Low-Pressure Solubility and Thermodynamics of Solvation of Carbon Dioxide, Ethane, and Hydrogen in 1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)amide between Temperatures of 283 K and 343 K

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The solubility of carbon dioxide, ethane, and hydrogen was determined experimentally in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide—a room-temperature ionic liquid—as a function of temperature between 283 K and 343 K and close to atmospheric pressure. Carbon dioxide is the most soluble, and hydrogen is the least soluble of the gases studied with mole fraction solubilities of the order of 10^{-2} and 10^{-4}, respectively. All the mole fraction solubilities decrease with increasing temperature, behavior typical of exothermal processes of solvation. From the variation of Henry's law constants with temperature, the partial molar thermodynamic functions of solvation, such as the standard Gibbs energy, the enthalpy, and the entropy, are calculated. The total uncertainty of the experimental data is in all cases better than ±3 %.

Introduction

The objective of this work is to report reliable data on the low-pressure solubility of three gases, carbon dioxide, ethane, and hydrogen, as a function of temperature in one room-temperature ionic liquid, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide or [C_6mim][NTf_2]. This work is part of an international IUPAC task group that was established with the aim of organizing a systematic study of the thermodynamic and thermophysical properties of this common room-temperature ionic liquid. Well-characterized samples of [C_6mim][NTf_2] coming from the same source were supplied to the different research groups.

The knowledge of the solubility of different gases in ionic liquids is very important for several potential technological applications, namely for reaction systems or for the development of new separation processes. Furthermore, low-pressure solubility data as a function of temperature can be used to assess the solute−solvent molecular interactions. When expressed as Henry's law constant, K_H, gas solubility is in direct relation with the Gibbs energy of solvation, which represents the variation of the Gibbs energy when the solute is transferred, at constant temperature, from the pure perfect gas state at standard pressure into the standard state of infinite dilution of the solute in the solvent. From the variation with temperature of K_H, the enthalpy of solvation and the entropy of solvation can be derived and analyzed to obtain insight into the molecular interactions responsible for the observed macroscopic properties of the solutions.

In this paper, experimental solubilities of CO_2, C_2H_6, and H_2 are presented from $T = 283$ K to 343 K, near 1 bar, using a high-precision isochoric saturation method. Henry's law constants and thermodynamic properties of solvation were calculated.

Experimental Section

Materials. Two samples, 25 mL and 15 mL in volume, of the room-temperature ionic liquid [C_6mim][NTf_2] (CAS Registry number 382150-50-7) were supplied by the IUPAC task group. The ionic liquid was synthesized at the University of Notre Dame, Indiana (group of Prof. J. Brennecke), and dried at the National Institute of Standards and Technology in Boulder, Colorado. The minimum stated mole fraction purity is 0.995 as found by ^{1}H and ^{19}F NMR spectroscopy. The samples were dried under vacuum for 2 days and sent by NIST in a sealed container. A coulometric Karl Fisher titration (ASTM E1064-100 standard) was used to determine the water content of the sample, which is less than 20 ppm. An ion-selective electrode permitted the determination of a bromine content of less than 10 ppm. The ionic liquid was transferred directly from the sealed container to the gas solubility equipment and was degassed and dried under vacuum at temperatures higher than 300 K for at least 20 h.

The gases used have the following specifications: carbon dioxide from AGA/Linde Gaz with mole fraction purities of 0.99995; ethane from AGA/Linde Gaz, with a mole fraction purity of 0.995; and hydrogen from AGA/Linde Gaz, with a mole fraction purity of 0.999997. The gases were used as received from the manufacturer.

Apparatus and Operation. The experimental method used for the present gas solubility measurements is based on an isochoric saturation technique and has been described in previous publications.[1−3] In this technique, a known amount of gaseous solute is put in contact with a precisely determined quantity of degassed solvent at a constant temperature inside an accurately known volume. When thermodynamic equilibrium is attained at a given temperature, the pressure above the liquid solution is constant and is directly related to the solubility of the gas in the liquid.

A large surface of contact and an appropriate stirring of the liquid-phase guarantee a sufficient exchange between the liquid

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Table 1. Experimental Values of Gas Solubilities in [C_6mim][NTf_2] 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[a]

T	p	K_H	x_2	dev	T	p	K_H	x_2	dev	T	p	K_H	x_2	dev
K	10^2 Pa	10^5 Pa	10^{-4}	%	K	10^2 Pa	10^5 Pa	10^{-4}	%	K	10^2 Pa	10^5 Pa	10^{-4}	%
		CO_2					C_2H_6					H_2		
288.48	288.22	24.60	406.5	−0.3	283.32	801.32	55.34	180.2	−0.8	283.88	776.67	1182	8.457	+0.7
293.06	734.28	27.26	366.8	−0.8	293.02	832.06	63.58	156.8	+0.8	293.56	802.18	1263	7.921	−1.3
293.21	296.12	26.95	371.0	+0.7	303.44	823.56	72.86	136.7	+2.1	293.59	811.29	1258	7.946	−0.9
298.06	304.05	29.54	338.5	+1.3	303.47	865.39	74.74	133.2	−0.4	303.41	828.07	1333	7.502	−0.2
298.58	753.84	30.40	328.9	−0.6	313.29	440.43	86.43	115.1	−2.3	303.43	837.36	1300	7.691	+2.4
303.42	770.25	33.19	301.3	−0.3	313.37	895.69	84.00	118.4	+0.7	313.17	853.72	1446	6.917	−0.3
303.44	313.02	32.92	303.8	+0.5	323.23	881.68	95.29	104.2	−0.4	323.27	880.20	1582	6.319	+0.2
308.36	786.81	36.24	276.0	−0.5	323.33	926.30	95.24	104.3	−0.3	323.30	890.05	1580	6.328	+0.4
323.28	877.46	45.49	219.8	−0.2	333.26	956.05	105.2	94.27	+0.4	333.17	785.36	1788	5.592	−1.7
333.22	908.26	51.72	193.3	+0.1	343.21	985.73	116.0	85.42	+0.3	343.02	807.61	1924	5.198	+2.0
343.20	938.48	58.16	172.0	+0.0						343.02	942.09	1984	5.041	−1.1

[a] p is the experimental equilibrium pressure, and the percent deviation is relative to the correlations of the data reported in Table 2.

solution and the gaseous phase in equilibrium with it. The magnetic stirrer used in the equilibrium cell is normally coated in glass.[2−4] In the present work, a Teflon-coated magnetic bar was used for the carbon dioxide and the ethane measurements, the reason being the occurrence of very thin solid particles in the liquid phase when a glass-coated magnetic bar was used. It has been proved that these solid particles were due to grinding against the bottom of the equilibrium cell. The hydrogen measurements were nevertheless made with a glass-coated magnetic bar as the solubility proved to be less precise when using a Teflon-coated stirrer, probably due to a slight sorption of the gas by the polymer.

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

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

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 Z_2 is the compressibility factor for the pure gas. The solubility can then be expressed in mole fraction

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

or as Henry's law constant

$$K_H \equiv \lim_{x_2 \to 0} \frac{f_2(p,T,x_2)}{x_2} \cong \frac{\phi_2(p_{eq},T_{eq})p_{eq}}{x_2} \tag{3}$$

where f_2 is the fugacity of the solute and ϕ_2 is its fugacity coefficient. The fugacity coefficient, which is very close to unity in the present cases, was included in the calculation of the Henry's law constants for all the gases.

The total uncertainty associated with Henry's law constants calculated from the present experimental solubilities is estimated to be better than ±3 %.

Results and Discussion

For each gaseous solute studied, multiple experimental data points were obtained in the temperature interval between 283 K and 343 K in steps of approximately 10 K. The experimental solubilities for carbon dioxide, ethane, and hydrogen in [C_6mim][NTf_2] are reported in Table 1. The results are given as Henry's law constants and as mole fractions of solute. These last values are calculated from the experimental data of 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 the ones recommended by IUPAC,[5] and the values of the second virial coefficients for all the gases, necessary for the calculation of the compressibility factor and of the fugacity coefficient of the solute, were taken from the compilation by Dymond and Smith.[6] The density of the samples of [C_6mim][NTf_2] was measured in our laboratory with a precision better than 0.01 % using an Anton Paar densitometer (model DMA 512 P).[7] The density values were fitted to the function

Table 2. Parameters of Equation 5 Used To Smooth the Raw Experimental Results from Table 1 along with the Percent Average Absolute Deviation of the Fit (AAD)

gas	A_0	A_1	A_2	AAD %
CO_2	+3.636	$+1.583 \times 10^3$	-4.929×10^5	0.5
C_2H_6	+6.361	$+1.573 \times 10^1$	-1.933×10^5	0.9
H_2	+18.90	-6.413×10^3	$+8.682 \times 10^5$	1.0

$$\rho/\mathrm{kg{\cdot}m^{-3}} = 1.6541 - 0.9468 \times 10^{-3}(T/\mathrm{K}) \tag{4}$$

The present values of density of the ionic liquid as a function of temperature agree, to within the experimental uncertainties, with the data published by other research teams.[8,12]

To correlate the solubility as a function of temperature, Henry's law constants obtained from the experimental data were adjusted to power series in $1/T$:

$$\ln(K_H/10^5\ \mathrm{Pa}) = \sum_{i=0}^{n} A_i(T/\mathrm{K})^{-i} \tag{5}$$

The coefficients A_i as well as the average absolute deviations obtained are collected in Table 2. The average absolute deviations characterize the precision of the data, which is of the order of 1 %.

In Figure 1 are represented the solubility data expressed in mole fraction as a function of temperature. Carbon dioxide and ethane are the most soluble gases with a mole fraction solubility of the order of 10^{-2}. Hydrogen is much less soluble with a mole fraction solubility of the order of 10^{-4}. The solubility of the three gases decreases with increasing temperature in the range covered by this work.

The solubility of carbon dioxide in [C_6mim][NTf_2] has been determined by other research groups, as a function of temper-

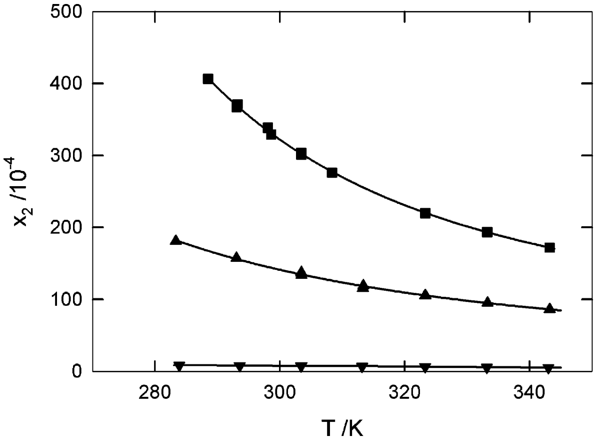

Figure 1. Mole-fraction gas solubilities in [C$_6$mim][NTf$_2$] at 0.1 MPa partial pressure of the solute, as a function of temperature: ■, carbon dioxide; ▲, ethane; ▼, hydrogen. Lines represent the correlations of the data using the parameters in Table 2.

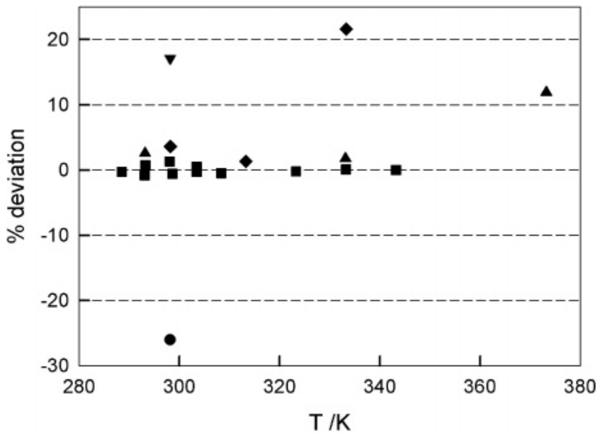

Figure 2. Deviations of the literature values to the correlation of Henry's law constants obtained in this work for carbon dioxide in [C$_6$mim][NTf$_2$]: ■, this work; ▲, Kumelan et al., 2006;[12] ▼, Balthus et al., 2004;[9] ◆, Aki et al., 2004;[11] ●, Kim et al., 2005.[10]

ature, using different experimental techniques. It is possible to compare 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 Figure 2. As it can be observed, only two sets of data, reported by Baltus et al.[9] and by Kim et al.,[10] exhibit a difference of more than 10 % from the present data. The values reported by Aki et al.[11] and by Kumelan et al.[12] (this last paper reports the solubility measurements made within the frame of the IUPAC task group referred to above) deviate from the present work by less than 5 %, except for two points at their higher-temperature end, one of which is at a temperature not covered by the present study. After a careful analysis of the present data and in light of the comparisons made, we consider that the present values have an accuracy better than ±5 %.

The solubility of hydrogen in [C$_6$mim][NTf$_2$] was also determined by Kumelan et al.,[13] using a different sample of the ionic liquid. The values reported by Kumelan et al. for the solubility of hydrogen at 293.2 K and at 333.2 K could be compared with the ones obtained here. It is observed that at the lowest temperature the values measured by Kumelan et al. underestimate the solubility of hydrogen, reporting a Henry's law constant which is 55 % higher than the one obtained here ($K_H = 1929 \times 10^5$ Pa[13] compared with $K_H = 1244 \times 10^5$ Pa, the value of the present work). This deviation is significantly lower at 333.2 K where a negative deviation of −11 % is found ($K_H = 1567 \times 10^5$ Pa[13] compared with $K_H = 1758 \times 10^5$ Pa). Furthermore, we observe a decrease with the temperature of the solubility of H$_2$ in [C$_6$mim][NTf$_2$] and the opposite behavior is found by Kumelan et al.[13] A similar discrepancy between the results obtained by the two research groups, which can not only be attributed to the uncertainty of the experimental measurements reported here, has already been found for the solubility of hydrogen in other ionic liquids[3] and can be surely endorsed to the difficulties in measuring such a low-solubility gas.

The variation of the solubility for the three gases studied with temperature, expressed in 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 solution.[14] The Gibbs energy of solvation is given by

$$\Delta_{sol}G^{\infty} = RT \ln(K_H/p^0) \tag{6}$$

where p^0 is the standard state pressure. The partial molar differences in enthalpy and entropy can be obtained by calculating the corresponding partial derivatives of the Gibbs energy with respect to temperature

$$\Delta_{sol}H^{\infty} = -T^2 \partial/\partial T(\Delta_{sol}G^{\infty}/T) = -RT^2 \partial/\partial T[\ln(K_H/p^0)] \tag{7}$$

$$\Delta_{sol}S^{\infty} = (\Delta_{sol}H^{\infty} - \Delta_{sol}G^{\infty})/T = -RT\, \partial/\partial T[\ln(K_H/p^0)] - R\ln(K_H/p^0) \tag{8}$$

The values for the Gibbs energy, enthalpy, and entropy of solvation are given in Table 3 for carbon dioxide, ethane, and hydrogen in [C$_6$mim][NTf$_2$] at seven discrete temperatures between 283 K and 343 K.

The Gibbs energy of solvation increases with increasing temperature in a similar manner for all the gases studied. This variation

Table 3. Thermodynamic Functions of Solvation for CO$_2$, C$_2$H$_6$, and H$_2$ in [C$_6$mim][NTf$_2$] at Several Discrete Temperatures between 283 K and 343 K[a]

T	$\Delta_{sol}G^{\infty}$	$\Delta_{sol}H^{\infty}$	$\Delta_{sol}S^{\infty}$	T	$\Delta_{sol}G^{\infty}$	$\Delta_{sol}H^{\infty}$	$\Delta_{sol}S^{\infty}$	T	$\Delta_{sol}G^{\infty}$	$\Delta_{sol}H^{\infty}$	$\Delta_{sol}S^{\infty}$
K	kJ·mol^{-1}	kJ·mol^{-1}	J·mol^{-1}·K^{-1}	K	kJ·mol^{-1}	kJ·mol^{-1}	J·mol^{-1}·K^{-1}	K	kJ·mol^{-1}	kJ·mol^{-1}	J·mol^{-1}·K^{-1}
		CO$_2$				C$_2$H$_6$				H$_2$	
283	7.255	−14.9	−78.3	283	9.422	−10.9	−71.7	283	16.64	−3.34	−70.6
293	8.031	−14.5	−76.9	293	10.14	−10.8	−71.4	293	17.36	−4.39	−74.2
303	8.792	−14.0	−75.1	303	10.85	−10.6	−70.7	303	18.12	−5.56	−78.2
313	9.532	−13.2	−72.8	313	11.55	−10.3	−69.7	313	18.93	−6.86	−82.4
323	10.25	−12.3	−69.9	323	12.24	−9.87	−68.4	323	19.77	−8.29	−86.9
333	10.93	−11.2	−66.6	333	12.92	−9.34	−66.9	333	20.67	−9.86	−91.7
343	11.58	−9.93	−62.7	343	13.58	−8.70	−64.9	343	21.61	−11.6	−96.7

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

leads to negative enthalpies of solvation indicating an exothermal process of solvation. In the temperature range studied, the enthalpy of solvation is the most negative for carbon dioxide and hydrogen is the gas which has a less-exothermal solvation process. The enthalpy of solvation does not vary significantly with temperature. It becomes nevertheless noticeably more negative with increasing temperature for hydrogen, behaving in an opposite manner with temperature for the other two gases.

For the entropy of solvation, all the values are negative and lay between $-60\ \mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$ and $-100\ \mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$. The exception is again hydrogen for which the values are more negative in the whole temperature range and decrease with increasing temperature. For the other two gases, the variation of the entropy of solvation with temperature is not significant as it only slightly decreases with temperature.

Because the solubility data are sufficiently precise, the thermodynamic properties of solvation can be used to infer about the molecular mechanisms pertaining to the solvation of the different gases in [C_6mim][NTf_2]. 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. The values obtained for the thermodynamic properties of solvation of hydrogen (in Table 3), namely the different behavior of the enthalpy and the entropy of solvation with temperature, indicate that the solute−solvent molecular interactions are probably of a different nature in the solutions involving this gas. This result has already been observed in similar studies involving other ionic liquids based on alkylimidazolium cations.[2,3]

Conclusion

We report the solubility of three different gases, CO_2, C_2H_6, and H_2, in one ionic liquid, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, as a function of temperature. The results obtained here could be compared with values published in the literature by different research groups for carbon dioxide (four different sets of data) and for hydrogen (one set of data reported by other authors). These comparisons allow the estimation of a realistic value for the accuracy of the present values. 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 of ±5 %.

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, except for hydrogen, the order of magnitude and variation with temperature of the thermodynamic properties of solvation is similar, a behavior that points to similar molecular mechanisms of solvation for carbon dioxide and ethane in [C_6mim][NTf_2]. Carbon dioxide exhibits more negative enthalpies of solvation, a situation typical of the existence of stronger solute−solvent interactions, here dominated by specific electrostatic forces.[15]

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