

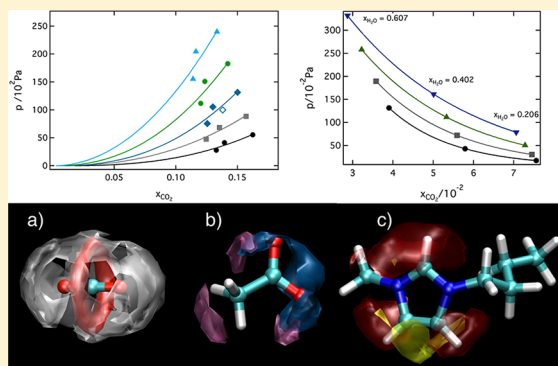
Effect of Water on the Carbon Dioxide Absorption by 1-Alkyl-3-methylimidazolium Acetate Ionic Liquids

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Supporting Information

ABSTRACT: The absorption of carbon dioxide by the pure ionic liquids 1-ethyl-3-methylimidazolium acetate ($[C_1C_2Im][OAc]$) and 1-butyl-3-methylimidazolium acetate ($[C_1C_4Im][OAc]$) was studied experimentally from 303 to 343 K. As expected, the mole fraction of absorbed carbon dioxide is high (0.16 at 303 K and 5.5 kPa and 0.19 at 303 and 9.6 kPa for $[C_1C_2Im][OAc]$ and $[C_1C_4Im][OAc]$, respectively), does not obey Henry's law, and is compatible with the chemisorption of the gas by the liquid. Evidence of a chemical reaction between the gas and the liquid was found both by NMR and by molecular simulation. In the presence of water, the properties of the liquid absorber significantly change, especially the viscosity that decreases by as much as 25% (to 78 mPa s) and 30% (to 262 mPa s) in the presence of 0.2 mol fraction of water for $[C_1C_2Im][OAc]$ and $[C_1C_4Im][OAc]$ at 303 K, respectively. The absorption of carbon dioxide decreases when the water concentration increases: a decrease of 83% in CO_2 absorption is found for $[C_1C_4Im][OAc]$ with 0.6 mol fraction of water at 303 K. It is proved in this work, by combining experimental data with molecular simulation, that the presence of water not only renders the chemical reaction between the gas and the ionic liquid less favorable but also lowers the (physical) solubility of the gas as it competes by the same solvation sites of the ionic liquid. The lowering of the viscosity of the liquid absorbent largely compensates these apparent drawbacks and the mixtures of $[C_1C_2Im][OAc]$ and $[C_1C_4Im][OAc]$ with water seem promising to be used for carbon dioxide capture.



1. INTRODUCTION

It has recently been shown that alkylimidazolium acetate ionic liquids can chemically absorb carbon dioxide,^{1–3} leading to solutions of almost 30 mol % CO_2 at atmospheric pressure.⁴ These ionic liquids are considered as potential absorbents for carbon dioxide and have even been studied as potential substitutes of amine-based solutions,⁵ as they associate selective absorption capabilities to negligible vapor pressures, low melting temperatures and good thermal stabilities.

The absorption of carbon dioxide in ionic liquids based on the acetate anion has been reported by several authors. Maginn et al.⁶ first studied the absorption of CO_2 in the $[C_1C_4Im][OAc]$ and proposed a mechanism for the chemical reaction of the gas with the ionic liquid based on NMR results. They proposed a first step of deprotonation of the imidazolium cation at the C2 position of the ring by the acetate anion followed by the association between the formed carbene and carbon dioxide. This simple mechanism was refuted by subsequent studies^{4,7,8} and, more recently, it has been shown that the mechanism of reaction between carbon dioxide and acetate based alkylimidazolium ionic liquids is more elaborate^{1–3} and also involves the formation of a complex anion.

Shiflett et al. reported experimental measurements of the absorption of carbon dioxide in $[C_1C_2Im][OAc]$,^{9,10} $[C_1C_4Im][OAc]$,¹⁰

and $[C_2C_2Im][OAc]$ ¹¹ and have mentioned the reversible formation of a chemical complex due to a Lewis acid base interaction. More recently, they have proved that the mechanisms proposed by Gurau et al.² and Besnard et al.³ using NMR spectroscopy and X-ray diffraction analysis and IR, Raman, and NMR spectroscopy, respectively, are compatible with the equilibrium measurements and models developed.¹¹

To improve the properties of gas absorbent including its selectivity for carbon dioxide, the research is focused on the addition of a molecular cosolvent, such as water, to the ionic liquid. The presence of water in ionic liquid affects the physicochemical properties of the liquid mixture, i.e., lowering the viscosity of the mixture,¹² an advantage for industrial applications. Contrary to many studies on the solubility of gases in pure ionic liquids, at both low and high pressures, very few data are available on ternary systems $[C_1C_4Im][OAc]$ + water + CO_2 ,^{2,11} even if they are more representative of real mixtures. Gurau et al.² have observed a fast release of the absorbed CO_2 upon the addition of water to $[C_1C_2Im][OAc]$, leading to the formation of $[C_1C_2Im][HCO_3]$. Shiflett et al.¹¹ observe that the addition

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of water to a solution of CO₂ in [C₂C₂Im][OAc] may lead to the formation of a bicarbonate salt that can prevent the regeneration of the ionic liquid upon the desorption of the gas. As far as the authors are aware, no research group has quantified the effect of water on the absorption of carbon dioxide by alkylimidazolium acetate ionic liquids as a function of the composition in water, temperature and pressure of the gas. Even if Chinn et al.¹³ report the carbon dioxide absorption by a mixture of [C₁C₄Im][OAc] + H₂O (14 wt %), again, no study of the effect of different concentrations of water is reported.

The aim of this work is to obtain a consistent and precise set of experimental data on the absorption of CO₂ by imidazolium acetate ionic liquids and to study the influence of water on the solubility of carbon dioxide in [C₁C₂Im][OAc] and [C₁C₄Im][OAc] at temperatures between 303 and 343 K. Moreover, the solvation of CO₂ and its solubility in the studied ionic liquids was investigated by molecular dynamic simulations. The analysis of the data enabled the access to the molecular mechanism of the carbon dioxide absorption in these ionic liquids. ¹H and ¹³C NMR spectroscopy provided further experimental evidence for the solvation mechanism proposed with or without the presence of water.

2. EXPERIMENTAL SECTION

Materials. The ionic liquids 1-ethyl-3-methylimidazolium acetate (98%), [C₁C₂Im][OAc], 1-butyl-3-methylimidazolium acetate, [C₁C₄Im][OAc] (98%) were supplied by SOLVIONIC. The carbon dioxide (AGA/Linde Gaz, with purity >0.99995 mol fraction) and the nitrogen (AGA/Linde Gaz, with purity >0.99995 mol fraction) were used as received. Water was distilled three times and degassed using melting–freezing cycles before use.

The water content of the ionic liquid sample was determined by coulometric Karl Fisher Titration using a Mettler Toledo DL31 titrator. Before each measurement the sample of ionic liquid was degassed and dried under vacuum at 303 K at least for 72 h. The quantity of water was determined to be 500 and 600 ppm for [C₁C₂Im][OAc] and [C₁C₄Im][OAc], respectively.

The temperature of decomposition of the ionic liquids was determined by a modulated DSC 2920 from TA Instruments. The value determined was 423 and 433 K for [C₁C₂Im][OAc] and [C₁C₄Im][OAc], respectively.

Mixtures of ionic liquids with different water contents were prepared gravimetrically. The ionic liquid was first introduced in a glass vial, and then the appropriate amount of water was added and the glass vial was sealed. The vial was completely filled with the liquid mixture to minimize the volume of the vapor phase in equilibrium with the liquid solution and so reduce the error in composition due to differential evaporation. The uncertainty of the mole fraction is estimated as ±0.0001.

Density Measurements. Densities were measured using a U-shaped vibrating-tube densimeter (Anton Paar, model DMA 512) operating in a static mode, following the procedure described in previous publications.^{8,14} Measurements of the pure ionic liquids and the mixtures ionic liquid + water were performed at pressures up to 25 MPa and in the temperature range from 293 to 353 K. The temperature was maintained constant within ±0.01 K by means of a recirculating bath equipped with a PID temperature controller (Julabo FP40-HP). For measuring the temperature, a 100 Ohm platinum resistance thermometer (precision of ±0.02 K and accuracy of ±0.04 K) was used. Its calibration was performed by verifying a water triple point (triple point cell by Hart Scientific) and by comparison against a 100 Ohm platinum resistance Hart Scientific

model 1502A. The pressure was measured using a precision pressure transmitter Druck, model PTX 610, working in a range from 0 to 70 MPa with an uncertainty 0.08% full scale. The uncertainty of the density measurement is estimated as 10^{−4} g cm^{−3}.¹⁴

Viscosity Measurements. The dynamic viscosities of pure ionic liquids and mixtures of ionic liquid + water were measured using an Anton Paar AMVn rolling ball viscosimeter at atmospheric pressure and temperatures between 293.15 and 363.15 K. The temperature was controlled to within 0.01 K and measured with accuracy better than 0.05 K. Before the measurements the 1.8 and 3 mm diameter capillary tubes were calibrated as a function of temperature and angle of measurement using a standard viscosity oil from Cannon (N35). The overall uncertainty on the viscosity is estimated as ±1.5%.

Gas-Absorption Measurements. The experimental apparatus used for the gas absorption measurements in pure ionic liquids was based on an isochoric saturation technique and has been described in previous publications.^{15–17} In this technique a known quantity of gaseous solute is put in contact with a precisely determined quantity of degassed solvent at a constant temperature inside an accurately known volume. When thermodynamic equilibrium is attained, the pressure above the liquid solution is directly related to the absorption of the gas by the liquid. Absorption of CO₂ was determined in the temperature range from 303.15 to 353.15 K. The method of data reduction was reported in previous publications.^{15,16}

A second cell was used to determine the absorption of carbon dioxide in the mixtures of ionic liquid + water. This cell is also a *pVT* constant volume cell and the experimental apparatus used for the present gas solubility measurements was based on an isochoric saturation method that has been described in a previous publication.^{18,19} In this technique a known quantity of gaseous solute is put into contact with a precisely determined quantity of degassed solvent at constant temperature inside an accurately known volume. As previously, when thermodynamic equilibrium is attained, the pressure above the liquid solution is constant and directly related to the solubility of the gas in the liquid. Details of the data reduction are given in our previous publications.^{18,19}

Molecular Simulations. Ionic liquids were represented by an all-atom force field, which is based on the AMBER/OPLS_AA framework.^{20,21} For the imidazolium cation, force field parameters were developed specifically.²² Acetate^{21,23} was represented with the potential models existing in the literature, whereas the potential model of Mallet et al.²⁴ was used for carbon dioxide.

The ionic liquid [C₁C₄Im][OAc] was simulated in periodic cubic boxes containing 127 ion pairs, using the molecular dynamics method implemented in the DL_POLY package.²⁰ Initial low-density configurations, with ions placed at random in periodic cubic boxes, were equilibrated to attain liquid-like densities and structures at 373 K and 1 bar. Temperature and pressure were maintained using a Nosé–Hoover thermostat and barostat, respectively. Once the equilibrium density was attained, simulation runs of 1 ns were performed, with an explicit cutoff distance of 16 Å for nonbonded interactions, from which 5000 configurations were stored. Structural quantities such as radial and spatial distribution functions were calculated from configurations generated during the production runs. Additionally, simulation boxes containing 200 ion pairs and 12 CO₂ molecules were prepared in the same manner, to calculate solute–solvent radial distribution functions between the gas and the

ionic liquid and the cation–anion interaction energy in the presence of CO₂.

The chemical potentials of CO₂ at 373 K in the two ionic liquids were calculated in a two-step procedure, as already described by Almantariotis et al.²⁵ First, for CO₂, a reduced-size version of the molecule was made by subtracting 0.8 Å from the C–O bond length and also from the Lennard-Jones diameters σ_O and σ_C . The resulting molecule is small enough so that its chemical potential can be calculated using the Widom test-particle insertion method²⁶ with efficient statistics (100 000 insertions into each of 5000 stored configurations of pure ionic liquids). Second, a stepwise finite difference thermodynamic integration procedure²⁷ was followed to calculate the free-energy difference between the initial, reduced versions of the carbon dioxide molecule and the final full-size model. The free energy calculation was performed on six intermediate steps along a linear path connecting the intermolecular parameters (bonds and diameters) of the reduced-size to those of the full-size molecule. This relatively modest number of intermediate steps is adequate because the starting point of the thermodynamic integration route is not too far from the final state. In the finite-difference thermodynamic integration scheme, derivatives (finite differences) of the total energy of the system with respect to the activation parameter were evaluated by a free-energy perturbation

Table 1. Parameters A_0 and A_1 of Linear Functions^a Used To Smooth the Experimental Densities at 0.1 MPa as a Function of Temperature

| IL | $A_0/\text{kg}\cdot\text{m}^{-3}$ | $A_1/\text{kg}\cdot\text{m}^{-3}\cdot\text{K}^{-1}$ | S/% |
|--|-----------------------------------|---|------|
| [C ₁ C ₂ Im][OAc] | 1281.0 | −0.6064 | 0.02 |
| [C ₁ C ₂ Im][OAc] + water ($x_{\text{water}} = 0.2000$) | 1278.3 | −0.5862 | 0.02 |
| [C ₁ C ₂ Im][OAc] + water ($x_{\text{water}} = 0.4040$) | 1282.6 | −0.5912 | 0.01 |
| [C ₁ C ₂ Im][OAc] + water ($x_{\text{water}} = 0.6028$) | 1290.2 | −0.6089 | 0.01 |
| [C ₁ C ₂ Im][OAc] + water ($x_{\text{water}} = 0.8020$) | 1295.4 | −0.6541 | 0.03 |
| [C ₁ C ₄ Im][OAc] | 1230.7 | −0.5927 | 0.01 |
| [C ₁ C ₄ Im][OAc] + water ($x_{\text{water}} = 0.1966$) | 1231.3 | −0.5888 | 0.01 |
| [C ₁ C ₄ Im][OAc] + water ($x_{\text{water}} = 0.3958$) | 1236.3 | −0.5846 | 0.06 |
| [C ₁ C ₄ Im][OAc] + water ($x_{\text{water}} = 0.6002$) | 1249.1 | −0.6230 | 0.01 |
| [C ₁ C ₄ Im][OAc] + water ($x_{\text{water}} = 0.7992$) | 1267.0 | −0.6765 | 0.01 |

^a $\rho_{\text{IL,phase}} = A_1 + A_0 \times T$.

expression in the NpT ensemble using a three-point formula with increments of 2×10^{-3} .

NMR Measurements. ¹H and ¹³C NMR data were collected at 25 or 40 °C on a Bruker AC 300 MHz spectrometer with the resonance frequency at 300.130 MHz for the ¹H nucleus. Samples of [C₁C₄Im][OAc] were recorded in solution using acetone-*d*₆ as a solvent. The deuterium in DMSO-*d*₆ was used for the external lock of the NMR magnetic field, and the residual proton in DMSO-*d*₆ was used as the ¹H NMR external reference at 2.5 ppm.

3. RESULTS AND DISCUSSION

Densities of the pure ionic liquids and of the mixtures of ionic liquid + water were obtained as a function of temperature from 293 to 353 K and of pressure from 0.1 to 25 MPa. The experimental data are presented in Table S-1 in the Supporting Information. The values of the density at atmospheric pressure (necessary for the calculation of the gas solubility) were adjusted to linear functions of temperature. The coefficients of the fits are listed in Table 1 together with the standard deviation, which is always better than 0.1%.

The densities as a function of pressure were correlated using the Tait equation:

$$\rho(T, p) = \left[\frac{\rho^0(T, p^0)}{1 - C \ln \left(\frac{B(T) + p}{B(T) + p^0} \right)} \right] \quad (1)$$

where $\rho^0(T, p^0)$ is the density value at a reference temperature T and at the pressure $p^0 = 0.1$ MPa; C is an adjustable parameter and $B(T)$ is a polynomial defined by

$$B(T) = \sum_{i=0}^2 B_i(T)^i \quad (2)$$

The parameters found for the present experimental data are listed in Table 2.

The volumetric data measured were used to calculate the excess molar volume of the mixtures of the ionic liquids [C₁C₂Im]-[OAc] and [C₁C₄Im][OAc] with water using the relation:

$$V^E = V_m^{\text{mix}} - \sum_i x_i \frac{M_i}{\rho_i} \quad (3)$$

where V_m^{mix} is the molar volume of the mixture, x_i the mole fraction of component i with molar mass M_i and density ρ_i . The values calculated are listed in Table S-2 of the Supporting Information. The uncertainty of the excess molar volumes, evaluated by propagation of the errors, is estimated to be $\pm 0.1 \text{ cm}^3 \text{ mol}^{-1}$.

Table 2. Tait Parameters C , B_0 , B_1 , and B_2 Used To Smooth the Experimental Densities as a Function of Pressure (to 25 MPa) and Temperature (from 293 to 453 K) along with the Percent Average Absolute Deviations of the Fit (AAD)

| IL | 10 ² C | B_0/MPa | $B_1/\text{MPa}\cdot\text{K}^{-1}$ | $10^3 B_2/\text{MPa}\cdot\text{K}^{-2}$ | AAD/% |
|---|-------------------|------------------|------------------------------------|---|-------|
| [C ₁ C ₂ Im][OAc] | −1.578 | +103.666 | +0.093 | +0.090 | 0.013 |
| [C ₁ C ₂ Im][OAc] + water ($x_{\text{water}} = 0.2000$) | +8.505 | +255.188 | +0.554 | −1.872 | 0.005 |
| [C ₁ C ₂ Im][OAc] + water ($x_{\text{water}} = 0.4040$) | +9.260 | +471.050 | −0.467 | −0.463 | 0.005 |
| [C ₁ C ₂ Im][OAc] + water ($x_{\text{water}} = 0.6028$) | +11.743 | +1305.881 | −4.581 | +5.228 | 0.013 |
| [C ₁ C ₂ Im][OAc] + water ($x_{\text{water}} = 0.8020$) | +7.618 | −106.151 | +2.913 | −5.582 | 0.014 |
| [C ₁ C ₄ Im][OAc] | +6.659 | −213.387 | +2.764 | −5.067 | 0.006 |
| [C ₁ C ₄ Im][OAc] + water ($x_{\text{water}} = 0.1966$) | +9.835 | +272.040 | +0.573 | −2.104 | 0.005 |
| [C ₁ C ₄ Im][OAc] + water ($x_{\text{water}} = 0.3958$) | +31.131 | −2763.812 | +24.953 | −0.043 | 0.047 |
| [C ₁ C ₄ Im][OAc] + water ($x_{\text{water}} = 0.6002$) | +3.908 | −553.792 | +4.486 | −7.639 | 0.008 |
| [C ₁ C ₄ Im][OAc] + water ($x_{\text{water}} = 0.7992$) | +3.823 | +336.813 | −0.957 | +0.719 | 0.009 |

As can be observed in Figure 1, the excess molar volumes are negative (with a minimum value around $-2 \text{ cm}^3 \text{ mol}^{-1}$) for all the mixtures studied in the range of temperature and pressure covered. The minimum of the excess molar volumes is found for mole fractions of water of around 0.7 for the two ionic liquids studied at all the temperatures and pressures. The variation of the excess molar volume with temperature or with pressure is represented in Figure 1 (plots a and b) for the example of $[\text{C}_1\text{C}_4\text{Im}][\text{OAc}]$. V^E becomes less negative when the temperature

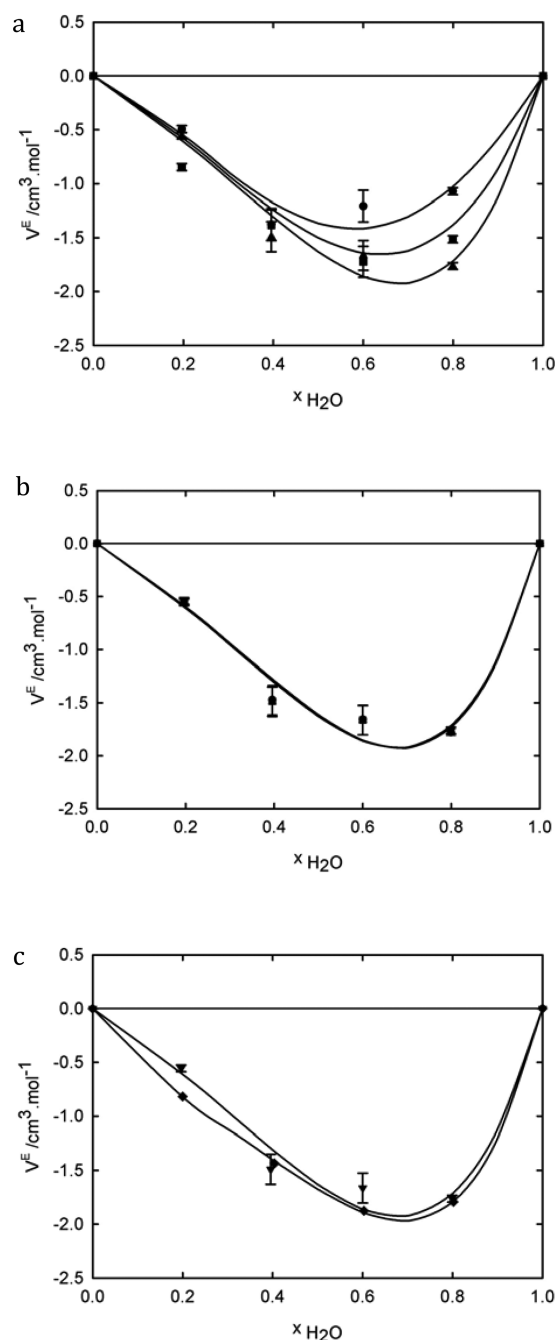


Figure 1. Excess molar volumes of the mixtures $[\text{C}_1\text{C}_4\text{Im}][\text{OAc}] + \text{water}$. (a) At atmospheric pressure as a function of the water mole fraction and as a function of the temperature: \blacktriangle , 293.15 K; \blacksquare , 323.15 K; \bullet , 353.15 K. (b) At 293.15 K as a function of the water mole fraction and as a function of pressure: \bullet , 1 bar; \blacktriangledown , 10 bar; \blacklozenge , 100 bar. (c) Water at 293.15 K and at atmospheric pressure for \blacktriangle , $[\text{C}_1\text{C}_2\text{Im}][\text{OAc}]$; \blacksquare , $[\text{C}_1\text{C}_4\text{Im}][\text{OAc}]$.

increases, the variation with pressure being negligible for the ionic liquids studied. Furthermore, it is observed that the excess molar volume does not vary significantly with the size of the alkyl side-chain of the cation (Figure 1, plot c).

Experimental values of the viscosity of the pure ionic liquids and of the mixtures of ionic liquids + water are reported in Table S-3 in the Supporting Information. From the comparison of the viscosities of $[\text{C}_1\text{C}_2\text{Im}][\text{OAc}]$ and $[\text{C}_1\text{C}_4\text{Im}][\text{OAc}]$ it can be concluded that it diminishes when the length of the alkyl side chain decreases in the cation, as observed in other families of ionic liquids based on the imidazolium cation. It was noted that the high viscosity of ionic liquids with anion acetate significantly decreases by increasing the temperature from 293 to 363 K. The dependence of the viscosity with the temperature for the pure ionic liquids and for their mixtures with water is represented by Vogel–Fulcher–Tammann (VFT) equations of the form

$$\eta = A \times T^{1/2} \exp\left(\frac{k}{T - T_0}\right) \quad (4)$$

The parameters obtained for the fit of the viscosity data measured herein are listed in Table 3.

Table 3. Correlation Parameters of the VFT Equation (k , A , and T_0) with the Percent Average Absolute Deviation of the Fit (AAD) for the Viscosity of ILs as a Function of Temperature Determined from Measurements between 293 and 373 K

| IL | k/K | $10^{-3}A/\text{mPa}\cdot\text{s}\cdot\text{K}^{-1/2}$ | T_0/K | AAD/% |
|---|--------------|--|----------------|-------|
| $[\text{C}_1\text{C}_2\text{Im}][\text{OAc}]$ | 663 | 10.33 | 199 | 0.3 |
| $[\text{C}_1\text{C}_2\text{Im}][\text{OAc}] + \text{water}$ ($x_{\text{water}} = 0.2088$) | 1042 | 1.99 | 164 | 0.6 |
| $[\text{C}_1\text{C}_2\text{Im}][\text{OAc}] + \text{water}$ ($x_{\text{water}} = 0.4000$) | 890 | 3.96 | 169 | 0.3 |
| $[\text{C}_1\text{C}_2\text{Im}][\text{OAc}] + \text{water}$ ($x_{\text{water}} = 0.6014$) | 1078 | 1.83 | 148 | 0.3 |
| $[\text{C}_1\text{C}_2\text{Im}][\text{OAc}] + \text{water}$ ($x_{\text{water}} = 0.8023$) | 1279 | 0.57 | 126 | 0.7 |
| $[\text{C}_1\text{C}_4\text{Im}][\text{OAc}]$ | 1081 | 2.45 | 185 | 1.2 |
| $[\text{C}_1\text{C}_4\text{Im}][\text{OAc}] + \text{water}$ ($x_{\text{water}} = 0.1843$) | 1128 | 1.95 | 177 | 0.3 |
| $[\text{C}_1\text{C}_4\text{Im}][\text{OAc}] + \text{water}$ ($x_{\text{water}} = 0.3889$) | 927 | 3.86 | 183 | 0.5 |
| $[\text{C}_1\text{C}_4\text{Im}][\text{OAc}] + \text{water}$ ($x_{\text{water}} = 0.5951$) | 1021 | 2.07 | 168 | 0.3 |
| $[\text{C}_1\text{C}_4\text{Im}][\text{OAc}] + \text{water}$ ($x_{\text{water}} = 0.8004$) | 751 | 3.08 | 175 | 0.3 |

The addition of water also significantly lowers the viscosity of the liquid. For example, the addition of 0.2 mol fraction of water leads to a decrease of the viscosity of more than 25% (to 77.9 mPa s) and 30% (to 262.3 mPa s) for $[\text{C}_1\text{C}_2\text{Im}][\text{OAc}]$ and $[\text{C}_1\text{C}_4\text{Im}][\text{OAc}]$ at 303 K, respectively. The viscosity also significantly lowers with temperature and the same mixtures exhibit viscosities of 20.8 mPa s and 48.7 mPa s at 333 K for $[\text{C}_1\text{C}_2\text{Im}][\text{OAc}] + \text{H}_2\text{O}$ ($x_{\text{H}_2\text{O}} = 0.2$) and $[\text{C}_1\text{C}_4\text{Im}][\text{OAc}] + \text{H}_2\text{O}$ ($x_{\text{H}_2\text{O}} = 0.2$), respectively. These facts can constitute a significant advantage for using these liquid mixtures as absorbents for carbon dioxide capture, provided that the absorption capacity is maintained.

As stressed in a previous work,²⁸ simple exponential representations are not sufficient to correlate the viscosity of mixtures

of ionic liquids with molecular compounds in the entire composition range and equations normally used to describe the viscosity of electrolyte solutions can not be applied to the mixtures studied here. We have used the empirical Grunberg–Nissan equation²⁹ to describe the viscosity of the studied mixtures, η_{mix} :

$$\ln \eta_{\text{mix}} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + \ln(\eta_{\text{mix}}/\eta^{\text{id}}) \quad (5)$$

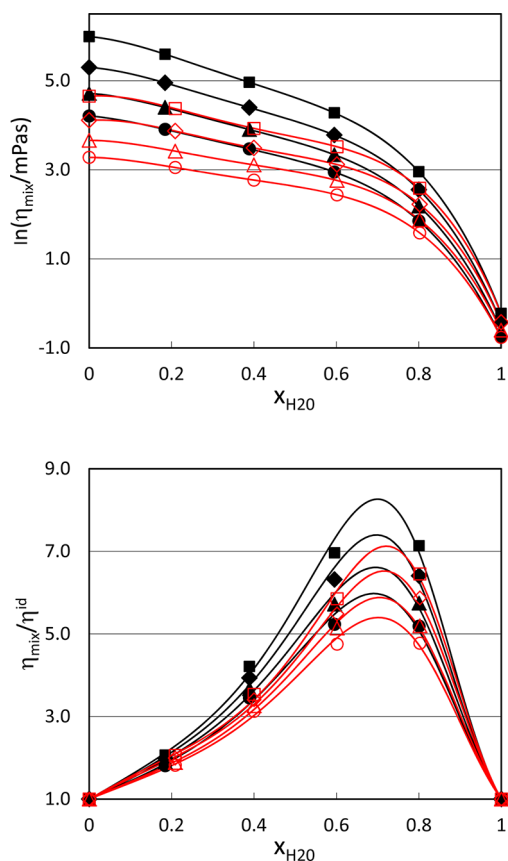


Figure 2. Logarithm of the viscosity (upper plot) and real to ideal ratio of (ionic liquid + water) mixtures (lower plot) as a function of mole fraction composition of water and at different temperatures: ■, {[C₁C₄Im][OAc] + H₂O} at 303 K; ◆, {[C₁C₄Im][OAc] + H₂O} at 313 K; ▲, {[C₁C₂Im][OAc] + H₂O} at 323 K; ●, {[C₁C₄Im][OAc] + H₂O} at 333 K; □, {[C₁C₂Im][OAc] + H₂O} at 303 K; ◇, {[C₁C₂Im][OAc] + H₂O} at 313 K; △, {[C₁C₂Im][OAc] + H₂O} at 323 K; ○, {[C₁C₂Im][OAc] + H₂O} at 333 K.

Table 4. Parameters *A*, *B*, and *C* of the Redlich–Kister-Type Fittings, Eq 6, Used To Fit the Experimental Viscosity Deviations Calculated from the Data of Table 4 along with the Standard Error of the Estimation

| <i>T</i> /K | <i>A</i> | <i>B</i> | <i>C</i> | std dev |
|---|----------|----------|----------|---------|
| [C ₁ C ₂ Im][OAc] | | | | |
| 303 | 6.0850 | −5.9222 | 5.4257 | 0.03 |
| 313 | 5.8974 | −5.6094 | 4.8395 | 0.04 |
| 323 | 5.7138 | −5.2878 | 3.8018 | 0.03 |
| 333 | 5.4774 | −5.0017 | 3.4375 | 0.04 |
| [C ₁ C ₄ Im][OAc] | | | | |
| 303 | 4.5035 | −5.9547 | 6.9542 | 0.05 |
| 313 | 6.6192 | −5.6196 | 4.1411 | 0.05 |
| 323 | 6.2792 | −5.2901 | 3.7429 | 0.05 |
| 333 | 5.9831 | −5.0228 | 3.2402 | 0.05 |

where x_i and η_i are the mole fraction and the viscosity of component *i*, respectively and $(\eta_{\text{mix}}/\eta^{\text{id}})$ is the ratio between the real and ideal viscosities of the mixture. This last term is calculated by a Redlich–Kister type equation:

$$\ln(\eta_{\text{mix}}/\eta^{\text{id}}) = x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2)^2] \quad (6)$$

where η^{id} is calculated here by the composition-weighted geometrical mean of the viscosities of the pure components, $\eta^{\text{id}} = \eta_1^{x_1} \eta_2^{x_2}$. The $\ln \eta_{\text{mix}}$ values and the corresponding ratio $(\eta_{\text{mix}}/\eta^{\text{id}})$ are plotted in Figure 2 as a function of the water mole fraction at different temperatures studied for [C₁C₂Im][OAc] and [C₁C₄Im][OAc]; the parameters *A*, *B*, and *C* of eq 5 at the

Table 5. Experimental Values of CO₂ in ILs Expressed as CO₂ Mole Fraction x_2 and the Experimental Equilibrium Pressure *p*

| <i>T</i> /K | 10 ^{−2} <i>p</i> /Pa | x_2 | <i>T</i> /K | 10 ^{−2} <i>p</i> /Pa | x_2 |
|---|-------------------------------|--------|---|-------------------------------|--------|
| [C ₁ C ₂ Im][OAc] | | | [C ₁ C ₄ Im][OAc] | | |
| 303.34 | 27.96 | 0.1415 | 303.54 | 96.26 | 0.1904 |
| 303.30 | 41.36 | 0.1485 | 303.54 | 206.49 | 0.2188 |
| 303.34 | 55.44 | 0.1624 | 303.54 | 99.40 | 0.1932 |
| 313.36 | 47.70 | 0.1383 | 303.53 | 176.61 | 0.2155 |
| 313.31 | 68.45 | 0.1443 | 313.54 | 265.72 | 0.2069 |
| 313.34 | 88.55 | 0.1570 | 313.53 | 144.58 | 0.1851 |
| 323.37 | 75.52 | 0.1339 | 313.51 | 231.30 | 0.2043 |
| 323.30 | 105.20 | 0.1387 | 323.58 | 191.61 | 0.1730 |
| 323.37 | 131.48 | 0.1501 | 323.55 | 329.27 | 0.1945 |
| 333.38 | 111.68 | 0.1283 | 323.50 | 197.16 | 0.1759 |
| 333.29 | 150.99 | 0.1319 | 333.45 | 255.55 | 0.1659 |
| 333.37 | 182.75 | 0.1421 | 333.51 | 354.35 | 0.1676 |
| 343.41 | 155.51 | 0.1217 | 343.50 | 309.06 | 0.1527 |
| 343.25 | 204.60 | 0.1241 | 343.57 | 463.78 | 0.1690 |
| 343.23 | 239.86 | 0.1334 | 343.52 | 255.55 | 0.1659 |
| [C ₁ C ₂ Im][OAc] + H ₂ O ($x_{\text{H}_2\text{O}} = 0.2059$) | | | 343.15 | 418.30 | 0.1676 |
| 303.33 | 17.49 | 0.0756 | [C ₁ C ₄ Im][OAc] + H ₂ O ($x_{\text{H}_2\text{O}} = 0.2045$) | | |
| 313.34 | 30.68 | 0.0745 | 303.33 | 58.60 | 0.1205 |
| 323.37 | 50.62 | 0.0728 | 313.34 | 92.57 | 0.1160 |
| 333.35 | 78.74 | 0.0706 | 323.35 | 136.00 | 0.1104 |
| [C ₁ C ₂ Im][OAc] + H ₂ O ($x_{\text{H}_2\text{O}} = 0.4016$) | | | 333.37 | 187.52 | 0.1040 |
| 303.33 | 43.25 | 0.0579 | 343.39 | 244.97 | 0.0971 |
| 313.36 | 72.23 | 0.0559 | [C ₁ C ₄ Im][OAc] + H ₂ O ($x_{\text{H}_2\text{O}} = 0.4054$) | | |
| 323.37 | 111.56 | 0.0533 | 303.28 | 45.50 | 0.0656 |
| 333.40 | 161.49 | 0.0501 | 313.29 | 72.23 | 0.0635 |
| [C ₁ C ₂ Im][OAc] + H ₂ O ($x_{\text{H}_2\text{O}} = 0.6066$) | | | 323.20 | 112.07 | 0.0606 |
| 303.34 | 131.75 | 0.0390 | 333.0 | 159.95 | 0.0572 |
| 313.35 | 189.64 | 0.0358 | 342.99 | 216.16 | 0.0534 |
| 323.40 | 258.14 | 0.0322 | [C ₁ C ₄ Im][OAc] + H ₂ O ($x_{\text{H}_2\text{O}} = 0.6462$) | | |
| 333.47 | 331.86 | 0.0287 | 303.35 | 133.88 | 0.0320 |
| [C ₁ C ₂ Im][OAc] + H ₂ O ($x_{\text{H}_2\text{O}} = 0.8015$) | | | 313.35 | 190.29 | 0.0294 |
| 303.35 | 378.6 | 0.0146 | 323.36 | 256.25 | 0.0264 |
| 313.37 | 452.91 | 0.0129 | 333.30 | 331.28 | 0.0233 |
| 323.41 | 533.51 | 0.0114 | 343.19 | 410.94 | 0.0205 |
| 333.48 | 620.21 | 0.0101 | [C ₁ C ₄ Im][OAc] + H ₂ O ($x_{\text{H}_2\text{O}} = 0.8015$) | | |
| 343.55 | 716.36 | 0.0091 | 303.35 | 378.6 | 0.0146 |
| | | | 313.37 | 452.91 | 0.0129 |
| | | | 323.41 | 533.51 | 0.0114 |
| | | | 333.48 | 620.21 | 0.0101 |
| | | | 343.55 | 716.36 | 0.0091 |

different temperatures for the two ionic liquids are listed in Table 4.

According to eq 6, used previously to correlate the viscosity of liquid mixtures containing ionic liquids,²⁸ the viscosity ratio ($\eta_{\text{mix}}/\eta^{\text{id}}$) is 1 for the pure components and mixtures with ideal viscosity. For real mixtures with a water mole fraction composition between 0.6 and 0.8, the real to ideal ratio can reach values larger than 7 for $\{[\text{C}_1\text{C}_4\text{Im}][\text{OAc}] + \text{H}_2\text{O}\}$ at 303 K, the mixture that shows a larger deviation from the ideal viscosity. As seen in Figure 2, the behaviors, in terms of the viscosity, of the two ionic liquids when mixed with water are similar in the temperature range covered.

The quantities of carbon dioxide absorbed by the pure ionic liquids and by the mixtures of the ionic liquids + water are listed in Table 5 at different temperatures (from 303 to 343 K) and equilibrium pressures (varying from 2.50 to 24.0 kPa for $[\text{C}_1\text{C}_2\text{Im}][\text{OAc}]$ and from 9.50 to 47 kPa for $[\text{C}_1\text{C}_4\text{Im}][\text{OAc}]$). The results are depicted in Figure 3 for the two ionic

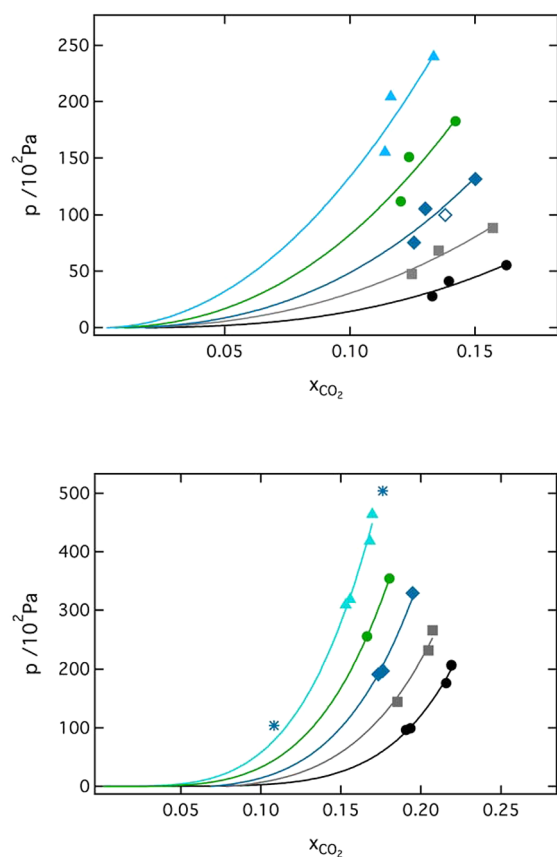


Figure 3. Absorption of carbon dioxide by $[\text{C}_1\text{C}_2\text{Im}][\text{OAc}]$ (upper plot) and $[\text{C}_1\text{C}_4\text{Im}][\text{OAc}]$ (bottom plot) at different temperatures. This work: ●, 303 K; ■, 313 K; ◆, 323 K; ●, 333 K; ▲, 343 K. ◇: Shiflett and Yokozeki, 2009, 323 K. *, Shiflett et al., 2008, 323 K.

liquids at the different temperatures and as a function of the pressure. It is observed that the solubility decreases when the alkyl side chain of the cation decreases and when the temperature increases. The variation of the solubility with the pressure does not obey Henry's law, as previously demonstrated by other authors, the variation of the mole fraction with pressure being compatible with the chemical absorption of the gas by the ionic liquid.

As can be seen in the upper plot of Figure 4, the addition of water to the ionic liquids causes a decrease on the absorption of

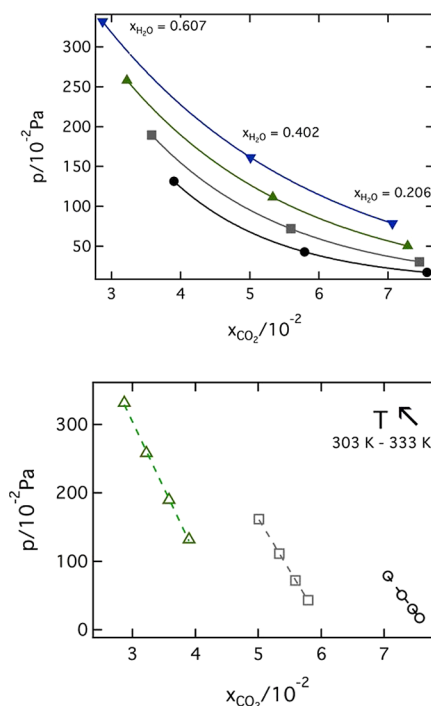


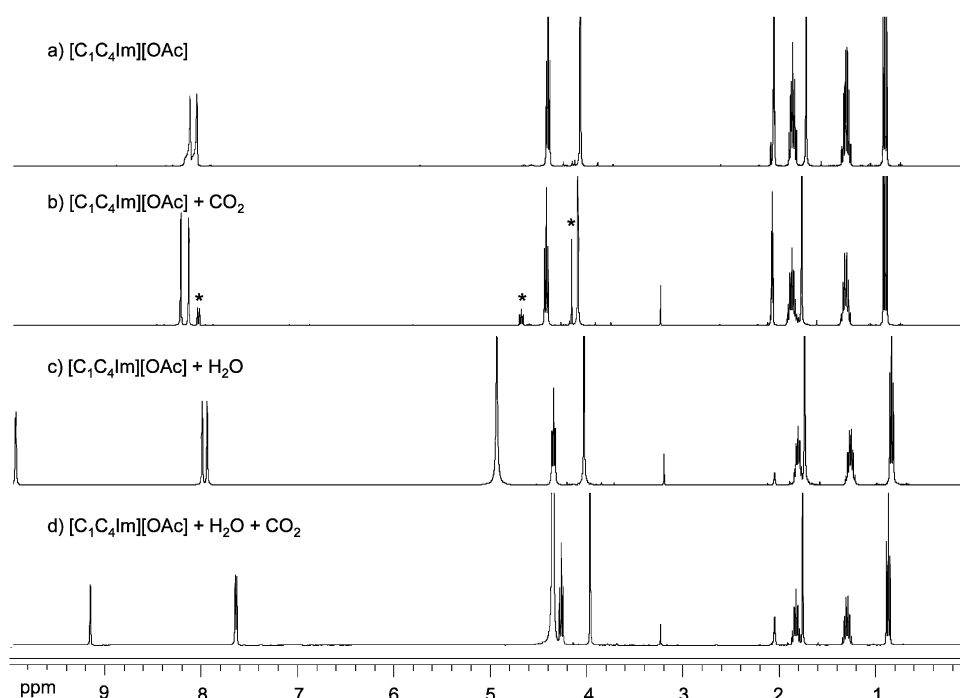
Figure 4. Absorption of carbon dioxide by mixtures of $[\text{C}_1\text{C}_2\text{Im}][\text{OAc}] + \text{H}_2\text{O}$ at different compositions at different temperatures. Upper plot: representation as a function of composition for set temperatures: ●, 303 K; ■, 313 K; ▲, 323 K; ▼, 333 K. Lower plot: representation as a function of temperature for set compositions of water in the ionic liquid: △, $x_{\text{H}_2\text{O}} = 0.6$; □, $x_{\text{H}_2\text{O}} = 0.6$; ○, $x_{\text{H}_2\text{O}} = 0.6$.

carbon dioxide. The lower plot of Figure 4 illustrates the fact that, for each composition studied, the carbon dioxide absorption decreases with temperature. Furthermore, the variations of the solubility with the temperature seem quite similar for all the solutions of absorbent (ionic liquid + water), which means that the energetics of absorption of the gas does not significantly change with the quantity of water present in the system. Wang et al.³⁰ have studied the dissolution behavior of CO_2 in the ionic liquid triethylbutylammonium acetate $[\text{N}_{2224}][\text{OAc}]$. They found evidence of the formation of a complex between the ionic liquid and water and a conservation of the carbon dioxide absorption capacity of the liquid.

Although we did not specifically quantify the recyclability of the liquid absorbents (pure ionic liquids or mixtures of ionic liquids with water), we have used repeatedly the ionic liquid after desorption of the gas by putting the solution under primary vacuum. No difference in the absorption capacity of the ionic liquid was found even if the composition of water, for the mixtures studied, was modified by differential evaporation of the molecular liquid.

In Figure 5 are depicted the ^1H and ^{13}C NMR spectra of pure $[\text{C}_1\text{C}_4\text{Im}][\text{OAc}]$ and of $[\text{C}_1\text{C}_4\text{Im}][\text{OAc}]$ saturated with carbon dioxide, with and without addition of water. The exact chemical shifts for each system are reported in the Supporting Information. The NMR spectra show that, in the absence of water, CO_2 causes the formation of a new species, structurally very similar with the pure ionic liquid. The signals corresponding to this new species formed are marked with * and ◆ in Figure 5, upper plot b and lower plot b, respectively. The fact that all the signals corresponding to the ionic liquid remain intact (no observable change in the chemical shifts of the protons and carbons in the sample of the pure ionic liquids and in the mixture)

Upper plot



Lower plot

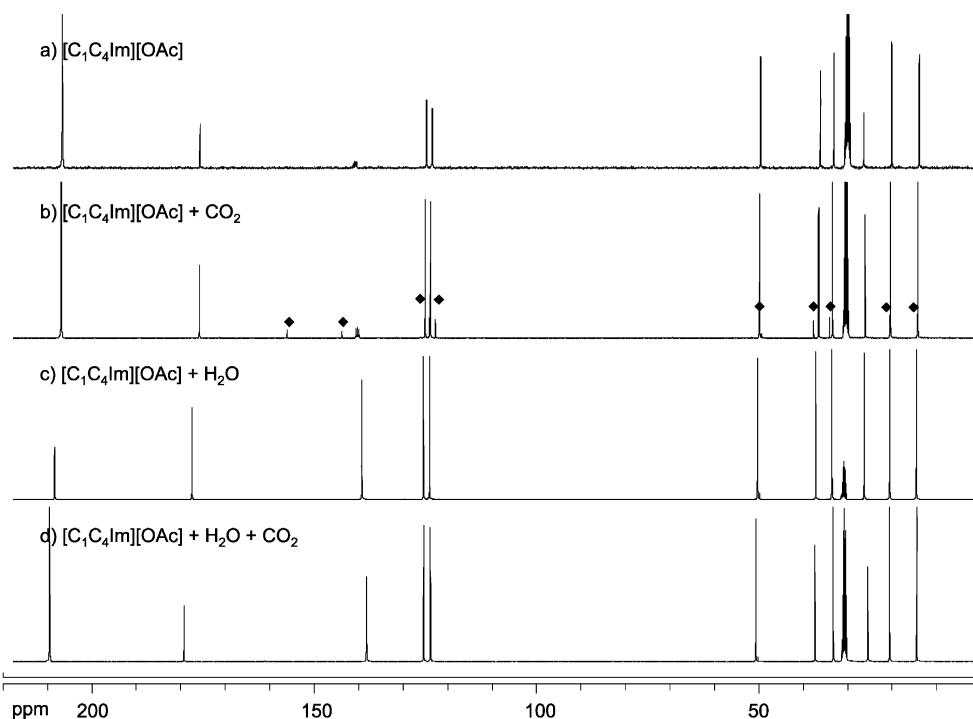


Figure 5. ^1H NMR spectra of various samples of 1-butyl-3-methylimidazolium acetate (upper plot) and ^{13}C NMR spectra of various samples of 1-butyl-3-methylimidazolium acetate (lower plot).

indicates that the observed high gas absorption is a consequence of the chemical reaction (or at least of the strong complexation) with the imidazolium cation, leading to the formation of a new chemical species. This species could not be clearly identified but a mechanism of formation through the abstraction of H_2 of the imidazolium cation, as suggested by Maginn,⁶ cannot be excluded.

Recently, several authors^{1–3} have also independently reported experimental data that lead to the conclusion that there is a chemical reaction between carbon dioxide and acetate based ionic liquids. Contrary to these conclusions, Shiflett et al.⁹ had reported that their ^1H NMR spectra of pure $[\text{C}_1\text{C}_4\text{Im}][\text{OAc}]$ and $[\text{C}_1\text{C}_4\text{Im}][\text{OAc}] + \text{CO}_2$ are the same, within the experimental

uncertainty, leading to the conclusion that any mechanism involving chemical reaction is minor. This observation was further supported by Carvalho et al.,⁷ who ascribed high CO₂ absorption only to strong interactions in the system evidenced by ¹³C NMR. However, we proved that high CO₂ absorption in pure [C₁C₄Im][OAc] is not only the consequence of strong interaction. Moreover, chemical reaction is the major pathway, because 12% molar could be ascribed to the new chemical species formed, the remaining 8% molar (the gas solubility being around 20% molar) can be attributed to the physical solubility of the gas.

In the presence of water ([C₁C₄Im][OAc] + H₂O + CO₂), the formation of a new ionic liquid form was not detected (Figure 5 upper plot d and lower plot d), indicating a different solubility mechanism of CO₂ in imidazolium acetate ionic liquids in the presence of water. The comparison between the two spectra, Figure 5 lower plot c and lower plot d, shows a slight downfield shift of the carbonyl carbon of the acetate anion (C=O, from 177.5 to 179.4 ppm), due to CO₂, indicating the presence of a Lewis acid/base interaction. Furthermore, a minor upfield shift is observed also for the methyl carbon of the acetate (CH₃, from 26.3 to 25.6 ppm). Also the position of C2 of the imidazolium cation is shifted slightly upfield (from 139.2 to

138.3 ppm) due to interactions of CO₂ with the cation. For comparison, to the sample of pure [C₁C₄Im][OAc] was added acetic acid, which resulted in an additional signal of H(OAc) at 11.5 ppm. Because this peak is seen in none of the spectra in the upper plot of Figure 5, we have concluded that either there is no formation of AcOH or it is formed in such a lower amount that it cannot be detected by NMR. Furthermore, CO₂ is seen in none of the ¹³C NMR spectra (possibly at about 120–130 ppm), which could be attributed to the high mobility of this molecule in solution. Here we can conclude that in the presence of water, both paths (chemical reaction involving cation and interaction of CO₂ and acetate) are disfavored, because there is competition between water and CO₂ for the same interaction site (OAc).

To get further insight on the mechanisms responsible for the difference in carbon dioxide absorption in the ionic liquid [C₁C₄Im][OAc] and the effect of water on the microscopic structure of the pure ionic liquid and on the CO₂ solutions, these systems were investigated using molecular dynamic simulations. Molecular dynamics simulations were done in a condensed phase and took into account all the two-body interactions from the environment of each molecule or ion, labeled as depicted in Figure 6. The radial distribution functions presented in Figure 6 (solid lines refer to the pure ionic liquid and dotted lines to the mixture CO₂ + IL) indicate that the presence of CO₂ does not affect the structure of the ionic liquid. Carbon dioxide is solvated preferentially in the vicinity of the anion and in the nonpolar region of imidazolium ionic liquids.

The structural features of the mixture of CO₂ + IL can be perceived and confirmed in the 3-dimensional spatial distribution functions depicted in Figure 7. In Figure 7a is represented the distribution of the local density of the cationic and the anionic atomic sites around CO₂ in [C₁C₄Im][OAc]. As already deduced from the radial distribution functions, the spatial distribution function shows that CO₂ is mainly solvated by the anion and the terminal carbon atoms of CT_{Im}. Looking at the distribution of atomic density around acetate (Figure 7b) it is found that both carbon dioxide and the cation (position C2_{Im}) interact with the oxygen atoms of the anion. Figure 7c confirms these observations.

Calculations of the free energy of solvation of CO₂ in [C₁C₄Im][OAc] at 373 K following a procedure described and tested elsewhere²⁵ give access to the Henry's law constants, K_{H} , that allow us to calculate the gas solubility at a partial pressure of gas, $p_{\text{gas}} = 1$ bar. The results obtained show a great disparity between the experimentally determined solubility (0.13 mol fraction solubility of carbon dioxide extrapolated to 373 K using the values in Table 5 compared with 0.002 ± 0.001 calculated here). This disparity constitutes another evidence of

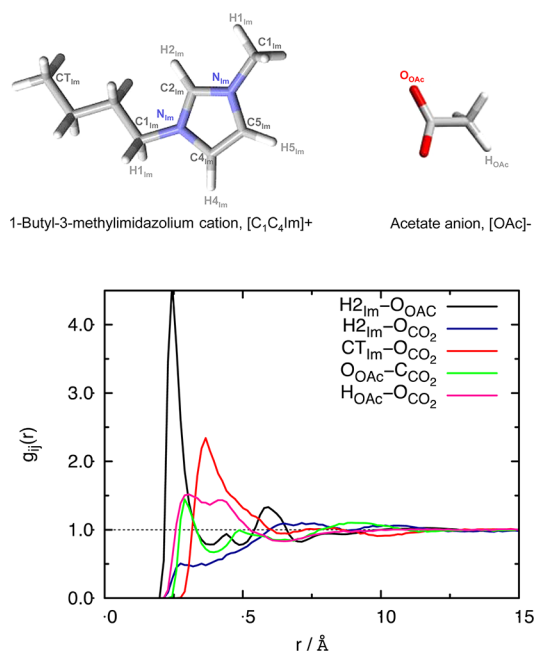


Figure 6. Preferential interaction sites between CO₂ and [C₁C₄Im][OAc].

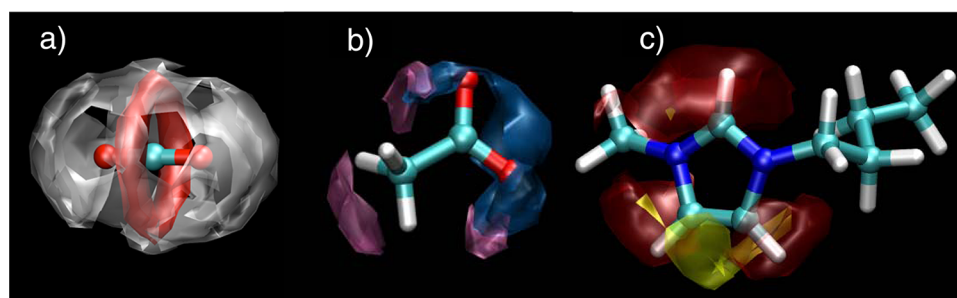


Figure 7. Spatial distribution functions between selected atomic sites in [C₁C₄Im][OAc], and CO₂. (a) Iso-surface corresponding to a local density of twice the average density of the CT_{Im} (gray) and of the O_{Ac} (red), (b) Iso-surface corresponding to a local density of 3-times the average density of the H2_{Im} (blue) and C_{CO2} (purple), (c) Iso-surface around C₁C₄Im⁺ corresponding to a local density of twice the average density of the O_{CO2} (yellow) and of twice of the O_{Ac} (red).

the chemical nature of the absorption of carbon dioxide by the ionic liquid rich mixtures. To evaluate the physical interactions present in solution, the overall system configuration energy of the mixtures $\text{CO}_2 + \text{IL}$ was decomposed, as represented in Figure 8. It can be observed that the presence of CO_2 increases

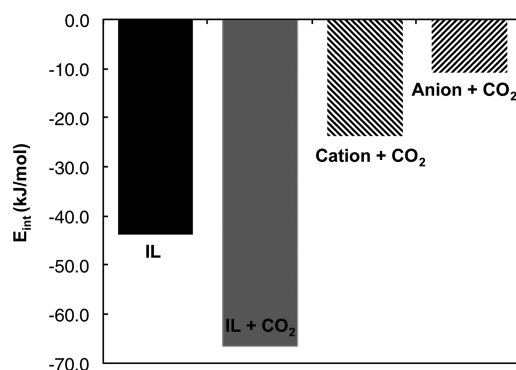


Figure 8. (a) Comparison of the cation–anion interaction energies in pure ionic liquids and in the mixtures with CO_2 . The values are normalized by a number of the amount of substance of IL in moles. (b) Anion– CO_2 and cation– CO_2 interaction energies in the mixtures $\text{IL} + \text{CO}_2$ (normalized by the number of CO_2 molecules). Exact values are reported in Table S-4 on the Supporting Information.

the cation–anion interactions, which causes stronger ion pair association. Surprisingly, CO_2 was found to interact stronger with the cation than with the anion constituting the ionic liquid.

4. CONCLUSION

The chemical absorption of carbon dioxide by the pure ionic liquids 1-ethyl-3-methylimidazolium acetate ($[\text{C}_1\text{C}_2\text{Im}][\text{OAc}]$) and 1-butyl-3-methylimidazolium acetate ($[\text{C}_1\text{C}_4\text{Im}][\text{OAc}]$) was evidenced by the measurement of the quantities of gas absorbed from 303 to 343 K, by the NMR study of the solutions and by molecular simulation calculations.

The study of the influence of the presence of water on the capability of the ionic liquid to absorb carbon dioxide was studied herein as a function of the concentration of water and as a function of temperature. The properties of the liquid absorber significantly change particularly the viscosity that decreases by as much as 25% and 30% in the presence of 0.2 mol fraction of water for $[\text{C}_1\text{C}_2\text{Im}][\text{OAc}]$ and $[\text{C}_1\text{C}_4\text{Im}][\text{OAc}]$ at 303 K, respectively. The absorption of carbon dioxide also decreases when the water concentration increases: a decrease of 83% in CO_2 absorption is found for $[\text{C}_1\text{C}_4\text{Im}][\text{OAc}]$ with 0.6 mol fraction of water at 303 K. Because for low concentrations of water (p.e. 0.2 mol fraction) the viscosity decreases very significantly and the carbon dioxide absorption capacity only slightly, we consider that the mixtures of acetate based ionic liquids with water can be considered as promising absorbers for CO_2 capture.

By combining experimental data with molecular simulation, we have proved that the presence of water not only renders the chemical reaction between the gas and the ionic liquid less favorable but also lowers the (physical) solubility of the gas as it competes by the same solvation sites of the ionic liquid.

Only one other study of the effect of water on the carbon dioxide absorption capacity of acetate based ionic liquids was found in the literature. Wang et al.³⁰ have reported the reversible CO_2 absorption in triethylbutylammonium acetate and its mixtures with water. Although the presence of water affects the

viscosity of the ionic liquid, it does not seem to affect the carbon dioxide absorption capacity in their case.

■ ASSOCIATED CONTENT

Supporting Information

Tables of the experimental densities (ρ) of the pure ILs and of the ILs + water between 293 and 353 K and up to 25 MPa; values of the calculated excess molar volumes V_m^E for $[\text{C}_1\text{C}_2\text{Im}][\text{OAc}] + \text{water}$ and $[\text{C}_1\text{C}_4\text{Im}][\text{OAc}] + \text{water}$ as a function of the composition, expressed in mole fraction of water, x_{water} , and as a function of temperature; experimental viscosities (η) of the pure ILs and of the mixtures (IL + water) as a function of the temperature at atmospheric pressure; calculated values of the cation–anion interaction energies for pure ionic liquids and in the mixture with CO_2 and cation– CO_2 and anion– CO_2 interactions energies; NMR chemical shifts of the different samples of ionic liquids. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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