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Influence of water on the carbon dioxide absorption by 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide

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ABSTRACT

The effect of the addition of water on the absorption of carbon dioxide by the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide was studied experimentally by measuring the low-pressure carbon dioxide solubility and the viscosity of the liquid solvent at temperatures from 303 to 323 K. Water is only partially miscible with the ionic liquid up to a mole fraction of 0.302 at 293 K, 0.321 at 303 K and 0.381 at 323 K. It was observed that the solubility of carbon dioxide decreases with the quantity of water from a mole fraction of 2.63×10^{-2} for the pure ionic liquid at 303.4 K to a value of 1.88×10^{-2} , a reduction of 30% of the solubility, for a mole fraction of water of 0.28. The viscosity of the liquid solvent also decreases, up to 40% at 303 K, from 28.6 mPa s for the pure ionic liquid to 16.4 mPa s for a water mole fraction of 0.302.

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1. Introduction

Due to their specific properties and variety, ionic liquids have a large number of potential applications both in processes (synthesis, catalysis, separations) [1] and in devices (optical, lubricants, batteries) [2].

Ionic liquids are considered as promising media for gas separations [3] as they are able, in many cases, to selectively and efficiently absorb one gas in a mixture. In an industrial gas absorption process, it is desirable to achieve high solutes capacities and/or high selectivity and also fast absorption rates [4]. Selectivity and absorption can be increased by chemically modifying the ionic liquids [5], by mixing two ionic liquids [6] or by adding a molecular compound that can act as a co-solvent or as an antisolvent of the gas. The addition of a molecular compound to an ionic liquid changes the physico-chemical properties of the liquid mixture, fact that can constitute an advantage, namely as far as the viscosity is concerned [7]. The presence of a molecular species lowers the viscosity of the mixture containing a more viscous ionic liquid and, if the gas solubility is not significantly affected, gas absorption can be enhanced by the improvement of the mass transfer in the system.

Another successful application of ionic liquids concerns their use as media for homogeneous or heterogeneous catalysis [8,9] either as solvents and/or as catalysts. Due to their non-volatility, evaporation of the organic and/or inorganic species can facilitate separation after reaction. However, this is not always possible in particular in the case of high-boiling or thermally labile compounds. Liquid–liquid extraction is also not desirable if the process aims to decrease environmental impact by decreasing the use of organic solvents. To avoid these problems, carbon dioxide, generally at high pressures, can be added to induce liquid–liquid phase separation in the mixture [10,11].

The knowledge of the phase equilibria involved in the systems ionic liquid/gas/molecular liquid is of prime importance. The solubility of gases in pure ionic liquids has been the subject of many studies both at low and high pressures. On the contrary, very few data are available on ternary systems even if they are more representative of real mixtures. Hert et al. [12] have focussed on ternary systems composed of two gases and one ionic liquid, and have observed an enhancement of oxygen and methane solubility in an ionic liquid due to the presence of carbon dioxide. Gmehling and co-workers have investigated the usefulness of replacing traditional separation entrainers by ionic liquids by measuring the vapour–liquid equilibria of one ionic liquid and two molecular compounds [13,14].

The majority of experimental data on ternary systems composed of an ionic liquid, a molecular solvent and a gas concern the high-pressure behaviour of carbon dioxide in binary mixtures con-

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taining one ionic liquid. As explained by Roth [15] the molecular component is generally heavy and has a technological interest, e.g. for pharmaceutical industry [16,17], for hydrogenation [18] or for enzymatic synthesis [19]. Other studies involve ternary mixtures of one ionic liquid, supercritical carbon dioxide and a small organic molecule, this latter acting as a cosolvent for CO₂ [20–22]. Fu et al. [23] have focussed on the effect of the presence of water on the CO₂ solubility in 1-butyl-3-methyl imidazolium hexafluorophosphate at pressures varying from 1 to 25 MPa. These authors have observed an average variation of the solubility of 6.7% with the addition of water (water mass fraction varying from 0.0067 to 1.6%). Similarly, Bermejo et al. [24] studied the influence of water on the high pressure solubility of carbon dioxide in two hygroscopic imidazolium based ionic liquids containing a nitrate anion. It was observed that the presence of water reduces the absolute solubility of CO₂. Ren et al. [25] have studied the effect of water on the absorption of SO₂ from a simulated flue gas and found that the presence of the molecular solvent does not decrease the absorption efficiency and causes the viscosity to decrease greatly.

Low-pressure vapour liquid equilibria data on ternary systems composed of an ionic liquid, a molecular compound and a gaseous solute are scarce. Our group [26] has quantified experimentally the influence of the presence of acetonitrile on the low pressure carbon dioxide solubility in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, [C₂mim][NTf₂]. A slight decrease of the solubility of the gaseous component in the liquid phase was observed with the presence of acetonitrile in the liquid phase. The work of Camper et al. [27] on the carbon dioxide capture in a mixture composed of an ionic liquid and an amine can be mentioned. Even though, not only physical but also chemical absorption is present in this case. To the best of our knowledge, no other studies were published on these equilibria.

We report in this paper a study on the vapour–liquid equilibria for the binary system 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide [C₂mim][NTf₂] + water at 292, 303 and 323 K, allowing the determination of the miscibility gap in each case. The study of the ternary system [C₂mim][NTf₂] + water + CO₂ at two temperatures (303 and 323 K) permits the quantification of the effect of the presence of water on the carbon dioxide absorption by the ionic liquid. The characterization of the saturation properties of the mixture provides insights about the molecular mechanisms involved during the solvation of the gas in the liquid mixture. Previous studies [28–30] have shown that ionic liquids exhibit medium-range ordering with the existence of persistent nanoscale domains in the liquid phase. The knowledge of the variation of the gas solubility in ionic liquid + water mixtures can help understanding how the presence of this molecular compound will affect this nanostructure. Carbon dioxide was chosen as it is a gas of technological interest and also probably the most studied gaseous solute in ionic liquid, thus allowing easy comparisons of the results. Water was considered as the molecular component as it is a green solvent, easy to add as a cosolvent and also because it is an impurity commonly present in the ionic liquid samples.

2. Experimental

2.1. Materials

The ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, [C₂mim][NTf₂], was prepared using the standard synthesis procedures described by Bonhôte et al. [31]. The bromide content of the ionic liquid sample was determined using ion chromatography [32] and was less than 5 ppm. Before each measurement, it was degassed and dried by evacuating it under

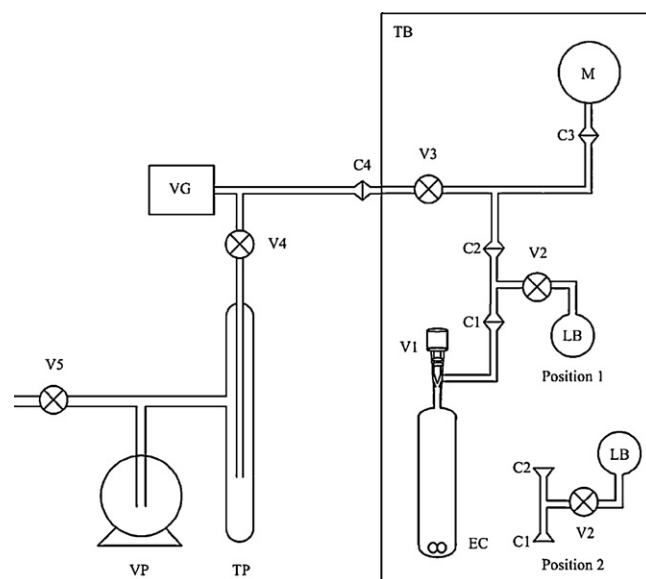


Fig. 1. Vapour pressure apparatus: VP, vacuum pump; TP, cold trap; VG, vacuum gauge Pirani; M, precise manometer; EC, equilibrium cell; LB, liquid bulb; C_i, mobile connections; V_i, constant volume glass valves.

vacuum (pressure of 1 Pa) for 15 h at 303 K. After this the water content was determined by coulometric Karl-Fisher titration using a Mettler Toledo DL31 titrator. A reference value of 45 ppm of water was obtained. As this quantity is negligible compared to the water quantities added to the ionic liquid in the gas solubility experiments, the ionic liquid after degassing was considered as totally dried for the calculations. The carbon dioxide was purchased from AGA/Linde Gaz (>0.99995 mole fraction) and was used as received. Water was triply distilled and before use, it was degassed using melting–freezing cycles.

Two *pVT* apparatus were used in this work. The first one (vapour pressure apparatus) allows the study of the vapour liquid equilibrium of the binary system [C₂mim][NTf₂] + water through the measurement of its vapour pressure as a function of the composition of the liquid phase. The second one (gas solubility apparatus) has the advantage to permit in a same experiment both the measurement of the vapour pressure of the binary mixture [C₂mim][NTf₂] + water and of the low-pressure gas solubility in this mixture.

2.2. Methods

The miscibility gap in the mixtures of [C₂mim][NTf₂] + water was determined at different temperatures using a *pVT* method. Two different measuring cells were used, both equipped with precision manometers one placed in an air thermostat [33] and another placed in a water bath.

The first cell is represented in Fig. 1. Precisely known quantities of ionic liquid and water, previously degassed under vacuum and by successive melting and freezing cycles (LB in position 1), respectively, are put in contact, under their own vapour pressure, inside the equilibrium cell, EC (LB in position 2). The two components are mixed at constant temperature and in the constant and accurately known volume of the apparatus. When thermodynamic equilibrium is reached, the vapour pressure is recorded. The composition of the liquid mixture is modified by evacuating the molecular compound, the new composition of the mixture being calculated gravimetrically. The equilibrium cell and the manometer are housed in an air thermostat whose temperature was controlled to within ±0.01 K and measured with a calibrated 100 Ω platinum

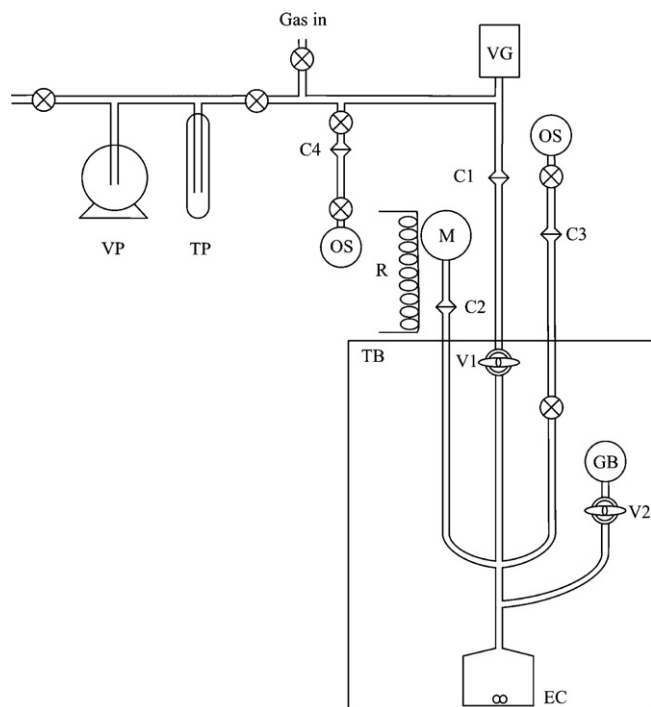


Fig. 2. Gas solubility apparatus: VP, vacuum pump; TP, cold trap; VG, vacuum gauge Pirani; GB, gas bulb; OS, molecular solvent bulb; M, precision manometer; TB, thermostated bath; EC, equilibrium cell; R, heating element; V₁, V₂, constant volume glass valves; C₁, mobile connections.

resistance thermometer from Hart Scientific (Secondary Reference Temperature Standard, model 1502A, accuracy of ± 0.018 K at 273 K). The air thermostat allows to work from 288 to 313 K. The pressure was measured using a quartz spiral manometer from Ruska (model 2465, uncertainty $\pm 10^{-5}$ bar).

The second cell used to determine the miscibility gap of the $[\text{C}_2\text{mim}][\text{NTf}_2] + \text{water}$ mixtures is also a pVT constant volume cell and is the same used during the gas solubility measurements. It is based on an isochoric saturation method that has been described in a previous publication [26] and is depicted in Fig. 2. In this technique, a known quantity of gaseous solute is put into contact with a precisely determined quantity of degassed solvent ($[\text{C}_2\text{mim}][\text{NTf}_2] + \text{water}$ mixture) at constant temperature inside an accurately known volume. 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.

A known quantity of carbon dioxide is first introduced in the calibrated gas bulb (GB) and is isolated from the rest of the installation by closing the glass valve V₂. The ionic liquid is then introduced in the equilibrium cell through connection C₂ by means of a syringe, its mass being determined with a precision of 1×10^{-4} g. It is degassed and dried. Water is introduced in the OS bulb and degassed by successive melting/freezing cycles while vacuum pumping non-condensable gases through connection C₄. This degassed liquid is then transferred to the equilibrium cell under its own vapour pressure through connection C₃. The amount of liquid introduced in the equilibrium cell at this stage is determined by weighing the OS bulb right after degassing the solvent and then after its introduction into the equilibrium cell. A small quantity of organic solvent is lost in the glass tubing between the OS bulb and the equilibrium cell during the transfer. This quantity is minimized by working at low temperature and can be easily estimated. It is taken into account for the estimation of the mixture composition uncertainty (± 0.0004 on the mole fraction). The gas/liquid equilibrium process starts by bringing into contact the solvent mixture

(previously equilibrated by stirring the two liquids at constant temperature and waiting for a constant pressure to be reached) with the gaseous solute by opening valve V₂ (a constant volume valve) in the constant volume of the equilibrium section.

The whole equilibrium section is maintained at constant temperature to within ± 0.01 K using a liquid thermostat and a PID temperature controller and its value is measured accurately by means of a calibrated (against a primary standard RTD from Tinsley with a precision of ± 0.02 K) 100Ω platinum resistance sensor associated to a 6 1/2 digit multimeter (Keithley model 2000). The pressure is measured using a Druck manometer RPT 350 model, calibrated for pressures between 35 and 3500 mbar with a precision of 0.01% full scale. This apparatus has been improved [26] by including a precise control of the temperature in the manometer which is placed outside the thermostated bath. The temperature in the manometer is maintained to within ± 0.1 K at 4°C above the temperature of the thermostated bath and is measured using miniature 100Ω platinum resistance sensors placed at different points of the apparatus and guaranteeing that a temperature gradient of less than 0.2 K is maintained. In this equilibrium cell, the pressure of the liquid mixture at different temperatures is measured before bringing into contact the solvent mixture (ionic liquid + water) with the gaseous solute to quantify the gaseous absorption.

Details of the data reduction are given in our previous paper [26]. As it has been recently demonstrated by Longinotti et al. [34], two possible thermodynamic treatments can be used to describe the solubility of gases in ionic liquids. If the ionic liquid is considered as a molecular solvent, like we did in this work, the gas solubility can be expressed as mole fraction of the gas in the liquid mixture, x_2 , calculated through:

$$x_2 = \frac{n_2^{\text{liq}}}{(n_{\text{solv}}^{\text{liq}} + n_2^{\text{liq}})} \quad (1)$$

where $n_{\text{solv}}^{\text{liq}} = n_1^{\text{liq}} + n_3^{\text{liq}}$ 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. For the calculations, the validity of the Raoult's law for the system gas/liquid solvent (ionic liquid + water) was assumed which means the carbon dioxide partial pressure, p_2 , can be calculated from x_2 and $p_{\text{solv}}^{\text{sat}}$, the vapour pressure of the liquid solution (determined in the first part of the experiment) using the following equation:

$$p_2 = x_2^{\text{solv}} p_{\text{solv}}^{\text{sat}} \quad (2)$$

The amount of solute present in the liquid solution is calculated from two pVT measurements: first when the gas is introduced in the calibrated bulb with volume V_{GB} , and second when thermodynamic equilibrium is reached:

$$\begin{aligned} n_2^{\text{liq}} &= n_2^{\text{tot}} - n_2^{\text{gas}} \\ &= \frac{p_{\text{ini}} V_{\text{GB}}}{[Z_2(p_{\text{ini}}, T_{\text{ini}})RT_{\text{ini}}]} - \frac{[p_{\text{eq}} - x_{\text{solv}} p_{\text{solv}}^{\text{sat}}](V_{\text{tot}} - V_{\text{liq}})}{[Z_{23}(p_{\text{eq}}, T_{\text{eq}})RT_{\text{eq}}]} \end{aligned} \quad (3)$$

where p_{ini} and T_{ini} are the pressure and temperature in the first pVT determination and p_{eq} and T_{eq} are the pressure and temperature at the equilibrium. V_{tot} is the total volume of the equilibration cell and V_{liq} is the volume occupied by the liquid solution. V_{liq} is always considered as equal to the volume of the pure solvent as it is assumed that the gas dissolved does not change significantly the volume of the liquid phase. In the case of multicomponent liquid solvents, this volume has to be determined as, apart from the molar volumes of the two components of the solvent mixture, it is necessary to take into account the volume change on mixing. Z_2 is the compressibility factor for the pure gas and Z_{23} is the compressibility factor for

the vapour phase in equilibrium with the solution (equals Z_2 in the case of the solubility of gases in pure ionic liquids) given by

$$Z_{23} = 1 + \frac{P}{RT}(y_2 B_{22} + y_3 B_{33} + y_2 y_3 \delta_{23}) \quad (4)$$

where B_{22} and B_{33} are the second virial coefficients for CO_2 and H_2O , respectively and $\delta_{23} = 2B_{23} - B_{22} - B_{33}$ with B_{23} being the crossed virial coefficient considered, in the present case, as the average between B_{22} and B_{33} .

The amount of solvent present in the liquid phase, $n_{\text{sol}}^{\text{liq}}$ can be calculated from (by assuming, once again, the validity of Raoult's law for the solute and the solvent in equilibrium):

$$n_{\text{sol}}^{\text{liq}} = n_{\text{sol}}^{\text{tot}} - n_{\text{sol}}^{\text{gas}} = n_{\text{sol}}^{\text{tot}} - \frac{x_{\text{sol}} p_{\text{sol}}^{\text{sat}} (V_{\text{tot}} - V_{\text{liq}})}{[Z_{23}(p_{\text{eq}}, T_{\text{eq}})RT_{\text{eq}}]} \quad (5)$$

where $n_{\text{sol}}^{\text{tot}}$ is the total amount of solvent initially introduced in the equilibrium cell and Z_{23} is the compressibility factor for the solvent calculated using Eq. (4).

The equilibrium compositions are calculated iteratively with the process starting with initial guesses for the mole fractions in both phases and continuing with the determination of the quantities of solute and solvent present in the liquid solution and in the vapour in equilibrium with it (Eqs. (3) and (5)), provided that the vapour pressure of the solvent is known as well as its molar volume.

From the mole fraction solubility, the Henry's law constant, K_H , can be calculated through [35]:

$$K_H \equiv \lim_{x_2 \rightarrow 0} \frac{f_2(p, T, x_2)}{x_2} \cong \frac{\phi_2(p_{\text{eq}}, T_{\text{eq}})p_{\text{eq}}}{x_2} \quad (6)$$

where f_2 is the fugacity of the solute and ϕ_2 its fugacity coefficient.

Another way of calculating the gas solubility in an ionic liquid is, as pointed out by Longinotti et al. [34], to consider the ionic character of the solvent and so the solute mole fraction is defined as

$$x_2 = \frac{n_2^{\text{liq}}}{(2n_{\text{sol}}^{\text{liq}} + n_2^{\text{liq}})} \quad (7)$$

As the quantity of carbon dioxide dissolved in the liquid is two orders of magnitude lower than the solvent quantity in this phase, the mole fraction calculated by considering the liquid solvent as a molecular liquid is twice as high as if the solvent is treated as a mixture of a cation and an anion.

For the calculations, we assume that Raoult's law is valid for the system gas/liquid solvent (=ionic liquid + water). We also consider that the gas dissolved does not change significantly the volume of the liquid phase. The volume change on mixing the two liquids is considered. The excess molar volumes of the binary system $[\text{C}_2\text{mim}][\text{NTf}_2] + \text{water}$ were previously calculated by our group at 303 and 323 K [36]. The influence of this correction on the gas solubility is low as the excess molar volumes are small: the maximum excess molar volume obtained is only $1.1 \text{ cm}^3 \text{ mol}^{-1}$ at 323 K for a water mole fraction around 0.13. The virial equation was used to describe the vapour phase. The second virial coefficients for carbon dioxide and water are taken from Dymond and Smith [37]. The cross virial coefficient is taken as the average between the second virial coefficient of water and carbon dioxide.

Mixtures of different water compositions were prepared gravimetrically in order to determine the influence on viscosity of the presence of water in $[\text{C}_2\text{mim}][\text{NTf}_2]$. The ionic liquid was first introduced in a glass vial and then the appropriate amount of water was added and the glass vial 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 as ± 0.0001 .

Table 1

Vapour pressures, $p_{\text{sol}}^{\text{sat}}$, of the $[\text{C}_2\text{mim}][\text{NTf}_2] + \text{water}$ mixtures as a function of the composition, expressed in water mole fraction, x_{water} .

Vapour pressure apparatus			
T = 292.75 K		T = 303.20 K	
x_3	$p_{\text{sol}}^{\text{sat}}$ (10 ² Pa)	x_{water}	$p_{\text{sol}}^{\text{sat}}$ (10 ² Pa)
0.0000	00.00	0.0000	00.00
0.2420	18.16	0.1750	21.46
0.2720	20.81	0.2050	26.08
0.2930	21.78	0.3110	38.94
0.5480	22.81	0.5140	42.70
0.6430	22.80	0.6760	42.55
0.7410	22.86	0.7290	42.63
1.0000	22.83 ^a	1.0000	42.61 ^a
Gas solubility apparatus			
T = 303.46 K		T = 323.35 K	
x_3	$p_{\text{sol}}^{\text{sat}}$ (10 ² Pa)	x_{water}	$p_{\text{sol}}^{\text{sat}}$ (10 ² Pa)
0.0000	00.00	0.0000	00.00
0.1163	19.64	0.1151	44.80
0.1283	21.11	0.1278	46.96
0.1775	27.09	0.1760	63.83
0.1989	24.43	0.2142	76.46
0.2365	33.44	0.2358	72.98
0.2396	29.38	0.2791	95.55
0.2807	40.12	0.2842	84.16
0.2850	39.59	1.0000	123.44 ^a
1.0000	42.46 ^a		

^a These values are taken from literature [38].

The viscosity of the mixtures was measured at 303 K and at 323 K, the temperature being controlled to within 0.01 K and measured with an accuracy better than 0.05 K, using a rolling ball viscometer from Anton Paar, model AMVn, equipped with a capillary tube of 1.8 mm in diameter. Before starting the measurements, we have calibrated the tube as a function of temperature and angle of measurement, with a standard viscosity oil from Cannon (N35). The overall uncertainty on the viscosity is estimated as $\pm 1.5\%$.

3. Results and discussion

The vapour pressure of the $[\text{C}_2\text{mim}][\text{NTf}_2] + \text{water}$ mixtures was measured as a function of composition at 293 and 303 K using the vapour pressure apparatus and at 303 and 323 K using the gas solubility apparatus. The experimental data are presented in Table 1 and are depicted in Fig. 3.

For the pure ionic liquid, the vapour pressure is not measurable and will be considered as equal to zero. An increase of the vapour pressure is first observed with the addition of water to the ionic liquid. After a water mole fraction corresponding to the solubility of water in the ionic liquid, the pressure in equilibrium with the liquid mixture becomes stable with composition and equals the vapour pressure of pure water at the considered temperature (as the solubility of the ionic liquid in the aqueous phase is considered as negligible, causing a variation on the vapour pressure smaller than the experimental uncertainty). These values can be found in literature [38]: 22.73 mbar at 292.75 K, 43.25 mbar at 303.33 K and 126.49 mbar at 323.35 K. As expected, the $[\text{C}_2\text{mim}][\text{NTf}_2] + \text{water}$ mixtures exhibit large positive deviations to Raoult's law as represented in the lower plot of Fig. 3. For the calculation of the water solubility at the different temperatures, a linear variation of the pressure with composition was considered, the water solubility in the ionic liquid being calculated by the intersection of the vapour pressure of water at a given temperature and the line describing the vapour pressure of the mixture at the same temperature. The average deviations from this linear behaviour of the vapour pres-

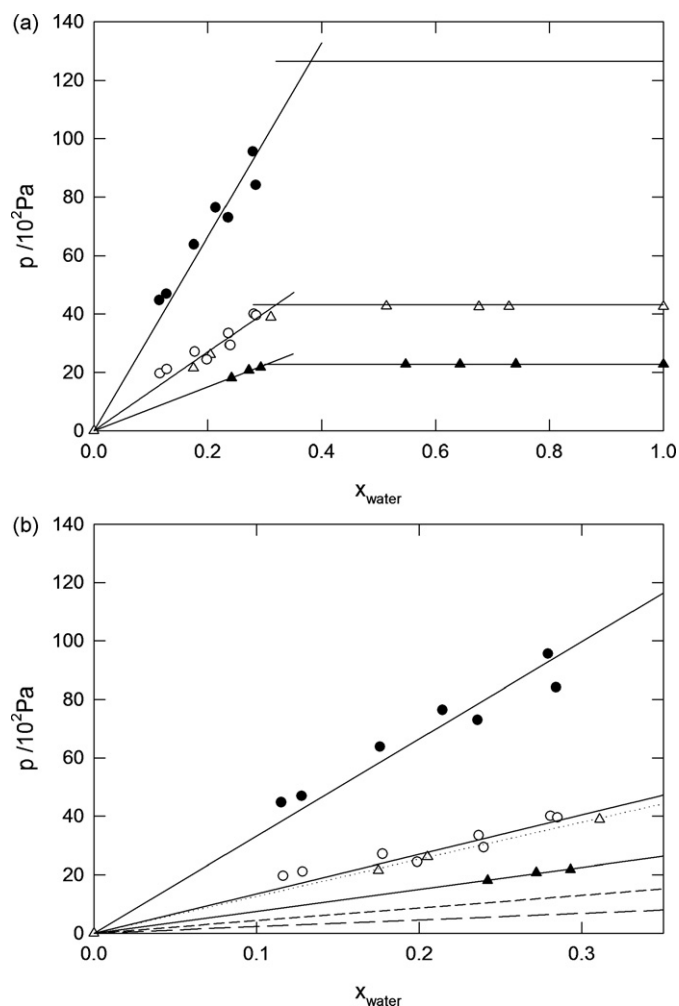


Fig. 3. (a) Vapour pressures of the $[\text{C}_2\text{mim}][\text{NTf}_2] + \text{water}$ mixtures, p , as a function of the composition, expressed in water mole fraction, x_{water} , measured with the two different pVT cells. In the air thermostat: (▲) $T = 292.75 \text{ K}$; (△) $T = 303.20 \text{ K}$ and in the liquid thermostat: (○) $T = 303.46 \text{ K}$; (●) $T = 323.35 \text{ K}$. (b) Deviations of the vapour pressures to Raoult's law at the different temperatures. The dash and dotted lines correspond to the Raoult's law: long dash line, $T = 292.75 \text{ K}$; short dash line, $T = 303.33 \text{ K}$; dotted line, $T = 323.35 \text{ K}$.

sure of the mixture can be as high as 10% at 323.35 K. Part of these deviations can be attributed to the precision of the pressure measurement and of the liquid mixture composition. Higher deviations are obtained in the case of the pVT cell placed in the water thermostat as the mixtures are prepared independently while in the case of the air thermostat cell, the different compositions are obtained by evaporation of controlled amounts of water. The value of 10% will be considered as the overall uncertainty of the experimental apparatus and covers both the precision and the accuracy of the measurement. The water solubilities in $[\text{C}_2\text{mim}][\text{NTf}_2]$ obtained in this work are $x_{\text{water}} = 0.302$ at 292.75 K, $x_{\text{water}} = 0.321$ at 303.33 K, and $x_{\text{water}} = 0.381$ at 323.35 K.

Water solubility in $[\text{C}_2\text{mim}][\text{NTf}_2]$ was determined by other authors using a variety of experimental apparatus. These literature data are presented, along with the values obtained in the present work in Fig. 4. Doker and Gmehling [14] and Kato and Gmehling [39] have studied, at 353 K, the vapour liquid equilibrium of the binary system with a static VLE apparatus. Freire et al. [40] and Bonhôte et al. [31] have detected visually the transition from one to two liquid phases and measured the water quantity in the ionic liquid rich phase by Karl-Fisher titration. Finally, our group [36] has previously determined the liquid–liquid miscibility of the system

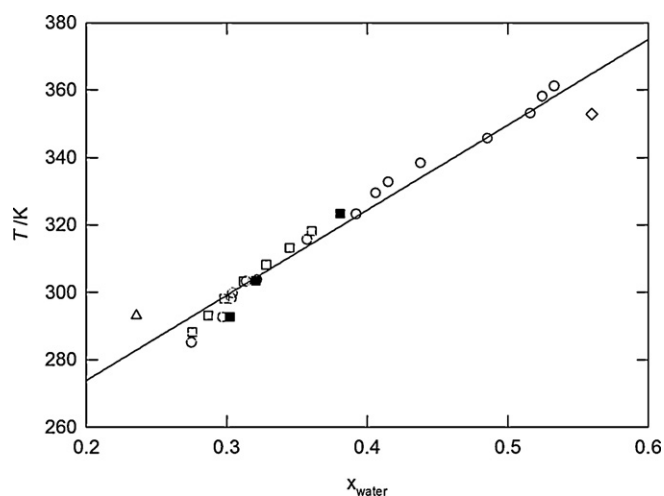


Fig. 4. Water solubility in $[\text{C}_2\text{mim}][\text{NTf}_2]$ as a function of temperature. Comparison with literature data: (■) this work, air thermostat; (●) this work, water thermostat; (□) Freire et al. [40]; (○) Wang et al. [36]; (◇) Doker and Gmehling [14] and Kato and Gmehling [39]; (△) Bonhôte et al. [31].

$[\text{C}_2\text{mim}][\text{NTf}_2] + \text{water}$ from 285 to 361 K using a standard nephelometric method. A linear increase of the water solubility is observed with temperature (average deviation of 1.1%). The most important deviations are observed with the experimental data obtained by Bonhôte et al. (3.5%), Doker and Gmehling (3.4%) and Kato and Gmehling (3.4%). The water solubilities measured in the present work are coherent with the literature data (average deviation from the linear fit of 1.7%).

The low-pressure solubility of carbon dioxide was measured in $[\text{C}_2\text{mim}][\text{NTf}_2] + \text{water}$ mixtures of different compositions at 303 and 323 K. The experimental data are reported in Table 2 in terms of mole fraction and Henry's law constants. The variation of this coefficient with the water mole fraction is presented in Fig. 5. The Henry's law varies from 38 bar for the pure ionic liquid to 56 bar for a water mole fraction of 0.27 at 303 K (corresponding to carbon dioxide mole fractions varying from 2.6×10^{-2} to 1.8×10^{-2}) and from 54 bar for the pure ionic liquid to 75 bar for a water mole fraction of 0.27 at 323 K (corresponding to carbon dioxide mole fractions varying from 1.9×10^{-2} to 1.3×10^{-2}). The same order of

Table 2

Experimental values of gas solubilities in several $[\text{C}_2\text{mim}][\text{NTf}_2] + \text{water}$ binary mixtures, as a function of the water mole fraction, x_{water} , expressed both as Henry's law constants, K_{H} , and as CO_2 mole fraction, x_{CO_2} , corrected for a partial pressure of solute of 0.1 MPa. p_{eq} is the equilibrium pressure.

x_{water}	p_{eq} (10^2 Pa)	K_{H} (10^5 Pa)	x_{CO_2} (10^{-2})
$T = 303.40 \text{ K}$			
0.0000		38.05 ^a	2.628 ^a
0.1128	609.36	45.85	2.181
0.1259	477.84	43.34	2.307
0.1731	572.41	48.57	2.059
0.1949	662.71	47.36	2.111
0.2341	669.25	53.15	1.881
0.2749	673.74	56.06	1.784
0.2800	658.15	53.22	1.879
$T = 323.26 \text{ K}$			
0.0000		53.65 ^a	1.864 ^a
0.1097	690.69	62.50	1.600
0.1244	558.84	60.89	1.642
0.1691	657.68	62.17	1.609
0.2067	782.70	71.24	1.404
0.2297	762.61	66.26	1.509
0.2306	741.77	69.09	1.447
0.2705	788.91	75.44	1.326

^a These values are taken from literature [26].

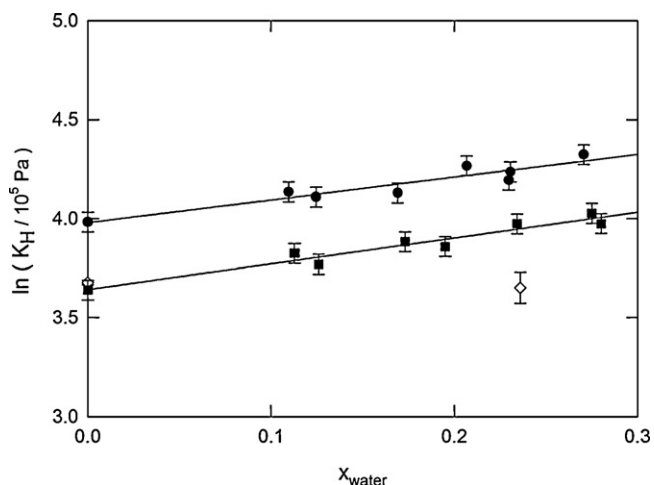


Fig. 5. Henry's law constants, K_H , for carbon dioxide in the $[\text{C}_2\text{mim}][\text{NTf}_2]$ + water mixtures as a function of the composition expressed in water mole fraction, x_{water} : (○) $T=303.40$ K, this work; (●) $T=323.26$ K, this work; (◇) $T=303$ K [43].

magnitude was measured by our group for the solubility of carbon dioxide in several ionic liquids [41,42] with an overall uncertainty of 5%. A similar linear decrease of the solubility (linear increase of the logarithm of the Henry's law constant) with the water mole fraction is observed at the two considered temperatures. Water acts in this mixture as an antisolvent. A decrease of the solubility is observed with temperature, corresponding to an exothermic solvation process. Such a result was already observed for carbon dioxide and others gases in ionic liquids and in mixtures of ionic liquid and a molecular solvent [41,42,26] but is not in line with the results determined by Scovazzo et al. [43] that show no difference on carbon dioxide solubility between the dried ionic liquid and the water saturated solvent.

The present results can be compared to literature studies where mixtures of an ionic liquid, a molecular solvent and a high pressure gas are studied [23,24]. Fu et al. [23] have not observed a regular variation of the carbon dioxide solubility with the water mole fraction in $[\text{C}_4\text{mim}][\text{PF}_6]$. An average variation of 6.5% on the solubility with a maximum variation of 15% was measured while in our case, a 47% decrease of the Henry's law constant for a water mole fraction of 0.27 is observed at 303 K. On the contrary, Bermejo et al. [24] have observed a decrease of the carbon dioxide solubility in the presence of water. As it has been demonstrated by our group, using molecular simulation calculations, both carbon dioxide [44] and water [45] are preferentially solvated in the charged domains of the ionic liquids, the decrease of the carbon dioxide solubility in the presence of water being attributed to the competition of the two molecular components by the same ionic liquid solvation sites. It is expected that the interaction between the gaseous solute and water is significant and surely influences the behaviour of the ternary system [46].

The effect of the addition of water on the low-pressure carbon dioxide solubility in different ionic liquids can be compared with the effect of the addition of other solvents. This comparison is illustrated in Fig. 6. The molecular compound added to the ionic liquid can act as a cosolvent, as in the case of acetone in $[\text{C}_4\text{mim}][\text{PF}_6]$ [20], its presence increasing the solubility of carbon dioxide or as antisolvent as in the cases of water (this work) or acetonitrile in $[\text{C}_2\text{mim}][\text{NTf}_2]$ [26] and water [23] and methanol [47] in $[\text{C}_4\text{mim}][\text{PF}_6]$. For $[\text{C}_2\text{mim}][\text{NTf}_2]$, the ionic liquid studied in this work, the reduction of the solubility of carbon dioxide is more pronounced in the case of water than in the case of acetonitrile.

The viscosities of the mixtures of $[\text{C}_2\text{mim}][\text{NTf}_2]$ + water at two different temperatures are reported in Table 3. As expected, the

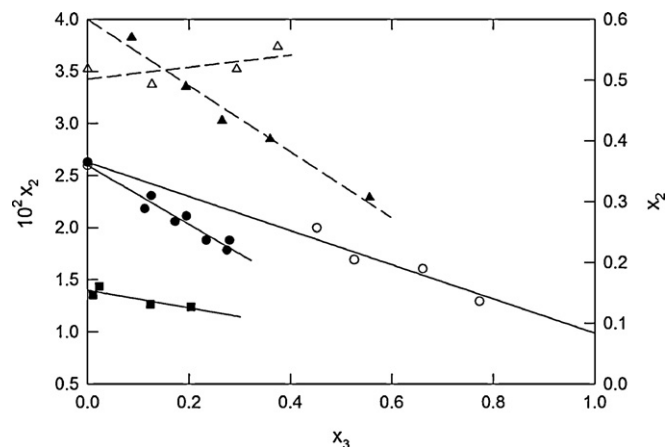


Fig. 6. Mole fraction of carbon dioxide in the liquid phase, x_2 , as a function of the molecular solvent mole fraction, x_3 : (●) $[\text{C}_2\text{mim}][\text{NTf}_2]$ + water, $T=303.40$ K, $p=10^5$ Pa, this work; (○) $[\text{C}_2\text{mim}][\text{NTf}_2]$ + acetonitrile, $T=303.48$ K, $p=10^5$ Pa [26]; (■) $[\text{C}_4\text{mim}][\text{PF}_6]$ + water, $T=303.15$ K, high pressure measurements, recalculated at 10^5 Pa [23]; (△) right axis, $[\text{C}_4\text{mim}][\text{PF}_6]$ + acetone, $T=313.15$ K, $p=7$ MPa [20]; (▲) right axis, $[\text{C}_4\text{mim}][\text{PF}_6]$ + methanol, $T=313.15$ K, $p=7.5$ MPa [47].

Table 3

Viscosities of the $[\text{C}_2\text{mim}][\text{NTf}_2]$ + water mixtures, η , as a function of the composition, expressed in water mole fraction, x_{water} .

$T=303.15$ K		$T=323.15$ K	
x_{water}	η (mPa s)	x_{water}	η (mPa s)
0.0000	28.6	0.0000	15.9
	28.7 ^a		16.2 ^a
0.1074	23.8	0.1074	13.6
0.2228	19.4	0.2228	11.4
0.3027	16.4	0.3027	9.90
0.305	16.8 ^a	0.305	10.8 ^a

^a These values are taken from literature [7].

variation of the viscosity of the mixtures is more important at the lower temperature studied as the difference in viscosities between the pure ionic liquid and that of pure water is bigger at 303 K. The values obtained in this work were compared with those previously published by Jacquemin et al. [7], measured using a rheometer. The viscosity of the pure ionic liquid measured here agrees with the previously published value to within $\pm 1\%$ but significant differences were found for the viscosities of the water saturated mixtures. In that case, differences up to 10% were found at the higher temperatures. These differences are attributed to errors in the composition of the mixtures due to the water evaporation in the rheometer. The errors of the composition of the mixtures are expected to be much lower in the closed capillary tube of the falling body viscometer used in this work. The present data can also be compared to the work of Widegren et al. [48] who measured the viscosity of mixtures of $[\text{C}_2\text{mim}][\text{NTf}_2]$ + water at various compositions and at 293 K using a capillary viscosimeter. These authors observe, at 293 K, a decrease of the viscosity of the ionic liquid with the water content that is more important than the one we observe at higher temperatures (33% of decrease between the pure ionic liquid and a mixture with a water mole fraction of 0.22 instead of 28% for a water mole fraction of 0.22 at 323 K). This result is coherent with our conclusions at 303 and 323 K.

4. Conclusions

This work permits the quantitative evaluation of the effect of water on the solubility of carbon dioxide in the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, $[\text{C}_2\text{mim}][\text{NTf}_2]$. It is observed that the solubility decreases with the

mole fraction concentration of water from $x_2 = 2.63 \times 10^{-2}$ for the pure ionic liquid to $x_2 = 1.88 \times 10^{-2}$ for a water mole fraction of 0.28 (values at 303 K), a reduction of approximately 30% on the carbon dioxide solubility. The ionic liquid studied is only partially miscible with water that forms a single phase with $[C_2mim][NTf_2]$ up to mole fractions of 0.381 at 323.35 K, as determined in this work.

The viscosities of the mixtures of $[C_2mim][NTf_2]$ with water were also determined and it was observed that they are approximately 40% lower (from 28.6 to 16.4 mPa s), for example for a water mole fraction of 0.30 at 303 K, than that of the pure ionic liquid. It is thus concluded that the viscosity of the ionic liquid medium can be significantly reduced while maintaining the same order of magnitude for the low-pressure solubility of carbon dioxide. As the viscosity can considerably modify the transport of the gas in the liquid medium, this modification of the thermophysical properties of the solvent can substantially affect the characteristics of the ionic liquid medium as an absorbent for carbon dioxide.

List of symbols

B	virial coefficient
f	fugacity
K_H	Henry's law constant
n	mole quantity
p	pressure
T	temperature
V	volume
x	mole fraction in the liquid phase
y	mole fraction in the vapour phase
Z	compressibility factor

Greek letters

η	viscosity
Φ	fugacity coefficient

Subscripts

eq	at equilibrium
i	component
ini	initial
solv	ionic liquid + water

Superscripts

gas	in the gas phase
liq	in the liquid phase
tot	total quantity

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