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Influence of Fluorination on the Solubilities of Carbon Dioxide, Ethane and Nitrogen in 1-*n*-Fluoro-alkyl-3-methylimidazolium Bis(*n*-fluoroalkylsulfonyl)amide Ionic Liquids

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Abstract

The effect on gas solubilities of adding partially fluorinated alkyl side-chains either on imidazolium-based cations or in bis(perfluoroalkylsulfonyl)amide anions was studied. The aim was to gain knowledge of the mechanisms of dissolution of gases in fluorinated ionic liquids and, if possible, to improve physical absorption of carbon dioxide in ionic liquids. We have determined experimentally, in the temperature range of 298 K to 343 K and at pressures close to atmospheric, the solubility and thermodynamics of solvation of carbon dioxide, ethane and nitrogen in the ionic liquids 1-octyl-3-methylimidazolium bis[trifluoromethylsulfonyl]amide ([C₈mim][NTf₂]), 1-octyl-3-methylimidazolium bis[pentafluoroethylsulfonyl]amide ([C₈mim][BETI]), 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-3-methylimidazolium bis[trifluoromethylsulfonyl]amide ([C₈H₄F₁₃mim][NTf₂]) and 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-3-methylimidazolium bis[pentafluoroethylsulfonyl]amide ([C₈H₄F₁₃mim][BETI]). Ionic liquids with partial fluorination on the cation were found to exhibit higher carbon dioxide and nitrogen mole fraction solubilities but lower ethane solubilities, compared to their hydrogenated counterparts. Molecular simulation provided insights about the mechanisms of solvation of the different gases in the ionic liquids.

Introduction

Ionic liquids are capable of selectively dissolving carbon dioxide when this gas is mixed with nitrogen, oxygen or methane.¹ We have previously observed that the presence of fluorinated alkyl side-chains in the (imidazolium) cation² or in the anion³ of different ionic liquids enhances the physical absorption of carbon dioxide. Previous studies on the physicochemical properties of perfluorinated organic liquids^{4,5} have shown that gases like carbon dioxide are strongly absorbed because the structure of the liquids is dominated by the presence of a backbone of strong C-F bonds that cause a loss in molecular flexibility and a decrease in polarity.⁶ In ionic liquids, the capacity and selectivity toward gas absorption can be tuned either by choosing appropriately the cation-anion pairs⁷ or by modifying the ions, including chemical structures that render the liquid specific for a given task.^{8,9}

Recent works have reported the physicochemical properties^{10,11,12} and possible applications¹³ including the gas absorption^{14,15,16,17,18}, of a large variety of ionic liquids containing fluorinated or partially fluorinated chains. The liquids studied therein are varied, with cations and anions presenting a diversity of molecular structures, the only common point being the presence of fluorinated moieties. It is difficult, in their case, to establish rational relations between the structure of the liquids and their capacity of selectively absorbing gases. To our knowledge, no study of the dependence of the solvation properties on the molecular interactions and structures was yet reported.

The purpose of this work is to study the capacity and clarify the molecular mechanisms underlying the solubility of carbon dioxide, ethane and nitrogen in ionic liquids containing fluorinated moieties. As a progression of our previous work^{2,3}, we report here carbon dioxide, ethane and nitrogen solubilities in a family of imidazolium-based ionic liquids containing fluoroalkyl chains on the cation, combined with fluorinated anions: 1-octyl-3-methylimidazolium bis[trifluoromethylsulfonyl]amide, [C₈mim][NTf₂]; 1-octyl-3-methylimidazolium bis[pentafluoroethylsulfonyl]amide, [C₈mim][BETI]; and 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-3-methylimidazolium bis[trifluoromethylsulfonyl]amide; [C₈H₄F₁₃mim][NTf₂]. From the low pressure solubility values, it is possible to estimate the ideal selectivities of these ionic liquids for CO₂/N₂ and CO₂/C₂H₆ separation.

Experimental Section

Materials. The gases used for the solubility measurements were carbon dioxide from AGA/Linde Gaz, with mole fraction purity of 0.99995; ethane from AGA/Linde Gaz, mole fraction purity of 0.995; and nitrogen from SAGA, mole fraction purity 0.9998. All gases were used without further purification.

The sample of 1-octyl-3-methylimidazolium bis[trifluoromethylsulfonyl]amide ($[\text{C}_8\text{mim}][\text{NTf}_2]$) (Figure 1) was synthesised using previously reported procedures¹⁹ and presents a mole fraction purity of 0.99. A volumetric Karl-Fisher titration using a Mettler Toledo DL32 titrator was used for determining the water content of an ionic liquid sample kept under a primary vacuum during at least 24 hours. The value found was 110 ppm of water. The halide content of the ionic liquid was determined using suppressed ion chromatography (IC) and it was found to be less than 5 ppm of chloride.

Room-temperature ionic liquid 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-3-methylimidazolium bis[trifluoromethylsulfonyl]amide ($[\text{C}_8\text{H}_4\text{F}_{13}\text{mim}][\text{NTf}_2]$) (Figure 1) was synthesized as described in our previous work² with a minimum mole fraction purity of 0.99, as found by ¹H and ¹⁹F NMR spectrometry. A coulometric Karl Fisher titration (model Mettler Toledo DL32, standard method KF) was used to determine the water content of the sample, which was less than 55 ppm. The iodide ion content was found to be less than 400 ppm as determined by ionic chromatography.

Room-temperature ionic liquid 1-octyl-3-methylimidazolium bis[pentafluoroethylsulfonyl]amide ($[\text{C}_8\text{mim}][\text{BETI}]$) (Figure 1) and was synthesized by metathesis in water of 1-octyl-3-methylimidazolium chloride ($[\text{C}_8\text{mim}][\text{Cl}]$) and lithium bis[pentafluoroethylsulfonyl]amide salt (LiBETI). $[\text{C}_8\text{mim}][\text{Cl}]$ was synthesized with minimum mole fraction of 0.98, after purification, and lithium bis[trifluoromethanesulfonyl]amide salt was purchased from Iolitec without any additional treatment, puriss. > 0.97. All solvents used are of analytical grade.

In the synthesis procedure, (14.30 g or 61.96 mmol) of $[\text{C}_8\text{mim}][\text{Cl}]$ were dissolved in approximately 200 mL of distilled water and the solution was kept at ambient temperature before a dropwise addition of lithium bis[pentafluoroethylsulfonyl]amide salt (25 g or 64.58 mmol), in approximately 5 mol % excess. After one hour at ambient temperature, the product was extracted with dichloromethane (140 mL). The water was decanted and the organic phase was then washed with water (5 x 40 mL) until no chloride was detected using a silver nitrate test. The organic solvent was removed by rotary evaporation for obtaining 1-octyl-3-

methylimidazolium bis[pentafluoroethylsulfonyl]amide ionic liquid ([C₈mim][BETI]). Finally, the ionic liquid was dried under vacuum of 0.3 mm Hg at 40°C overnight to give a yellow liquid (60.68 mmol, global yield of 98%).

Ionic liquid 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-3-methylimidazolium bis[pentafluoroethylsulfonyl]amide ([C₈H₄F₁₃mim][BETI]) (Figure 1) was synthesized by metathesis in water of 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-3-methylimidazolium iodide ([C₈H₄F₁₃mim][I]), prepared as described in our previous work,⁹ and lithium bis[pentafluoroethylsulfonyl]amide salt (LiBETI). Lithium bis[trifluoroethanesulfonyl]amide salt was purchased from Iolitec without any additional treatment, puriss. > 0.97. All solvents used are of analytical grade.

We dissolve (19.80 g or 35.60 mmol) of [C₈H₄F₁₃mim][I] in approximately 300 mL of distilled water and the solution was heated up to 60°C before a dropwise addition of lithium bis[pentafluoroethylsulfonyl]amide (14.50 g or 37.46 mmol), in approximately 5 mol % excess. After one hour at 60°C, the liquid mixture was cooled down to room temperature and the product was extracted with dichloromethane (700 mL). The water was decanted and the organic phase was then washed with water (4 x 70 mL) until no iodide was detected using a silver nitrate test. The organic solvent was removed by rotary evaporation for obtaining 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-3-methylimidazolium bis[pentafluoroethylsulfonyl]amide ionic liquid ([C₈H₄F₁₃mim][BETI]). Finally, the ionic liquid was dried under vacuum of 0.3 mmHg at 40°C overnight to give a brown solid at ambient temperature (28.24 mmol, global yield of 79%).

The minimum mole fraction purity for both ionic liquids, [C₈mim][BETI] and [C₈H₄F₁₃mim][BETI] was estimated to be 0.96, by ¹H and ¹⁹F NMR spectrometry and elemental analysis. The water content of the sample, is less than 10 ppm for [C₈mim][BETI] and 65 ppm for [C₈H₄F₁₃mim][BETI], respectively. The total halogen content was found to be 0.65 wt.% 0.66 wt.%, respectively.

Thermal characterization. We use Differential Scanning Calorimetry (DSC, Modulated 2920, TA Instruments) to study the melting points and decomposition temperatures for all ionic liquids. For [C₈mim][BETI] a melting temperature was not detected (below 223.15 K), applying a scan rate of 5K min⁻¹. Additionally, the sample possesses extremely high thermal stability as its thermal decomposition was detected at T_{onset} of 636.15 K. The scan rate during thermal decomposition was 2 K min⁻¹. [C₈H₄F₁₃mim][BETI] shows a melting temperature at 311.15 K and a cold

crystallization temperature at 263.15 K. The glass transition temperature was found to be approximately 223 K. The ionic liquid decomposes in many by-products at the onset temperature of 626.15 K; more than four peaks were observed in thermograph during decomposition of the sample. For all phase transition and decomposition temperatures a scan rate of 2 K min⁻¹ was applied. All ionic liquids were kept before each measurement under primary vacuum at 303 K for at least 24 h at 303 K.

Density measurements. Densities of [C₈mim][BETI] and [C₈H₄F₁₃mim][BETI] at temperatures from 293 K to 343 K and pressures up to 25 MPa were measured using a U-shape vibrating-tube densimeter (Anton Paar, model DMA 512) operating in a static mode, following the procedure described previously.^{17,19} The uncertainty of the density measurement is estimated as 0.1 kg·m⁻³. Due to the high viscosity of both ionic liquids, [C₈mim][BETI] and [C₈H₄F₁₃mim][BETI], (at ambient conditions $\eta > 100$ mPa·s), systematic deviations on the density measurements depending on the fluid viscosity occur. Using the available correlations from Anton Paar,²⁰ corrections have been made considering the viscosity of the ionic liquid samples at atmospheric pressure.

Viscosity measurements. The dynamic viscosities of [C₈mim][BETI] and [C₈H₄F₁₃mim][BETI], previously dried under vacuum, were measured using an Anton Paar AMVn rolling ball viscometer, as a function of the temperature from 293.15 K to 363.15 K (controlled to within 0.01 K and measured with an accuracy better than 0.05 K) at atmospheric pressure. Before starting the measurements, both, 1.8 and 3.0 mm diameter capillaries tubes, used for viscosity measurements, were calibrated as a function of temperature and angle of measurement using as reference a standard viscosity fluid from Cannon (N35). The overall uncertainty on the viscosity measurements is estimated as $\pm 1.5\%$.

Gas-solubility Measurements. Gas solubility was measured in an apparatus based on an isochoric saturation technique described previously.^{20,21} An amount of solvent previously degassed is put in contact with the gas at a constant temperature, inside an accurately known volume. At thermodynamic equilibrium, the solubility of the gas can be calculated from the pressure above the liquid solution. A gravimetrically known quantity of ionic liquid is introduced in the equilibration cell, V_{liq} , while the amount of solute that is present in the liquid phase, n_2^{liq} (subscript 2 stands for solute and subscript 1 for solvent), is calculated by two pVT measurements, one at the

beginning when the gas is introduced in a calibrated bulb with volume V_{GB} and another after thermodynamic equilibrium is attained:

$$n_2^{\text{liq}} = \frac{p_{\text{ini}} V_{GB}}{Z_2(p_{\text{ini}}, T_{\text{ini}}) RT_{\text{ini}}} - \frac{p_{\text{eq}} (V_{\text{Tot}} - V_{\text{liq}})}{Z_2(p_{\text{eq}}, T_{\text{eq}}) RT_{\text{eq}}} \quad (1)$$

where p_{ini} and T_{ini} are the pressure and temperature in the first pVT determination and p_{eq} and T_{eq} are the pressure and temperature at thermodynamic equilibrium. V_{Tot} is the total volume of the equilibration cell, and Z_2 is the compressibility factor for the pure gas. The solubility can then be expressed in mole fraction:

$$x_2 = \frac{n_2^{\text{liq}}}{n_1^{\text{liq}} + n_2^{\text{liq}}} \quad (2)$$

where n_2^{liq} is the amount of solute dissolved in the ionic liquid and $n_1^{\text{liq}} = n_1^{\text{tot}}$ is the total amount of ionic liquid. The Henry's law constant can be calculated using the following equation:

$$K_H = \lim_{x_2 \rightarrow 0} \frac{f_2(p, T, x_2)}{x_2} \approx \frac{\varphi_2(p, T) p}{x_2} \quad (3)$$

where f_2 is the fugacity of the solute and φ_2 is its fugacity coefficient. The fugacity coefficient, which is very close to unity in the present cases, was included in the calculation of the Henry's law constants for all the gases.

The total uncertainty associated with Henry's law constants calculated from the present experimental solubilities is estimated to be better than $\pm 5\%$.

Molecular Simulation. We have used an all-atom force field, bases in the OPLS-AA framework, specifically developed to represent the ionic liquids.^{22,23,24} This model contains all the parameters needed to simulate the ions $\text{C}_8\text{C}_{1\text{im}}^+$, $\text{C}_8\text{H}_4\text{F}_{13}\text{C}_{1\text{im}}^+$, NTf_2^- , and BETI^- . Molecular dynamics simulations were run in periodic cubic boxes containing 256 ion pairs of ionic liquids $[\text{C}_8\text{C}_{1\text{im}}][\text{BETI}]$ or $[\text{C}_8\text{H}_4\text{F}_{13}\text{C}_{1\text{im}}][\text{BETI}]$, using

the DL_POLY code.²⁵ Equilibration runs started from low-density initial configurations (in cubic lattices) and consisted of 500 ps trajectories, with a 2 fs timestep, at constant NpT at 423 K and 1 bar (Nosé-Hoover thermostat and isotropic barostat). At the final densities of the ionic liquid state, the length of the side of the simulation boxes is approximately 56 Å and 59 Å for the ionic liquids with the fully hydrogenated and partially fluorinated cation, respectively. Trajectories of 1 ns were generated starting from the equilibrated configurations. Additionally, simulation boxes containing 246 ion pairs of the liquids [C₈C₁im][BETI], [C₈H₄F₁₃C₁im][BETI], [C₈C₁im][NTf₂] and [C₈H₄F₁₃C₁im][NTf₂] and 4 CO₂ or C₂H₆ molecules were equilibrated and then used to calculate solute-solvent radial distribution functions between the gas and the solvent ions, also from 1 ns trajectories. The potential model of Harris and Yung²⁶ was used for CO₂ whereas the parameters for C₂H₆ were those of the OPLS_AA model.^{27,28}

The chemical potential of CO₂ in the two ionic liquids [C₈C₁im][BETI] and [C₈H₄F₁₃C₁im][BETI], was calculated in a two-step procedure, as in our previous work.² First, for CO₂, a compact version of the molecule was created by shortening the C-O bond length by 1 Å. The Lennard-Jones diameters σ_o and σ_c were also reduced by 1 Å. The chemical potential of this compact version of CO₂ can be calculated efficiently by Widom test-particle insertion.²⁹ Simulation runs of 600 ps at 373 K were performed, and 3000 configurations were stored. In each of these stored snapshots, 10⁵ insertions were attempted. Following this initial calculation by test-particle insertion, a stepwise finite difference thermodynamic integration procedure³⁰ was used to calculate the free-energy difference between the compact of the carbon dioxide molecule and the full-size model, on eight intermediate steps.

Results and Discussion

We present in Table 1 of the Supporting Information the experimental densities of the ionic liquids, [C₈mim][BETI] and [C₈H₄F₁₃mim][BETI], at temperatures from 293 K to 343 K and at pressures up to 25 MPa. The values of density at atmospheric pressure were adjusted to linear functions of temperature as follows:

$$\rho_{[\text{C}_8\text{mim}][\text{BETI}]} / \text{kg} \cdot \text{m}^{-3} = 1680.8 - 957.57 \times 10^{-3} (T/\text{K}) \quad (4)$$

$$\rho_{[\text{C}_8\text{H}_4\text{F}_{13}\text{mim}][\text{BETI}]} / \text{kg} \cdot \text{m}^{-3} = 2133.8 - 1300.11 \times 10^{-3} (T/\text{K}) \quad (5)$$

The standard deviation of the fits is always better than 0.05%.

The values determined for [C₈mim][BETI] could be compared with those of the literature. The value of 1397.2 kg·m⁻³ at 296.15 K obtained in this work is 4.3% higher than the value reported by Qu *et al.*,²¹ however, these authors do not provide information about the measurement technique employed. To our knowledge, published values for the density of ionic liquid [C₈H₄F₁₃mim][BETI], originally synthesized in the present work, do not exist in literature data.

The effect on densities of adding longer fluoroalkyl chains on the anion NTf₂⁻ can be clarified by the comparison of the density values of [C₈mim][BETI] and those published by Almantariotis *et al.*² for the ionic liquid [C₈mim][NTf₂]. As it can be seen in Figure 1 of the Supporting Information, an increase of about 5% on the density is observed when changing NTf₂⁻ anion with BETI⁻ anion. A similar trend on the density was obtained in the case of the partial fluorinated cation ionic liquids ([C₈H₄F₁₃mim])³¹ where an increase on density of about 1.7% was found.

We determined the dynamic viscosities, as a function of temperature from 293 K to 363 K, of dried samples of the ionic liquids [C₈mim][BETI] and [C₈H₄F₁₃mim][BETI]. Experimental data are listed in Table 2 of the Supporting Information together with viscosities of ionic liquids [C₈mim][NTf₂] and [C₈H₄F₁₃mim][NTf₂] measured previously in our laboratory² to compare the effects of changing the anion from NTf₂⁻ to BETI⁻. The measured viscosities are correlated as a function of temperature using a Vogel–Fulcher–Tamman (VFT) equation, as previously described⁸ (with standard deviations of 0.4% and 0.5%, respectively):

$$\eta_{[\text{C}_8\text{mim}][\text{BETI}]} / \text{mPa} \cdot \text{s} = (2.81 \times 10^{-3}) \times (T / \text{K})^{\frac{1}{2}} \exp \left[\frac{1113}{(T / \text{K}) - 162} \right] \quad (6)$$

$$\eta_{[\text{C}_8\text{H}_4\text{F}_{13}\text{mim}][\text{BETI}]} / \text{mPa} \cdot \text{s} = (2.06 \times 10^{-3}) \times (T / \text{K})^{\frac{1}{2}} \exp \left[\frac{1337}{(T / \text{K}) - 170} \right] \quad (7)$$

The present data are higher than those reported by Qu *et al.*²¹ At 313.15 K, the deviation between both series of data is 16.5%, which decreases to 12.5% at 373.15 K, a deviation probably caused, among others, by the amount of water present in the sample used by the authors.

Viscosity is affected by the addition of fluoroalkyl chains on the cation or on the anion. The trend obtained in this work is η [C₈H₄F₁₃mim][BETI] > η [C₈mim][BETI] > η [C₈H₄F₁₃mim][NTf₂] > η [C₈mim][NTf₂], as can be observed in Table 2 of the Supporting Information. Viscosities of all ionic liquids are represented graphically in Figure 2 of the Supporting Information where it is clear that the fluorination of the cation alters the viscosity more significantly than the fluorination on the anion of the ionic liquids studied.

Multiple experimental data points for solubilities of carbon dioxide, ethane and nitrogen in [C₈mim][NTf₂], [C₈H₄F₁₃mim][NTf₂], [C₈mim][BETI] and [C₈H₄F₁₃mim][BETI] were obtained in the temperature interval between 298 K and 343 K, in steps of approximately 10 K. The mole fraction solubilities together with the calculated Henry's law constants are reported in Table 1. In all cases, mole fractions are corrected for a partial pressure of solute of 0.1 MPa. The relative atomic masses used are the ones recommended by IUPAC³² and the second virial coefficients for carbon dioxide, ethane and nitrogen, were taken from the compilation by Dymond and Smith.³³

The Henry's law constants, calculated from the experimental data, were adjusted to power series in 1/T in order to obtain representative values of the solubility

$$\ln[K_H(T)/10^5 \text{ Pa}] = \sum_{i=0}^n A_i (T/K)^{-i} \quad (8)$$

The coefficients A_i as well as the standard deviations of the fits, considered as a measure of the precision of the data, are collected in Table 2. The Henry's law constants, calculated from the CO₂, C₂H₆ and N₂ solubility measurements described in this work, are considered to be precise to within less than 1%, 2.1% and 4.4%, respectively.

We present in Figure 2 the experimental solubility data, expressed in gas mole fraction, as a function of temperature of the three gases in the four ionic liquids. To facilitate the comparison, the data, expressed in mole fraction and in molality, for the three gases and the four ionic liquids at 323 K is depicted in Figure 3. Carbon dioxide is the most soluble gas in all of the ionic liquids, followed by ethane. Both gases present a mole fraction solubility of the order of about 10⁻², one order of magnitude higher than the mole fraction solubility of nitrogen. In our previous work,^{2,3} we compared the mole fraction gas solubility of CO₂ in [C₈H₄F₁₃mim][NTf₂] and in

[C₈mim][NTf₂], observing that the fluorination of the cation increases the solubility of CO₂ about 20% in the temperature range studied. Since systematic increase of fluorination is a proven method^{2,6} for absorbing higher quantities of CO₂ (in mole) it is of great interest to study the effect of increasing fluoroalkyl groups on the anion NTf₂⁻. This study can be done by comparing the solubility of carbon dioxide in ionic liquids with the same cation associated with the NTf₂⁻ or with the BETI⁻ anion. From the different in the solubility of CO₂ in the ionic liquids [C₈mim][NTf₂] and [C₈mim][BETI] reported herein, we have observed a lower increase on CO₂ solubility (approximately 11%) upon the fluorination of the anion than that previously reported linked with the partial fluorination of the cation. At 303 K, the Henry's law constants are equal to 33.3 ± 0.1 bar and 30.2 ± 0.1 bar for CO₂ in [C₈mim][NTf₂] and [C₈mim][BETI], respectively. The ionic liquid [C₈H₄F₁₃mim][BETI] (with higher degree of fluorination both in the cation and in the anion, does not exhibit higher CO₂ uptake, compared to [C₈H₄F₁₃mim][NTf₂], since at 303 K, values of $K_H = 28.3 \pm 0.2$ bar and 27.9 ± 0.3 bar were calculated, respectively.

Experimental C₂H₆ solubility data, expressed as a mole fraction for a partial pressure of the solute of 0.1 MPa, as a function of temperature, are also depicted in Figure 2 and compared at 323 K with the other two gases in Figure 3. The gas mole fraction solubility is higher in cation-hydrogenated imidazolium ionic liquids when compared with their partially fluorinated counterparts. More precisely, a high solubility of C₂H₆ was found in [C₈mim][BETI] with a value of $K_H = 48.4 \pm 0.6$ bar calculated at 303 K. That last value is significantly lower compared to the values found for C₂H₆ solubility in [C₈mim][NTf₂] ($K_H = 59.9 \pm 0.4$ bar) and [C₈H₄F₁₃mim][NTf₂] ($K_H = 79.8 \pm 0.5$ bar), almost 23% and 33%, respectively. The low C₂H₆ solubility in [C₈H₄F₁₃mim][NTf₂] could be explained by analogy with the behaviour of C₂H₆ in liquid perfluorinated hydrocarbons³⁴. However, C₂H₆ uptake was found to be similar in both ionic liquids, [C₈mim][NTf₂] and [C₈H₄F₁₃mim][BETI], especially at the higher temperatures studied.

In Figure 2, N₂ solubility data, expressed as a mole fraction for a partial pressure of the solute of 0.1 MPa, in ionic liquids [C₈mim][NTf₂], [C₈H₄F₁₃mim][NTf₂] and [C₈mim][BETI] as a function of temperature are also plotted. [C₈H₄F₁₃mim][NTf₂] exhibits the highest gas absorption, with a value of $K_H = 525 \pm 8$ bar at 303 K, followed by [C₈mim][BETI]. The gas mole fraction in all ionic liquids has values between 2×10^{-3} and 6×10^{-4} , in the temperature range covered. The solubility of N₂ increases for the

ionic liquids with fluorinated cations, like in the case of CO₂. This behaviour can be explained by the rigidity of the fluorinated chains that leads to a larger free volume in the ionic liquids having fluorinated cations.^{6,35,36}

In Figure 3, the solubility of the three gases in the four ionic liquids is also plotted in molality. Although the observations described above do not significantly change, it is worthwhile to notice that the differences between the different ionic liquids as absorbents of carbon dioxide are much smaller. We have decided to analyze the differences in terms of mole fraction as it is a more appropriate unit when addressing the physical-chemical study of the gas dissolution processes³⁷.

By the analysis of the thermodynamic properties of solvation listed in Table 3, we can observe that the comportment of CO₂ in the ionic liquids studied is explained by a more favorable entropy of solvation as the enthalpies of solvation calculated are similar for the four ionic liquids and even slightly less negative for [C₈H₄F₁₃mim][BETI], the ionic liquid in which CO₂ is the most soluble. The behavior of ethane is more complicated to explain as, even if the gas is less soluble than CO₂ in the liquids studied, the enthalpy of dissolution is more favorable for C₂H₆. In this case, the dissolution process is explained by a balance between enthalpic and entropic factors. In the case of N₂, a gas one order of magnitude less soluble in the ionic liquids, the enthalpy of dissolution is much less negative than for the other gaseous solutes.

In previous works, the solubility of CO₂ was studied in ionic liquids with fluoroalkyl groups^{14,38} but no attention has been given to the effect of fluorination on the solubility of other gases. Only Bara *et al.*³⁹ have discussed the effect of the partial fluorination of imidazolium cations on the gas separation using membrane-supported ionic liquids. Comparison between [C₈mim][NTf₂] and [C₈H₄F₁₃mim][NTf₂] reveals an improvement on ideal selectivity for CO₂ / CH₄ separation (9 and 13, respectively) and a decrease of the selectivity for CO₂ / N₂ separation (27 and 16, respectively). The calculated ideal gas selectivities are listed in Table 4. We find the same trends as Bara *et al.*³⁹ but unfortunately, pure gas solubilities of CO₂, CH₄ and N₂ are not communicated, so direct comparison with our experimental data was not possible.

In order to explain the molecular mechanisms of solvation of CO₂ in ionic liquids [C₈mim][BETI] and [C₈H₄F₁₃mim][BETI], we have performed some molecular dynamics simulations. The free energy of solvation of CO₂ in both ionic liquids was calculated at 373.15 K, yielding to values of $K_H = 80.3 \pm 0.8$ bar and $K_H = 58.3 \pm 0.6$ bar respectively. Then, from the values of Henry's constants mole fractions of CO₂ in ionic

liquids of $x_{\text{CO}_2} = (1.24 \pm 0.1) \times 10^{-2}$ and $x_{\text{CO}_2} = (1.72 \pm 0.2) \times 10^{-2}$ at partial pressure of the gas $p_{\text{CO}_2} = 0.1$ MPa were calculated, as seen in Figure 3. The comparison of simulation results with experiment serves to validate our calculation procedure and the force field developed during our work, especially the one for the originally synthesized $[\text{C}_8\text{H}_4\text{F}_{13}\text{mim}][\text{BETI}]$. The solubility of CO_2 in both ionic liquids was correctly predicted while molecular simulation predicts that the CO_2 solubility is more important in $[\text{C}_8\text{H}_4\text{F}_{13}\text{mim}][\text{BETI}]$. Quantitatively, perfect agreement with experiment was obtained in the case of the CO_2 solubility in $[\text{C}_8\text{mim}][\text{BETI}]$ validating the force field model to describe CO_2 – ionic liquid interactions. In the case of the CO_2 solubility in $[\text{C}_8\text{H}_4\text{F}_{13}\text{mim}][\text{BETI}]$, an overestimation of about 21% was observed.

The molecular structure of the solutions was studied by calculating the site–site solute–solvent radial distribution functions for CO_2 and C_2H_6 in all ionic liquids. As observed in Figure 5a, CO_2 is more probably solvated near the imidazolium ring of the cation when the longer alkyl side-chains are hydrogenated and is more probably dislocated towards the fluorinated chains when they exist in the cation (higher peaks in Figures 5b and 5c). In this last case, CO_2 is found at larger distances from the carbon backbone as the fluor atoms are larger than the hydrogen atoms in the alkyl side-chain of the cation.

Site–site solute–solvent radial distribution functions for C_2H_6 in all ionic liquids are plotted in Figure 6. Ethane is more probably solvated, as expected, near the alkyl side-chains of the cation (Figures 6b and 6c) with no particular affinity being found for each of the anions studied herein.

Conclusions

The present work shows that the ideal selectivity of carbon dioxide absorption in ionic liquids can be considerably increased by using as absorbents imidazolium-based ionic liquids with fluorinated moieties in the cation or in the anion.

We have observed that the mole fraction absorption of carbon dioxide increases with the increase of the fluorination of the ionic liquid, independently on whether it is placed on the cation or on the anion. The CO_2 mole fraction solubility increases by 10% at 303 K when changing from $[\text{C}_8\text{mim}][\text{NTf}_2]$ to $[\text{C}_8\text{mim}][\text{BETI}]$ (increase of the fluorination in the anion with hydrogenated chains in the cation) but only by less than 2% when changing from $[\text{C}_8\text{H}_4\text{F}_{13}\text{mim}][\text{NTf}_2]$ to $[\text{C}_8\text{H}_4\text{F}_{13}\text{mim}][\text{BETI}]$ (increase of the fluorination in the anion with

fluorinated chains in the cation). The fluorination in the imidazolium cation affects more significantly the CO₂ uptake (expressed in mole fraction of gas) in NTf₂⁻ based ionic liquids than in BETI⁻ based ionic liquids. We have observed an increase of the CO₂ mole fraction solubility of 20 % at 303 K when changing from [C₈mim][NTf₂] to [C₈H₄F₁₃mim][NTf₂] but only of 7% when changing from [C₈mim][BETI] to [C₈H₄F₁₃mim][BETI].

Ethane is much less soluble in the ionic liquids studied in this work. The fluorination of the ions constituting the ionic liquid have a larger relative effect on the gas uptake, the presence of fluorinated moieties, in the cation or in the anion, causing a decrease on the mole fraction solubility of the gas of 24 % when changing the NTf₂⁻ for the BETI⁻ anion (independently on the cation) or by 33 % when changing the C₈mim⁺ for the C₈H₄F₁₃mim⁺ cation (independently of the anion).

As a consequence of the behaviors described above, the ideal selectivity for the carbon dioxide/ethane absorption increases when the ionic liquids contains fluorinated chains in the cation and is practically constant (with only a slight decreases) when the fluorination in the anion increases.

The results obtained could be explained by complementing the experimental data on gas solubility with molecular simulation studies that provided accurate information about the molecular structure of the solutions. As observed before for other fluorinated ionic liquids, the higher solubility of carbon dioxide in fluorinated ionic liquids^{2,3} when compared with their hydrogenated counterparts corresponds, at the molecular level, to an increased affinity of this gas towards fluorinated alkyl chains.⁶ Carbon dioxide is, nevertheless, also solvated near the charged parts of the ionic liquid, as observed before.² In the case of ethane, the gas interacts preferentially with the non-polar domain of the ionic liquids, its solubility being lowered, as expected⁴⁰, in the fluorinated ionic liquids.

Supporting Information

Includes a table and a figure with the experimental densities of the ionic liquids [C₈mim][BETI] and [C₈H₄F₁₃mim][BETI] between 293 and 343 K up to 25 MPa; and a table and a figure with the experimental dynamic viscosities of [C₈H₄F₁₃mim][NTf₂], [C₈mim][NTf₂], [C₈mim][BETI] and [C₈H₄F₁₃mim][BETI], as a function of temperature at atmospheric pressure.

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Figure 1. a) Chemical structure of the ionic liquid 1-octyl-3-methylimidazolium bis[pentafluoroethylsulfonyl]amide ($[C_8mim][BETf]$); b) Chemical structure of the ionic liquid 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-3-methylimidazolium bis[pentafluoroethylsulfonyl]amide ($[C_8H_4F_{13}mim][BETf]$).

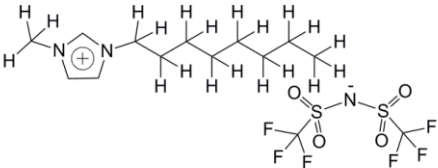
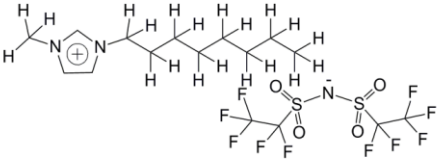
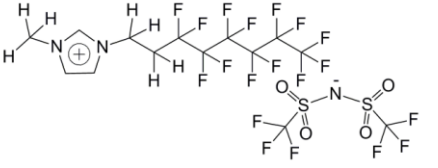
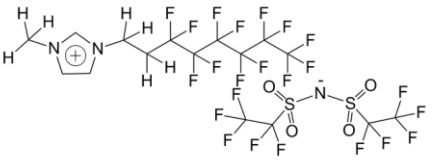
	1-octyl-3-methylimidazolium bis[trifluoromethylsulfonyl]amide	$[C_8mim][NTf_2]$
	1-octyl-3-methylimidazolium bis[pentafluoroethylsulfonyl]amide	$[C_8mim][BETf]$
	1-(3,3,4,4,5,5,6,6,7,7,8,8,8- tridecafluorooctyl)-3- methylimidazolium bis[trifluoromethylsulfonyl]amide	$[C_8H_4F_{13}mim][NTf_2]$
	1-(3,3,4,4,5,5,6,6,7,7,8,8,8- tridecafluorooctyl)-3- methylimidazolium bis[pentafluoroethylsulfonyl]amide	$[C_8H_4F_{13}mim][BETf]$

Figure 2. Gas solubilities in \blacklozenge [C₈H₄F₁₃mim][BETI]; \blacksquare [C₈H₄F₁₃mim][NTf₂]; \blacktriangle [C₈mim][BETI]; \bullet [C₈mim][NTf₂] as a function of temperature, expressed as mole fraction at a partial pressure of solute at 0.1MPa. Upper plot: Carbon dioxide; middle plot: ethane; lower plot: nitrogen. Open symbols stand for previous measurements.²

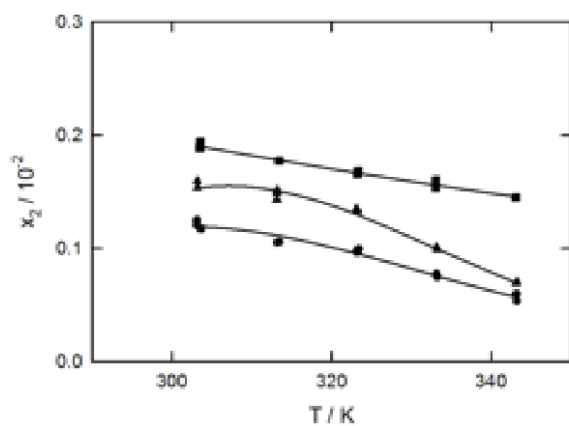
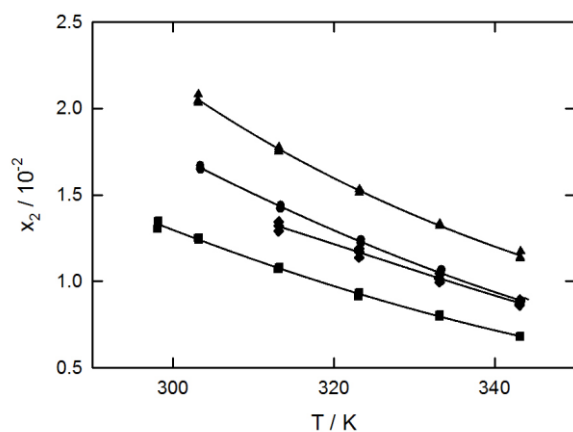
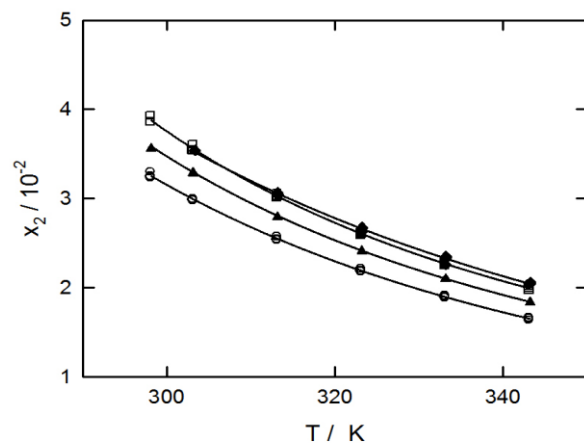


Figure 3. Comparison of the solubility of the three gases at 323 K in the four ionic liquids studied herein expressed in mole fraction of gas (upper plot) and in molality (lower plot) at 1 bar partial pressure of gas. The values for the solubility of CO₂ in [C₈mim][NTf₂] and in C₈H₄F₁₃mim][NTf₂] are taken from a previous work.²

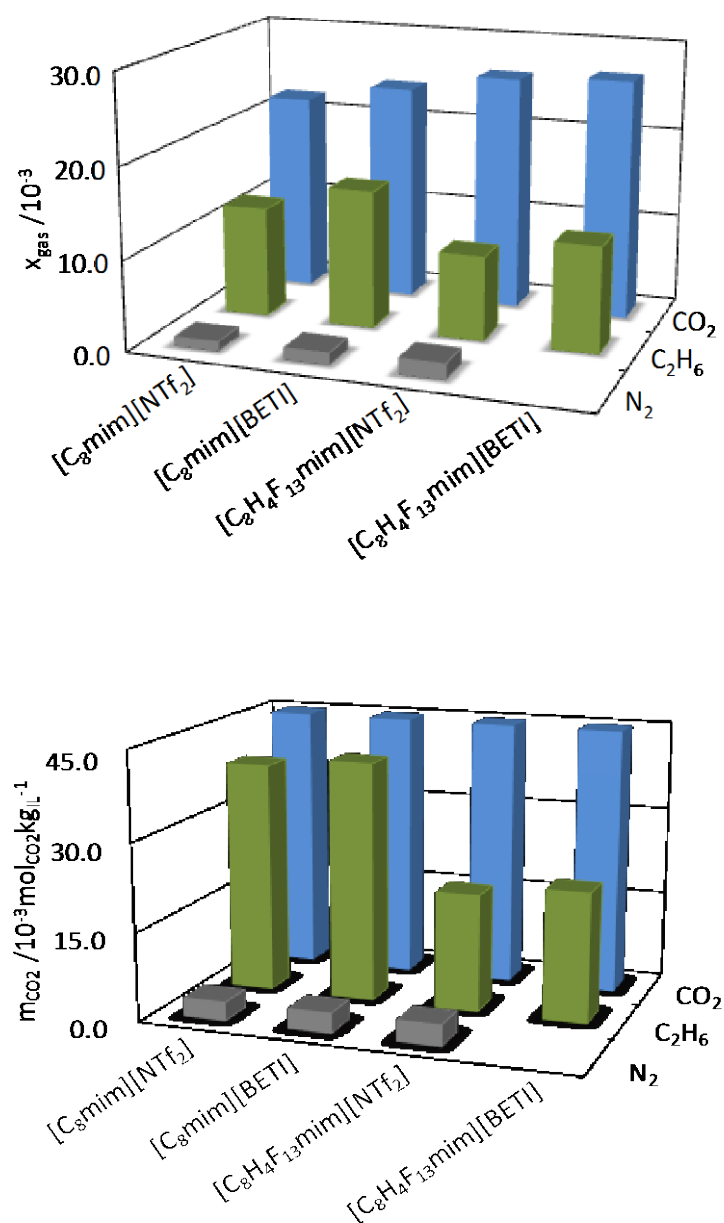


Figure 4. Carbon dioxide solubility in ionic liquids \blacktriangle $[\text{C}_8\text{mim}][\text{BETI}]$ and \blacklozenge $[\text{C}_8\text{H}_4\text{F}_{13}\text{mim}][\text{BETI}]$ as a function of temperature expressed as mole fraction of carbon dioxide at a partial pressure of 0.1 MPa (left hand-side plot) and as Henry's law constants (right hand-side plot). Full symbols are experimental results and open symbols are molecular simulation calculations at 373.15 K

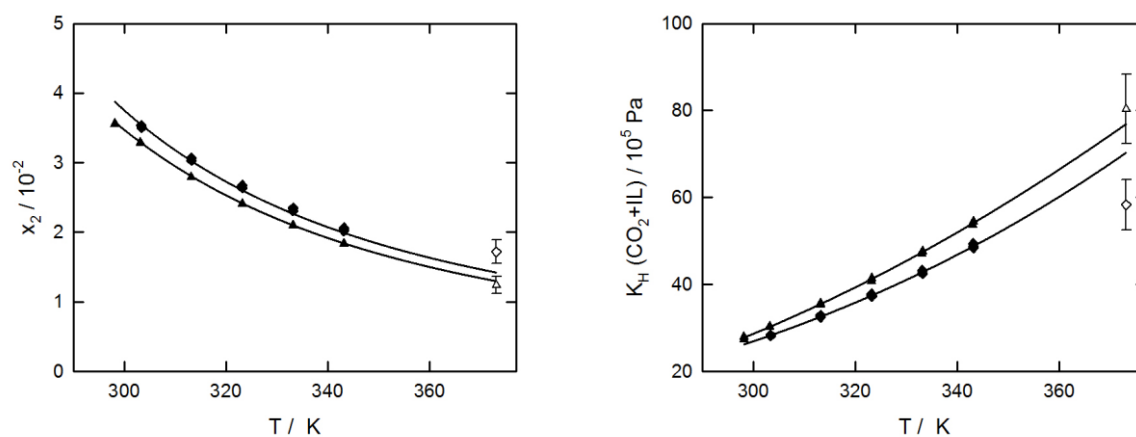


Figure 5. Solute-solvent site-site radial distribution functions of carbon dioxide in the ionic liquids $[\text{C}_8\text{mim}][\text{NTf}_2]$, $[\text{C}_8\text{H}_4\text{F}_{13}\text{mim}][\text{NTf}_2]$, $[\text{C}_8\text{mim}][\text{BETI}]$ and $[\text{C}_8\text{H}_4\text{F}_{13}\text{mim}][\text{BETI}]$.

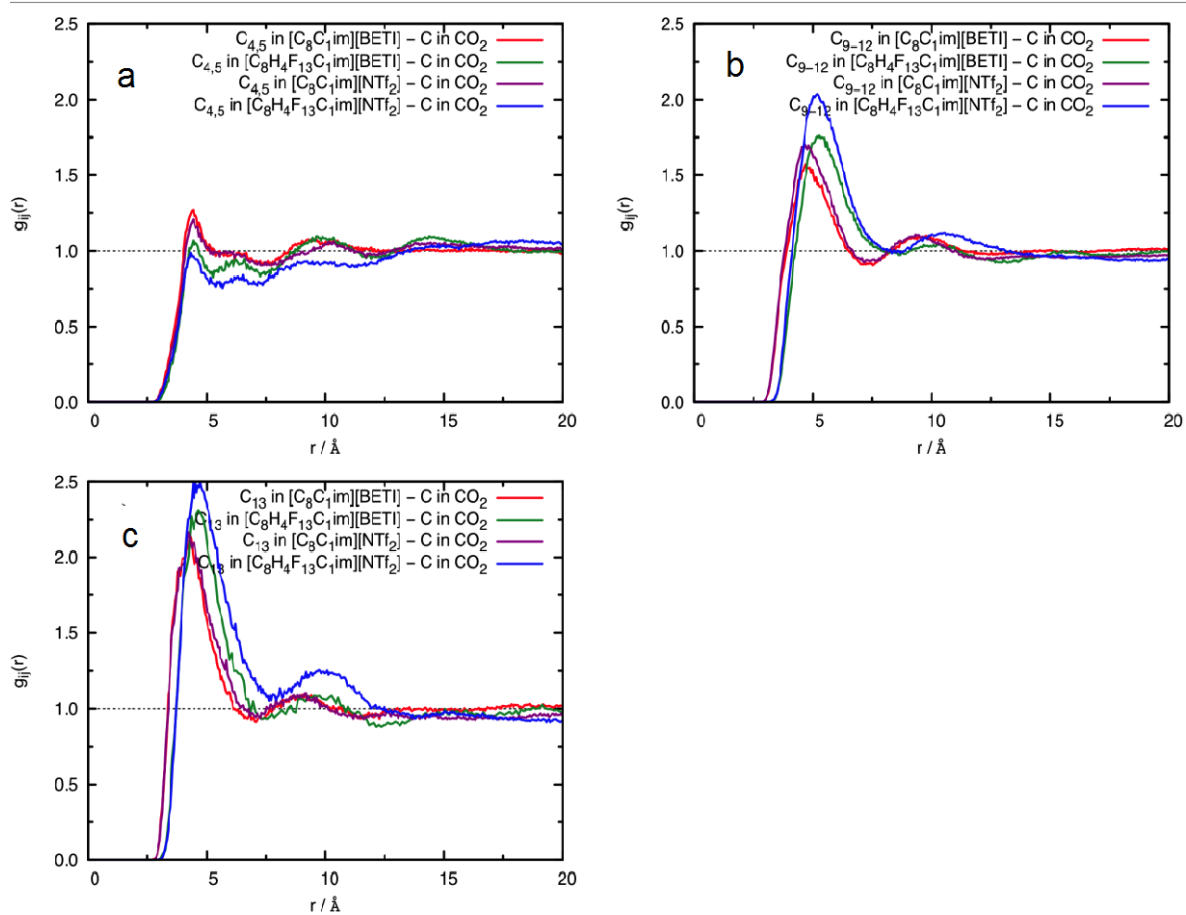


Figure 6. Solute-solvent site-site radial distribution functions of ethane in the ionic liquids $[\text{C}_8\text{mim}][\text{NTf}_2]$, $[\text{C}_8\text{H}_4\text{F}_{13}\text{mim}][\text{NTf}_2]$, $[\text{C}_8\text{mim}][\text{BETI}]$ and $[\text{C}_8\text{H}_4\text{F}_{13}\text{mim}][\text{BETI}]$.

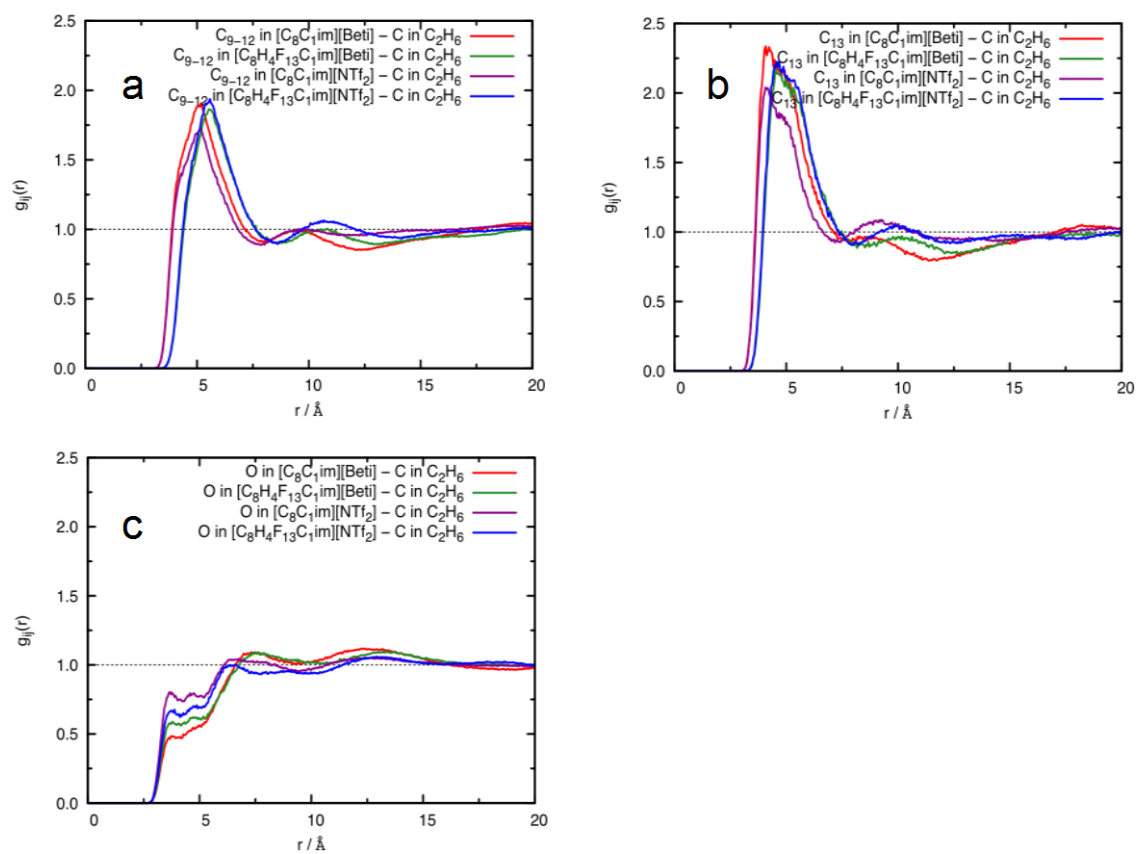


TABLE 1. Experimental values of carbon dioxide, ethane and nitrogen solubility in [C₈mim][NTf₂], [C₈H₄F₁₃mim][NTf₂], [C₈mim][BETI] and [C₈H₄F₁₃mim][BETI] expressed both as Henry's law constant, K_H , and as mole fraction, x_2 , corrected for a partial pressure of solute of 0.1 MPa. p is the experimental equilibrium pressure and the per cent deviation is relative to the correlations of the data reported in Table 2

T / K	$p / 10^2 \text{ Pa}$	$K_H / 10^5 \text{ Pa}$	$x_2 / 10^{-2}$	dev / %
[C ₈ mim][BETI] – CO ₂				
298.14	659.38	27.9	3.56	–0.7
298.14	696.27	28.0	3.56	–0.7
298.14	611.35	27.3	3.65	+1.8
303.14	673.65	30.3	3.29	–0.2
303.15	711.06	30.3	3.28	–0.4
303.16	625.57	30.1	3.30	+0.3
313.16	702.24	35.7	2.79	–0.6
313.16	740.27	35.7	2.79	–0.5
313.16	651.73	35.3	2.82	+0.5
323.20	729.85	41.4	2.41	–0.4
323.18	768.62	41.3	2.41	–0.3
323.15	676.99	40.8	2.44	+1.1
333.15	756.64	47.6	2.09	–0.3
333.19	796.40	47.5	2.10	–0.1
333.08	701.91	47.0	2.12	+0.8
343.17	783.18	54.4	1.83	–0.5
343.21	823.91	54.5	1.83	–0.6
343.06	726.34	53.6	1.86	+0.8
[C ₈ H ₄ F ₁₃ mim][BETI] – CO ₂				
303.37	645.10	28.1	3.54	+0.6
303.38	637.29	28.4	3.50	–0.4
313.17	630.40	32.5	3.06	+0.2

313.17	684.49	32.5	3.07	+0.3
313.20	682.48	32.9	3.03	-0.9
323.21	654.24	37.3	2.67	+0.5
323.22	710.13	37.3	2.67	+0.4
323.20	707.75	37.8	2.64	-0.9
333.19	677.78	42.6	2.34	+0.5
333.19	735.13	42.4	2.35	+0.9
333.11	732.53	43.2	2.31	-1.0
343.18	701.18	48.7	2.05	+0.2
343.20	760.14	48.4	2.06	+0.9
343.10	757.30	49.4	2.02	-1.3

[C₈mim][NTf₂] – C₂H₆

303.41	717.10	60.3	1.65	+0.6
303.44	717.33	60.3	1.65	+0.5
303.41	513.41	59.5	1.67	-0.8
303.40	766.76	59.4	1.67	-0.9
303.40	782.68	60.0	1.65	+0.1
313.40	744.59	69.9	1.42	+0.9
313.41	534.14	69.0	1.44	-0.5
313.37	795.22	69.9	1.42	+0.8
323.40	771.87	81.4	1.22	+0.7
323.41	554.74	80.1	1.24	-1.0
333.36	798.97	95.2	1.04	+0.4
333.40	575.23	93.3	1.07	-1.8
333.30	869.77	95.2	1.05	+0.4
343.33	826.11	113	0.88	+0.6

[C₈H₄F₁₃mim][NTf₂] – C₂H₆

298.14	631.11	74.2	1.34	+0.5
298.08	715.48	76.2	1.30	-2.1
298.14	634.05	73.6	1.35	+1.4
303.17	584.05	79.4	1.25	+0.8

303.19	642.66	80.1	1.24	-0.1
313.20	604.82	91.9	1.08	+0.5
313.10	665.23	92.9	1.07	-0.7
323.18	625.40	106	0.93	+0.8
323.08	688.08	109	0.91	-1.8
333.17	645.92	123	0.81	+1.3
333.15	710.45	125	0.80	+0.1
343.15	666.54	146	0.68	-0.3
343.19	733.06	146	0.68	-0.3

[C₈mim][BETI] – C₂H₆

303.16	729.24	47.7	2.08	+1.4
303.13	487.34	48.6	2.04	-0.3
303.17	557.63	48.8	2.03	-0.8
313.14	757.55	55.9	1.78	+0.6
313.18	505.59	56.4	1.76	-0.2
313.16	578.77	56.8	1.75	-1.0
323.16	785.44	64.9	1.53	+0.4
323.22	523.55	64.9	1.53	+0.5
323.16	599.66	65.7	1.51	-0.8
333.16	813.15	75.4	1.32	-0.2
333.18	541.27	74.6	1.33	+0.9
333.17	620.30	75.3	1.32	-0.1
343.16	840.82	88.0	1.13	-1.6
343.24	558.86	84.8	1.17	+2.2
343.16	641.00	87.3	1.14	-0.8

[C₈H₄F₁₃mim][BETI] – C₂H₆

313.15	626.55	75.3	1.32	+0.2
313.13	504.40	77.0	1.29	-2.1
313.15	577.13	73.9	1.35	+2.1
323.13	647.77	84.9	1.17	+0.3
323.13	521.59	87.4	1.14	-2.7

323.15	596.83	83.6	1.19	+1.9
333.11	669.26	97.7	1.02	+0.0
333.12	538.81	100	0.99	-2.3
333.16	616.55	94.9	1.05	+3.0
343.12	690.96	115	0.87	-0.7
343.11	556.09	116	0.86	-1.5
343.15	636.60	112	0.89	+2.1

[C₈mim][NTf₂] – N₂

303.13	595.64	828	0.12	+1.2
303.12	675.75	802	0.12	+4.4
303.63	683.52	854	0.12	+0.5
313.17	697.85	952	0.11	-5.7
313.49	705.49	946	0.11	-1.3
323.22	634.31	1019	0.10	+3.1
323.21	719.77	1042	0.10	+0.8
323.37	727.39	1006	0.10	+0.8
333.20	653.69	1340	0.07	-1.4
333.18	741.68	1297	0.08	+1.8
343.21	673.10	1878	0.05	-6.1
343.18	763.64	1685	0.06	+4.6

[C₈H₄F₁₃mim][NTf₂] – N₂

303.48	629.07	530	0.19	-0.9
303.50	700.68	529	0.19	-0.7
303.53	687.43	515	0.19	+2.0
313.40	649.29	565	0.18	-0.5
313.45	723.29	564	0.18	-0.4
323.23	669.32	606	0.17	-0.9
323.29	745.60	595	0.17	+0.9
333.06	689.32	652	0.15	-1.6
333.10	767.79	625	0.16	+2.7
343.09	709.67	689	0.15	-0.5

[C ₈ mim][BETI] – N ₂				
303.15	663.54	627	0.16	+3.4
303.15	679.26	651	0.15	-0.5
313.15	685.29	671	0.15	-1.9
313.15	658.21	660	0.15	-0.3
313.12	701.51	699	0.14	-5.9
323.16	707.14	747	0.13	+2.6
323.15	679.21	754	0.13	+1.7
323.15	723.91	743	0.13	+3.0
333.16	700.49	1014	0.10	-1.5
333.13	746.59	990	0.10	+0.7
343.17	721.70	1424	0.07	+0.1
343.12	769.31	1438	0.07	-1.0

TABLE 2. Parameters of equation (8) used to smooth the experimental results on K_H from Table 1 along with the standard deviation of the fit, s .

Ionic Liquid	A_0	A_1	A_2	s
[C₈mim][NTf₂]				
C ₂ H ₆	+ 18.02	– 7.165 × 10 ³	+ 8.921 × 10 ⁵	0.9
N ₂	+ 57.35	– 3.052 × 10 ⁴	+ 4.602 × 10 ⁶	4.4
[C₈H₄F₁₃mim][NTf₂]				
C ₂ H ₆	+ 16. 36	– 5.973 × 10 ³	+ 7.098 × 10 ⁵	0.9
N ₂	+ 10. 52	– 1.963 × 10 ³	+ 2.035 × 10 ⁵	1.6
[C₈mim][BETI]				
CO ₂	+ 8.17	– 1.359 × 10 ³	– 2.538 × 10 ⁴	0.8
C ₂ H ₆	+ 11.78	– 3.398 × 10 ³	+ 3.093 × 10 ⁵	1.0
N ₂	+ 78.76	– 4.439 × 10 ⁴	+ 6.816 × 10 ⁶	2.8
[C₈H₄F₁₃mim][BETI]				
CO ₂	+ 10.18	– 2.807 × 10 ³	+ 2.227 × 10 ⁵	0.8
C ₂ H ₆	+ 22. 07	– 1.003 × 10 ⁴	+ 1.400 × 10 ⁶	2.1

TABLE 3. Thermodynamic properties of solvation in the temperature range 303 K—343 K. In italics are included the values calculated from data reported in reference²

	$\Delta_{\text{soln}}H/\text{kJmol}^{-1}$	$-T\Delta_{\text{soln}}S/\text{kJmol}^{-1}$
<i>[C₈mim][NTf₂] + CO₂</i>	<i>- 12.9</i>	<i>23.1</i>
[C ₈ mim][NTf ₂] + C ₂ H ₆	- 13.7	25.5
[C ₈ mim][NTf ₂] + N ₂ *	- 9.3	27.0
<i>[C₈H₄F₁₃mim][NTf₂] + CO₂</i>	<i>- 12.5</i>	<i>22.3</i>
[C ₈ H ₄ F ₁₃ mim][NTf ₂] + C ₂ H ₆	- 13.1	25.6
[C ₈ H ₄ F ₁₃ mim][NTf ₂] + N ₂	- 5.9	23.0
[C ₈ mim][BETI] + CO ₂	- 12.6	22.6
[C ₈ mim][BETI] + C ₂ H ₆	- 12.6	23.8
[C ₈ mim][BETI] + N ₂	- 9.2	25.5
[C ₈ H ₄ F ₁₃ mim][BETI] + CO ₂	- 11.9	21.6
[C ₈ H ₄ F ₁₃ mim][BETI] + C ₂ H ₆ *	- 7.2	24.0

* in the temperature range 303—323 K

TABLE 4. Ideal gas selectivities of ionic liquids containing on the cation fluoroalkyl groups alkyl groups, combined with [NTf₂] and [BETI] anions at 303 K

Ionic Liquid	CO ₂ /C ₂ H ₆	CO ₂ /N ₂	CO ₂ /N ₂ ^a	CO ₂ /CH ₄ ^a
[C ₈ mim][NTf ₂]	1.8	24.9	27	9
[C ₈ H ₄ F ₁₃ mim][NTf ₂]	2.9	18.7	16	13
[C ₈ mim][BETI]	1.6	21.2	-	-
[C ₈ H ₄ F ₁₃ mim][BETI]	2.3 ^b	-	-	-

^a: values taken by ref.³⁹

^b: measured at 313 K

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