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Thermophysical Characterization of Two DyethylMethylAmmonium Ionic Liquids

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Abstract: Density (ρ), speed of sound (U), and derived magnitudes of two diethylmethylammonium ILs against temperature have been studied in this work. The chosen ILs were diethylmethylammoniumtrifluoromethanesulfonate, $[C_2C_2C_1N][OTf]$, and diethylmethylammoniummethanesulfonate $[C_2C_2C_1N][MeSO_3]$. In order to analyze the influence of water content, saturated and dried samples of these ILs were studied. ILs were dried using a vacuum pump, and the saturation level (28% and 6% in weight for $[C_2C_2C_1N][MeSO_3]$ and $[C_2C_2C_1N][OTf]$, respectively) was achieved by keeping the ILs in an open bottle at ambient temperature. Direct measurements of density and speed of sound were taken with an Anton Paar DSA 5000. Linear equations were used to express the correlation with temperature of both properties and the thermal expansion coefficient, α_P, and the adiabatic bulk modulus constant, K_S, have been also obtained.

Additionally, results were compared with previous literature data in order to have a deeper understanding of the liquid properties and to detect possible anomalous behaviours.

The effect of water content is different on both properties. Thus, the density of the samples slightly increases when water is removed whereas opposite behaviour was found with regard to the speed of sound, which decreases when the water content was completely removed.

Keywords: density; velocity of sound; adiabatic bulk modulus constant; thermal expansion coefficient.

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1. Introduction

Ionic Liquids (ILs) are being the focus of attention recently, since they are a green and affordable alternative to many substances that are currently used in the industrial field as solvents, lubricants between other materials, due to his eco-friendly characteristics and low or null volatility. However, the enormous amount of different ionic liquids and the huge differences between them means many of their possible applications are yet to be discovered.

In this work, density and speed of sound of the ionic liquids diethylmethylammonium trifluoromethanesulfonate, $[C_2C_2C_1N][OTf]$, and diethylmethylammonium methanesulfonate $[C_2C_2C_1N][MeSO_3]$ have been measured directly in temperature range, using an Anton Paar DSA 5000.

Using the density and speed of sound, the related magnitudes adiabatic bulk modulus (K_S) and thermal coefficient $\boldsymbol{\alpha}_P$ can be obtained.

Low values of adiabatic bulk modulus imply good low temperature fluidity [2]. The temperature fluidity is a very important parameter to decide the quality of lubricant oil. Also, the adiabatic bulk modulus can be used like as predictive parameter for pressure-viscosity coefficient [3].

The coefficient of thermal expansion (α_p) leads to useful information on the dependence of the volumetric properties on temperature and pressure.

Measurements were taken for both ionic liquids with two different water content, saturated and dried, in order to analyse the influence of this water content on the samples.

2. Materials and Methods

2.1. Products

The chemicals used in this study are commercially available and supplied by IoLiTec; Diethylmethylammoniumtrifluoromethanesulfonate (([$C_2C_2C_1N$][OTf]) with a molar mass of M_w = 237 g/mol and a chemical purity of >98 %; and Diethylmethylammoniummethanesulfonate ([$C_2C_2C_1N$][$MeSO_3$]) with a molar mass of M_w = 183 g/mol and a chemical purity of >98 %.

For drying the samples, ILs have been subjected to high vacuum for 48 hours at ambient temperature, to remove most of the water content (after this process, water content of 0.06% in the case of [$C_2C_2C_1N$][$MeSO_3$] and 0.03% for [$C_2C_2C_1N$][OTf] were measured). Given the high hygroscopicity of these ILs, saturated samples have been obtained by exposing them to the atmosphere during 67 days (reaching a water content of 28% in the case of [$C_2C_2C_1N$][$MeSO_3$] and 6% for [$C_2C_2C_1N$][OTf]).

2.2. Apparatus

The amount of water was measured by using a Karl Fisher titrator (Mettler Toledo C20), which 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 [1]:

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

The coefficient of thermal expansion is related to variation of the density with temperature [4]:

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

Measurements were performed from (288 to 333)K at 992 hPa (according to the day's pressure), with a range of 5K, with the exception of [$MeSO_3$]$^-$ which 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 and for density measurements is 10^{-6} g/cm^3.

Measurement of the samples in this work have been made in temperature range from (298 to 333)K for the [$C_2C_2C_1N$][$MeSO_3$] and from (288 to 333)K for the [$C_2C_2C_1N$][OTf]; every 5K.

3. Results

Figure 1 shows the density of the [$C_2C_2C_1N$][OTf] and [$C_2C_2C_1N$][$MeSO_3$] as a function of the temperature. The anion [OTf]$^-$ confers higher values of density than [$MeSO_3$]$^-$, for both saturated and dried samples. Density decreases with temperature for all the samples, as it should be expected and it seems that there is no influence of the water on this temperature dependence taking into account that densities values show the same slope with temperature for dried and saturated samples).

Furthermore, the addition of water decreases the density of both ILs. Results are comparable with other bibliographic references [5-7].

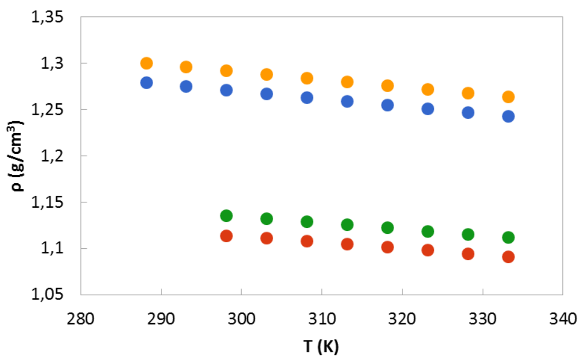

Figure 1. Density versus the temperature at 0.1 MPa, for dried (•) and saturated (•) [$C_2C_2C_1N$][OTf] and dried (•) and saturated (•) [$C_2C_2C_1N$][$MeSO_3$] ILs.

In the case of speed of sound (Figure 2), similar behaviors have been observed, that is a decrease of this parameter with the temperature for all the studied fluids, being in good agreement with other previous works [1]. The IL [$C_2C_2C_1N$][OTf] shows lower values of speed of sound than [$C_2C_2C_1N$][$MeSO_3$] in all the temperature interval studied.

It is observed a big influence of the water contain on the speed of sound; in the [$C_2C_2C_1N$][OTf] a small increase in water (6% of saturation) is accompanied by a small increase in the speed of sound, but for the [$C_2C_2C_1N$][$MeSO_3$] the change in the sound of speed was clearly higher (28% of saturation).

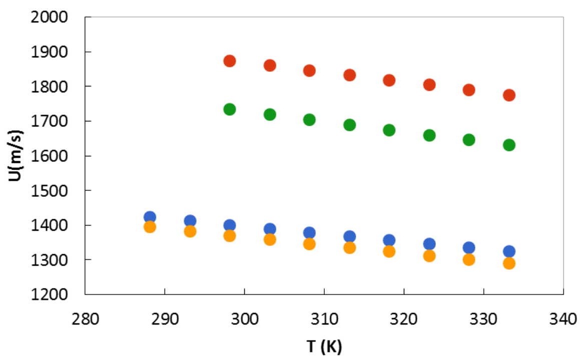

Figure 2. Speed of sound versus the temperature at 0.1 MPa, for dried (•) and saturated (•) [$C_2C_2C_1N$][OTf] and for dried (•) and saturated (•) [$C_2C_2C_1N$][$MeSO_3$] ILs.

Figure 3 shows the adiabatic bulk modulus for both selected ILs dried and saturated, which decreases linearly with temperature for all the fluids. The IL [$C_2C_2C_1N$][OTf] shows lower values of this parameter than [$C_2C_2C_1N$][$MeSO_3$]. Similarly that the speed of sound, a big influence of the water contain is also observed in adiabatic bulk modulus.

Adiabatic bulk modulus low values translate into good low temperature fluidity. [$C_2C_2C_1N$][$MeSO_3$] has twice as much K_S as a good lubricant [1], but [$C_2C_2C_1N$][OTf] has a closer value to regular lubricants [2]. An interesting property of the [$C_2C_2C_1N$][OTf] is that his K_S is almost constant with the percentage of water in the IL. In addition, small variations on the value of K_S with temperature were detected.

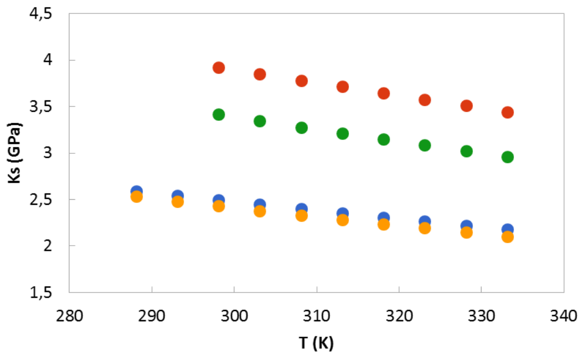

Figure 3. Adiabatic bulk modulus versus the temperature at 0.1 MPa, for dried (•) and saturated (•) [$C_2C_2C_1N$][OTf] and dried (•) and saturated (•) [$C_2C_2C_1N$][$MeSO_3$] ILs.

Using equation (2) the thermal expansion coefficient has been calculated. The IL [$C_2C_2C_1N$][OTf] presents higher values of α_P than [$C_2C_2C_1N$][$MeSO_3$]. For both ILs, a positive slope can be seen, and similarly than adiabatic bulk modulus, the effect of water is negligible for [$C_2C_2C_1N$][OTf], but not for [$C_2C_2C_1N$][$MeSO_3$]. This can be explained by the higher hygroscopicity of the last IL.

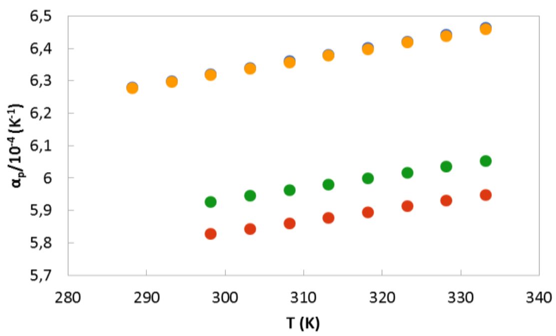

Figure 4. Coefficient of thermal expansion versus the temperature at 0.1 MPa, for dried (•) and saturated (•) [$C_2C_2C_1N$][OTf] and dried (•) and saturated (•) [$C_2C_2C_1N$][$MeSO_3$] ILs.

5. Conclusions

Density of [$C_2C_2C_1N$][OTf] is higher than [$C_2C_2C_1N$][$MeSO_3$] and decreases linearly with temperature. Saturated samples present lower values of density than dried samples for both ILs.

Speed of sound [$C_2C_2C_1N$][OTf] is lower than [$C_2C_2C_1N$][$MeSO_3$] and also decreases linearly with temperature. However, it is observed a big influence of the water contain on this property.

Thermal expansion coefficients behave as expected. Because the density decreases with temperature, the thermal coefficient expansion increases. The saturated sample has a greater thermal expansion coefficient than the dry sample for the [$C_2C_2C_1N$][OTf]. On the other hand, the saturated sample has a lower thermal expansion coefficient than the dry sample for the [$C_2C_2C_1N$][$MeSO_3$].

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

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