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Solubility of carbon dioxide and ethane in three ionic liquids based on the bis{(trifluoromethyl)sulfonyl}imide anion

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Abstract

The objective of this work was to study the influence of changing the cation of the ionic liquid (IL) on gas solubility. For this purpose, the low-pressure solubility of carbon dioxide and of ethane in three ILs based on the bis{(trifluoromethyl)sulfonyl}imide anion ([NTf₂][−]) was determined experimentally. Solubility data is reported for 1-ethyl-3-methylimidazolium ([C₁C₂Im]⁺), 1-butyl-1-methylpyrrolidinium ([C₁C₄pyrr]⁺) and propylcholinium ([N_{1132-OH}]⁺) bis{(trifluoromethyl)sulfonyl}imide ILs between 300 and 345 K. These data are precise to within ±1% and accurate to within ±5%. In these ILs, carbon dioxide (mole fraction solubility between 1 and 3 × 10^{−2}, molarity between 0.03 and 0.1 mol L^{−1}) is one order of magnitude more soluble than ethane. The effect of changing the cation is small but significant. Changing the cation has a similar effect on both gases even if the differences are more pronounced in the case of ethane with the order of solubility [C₁C₄pyrr][NTf₂] > [C₁C₂Im][NTf₂] > [N_{1132-OH}][NTf₂]. For all the systems, the solubility decreases with temperature corresponding to exothermic processes of solvation and negative enthalpies and entropies of solvation were calculated. The properties of solvation of the two gases in [C₁C₄pyrr][NTf₂] do not vary significantly with temperature while important variations are depicted for both gases in [C₁C₂Im][NTf₂].

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1. Introduction

The aim of this work is to contribute to the study of the interactions between ionic liquids (ILs) containing the anion bis{(trifluoromethyl)sulfonyl}imide ([NTf₂][−]) and two gaseous solutes, carbon dioxide and ethane through the experimental determination of gas solubility. Gas solubilities were measured as a function of temperature and at pressures close to atmospheric, using an isochoric saturation method. The data obtained provides important information for the characterization of solute–solvent interactions and so contribute to understand the mechanisms of dissolution. From a practical point of view, gas solubility can be useful in the calculation of (vapour + liquid) equilibria and thus pertinent to the development of new reaction and separation processes.

Our research group has previously studied the solubility of a selection of gases in two ILs namely 1-butyl-3-methylimidazolium tetrafluoroborate [C₁C₄Im][BF₄] [1] and 1-butyl-3-methylimidazolium hexafluorophosphate [C₁C₄Im][PF₆] [2] as a function of temperature from 303 to 343 K. In these two liquids, carbon dioxide was found to be the most soluble of the gases investigated, followed by ethane and methane. Other solutes including oxygen, argon, nitrogen, hydrogen and carbon monoxide showed much lower solubility. We have also studied the influence of changing the anion in 1-butyl-3-methylimidazolium-based ILs on the solubility of gaseous solutes [3]. It was observed that the gas solubilities in [C₁C₄Im][BF₄] and [C₁C₄Im][PF₆] are significantly lower than those in [C₁C₄Im][NTf₂].

The influence of changing the cation on the solubility of gases has also been previously investigated [4] through the study of carbon dioxide and hydrogen in three ILs composed of [NTf₂][−] with either an imidazolium cation (1-ethyl-3-methylimidazolium, [C₁C₂Im]⁺ and [C₁C₄Im]⁺) or an ammonium

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Fig. 1. Structural formula of the three ILs investigated in this work. (a) bis[(trifluoromethyl)sulfonyl]imide anion; (b) 1-ethyl-3-methylimidazolium cation; (c) 1-butyl-1-methylpyrrolidinium cation; and (d) propylcholinium cation.

cation (butyl-trimethylammonium, $[N_{4111}]^+$). In contrast with variation with the IL anion, the cation influence was found to be much smaller. Both gases studied were found more soluble in the ammonium-based IL studied than in the two imidazolium-based ILs. Moreover, a slight increase of the solubility was systematically observed when increasing the chain length on the imidazolium cation.

Herein, it is our aim to continue the study of the influence of changing the cation of the IL on the solubility of gaseous solutes. We have chosen three ILs based on the $[NTf_2]^-$ anion combined with either an aromatic ring ($[C_1C_2Im]^+$) or a cycle (1-butyl-1-methylpyrrolidinium, $[C_1C_4pyrr]^+$) and hydroxyl functionalised acyclic (propylcholinium $[N_{1132-OH}]^+$) tetraalkylammonium cation as shown in Fig. 1.

The solubility of carbon dioxide in a variety of ILs has been determined at low pressures [1–10] and high pressures (up to 73 MPa) [11–24]. In particular, the system (carbon dioxide + $[C_1C_2Im][NTf_2]$), also investigated in this work, was studied by several authors [7–10,14,17]. Camper et al. [7,8,10] have determined the solubility of carbon dioxide experimentally in this IL from 303 to 343 K and at low pressures by isochoric pVT measurements. The reported Henry's law constants (4.0 MPa at 303 K and 7.7 MPa at 343 K) increase when increasing temperature corresponding to a decrease of the solubility with temperature. Morgan et al. [9], whose main focus was to determine the experimental diffusivity of carbon dioxide in a variety of ILs, also measured the solubility of this gas by passing it through a supported IL film and measuring the gas pressure after the membrane at equilibrium. At 313 K, the solubility of carbon dioxide in $[C_1C_2Im][NTf_2]$ was found to be $0.1 \text{ mol L}^{-1} \text{ atm}^{-1}$ which corresponds to a Henry's law constant of 4.1 MPa. Cadena et al. [14] used a gravimetric microbalance to determine the solubility of carbon dioxide in $[C_1C_2Im][NTf_2]$ between 283 and 323 K and at pressures up to 1.4 MPa. Their measured Henry's law constants increase with temperature and vary from 2.53 to 5.15 MPa. Finally, Kim et al. [17] have measured the solubility of carbon dioxide in $[C_1C_2Im][NTf_2]$ at 298.15 K and up to 1 MPa with a method

similar to that of Cadena et al. [14]. Therein, the Henry's law constant calculated by extrapolating their data at atmospheric pressure was nearly 30% higher than that reported by Cadena et al. [14] at the same temperature. To the best of our knowledge, only Anthony et al. [12] have measured the solubility of carbon dioxide in $[C_1C_4pyrr][NTf_2]$ and reported Henry's law constants at 283, 298 and 323 K of 3.02, 3.86 and 5.61 MPa, respectively.

In comparison, the solubility of ethane in ILs has been far less studied than the solubility of carbon dioxide [1,2,8,10,11]. Camper et al. [8,10] have studied the system ethane + $[C_1C_2Im][NTf_2]$ which is also reported herein. Henry's law constants of 10.7 MPa at 303 K and of 16.8 MPa at 313 K were found with the solubility decreasing with increasing temperature.

The solubility of carbon dioxide and ethane has been investigated in a wide range of imidazolium-based ILs including $[C_1C_2Im][NTf_2]$ [8,10], $[C_1C_4Im][NTf_2]$ [22], $[C_1C_4Im][BF_4]$ [1,10], $[C_1C_4Im][PF_6]$ [2,10,11], 1-ethyl-3-methylimidazolium dicyanamide ($[C_1C_2Im][dca]$) [10] and 1-ethyl-3-methylimidazolium triflate ($[C_1C_2Im][OTf]$) [10]. In all these ILs, carbon dioxide exhibits a higher solubility than ethane.

In general, changing the anion of the IL has a larger impact on the gas solubility than modifying the cation [3,6,12,14,15]. The presence of the $[NTf_2]^-$ anion systematically increases the solubility of carbon dioxide [3,6,12,14] this anion showing a larger affinity for this solute regardless of whether the liquid is based on the imidazolium, pyrrolidinium or ammonium cations [12]. The effect of changing the cation of the IL on the solubility of gases is less significant [12,15]. A slight increase of the solubility of carbon dioxide when increasing the alkyl side chain length in the imidazolium cation was observed [6,15,23]. In addition, Anthony et al. [12] compared the solubility of carbon dioxide in three ILs containing the anion $[NTf_2]^-$ and either an imidazolium, an ammonium or a pyrrolidinium cation. Replacing the imidazolium cation with either the tetraalkylammonium-based cations resulted in a decrease in the solubility of carbon dioxide of between 15 and 30%. Interestingly, Baltus et al. [6] have observed, using a quartz crystal microbalance, a significantly greater carbon dioxide solubility in imidazolium-based ILs having fluorine-substituted cation as compared with the corresponding IL with a nonfluorinated cation. In this case the Henry's constant differs by a factor of seven between $[C_1C_8Im][NTf_2]$ and the corresponding fluorine-substituted IL $[C_1(C_8F_3)Im][NTf_2]$. This observation is compatible with the known affinity of carbon dioxide by fluorinated solvents [37].

In the present work, the selected ILs with the exception of $[C_1C_2Im][NTf_2]$ are not commonly studied. The solubility of carbon dioxide and ethane, was precisely determined as a function of temperature from 303 to 343 K and at pressures close to atmospheric using a high precision isochoric saturation method. The knowledge of the variation with temperature of the solubility allows the calculation of the thermodynamic properties of solvation.

2. Experimental

The IL $[C_1C_2Im][NTf_2]$ was prepared at the QUILL research center at Belfast, using the standard synthesis procedures described by Bonhôte et al. [25]. The bromide content of this IL sample was determined using ion chromatography (IC) [26] and was found to be below the 5 ppm detection limit. The water content was determined before and after the solubility measurements by volumetric Karl-Fisher titration using a Mettler Toledo DL31 titrator. A reference value of 45 ppm (w/w) of water was obtained after drying the liquid in vacuo at 303 K for 8 h. The bromide content of the $[C_1C_4pyrr][NTf_2]$ and chloride content of the $[N_{1132-OH}][NTf_2]$ samples were also determined using IC and were found to lay below the detection limit of 5 ppm. The water contents of these samples, determined as previously were respectively of 70 and 45 ppm (w/w) after the same treatment as previously.

The carbon dioxide (>0.99995 mol fraction) and ethane (>0.995 mol fraction) were purchased from AGA/Linde Gaz and were used as received.

The experimental apparatus used for the low-pressure gas solubility measurements is based on an isochoric saturation technique that has been described in previous publications [1–4]. In this technique, a known quantity of gaseous solute is placed in contact with a precisely determined quantity of degassed solvent 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.

The quantity of IL introduced in the equilibration cell is determined gravimetrically, V_{liq} being calculated from the density of the IL. The amount of solute present in the liquid solution, n_2^{liq} , is calculated by the difference between the pVT measured when the gas is initially introduced in a calibrated bulb with volume V_{GB} and then after thermodynamic equilibrium is reached (it is assumed that the volume of the saturated solution is the same of that of the pure IL):

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

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

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

or as Henry's law constant:

$$K_H = \lim_{x_2 \rightarrow 0} \frac{f_2(p, T, x_2)}{x_2} \cong \frac{\phi_2(p_{eq}, T_{eq})p_{eq}}{x_2} \quad (3)$$

where f_2 is the fugacity of the solute and ϕ_2 its fugacity coefficient calculated in the usual way [36]. In all cases, the subscript 2 denotes the solute and subscript 1 denotes the solvent.

The Henry's law constants can be exactly converted to the Gibbs energy of solvation, $\Delta_{solv}G^\infty$, corresponding to the change in Gibbs energy when the solute is transferred, at constant temperature, from the pure perfect gas state at the standard pressure to the standard state of infinite dilution of the solute in the solvent:

$$\Delta_{solv}G^\infty = RT \ln \left(\frac{K_H}{p^0} \right) \quad (4)$$

where p^0 is the standard state pressure. From the temperature variation of K_H , other thermodynamic properties of solvation can be calculated, which in the case of gaseous solutes at low pressures, can be approximated to the thermodynamic properties of solution [35]. The differences in enthalpy and entropy between the two standard states referred above ($\Delta_{solv}H^\infty$ and $\Delta_{solv}S^\infty$, respectively) can be obtained by taking the corresponding partial derivatives of the Gibbs energy with respect to temperature:

$$\begin{aligned} \Delta_{solv}H^\infty &= -RT^2 \frac{\partial}{\partial T} \left[\ln \left(\frac{K_H}{p^0} \right) \right], \\ \Delta_{solv}S^\infty &= -RT \frac{\partial}{\partial T} \left[\ln \left(\frac{K_H}{p^0} \right) \right] - R \ln \left(\frac{K_H}{p^0} \right) \end{aligned} \quad (5)$$

The densities of the three ILs investigated, necessary for the calculation of V_{liq} in Eq. (1), were determined in house from 293 to 343 K, with an overall precision of 0.01% using an Anton Paar densitometer (model DMA 512 P) [29].

3. Results and discussion

For each system, multiple experimental data points were obtained between 293 and 343 K in steps of approximately 10 K. The experimental solubilities of carbon dioxide and ethane in $[C_1C_2Im][NTf_2]$, $[C_1C_4pyrr][NTf_2]$ and $[N_{1132-OH}][NTf_2]$ are reported in Table 1. The solubility results are expressed as mole fractions of solute and as Henry's law constants. The mole fraction solubilities, at the reference pressure of 0.1 MPa, are calculated from the experimental data on K_H (at slightly different total pressures) assuming a partial pressure of the gaseous solute equal to 0.1 MPa. The relative atomic masses used are those recommended by IUPAC [27] and the values of the second virial coefficients, necessary for the calculation of the compressibility factor, were taken from the compilation by Dymond and Smith [28].

The density values were fitted to linear functions of the temperature (the average absolute deviation of the fit is 0.005%):

$$\rho_{[C_1C_2Im][NTf_2]} (\text{kg m}^{-3}) = 1817.0 - 1.0009(T/K) \quad (6)$$

$$\rho_{[C_1C_4pyrr][NTf_2]} (\text{kg m}^{-3}) = 1658.9 - 0.8872(T/K) \quad (7)$$

$$\rho_{[N_{1132-OH}][NTf_2]} (\text{kg m}^{-3}) = 1719.6 - 0.9032(T/K) \quad (8)$$

The measured density of $[C_1C_2Im][NTf_2]$ can be compared with previously published data [30–33]. The largest deviation found is of 0.2% between the present data and those of Refs. [32,33]. The density of $[C_1C_4pyrr][NTf_2]$ was measured by Anthony et al. [12] and shows a deviation from the present data

Table 1

Experimental values of gas solubilities in the three ILs investigated expressed both as Henry's law constants, K_H and as mole fraction, x_2 , corrected for a partial pressure of solute of 0.1 MPa

T (K)	p ($\times 10^2$ Pa)	K_H ($\times 10^5$ Pa)	x_2 ($\times 10^{-3}$)	Deviation (%)
[C₁C₂Im][NTf₂] + CO₂				
303.63	479.17	38.08	26.14	−0.3
303.87	464.06	38.61	25.78	+0.6
313.87	495.92	45.85	21.72	−0.1
313.92	492.93	46.22	21.55	+0.6
313.95	500.63	45.43	21.92	−1.2
323.96	519.63	54.15	18.40	−0.1
323.98	520.40	54.64	18.23	+0.7
324.05	433.03	53.92	18.48	−0.7
324.12	521.60	54.47	18.29	+0.2
334.07	542.17	62.93	15.84	−0.5
334.10	546.15	63.43	15.71	+0.3
334.16	448.41	63.90	15.60	+0.9
343.99	563.75	72.51	13.75	−0.3
344.23	570.97	72.90	13.68	−0.1
[C₁C₂Im][NTf₂] + C₂H₆				
304.14	442.33	150.5	6.599	−0.3
304.15	442.25	149.6	6.639	+0.3
314.25	456.31	171.5	5.793	−0.2
314.29	456.29	170.7	5.821	+0.3
324.43	470.27	196.5	5.060	+0.1
324.44	470.31	196.9	5.049	−0.1
334.58	484.23	229.4	4.337	−1.1
334.63	484.07	224.8	4.425	+0.9
344.70	497.70	261.8	3.802	+0.1
[C₁C₄pyrr][NTf₂] + CO₂				
303.78	486.78	36.65	27.15	+0.0
313.80	509.47	43.63	22.82	+0.7
313.85	505.34	42.99	23.16	−0.9
323.94	531.34	51.21	19.45	+0.8
323.96	526.15	50.64	19.67	−0.3
334.04	545.97	58.47	17.04	−0.7
334.04	552.17	59.08	16.87	+0.4
334.10	546.17	58.67	16.99	−0.4
344.04	565.53	67.57	14.75	+0.1
344.05	565.45	67.39	14.79	−0.2
344.15	572.64	67.81	14.70	+0.3
[C₁C₄pyrr][NTf₂] + C₂H₆				
304.24	388.75	105.2	9.441	+0.2
314.25	401.63	120.2	8.269	−0.2
324.40	414.36	136.2	7.300	−0.7
334.51	427.15	156.9	6.340	+1.1
344.69	439.26	173.7	5.730	−0.5
[N₁₁₃₂-OH][NTf₂] + CO₂				
304.16	467.00	41.75	23.84	+0.2
314.26	487.52	50.15	19.85	+0.1
324.46	507.04	59.44	16.76	−0.5
324.47	507.04	59.42	16.77	−0.6
334.61	526.21	70.83	14.07	+0.7
334.68	526.33	70.91	14.05	+0.7
344.84	543.86	81.66	12.21	−0.6
[N₁₁₃₂-OH][NTf₂] + C₂H₆				
304.15	436.37	159.9	6.209	−1.2
304.22	436.77	164.2	6.047	+1.4
314.21	450.39	189.3	5.248	+1.6
314.28	450.10	183.1	5.427	−1.9
324.35	463.70	211.8	4.694	−1.0
324.39	463.91	215.4	4.617	+0.6
334.36	477.05	245.2	4.057	+0.3
334.59	477.37	246.8	4.031	+0.6
344.74	490.48	278.4	3.575	−0.4

p is the experimental equilibrium pressure and the per cent deviation is relative to the correlations of the data reported in Table 2.

Fig. 2. Mole fraction gas solubilities of carbon dioxide (upper plot) and of ethane (lower plot) in the three ILs at 0.1 MPa partial pressure as a function of temperature: (■) [C₁C₂Im][NTf₂]; (▲) [C₁C₄pyrr][NTf₂]; and (●) [N₁₁₃₂-OH][NTf₂]. The curves represent Eq. (9) with parameters shown in Table 2.

of 0.02% at 293 K and of 0.3% at 323 K. To our knowledge, no density data were previously published for [N₁₁₃₂-OH][NTf₂].

To get representative values of the solubility, the Henry's law constants presented in Table 1 were correlated as a function of temperature by an empirical equation of the type:

$$\ln[K_H(T)/10^5 \text{ Pa}] = \sum_{i=0}^n A_i (T/K)^{-i} \quad (9)$$

The coefficients A_i obtained are listed in Table 2 together with the average absolute deviations obtained. When a sufficiently large number of independent experimental determinations are available, these deviations are a good approximation to the statistical error estimation obtained from the propagation of the experimental uncertainties in pressure, temperature and IL mass. These values can thus be regarded as an estimation of the precision of the solubility data considered in the present case as $\pm 1\%$.

In Fig. 2 the solubility, expressed in mole fraction, for the two gases in the ILs as a function of temperature is presented. In the three ILs investigated, carbon dioxide (mole fraction sol-

Table 2

Parameters of Eq. (9) which describes the experimental results on K_H from Table 1 along with the per cent average absolute deviation of the fit (AAD)

System	A_0	A_1	A_2	AAD (%)
$[C_1C_2Im][NTf_2] + CO_2$	+7.595	-6.716×10^2	-1.604×10^5	0.5
$[C_1C_2Im][NTf_2] + C_2H_6$	+16.22	-5.639×10^3	$+6.780 \times 10^5$	0.4
$[C_1C_4pyrr][NTf_2] + CO_2$	+8.579	-1.429×10^3	-2.514×10^4	0.4
$[C_1C_4pyrr][NTf_2] + C_2H_6$	+9.487	-1.644×10^3	$+5.279 \times 10^4$	0.5
$[N_{1132-OH}][NTf_2] + CO_2$	+9.478	-1.748×10^3	$+8.673 \times 10^1$	0.4
$[N_{1132-OH}][NTf_2] + C_2H_6$	+12.16	-2.992×10^4	$+2.554 \times 10^5$	1.0

ubility between 1 and 3×10^{-2} , molarity between 0.03 and 0.1 mol L^{-1}) is one order of magnitude more soluble than ethane (mole fraction solubility between 4 and 10×10^{-3} , molarity between 0.01 and 0.04 mol L^{-1}). This is in good agreement with the data reported by Camper et al. [8,10] for the ionic liquid $[C_1C_2Im][NTf_2]$ and is compatible with the values reported for other imidazolium-based ILs [1,2,10,11]. The higher solubility of carbon dioxide in the ILs has been explained by the importance of the solute–solvent electrostatic interactions [34].

The present results indicate that the presence of the pyrrolidinium cation increases the solubility of both gases while the

lower solubilities were measured in the ammonium-based IL containing an alcohol function. The influence of changing the cation is more significant for ethane than for carbon dioxide solubility. For example, the presence of pyrrolidinium cation increases the solubility of ethane by nearly 50% compared with the solubility in the two other ILs investigated. The carbon dioxide solubility only increases at most 21% in the presence of this cation.

Fig. 3 shows deviation plots with differences between the various literature sources and the correlation of the present data for the systems: $[C_1C_2Im][NTf_2]$ + carbon dioxide and $[C_1C_2Im][NTf_2]$ + ethane in order to estimate the accuracy of the data in this work. For $[C_1C_2Im][NTf_2]$ + carbon dioxide (Fig. 3a), the values reported by Cadena et al. [14], by Camper et al. [7,10] and by our research group in a previous study [4] (using the same type of experimental apparatus but another sample of IL) deviate from the present work less than 5%. Another set of data from Camper et al. [8] for the same system show a larger deviation specially at the higher temperature end. Finally, two sets of data, reported by Kim et al. [17] and by Morgan et al. [9], exhibit a difference of more than 5% from the present data. These higher deviations can be explained, in the case of Morgan et al. [9] by a 10% error claimed by the authors for their experimental solubilities. Concerning the data of Kim et al. [17], a pressure extrapolation was necessary to calculate the Henry's

Fig. 3. Percent deviations from the literature values to the correlation of the Henry's law constants obtained in this work for carbon dioxide in $[C_1C_2Im][NTf_2]$ (a) and for ethane in $[C_1C_2Im][NTf_2]$ (b): (■) this work; (○) Jacquemin et al. [4]; (□) Camper et al. [7,10]; (▲) Camper et al. [8]; (◆) Morgan et al. [9]; (●) Cadena et al. [14]; and (▼) Kim et al. [17].

Fig. 4. Literature values of Henry's law constants as a function of temperature for carbon dioxide in $[C_1C_2Im][NTf_2]$: (○) Jacquemin et al. [4]; $[C_1C_4Im][NTf_2]$: (●) Jacquemin et al. [4]; $[N_{4111}][NTf_2]$: (□) Jacquemin et al. [4]; $[N_{1444}][NTf_2]$: (▲) Anthony et al. [12]; and $[C_1C_4pyrr][NTf_2]$: (△) Anthony et al. [12]. The curves represent Eq. (9) with parameters shown in Table 2: (—), $[C_1C_2Im][NTf_2]$; (---), $[N_{1132-OH}][NTf_2]$; (· · ·), $[C_1C_4pyrr][NTf_2]$.

law constants from their high-pressure measurements at 298 K. The precision of this fit can explain the differences found in the solubilities.

Fig. 3b presents the deviations between the present set of data and those previously reported for $[C_1C_2mim][NTf_2]$ + ethane. This system has been investigated by Camper et al. [8,10] at 303 and 313 K and agree to within 4% with the present set of data.

Only Anthony et al. [12] report the solubility of CO_2 in $[C_1C_4pyrr][NTf_2]$ at three temperatures from 283 to 323 K. Their Henry's law constants, obtained by extrapolation of high-pressure data, agree with the ones obtained in the present work to within 10% at 323 K. At the lower temperatures considered by these authors, not studied in the present work, deviations up to 22% are calculated between their data and the extrapolation at lower temperatures of our solubility data. Because of these extrapolations, these values were not considered in the estimation of the accuracy of the present data.

Table 3

Thermodynamic functions of solvation for the carbon dioxide and ethane in the three ILs investigated at several discrete temperatures between 305 and 345 K

T (K)	$\Delta_{sol}G^\infty$ (kJ mol $^{-1}$)	$\Delta_{sol}H^\infty$ (kJ mol $^{-1}$)	$\Delta_{sol}S^\infty$ (J mol $^{-1}$ K $^{-1}$)
$[C_1C_2Im][NTf_2]$ + CO_2			
305	9.308	−14.3	−77.5
315	10.08	−14.0	−76.6
325	10.84	−13.8	−75.8
335	11.59	−13.5	−75.0
345	12.34	−13.3	−74.3
$[C_1C_2Im][NTf_2]$ + C_2H_6			
305	12.73	−9.92	−74.3
315	13.50	−11.1	−78.1
325	14.29	−12.2	−81.5
335	15.12	−13.2	−84.6
345	15.99	−14.2	−87.5
$[C_1C_4pyrr][NTf_2]$ + CO_2			
305	9.186	−13.3	−73.6
315	9.922	−13.2	−73.4
325	10.66	−13.2	−73.3
335	11.39	−13.1	−73.2
345	12.12	−13.1	−73.1
$[C_1C_4pyrr][NTf_2]$ + C_2H_6			
305	11.83	−10.8	−74.2
315	12.57	−10.9	−74.5
325	13.32	−11.0	−74.7
335	14.07	−11.0	−75.0
345	14.82	−11.1	−75.2
$[N_{1132-OH}][NTf_2]$ + CO_2			
305	9.500	−14.5	−78.9
315	10.29	−14.5	−78.9
325	11.08	−14.5	−78.9
335	11.86	−14.5	−78.9
345	12.65	−14.5	−78.9
$[N_{1132-OH}][NTf_2]$ + C_2H_6			
305	12.93	−11.0	−78.3
315	13.72	−11.4	−79.7
325	14.52	−11.8	−81.0
335	15.34	−12.2	−82.2
345	16.17	−12.6	−83.3

$\Delta_{sol}G^\infty$ is the Gibbs energy of solvation, $\Delta_{sol}H^\infty$ the enthalpy of solvation and $\Delta_{sol}S^\infty$ the entropy of solvation. The values are consistent with $p^0 = 0.1$ MPa.

After a careful analysis of the present data and in light of the comparisons made, the present values are considered to be precise to within $\pm 1\%$ with an estimated accuracy better than $\pm 5\%$.

The effect of changing the cation of the IL is significant as can be observed in Fig. 4 where Henry's law constants obtained for carbon dioxide in this study and with imidazolium-, ammonium- or pyrrolidinium-based ILs are depicted. The results obtained in $[C_1C_2Im][NTf_2]$ (two sets of data obtained with two different samples [4]) and $[C_1C_4Im][NTf_2]$ confirm a slight increase of the solubility of carbon dioxide when increasing the chain length on the imidazolium ring of the cation. This phenomenon was already observed by other authors [6,15,23]. It can also be observed in this figure that the solubility of carbon dioxide in $[C_1C_4Im][NTf_2]$ and in $[C_1C_4pyrr][NTf_2]$ (ILs with two different cycles – one aromatic and one non-aromatic – but with the same alkyl chains on these cycles) is comparable. Concerning the ammonium cations, the addition of an alcohol function – comparison between $[N_{4111}][NTf_2]$ and $[N_{1132-OH}][NTf_2]$ – increases the Henry's law constant (solubility decreases). The higher solubility, measured by our group, for carbon dioxide in the IL with the pyrrolidinium cation, compared to the solubility in ammonium cation, was also observed by Anthony et

Fig. 5. Enthalpy of solvation of carbon dioxide (upper plot) and ethane (lower plot) in the three considered ILs as a function of temperature: (■) $[C_1C_2Im][NTf_2]$; (▲) $[C_1C_4pyrr][NTf_2]$; and (●) $[N_{1132-OH}][NTf_2]$.

al. [12]. Finally, the variations of the solubility caused by the change of the cation are slightly more important at higher temperatures. For example, carbon dioxide is 14% more soluble in pyrrolidinium-based IL than in ammonium-based IL at 303 K, it is 21% more soluble at 344 K.

The variation with temperature of the solubility, expressed in Henry's law constant, is directly related with the thermodynamic properties of solvation through Eqs. (4) and (5) and constitute a reasonable approximation, for the case of gaseous solutes at low pressure, of the thermodynamic properties of solution [35]. The values for the partial molar Gibbs energy, enthalpy and entropy of solvation are given for the six investigated systems in Table 3. Figs. 5 and 6 present the variation with temperature of the enthalpy and entropy of solvation for the considered systems, respectively.

The negative enthalpies of solvation calculated correspond to exothermic processes of solvation which means that the solvation is thus favoured at lower temperatures. More negative values were calculated for systems involving carbon dioxide. As can be observed in Fig. 6, all the systems investigated exhibit negative entropies of solvation. The properties of solvation of the two gases in $[C_1C_4pyrr][NTf_2]$ do not vary significantly with

temperature while important variations of these properties with temperature are depicted for both gases in $[C_1C_2Im][NTf_2]$. In $[N_{1132-OH}][NTf_2]$, for the case of carbon dioxide, no significant variation of the properties is observed while they decrease for the case of ethane.

4. Conclusions

In this paper, the effect of changing the cation of the IL on the low-pressure solubility of two gaseous solutes, carbon dioxide and ethane, was investigated. The solubility of these gases was measured as a function of temperature using an accurate isochoric saturation method in $[C_1C_4pyrr][NTf_2]$, $[C_1C_2Im][NTf_2]$ and $[N_{1132-OH}][NTf_2]$. Carbon dioxide with mole fractions solubility between 1 and 3×10^{-2} , was found to be one order of magnitude more soluble than ethane. These data have been shown to be precise to within $\pm 1\%$ and accurate to within $\pm 5\%$. For all the systems, the solubility decreases with increasing temperature which corresponds to exothermic processes of solvation.

Although the effect of changing the cation on the solubility is less significant than the effect of changing the anion, it is still noticeable. Both gases appear as more soluble in the pyrrolidinium-based IL and less soluble in the ammonium-based IL studied, an observation already made by Anthony et al. [12]. Changing the cation has a similar effect on both gases.

Negative enthalpies (exothermic processes) and entropies of solvation were calculated for all the systems investigated. The properties of solvation of the two gases in $[C_1C_4pyrr][NTf_2]$ do not vary significantly with temperature while important variations are depicted for both gases in $[C_1C_2Im][NTf_2]$.

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Fig. 6. Entropy of solvation of carbon dioxide (upper plot) and ethane (lower plot) in the three considered ILs as a function of temperature: (■) $[C_1C_2Im][NTf_2]$; (▲) $[C_1C_4pyrr][NTf_2]$; and (●) $[N_{1132-OH}][NTf_2]$.

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