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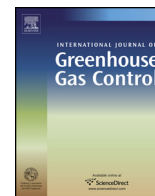


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## Absorption of carbon dioxide by ionic liquids with carboxylate anions



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## ABSTRACT

Experimental values of the absorption of carbon dioxide in two ionic liquids with carboxylate anions – the 1-butyl-3-methylimidazolium levulinate [ $C_1C_4Im][LEV]$ ] and the 1-butyl-1-methylpyrrolidinium acetate [ $C_1C_4Pyrro][OAc]$ ] – are reported as a function of temperature and at pressures close to atmospheric. Mole fraction absorption of carbon dioxide in [ $C_1C_4Im][LEV]$ ] and [ $C_1C_4Pyrro][OAc]$ ] is equal to  $0.93 \times 10^{-2}$  and  $1.10 \times 10^{-2}$  at 303.15 K and 89.2 kPa and 353.15 K and 67.1 kPa, respectively. The effect of the presence of controlled amounts of water on the absorption of carbon dioxide was measured for [ $C_1C_4Pyrro][OAc]$ . The presence of a 0.35 mole fraction of water in [ $C_1C_4Pyrro][OAc]$  decreases the viscosity of the ionic liquid phase and dramatically increases the amount of carbon dioxide absorbed, pointing toward a chemical reaction between the gas and the liquid absorbent. Increasing the amounts of water lowers the viscosity further but also the absorption capacity of the ionic liquid. Molecular dynamics simulations were used to interpret the molecular mechanism of solvation of carbon dioxide in [ $C_1C_4Pyrro][OAc]$ . Results show that carbon dioxide is solvated preferentially in the non-polar domain of the solvent, and that the  $CO_2$ –anion interactions dominate over the  $CO_2$ –cation interactions. Molecular simulations could reproduce the experimental solubility of  $CO_2$  in [ $C_1C_4Im][TFA]$  (known to be a physical process), but not in [ $C_1C_4Pyrro][OAc]$  and reinforcing the conclusion that the higher solubility of carbon dioxide in the acetate based ionic liquid can be ascribed to a chemical reaction.

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## 1. Introduction

Ionic liquids are considered as promising media for gas separations (Costa Gomes and Husson, 2010) as they are able to selectively and efficiently absorb one gas in a mixture. In particular, they have been indicated as possible alternatives for carbon dioxide removal from flue-gas streams (Ramdin et al., 2012) by chemical (Bates et al., 2002) or physical absorption (Shiflett et al., 2010). Several properties are significant for the evaluation of ionic liquids as liquid absorbers for gaseous solutes – the absorption capacity, the selectivity and the mass transfer – as they will determine the design and cost of possible industrial processes (Henley et al., 2011).

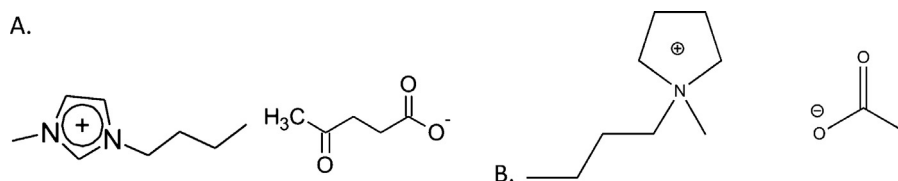
We are interested in exploring the use of ionic liquids having carboxylate anions for the absorption of carbon dioxide, as they seem

to be capable of chemically coordinating this gas hence showing a high absorption capacity (Maginn, 2005; Shiflett et al., 2008). This chemical reaction, evidenced by several authors for acetate based ionic liquids (Stevanovic et al., 2012; Gurau et al., 2011; Besnard et al., 2012), seems to be reversible and so it is possible to recycle the absorbent at a relatively low energy cost. Nevertheless, ionic liquids based on the acetate anions and on the imidazolium cations have shown some drawbacks linked to the possibility of proton transfer between the anion and the cation (due to the acidity of the hydrogen in the position  $C_2$  of the imidazolium ring). Although the equilibrium constant of this reaction seems relatively unimportant, submitting the ionic liquid to repeated pressure cycles displaces the equilibrium in the sense of the formation of acetic acid, a volatile product. This means that these ionic liquids can, to some extent, be considered as protic ionic liquids (Greaves and Brummond, 2008) and so they are in reality a liquid mixture of different molecular compounds and ions, the composition of the mixture depending on the conditions at which it has been kept.

In this work, we have studied the absorption of carbon dioxide by two ionic liquids having carboxylate anions. Firstly, we have considered the 1-butyl-1-methylpyrrolidinium acetate

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**Fig. 1.** Ionic liquids used in this work. (A) 1-Butyl-3-methylimidazolium levulinate [ $C_1C_4Im][LEV]$ ] and (B) 1-butyl-1-methylpyrrolidinium acetate [ $C_1C_4Pyrro][OAc]$ ].

[ $C_1C_4Pyrro][OAc]$ , an ionic liquid based on the acetate anion but having no acidic proton in the cation. Due to its low fluidity we have studied the absorption capacity of the mixtures of this ionic liquid with water. Secondly, we have studied an ionic liquid with a heavier carboxylic anion, the 1-butyl-3-methylimidazolium levulinate [ $C_1C_4Im][LEV]$ ], in order to check if the absorption mechanism was the same as in the case of the acetate-based imidazolium ionic liquids. We predict a considerable advantage on the use of this ionic liquid linked to the fact that, if the cation–anion proton transfer occurs, a molecular species of low volatility is formed (as levulinic acid is much less volatile than acetic acid).

In order to contribute to the understanding of the mechanisms of solvation of carbon dioxide in this family of ionic liquids, the absorption of carbon dioxide in [ $C_1C_4Pyrro][OAc]$  was compared with the solvation of  $CO_2$  by 1-butyl-3-methylimidazolium trifluoroacetate [ $C_1C_4Im][TFA]$ ]. In this last ionic liquid, the absorption of carbon dioxide is purely physical and so linked to the gas–liquid molecular interactions and to the molecular structure of the solution.

Absorption of carbon dioxide by [ $C_1C_4Im][LEV]$ ] was first studied by Yokozeki et al. (2008) and the value of absorption was found to be equal to 0.245 at 298.1 K and at 100.2 kPa, when expressed in mole fraction of gas. Absorption of gas in [ $C_1C_4Pyrro][OAc]$ ] was not yet reported but a cation–anion proton transfer has been suggested (transfer of a proton from the butyl chain of the cation to the anion) with the release of acetic acid, methyl pyrrolidine and butane (Yoshizawa-Fujita et al., 2006). It seems then that the low acidity of the protons in the alkyl side-chain in the pyrrolidinium cation is sufficient to cause a cation–anion proton transfer.

Values of absorption of carbon dioxide in [ $C_1C_4Im][TFA]$ ] are available in the literature and were found to be significantly lower than in ionic liquids based on the acetate anion and an imidazolium cation (Shiflett et al., 2009; Carvalho et al., 2009; Cabaco et al., 2011). Many explanations have been proposed to interpret this difference in solubility mainly based on the stronger  $CO_2$ – $OAc^-$  interaction than  $CO_2$ – $TFA^-$  which can be attributed to the lower electron density, and therefore lower donor ability, of the trifluoroacetate anion when compared with the acetate anion. The exact mechanism of carbon dioxide absorption by these ionic liquids is, nevertheless, still not well understood.

We investigate the absorption of carbon dioxide and its solubility in [ $C_1C_4Pyrro][OAc]$ ] and the [ $C_1C_4Im][TFA]$ ] by molecular dynamic simulations. The comparison of the molecular structures and interactions of the solutions of carbon dioxide in the two ionic liquids ([ $C_1C_4Im][TFA]$ ] and [ $C_1C_4Pyrro][OAc]$ ]) is expected to clarify the molecular mechanism of the  $CO_2$  absorption.  $^1H$  and  $^{13}C$  NMR spectroscopy provided further experimental evidence for the solvation mechanism proposed.

## 2. Materials

The [ $C_1C_4Pyrro][OAc]$ ] was purchased from Solvionic with mole fraction purities of 0.995. The [ $C_1C_4Im][LEV]$ ] samples were synthesized at the laboratory of Chemistry, Catalysis, Polymers and Processes of Lyon.

During the synthesis of 1-butyl-3-methylimidazolium levulinate, [ $C_1C_4Im][LEV]$ ], all the operations were performed in the absence of oxygen and of water and under a purified argon atmosphere using glove box (Jacomex or MBraun) or vacuum-line techniques. 1-Methylimidazole (>99%, Aldrich) was distilled prior to use. Chlorobutane (>99%, Aldrich) was used without further purification. Sodium levulinate was previously synthesized at the laboratory LMOPS, Lyon, France and was used without further purification.

For the synthesis of the 1-butyl-3-methylimidazolium chloride, [ $C_1C_4Im][Cl]$ ], the first operation consisted on the slowly addition of 1-chlorobutane (106 mL, 1.01 mol) to 1-methylimidazole (50 mL, 0.63 mol) under strong stirring. The mixture was left stirring for 2 days at 343.15 K. The hot solution was then transferred drop wise via a cannula into dry toluene (200 mL) at 273.15 K under vigorous mechanical stirring. The white precipitate formed was then filtered and washed repeatedly with dry toluene ( $3 \times 200$  mL) and dried overnight under vacuum giving a white solid (95.6 g, 0.55 mol, 87%) (Magna et al., 2003).

To obtain the final product, 1-butyl-3-methylimidazolium levulinate, [ $C_1C_4Im][LEV]$ ], sodium levulinate (32.9 g, 0.24 mol) was dissolved in water (60 mL). 1-Butyl-3-methylimidazolium chloride, [ $C_1C_4Im][Cl]$ ] (34.4 g, 0.20 mol), was dissolved in dichloromethane (170 mL). The aqueous phase was added drop wise to the organic phase under strong stirring, at 303.15 K. The mixture was left stirring during 60–70 h at 303.15 K. After separating the two phases and drying the aqueous one, a dark viscous fluid was obtained (4.2 g, 0.08 mol, 41%).

The water contents of the degassed sample were determined, with a precision of  $\pm 5$  ppm, using a coulometric Karl Fisher titrator (Mettler Toledo DL31). The ionic liquids were kept under vacuum for 72 h at 303 K before each measurement. The water content of the degassed samples was found to be 365 ppm for [ $C_1C_4Im][LEV]$ ].

The temperature of decomposition of the ionic liquids used herein (represented in Fig. 1) was determined using a modulated DSC 2920 from TA Instruments and was found to be 448 K for [ $C_1C_4Im][LEV]$ ] and 518 K for [ $C_1C_4Pyrro][OAc]$ ], respectively. The temperature of fusion for [ $C_1C_4Pyrro][OAc]$ ], an ionic liquid which is solid at room temperature, was found to be 353 K.

Mixtures of [ $C_1C_4Pyrro][OAc]$ ] and water of different compositions were prepared gravimetrically. The [ $C_1C_4Pyrro][OAc]$ ] 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 in order 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 at  $\pm 0.0001$ . The molar fraction of water in the prepared mixtures was 0.35–0.85.

The gases used for this study were used as received from the manufacturer. Carbon dioxide was obtained from AGA/Linde Gas with mole fraction purity of 0.99995.

## 3. Density measurements

Densities were measured using a U-shape vibrating-tube densimeter (Anton Paar, model DMA 512) operating in a static

mode, following the procedure described in previous publications (Jacquemin et al., 2006a, 2007). Measurements for  $[C_1C_4Im][LEV]$  and  $[C_1C_4Pyrro][OAc]$  + water were performed for pressures up to 25 MPa and at temperatures from 293 to 343 K.

The temperature in the densimeter was maintained constant to within  $\pm 0.01$  K by means of a recirculating bath equipped with a PID temperature controller (Julabo FP40-HP). For measuring the temperature, a 100  $\Omega$  platinum resistance thermometer (precision of  $\pm 0.02$  K and accuracy of  $\pm 0.04$  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  $\Omega$  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 function of temperature and pressure determined by calibration between temperatures of 293 and 343 K (and pressures of 0.1 and 25 MPa), using as calibration fluids *n*-heptane, bromobenzene and 2,4-dichlorotoluene following the recommendations by Schilling et al. (Schilling et al., 2008). Density measurements were performed in steps of 10 K. The uncertainty of the density measurements is estimated as  $10^{-4}$  g cm $^{-3}$ .

The density of the pure  $[C_1C_4Pyrro][OAc]$  was calculated using a group contribution model developed by Jacquemin et al. (Jacquemin et al., 2008a,b).

#### 4. Viscosity measurements

The dynamic viscosities of the two systems,  $[C_1C_4Im][LEV]$  previously dried under vacuum and  $[C_1C_4Pyrro][OAc]$  + water 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) and at atmospheric pressure. Before starting the measurements, the 3 mm diameter capillary tube was calibrated as a function of temperature and angle of measurement using standard viscosity oil from Cannon (N35). The overall uncertainty in the viscosity is estimated as  $\pm 1.5\%$ .

#### 5. Gas-absorption measurements

The experimental method used for the gas absorption measurements in pure ionic liquids is based on an isochoric saturation technique and has been described in previous publications (Jacquemin et al., 2006b,c). 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 constant and is directly related to the absorption of the gas in the liquid.

The quantity of ionic liquid introduced in the equilibration cell is determined gravimetrically. This quantity is equal to the amount of solvent present in the liquid solution,  $n_1^{liq}$ , as the ionic liquid does not present a measurable vapour pressure. The amount of solute present in the liquid solution,  $n_2^{liq}$  (subscripts 1 and 2 stand for solvent and solute, respectively), is calculated by the difference between two, pressure, volume, temperature, *pVT*, measurements: first when the gas is introduced in a calibrated bulb with volume  $V_{GB}$  and second after thermodynamic equilibrium is reached:

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

where  $p_{ini}$  and  $T_{ini}$  are the pressure and temperature in the first *pVT* determination, respectively and  $p_{eq}$  and  $T_{eq}$  are the pressure and temperature at the equilibrium, respectively.  $V_{tot}$  is the total volume of the equilibration cell,  $V_{liq}$  is the volume of the liquid

solution and  $Z_2$  is the compression factor for the pure gas. The solubility can then be expressed in mole fraction, which is calculated from the following equation:

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

where  $n_2^{liq}$  is the amount of solute dissolved in the ionic liquid and  $n_1^{liq} = n_1^{tot}$  is the total amount of ionic liquid. We consider that the volume of the ionic liquid does not change when the gas is solubilized and so the volume of the liquid solution is equal to the molar volume of the pure ionic liquid.

A second experimental method is used for the gas absorption measurements in the mixtures ionic liquid + water. This one is also based on an isochoric saturation technique and has been described in previous publications (Hong et al., 2006; Husson et al., 2010).

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.

The gas absorption can be expressed as mole fraction of the gas in the liquid mixture,  $x_2$  calculated through:

$$x_2 = \frac{n_2^{liq}}{n_{solv}^{liq} + n_2^{liq}} \quad (3)$$

where  $n_{solv}^{liq} = n_1^{liq} + n_3^{liq}$  is the amount of solvent in the liquid phase with  $n_1^{liq}$  being the amount of ionic liquid which due to its negligible vapour pressure is equal to the total quantity of ionic liquid introduced in the equilibrium cell and  $n_3^{liq}$  the amount of water in the liquid solution.

#### 6. Molecular simulations

The microscopic structures and interactions in the mixtures of ionic liquids ( $[C_1C_4Im][TFA]$  and  $[C_1C_4Pyrro][OAc]$ ) and carbon dioxide were investigated by molecular dynamics simulations. Ionic liquids were represented by an all-atom force field, which is based on the AMBER/OPLS-AA framework (Smith and Todorov, 2007; Jorgensen et al., 1996). For imidazolium cation force field parameters were developed specifically (Canongia Lopes et al., 2004), meanwhile for the pyrrolidinium cation they were retrieved from the force field for amines (Rizzo and Jorgensen, 1999). Acetate (Jorgensen et al., 1996; Yu et al., 2004) and trifluoroacetate (Liu et al., 2006) were represented with the potential models existing in the literature, whereas the potential model of Harris and Yung (Mallet et al., 2008) was used for carbon dioxide.

The ionic liquids  $[C_1C_4Im][TFA]$  and  $[C_1C_4Pyrro][OAc]$  were simulated in periodic cubic boxes containing 127 ion pairs, using the molecular dynamics method implemented in the DL.POLY package (Smith and Todorov, 2007). 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 attained, simulations runs of 1 ns were performed, with an explicit cutoff distance of 16 Å for non-bonded 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 carbon dioxide 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 carbon dioxide.

The chemical potentials of carbon dioxide at 373 K in the two ionic liquids were calculated in a two-step procedure, as already described by [Almantariotis et al. \(2010\)](#). First, for carbon dioxide, 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  $\sigma_O$  and  $\sigma_C$ . The resulting molecule is small enough so that its chemical potential can be calculated using the Widom test-particle insertion method with efficient statistics (100,000 insertions into each of 5000 stored configurations of pure ionic liquids). Second, a stepwise finite difference thermodynamic integration procedure 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 expression in the  $NpT$  ensemble using a three-point formula with increments of  $2 \times 10^{-3}$ .

## 7. NMR measurements

$^1\text{H}$  and  $^{13}\text{C}$  NMR data were collected at 298.15 K or 313.15 K on a Bruker AC 400 MHz spectrometer. Spectra of  $[\text{C}_1\text{C}_4\text{Im}][\text{LEV}]$  and  $[\text{C}_1\text{C}_4\text{Pyrro}][\text{OAc}]$  samples were recorded in solution using acetone- $d_6$  and  $\text{CDCl}_3$  as solvents, respectively. A coaxial capillary tube loaded with DMSO- $d_6$  was inserted into the 5 mm NMR tube filled with the  $[\text{C}_1\text{C}_4\text{Pyrro}][\text{OAc}]$  + water sample to avoid any contact between the deuterated solvent and the analyzed mixture. 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  $^1\text{H}$  NMR external reference at 2.5 ppm.

## 8. Results and discussion

The experimental values obtained for the density of  $[\text{C}_1\text{C}_4\text{Im}][\text{LEV}]$  and  $[\text{C}_1\text{C}_4\text{Pyrro}][\text{OAc}]$  + water as a function of pressure and at temperatures from 293 to 353 K are reported in Table S2 of Supplementary information. The values of density at atmospheric pressure (necessary for the calculation of the gas solubility) were adjusted to linear functions of temperature:

$$\rho_{[\text{C}_1\text{C}_4\text{Im}][\text{LEV}]} (\text{kg m}^{-3}) = 1281.7 - 0.6112 (T/\text{K}) \quad (4)$$

$$\rho_{[\text{C}_1\text{C}_4\text{Pyrro}][\text{OAc}]+\text{H}_2\text{O}(\chi=0.4)} (\text{kg m}^{-3}) = 1186.3 - 0.5669 (T/\text{K}) \quad (5)$$

$$\rho_{[\text{C}_1\text{C}_4\text{Pyrro}][\text{OAc}]+\text{H}_2\text{O}(\chi=0.6)} (\text{kg m}^{-3}) = 1198.7 - 0.5858 (T/\text{K}) \quad (6)$$

$$\rho_{[\text{C}_1\text{C}_4\text{Pyrro}][\text{OAc}]+\text{H}_2\text{O}(\chi=0.8)} (\text{kg m}^{-3}) = 1233.0 - 0.6689 (T/\text{K}) \quad (7)$$

the standard deviation of the fits is always better than 0.1%. The density of  $[\text{C}_1\text{C}_4\text{Im}][\text{LEV}]$  was compared to both the acetate based ionic liquids with imidazolium cations studied in our previous work ([Stevanovic et al., 2012](#)) and was found to be lower than  $[\text{C}_1\text{C}_2\text{Im}][\text{OAc}]$  and higher than  $[\text{C}_1\text{C}_4\text{Im}][\text{OAc}]$ . Mixtures of  $[\text{C}_1\text{C}_4\text{Pyrro}][\text{OAc}]$  + water present, as expected, lower densities than mixtures of  $[\text{C}_1\text{C}_2\text{Im}][\text{OAc}]$  + water or  $[\text{C}_1\text{C}_4\text{Im}][\text{OAc}]$  + water ([Stevanovic et al., 2012](#)) for an equivalent mole fraction of water. The density increases when the quantity of water increases as it was observed previously for the systems  $[\text{C}_1\text{C}_2\text{Im}][\text{OAc}]$  + water and

$[\text{C}_1\text{C}_4\text{Im}][\text{OAc}]$  + water. The densities measured herein as a function of pressure were correlated using the Tait equation:

$$\rho(T, P) = \left[ \frac{\rho^0(T, p^0)}{1 - C \ln((B(T) + p)/(B(T) + p^0))} \right] \quad (8)$$

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  $B(T)$  a polynomial defined by:

$$B(T) = \sum_{i=0}^2 B_i(T)^i \quad (9)$$

The parameters found for the present data are listed in Table 1.

The dynamic viscosity was measured for the systems  $[\text{C}_1\text{C}_4\text{Im}][\text{LEV}]$  and  $[\text{C}_1\text{C}_4\text{Pyrro}][\text{OAc}]$  + water, and is listed in Table 2 as a function of temperature from 293 to 373 K. The Vogel–Fulcher–Tamman (VFT) equation was used to correlate the experimental viscosities as a function of temperature:

$$\eta_{[\text{C}_1\text{C}_4\text{Im}][\text{LEV}]} (\text{mPa s}) = (2.07 \times 10^{-3}) (T/\text{K})^{1/2} \exp \left[ \frac{1197}{(T/\text{K}) - 190} \right] \quad (10)$$

$$\eta_{[\text{C}_1\text{C}_4\text{Pyrro}][\text{OAc}]+\text{H}_2\text{O}(\chi=0.4)} (\text{mPa s}) = (2.54 \times 10^{-3}) (T/\text{K})^{1/2} \times \exp \left[ \frac{985}{(T/\text{K}) - 183} \right] \quad (11)$$

$$\eta_{[\text{C}_1\text{C}_4\text{Pyrro}][\text{OAc}]+\text{H}_2\text{O}(\chi=0.6)} (\text{mPa s}) = (1.01 \times 10^{-3}) (T/\text{K})^{1/2} \times \exp \left[ \frac{1173}{(T/\text{K}) - 164} \right] \quad (12)$$

$$\eta_{[\text{C}_1\text{C}_4\text{Pyrro}][\text{OAc}]+\text{H}_2\text{O}(\chi=0.8)} (\text{mPa s}) = (1.97 \times 10^{-3}) (T/\text{K})^{1/2} \times \exp \left[ \frac{868}{(T/\text{K}) - 177} \right] \quad (13)$$

As expected, the viscosities of the ionic liquids depend both on the nature of the anion and the cation. Values of viscosity, at 303.15 K, of  $[\text{C}_1\text{C}_4\text{Im}][\text{LEV}]$  are equal to 1441 mPa s, so 3.6 and 13.7 times higher than values of  $[\text{C}_1\text{C}_4\text{Im}][\text{OAc}]$  and  $[\text{C}_1\text{C}_2\text{Im}][\text{OAc}]$ , respectively ([Stevanovic et al., 2012](#)). The system  $[\text{C}_1\text{C}_4\text{Pyrro}][\text{OAc}]$  + water (for a mole fraction of water equal to 0.4) presents a viscosity of 330.4 mPa s at 293.15 K, a value 1.1 and 3.7 times higher than those of  $[\text{C}_1\text{C}_4\text{Im}][\text{OAc}]$  + water and  $[\text{C}_1\text{C}_2\text{Im}][\text{OAc}]$  + water. The viscosity of the mixture  $[\text{C}_1\text{C}_4\text{Pyrro}][\text{OAc}]$  + water decreases with the addition of water, the viscosity, for a mole fraction of water equal to 0.8 being as low as 45.43 mPa s at 293 K, 2.1 and 7.3 times lower than for mole fractions of water equal to 0.6 and 0.4, respectively.

For both  $[\text{C}_1\text{C}_4\text{Im}][\text{LEV}]$ ,  $[\text{C}_1\text{C}_4\text{Pyrro}][\text{OAc}]$  and for the mixtures of  $[\text{C}_1\text{C}_4\text{Pyrro}][\text{OAc}]$  + water, multiple experimental data points on the absorption of carbon dioxide were obtained in the temperature interval between 303.15 K and 343.15 K in steps of approximately 10 K. The pure ionic liquid  $[\text{C}_1\text{C}_4\text{Pyrro}][\text{OAc}]$  was only studied at 353 K. For the  $[\text{C}_1\text{C}_4\text{Pyrro}][\text{OAc}]$  + water mixtures, measurements of the  $\text{CO}_2$  absorption were made at 303.15 and 313.15 K for mole fractions of water equal to 0.35, 0.6 and 0.85. The experimental values are reported in Table 3.

The absorption of carbon dioxide in pure  $[\text{C}_1\text{C}_4\text{Im}][\text{LEV}]$  is represented in Fig. 2 as a function of pressure for the different temperatures studied. The gas is absorbed up to a  $0.93 \times 10^{-2}$  mole fraction at 303.15 K and 67.1 kPa. Absorption of carbon dioxide in  $[\text{C}_1\text{C}_4\text{Im}][\text{LEV}]$  increases when the partial pressure of gas increases



**Table 1**

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 353 K). AAD indicated the percent average absolute deviation of the fit.

Ionic liquid	$10^2 \times C$	$B_0$ (MPa)	$B_1$ (MPa K <sup>-1</sup> )	$10^3 \times B_2$ (MPa K <sup>-2</sup> )	AAD (%)
[C <sub>1</sub> C <sub>4</sub> Pyrro][OAc] + water ( $x_{\text{water}} = 0.4077$ )	-2.137	+278.999	-2.339	+3.808	0.016
[C <sub>1</sub> C <sub>4</sub> Pyrro][OAc] + water ( $x_{\text{water}} = 0.6028$ )	-1.527	-107.704	+0.136	+0.007	0.016
[C <sub>1</sub> C <sub>4</sub> Pyrro][OAc] + water ( $x_{\text{water}} = 0.8027$ )	-2.005	-136.864	+0.230	-0.158	0.020

**Table 2**

Experimental dynamic viscosities,  $\eta$ , of the ionic liquids [C<sub>1</sub>C<sub>4</sub>Im][LEV] and [C<sub>1</sub>C<sub>4</sub>Pyrro][OAc] + water mixtures as a function of temperature at atmospheric pressure.

$T$ (K)	$\eta^{\text{exp}}$ (mPa s)	$\delta$ (%)	$T$ (K)	$\eta^{\text{exp}}$ (mPa s)	$\delta$ (%)
<b>[C<sub>1</sub>C<sub>4</sub>Im][LEV]</b>			<b>[C<sub>1</sub>C<sub>4</sub>Pyrro][OAc] + water (<math>x_{\text{water}} = 0.4077</math>)</b>		
303.15	1441	+0.0	293.15	330.4	+0.0
313.15	619.6	-0.2	303.15	160.12	-0.2
323.15	300.2	+0.7	313.15	86.23	+0.4
333.15	165.0	-0.9	323.15	51.09	+0.4
			333.15	32.67	-0.2
			343.15	22.10	-0.5
			353.15	15.73	-1.2
			363.15	11.52	-0.8
			373.15	8.644	+0.6
<b>[C<sub>1</sub>C<sub>4</sub>Pyrro][OAc] + water (<math>x_{\text{water}} = 0.6028</math>)</b>			<b>[C<sub>1</sub>C<sub>4</sub>Pyrro][OAc] + water (<math>x_{\text{water}} = 0.8027</math>)</b>		
293.15	152.7	+0.1	293.15	45.43	+0.0
303.15	81.31	-0.6	303.15	26.05	+0.2
313.15	45.97	+1.5	313.15	16.32	-0.2
323.15	29.13	-0.7	323.15	10.90	-0.3
333.15	18.89	+0.5	333.15	7.665	-0.2
343.15	13.23	-1.1			
353.15	9.512	-1.3			

and when the temperature decreases. It is observed in Fig. 2 that the carbon dioxide absorption progress linearly with the pressure for all temperatures studied, indicating that Henry's law is verified and that carbon dioxide is only physically dissolved in that case. Compared to the imidazolium acetate ionic liquids studied previously by our research group (Stevanovic et al., 2012), which are able to both chemically and physically absorb carbon dioxide, absorption in the [C<sub>1</sub>C<sub>4</sub>Im][LEV] was found to be one order of magnitude lower.

The results presented herein on the absorption of CO<sub>2</sub> in the mixtures [C<sub>1</sub>C<sub>4</sub>Pyrro][OAc] + water are presented in Fig. 3. The absorption of carbon dioxide decreases when the mole fraction of water increases, the absorbed quantity of gas varying from  $10.9 \times 10^{-2}$  to  $0.9 \times 10^{-2}$  at 303.15 K and 9.4 kPa and 303.15 K and 63.8 kPa for water mole fractions equal to 0.35 and 0.85, respectively.

In order to compare the absorption of carbon dioxide in all studied systems, experimental data were extrapolated linearly to

**Table 3**

Experimental values of carbon dioxide in [C<sub>1</sub>C<sub>4</sub>Pyrro][LEV], [C<sub>1</sub>C<sub>4</sub>Pyrro][OAc] and [C<sub>1</sub>C<sub>4</sub>Pyrro][OAc] + water expressed as carbon dioxide mole fraction,  $x_2$ ,  $p$  is the experimental equilibrium pressure,  $K_H$  the Henry's law constants and dev is the estimation of the precision of the experimental data.

$T$ (K)	$p$ (10 <sup>2</sup> Pa)	$x_2^{\text{exp}}$	$K_H$ (10 <sup>5</sup> Pa)	$x_2$ (10 <sup>-2</sup> )	dev (%)
<b>[C<sub>1</sub>C<sub>4</sub>Pyrro][LEV]</b>					
303.16	670.78	0.0093	72.2	1.38	-0.1
313.28	633.60	0.0078	81.4	1.22	+1.9
313.28	691.26	0.0083	82.9	1.20	+0.1
313.31	696.99	0.0082	84.4	1.18	-1.7
323.32	658.57	0.0066	99.5	1.00	+0.1
323.34	717.90	0.0073	97.4	1.02	+2.3
323.34	723.84	0.0070	102.5	0.97	-2.7
333.35	683.20	0.0056	122.3	0.82	+1.4
333.36	750.17	0.0060	124.1	0.80	+0.0
333.41	747.00	0.0059	125.7	0.79	-1.2
<b>[C<sub>1</sub>C<sub>4</sub>Pyrro][OAc]</b>					
353.55	891.8	0.011	84.5	0.012	
353.18	434.26	0.005	88.8	0.011	
<b>[C<sub>1</sub>C<sub>4</sub>Pyrro][OAc] + water (<math>x_{\text{water}} = 0.35</math>)</b>					
303.34	94.00	0.109			
313.35	147.00	0.103			
<b>[C<sub>1</sub>C<sub>4</sub>Pyrro][OAc] + water (<math>x_{\text{water}} = 0.6</math>)</b>					
303.32	154.00	0.057			
313.72	221.00	0.053			
<b>[C<sub>1</sub>C<sub>4</sub>Pyrro][OAc] + water (<math>x_{\text{water}} = 0.85</math>)</b>					
303.35	638	0.009			
313.36	709	0.008			

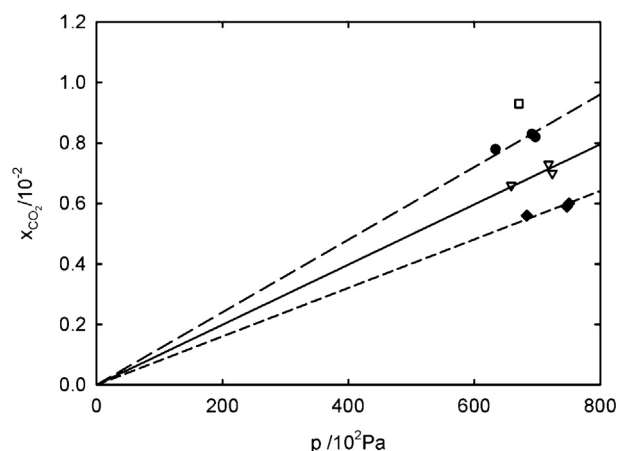


Fig. 2. Mole fraction absorption of carbon dioxide in the  $[C_1C_4Im][LEV]$  as a function of the temperature: ( $\square$ ), 303.15 K; ( $\bullet$ ), 313.15 K; ( $\nabla$ ), 323.15 K; and ( $\blacklozenge$ ), 333.15 K.

353.15 K for all systems except for  $[C_1C_4Pyrro][OAc]$ . In that case, it is assumed that the pressure differences do not affect significantly the values of absorption of carbon dioxide in the different systems studied and so they can be compared at the different temperatures studied. Results are presented in Fig. 4. The absorption of carbon dioxide in the mixtures  $[C_1C_4Pyrro][OAc]$  + water for water mole fractions equal to 0.35 and 0.60 is one order of magnitude higher than in the three other systems. Values are comparable to these found for the systems  $[C_1C_2Im][OAc]$  + water and  $[C_1C_4Im][OAc]$  + water studied previously (Stevanovic et al., 2012). It implies that the system  $[C_1C_4Pyrro][OAc]$  + water can react chemically with carbon dioxide when the amount of water present is sufficient. Absorption of carbon dioxide in pure  $[C_1C_4Pyrro][OAc]$  was found to be lower than in mixtures of  $[C_1C_4Pyrro][OAc]$  + water for water mole fraction equal to 0.35 and 0.60. Absorption of carbon dioxide in pure  $[C_1C_4Pyrro][OAc]$  is also one order of magnitude lower than in  $[C_1C_2Im][OAc]$  and  $[C_1C_4Im][OAc]$ . It appears that pure  $[C_1C_4Pyrro][OAc]$  is only able to physically absorb carbon dioxide and the mechanism of chemical reaction between  $[C_1C_4Pyrro][OAc]$  + water and carbon dioxide is different from that of the systems with the ionic liquids  $[C_1C_2Im][OAc]$  and  $[C_1C_4Im][OAc]$ , these two ionic liquids reacting chemically with carbon dioxide with and without water present.

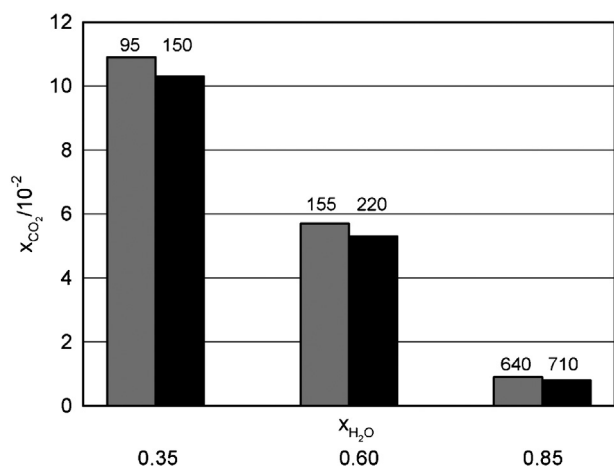


Fig. 3. Mole fraction absorption of carbon dioxide in the systems  $[C_1C_4Pyrro][OAc]$  + water as a function of the temperature: ( $\blacksquare$ ) 303.15 K and ( $\blacksquare$ ) 313.15 K. The number above each bar represents the equilibrium pressure in  $10^2$  Pa.

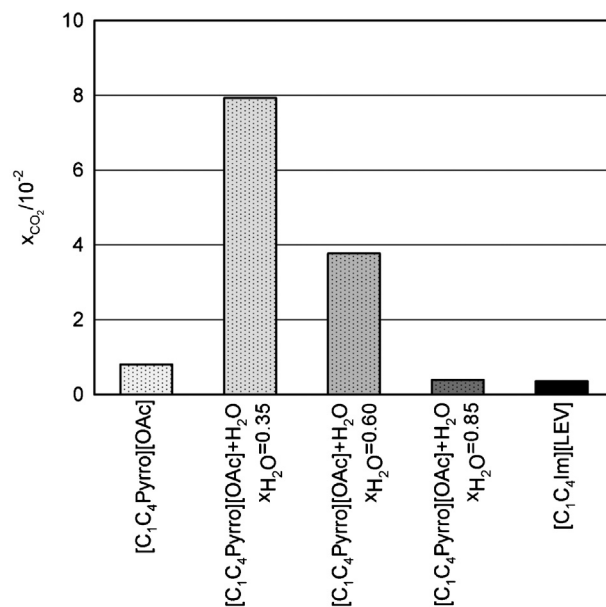


Fig. 4. Mole fraction absorption of carbon dioxide in the ionic liquids and ionic liquids + water systems studied herein, at 353.15 K: ( $\square$ ),  $[C_1C_4Pyrro][OAc]$ ; ( $\blacksquare$ ),  $[C_1C_4Pyrro][OAc]$  + water ( $x_{H_2O} = 0.35$ ); ( $\blacksquare$ ),  $[C_1C_4Pyrro][OAc]$  + water ( $x_{H_2O} = 0.60$ ); ( $\blacksquare$ ),  $[C_1C_4Pyrro][OAc]$  + water ( $x_{H_2O} = 0.80$ ); ( $\blacksquare$ ),  $[C_1C_4Im][LEV]$ . Values are obtained by extrapolating linearly experimental data to 353.15 K for all systems except for  $[C_1C_4Pyrro][OAc]$ .

Absorption of carbon dioxide in  $[C_1C_4Im][LEV]$  is comparable to the absorption in pure  $[C_1C_4Pyrro][OAc]$  or in the mixture  $[C_1C_4Pyrro][OAc]$  + water for water molar fraction equal to 0.85.

In order to explain the difference in carbon dioxide absorption in the studied ionic liquids as well as the effect of water on the microscopic structure of the pure ionic liquids and in their mixtures with carbon dioxide, we have used molecular dynamics simulations. Two ionic liquids were considered, the 1-butyl-3-methyl trifluoroacetate  $[C_1C_4Im][TFA]$  and the  $[C_1C_4Pyrro][OAc]$ . In the first case, it is well known that the absorption of  $CO_2$  is purely physical (Carvalho et al., 2009) and we expect that the comparison between the behaviors of the two ionic liquids will contribute to the understanding of the mechanisms of gas absorption in  $[C_1C_4Pyrro][OAc]$ .

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 Fig. 5.

Initially, the microscopic structure of the pure ionic liquids  $[C_1C_4Im][TFA]$  and  $[C_1C_4Pyrro][OAc]$ , was perceived by the analysis of the site-site radial distribution function – probability of finding two selected atomic sites at a certain distance is represented in Fig. 6 for several representative atomic sites in the pure ionic liquids. From the plots in Fig. 6 it can be observed that in the imidazolium ionic liquid, the cation and the anion interact preferentially through the  $H_{2Im}$  hydrogen of the  $C_1C_4Im^+$  and the  $O_{TFA}$  oxygen of  $TFA^-$ , where negative charge is concentrated. The oxygen atom of the anion  $TFA^-$  is also found with significant probability in the vicinity of the nitrogen  $N_{Im}$  of imidazolium cation. This result was expected and is consistent with other imidazolium liquids reported in literature.

Likewise, in the pyrrolidinium ionic liquid the interaction between the partially positive  $N_{Pyrro}$  (as well as  $C1_{Pyrro}$ ) and the oxygen of the  $OAc^-$  are of the most importance. The other interaction sites between the cation and the anion are present, but less expressed. However, the distance between these cation and anion atomic sites are shorter for the imidazolium ionic liquid (Stevanovic et al., 2012) than for the pyrrolidinium based one, in accordance

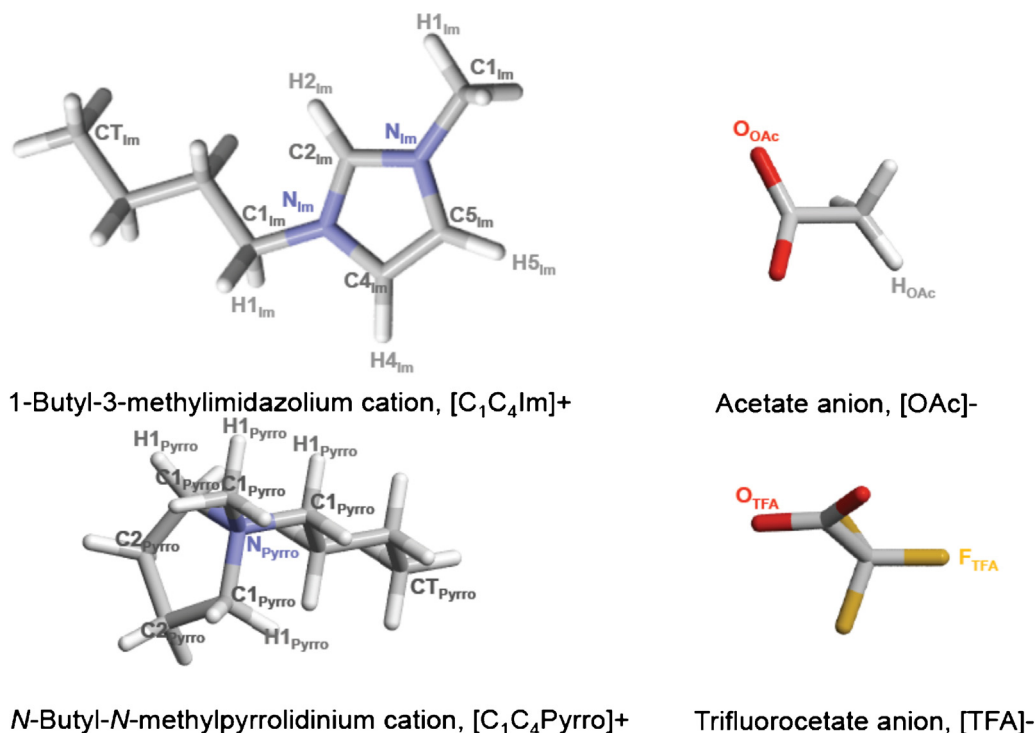


Fig. 5. Atom labeling in 1-butyl-3-methylimidazolium and N-butyl-N-methylpyrrolidinium cations and acetate and trifluoroacetate anions.

with accessibility and acidity of imidazolium  $H2_{Im}$  and therefore stronger acid-base interactions in the former case.

The molecular simulation results indicate that the presence of carbon dioxide does not affect the most significant interaction sites present in the pure ionic liquids. This can be also deduced from the plots in Fig. 6, where solid lines refer to the pure ionic liquid and dotted lines to the mixture ( $CO_2$  + ionic liquid). In the  $[C_1C_4Im][TFA]$ , both peaks, one corresponding to the interactions of the terminal carbon atoms of the alkyl chain of the cation  $CT_{Im}$  and the oxygen of  $CO_2$  ( $O_{CO_2}$ ), and the other between the oxygen of the anion ( $O_{OAc}$ ) and carbon of carbon dioxide ( $C_{CO_2}$ ) are of significant importance. This indicates that carbon dioxide is solvated preferentially in the vicinity of the anion and in the non-polar region of imidazolium ionic liquids. Carbon dioxide was found to be solvated similarly in  $[C_1C_4Im][TFA]$  and in  $[C_1C_4Im][OAc]$  as demonstrated in our previous work (Stevanovic et al., 2012). Analogously in  $[C_1C_4Pyrro][OAc]$ , there is a high probability of finding carbon dioxide near oxygen of  $OAc^-$  and  $CT_{Pyrro}$ . No significant difference in solvation of carbon dioxide in both types of ionic

liquid, imidazolium (Stevanovic et al., 2012) and pyrrolidinium, was observed.

These structural features of the mixture of ( $CO_2$  + ionic liquid) can be perceived and confirmed also in 3 dimensional spatial distribution functions in Fig. 7. In Fig. 7a and d is represented the distribution of the local density of the cationic and the anionic atomic sites around carbon dioxide in  $[C_1C_4Im][TFA]$  and  $[C_1C_4Pyrro][OAc]$ , respectively. As already deduced from the radial distribution functions, for the two ionic liquids studied the spatial distribution function shows that carbon dioxide is mainly solvated by the anion ( $O_{OAc}$  or  $O_{TFA}$ , red) and the terminal carbon atoms of  $CT_{Im}$  or  $CT_{Pyrro}$  (gray). Looking at distribution of atomic density around acetate or trifluoroacetate (Fig. 7b and e) is expected to find  $C_{CO_2}$  (cyan) and  $C2_{Im}$  or  $N_{Pyrro}$  (blue) interacting with the oxygen atoms of the anion. From Fig. 7c and f we can observe that the presence of the oxygen of carbon dioxide around the cation is minor.

Calculations of the free energy of solvation of carbon dioxide in  $[C_1C_4Im][TFA]$  and  $[C_1C_4Pyrro][OAc]$  at 373 K give access

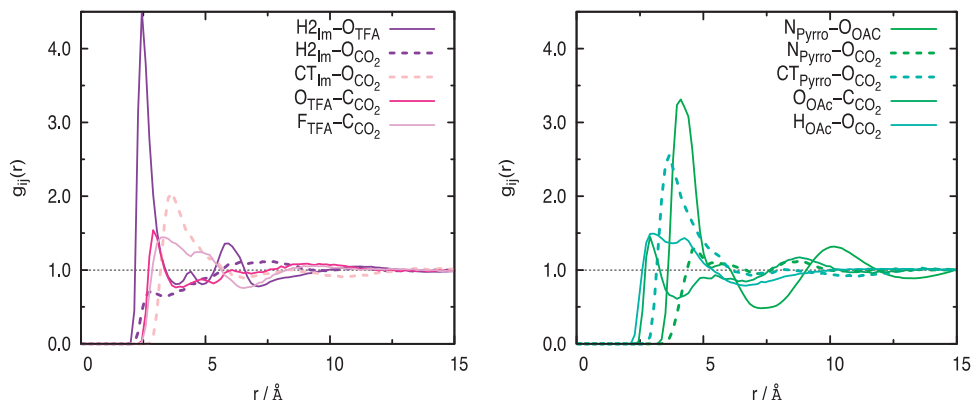
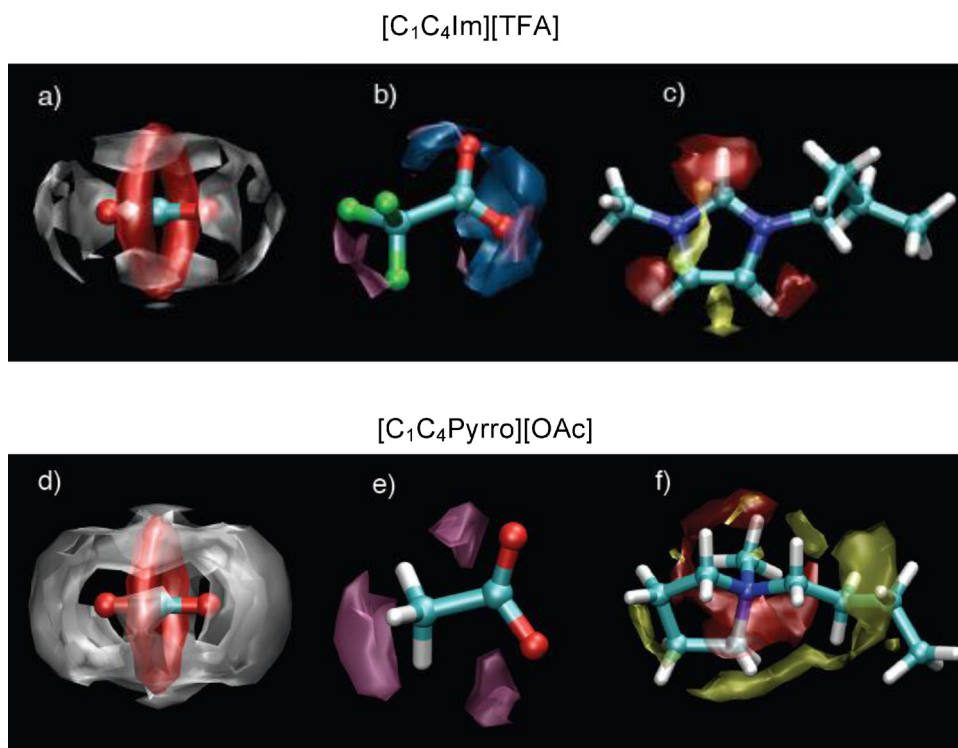


Fig. 6. Preferential interaction sites between ionic liquid and carbon dioxide. On the left-hand side:  $[C_1C_4Im][TFA]$  and on the right-hand side:  $[C_1C_4Pyrro][OAc]$ .





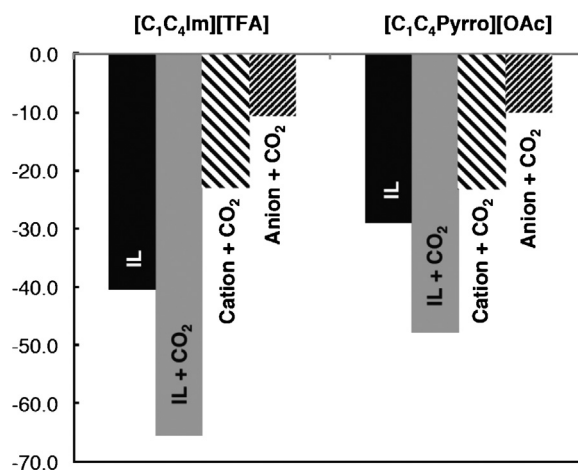
**Fig. 7.** Spatial distribution functions between selected atomic sites in  $[C_1C_4Im][TFA]$ ,  $[C_1C_4Pyrro][OAc]$  and carbon dioxide. (a and d) Around carbon dioxide: iso-surface corresponding to a local density of twice the average density of the  $CT_{Im}$  or  $CT_{pyrro}$  (gray) and of the  $O_{OAc}$  or  $O_{TFA}$  (red). (b and e) Around  $OAc^-$  or  $TFA^-$ . Iso-surface corresponding to a local density of 3-times the average density of the  $H2_{Im}$  (blue) and  $CCO_2$  (purple). Figure c and f: around  $C_1C_4Im^+$  or  $C_1C_4Pyrro^+$ . Iso-surface corresponding to a local density of twice the average density of the  $O_{CO_2}$  (yellow) and of 4-times of the  $O_{OAc}$  or  $O_{TFA}$  (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

to the Henry's law constants,  $K_H$ , that allow us to calculate the gas solubility at a partial pressure of gas  $p_{gas} = 1$  bar. The results are summarized in Table 4, where a comparison with the experimental values is also reported. The results of the simulations agree with the experiments for  $[C_1C_4Im][TFA]$ . Whereas, simulations made previously (Stevanovic et al., 2012) did not reproduce experimental trends for  $[C_1C_4Im][OAc]$ . Solubilities calculated for  $[C_1C_4Im][TFA]$  were found to be the same than for  $[C_1C_4Im][OAc]$  studied previously (Stevanovic et al., 2012), within the incertitude of simulations. This implies that the nature of the cation does not affect the solubility of carbon dioxide significantly.

The disparity in the solubility of carbon dioxide in the studied ionic liquids can be ascribed either to the structural difference in ionic liquids or/and different strength and nature of interactions. As the structural analysis showed no significant difference between  $[C_1C_4Im][TFA]$  and  $[C_1C_4Pyrro][OAc]$ , the strength of interactions  $CO_2$ -solute must be of significant importance.

In order to explain such a difference in the solubility of carbon dioxide the simulation results were examined in detail. The overall system configuration energy of the mixtures ( $CO_2$  + ionic liquid) was decomposed to the energy between each pair of species,

represented in Fig. 8. The overall cation–anion interactions are stronger for the pair  $[C_1C_4Im]^+[TFA]^-$  than for  $[C_1C_4Pyrro]^+[OAc]^-$ . These observations were already made from the analysis of the site-site radial distribution functions in Fig. 6. The presence of carbon dioxide increases the cation–anion interactions thus favoring the ion pair association. No significant difference in the interaction energy between carbon dioxide and cation/anion was observed for the two ionic liquids. Surprisingly, carbon dioxide was found to have a more favorable energy of interaction with the cation than with the anion of the ionic liquids.



**Fig. 8.** Comparison of the cation–anion, cation– $CO_2$  and anion– $CO_2$  interaction energies in pure ionic liquids and in the mixtures with carbon dioxide. The values are normalized by a number of the amount of substance of ionic liquid in moles. In the mixtures  $IL + CO_2$  interaction energies are normalized by number of  $CO_2$  molecules. Exact values are reported in Table S1 (ESI).

**Table 4**

Comparison of experimental solubilities of carbon dioxide in ionic liquids and calculated by molecular dynamic simulations expressed in mole fraction:  $[C_1C_4Im][TFA]$  and  $[C_1C_4Pyrro][OAc]$ .

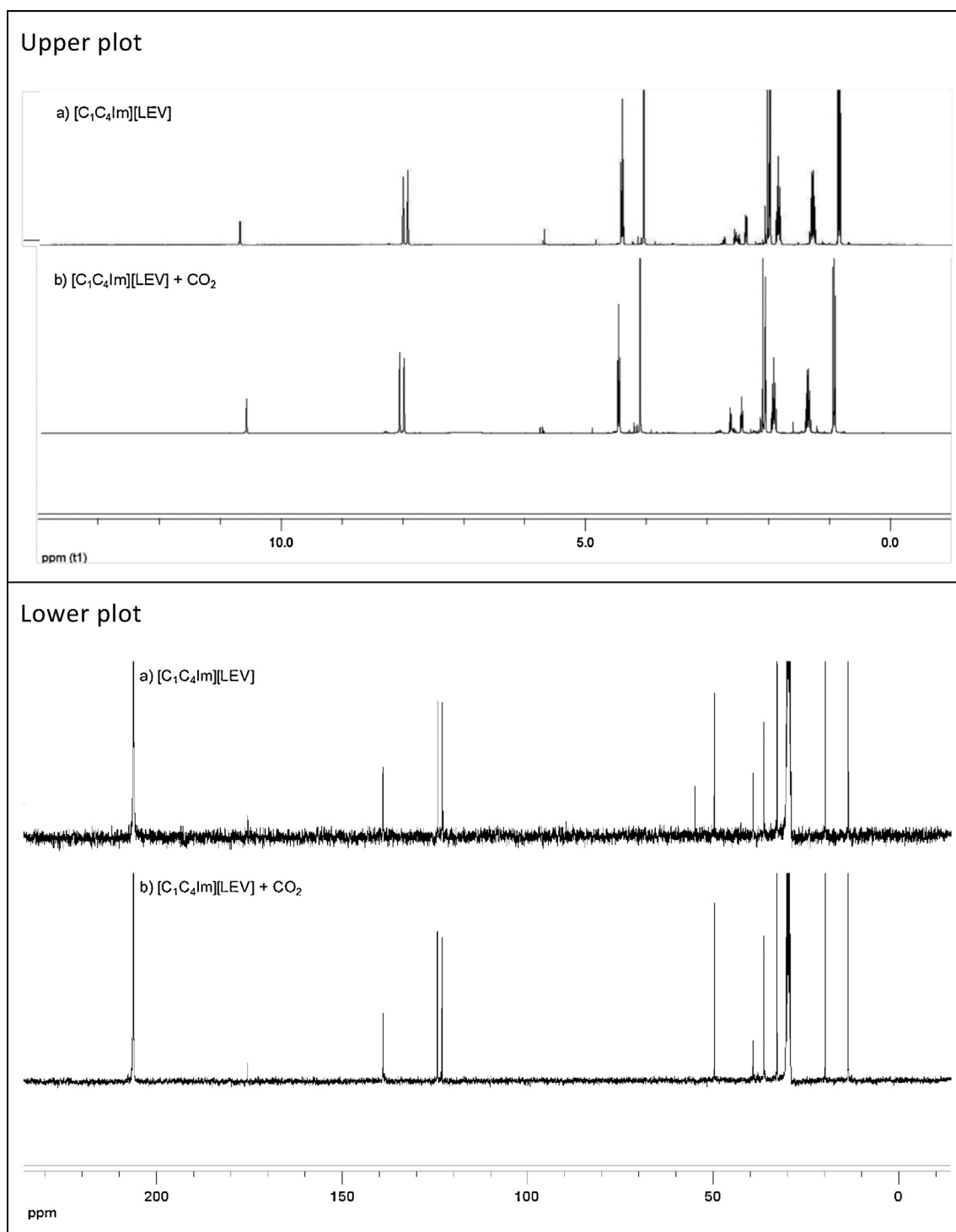
Ionic liquid	Calculated, $x_{sim}^a$	Experimental, $x_{exp}$
$[C_1C_4Im][TFA]$	$0.004 \pm 0.001$	$0.005^c$
$[C_1C_4Pyrro][OAc]$	$0.002 \pm 0.001^b$	$0.012^d$

<sup>a</sup> 373 K.

<sup>b</sup> Extrapolated to 373 K.

<sup>c</sup> 298 K.

<sup>d</sup> 353 K.

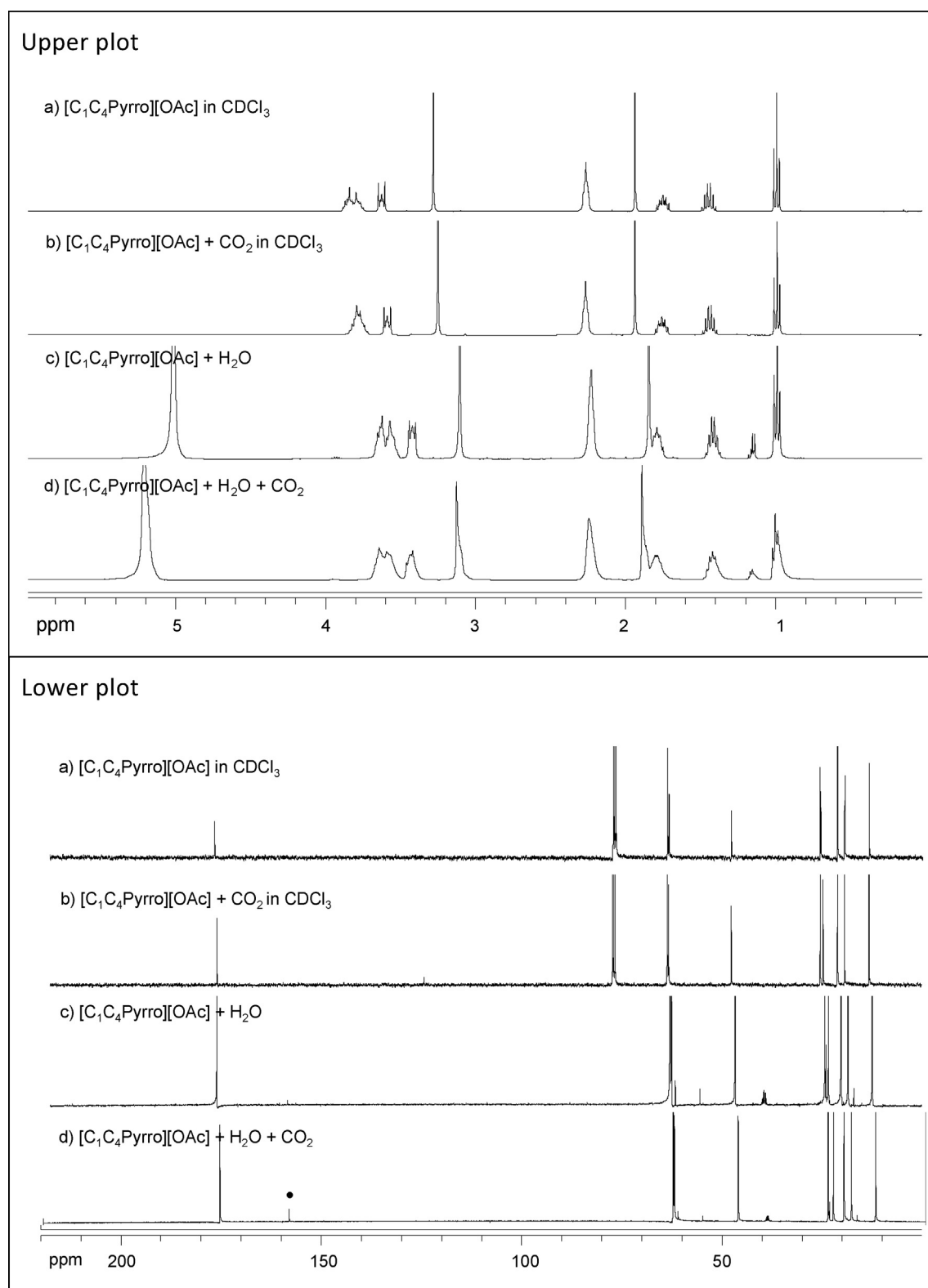


**Fig. 9.**  $^1H$  NMR (upper plot) and  $^{13}C$  NMR spectra (lower plot) of various samples of  $[C_1C_4Im][LEV]$  in acetone- $d_6$ .

Molecular simulation reproduces the correct carbon dioxide solubility in  $[C_1C_4Im][TFA]$ , but not in  $[C_1C_4Pyrro][OAc]$ , meaning that in the later case some mechanism of gas absorption other than physical absorption (the only implemented in the molecular simulations), prevails.

To obtain further information about the interaction of carbon dioxide and the ionic liquids, which could help to interpret the trends of the experimental values of carbon dioxide absorption,  $^1H$  and  $^{13}C$  NMR spectra of pure and carbon dioxide-saturated ionic liquids were recorded at atmospheric pressure. Fig. 9 shows NMR spectra of pure  $[C_1C_4Im][LEV]$  and  $[C_1C_4Im][LEV]$  saturated

with carbon dioxide. Comparison of the spectra (a) and (b) in the upper and lower plots of Fig. 9 shows no noticeable changes neither in  $^1H$  or in  $^{13}C$  chemical shifts upon saturation of the ionic liquid with carbon dioxide. This observation proves that no chemical reaction is involved in the carbon dioxide absorption by  $[C_1C_4Im][LEV]$ , in agreement with the lower values of absorption found compared to the imidazolium acetate based ionic liquids (Stevanovic et al., 2012). Furthermore, the small peak in spectrum (b) of the lower plot in Fig. 9 at around 175 ppm is the clear signature of free  $CO_2$  in solution (Tomizaki et al., 2010).



**Fig. 10.**  $^1\text{H}$  NMR spectra (upper plot) and  $^{13}\text{C}$  NMR spectra (lower plot) of various samples of  $[\text{C}_1\text{C}_4\text{Pyrro}][\text{OAc}]$ . Samples (a) and (b) were recorded in solution in  $\text{CDCl}_3$  while samples (c) and (d) were recorded in a coaxial tube loaded with  $\text{DMSO}-d_6$ .

To obtain further insight into the mechanism of carbon dioxide absorption by pyrrolidinium acetate,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of pure  $[\text{C}_1\text{C}_4\text{Pyrro}][\text{OAc}]$ , of the  $[\text{C}_1\text{C}_4\text{Pyrro}][\text{OAc}] + \text{H}_2\text{O}$  mixtures and of the solutions containing  $\text{CO}_2$  in these liquids were recorded and are depicted in Fig. 10. Since  $[\text{C}_1\text{C}_4\text{Pyrro}][\text{OAc}]$  is a solid at

room conditions with a melting point at 353 K, the pure ionic liquid was dissolved in  $\text{CDCl}_3$  before the NMR spectra of the solution were recorded. Comparison of the spectra (a) and (b) in the upper and lower plots of Fig. 10 shows no noticeable changes, neither in  $^1\text{H}$  or in  $^{13}\text{C}$  chemical shifts upon saturation of the mixture

with carbon dioxide. This indicates that, without the presence of water, the mechanism of absorption is different from the mechanism in  $[C_1C_4Im][OAc]$  in which chemical reactions with acetate were observed previously (Stevanovic et al., 2012). Contrary to  $[C_1C_4Im][OAc]$ , solubility measurements showed that the presence of water in  $[C_1C_4Pyrro][OAc]$  increases dramatically the absorption of gas when compared with that in the pure ionic liquid. This is another evidence that the mechanism of absorption of the gas is different in the two ionic liquids containing the acetate anion. An additional peak appears in the  $^{13}C$  NMR spectrum at 158.5 ppm (● in the lower plot labeled d) in Fig. 10) when the ionic liquid + water mixture is saturated with  $CO_2$ . Most probably, this peak corresponds to the formed  $HCO_3^-$ , as proved independently by dissolving  $NaHCO_3$  in the ionic liquid (Fig. S1 in Supplementary information). This observation is in agreement with previously established results, which showed that solubility of carbon dioxide in triethylbutylammonium acetate is excluded by chemical reaction involving cation (Wang et al., 2011), but instead involves the acetate anion. Although the reaction is possible only in the presence of water, excess water displaces equilibrium toward the reactants and decreases the absorption, as proved by the experimental measurements herein. This work shows that there should be an optimum concentration of water around mole fraction concentrations of 0.35.

## 9. Conclusions

This work presents an original study of the physico-chemical properties of the ionic liquids  $[C_1C_4Im][LEV]$ ,  $[C_1C_4Pyrro][OAc]$  and  $[C_1C_4Pyrro][OAc]$  + water. Our aim is to study the absorption mechanisms of carbon dioxide in these solvents. These mechanisms are relevant to propose alternative processes for carbon dioxide capture.

We have observed that the ionic liquid  $[C_1C_4Im][LEV]$  presents a higher viscosity than the imidazolium acetate based ionic liquids, which can constitute a disadvantage for industrial processes needing high fluidities. The mixtures  $[C_1C_4Pyrro][OAc]$  + water present also higher values of absorption than  $[C_1C_2Im][OAc]$  + water and  $[C_1C_4Im][OAc]$  + water for the same water molar composition.

We have observed that absorption of carbon dioxide in the pure ionic liquids is of the order of  $10^{-2}$  when expressed in mole fraction of gas, indicating that no chemical reaction between carbon dioxide and ionic liquids are involved unlike in the case of imidazolium acetate based ionic liquids. Absence of chemical reaction is confirmed by comparison between the NMR spectra of pure ionic liquids and those of carbon dioxide saturated ionic liquids.

The mixtures  $[C_1C_4Pyrro][OAc]$  + water present values for the carbon dioxide absorption one order of magnitude higher than that in the pure ionic liquids. These values, comparable to those that can be found in the systems  $[C_1C_2Im][OAc]$  + water and  $[C_1C_4Im][OAc]$  + water, point toward the existence of chemical reaction between  $[C_1C_4Pyrro][OAc]$  and carbon dioxide but only in the presence of water. The NMR study reported here proves that, in the case of  $[C_1C_4Pyrro][OAc]$  + water, the mechanism of  $CO_2$  absorption is different from that previously reported for  $[C_1C_4Im][OAc]$  + water mixtures.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ijggc.2013.04.017>.

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