Solubility of H_2 in the Ionic Liquid [hmim][Tf_2N]

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New experimental results are presented for the solubility of hydrogen in the ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf_2N]) for temperatures from (293 to 413) K and pressures up to about 10 MPa. The extended Henry's law is applied to correlate the solubility pressures. The solubility of H_2 in [hmim][Tf_2N] is low and increases toward higher temperatures. For example, at $T \approx 293$ K (413 K) and $p \approx 9$ MPa, only about 0.106 mol (0.170 mol) of the gas is dissolved in 1 kg of the ionic liquid.

Introduction

Recently, we presented experimental results for the solubility of the single gases carbon dioxide, carbon monoxide, hydrogen, and oxygen in the ionic liquid 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) as well as for the solubility of carbon dioxide in the ionic liquid [hmim][Tf_2N].[1−5] This contribution extends that work to the solubility of hydrogen in [hmim][Tf_2N]. No experimental information on this particular gas solubility is so far available in the open literature. Experimental results are reported for temperatures T between 293 K and 413 K and pressures p up to ~10 MPa. The experimental data are used to determine Henry's constant of hydrogen in [hmim][Tf_2N].

Experimental Section

The apparatus and the measuring technique were the same as in the previous work;[1−8] therefore, no descriptions are repeated here.

Hydrogen (mole fraction ≥ 99.999 %) was purchased from Messer-Griesheim, Ludwigshafen, Germany. It was used without further purification. [hmim][Tf_2N] ($C_{12}H_{19}N_3F_6O_4S_2$, high purity, mass fraction ≥ 99 %) was supplied by Merck KGaA, Darmstadt, Germany. It was degassed and dried under vacuum as described previously.[1] ^{1}H and ^{19}F NMR spectroscopic investigations were carried out, proving that the impurities of that sample were below 0.005 mole fraction. The water content of the sample was less than 0.0005 mass fraction, as determined by Karl Fischer titration analysis before and after the measurements. The ionic liquid was collected after the measurement and reconditioned (i.e., degassed and dried under vacuum) for further use, as no signs of degradation were observed under the chosen experimental conditions. The aforementioned analytical results of the ionic liquid sample purchased from Merck were in perfect agreement with the results of the sample of that ionic liquid, which was used in a previous investigation,[5] synthesized at the group of J. F. Brennecke at the University of Notre Dame (Notre Dame, IN), and purified by the National Institute of Standards and Technology (Boulder, CO).

The solubility of hydrogen in [hmim][Tf_2N] was measured at temperatures from (~293 to ~413) K in intervals of approximately 40 K. The experimental results are given in Table 1. Figure 1 shows the experimental data plotted as the pressure required to dissolve hydrogen versus the gas molality m_{H_2} (i.e., the number of moles of H_2 per kilogram of [hmim][Tf_2N]). Gas molality is easily converted to mole fraction when the molar mass of the solvent is known. The relative molar mass of [hmim][Tf_2N] is 447.42. As can be seen from Figure 1, the solubility pressure nearly linearly increases with increasing molality of hydrogen in the liquid phase (typical "physical" gas solubility behavior).

Table 1 also contains the experimental uncertainties for the gas molalities as well as for the solubility pressures estimated from a Gauss error propagation calculation. The relative uncertainty in the amount of dissolved hydrogen is on average (at maximum) about 0.35 % (0.5 %). The relative uncertainty in the pressure decreases from about 1.2 % at low pressures to about 0.5 % at the higher pressures. The solubility of hydrogen increases by about 63 % when the temperature increases from (293 to 413) K. The system (H_2 + [hmim][Tf_2N]) is one of the few examples where at around room temperature the gas solubility increases with increasing temperature. Such a behavior was also observed for the system (H_2 + [bmim][PF_6]).[3]

Correlation

The vapor pressure of the ionic liquid [hmim][Tf_2N] is negligibly small. Therefore, the gaseous phase is here regarded as pure hydrogen, and the vapor−liquid equilibrium condition is only applied to hydrogen.[1] That equilibrium condition results in the extended Henry's law. Since the solubility of hydrogen in the ionic liquid is very small, the liquid mixture is treated as an ideal solution, and the extended Henry's law (on the molality scale basis) simplifies to

$$k_{H,H_2}(T, p)\,\frac{m_{H_2}}{m^\circ} = f_{H_2}(T, p) \qquad (1)$$

$k_{H,H_2}(T, p)$ is Henry's constant of hydrogen in [hmim][Tf_2N] (based on the molality scale), $f_{H_2}(T, p)$ is the fugacity of hydrogen in the vapor phase, and $m^\circ = 1$ mol·kg^{-1}.

The influence of pressure on the Henry's constant of hydrogen in [hmim][Tf_2N] is expressed by

$$k_{H,H_2}(T, p) = k^{(0)}_{H,H_2}(T)\,\exp\left(\frac{v^{\infty}_{H_2}p}{RT}\right) \qquad (2)$$

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Table 1. Experimental Results for the Solubility of Hydrogen in [hmim][Tf$_2$N]

T	m_{H_2}	p	f_{H_2}/m_{H_2}
K	mol·kg^{-1}	MPa	MPa/(mol·kg^{-1})
293.2 ± 0.1	0.01713 ± 0.00009	1.476 ± 0.020	86.94 ± 1.27
	0.02984 ± 0.00011	2.557 ± 0.030	86.97 ± 1.06
	0.04684 ± 0.00016	4.048 ± 0.034	88.49 ± 0.77
	0.06284 ± 0.00020	5.337 ± 0.037	87.63 ± 0.65
	0.08051 ± 0.00030	6.822 ± 0.046	88.18 ± 0.65
	0.09812 ± 0.00034	8.307 ± 0.050	88.88 ± 0.59
	0.11526 ± 0.00038	9.819 ± 0.054	90.23 ± 0.54
333.2 ± 0.1	0.03213 ± 0.00012	2.264 ± 0.021	71.35 ± 0.69
	0.05060 ± 0.00016	3.544 ± 0.032	71.40 ± 0.66
	0.06678 ± 0.00021	4.720 ± 0.035	72.52 ± 0.56
	0.08695 ± 0.00030	6.157 ± 0.041	73.22 ± 0.53
	0.10752 ± 0.00035	7.601 ± 0.045	73.67 ± 0.48
	0.13135 ± 0.00042	9.305 ± 0.050	74.52 ± 0.44
373.15 ± 0.1	0.02641 ± 0.00010	1.591 ± 0.018	60.73 ± 0.74
	0.04718 ± 0.00015	2.866 ± 0.029	61.63 ± 0.65
	0.07446 ± 0.00026	4.499 ± 0.036	61.81 ± 0.53
	0.10165 ± 0.00033	6.179 ± 0.040	62.71 ± 0.44
	0.12777 ± 0.00040	7.746 ± 0.044	63.03 ± 0.40
	0.14880 ± 0.00046	9.077 ± 0.048	63.86 ± 0.37
413.2 ± 0.1	0.03070 ± 0.00011	1.620 ± 0.018	53.18 ± 0.62
	0.05729 ± 0.00018	3.050 ± 0.029	54.00 ± 0.54
	0.09234 ± 0.00030	4.918 ± 0.036	54.49 ± 0.43
	0.12509 ± 0.00039	6.638 ± 0.041	54.74 ± 0.37
	0.15232 ± 0.00058	8.098 ± 0.051	55.22 ± 0.39
	0.17841 ± 0.00064	9.508 ± 0.054	55.71 ± 0.36

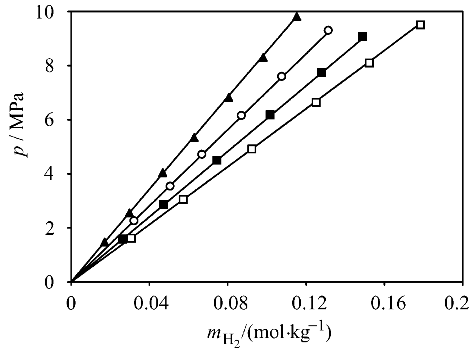

Figure 1. Total pressure above solutions of (H_2 + [hmim][Tf$_2$N]): [▲, T = 293.2 K; ○, T = 333.2 K; ■, T = 373.15 K; □, T = 413.2 K] experimental results, this work; —, correlation, this work.

where $k^{(0)}_{H,H_2}(T)$ is Henry's constant of hydrogen in [hmim][Tf$_2$N] at zero pressure, $v^{\infty}_{H_2}$ is the partial molar volume of hydrogen at infinite dilution in [hmim][Tf$_2$N], and R is the universal gas constant.

The fugacity of pure hydrogen f_{H_2} at equilibrium temperature and pressure is the product of the total pressure p and the fugacity coefficient $\phi_{H_2}(T, p)$:

$$f_{H_2}(T, p) = p\phi_{H_2}(T, p) \tag{3}$$

$\phi_{H_2}(T, p)$ is calculated from the virial equation of state, truncated after the second virial coefficient.[3] Within the investigated temperature range, the second virial coefficient of hydrogen is positive and small. Therefore, the fugacity coefficient of hydrogen is larger than 1 but does not deviate much from 1 (by about 6 % at maximum).

Henry's constant of hydrogen in [hmim][Tf$_2$N] at zero pressure $k^{(0)}_{H,H_2}(T)$ is obtained by an extrapolation of the new experimental results for the solubility pressure of H_2 in [hmim][Tf$_2$N]:

$$k^{(0)}_{H,H_2}(T) = \lim_{p \to p^s_{[\mathrm{hmim}][\mathrm{Tf_2N}]} = 0} \left[\frac{f_{H_2}(T, p)}{(m_{H_2}/m^\circ)}\right] \tag{4}$$

The experimental results for $f_{H_2}/(m_{H_2}/m^\circ)$ as well as their experimental uncertainty are also given in Table 1. Figure 2 shows isothermal plots of $f_{H_2}/(m_{H_2}/m^\circ)$ versus the total pressure above the liquid solution. The experimental uncertainty is also shown, but only when the error bars are larger than the symbols which represent the experimental data. As usual, a linear regression was applied to determine Henry's constant by an extrapolation.

Table 2 lists the numerical values for Henry's constants (at zero pressure) resulting from the extrapolations. The estimated relative uncertainty of these numbers is 0.85 %. Henry's constant of hydrogen in [hmim][Tf$_2$N] (at zero pressure) decreases from 86.3 MPa at 293.2 K to 52.9 MPa at 413.2 K.

The final results for the Henry's constant (at zero pressure) of hydrogen in [hmim][Tf$_2$N] (on the molality scale) are correlated within the estimated uncertainty range by

$$\ln\{k^{(0)}_{H,H_2}(T)/\mathrm{MPa}\} = 2.7778 + 492/(T/K) \tag{5}$$

Figure 3 shows the Henry's constant (at zero pressure) plotted versus the inverse absolute temperature together with the correlation curve (eq 5). The experimental uncertainty is not shown because the error bars are smaller than the symbols that represent the experimental data.

The new experimental results for the solubility pressure data for the system (H_2 + [hmim][Tf$_2$N]) were correlated with the results for the Henry's constant (at zero pressure), given in eq 5, and the partial molar volume of hydrogen in [hmim][Tf$_2$N]. The correlation resulted in

$$v^{\infty}_{H_2}/(\mathrm{cm^3 \cdot mol^{-1}}) = -10.7 + 0.076(T/\mathrm{K}) \tag{6}$$

Figure 1 illustrates the good agreement between the experimental data and the correlation for the total pressure. The average absolute (relative) deviation does not exceed 0.03 MPa (0.5 %).

The knowledge of Henry's constant $k_{H,H_2}(T, p)$ allows for the calculation of some interesting solution thermodynamic properties, $\Delta_{sol}X$, of H_2 in [hmim][Tf$_2$N], where, for example, $X = G$ (the molar Gibbs energy), H (the molar enthalpy), or S (the molar entropy).[1] At standard temperature and pressure (T° = 298.15 K, p° = 0.1 MPa), the following numerical values for those properties (based on the molality scale) result from the correlation equations given above:

$$\Delta_{sol}G^\circ = (16.686 \pm 0.021)\ \mathrm{kJ \cdot mol^{-1}} \tag{7}$$

$$\Delta_{sol}H^\circ = (4.09 \pm 0.12)\ \mathrm{kJ \cdot mol^{-1}} \tag{8}$$

$$\Delta_{sol}S^\circ = (-42.2 \pm 0.4)\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}} \tag{9}$$

Comparison with Literature Data

There is some experimental information on the solubility of hydrogen in several ionic liquids (e.g., [bmim][PF$_6$]) available in the open literature (cf., for example, refs 3 and 9−12). Moreover, a couple of authors published experimental data on the solubility of several gases (e.g., carbon dioxide,[5,13−16] carbon monoxide,[17] or oxygen[16]) in [hmim][Tf$_2$N]. However, the present work is the first to report experimental data for the solubility of hydrogen in [hmim][Tf$_2$N].

In Figure 4, the temperature-dependent (zero pressure)

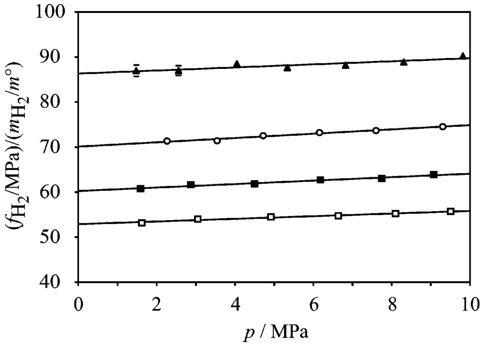

Figure 2. Influence of the total pressure on the ratio of H_2 fugacity (in the gaseous phase) to H_2 molality (in the liquid phase): [▲, $T = 293.2$ K; ○, $T = 333.2$ K; ■, $T = 373.15$ K; □, $T = 413.2$ K] experimental results, this work; —, linear fit.

Table 2. Henry's Constant of Hydrogen in [hmim][Tf$_2$N]^a

T/K	$k^{(0)}_{H,H_2}$/MPa
293.2	86.3 ± 0.7
333.2	70.1 ± 0.6
373.15	60.3 ± 0.5
413.2	52.9 ± 0.45

[a] At zero pressure, on the molality scale.

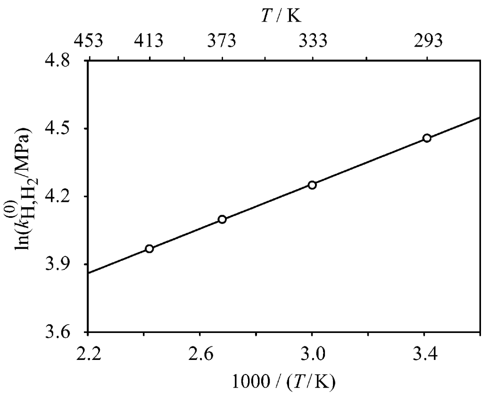

Figure 3. Henry's constant of H_2 in [hmim][Tf$_2$N] (at zero pressure, on the molality scale): ○, extrapolated experimental results, this work; —, correlation, this work.

Henry's constant of hydrogen in [hmim][Tf$_2$N] is compared with the (zero pressure) Henry's constant of carbon dioxide in that particular ionic liquid.[5] In addition, the (zero pressure) Henry's constant of hydrogen,[3] carbon dioxide,[1] carbon monoxide,[2] and oxygen[4] in [bmim][PF$_6$] are given in that figure. The (zero pressure) Henry's constant of hydrogen in [hmim][Tf$_2$N] differs from that in [bmim][PF$_6$] by about −37 % at 293 K to about −29 % at 413 K. The difference between the (zero pressure) Henry's constant of carbon dioxide in [hmim][Tf$_2$N] and the one in [bmim][PF$_6$] amounts to about +4 % at 293 K to −15 % at 372 K. In [bmim][PF$_6$], among the gases mentioned above, carbon dioxide is the most soluble, followed by oxygen, carbon monoxide, and finally hydrogen. As is common for many (gas+solvent) systems in a temperature area around room temperature, the solubility (the Henry's constant) of carbon dioxide in [bmim][PF$_6$] decreases (increases) with rising temperature. However, for the sparsely soluble gases (O_2 and CO) there is nearly no influence of temperature on the solubility in the ionic liquid [bmim][PF$_6$]. For the least soluble gas (H_2), the solubility increases with increasing temperature. In [hmim][Tf$_2$N], the same qualitative behavior for the gas solubility as well as for the influence of temperature on that gas solubility is observed—at least for H_2 and CO_2, whose (temperature-dependent) solubilities have been investigated so far.

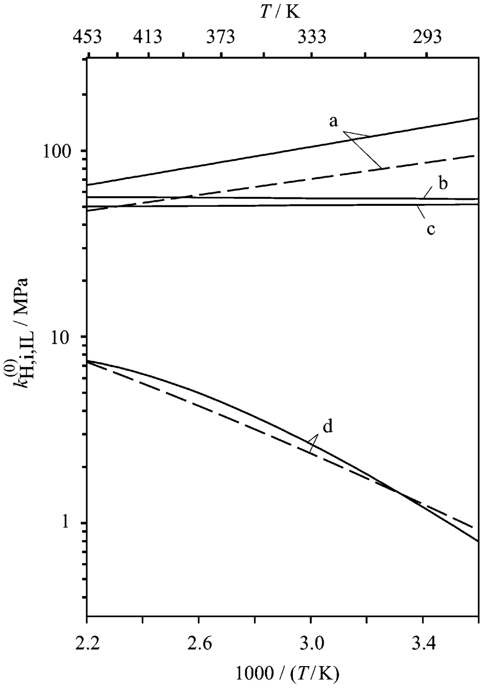

Figure 4. Henry's constant (at zero pressure, on the molality scale) of gas a = H_2, b = CO, c = O_2, and d = CO_2 in the ionic liquid IL {—, [bmim][PF$_6$]; — —, [hmim][Tf$_2$N]}. Correlation results based on experimental data from this work and refs 1−5.

Conclusions

New experimental results for the solubility of hydrogen in the ionic liquid [hmim][Tf$_2$N] are presented for temperatures from (293 to 413) K and pressures up to about 10 MPa. The new experimental results for the solubility pressure were correlated with an average relative deviation of about 0.5 % (with gas molality and temperature preset) by means of the extended Henry's law. The solubility of hydrogen in [hmim][Tf$_2$N] is remarkably lower than the solubility of carbon dioxide in that ionic liquid, which was investigated previously.[5] The solubility of hydrogen (carbon dioxide) increases (decreases) with rising temperature. For example, at $T \approx 333$ K (413 K) and $p \approx 9$ MPa, about 0.127 (0.170) mol of hydrogen is dissolved in 1 kg of [hmim][Tf$_2$N], whereas at those temperatures and pressure about 4.2 (1.7) mol of carbon dioxide is dissolved in 1 kg of that ionic liquid.

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