

## VOLUMETRIC PROPERTIES OF A PYRROLIDINIUM-BASED AND TWO IMIDAZOLIUM-BASED IONIC LIQUIDS AT HIGH PRESSURES

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**Introduction:** In order to select the most suitable ionic liquids (ILs) for certain applications it is necessary to know some of their thermophysical properties, such as density or viscosity. In this work we have performed density measurements of three ILs: 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate  $[C_4C_1\text{Pyrr}][CF_3SO_2]$ , 1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide  $[C_4C_1C_1\text{Im}][NTf_2]$ , and 1-butyl-2,3-dimethylimidazolium tris(pentafluoroethyl)trifluorophosphate  $[C_4C_1C_1\text{Im}][[(C_2F_5)_3PF_3]$ , from 278.15 K to 398.15 K and at pressures up to 120 MPa. From these measurements we have obtained other volumetric properties such as isothermal compressibility and isobaric thermal expansivity.

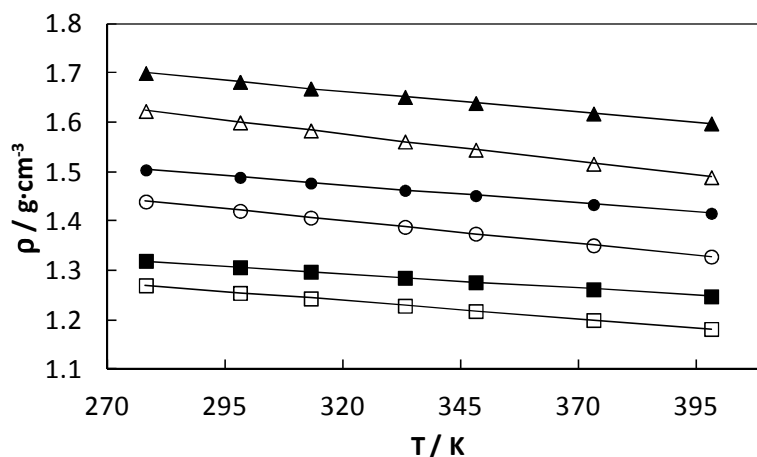
**Experimental:** Samples of ILs were kindly provided by Merck with purities higher than 98%. ILs were dried and degassed under vacuum for at least 48 hours, under agitation and using a vacuum system with a rotary pump Edwards RV3 before carrying out the measurement of density values at high pressure. A Karl-Fischer coulometric titrator (Mettler Toledo DL32) was employed to measure the water content in the samples before and after density measurements.

The experimental device consists of a fully automated vibrating tube densimeter Anton Paar HPM. The densimeter was calibrated [1] following the procedure described by Lagourette et al. [2] and modified by Comuñas et al. [3]. The expanded ( $k=2$ ) uncertainty of the density with this technique was rigorously calculated by Segovia et al. [1] finding that it is  $0.7 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$  for temperatures below  $T = 373.15 \text{ K}$ ,  $5 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$  at  $T = (373.15 \text{ and } 398.15) \text{ K}$  and  $p = 0.1 \text{ MPa}$ , and  $3 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$  in other cases, i.e. at  $T \geq 373.15 \text{ K}$  and  $p > 0.1 \text{ MPa}$ . More details of the system were given previously [1].

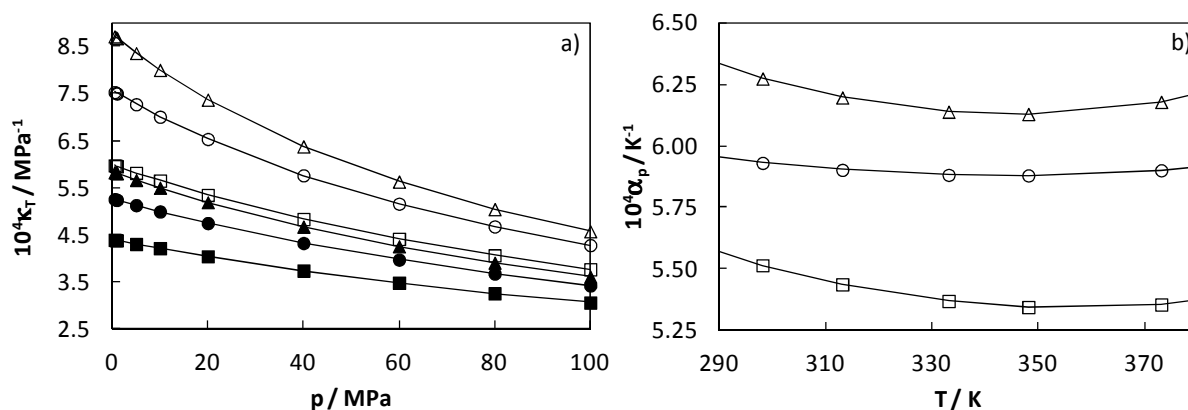
**Results and discussion:** Experimental density results at 0.1 MPa and 120 MPa in the whole temperature range for ILs are presented in figure 1. The modified Tamman-Tait equation [1] was employed to correlate experimental density values with temperature and pressure, obtaining absolute average deviation (AAD) lower than 0.018 %. It can be observed that  $[C_4C_1\text{Pyrr}][CF_3SO_2]$  is the IL with the lowest density, whereas for the ILs with the  $[C_4C_1C_1\text{Im}]^+$  cation, the density is higher for that with  $[(C_2F_5)_3PF_3]^-$  anion.

Isothermal compressibility shows system modification when it is subjected to pressure changes at constant temperature. This property is defined by  $\kappa_T(T,p) = 1/\rho \cdot (\partial\rho/\partial p)_T$  and can be obtained from the modified Tammann-Tait equation by simple analytical derivation. In figure 2.a) it is plotted the isothermal compressibility as a function of pressure at two

temperatures for the three ILs. It was found the following trend for  $\kappa_T$ :  $[C_4C_1C_1Im][[(C_2F_5)_3PF_3]] > [C_4C_1C_1Im][NTf_2]] > [C_4C_1Pyrr][CF_3SO_2]$ .



**Figure 1.** Experimental density,  $\rho$ , at 0.1 MPa (empty symbols) and 120 MPa (filled symbols)  $[C_4C_1C_1Im][CF_3SO_2]$  ( $\square$ ),  $[C_4C_1C_1Im][NTf_2]$  ( $\circ$ ),  $[C_4C_1C_1Im][[(C_2F_5)_3PF_3]]$  ( $\triangle$ ).



**Figure 2.** (a) Isothermal compressibility,  $\kappa_T$ , at 313.15 K (filled symbols) and at 398.15 K (empty symbols); and (b) isobaric thermal expansivity,  $\alpha_p$ , at 40 MPa for  $[C_4C_1C_1Im][CF_3SO_2]$  ( $\square$ ),  $[C_4C_1C_1Im][NTf_2]$  ( $\circ$ ),  $[C_4C_1C_1Im][[(C_2F_5)_3PF_3]]$  ( $\triangle$ ).

Isobaric thermal expansivity shows the fractional change in density when temperature increases at constant pressure. It was obtained from the isobaric densities by derivation, as it is recommended by several authors [4-6]. Thus, isobaric densities were fitted through eq. 1:

$$\ln(\rho) = A + BT + CT^2 + DT^3 \quad (1)$$

Therefore, isobaric thermal expansivity coefficient is given by:

$$\alpha_p = -(B + 2CT + 3DT^2) \quad (2)$$

In figure 2.b) it is plotted the isobaric thermal expansivity coefficient,  $\alpha_p$ , at 40 MPa as a function of temperature for the three ILs. It can be observed a minimum in the behaviour of  $\alpha_p$  with temperature for all the ILs. This behaviour was found previously in the literature [5-7]. The following trend was found for  $\alpha_p$ :  $[\text{C}_4\text{C}_1\text{C}_1\text{Im}][(\text{C}_2\text{F}_5)_3\text{PF}_3] > [\text{C}_4\text{C}_1\text{C}_1\text{Im}][\text{NTf}_2] > [\text{C}_4\text{C}_1\text{Pyrr}][\text{CF}_3\text{SO}_2]$ .

**Conclusions:** Experimental density values were determined for  $[\text{C}_4\text{C}_1\text{Pyrr}][\text{CF}_3\text{SO}_2]$ ,  $[\text{C}_4\text{C}_1\text{C}_1\text{Im}][\text{NTf}_2]$  and  $[\text{C}_4\text{C}_1\text{C}_1\text{Im}][(\text{C}_2\text{F}_5)_3\text{PF}_3]$  in a temperature range from 273.15 K to 298.15 K and pressures up to 120 MPa. Isothermal compressibility,  $\kappa_T$ , and isobaric thermal expansivity,  $\alpha_p$ , were obtained from these data and follow the same sequence:  $[\text{C}_4\text{C}_1\text{C}_1\text{Im}][(\text{C}_2\text{F}_5)_3\text{PF}_3] > [\text{C}_4\text{C}_1\text{C}_1\text{Im}][\text{NTf}_2] > [\text{C}_4\text{C}_1\text{Pyrr}][\text{CF}_3\text{SO}_2]$ . The behaviour of  $\alpha_p$  with temperature along isobars presents a minimum in the studied temperature and pressure range.

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