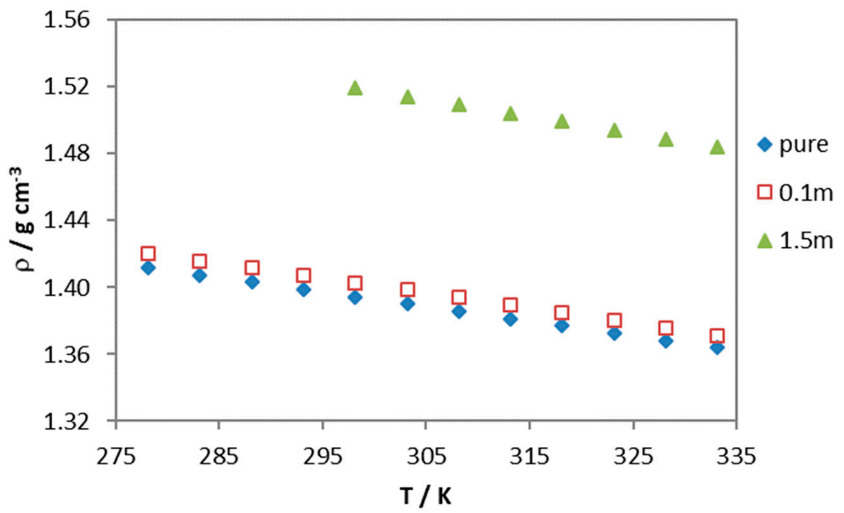

Figure 1. Density versus temperature at 0.1 MPa, for pure 1-butyl-1-methylpyrrolidinium-bis-[(trifluoromethyl)-sulfonyl]-imide ([bmpyr] [TFSI]) and the lowest (0.1 m) and highest (1.5 m) mixture concentration samples.

With regards to the speed of sound (Figure 2), similar behaviours were observed, with a decrease in this parameter with the temperature for pure IL and its mixtures. The result for pure IL was in very good agreement with previous works [8].

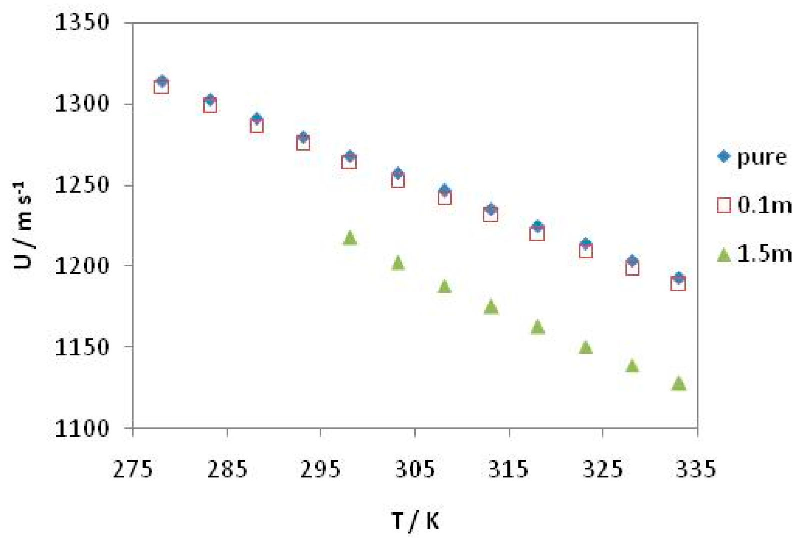

Figure 2. Speed of sound versus the temperature at 0.1 MPa, for pure [bmpyr] [TFSI] and the lowest (0.1 m) and highest (1.5 m) mixture concentrations.

To the best of our knowledge, there are no experimental data on density and/or speed of sound for these mixtures.

Figure 3 shows the adiabatic bulk modulus for the selected IL and its mixtures, which decreased linearly with temperature for all the fluids. Pure IL and the 0.1 m mixture had the same values; meanwhile, 1.5 m had lower bulk modulus values than the previous ones when increasing the temperature, and even had a different slope. Adiabatic bulk modulus low values translate to good low-temperature fluidity. All the studied compounds have close values to regular lubricants [3].

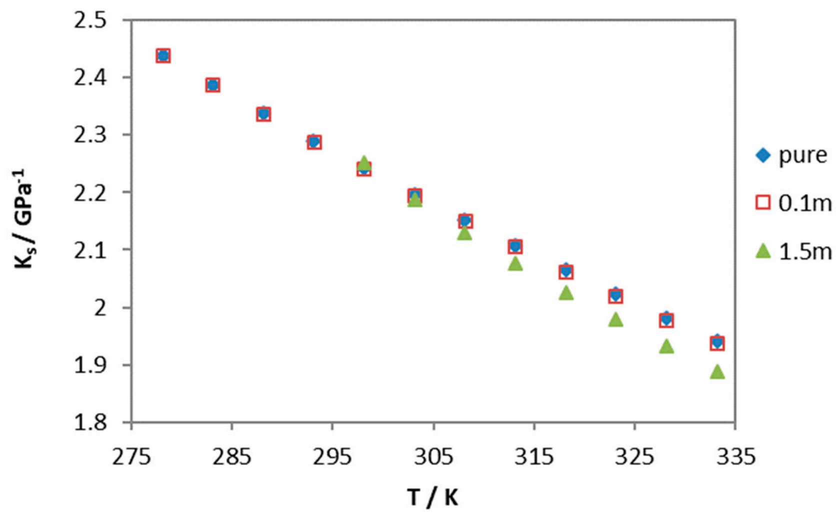

Figure 3. Adiabatic bulk modulus versus the temperature at 0.1 MPa for pure [bmpyr] [TFSI] and the lowest (0.1 m) and highest (1.5 m) mixture concentrations.

The thermal expansion coefficient is represented in Figure 4. The highest values of α_P were found when saturation was reached. For all the compounds, a positive slope can be seen.

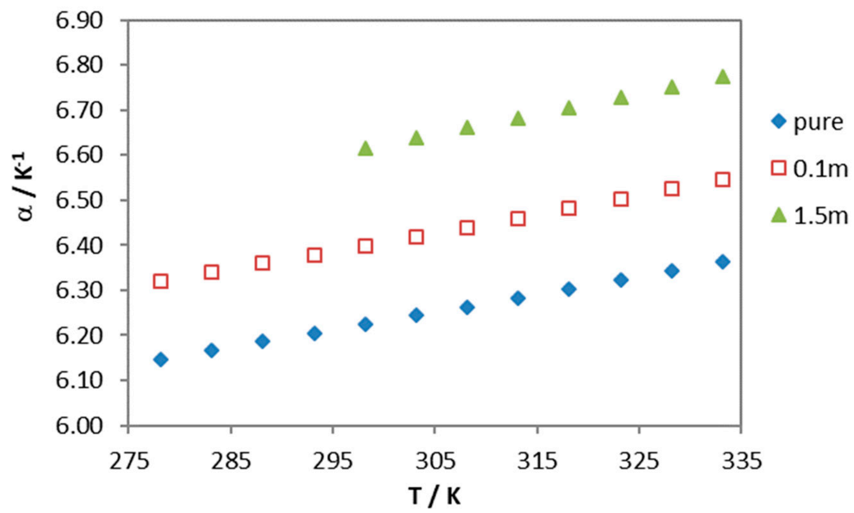

Figure 4. Coefficient of thermal expansion versus the temperature at 0.1 MPa for pure [bmpyr] [TFSI] and the lowest (0.1 m) and highest (1.5 m) mixture concentrations.

Electrical conductivity for liquid mixtures of [bmpyr] [TFSI] + LiTFSI is represented in Figure 5. Similar values of conductivity of pure [bmpyr] [TFSI] have been found by other authors [6,9]. A clear decrease in electrical conductivity was detected when increasing the salt concentration.

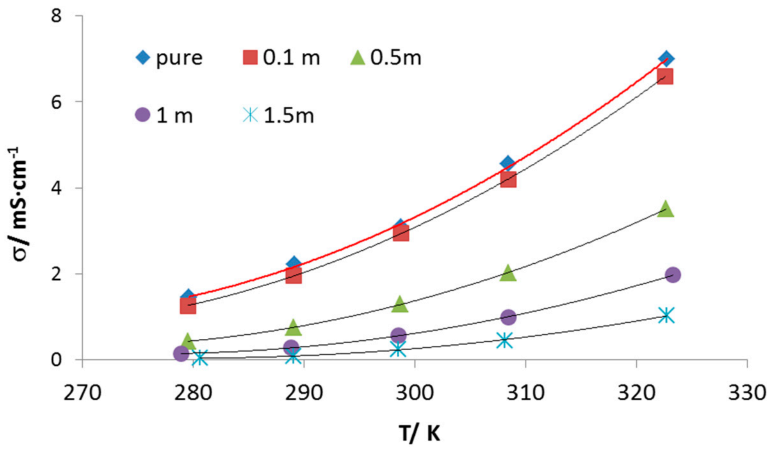

Figure 5. Conductivity versus temperature for pure [bmpyr] [TFSI] and its mixtures with [Li] [TFSI], lines correspond to the Vogel–Fulcher–Tammann (VFT) [10] fitting curves.

Literature about liquid mixtures of ILs and salts is scarce, Martinelli et al. [10] studied electrical conductivity of the same system [bmpyr] [TFSI] + LiTFSI, and although these authors performed the experiments with different salt concentrations, they detected the same behaviours that were observed in this work: conductivity decreases when salt concentration increases. This effect is attributed to an increase in viscosity with the addition of salt, typically observed in IL-salt mixtures.

4. Conclusions

The density of mixtures is higher than that of pure IL and decreases linearly with concentration and temperature.

Speed of sound of mixtures is lower than that of pure [bmpyr] [TFSI], and also decreases linearly with concentration and temperature.

Similar adiabatic bulk modulus values have been found for the studied samples, behaviour that agrees with regular lubricant values.

Because the density decreases with temperature, the thermal coefficient expansion increases, as expected, and saturated samples have greater thermal expansion coefficients than pure samples.

Conductivity increases exponentially with temperature, following the VFT equation.

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Conflicts of Interest: The authors declare no conflict of interest.

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