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# Influence of the Cation on the Solubility of CO<sub>2</sub> and H<sub>2</sub> in Ionic Liquids Based on the Bis(trifluoromethylsulfonyl)imide Anion

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**Abstract** Experimental values for the solubility of carbon dioxide and hydrogen in three room temperature ionic liquids based on the same anion—(bistrifluoromethylsulfonyl)imide [Ntf<sub>2</sub>]<sup>-</sup>—and three different cations—1-butyl-3-methylimidazolium, [C<sub>4</sub>mim]<sup>+</sup>, 1-ethyl-3-methylimidazolium, [C<sub>2</sub>mim]<sup>+</sup> and trimethyl-butylammonium, [N<sub>4111</sub>]<sup>+</sup>—are reported between 283 and 343 K and close to atmospheric pressure. Carbon dioxide, with a mole-fraction solubility of the order of 10<sup>-2</sup>, is two orders of magnitude more soluble than hydrogen. The solubility of CO<sub>2</sub> is very similar in the three ionic liquids although slightly lower in the presence of the [C<sub>2</sub>mim]<sup>+</sup> cation. In the case of H<sub>2</sub>, noticeable differences were observed with larger mole fraction solubilities in the presence of [N<sub>4111</sub>]<sup>+</sup> followed by [C<sub>4</sub>mim]<sup>+</sup>. All of the mole-fraction solubilities decrease with increasing temperature. From the variation of Henry's law constants with temperature, the thermodynamic functions of solvation were calculated. The precision of the experimental data, considered as the average absolute deviation of the Henry's law constants from appropriate smoothing equations, is always better than ±1%.

**Keywords** Solubility · Carbon dioxide · Hydrogen · Ionic liquids · Ntf<sub>2</sub>

## 1 Introduction

In the present paper we report original low-pressure solubility measurements of two gases in three ionic liquids. The main objective of this project is to identify the effect of cation substitution of the ionic liquid on gas solubility.

Knowledge of the gas solubility in this new family of liquid solvents is useful both from practical and fundamental points of view. Gas solubility data are valuable in view of the use of room temperature ionic liquids as reaction systems or in separation processes. They also

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provide a reliable way to calculate the thermodynamic properties of a solution and to assess the molecular mechanisms involved in the solvation process.

Three ionic liquids were chosen for this study: 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide,  $[\text{C}_2\text{mim}][\text{Ntf}_2]$ ; 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide,  $[\text{C}_4\text{mim}][\text{Ntf}_2]$ ; and butyltrimethylammonium bis(trifluoromethylsulfonyl)imide,  $[\text{N}_{4111}][\text{Ntf}_2]$ .

The solubility of gases in 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide has been determined by other research groups using different techniques, and Henry's law constants could be determined both from data obtained at pressures close to atmospheric [1–4] or by extrapolation of values obtained at higher pressures [5–9]. Carbon dioxide is the most studied gaseous solute and the values reported in the literature for the Henry's law constants agree to within  $\pm 20\%$ . Hydrogen solubility was measured only by Dyson et al. [5] at 298 K. No results are available in literature for gas solubilities in ionic liquids based on the ammonium cation studied in this work.

In this paper, experimental solubilities of carbon dioxide and hydrogen in three ionic liquids sharing the  $[\text{Ntf}_2]$  anion are reported as a function of temperature between 283 and 343 K near 0.1 MPa using a high precision isochoric saturation method [10–13]. These solubility data allow the calculation of the Henry's law constants as a function of temperature, and from them the thermodynamic properties of solvation. The Gibbs energy of solvation, considered as the change in Gibbs energy when the solute is transferred at constant temperature from a pure perfect gas at 0.1 MPa to the infinitely dilute standard state in the solvent, is calculated directly from the Henry's law constants, and the standard enthalpy and entropy of solvation from their variation with temperature.

## 2 Experimental

### 2.1 Materials

The samples of the three selected ionic liquids based on the  $[\text{Ntf}_2]$  anion (minimum stated purity of 0.99 in mole fraction) were supplied by the group of Prof. P. Wasserscheid (University of Erlangen-Nürnberg, Germany). The  $[\text{C}_2\text{mim}][\text{Ntf}_2]$  and  $[\text{C}_4\text{mim}][\text{Ntf}_2]$  were synthesized via ion exchange from  $[\text{C}_2\text{mim}][\text{Br}]$  and  $[\text{C}_4\text{mim}][\text{Cl}]$ , respectively. Halide content analysis indicated values lower than 50 ppm for both bromide and chloride. The ionic liquid  $[\text{N}_{4111}][\text{Ntf}_2]$  did not contain any chloride or bromide ions.

All samples were kept under vacuum for 15 h at 303 K before each measurement. A volumetric Karl Fisher titration (Mettler Toledo DL31) was performed before and after each series of measurements and it was found that there was no variation of the quantity of water in the samples. In all cases, the water contents were approximately  $50 \pm 5$  ppm.

The carbon dioxide and hydrogen used for this study were supplied by AGA/Linde Gaz with mole fraction purities of 0.99995 and 0.9998, respectively. All gases were used as received from the manufacturer.

### 2.2 Procedure

The experimental method used for these gas solubility measurements is based on an isochoric saturation technique that has been described in previous publications [10–13]. In this technique, a known quantity of a gaseous solute is put into contact with a precisely determined quantity of degassed solvent at a constant temperature inside a cell of accurately

known volume. When thermodynamic equilibrium is attained, the pressure above the liquid solution is constant and is directly related to the solubility of the gas in the liquid.

The quantity of ionic liquid introduced into the equilibration cell,  $V_{\text{liq}}$ , is determined gravimetrically. The amount of solute present in the liquid solution,  $n_2^{\text{liq}}$  (subscript 2 stands for solute and subscript 1 stands for solvent), is calculated by the difference between two  $pVT$  measurements, the first when the gas is introduced into a calibrated bulb with volume  $V_{\text{GB}}$  and the second after thermodynamic equilibrium is reached:

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

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

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

or as the Henry's law constant:

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

where  $f_2$  is the fugacity of the solute and  $\phi_2$  its fugacity coefficient.

### 3 Results and Discussion

For each system studied, multiple experimental data points were obtained in the temperature interval between 283 and 343 K in steps of approximately 10 K. The experimental solubilities, expressed as mole fraction of carbon dioxide and hydrogen in the three selected ionic liquids are reported in Table 1 and Table 2. Henry's law constants can be calculated from the experimental values and are used to determine the mole fraction solubility, assuming a partial pressure of the gaseous solute equal to 0.1 MPa.

The relative atomic masses used are the ones recommended by IUPAC [14] and the values of the second virial coefficients for all the gases, necessary for the calculation of the compressibility factor, were taken from the compilation by Dymond and Smith [15]. The densities of the ionic liquid samples used as solvents during the present measurements were determined as a function of temperature with a precision of 0.01% using an Anton Paar vibrating-tube densitometer (model DMA 512 P) [16].

$$\rho_{[\text{C}_2\text{mim}][\text{Ntf}_2]}/\text{kg}\cdot\text{m}^{-3} = 1816.5 - 1001.3 \times 10^{-3}(T/\text{K}) \quad (4)$$

$$\rho_{[\text{C}_4\text{mim}][\text{Ntf}_2]}/\text{kg}\cdot\text{m}^{-3} = 1722.7 - 9549.6 \times 10^{-4}(T/\text{K}) \quad (5)$$

$$\rho_{[\text{N}_{4111}][\text{Ntf}_2]}/\text{kg}\cdot\text{m}^{-3} = 1654.9 - 8820.0 \times 10^{-4}(T/\text{K}). \quad (6)$$

**Table 1** Experimental results for the solubility of H<sub>2</sub> in the ionic liquids 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, where  $p$  is the experimental equilibrium pressure and the per cent deviation is relative to the correlations of the data reported in Table 3

$T/K$	$p/10^2$ Pa	$K_H/10^5$ Pa	$x_2/10^{-4}$	dev %
<b>[N<sub>4111</sub>][Ntf<sub>2</sub>]</b>				
282.93	790.55	1117	8.956	-0.0
292.61	816.51	1130	8.854	-0.0
303.35	461.05	1169	8.562	+0.4
303.38	845.38	1175	8.518	-0.1
303.40	826.75	1175	8.516	-0.2
313.29	871.97	1239	8.078	-0.1
313.29	475.04	1232	8.122	+0.5
323.16	898.44	1327	7.543	-0.1
323.18	489.00	1330	7.521	-0.4
323.24	878.71	1328	7.534	-0.2
333.07	925.01	1438	6.960	-0.2
333.27	904.94	1431	6.991	+0.4
343.02	925.01	1570	6.374	+0.0
<b>[C<sub>4</sub>mim][Ntf<sub>2</sub>]</b>				
283.45	761.03	1274	7.855	-0.0
293.30	748.70	1328	7.537	-0.2
293.41	786.80	1334	7.502	+0.2
303.24	812.22	1427	7.013	+0.3
303.42	773.63	1422	7.038	-0.2
313.31	838.26	1551	6.450	-0.2
323.25	822.43	1735	5.767	+0.7
323.28	864.01	1717	5.829	-0.4
333.12	889.40	1925	5.197	-0.3
343.08	915.05	2181	4.587	-0.4
343.13	871.18	2201	4.545	+0.5
<b>[C<sub>2</sub>mim][Ntf<sub>2</sub>]</b>				
282.98	806.80	1351	7.404	+0.2
293.10	834.59	1428	7.006	-0.4
303.38	801.90	1534	6.524	-0.0
303.43	433.75	1535	6.519	-0.1
304.35	865.47	1539	6.500	+0.4
313.19	826.88	1677	5.966	+0.1
313.28	446.86	1685	5.939	-0.3
323.18	460.01	1867	5.358	+0.1
325.15	857.35	1910	5.239	+0.1
333.03	877.36	2104	4.756	-0.0
333.09	473.13	2103	4.758	+0.1
343.05	902.80	2395	4.178	-0.0
343.07	486.32	2397	4.174	-0.1

**Table 2** Experimental results for the solubility of CO<sub>2</sub> in the ionic liquids 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, where  $p$  is the experimental equilibrium pressure and the per cent deviation is relative to the correlations of the data reported in Table 3

$T/K$	$p/10^2$ Pa	$K_H/10^5$ Pa	$x_2/10^{-4}$	dev %
<b>[N<sub>4111</sub>][Ntf<sub>2</sub>]</b>				
282.94	692.44	23.78	418.0	+0.2
290.17	725.19	27.93	356.1	-0.3
303.38	360.61	36.13	275.5	+0.3
303.38	779.81	36.20	274.9	+0.1
303.39	753.25	36.34	273.9	-0.3
313.24	383.51	43.33	229.8	+0.2
313.28	818.72	43.51	228.9	-0.1
323.15	405.20	51.36	194.0	+0.1
323.19	824.23	51.54	193.3	-0.1
333.09	425.91	60.28	165.3	+0.0
343.00	445.54	69.95	142.5	-0.0
343.07	890.12	70.02	142.4	-0.0
<b>[C<sub>4</sub>mim][Ntf<sub>2</sub>]</b>				
283.36	675.30	23.91	415.7	+0.4
293.25	715.64	29.95	332.1	-0.2
303.21	752.47	36.41	273.3	-0.2
303.23	958.23	36.57	272.2	-0.6
303.26	933.69	36.45	273.1	-0.2
313.36	1001.18	43.51	228.9	-0.3
313.39	971.94	43.23	230.3	+0.4
323.22	820.01	50.76	196.3	-0.3
323.48	1042.44	51.08	195.0	-0.5
323.61	1008.86	50.19	198.5	+1.4
333.70	1082.50	59.09	168.6	-0.8
333.76	1044.78	57.69	172.7	+1.7
343.78	1120.07	66.52	149.9	-0.1
343.79	1080.57	67.01	148.8	-0.8
<b>[C<sub>2</sub>mim][Ntf<sub>2</sub>]</b>				
283.43	650.50	24.88	399.6	+0.2
293.39	691.74	31.06	320.3	-0.2
303.39	729.85	37.90	262.6	-0.1
323.22	799.32	53.75	185.3	+0.3
343.07	863.61	72.99	136.6	-0.1

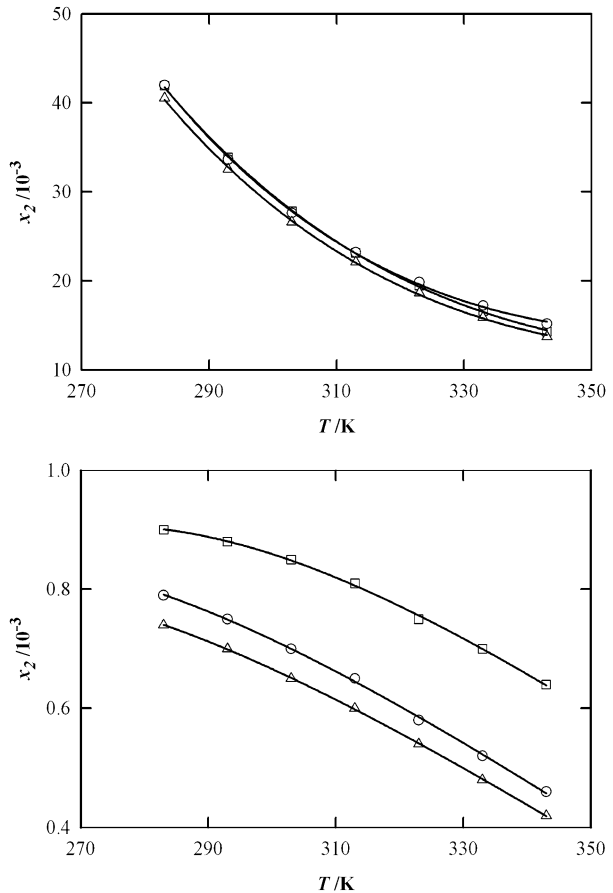
The Henry's law constants obtained from the experimental data were correlated as a function of temperature by an empirical equation of the type:

$$\ln[K_H/10^5 \text{ Pa}] = \sum_{i=0}^n A_i (T/K)^{-i}. \quad (7)$$

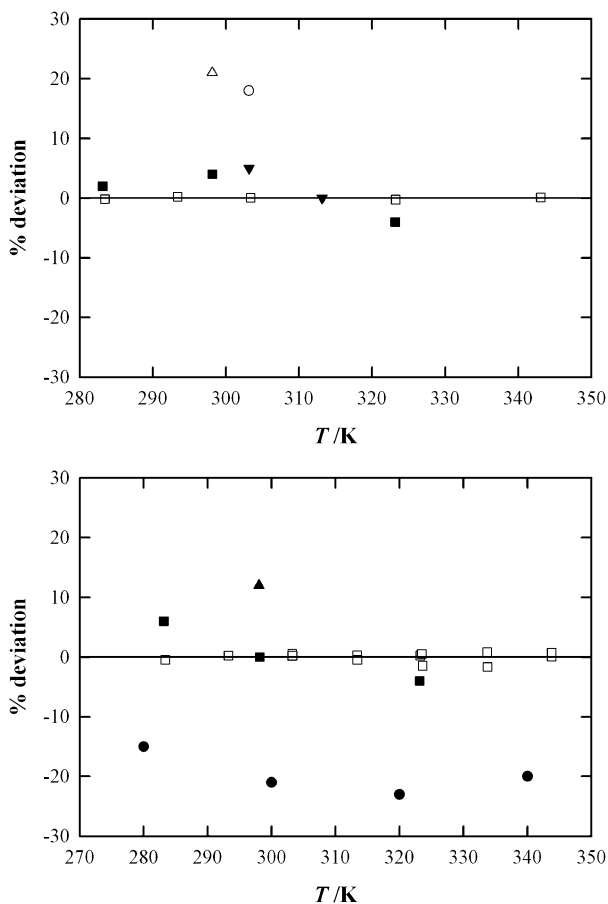
**Table 3** Parameters of Eq. 7 used to smooth the experimental  $K_H$  results from Tables 1 and 2, along with the per cent average absolute deviation of the fit (AAD)

Gas	$A_0$	$A_1$	$A_2$	AAD %
<b>[N<sub>4111</sub>][Ntf<sub>2</sub>]</b>				
H <sub>2</sub>	+18.26	$-6.372 \times 10^3$	$+9.027 \times 10^5$	0.2
CO <sub>2</sub>	+8.769	$-1.394 \times 10^3$	$-5.364 \times 10^4$	0.2
<b>[C<sub>4</sub>mim][Ntf<sub>2</sub>]</b>				
H <sub>2</sub>	+21.10	$-7.674 \times 10^3$	$+1.054 \times 10^6$	0.3
CO <sub>2</sub>	+5.006	$+8.455 \times 10^2$	$-3.863 \times 10^5$	0.6
<b>[C<sub>2</sub>mim][Ntf<sub>2</sub>]</b>				
H <sub>2</sub>	+21.24	$-7.668 \times 10^3$	$+1.046 \times 10^6$	0.2
CO <sub>2</sub>	+7.935	$-8.376 \times 10^2$	$-1.417 \times 10^5$	0.2

**Fig. 1** Mole fraction gas solubilities of CO<sub>2</sub> (upper plot) and H<sub>2</sub> (lower plot) at 0.1 MPa partial pressure of the solute as a function of temperature in: □, [N<sub>4111</sub>][Ntf<sub>2</sub>]; ○, [C<sub>4</sub>mim][Ntf<sub>2</sub>]; △, [C<sub>2</sub>mim][Ntf<sub>2</sub>]. Lines represent smoothed data using the parameters in Table 3



**Fig. 2** Deviations from the literature values of the correlation of the Henry's law constants obtained in this work for carbon dioxide in  $[\text{C}_2\text{mim}][\text{NTf}_2]$  (upper plot) and in  $[\text{C}_4\text{mim}][\text{NTf}_2]$  (lower plot):  $\square$ , this work,  $\blacksquare$ , Cadena et al., 2004 [1] and Anthony et al., 2005 [7];  $\circ$ , Kim et al., 2005 [6];  $\triangle$ , Morgan et al., 2005 [8];  $\blacktriangledown$ , Camper et al., 2005 and 2006 [3, 4];  $\bullet$ , Lee and Outcalt, 2006 [9];  $\blacktriangle$ , Baltus et al., 2004 [2]



The  $A_i$  coefficients obtained are listed in Table 3 together with the average absolute deviations obtained for each solute. These values can be regarded as an estimation of the precision of the experimental data, which in the present case is always better than 1%.

In Fig. 1 are illustrated the solubility data, expressed in mole fraction, for carbon dioxide and hydrogen in the selected ionic liquids as a function of temperature. As it can be observed, carbon dioxide is two orders of magnitude more soluble than hydrogen (mole-fraction solubilities of  $10^{-2}$  and  $10^{-4}$ , respectively). The solubility of the two gases in the three ionic liquids decreases with increasing temperature in the range covered by this work.

The solubility of carbon dioxide in  $[\text{C}_2\text{mim}][\text{NTf}_2]$  has been determined by different research groups, often as a function of temperature, using different experimental techniques. It is then possible to compare some of the present results with those of other authors, the comparison providing guidance to estimate the accuracy of the data in this work. A deviation plot showing differences between the various literature sources and the correlation of the present data is represented in the upper plot of Fig. 2. As it can be observed, only two sets of values, those reported by Kim et al. [6] and by Morgan et al. [8], exhibit a difference of more than 10% from the present data. The values reported by Cadena et al. [1] and by Camper et al. [3] deviate from the present work by less than 5%. In the lower plot of Fig. 2, a similar deviation plot illustrates the solubility of  $\text{CO}_2$  in  $[\text{C}_4\text{mim}][\text{NTf}_2]$ . For this ionic liquid, the



**Table 4** Thermodynamic functions of solvation for H<sub>2</sub> in the three ionic liquids at several discrete temperatures between 283 and 343 K.  $\Delta_{\text{solv}}G^\infty$  is the Gibbs energy of solvation,  $\Delta_{\text{solv}}H^\infty$  the enthalpy of solvation and  $\Delta_{\text{solv}}S^\infty$  the entropy of solvation. The values are consistent with  $p^\circ = 0.1$  MPa

$T/\text{K}$	$\Delta_{\text{solv}}G^\infty/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{solv}}H^\infty/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{solv}}S^\infty/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
<b>[N<sub>4111</sub>][Ntf<sub>2</sub>]</b>			
283	16.51	+0.06	-58.1
293	17.13	-1.75	-64.4
303	17.80	-3.44	-70.1
313	18.53	-5.02	-75.2
323	19.30	-6.51	-79.9
333	20.12	-7.90	-84.2
343	20.99	-9.22	-88.0
<b>[C<sub>4</sub>mim][Ntf<sub>2</sub>]</b>			
283	16.82	-1.86	-66.0
293	17.52	-3.98	-73.4
303	18.29	-5.95	-80.0
313	19.12	-7.80	-86.0
323	20.00	-9.54	-91.5
333	20.94	-11.2	-96.4
343	21.93	-12.7	-101
<b>[C<sub>2</sub>mim][Ntf<sub>2</sub>]</b>			
283	16.97	-2.28	-68.0
293	17.68	-4.37	-75.3
303	18.47	-6.33	-81.9
313	19.32	-8.17	-87.8
323	20.23	-9.89	-93.2
333	21.18	-11.5	-98.2
343	22.19	-13.0	-103

values of Cadena et al. [1] agree with the ones obtained in the present work to within 5%, but the solubilities reported by both Baltus et al. [2] and Lee and Outcalt [9] deviate by more than 10% from the ones measured here. After a careful analysis of the present data, and in light of the comparisons made, we consider that the present values are precise to within  $\pm 1\%$  and have an accuracy of better than  $\pm 5\%$ .

The variation with temperature of the solubility for the two gases studied in the three ionic liquids, expressed in terms of the Henry's law constant, is directly related to the thermodynamic properties of solvation which, in the case of gaseous solutes at low pressures, are practically identical to the thermodynamic properties of the solution [17]. The Gibbs energy of solvation is given by

$$\Delta_{\text{solv}}G^\infty = RT \ln(K_{\text{H}}/p^\circ) \quad (8)$$

where  $p^\circ$  is the standard state pressure. The partial molar differences in enthalpy and entropy between the two states can be obtained by calculating the corresponding partial derivatives

**Table 5** Thermodynamic functions of solvation for CO<sub>2</sub> in the three ionic liquids at several discrete temperatures between 283 and 343 K.  $\Delta_{\text{solv}}G^\infty$  is the Gibbs energy of solvation,  $\Delta_{\text{solv}}H^\infty$  the enthalpy of solvation and  $\Delta_{\text{solv}}S^\infty$  the entropy of solvation. The values are consistent with  $p^0 = 0.1$  MPa

$T/\text{K}$	$\Delta_{\text{solv}}G^\infty/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{solv}}H^\infty/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{solv}}S^\infty/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
<b>[N<sub>4111</sub>][Ntf<sub>2</sub>]</b>			
283	7.464	-14.7	-78.5
293	8.247	-14.6	-78.1
303	9.026	-14.5	-77.8
313	9.802	-14.4	-77.5
323	10.58	-14.4	-77.2
333	11.35	-14.3	-76.9
343	12.11	-14.2	-76.7
<b>[C<sub>4</sub>mim][Ntf<sub>2</sub>]</b>			
283	7.460	-15.67	-81.7
293	8.264	-14.90	-79.0
303	9.042	-14.17	-76.6
313	9.797	-13.49	-74.4
323	10.53	-12.86	-72.4
333	11.25	-12.3	-70.6
343	11.94	-11.7	-68.9
<b>[C<sub>2</sub>mim][Ntf<sub>2</sub>]</b>			
283	7.543	-15.3	-80.7
293	8.345	-15.0	-79.7
303	9.137	-14.7	-78.8
313	9.921	-14.5	-78.0
323	10.70	-14.3	-77.3
333	11.47	-14.0	-76.6
343	12.23	-13.8	-76.0

of the Gibbs energy with respect to temperature

$$\Delta_{\text{solv}}H^\infty = -T^2\partial/\partial T(\Delta_{\text{solv}}G^\infty/T) = -RT^2\partial/\partial T[\ln(K_H/p^0)] \quad (9)$$

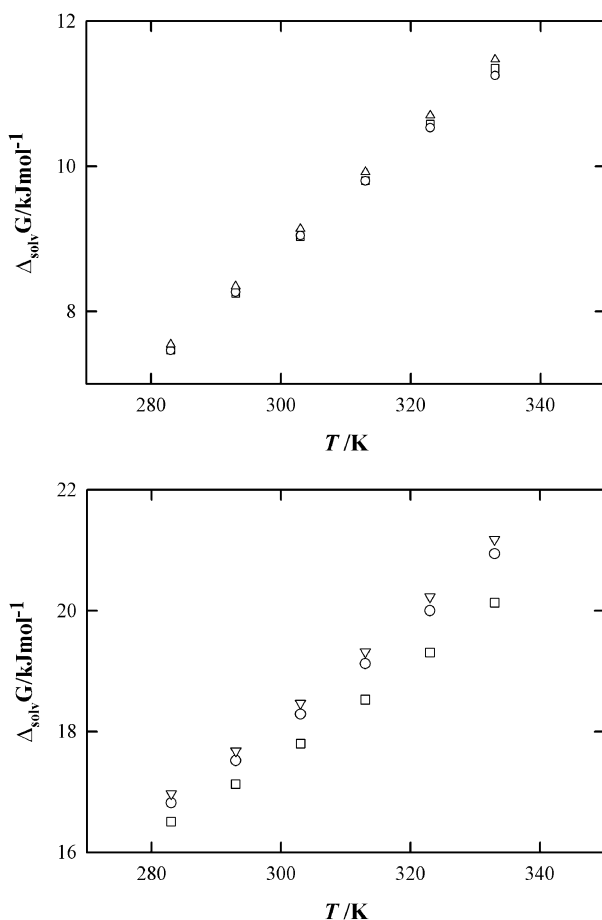
$$\Delta_{\text{solv}}S^\infty = (\Delta_{\text{solv}}H^\infty - \Delta_{\text{solv}}G^\infty)/T = -RT\partial/\partial T[\ln(K_H/p^0)] - R\ln(K_H/p^0). \quad (10)$$

The values of the Gibbs energy, enthalpy and entropy of solvation are given in Tables 4 and 5 for the two gases in the three ionic liquids at seven discrete temperatures between 283 and 343 K.

The Gibbs energy of solvation is depicted in Fig. 3 for carbon dioxide (upper plot) and for hydrogen (lower plot) in the ionic liquids studied. As it can be observed, the Gibbs energy of solvation increases with increasing temperature for both gases in a similar manner for all the ionic liquids studied. This variation leads to negative enthalpies of solvation, indicating an exothermal solvation process. In the temperature range studied, and as can be observed in Fig. 4, the enthalpy of solvation is more negative for carbon dioxide than for hydrogen. For the first gas, it does not vary significantly with temperature but, in the

**Fig. 3** Gibbs energy of solvation of CO<sub>2</sub> (upper plot) and H<sub>2</sub> (lower plot) at 0.1 MPa partial pressure of the solute as a function of temperature in:

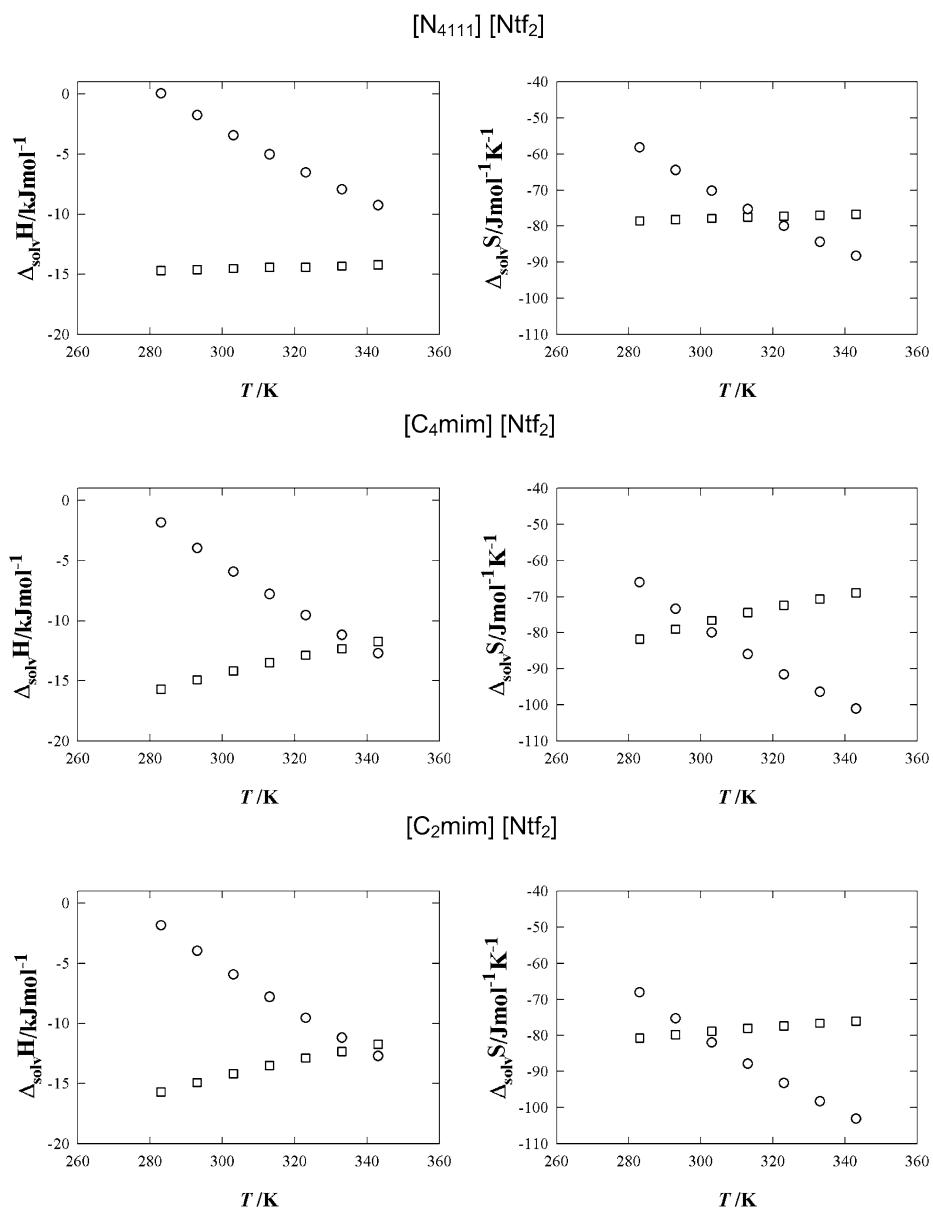
- , [N<sub>4111</sub>][Ntf<sub>2</sub>];  
 ○, [C<sub>4</sub>mim][Ntf<sub>2</sub>];  
 ∇, [C<sub>2</sub>mim][Ntf<sub>2</sub>]



case of hydrogen, it decreases significantly with temperature. For the three ionic liquids studied, the enthalpy of solvation for hydrogen approaches zero for the lower temperatures studied.

The entropy of solvation in Fig. 4, is noticeably more negative for the imidazolium based ionic liquids and varies between  $-60$  and  $-100$  J·mol<sup>-1</sup>·K<sup>-1</sup>. For all of the ionic liquids, its variation with temperature is more important for hydrogen than for carbon dioxide in the temperature range covered by this work.

Because the solubility data are sufficiently precise, the thermodynamic properties of solvation can be used to make inferences about the molecular mechanisms pertaining to the solvation of the gases in the three ionic liquids. These properties provide valuable information both about the solute–solvent interactions and about the molecular structure of the solutions: the enthalpy of solution is closely related with the cross gas–ionic liquid molecular interactions, and the entropy of solvation gives indications about the structure of the solvent molecules surrounding the solute.



**Fig. 4** Enthalpy of solvation (*left*) and entropy of solvation (*right*) of the gases in ionic liquids based in the [Ntf<sub>2</sub>] anion as a function of temperature: □, CO<sub>2</sub>; ○, H<sub>2</sub>

## 4 Conclusions

We report the solubility of carbon dioxide and of hydrogen, as a function of temperature, in three ionic liquids sharing the bis(trifluoromethylsulfonyl)amide anion. The results obtained here can be compared with values published in the literature by different research groups. These comparisons allow the estimation of a realistic value for the accuracy of the present

data. Together with a careful analysis of the sources and order of magnitude of the errors associated with our experimental technique, we consider that the accuracy of all the values presented in this paper is  $\pm 5\%$ .

Changing the cation of the ionic liquid has only a minor effect on the solubility of carbon dioxide. It is nevertheless noticeable that this gas is slightly less soluble in  $[\text{C}_2\text{mim}][\text{NTf}_2]$ . For hydrogen, its solubility is also similar in the three ionic liquids, with the differences in solubility being similar to the ones found for carbon dioxide. The relative order of the hydrogen solubility is the same as this gas is more soluble in  $[\text{N}_{4111}][\text{Ntf}_2]$  followed by  $[\text{C}_4\text{mim}][\text{NTf}_2]$ . It can be concluded that the effect of the ionic liquid cation on the solubility of both hydrogen and carbon dioxide is similar.

The data obtained here make it possible to calculate and analyze the thermodynamic properties of solvation, which allow us to assess the molecular interactions in solution. It was observed that, although the order of magnitude of the properties of solvation is similar, their variation with temperature is quite different, pointing to probable differences in the mechanisms of solvation for the two gases studied. These differences have already been noticed for other ionic liquids [12, 13, 18].

The behavior of each gas in the presence of the imidazolium based ionic liquids is very similar. For  $[\text{N}_{4111}][\text{Ntf}_2]$  as solvent, it is observed that the solvation of hydrogen is less exothermal than in the imidazolium-based ionic solvents. The entropies of solvation, of hydrogen and carbon dioxide are also less negative for  $[\text{N}_{4111}][\text{Ntf}_2]$ . The fact that the enthalpies of solvation are more negative for the imidazolium-based ionic liquids is explained by the existence of stronger solute-solvent interactions that are dominated by specific electrostatic forces [19].

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