# Isobaric Thermal Expansivity for Ionic Liquids with a Common Cation as a Function of Temperature and Pressure[†]

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Isobaric thermal expansivity $\alpha_p$ as a function of temperature and pressure was determined by means of a calorimetric method for a set of ionic liquids with a common cation within the temperature and pressure intervals (278.15 to 348.15) K and (5 to 50) MPa. The selected common cation was 1-butyl-3-methylimidazolium, whereas the chosen anions were tetrafluoroborate, bis(trifluoromethylsulfonyl)imide, hexafluoroantimonate, trifluoromethanesulfonate, and methylsulfate. The results are compared with available literature data, obtained from density measurements. An unusual, negative dependence of $\alpha_p$ against temperature was found for all liquids over the whole temperature and pressure interval. The results are discussed in terms of the differences in the chemical nature of the anions.

## Introduction

Room temperature ionic liquids (RTILs) have received great attention in the last years.[1−3] They are salts, usually formed by an organic cation and an organic or inorganic anion, that are liquid at room temperature.[4] This interest comes mainly from their unique physical and chemical properties such as an extremely low vapor pressure, specific solvent abilities, and low melting temperature. In addition, and unlike other ionic compounds, they usually present a high thermal stability over an extended temperature range. On the another hand, an enormous amount of possible ionic liquids exist, since it is possible to make a huge quantity of combinations between different cations and anions, which allows us to choose a particular ionic liquid that fulfills the exigencies required for some concrete application. These characteristics make RTILs potential environmentally friendly substitutes to traditional solvents. Therefore, the study of physical properties of RTILs is very important from both a fundamental and applied research point of view. As a consequence, in the last years, there was a lot of work devoted to the study of physical properties of these liquids, the density being the most widely studied, due to its experimental accessibility. Most of these data were reported at atmospheric pressure, although there is a considerable amount of work which reports density as a function of temperature $T$ and pressure $p$ over extended $T$, $p$ ranges.[5−13] It was found that density of RTILs is usually between (1000 and 2000) $\mathrm{kg \cdot m^{-3}}$, whereas its dependencies against temperature and pressure (given by the isobaric thermal expansivity $\alpha_p$ and isothermal compressibility $\kappa_T$) are significantly milder than those found for common organic solvents—both thermodynamic coefficients present values about a half of those of molecular liquids. In addition, some studies[6,7] point to the fact that $\alpha_p$ of RTILs presents a negative temperature dependency, opposite to that found for usual organic solvents at moderate pressures,[14−21] although it would be desirable to have some more evidence to confirm this anomalous behavior. It is the aim of this work to contribute to the knowledge of the behavior of $\alpha_p$ against temperature and pressure for RTILs. To this end, $\alpha_p$ was determined through a calorimetric method[19−22] in the range (278.15 to 348.15) K and (5 to 50) MPa for a set of RTILs with a common cation. 1-Butyl-3-methylimidazolium, [$C_4$mim], was the selected cation, whereas tetrafluoroborate, [$BF_4$], bis(trifluoromethylsulfonyl)imide, [$NTf_2$], hexafluoroantimonate, [$SbF_6$], trifluoromethanesulfonate, [$CF_3SO_3$], and methylsulfate, [$MeSO_4$], were the chosen anions. The reported data are compared with the literature, obtained from experimental measure of density,[5−13] and finally, the $\alpha_p$ values as well as their behavior against temperature and pressure are qualitatively discussed in terms of the chemical nature of the anion.

## 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 due to the quality of literature data.[23,24] [$C_4$mim][$BF_4$], [$C_4$mim][$NTf_2$], [$C_4$mim][$SbF_6$], and [$C_4$mim][$MeSO_4$] were purchased from Solvent Innovation, whereas [$C_4$mim][$CF_3SO_3$] was obtained from Merck. All RTILs present purities higher than 99 % in mass. All ionic liquids were dried and degassed under vacuum for at least 2 days prior to use at moderate temperature (333.15 K). After this procedure, the water mass fraction in ionic liquids was determined by means of Karl Fisher titration. A water mass fraction of $(250, 110, 220, 50, \text{and } 300) \cdot 10^{-6}$ was found for [$C_4$mim][$BF_4$], [$C_4$mim][$NTf_2$], [$C_4$mim][$SbF_6$], [$C_4$mim][$MeSO_4$], and [$C_4$mim][$CF_3SO_3$], respectively.

***Methodology.*** Isobaric thermal expansivity for the RTILs was determined through a Micro DSCII microcalorimeter from Setaram coupled with a Ruska 7610 pressure controller.[19−22] This calorimetric method for $\alpha_p$ determination is based on recording the heat exchanging between the cell which contains the RTIL and the calorimetric block caused by the variation of the pressure over the sample; $\alpha_p$ is determined from the next equation

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

where $V$, $T$, and $(d'Q/dp)$ denote volume, temperature, and variation of the heat introduced in the system against change

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

| | $[C_4mim][NTf_2]$ | $[C_4mim][SbF_6]$ | $[C_4mim][CF_3SO_3]$ | $[C_4mim][BF_4]$ | $[C_4mim][MeSO_4]$ |
|---|---|---|---|---|---|
| $a_0/10^{-3}\ K^{-1}$ | 0.9874 | 1.0554 | 1.0527 | 1.0156 | 1.0148 |
| $a_1/10^{-6}\ K^{-2}$ | −1.6047 | −2.2621 | −2.3603 | −2.1724 | −2.5036 |
| $a_2/10^{-9}\ K^{-3}$ | 1.8863 | 2.8376 | 3.0361 | 2.6161 | 3.2345 |
| $b_1/(MPa^{-1}\ 10^{-6}\ K^{-1})$ | −2.3783 | −1.6738 | −1.7450 | −1.4184 | −1.2379 |
| $b_2/(MPa^{-2}\ 10^{-9}\ K^{-1})$ | 10.5112 | 5.6131 | 6.9552 | 5.4010 | 4.6555 |
| $s/10^{-6}\ K^{-1}$ | 3 | 1 | 1 | 2 | 1 |

in pressure, respectively. The samples were introduced in the experimental cell, and when thermal stability at the measuring temperature was reached, a pressure ramp at 1.5 MPa·min$^{-1}$ was applied. This produced a heat flux $\phi^x$ between the sample and the calorimeter block to appear, which was detected by the flowmeters located around the

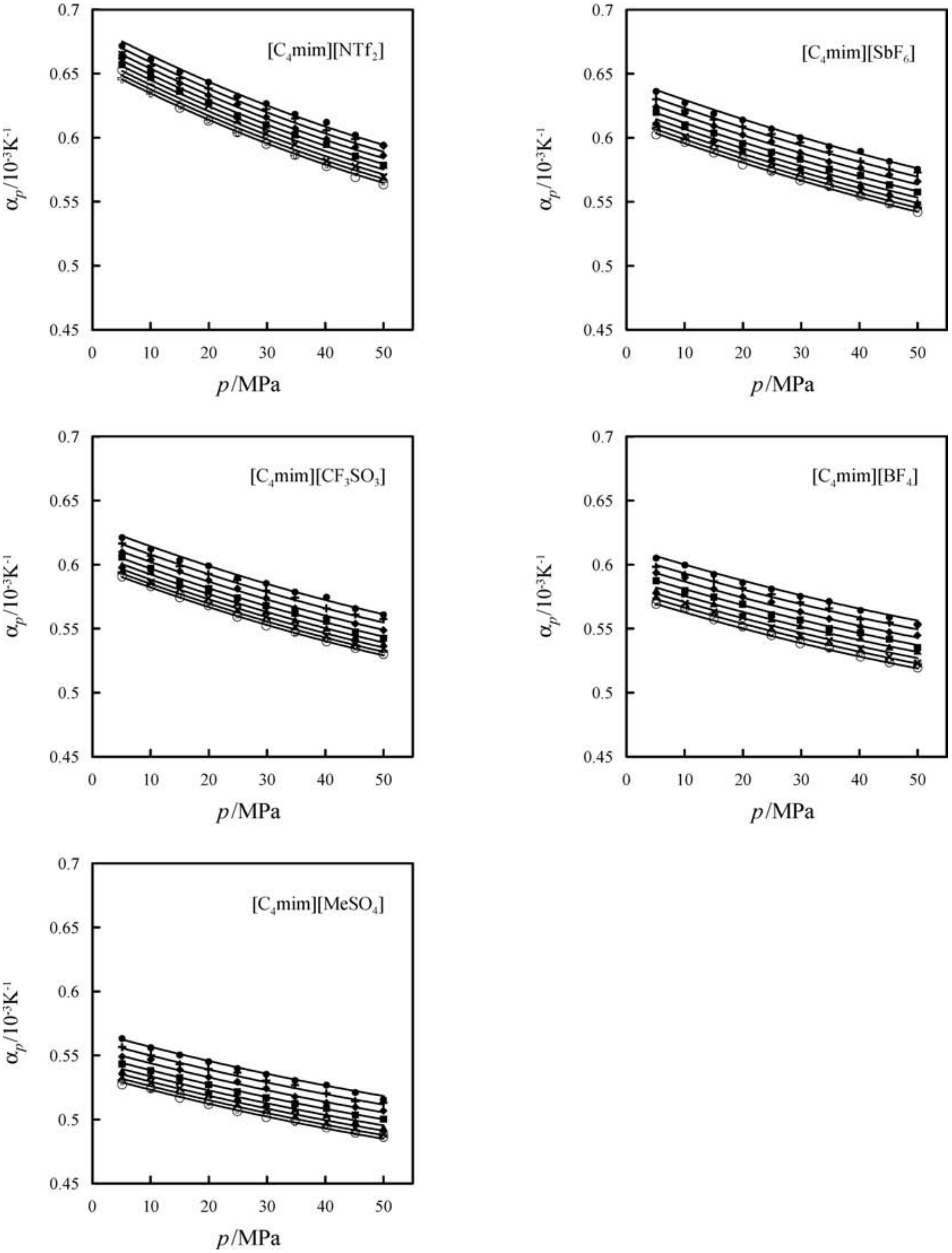

**Figure 1.** $\alpha_p$ values as a function of temperature at several pressures for: $[C_4mim][NTf_2]$, $[C_4mim][SbF_6]$, $[C_4mim][CF_3SO_3]$, $[C_4mim][BF_4]$, and $[C_4mim][MeSO_4]$. ●, $T = 278.15$ K; +, $T = 288.15$ K; ◆, $T = 298.15$ K; ■, $T = 308.15$ K; ▲, $T = 318.15$ K; ×, $T = 328.15$ K; open plus symbol, $T = 338.15$ K; ○, $T = 348.15$ K; −, calculated values from eq 3.

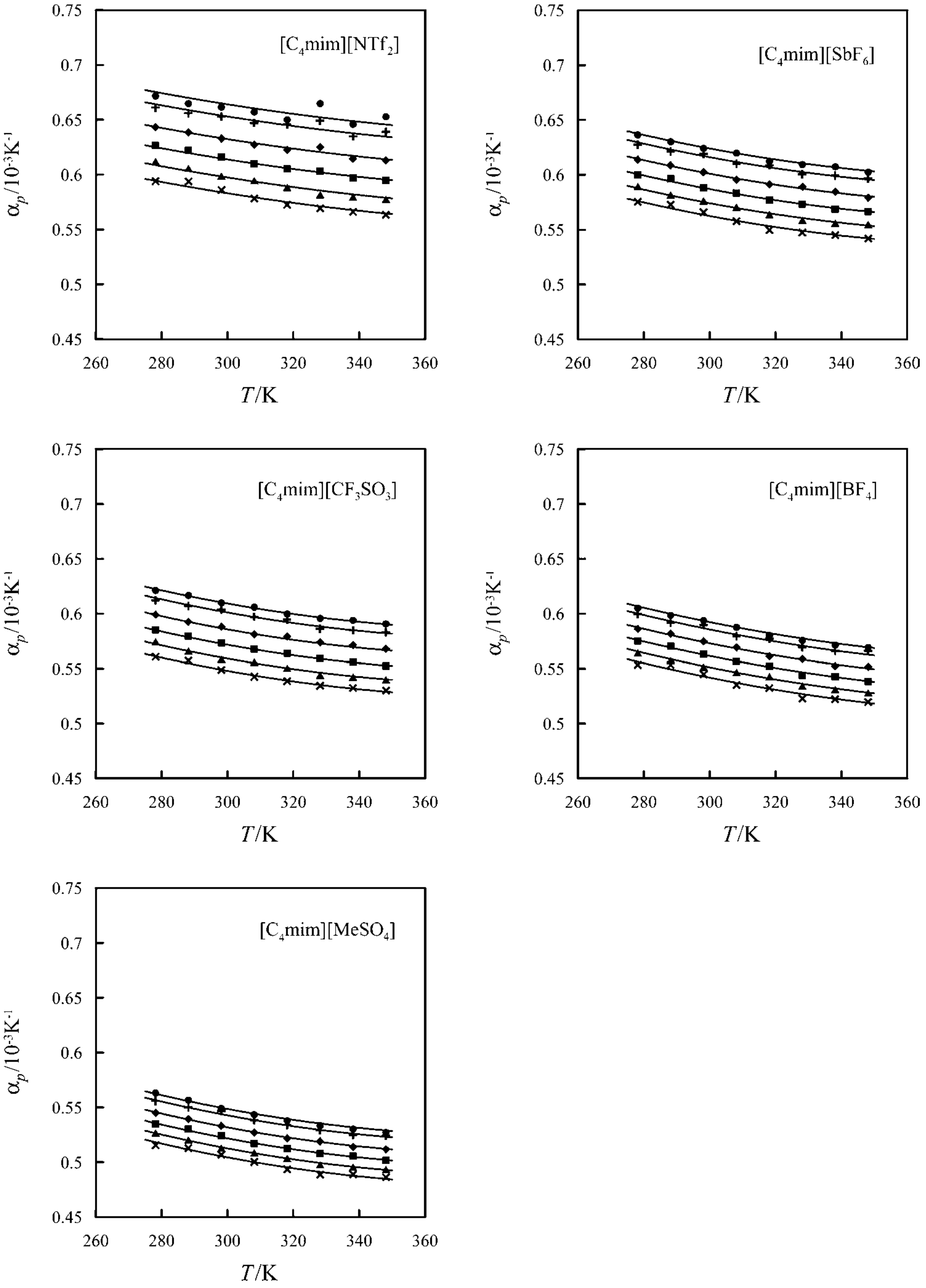

**Figure 2.** $\alpha_p$ values as function of pressure at several temperatures for: [C$_4$mim][NTf$_2$], [C$_4$mim][SbF$_6$], [C$_4$mim][CF$_3$SO$_3$], [C$_4$mim][BF$_4$], and [C$_4$mim][MeSO$_4$]. ●, $p = 5$ MPa; +, $p = 10$ MPa; ◆, $p = 20$ MPa; ■, $p = 30$ MPa; ▲, $p = 40$ MPa; ×, $p = 50$ MPa; —, calculated values from eq 3.

cell. For calibrating the instrument, two calibration liquids of known $\alpha_p$ were needed: water and *n*-hexane were selected because of the quality of the available literature data.[23,24] From the isobaric thermal expansivity of these two standards, $\alpha_p^{\mathrm{w}}$ and $\alpha_p^{\mathrm{h}}$, and from their heat flux $\phi^{\mathrm{w}}$ and $\phi^{\mathrm{h}}$, determined in two previous experiences, the isobaric thermal expansivity of the unknown liquid $\alpha_p^{\mathrm{x}}$ is obtained from the measured flux $\phi^{\mathrm{x}}$, through

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

The repeatability of $\alpha_p$ is estimated in $0.005 \cdot 10^{-3}$ K$^{-1}$, which together with the uncertainty stated for the calibration fluids yields for $\alpha_p$ an uncertainty of 2 %.

## Results and Discussion

The isobaric thermal expansivity was determined within the temperature and pressure interval (278.15 to 348.15) K and (5 to 50) MPa for [C$_4$mim][BF$_4$], [C$_4$mim][NTf$_2$], [C$_4$mim][SbF$_6$], [C$_4$mim][CF$_3$SO$_3$], and [C$_4$mim][MeSO$_4$]. The measurements were obtained 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 values were fitted to the next polynomial in $T$ and $p$

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

The $a_i$ and $b_i$ coefficients are given in the Table 1.

There are available literature ($p$, $\rho$, $T$) data for [C$_4$mim][BF$_4$], [C$_4$mim][NTf$_2$], and [C$_4$mim][CF$_3$SO$_3$],[5−13] which allow $\alpha_p$ to be determined by using the next relation

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

The comparison of the literature values with those of the present work was performed by making use of the average relative deviation $\Delta$, defined as

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

For [C$_4$mim][BF$_4$], a $\Delta$ value of 0.03 was found for the data of Cibulka et al.,[5] 0.09 for those of Coutinho et al.,[6] 0.03 for Rebelo et al.,[7] 0.03 for Tomida et al.,[8] 0.02 for Tekin et al.,[9] 0.02 for Machida et al.,[10] 0.004 for Sammamed et al.,[11] and 0.03 for Abdulagatov et al.[12] data. As for [C$_4$mim][NTf$_2$], the comparison with the data of Rebelo et al.[13] yields a $\Delta$ value of 0.04, whereas those of Cibulka et al.[5] show a $\Delta$ of 0.011. Finally, the data of [C$_4$mim][CF$_3$SO$_3$], reported by Coutinho et al.,[6] give a value of 0.10 for $\Delta$. These values are compatible with the stated uncertainty of this work and that of the literature, although it is worth noting that the latter presents a somewhat nonmeasurable character, derived from the fact that it is obtained from differentiation of a fitting equation, which involves a prejudiced dependence of the density against temperature, which could produce a misleading behavior of $\alpha_p$ against $T$. In that sense, the data of this work, since it is obtained directly, could cast light on the already visited problem[6,7,13] of the unusual (negative) dependence of $\alpha_p$ against $T$ for RTILs. Figure 1 shows $\alpha_p$ as a function of temperature at different pressures; $\alpha_p$ decreases as $T$ is raised at all measuring pressures for all studied RTILs, a fact which confirms the anomalous behavior of $\alpha_p$ against $T$. As for $\alpha_p$ pressure dependence, it is presented in Figure 2 at several temperatures for all studied liquids. It can be observed that $\alpha_p$ decreases as pressure is raised at all studied temperatures and all studied liquids, which is the common behavior found for other liquids.[14−21] On the other hand, the curves at different temperatures are almost parallel over the whole pressure range, a fact which contrasts with the much more complex $\alpha_p$ pressure dependence of common solvents—even relatively simple liquids as alkanes show curve crossing at high pressure.[14,16−19]

By simple inspection of Figures 1 and 2, it is easy to realize that there is a (weak) correlation between the molecular weight, MW, of the RTIL and the value of $\alpha_p$: the lower the MW, the smaller the $\alpha_p$ is, although there is one exception, namely, [C$_4$mim][MeSO$_4$], which shows the lower $\alpha_p$ value but its MW is bigger than that of [C$_4$mim][BF$_4$]. This correlation can be ascribed to the fact that increasing the molecular weight makes the ions that form the RTIL bigger; however, the charge per ion is the same (elementary charge), and as a consequence, the ionic character is more diluted. This would make the RTILs of large MW more similar to a molecular liquid than those of small MW. This is also supported by the $\alpha_p$ temperature and pressure dependencies. It is more anomalous, as compared to molecular solvents, as MW is lower: $\alpha_p$ decreases as temperature is raised in a slightly more pronounced way for low MW RTILs, whereas $\alpha_p$ against $p$ decreases in a lower extent for low MW RTILs.

## Conclusion

The $\alpha_p$ behavior against $T$ and $p$ was characterized for a set of RTILS with a common cation to study the influence of the anion over this magnitude. Low $\alpha_p$, as compared to typical molecular liquid values, were obtained. Moreover, unusual $\alpha_p$ behavior against $T$ and $p$ was obtained: $\alpha_p$ curves against $p$ remain almost parallel both at low and high pressure, whereas negative $\alpha_p$ temperature dependency was obtained for all RTILs over the whole pressure and temperature range. The decreasing of the molar mass produces both the $\alpha_p$ data and their dependency against $T$ and $p$ to differ in a greater extent from those found for usual organic solvents, a fact that could be ascribed to an increasing of the ionic character of the RTIL as the ions that form the liquid become smaller.

### 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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