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# Calorimetric and Volumetric Study on Binary Mixtures 2,2,2-Trifluoroethanol + (1-Butyl-3-methylimidazolium Tetrafluoroborate or 1-Ethyl-3-methylimidazolium Tetrafluoroborate)[†]

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This work was motivated by the fundamental interest in the study of mixtures containing ionic liquids and fluorinated alcohols but also by the possibility of the use of these mixtures in refrigeration applications. The study of the thermophysical properties of these mixtures will contribute to evaluate the reliability as an absorbent of several ionic liquids with the refrigerant 2,2,2-trifluoroethanol. Thus, densities, $\rho$, over the temperature ranges from (283.15 to 323.15) K and (293.15 to 323.15) K of 2,2,2-trifluoroethanol (TFE) + 1-butyl-3-methylimidazolium tetrafluoroborate ($[C_1C_4im][BF_4]$) and 1-ethyl-3-methylimidazolium tetrafluoroborate ($[C_1C_2im][BF_4]$) were measured at atmospheric pressure, respectively. Excess molar volumes, $V_m^E$, were calculated from the density values of the mixtures and of the pure compounds. In addition, mixing enthalpies (or excess molar enthalpies), $\Delta_{mix}H$, were measured for both systems at atmospheric pressure and at (293.15 and 333.15) K. Densities of $[C_1C_4im][BF_4]$ + TFE are lower than those for $[C_1C_2im][BF_4]$ + TFE. For both systems, mixing enthalpies are positive, being higher for $[C_1C_4im][BF_4]$ + TFE. Excess molar volumes were positive in the case of $[C_1C_4im][BF_4]$ + TFE between (283 and 323) K and slightly negative at 333 K, whereas for $[C_1C_2im][BF_4]$ + TFE they were negative in the (293 to 333) K temperature range. In light of the results reported herein, the system containing $[C_1C_2im][BF_4]$ is preferred to $[C_1C_4im][BF_4]$ for refrigeration by absorption. Nevertheless, other properties should be taken into account for the final choice of a refrigerant/absorbent pair.

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## Introduction

In industrial processes, steam or heat is classically produced by the combustion of fossil fuels, while at the same time, heat is rejected as waste. Since the energy crisis, for economical reasons, there has been an increasing interest in favor of heat pumps that allow the conversion of low-potential thermal sources (waste heat or renewable energy like solar energy) into useful energy (heat or cool). The conventional vapor compression cycle uses a mechanical gas compression step as an energy input for this antinatural conversion. In absorption pumps, this energy-consuming step is replaced by a chemical compression (combination of an absorber, a separator, and a pump) working with a binary mixture composed of a refrigerant and an absorbent.[1] This system has also the advantage to avoid toxic gases (e.g., hydrofluorocarbons and chlorofluorocarbons) classically used in mechanical compression. In 1988, Marcriss et al.[2] suggested about 40 refrigerants and 200 absorbents, and the investigations in new work fluids have continued up to our days.[3−6]

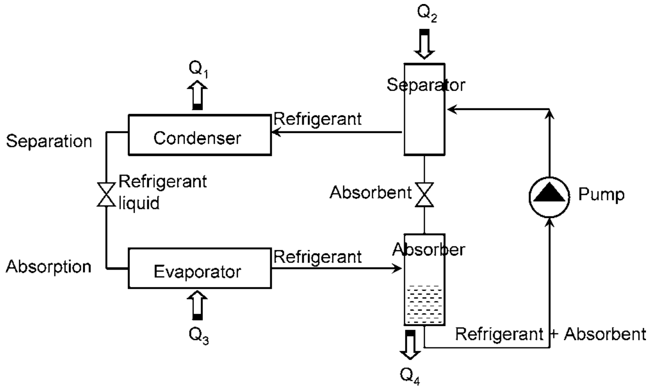

**Figure 1.** Schematic representation of an absorption pump.

A schematic representation of an absorption pump is shown in Figure 1. It is composed of absorption and separation processes. During the absorption step, the refrigerant—the more volatile component—is evaporated (endothermic process) and then absorbed (exothermic process) by the liquid absorbent—the less volatile component—which reduces the pressure in the system. In the separation step, the absorbent is then separated from the refrigerant (endothermic process), the latter being recondensed (exothermic process). A pump is necessary because of the pressure difference in the separation and absorption part of the system.[1]

The performance of an absorption system is dependent on the refrigerant/absorbent pair chosen and on its chemical and thermodynamic properties.[7] The knowledge of these properties is necessary to calculate the mass and energy balances in the

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process and to evaluate the COP (coefficient of performance) of the system. This factor is the ratio between the useful energy and the energy input of the process. Depending on the objective of the heat pump (cooling, heating, or heating and cooling), the useful energy is not the same: cooling capacity at evaporator, $Q_3$, for a refrigeration system; heating capacity at absorber, $Q_4$, and heating capacity at condenser, $Q_1$, for a heat system, and finally $Q_1$, $Q_3$, and $Q_4$ for a heating and cooling system. The energy input of the system is the energy input in the separator, $Q_2$, and the energy input in the pump. This last quantity is negligible compared to $Q_2$. So, to increase the COP of the process, $Q_2$ should be as low as possible, while the other energy quantities should be as high as possible.[1] Clearly, properties in favor of mass transfer (e.g., low viscosity) and energy efficiency (e.g., high vaporization enthalpy and low vapor pressure of the refrigerant) are required as well as properties making the refrigerant/absorbent pair environmentally safe (e.g., low toxicity, nonflammability).

The two couples classically used as refrigerant and absorbent, water/LiBr and $NH_3$/water, have many practical disadvantages, for example, the high vapor pressure of water as an absorbent that requires a costly rectifier unit, the viscosity and corrosiveness of LiBr, the limited miscibility between LiBr and water, or the toxicity and flammability of $NH_3$. For these reasons, there is a need for new refrigerant/absorbent pairs. The thermophysical properties of solutions containing fluorinated or partly fluorinated alcohols have received significant attention in view of practical applications as refrigerants[8−10] in heat machines with organic absorbents as water or polyglycol ethers. Such studies continue actively, especially among academic institutions.[11−14] In addition, other novel compounds such as ionic liquids (ILs) are being investigated as absorbents.[15] Ionic liquids are salts composed of large organic ions characterized by molecular structures that are asymmetric and flexible with a delocalization of the electrostatic charges. Because of their negligible vapor pressure, stability as a liquid in a wide temperature range, their good miscibility with refrigerants, and their nonflammability, they can be suitable candidates as absorbents.[2]

Kim et al.[15] have shown through the measurement of selected properties—heat capacities and vapor pressure—that mixtures of 2,2,2-trifluoroethanol (TFE) + 1-butyl-3-methylimidazolium bromide ($[C_1C_4im][Br]$) or $[C_1C_4im][BF_4]$ could be suitable candidates for working fluids in absorption pumps. Following this study, TFE was selected in the present work, as a refrigerant, and $[C_1C_4im][BF_4]$ and $[C_1C_2im][BF_4]$ were selected as absorbents. These classical ILs were also chosen because of their low viscosities (75.4 mPa·s for $[C_1C_4im][BF_4]$[16] and 30.1 mPa·s for $[C_1C_2im][BF_4]$[17] at 303 K) and full miscibility with TFE. The knowledge of the thermophysical properties of the refrigerant/absorbent couple is necessary to choose the best system and optimize the performance of the process. The objective of the present work is to determine calorimetric and volumetric properties of two pairs of TFE/IL that could potentially be used in absorption pumps.

We have measured densities of the mixtures TFE + IL over the whole composition range from (283.15 to 333.15) K at atmospheric pressure, and to have insight into the mixture at the molecular level, excess molar volumes were calculated from the density data. Then enthalpies of mixing for the same systems at (298.15 and 323.15) K were experimentally determined. This study constitutes a first step in the estimation of the potential of these couples to replace classical refrigerant/absorbent pairs. In a second step, properties such as viscosity, surface tension, or heat capacity, among others, would be required.

## Materials and Methods

***Materials.*** The chemicals used were supplied by Sigma-Aldrich. TFE has a purity > 99.9 %; $[C_1C_4im][BF_4]$ has a purity > 97.0 %; and $[C_1C_2im][BF_4]$ has a purity > 97.0 %. When received, all the compounds were transferred in a dry chamber to bottles equipped with septa in argon atmosphere for storage. Before use, the mass fraction of water in the ionic liquid samples was determined by coulometric Karl Fisher titration (Mettler Toledo DL 31) and was found to be $100 \cdot 10^{-6}$ and $200 \cdot 10^{-6}$ for $[C_1C_4im][BF_4]$ and $[C_1C_2im][BF_4]$, respectively.

***Volumetric Study.*** The molar volumes of the pure components and of the mixtures were calculated from density measurements performed using two U-shape vibrating-tube densimeters operating in a static mode and at atmospheric pressure, one located in Clermont-Ferrand, France, and the other in Vigo, Spain. In both cases, a sample of given composition was prepared, and its density was measured at all the considered temperatures.

The mixtures of $[C_1C_2im][BF_4]$ + TFE were studied in Clermont-Ferrand, France. Samples of binary mixtures were prepared in a series of glass vials stirred by a small glass sphere. Different quantities of IL were added in different vials that were filled with TFE avoiding any head space that would lead to a differential evaporation. The composition of the mixture was determined gravimetrically (± 0.0001 g). The error on the mole fraction, calculated by error propagation, is estimated to be $\pm 3 \cdot 10^{-5}$. Details of the experimental setup (Anton Paar DMA 512 P vibrating tube densimeter) and procedures can be found in Almantariotis et al.[18] The temperature was maintained to within ± 0.01 K by means of a circulating bath equipped with a PID temperature controller (Julabo model F25-HE). It was measured using a 100Ω Platinum resistance thermometer (precision of ± 0.02 K and accuracy of ± 0.04 K). Its calibration was performed by verifying a water triple point (triple point cell by Hart Scientific) and by comparison against a 100 Ω platinum resistance Hart Scientific model 1502A.

The measured period of vibration ($\tau$) of a U tube is related to the density ($\rho$) according to $\rho = A\tau^2 + B$, where $A$ and $B$ are parameters that are a function of temperature and pressure determined by calibration between temperatures of (293 and 343) K and at atmospheric pressure, using as calibration fluids *n*-heptane, bromobenzene, and 2,4-dichlorotoluene following the recommendations of Schilling et al.[19] for the calibration of vibrating U-tube densimeters for dense fluids. Taking into account the uncertainties in the temperature and period, the overall experimental uncertainty in the reported density values has been calculated by the law of propagation of uncertainty, resulting in a value of $\pm 4 \cdot 10^{-4}$ g·cm$^{-3}$.

The densities of the mixtures $[C_1C_4im][BF_4]$ + TFE were measured at Vigo University. For the preparation of the mixtures, the IL and TFE were introduced in septum sealed vials of 20 mL that were initially filled with argon. The binary mixtures were prepared by mass using a precision digital AND balance with an uncertainty of $\pm 5 \cdot 10^{-5}$ g. The vials were not totally filled leading to the presence of a vapor phase (typically 4 mL) containing TFE. The error on the mole fraction composition of the mixtures induced by the uncertainty of the balance ($\pm 9 \cdot 10^{-6}$) is small compared to the error due to this differential evaporation ($\pm 3 \cdot 10^{-5}$). The global uncertainty on the mole fraction composition is estimated as $\pm 3 \cdot 10^{-5}$. The samples were introduced in the densimeter cell under vacuum conditions. A scheme and details of the experimental setup (Anton Paar DMA 512 P/60 vibrating-tube densimeter) and procedures can be found in Piñeiro et al.[20] The calibration of the apparatus was performed, according to the procedure based on the method of Lagourette et al.,[21] by measuring the temperature dependence of the period, when the cell is under vacuum, as well as the period at all considered $T$, $P$ conditions for a chosen reference fluid, such as water, for which reliable and accurate densities are given at all $T$, $P$ conditions.[22] The water used in the calibration was purified using a Milli-Q system and degassed using a Branson 2210 ultrasonic bath. The temperature regulation is achieved through a jacket filled with water that surrounds the experimental cell, whose temperature is controlled by a Prolabo Thermostat. The temperature is measured by a CKT100 platinum thermometer, placed close to the experimental cell and previously calibrated, with an uncertainty estimated to be less than ± 0.05 K. Taking into account the uncertainties in the temperature and period, the accuracy of the water density, and the applied vacuum, the overall experimental uncertainty in the reported density values has been calculated by the law of propagation of uncertainty, resulting in a value of $\pm\, 4 \cdot 10^{-4}\ \mathrm{g \cdot cm^{-3}}$.

From the density of the mixtures as a function of composition and that of the pure components, it is possible to calculate the excess molar volume, $V_\mathrm{m}^\mathrm{E}$, of the mixtures by[23]

$$V_\mathrm{m}^\mathrm{E} = V_\mathrm{m}^\mathrm{mix} - \sum_i x_i \frac{M_i}{\rho_i} \tag{1}$$

where $V_\mathrm{m}^\mathrm{mix}$ is the molar volume of the mixture and $x_i$ is the mole fraction of component $i$ with molar mass $M_i$ and density $\rho_i$. The uncertainty of excess molar volumes, evaluated by propagation of the errors, is estimated to be less than $\pm\, 0.06\ \mathrm{cm^3 \cdot mol^{-1}}$.

***Calorimetric Study.*** Mixing enthalpies were determined by directly measuring the energy generated during the mixing using a high-precision differential scanning microcalorimeter from Setaram (micro DSC III). This flow calorimeter is based on the Calvet principle. The calorimetric signal is a differential heat flow rate measured by two thermopiles around two vessels: a measurement cell in which the two components are mixed and a reference cell containing the static pure ionic liquid. A scheme of the experimental setup is presented in Figure 2. The vessels are in a metallic block immersed in a liquid thermostat (undecane) placed in an inert atmosphere of dry nitrogen. The temperature inside the calorimeter block is controlled via Peltier effects thermoelements and measured near the vessels with an uncertainty of ± 0.001 K. Two variable-rate syringe pumps (KdScientific) were used to provide a constant flow rate of each fluid (typically between (0.2 and 7) $\mathrm{mL \cdot min^{-1}}$) with an uncertainty of ± 0.5 %. The two fluids are first introduced in a temperature prestabilizator whose temperature is controlled to within ± 0.1 K. Two stainless steel (Hastelloy C276) circulation mixing cells (850 $\mu$L) were used that were specially designed to allow an efficient mixing of viscous fluids. Each liquid is introduced in the upper part of the cell in one branch of a double helix ensuring a progressive contact between the two components. The energetic effect is measured in the lower part of the cell which corresponds to the mixing point. For each composition, several flow rates were tested to check the correct mixing of the fluids (reproducibility of the mixing enthalpy).

The calorimeter was first calibrated at each temperature with a cell provided by the manufacturer applying a Joule effect and using different values of electrical power. This calibration allows the conversion of the signal from applied tension to restituted power. The signal uncertainty is of ± 0.1 mW. The mixing system was then tested with the measurement at (298 and 323) K of the mixing enthalpy of the system water + ethanol already studied in the literature.[24] From this, a corrective factor (1.01) was applied to our signal. The uncertainty on the mixing enthalpy is finally estimated to be less than 1 %.

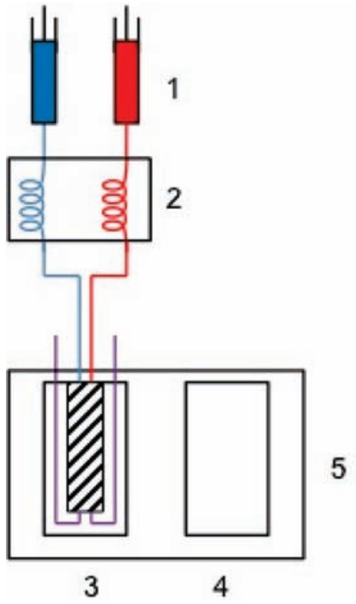

**Figure 2.** Schematic diagram of the mixing calorimeter: 1, syringe pumps; 2, preheater; 3, mixing cell; 4, reference cell; 5, DSC calorimeter.

**Table 1. Densities, $\rho$, and Excess Molar Volumes, $V_\mathrm{m}^\mathrm{E}$, for the Binary Systems $[\mathrm{C_1C_4im}][\mathrm{BF_4}]$ + TFE as a Function of the Composition Expressed in Ionic Liquid Mole Fraction, $x_\mathrm{IL}$, from (298.15 to 333.15) K**

| $x_\mathrm{IL}$ | $\rho$ / $\mathrm{g \cdot cm^{-3}}$ | $V_\mathrm{m}^\mathrm{E}$ / $\mathrm{cm^3 \cdot mol^{-1}}$ | $\rho$ / $\mathrm{g \cdot cm^{-3}}$ | $V_\mathrm{m}^\mathrm{E}$ / $\mathrm{cm^3 \cdot mol^{-1}}$ | $\rho$ / $\mathrm{g \cdot cm^{-3}}$ | $V_\mathrm{m}^\mathrm{E}$ / $\mathrm{cm^3 \cdot mol^{-1}}$ |
|---|---|---|---|---|---|---|
| | $T$ = 283.15 K | | $T$ = 293.15 K | | $T$ = 303.15 K | |
| 0.0000 | 1.4082 | 0.00 | 1.3911 | 0.00 | 1.3738 | 0.00 |
| 0.1032 | 1.3608 | 0.13 | 1.3469 | 0.09 | 1.3329 | 0.04 |
| 0.2129 | 1.3222 | 0.38 | 1.3101 | 0.33 | 1.2981 | 0.27 |
| 0.2990 | 1.2998 | 0.45 | 1.2888 | 0.39 | 1.2779 | 0.34 |
| 0.4022 | 1.2791 | 0.43 | 1.2690 | 0.39 | 1.2591 | 0.32 |
| 0.5028 | 1.2629 | 0.39 | 1.2534 | 0.35 | 1.2443 | 0.29 |
| 0.5808 | 1.2523 | 0.34 | 1.2433 | 0.31 | 1.2346 | 0.25 |
| 0.6912 | 1.2396 | 0.26 | 1.2312 | 0.21 | 1.2231 | 0.16 |
| 0.8062 | 1.2285 | 0.16 | 1.2205 | 0.13 | 1.2128 | 0.10 |
| 0.8945 | 1.2212 | 0.07 | 1.2133 | 0.08 | 1.2058 | 0.07 |
| 1.0000 | 1.2133 | 0.00 | 1.2059 | 0.00 | 1.1986 | 0.00 |
| | $T$ = 313.15 K | | $T$ = 323.15 K | | $T$ = 333.15 K | |
| 0.0000 | 1.3561 | 0.00 | 1.3380 | 0.00 | 1.3191 | 0.00 |
| 0.1032 | 1.3190 | −0.03 | 1.3049 | −0.12 | 1.2906 | −0.24 |
| 0.2129 | 1.2861 | 0.19 | 1.2743 | 0.07 | 1.2624 | −0.07 |
| 0.2990 | 1.2670 | 0.25 | 1.2564 | 0.13 | 1.2458 | −0.02 |
| 0.4022 | 1.2494 | 0.22 | 1.2397 | 0.12 | 1.2300 | −0.02 |
| 0.5028 | 1.2352 | 0.20 | 1.2264 | 0.09 | 1.2174 | −0.03 |
| 0.5808 | 1.2260 | 0.17 | 1.2175 | 0.08 | 1.2090 | −0.03 |
| 0.6912 | 1.2150 | 0.09 | 1.2070 | 0.03 | 1.1991 | −0.07 |
| 0.8062 | 1.2051 | 0.05 | 1.1976 | 0.00 | 1.1901 | −0.06 |
| 0.8945 | 1.1983 | 0.05 | 1.1909 | 0.03 | 1.1836 | 0.02 |
| 1.0000 | 1.1914 | 0.00 | 1.1844 | 0.00 | 1.1774 | 0.00 |

## Results and Discussion

Table 1 and 2 summarize the results for the density as a function of composition from 283.15 to 333 K with a step of 10 K, for the pure components and for the mixtures TFE + IL. The experimental densities were fitted as a function of temperature using the following polynomial equation

$$\rho(T)/\mathrm{g\cdot cm^{-3}} = \rho_0 + \rho_1 T + \rho_2 T^2 \qquad (2)$$

The parameters $\rho_0$, $\rho_1$, and $\rho_2$ of eq 2 are presented in Table 3 as well as the standard error of estimate, SEE, of the fits. SEE is defined as

$$\mathrm{SEE} = \sqrt{\sum_{i=1}^{n} \frac{(\rho_i^{\mathrm{exptl}} - \rho_i^{\mathrm{calcd}})^2}{n - k - 1}} \qquad (3)$$

where $\rho^{\mathrm{exptl}}$ and $\rho^{\mathrm{calcd}}$ are the experimental and the calculated (using eq 2) densities, respectively; $n$ is the number of experimental data points; and $k$ is the number of parameters in eq 2.

The two considered ionic liquids have densities between 1.2133 g·cm$^{-3}$ and 1.1774 g·cm$^{-3}$ for [$C_1C_4$im][$BF_4$] and between 1.2843 g·cm$^{-3}$ and 1.2546 g·cm$^{-3}$ for [$C_1C_2$im][$BF_4$] in the temperature ranges studied: (283 to 333) K and (293 to 333) K for [$C_1C_4$im][$BF_4$] and [$C_1C_2$im][$BF_4$], respectively. The density of pure [$C_1C_4$im][$BF_4$] was extensively studied in the literature (more than 800 experimental data points).[25] An analysis of all these data indicates relative deviations between our experimental densities and those of the literature of less than 1 % in the temperature range (283 to 333) K except in the case of the data of Harris et al.,[26] Suárez et al.,[27] Branco et al.,[28] and Huddleston et al.[29] Harris et al.[26] used two samples of [$C_1C_4$im][$BF_4$] with different content in water and halides. The scatter between the two samples is 1.1 %, and with our data the scatter is 1.0 % for one sample and 1.3 % for the other sample. These differences can be due not only to the different purity mixture but also to differences in the sample handling and in the experimental technique adopted. The errors in relating the temperature of the measurements to a common scale or the calibration should also be taken into account. The scatter of the density measurement data of Suárez et al.[27] and Branco et al.[28] can be due to the fact that these data were measured with a pyrex dilatometric tube under argon and with a micropycnometric technique, respectively. For Huddleston et al.[29] the deviations with our data can be due to water content (reported as 4530 ppm).

[$C_1C_2$im][$BF_4$] was far less studied (10 references were found in the literature), and the relative deviations between our experimental densities and those of the literature are typically less than 0.3 % as can be seen in Figure 3 in the temperature range (293 to 333) K. Only the data from Schreiner et al.[17] and Gardas et al.[30] present larger relative deviations (0.7 % and 1.5 %, respectively). These deviations can be due to the salt's purity, including water and halide content, differences in sample handling and the experimental technique adopted, errors in relating the temperature of the measurements to a common scale, or errors in calibration. Gardas et al.[30] report deviations ranging from −2.7 % to −3.1 % with the data of Zhang et al.[31] and also show positive deviations (1.7 %) from the values of Noda et al.[32]

**Table 2. Densities, $\rho$, for the Binary Systems [$C_1C_2$im][$BF_4$] + TFE as a Function of the Composition Expressed in Ionic Liquid Mole Fraction, $x_{IL}$, at (293.15 to 333.15) K**

| $x_{IL}$ | $T$/K | $\rho$/g·cm$^{-3}$ | $T$/K | $\rho$/g·cm$^{-3}$ | $T$/K | $\rho$/g·cm$^{-3}$ |
|---|---|---|---|---|---|---|
| 0.0000 | 293.14 | 1.3897 | 303.19 | 1.3724 | 313.15 | 1.3548 |
| 0.0990 | 293.15 | 1.3733 | 303.17 | 1.3591 | 313.15 | 1.3447 |
| 0.3050 | 293.16 | 1.3406 | 303.18 | 1.3294 | 313.16 | 1.3184 |
| 0.5164 | 293.17 | 1.3184 | 303.16 | 1.3089 | 313.19 | 1.2993 |
| 0.7550 | 293.14 | 1.2996 | 303.17 | 1.2913 | 313.16 | 1.2829 |
| 1.0000 | 293.10 | 1.2843 | 303.11 | 1.2765 | 313.15 | 1.2692 |

| $x_{IL}$ | $T$/K | $\rho$/g·cm$^{-3}$ | $T$/K | $\rho$/g·cm$^{-3}$ |
|---|---|---|---|---|
| 0.0000 | 323.15 | 1.3366 | 333.15 | 1.3178 |
| 0.0990 | 323.12 | 1.3305 | 333.20 | 1.3158 |
| 0.3050 | 323.15 | 1.3073 | 333.16 | 1.2964 |
| 0.5164 | 323.14 | 1.2902 | 333.15 | 1.2811 |
| 0.7550 | 323.20 | 1.2747 | 333.14 | 1.2668 |
| 1.0000 | 323.14 | 1.2618 | 333.23 | 1.2546 |

**Table 3. Parameters of the Polynomial Equation (Equation 2), Used to Fit the Experimental Densities as a Function of Temperature along with the Standard Error of Estimate (SEE)**

| $x_{IL}$ | $\rho_0$/g·cm$^{-3}$ | $\rho_1 \cdot 10^3$/g·cm$^{-3}$·K$^{-1}$ | $\rho_2 \cdot 10^7$/g·cm$^{-3}$·K$^{-2}$ | SEE $10^4$ |
|---|---|---|---|---|
| | | [$C_1C_4$im][$BF_4$] | | |
| 0.0000 | 1.7092 | −0.4551 | −21.475 | 1.136 |
| 0.1032 | 1.7207 | −1.1584 | −3.9749 | 0.412 |
| 0.2129 | 1.6952 | −1.4227 | 3.7108 | 0.359 |
| 0.2990 | 1.6538 | −1.395 | 5.1126 | 0.280 |
| 0.4022 | 1.6039 | −1.2886 | 4.993 | 0.781 |
| 0.5028 | 1.5791 | −1.2961 | 6.3229 | 0.895 |
| 0.5808 | 1.5518 | −1.2237 | 5.8539 | 0.724 |
| 0.6912 | 1.5154 | −1.1159 | 4.9997 | 0.380 |
| 0.8062 | 1.4953 | −1.0911 | 5.2535 | 0.469 |
| 0.8945 | 1.4881 | −1.1052 | 5.7429 | 0.810 |
| 1.0000 | 1.4694 | −1.0623 | 5.5708 | 0.390 |
| | | [$C_1C_2$im][$BF_4$] | | |
| 0.0000 | 1.6585 | −0.1442 | −26.364 | 0.622 |
| 0.0990 | 1.7492 | −1.1464 | −4.6343 | 0.719 |
| 0.3050 | 1.7018 | −1.3428 | 3.7796 | 0.626 |
| 0.5164 | 1.6692 | −1.4290 | 7.9226 | 0.781 |
| 0.7550 | 1.6062 | −1.2421 | 6.6927 | 0.632 |
| 1.0000 | 1.5804 | −1.2500 | 8.1728 | 1.048 |

In a refrigeration system, the hydrostatic principle is used to maintain the pressure difference between the components, and so an absorbent solution with higher density is preferred to minimize the overall height of the refrigerator. ILs have densities typically higher than those of classical solvents, but [$C_1C_4$im][$BF_4$] has a lower density than [$C_1C_2$im][$BF_4$], thus being preferred as an absorbant.

The density of pure TFE was measured both in the French and in the Spanish laboratories with values varying from 1.41

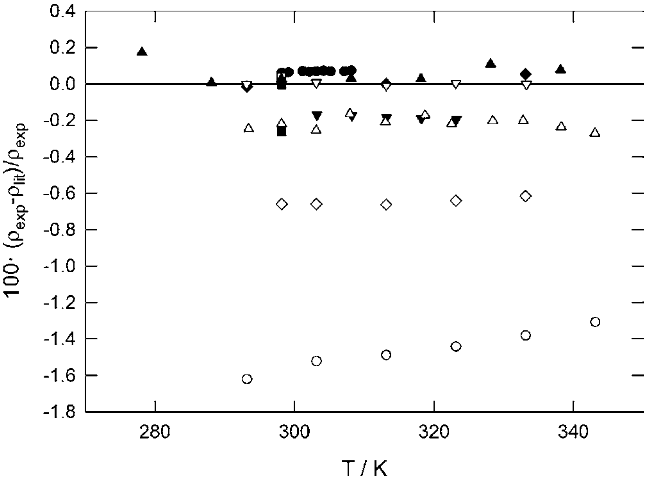

**Figure 3.** Relative deviations of the literature densities for [$C_1C_2$Im][$BF_4$] from our fitted data as a function of temperature. ▽, This work; ●, Navia et al.;[47] ○, Gardas et al.;[48] ▼, Wong et al.;[49] Δ, Klomfar et al.;[50] ■, Stoppa et al.;[51] □, Rilo et al.;[52] ◆, Taguchi et al.;[53] ◇, Schreiner et al.;[54] ▲, Stoppa et al.[55] Lines correspond to the fit of the data using the Redlich−Kister equation with two parameters.

**Table 4. Excess Molar Volumes, $V_m^E$, for the Binary Systems $[C_1C_2im][BF_4]$ + TFE as a Function of the Composition Expressed in Ionic Liquid Mole Fraction, $x_{IL}$, from (293.15 to 333.15) K**

| | *T*/K | | | | |
|---|---|---|---|---|---|
| $x_{IL}$ | 293.15 | 303.15 | 313.15 | 323.15 | 333.15 |
| | $V_m^E$/cm$^3$·mol$^{-1}$ | | | | |
| 0.0000 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 0.0990 | −0.22 | −0.29 | −0.37 | −0.49 | −0.63 |
| 0.3050 | −0.15 | −0.24 | −0.36 | −0.50 | −0.68 |
| 0.5164 | −0.18 | −0.26 | −0.36 | −0.48 | −0.63 |
| 0.7550 | −0.16 | −0.20 | −0.25 | −0.31 | −0.38 |
| 1.0000 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

g·cm$^{-3}$ at 283 K to 1.32 g·cm$^{-3}$ at 333 K. Deviations between the two sets of data of less than 0.1 % confirm the accuracy of the experimental apparatus and the validity of the calibration procedure and experimental method adopted. In the case of TFE, the relative deviations with the literature are less than 0.05 %[8,33−36] except for the data of Gente et al.[8] that show deviations of up to 1 % in the temperature range (283 to 333) K.

The excess molar volumes were calculated from the fitting of the experimental densities and are presented as a function of temperature and composition in Tables 1 and 4 for $[C_1C_4im][BF_4]$ and $[C_1C_2im][BF_4]$, respectively. The excess molar volumes were correlated, at each temperature, as a function of composition by a Redlich−Kister-type equation

$$V_m^E/\text{cm}^3\cdot\text{mol}^{-1} = x_{IL}x_{TFE}[A + B(x_{IL} - x_{TFE})] \qquad (4)$$

where $x_{IL}$ and $x_{TFE}$ are the mole fractions of IL and TFE, respectively. The parameters *A* and *B* are presented in Table 5 together with the standard error of estimate of the fitting.

As typically observed for mixtures composed of an IL and a molecular component, the excess molar volumes are small (less than 1 cm$^3$·mol$^{-1}$) compared to the molar volumes of the pure components. The excess molar volume for both mixtures studied here decreases almost linearly when the temperature increases as shown in Figure 4 for compositions of 0.5 in mole fraction. Strangely enough, positive excess molar volumes are found in the case of $[C_1C_4im][BF_4]$ + TFE in the lower temperature end (from (283.15 to 323.15) K) that become slightly negative at 333.15 K. In the case of $[C_1C_2im][BF_4]$ + TFE, excess molar volumes are negative for all the considered temperatures over the whole composition.

As observed in Figure 5, for the values at 333 K, a larger alkyl side chain in the cation of the ionic liquid causes an increase of the excess molar volume for the mixtures $[C_1C_nim][BF_4]$ + TFE. Garcia-Miaja et al.[37] have reported the same behavior as they observed an increase in the excess molar volumes of mixtures of ethanol with ionic liquids (based in imidazolium cations associated with different anions) when the number of carbon atoms of the alkyl side chains in the cation of the salt increases. Deng et al.[38] have made a systematic study of the excess molar volumes of mixtures of methanol + $[C_1C_nim][Ntf_2]$ ($n$ = 2 to 10) and have also observed a linear increase of $V_m^E$ (that becomes less negative) with *n*. The excess molar volume also increases when the size of the alkyl chain in the alcohol increases. In Figure 6 are represented the excess molar volumes of mixtures of $[C_1C_4im][BF_4]$ + *n*-alcohol ($n$ = 1 or 2), $V_m^E$ being smaller in the case of methanol. It seems as though the effect of the increasing alkyl chain is always the

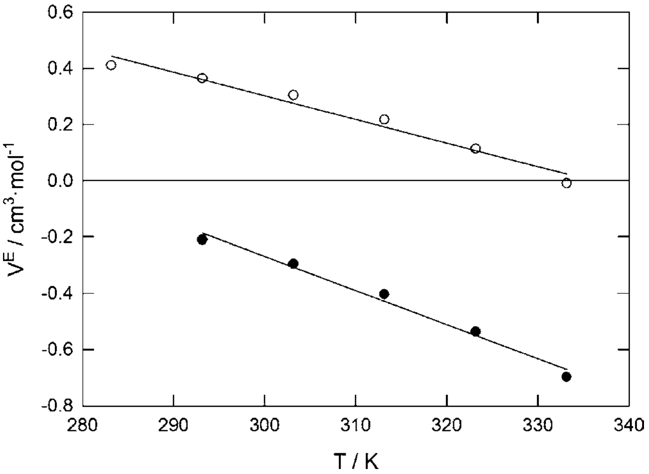

**Figure 4.** Excess molar volumes as a function of temperature when $x_{IL}$ = 0.5 for the mixtures: ●, $[C_1C_2Im][BF_4]$ + TFE; ○, $[C_1C_4Im][BF_4]$ + TFE.

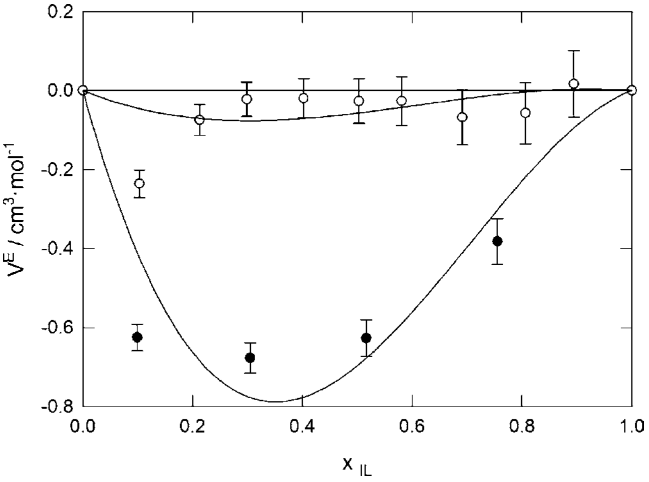

**Figure 5.** Excess molar volumes of the mixtures ionic liquid + TFE as a function of the ionic liquid mole fraction at 333 K: ●, $[C_1C_2Im][BF_4]$; ○, $[C_1C_4Im][BF_4]$.

**Table 5. Parameters *A* and *B* of the Redlich−Kister-Type Fittings, Equation 4, for the Correlation of the Experimental Excess Molar Volumes from Tables 1 and 4 as a Function of the Composition from (283.15 to 333.15) K along with the Standard Error of Estimate (SEE)**

| | $[C_1C_4im][BF_4]$ | | | | | |
|---|---|---|---|---|---|---|
| | *T* = 283.15 K | *T* = 293.15 K | *T* = 303.15 K | *T* = 313.15 K | *T* = 323.15 K | *T* = 333.15 K |
| *A*/cm$^3$·mol$^{-1}$ | 1.60 | 1.40 | 1.14 | 0.77 | 0.32 | −0.23 |
| *B*/cm$^3$·mol$^{-1}$ | −0.93 | −0.79 | −0.68 | −0.46 | −0.14 | 0.34 |
| SEE | 0.03 | 0.04 | 0.04 | 0.05 | 0.06 | 0.07 |

| | $[C_1C_2im][BF_4]$ | | | | |
|---|---|---|---|---|---|
| | *T* = 293.15 K | *T* = 303.15 K | *T* = 313.15 K | *T* = 323.15 K | *T* = 333.15 K |
| *A*/cm$^3$·mol$^{-1}$ | −0.84 | −1.18 | −1.61 | −2.15 | −2.79 |
| *B*/cm$^3$·mol$^{-1}$ | 0.38 | 0.68 | 1.08 | 1.61 | 2.26 |
| SEE | 0.07 | 0.08 | 0.09 | 0.11 | 0.13 |

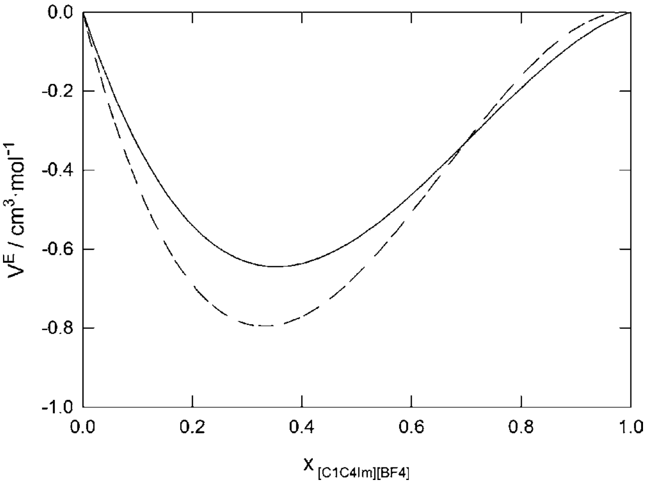

**Figure 6.** Excess molar volumes of the mixtures alcohol + $[C_1C_4Im][BF_4]$ at 303.15 K calculated from data published in the literature: dashed line, $[C_1C_4Im][BF_4]$ + $CH_3OH$;[56] full line, $[C_1C_4Im][BF_4]$ + $C_2H_5OH$.[57]

same on the excess molar volume of mixtures of alcohols and ionic liquids—$V_m^E$ increases with the presence of larger alkyl chains independently of whether they are placed in the cation or in the anion of the ionic liquid, or in the alcohol.

Comparison of Figures 5 and 6 permits an insight on the effect of the fluorination of the alcohol on the volumetric properties of the mixtures. Fluorination of the alcohol seems to contribute to an increase of the excess molar volume as can be observed by comparing the excess molar volumes of the systems ionic liquid + TFE with those obtained for systems composed of an IL and a nonfluorinated alcohol. To the best of our knowledge, no excess molar volumes were measured for mixtures of an IL and a fluorinated alcohol. Nevertheless, different studies have been published on the solubility of fluorinated and partially fluorinated alcohols in ionic liquids.[39,40] The phase behavior of the mixtures of different ionic liquids with partially fluorinated alcohols seems to be determined by the nanosegregated nature of the liquid salts,[41] but it has been suggested[39] that a certain degree of association between the fluorinated molecules might exist mainly due to the low affinity between the fluorinated moieties and the alkyl chains in the ionic liquids. Such "self aggregation" of the fluorinated alcohols in solution is compatible with the behavior found herein for the excess molar volumes of the ionic liquid + TFE mixtures, namely, the large difference between the mixtures containing $[C_1C_2im][Ntf_2]$ and those containing $[C_1C_4im][Ntf_2]$.

Table 6 summarizes the results of the mixing enthalpies for both systems at different compositions at (298 and 323) K. This property was fitted as a function of the composition, at each temperature, using a Redlich−Kister-type equation

$$\Delta_{mix}H/\mathrm{J\cdot mol^{-1}} = x_{IL}x_{TFE}[A' + B'(x_{IL} - x_{TFE}) + C'(x_{IL} - x_{TFE})^2] \quad (5)$$

Coefficients $A'$, $B'$, and $C'$ are presented in Table 7 along with the standard error of estimate of the fit. Figure 7 presents the variation of the mixing enthalpies as a function of the composition for the two systems at (298 and 323) K.

For both systems, the process of mixing is endothermic (positive mixing enthalpies). The curves presented in Figure 7 are asymmetric with an extremum for an IL mole fraction of approximately 0.3. For both ILs, the maximum mixing enthalpy is the same at 323 K (750 J·mol$^{-1}$), while it slightly differs at 298 K: 1.3 kJ·mol$^{-1}$ and 1.2 kJ·mol$^{-1}$ for $[C_1C_4im][BF_4]$ and for $[C_1C_2im][BF_4]$, respectively. The mixing enthalpy decreases with temperature varying from 1.3 J·mol$^{-1}$ at 298 K to 0.7 J·mol$^{-1}$ at 323 K for $[C_1C_4im][BF_4]$ + TFE for an IL mole fraction of 0.3.

Calorimetric measurements are presented in the literature for mixtures composed of an ionic liquid (imidazolium bistrifluoromethylsulfonylimide[42] and pyridinium tetrafluoroborate[43−45]) and an alcohol: positive enthalpies of mixing are calculated with a maximum typically between (2 and 3) kJ·mol$^{-1}$, increasing with the alcohol size and located in the molecular component rich region (ionic liquid mole fraction between 0.4 and 0.5). Some of these results—for systems composed of methanol or ethanol and an ionic liquid sharing the same anion $BF_4$ but with different cation—are presented in Figure 8. To the best of our knowledge, no mixing enthalpies were measured for mixtures of an ionic liquid and a fluorinated alcohol. As can be observed in Figure 8, the mixing enthalpies of the system ionic liquid + TFE are the same order of magnitude as those measured for the systems ionic liquid + nonfluorinated alcohol, the values measured herein being slightly lower.

**Table 6. Mixing Enthalpies, $\Delta_{mix}H$, for the Binary Systems $[C_1C_2im][BF_4]$ + TFE and $[C_1C_4im][BF_4]$ + TFE as a Function of the Composition Expressed in Ionic Liquid Mole Fraction, $x_{IL}$, at 298.15 K and 323.15 K**

| $[C_1C_4im][BF_4]$ | | | |
|---|---|---|---|
| $T$ = 298.15 K | | $T$ = 323.15 K | |
| $x_{IL}$ | $\Delta_{mix}H$/J·mol$^{-1}$ | $x_{IL}$ | $\Delta_{mix}H$/J·mol$^{-1}$ |
| 0.0878 | 726.97 | 0.0459 | 181.14 |
| 0.1614 | 1168.86 | 0.1137 | 474.82 |
| 0.2042 | 1276.85 | 0.2042 | 703.39 |
| 0.2779 | 1328.43 | 0.2779 | 747.69 |
| 0.3392 | 1264.11 | 0.3461 | 724.10 |
| 0.3908 | 1210.34 | 0.4350 | 642.56 |
| 0.4350 | 1143.79 | 0.5359 | 534.13 |
| 0.5065 | 996.29 | 0.6062 | 450.79 |
| 0.6581 | 676.25 | 0.6978 | 330.70 |
| 0.6919 | 605.85 | 0.8220 | 181.20 |
| 0.7549 | 496.45 | 0.8850 | 119.60 |
| 0.8089 | 380.35 | | |
| 0.9059 | 168.75 | | |

| $[C_1C_2im][BF_4]$ | | | |
|---|---|---|---|
| $T$ = 298.15 K | | $T$ = 323.15 K | |
| $x_{IL}$ | $\Delta_{mix}H$/J·mol$^{-1}$ | $x_{IL}$ | $\Delta_{mix}H$/J·mol$^{-1}$ |
| 0.0555 | 388.80 | 0.0555 | 224.01 |
| 0.1114 | 628.33 | 0.1114 | 390.18 |
| 0.1904 | 1073.15 | 0.1904 | 720.71 |
| 0.3199 | 1204.74 | 0.2477 | 756.82 |
| 0.4137 | 1142.03 | 0.3199 | 775.78 |
| 0.4847 | 1046.36 | 0.4137 | 714.29 |
| 0.5852 | 870.11 | 0.4847 | 646.82 |
| 0.7016 | 648.11 | 0.5852 | 525.61 |
| 0.7900 | 467.12 | 0.7016 | 379.81 |
| 0.9039 | 211.90 | 0.7900 | 264.57 |
| | | 0.9216 | 97.34 |

**Table 7. Parameters $A'$, $B'$, and $C'$ of the Redlich−Kister-Type Fittings, Equation 5, Used to Fit the Experimental Mixing Enthalpies from Table 6 as a Function of the Composition at (298.15 and 323.15) K along with the Standard Error of Estimate (SEE)**

| | $T$ = 298.15 K | | $T$ = 323.15 K | |
|---|---|---|---|---|
| | $[C_1C_4im][BF_4]$ | $[C_1C_2im][BF_4]$ | $[C_1C_4im][BF_4]$ | $[C_1C_2im][BF_4]$ |
| $A'$/J·mol$^{-1}$ | 4051 | 4162 | 2351 | 2593 |
| $B'$/J·mol$^{-1}$ | −4389 | −3095 | −2418 | −2242 |
| $C'$/J·mol$^{-1}$ | 2943 | 1086 | 1054 | 702 |
| SEE | 25 | 38 | 22 | 39 |

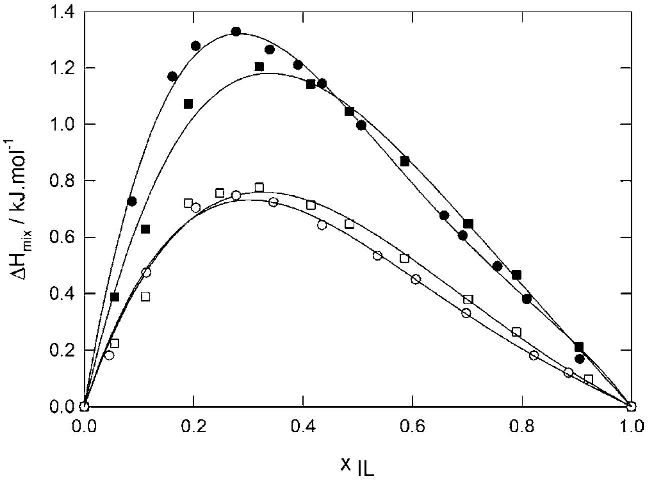

**Figure 7.** Mixing enthalpies as a function of the ionic liquid mole fraction: ●, $[C_1C_4im][BF_4]$ + TFE at 298.15 K; ○, $[C_1C_4im][BF_4]$ + TFE at 323.15 K; ■, $[C_1C_2im][BF_4]$ + TFE at 298.15 K; □, $[C_1C_2im][BF_4]$ + TFE at 323.15 K. Lines correspond to the fit of the data using three parameters of the Redlich−Kister-type equation.

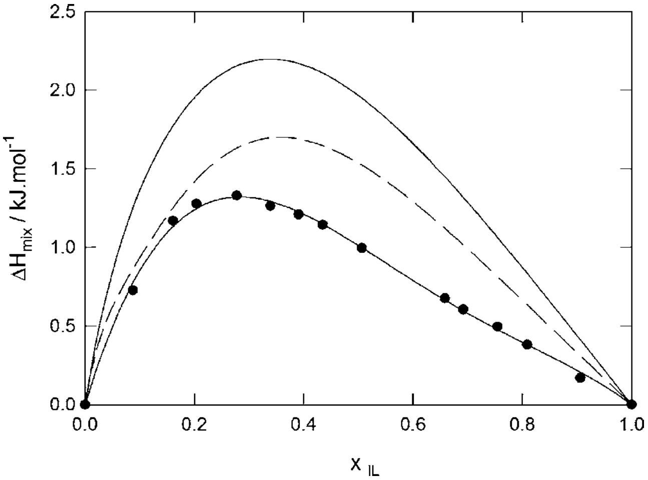

**Figure 8.** Mixing enthalpies of ionic liquid + alcohol binary mixtures as a function of the ionic liquid mole fraction. ●, $[C_1C_4im][BF_4]$ + TFE at 298.15 K (this work); full line, 1-butyl-3-methyl pyridinium tetrafluoroborate $[C_1C_4pyr][BF_4]$ + EtOH at 298 K;[43] dashed line, $[C_1C_4pyr][BF_4]$ + MeOH at 298 K. Lines correspond to the fit of the data using the Redlich−Kister equation with two parameters.

The enthalpy of mixing depends on the molecular interactions between the components of the mixture, its sign, and magnitude, roughly reflecting the balance between the interactions of pairs of like and unlike species in the mixture. In the present case, the enthalpy of mixing is positive which means that the interactions between the fluorinated alcohol and the ionic liquid are less favorable than the interactions of the pure substances. The differences between the two ionic liquids are not significantly different which means that in terms of the molecular interactions the two mixtures are not significantly different.

The mixing enthalpy of the system refrigerant/absorbent will also be necessary to calculate the energy output in the absorption step of the heat pump ($Q_4$). To increase the energetic efficiency of the process (increase of the COP), $Q_4$ should be as high as possible in absolute value especially in the case of heating systems. This quantity is negative and can be decomposed in two contributions

$$Q_4 = -\Delta_{vap}H(\mathrm{TFE}) + \Delta_{mix}H \qquad (6)$$

with $\Delta_{vap}H$(TFE) being the enthalpy of vaporization of the pure TFE. This term (43.97 kJ·mol$^{-1}$ at 298.15 K[46]) corresponds to the main contribution to $Q_4$, being preferable to have a negative or small positive enthalpy of mixing.

## Conclusions

Densities of ionic liquid + TFE mixtures were measured for two ionic liquids with different cations ($[C_1C_4im][BF_4]$ and $[C_1C_2im][BF_4]$) at several temperatures, and from these values, excess molar volumes were calculated. It was observed that the excess molar volumes decrease with increasing temperature and increase with the number of carbon atoms in the alkyl chains whether they are placed in the ionic liquid (in the cation or the anion) or in the alcohol. By comparing the values measured herein with others published in the literature for the same ionic liquids and for nonfluorinated alcohols, we could observe an increase in the excess molar volumes due to the presence of fluorine atoms in the alcohol.

Positive excess enthalpies were found for the same mixtures of ionic liquid + TFE, measured at different temperatures. These indicate an endothermic process of mixing, characteristic of less favorable molecular interactions between unlike pairs in the mixture.

The relations between the excess properties and the property changes of mixing permit a discussion of the molecular phenomena which give rise to the observed macroscopic property behavior. A rich fluid-phase behavior has been observed on the phase equilibrium of alkanes, fluorinated alkanes, and alkanols and partially fluorinated alkanols in various ionic liquids.[39,40] These macroscopic properties have been rationalized at a molecular level in terms of the different complex interactions between the fluorinated alcohols—composed of a polar headgroup, an alkylated "spacer", and a fluorinated moiety—and the ionic liquid—a nanosegregated fluid exhibiting nonpolar domains permeated by a polar network. Although these effects are less clear in the case of TFE, the smallest of the semifluorinated alcohols, the same arguments can be used to explain the peculiar behavior found for the excess molar volumes of the two mixtures studied as well as the enthalpy variations on mixing measured in both cases.

With respect to the industrial application (refrigeration by absorption), a system with an absorbent solution with higher density and with negative or small positive mixing enthalpy is preferred. Thus, in this case the system containing $[C_1C_2im][BF_4]$ is preferred to $[C_1C_4im][BF_4]$. Nevertheless, other properties should be taken into account, such as corrosion with respect to the material of the piping, pumps, and other components of the refrigeration system, not be toxic, to be thermally stable, to have low viscosity, etc.

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