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Thermophysical characterization of TFSI based ionic liquid and lithium salt mixtures

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Received: date; Accepted: date; Published: date

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. Thermophysical properties of the IL 1-butyl-1-methylpyrrolidinium bis[(trifluoromethyl)sulfonyl]imide ([bmpyr][TFSI]) and its mixtures with the 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 salt addition, whereas 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 can be 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

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 to 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 the bis(trifluoromethane)sulfonimide lithium salt (from 0.1 m to saturation level) have been measured directly in 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 like as predictive parameter for 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 a 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 a chemical purity of 99 %.This IL was used as supplied, *i.e.* 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 supplied by Merck with a molar mass of M_w = 287.09 g·mol^{-1} and a chemical purity of 99.9 %.

Saturated solutions have been reached by mixing both components with the help of an ultrasound bath during (24 to 48) h and by increasing molality in 0.5 mol kg^{-1} intervals until 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 is 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]:

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

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

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

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 5K, with the exception of the mixture 1.5 m whose measurements start in 298K due to its melting is close to room temperature. The expanded uncertainty for the speed of sound is 10^{-2}m·s^{-1} and for density measurements is 10^{-6} g·cm^{-3}.

Electrical conductivity (σ) was measured by using a conductimeter Crison Basic 30 in the temperature range (278, 288, 298, 308 and 323)K; heating from (298 to 323)K, cooling until 278K and heating again to 288K. The resolution is 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 as a function of temperature. As expected, density increases with the salt concentration. Density values for pure IL are in very good concordance with other authors [6,7].

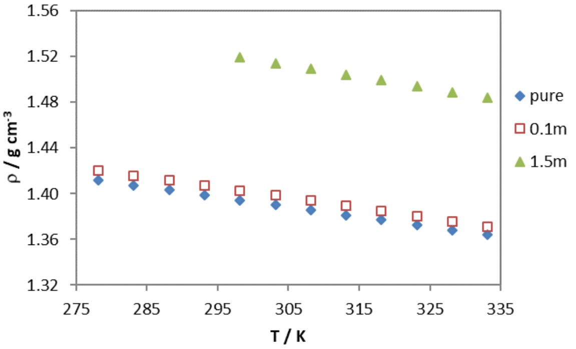

Figure 1. Density versus temperature at 0.1 MPa, for pure [bmpyr][TFSI] and the lowest (0.1 m) and highest (1.5 m) mixture concentration samples.

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

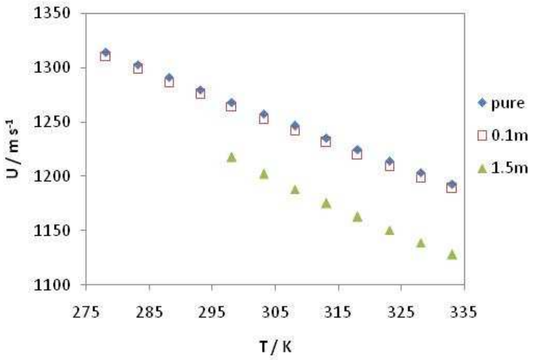

Figure 2. Speed of sound versus the temperature at 0.1 MPa, for pure [bmpyr][TFSI]and the lowest (0.1 m) and highest (1.5 m) mixture concentration.

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

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

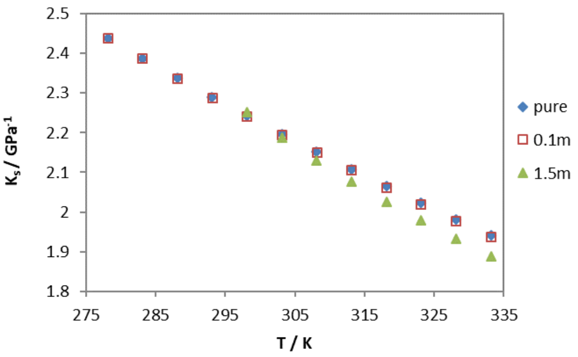

Figure 3. Adiabatic bulk modulus versus the temperature at 0.1 MPa for pure [bmpyr][TFSI]and the lowest (0.1 m) and highest (1.5 m) mixture concentration.

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

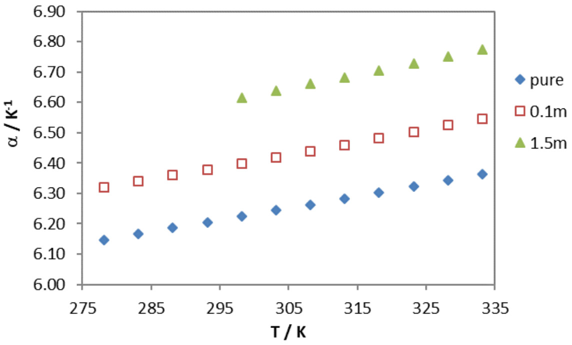

Figure 4. Coefficient of thermal expansion versus the temperature at 0.1 MPa for pure [BMPyr][TFSI]and the lowest (0.1 m) and highest (1.5 m) mixture concentration.

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]. Aclear decrease on electrical conductivity is detected when increasing on salt concentration.

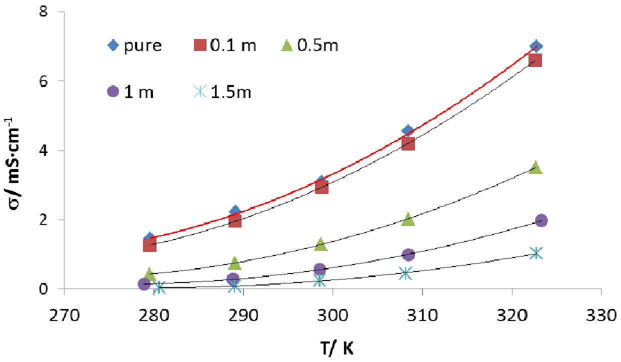

Figure 5. Electrical conductivity versus temperature for pure [BMPyr][TFSI] and its mixtures with [Li][TFSI], lines correspond to VFT [10] fitting curves.

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

4. Conclusions

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 withregular lubricant values.

Because the density decreases with temperature, the thermal coefficient expansion increases, as expected. The saturated sample has a greater thermal expansion coefficient than the pure sample.

Conductivity increases exponentially with temperature, following VFT equation.

Funding: This work was supported by Spanish Ministry of Economy and Competitiveness and FEDER Program through the projects MAT2014-57943-C3-1-P, MAT2014-57943-C3-3-P, MAT2017-89239-C2-1-P as well as by Xunta de Galicia through GRC ED431C 2016/001 project and the Galician Network of Ionic Liquids (ReGaLIs) ED431D 2017/06. P. Vallet and J. J. Parajó thank funding support of FPI Program from Spanish Ministy of Science, Education and Universities and I2C postdoctoral Program of Xunta de Galicia, respectively.

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

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