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Dependence against Temperature and Pressure of the Isobaric Thermal Expansivity of Room Temperature Ionic Liquids†

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The isobaric thermal expansivity α_p in the temperature and pressure intervals of (278.15 to 348.15) K and (5 to 50) MPa is reported for an assorted set of room temperature ionic liquids (RTILs) using a calorimetric method with an uncertainty of 2 %. The RTILs were selected to represent some of the most widely studied anions and cations; 1-butyl-3-methylpyridinium tetrafluoroborate [C$_4$mpyr][BF$_4$], 1-ethyl-3-methylimidazolium tetrafluoroborate [C$_2$mim][BF$_4$], 1-hexyl-3-methylimidazolium tetrafluoroborate [C$_6$mim][BF$_4$], 1-octyl-3-methylimidazolium tetrafluoroborate [C$_8$mim][BF$_4$], 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C$_2$mim][NTf$_2$], and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C$_6$mim][NTf$_2$] are analyzed. The same general trends were obtained for the studied liquids, although differences are found both in the magnitude and in the α_p behavior against temperature and pressure.

Introduction

Room temperature ionic liquids (RTILs) have been postulated as potential environmental-friendly substitutes to traditional solvents in many chemical processes, mainly because of their unique physical and chemical properties, the most remarkable of them being their extremely low vapor pressure, low melting temperature, and a high thermal stability over an extended temperature range. As a consequence, research about the physical properties of these compounds has received great attention in the last few years.[1−4] Most of the effort was spent in the study of physical properties of RTILs at atmospheric pressure, although in the last few years, there have been some works devoted to characterize the behavior against p and T, of several magnitudes, with the density ρ being the most widely studied.[5−12] As a result, it was concluded that the RTILs density dependencies against T and p, given by the isobaric thermal α_p expansivity and isothermal compressibility κ_T, differ significantly from those of other solvents. These differences were observed not only in the α_p and κ_T values themselves but also in the behavior of these magnitudes against temperature and pressure: there are several works[6,8] in which a negative temperature dependency for α_p over the whole pressure range is shown, where this behavior is not usually found for organic solvents at moderate pressures.[13−20] Moreover, by checking the α_p literature data,[5−12] it seems to be that this is not an isolated case, but the rule for RTILs.

It is the aim of this work to provide more experimental data of α_p against temperature and pressure for RTILs. Isobaric thermal expansivity was directly determined through a calorimetric method[18−22] in the range of (278.15 to 348.15) K and (5 to 50) MPa for a set of RTILs, selected to represent some of the most widely studied anions and cations: 1-butyl-3-methylpyridinium tetrafluoroborate [C$_4$mpyr][BF$_4$], 1-ethyl-3-methylimidazolium tetrafluoroborate [C$_2$mim][BF$_4$], 1-hexyl-3-methylimidazolium tetrafluoroborate [C$_6$mim][BF$_4$], 1-octyl-3-methylimidazolium tetrafluoroborate [C$_8$mim][BF$_4$], 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C$_2$mim][NTf$_2$], and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C$_6$mim][NTf$_2$] are analyzed. The reported data are compared with literature, obtained from the experimental measure of density,[5−12] and the obtained α_p values as well as their behavior against temperature and pressure are qualitatively discussed and related to the chemical nature of the anion and cation.

Experimental Section

Chemicals. Two standard liquids were required for the calibration of the calorimeter: Milli-Q water and hexane from Fluka (purity > 99.5 % in mass) were chosen because of the quality of literature data.[23,24] The ionic liquids [C$_4$mpyr][BF$_4$], [C$_2$mim][BF$_4$], [C$_6$mim][BF$_4$], [C$_8$mim][BF$_4$], [C$_2$mim][NTf$_2$], and [C$_6$mim][NTf$_2$] were purchased from Solvent Innovation. All RTILs present purities higher than 99 % in mass. All of them were dried and degassed under vacuum for at least 2 days prior to use. After this procedure, the water content in ionic liquids was determined by means of Karl Fisher titration, obtaining $1\cdot10^{-4}$, $2.5\cdot10^{-4}$, $1.7\cdot10^{-4}$, $1.1\cdot10^{-4}$, $7\cdot10^{-5}$, and

Table 1. Fitting Coefficients of the Isobaric Thermal Expansivity for the Studied Liquids

	[C$_4$mpyr] [BF$_4$]	[C$_2$mim] [BF$_4$]	[C$_6$mim] [BF$_4$]	[C$_8$mim] [BF$_4$]
$a_0\cdot10^3$/K^{-1}	0.9985	1.1113	1.0646	1.0236
$a_1\cdot10^6$/K^{-2}	−2.2003	−2.7749	−2.4545	−2.1215
$a_2\cdot10^9$/K^{-3}	2.7259	3.5510	3.1186	2.5775
$b_1\cdot10^6$/MPa$^{-1}\cdot$K^{-1}	−1.4139	−1.2462	−1.6361	−1.8742
$b_2\cdot10^9$/MPa$^{-2}\cdot$K^{-1}	5.2654	4.3832	6.2719	7.8586
$s\cdot10^6$/K^{-1}	1	1	2	1

	[C$_2$mim] [NTf$_2$]	[C$_6$mim] [NTf$_2$]
$a_0\cdot10^3$/K^{-1}	1.0181	1.0088
$a_1\cdot10^6$/K^{-2}	−1.7917	−1.6946
$a_2\cdot10^9$/K^{-3}	2.0954	1.9503
$b_1\cdot10^6$/MPa$^{-1}\cdot$K^{-1}	−2.0194	−2.3838
$b_2\cdot10^9$/MPa$^{-2}\cdot$K^{-1}	7.1836	10.192
$s\cdot10^6$/K^{-1}	2	2

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$6 \cdot 10^{-5}$ in mass fraction for [C_4mpyr][BF_4], [C_2mim][BF_4], [C_6mim][BF_4], [C_8mim][BF_4], [C_2mim][NTf_2], and [C_6mim][NTf_2], respectively.

Methodology. Isobaric thermal expansivity for the RTILs was obtained by using a Micro DSCII microcalorimeter from Setaram coupled with a Ruska 7610 pressure controller.[18−22] The method for determining α_p is based on recording the heat exchanging between the cell which contains the RTIL and the calorimetric block, which appears because of a pressure variation over the sample. α_p is thus determined using the next equation:[18]

$$\alpha_p = -\frac{1}{VT}\frac{d'Q}{dp} \tag{1}$$

where V, T, and $(d'Q)/(dp)$ denote volume, temperature, and variation of the heat introduced in the system against change in pressure, respectively. Once the sample was introduced in the experimental cell and thermal stability at the measuring temperature was achieved, a pressure ramp at 1.5 $MPa \cdot min^{-1}$ was applied. Because of this pressure change, a heat flux ϕ^x between the sample and the calorimeter block appeared, which was detected by the flow meters located around the cell. Two liquids of known α_p were needed to calibrate the apparatus:

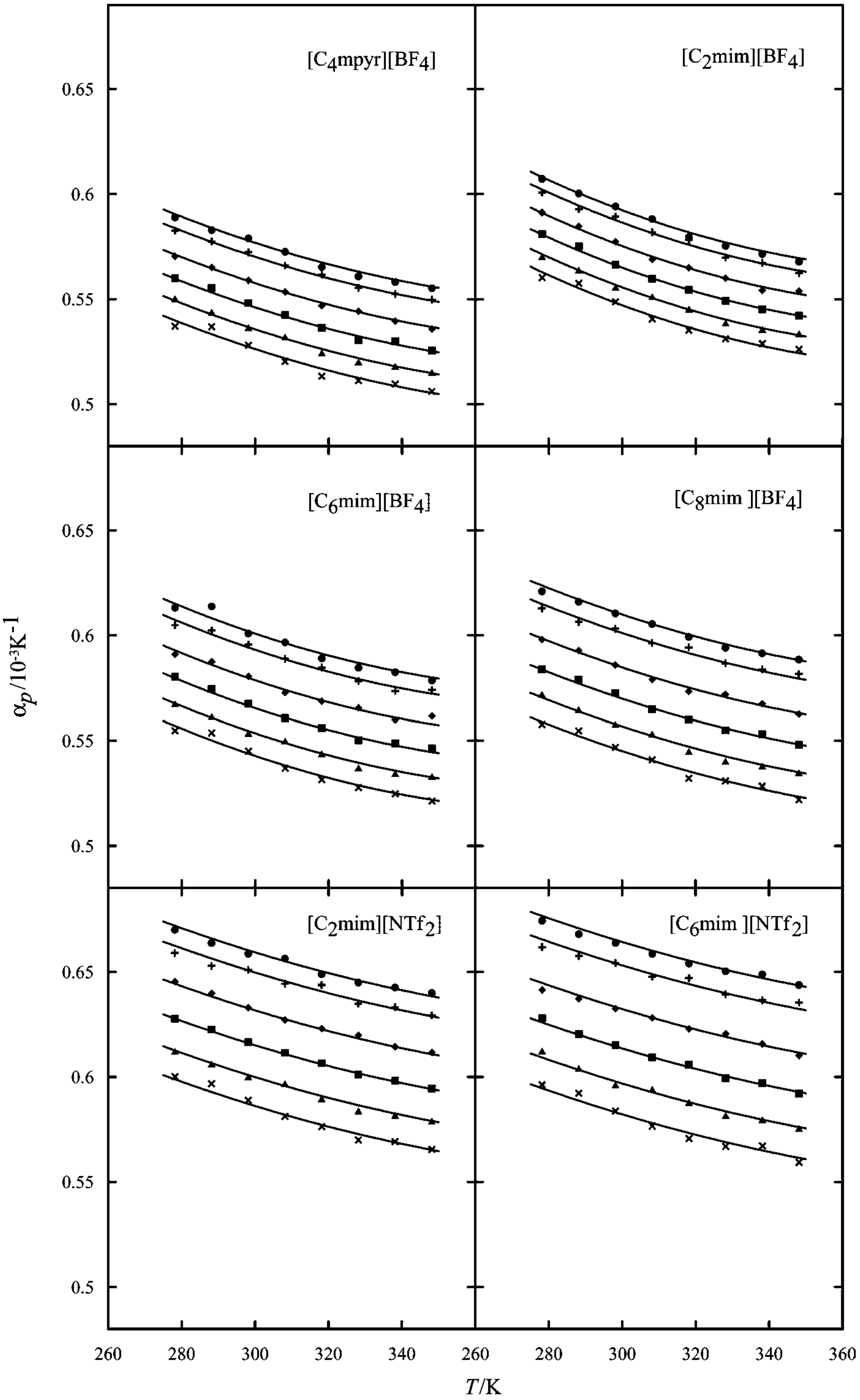

Figure 1. α_p values as function of temperature at several pressure for: [C_4mpyr][BF_4]; [C_2mim][BF_4]; [C_6mim][BF_4]; [C_8mim][BF_4]; [C_2mim][NTf_2]; [C_6mim][NTf_2]. ●, p = 5 MPa; +, p = 10 MPa; ◆, p = 20 MPa; ■, p = 30 MPa; ▲, p = 40 MPa; ×, p = 50 MPa.

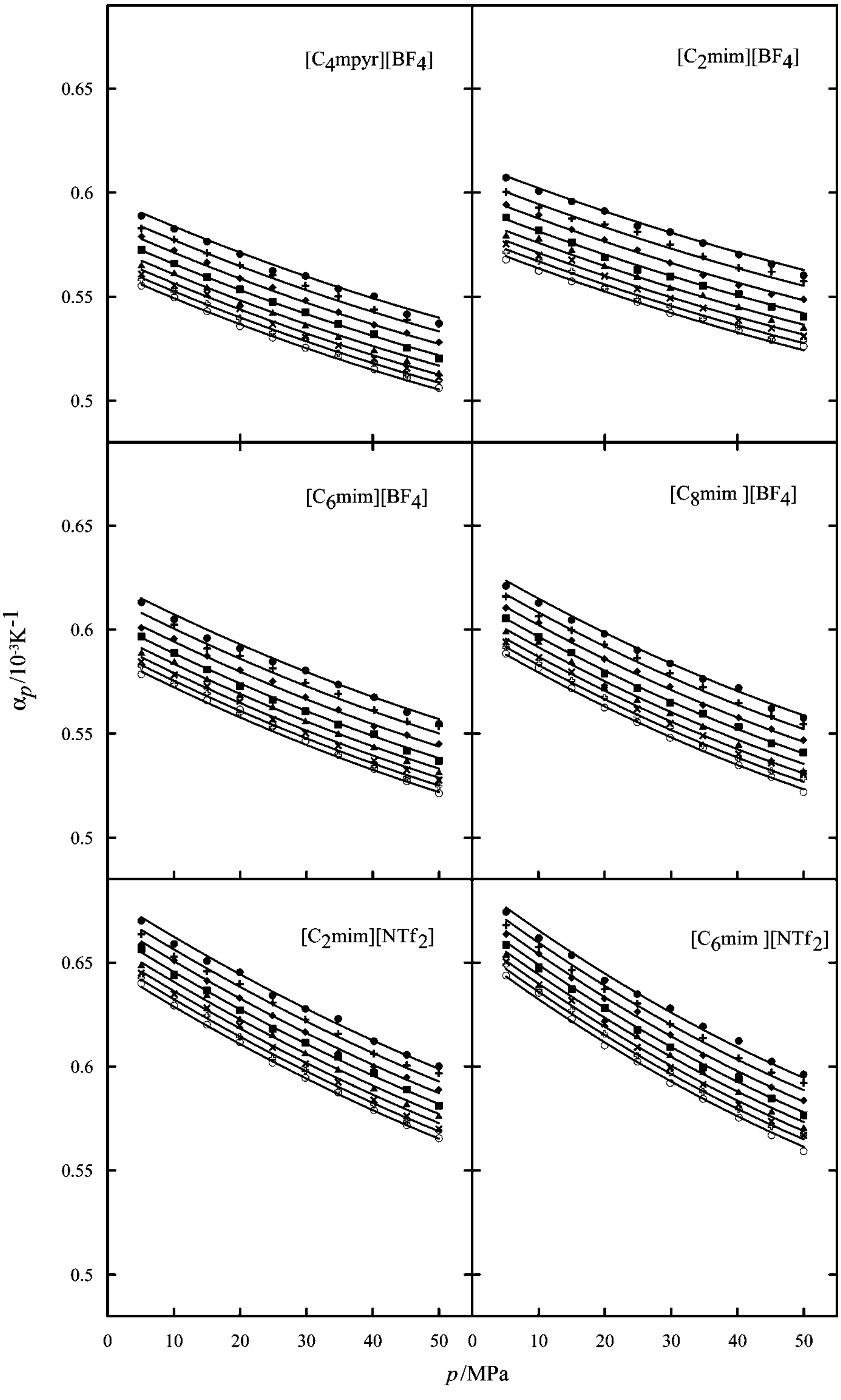

Figure 2. α_p values as function of pressure at several temperatures for: [C$_4$mpyr][BF$_4$]; [C$_2$mim][BF$_4$]; [C$_6$mim][BF$_4$]; [C$_8$mim][BF$_4$]; [C$_2$mim][NTf$_2$]; [C$_6$mim][NTf$_2$]. ●, T = 278.15 K; +, T = 288.15 K; ◆, T = 298.15 K; ■, T = 308.15 K; ▲, T = 318.15 K; ×, T = 328.15 K; open plus sign, T = 338.15 K; ○, T = 348.15 K.

water and *n*-hexane were selected because of the quality of the available literature data.[23,24] From the heat flux ϕ^w and ϕ^h, determined in two previous experiences for the calibration fluids, and from their isobaric thermal expansivity literature values, α_p^w and α_p^h, the isobaric thermal expansivity of the unknown liquid α_p^x is obtained from the measured flux ϕ^x, by means of:

$$\alpha_p^x = \alpha_p^w + \frac{\phi^w - \phi^x}{\phi^w - \phi^h}(\alpha_p^h - \alpha_p^w) \qquad (2)$$

The uncertainties in temperature and pressure were estimated in 0.01 K and 0.005 MPa, respectively. The repeatability of α_p is estimated in $5 \cdot 10^{-6}$ K^{-1}, but the main error of this measuring procedure comes from the α_p literature data for *n*-hexane.[24] The combination of all uncertainty sources for α_p yields an uncertainty of 2 %.

Results and Discussion

The isobaric thermal expansivity data were obtained within the temperature and pressure intervals of (278.15 to 348.15) K and (5 to 50) MPa in temperature and pressure steps of 10 K and 0.45 MPa, respectively. Data at representative temperatures and pressures are reported as Supporting Information. All experimental data were fitted to the next polynomial in T and p:

$$\alpha_p(p, T) = \sum_{i=0}^{2} a_i T^i + \sum_{i=1}^{2} b_i p^i \tag{3}$$

The a_i and b_i coefficients are given in the Table 1. It is interesting to note that the water content of RTILs should influence α_p in a different way depending on temperature. Pure water presents low α_p values at low temperatures (α_p equals zero at 277.13 K), but it increases strongly with temperature, being very similar to that of studied RTILs at 348.15 K (the highest temperature of this work). Thus, it is expected that water content affects mainly low temperature measurements, with high temperature ones relatively not influenced by these impurities.

There are available literature (p, ρ, T) data for [C_2mim][BF_4], [C_6mim][BF_4], [C_8mim][BF_4], [C_2mim][NTf_2], and [C_6mim][NTf_2],[5−12] which allow α_p to be determined by using the next relation:

$$\alpha_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \tag{4}$$

The literature values were compared to those of the present work by means of the percent average absolute deviation Δ, defined as:

$$\Delta = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{\alpha_{p,i}^{\text{exp}} - \alpha_{p,i}^{\text{lit}}}{\alpha_{p,i}^{\text{exp}}}\right| \tag{5}$$

For [C_2mim][BF_4], a Δ value of 0.9 % was found for the data of Sanmamed et al.,[5] 6 % for those of Coutinho et al.,[6] and 4 % for Machida et al.[7] For [C_6mim][BF_4], the comparison with the data of Sanmamed et al.[5] yields a Δ value of 0.7 %, whereas those of Machida et al.[7] show a Δ of 6 %. For [C_8mim][BF_4], a Δ value of 0.8 % was found for the data of Sanmamed et al.[5] and 6 % for those of Coutinho et al.[8] For [C_2mim][NTf_2], a Δ value of 21 % for the data of Coutinho et al.[6] and 3.6 % for those of Cibulka et al.[9] was obtained. Finally, for [C_6mim][NTf_2], the comparison with the data of Rebelo et al.[10,11] yields two Δ values of 8 % and 7 %. Most of these deviations are coherent with the stated uncertainty in this work and in literature. It must be noted that obtaining the α_p from eq 4 implies fitting against T of the density data; therefore, a somewhat subjective character is involved in this calculation, since one must select some fitting equation which predetermines the dependence of α_p against T. From this point of view, the data reported in this work are not affected by any a priori assumption because α_p is directly measured. Figure 1 shows α_p as a function of temperature at different pressures; negative temperature dependence is obtained for all cases. Figure 2 shows α_p as a function of pressure at several temperatures. α_p decreases against p, as it was found for molecular liquids;[12−21] but in contrast to them,[14,16−19] the curves remain almost parallel over the whole pressure range.

By simple inspection of Figures 1 and 2, it becomes evident that α_p is similar for the studied RTILs; it belongs to the interval of $(0.45 \text{ to } 0.7)\cdot 10^{-3}$ K^{-1} for all liquids over the whole temperature and pressure range. Moreover, no noticeable differences as regards to temperature dependence were found. As for pressure dependence, it was found that it correlates with the α_p value itself; as α_p is higher, the pressure dependence is more pronounced. With regards to the chemical nature of the RTILs, it can be observed that the increment of the chain length hardly affects α_p; as a general rule, it seems to be slightly higher for the cations with longer alkyl chains, but this effect is very small, and it can be detected only for low pressure. In contrast, the change of the imidazolium by the pyridinium ring has a noticeable effect, with the α_p being lower for the latter. The change of the anion also has an important effect: the bigger the anion, the higher α_p is.[21]

Conclusion

Isobaric thermal expansivity against temperature and pressure has been determined for a set of RTILs which includes the most widely studied cations and anions. Small and similar α_p values have been found for all studied RTILs, and negative dependency against T was obtained for all studied liquids over the whole pressure range. No important differences have been observed by changing the alkyl chain in the imidazolium ring of the RTIL, whereas substituting it by a pyridinium has a noticeable effect. As for the influence of the anion, a correlation between its size and α_p has been detected.

Supporting Information Available:

Experimental data for thermal expansivities for the studied RTILs as a function of temperature and pressure. This material is available free of charge via the Internet at http://pubs.acs.org.

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