Solubility of H_2 in the Ionic Liquid [bmim][PF_6]

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New experimental results are presented for the solubility of hydrogen in the ionic liquid 1-*N*-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) for temperatures from 313 K to 373 K and pressures up to about 9 MPa. The extended Henry's law is applied to correlate the solubility pressures. The solubility of H_2 in [bmim][PF_6] is low and increases slightly with temperature. For example, at $T \approx 313$ K (373 K) and $p \approx 9$ MPa, only about 0.078 mol (0.106 mol) of the gas is dissolved in 1 kg of the ionic liquid.

Introduction

Ionic liquids offer new opportunities as solvents in various areas, as, for example, the chemical and petroleum industries. In synthetic chemistry, research on ionic liquids is strongly driven by the idea that for any reaction to come into consideration there might exist an ionic liquid that will provide advantages over present-day solvents. So, the challenge is to find the ideal ionic liquid for the considered application. Important reactions that are currently proposed to be carried out in ionic liquids are, for example, hydrogenation and hydroformylation.

The use of ionic liquids requires the knowledge of their thermophysical properties, such as, for example, gas solubility data. However, reliable experimental information on such properties still lags behind the results reported on the effects that ionic liquids have on, for example, reaction kinetics and reaction product selectivity. Reliable information on the solubility of gases (e.g., hydrogen, carbon monoxide, oxygen, etc.) in ionic liquids is needed for the design and operation of respective processes and also for the development and test of computational methods such as computer simulations based on quantum chemistry approximations for the intermolecular pair potential. Recently, we presented experimental results on the solubility of the single gases carbon dioxide and carbon monoxide in the ionic liquid [bmim][PF_6].[1,2] This contribution extends that work to the solubility of hydrogen in that particular ionic liquid. Experimental results are reported for temperatures T between 313 K and 373 K and pressures p up to 9.1 MPa. The experimental data are used to determine Henry's constant of hydrogen in [bmim][PF_6]. The new results are compared with the very limited experimental information found in the literature.

Experimental Section

Apparatus and Measuring Technique. The experimental arrangement used in the present work was the same as in the previous work. For a detailed description of the experimental equipment and procedure, the reader is referred to previous papers (cf., for example, refs 3−5). Here, the basic experimental techniques and the experimental uncertainties are only given briefly.

In an experiment, a thermostated high-pressure cylindrical view cell (material = Hastelloy C4; volume = approximately 29.5 cm^3) with two sapphire windows is charged with hydrogen. The amount of the mass of hydrogen is determined via the volume of the cell and experimental p,T data by means of the virial equation of state;[6] details are given in the Modeling section. The ionic liquid is added to the cell by a calibrated high-pressure spindle press until the gas is completely dissolved in the liquid phase. The amount of solvent only slightly exceeds the minimum amount needed to dissolve the gas completely. After equilibration, which takes about 3 h, very small quantities of the liquid mixture are withdrawn stepwise from the cell through reversely turning the high-pressure spindle press until the first (very small) stable gas bubbles appear. The pressure inside the cell is then the equilibrium pressure required to dissolve the charged amount of the gas in the remaining amount of solvent at the preset temperature. As the liquid mixture is almost incompressible, the amount of that mixture and in particular the amount of dissolved gas, which are withdrawn from the cell to decrease the pressure, are negligibly small. The volume of the solvent needed to dissolve the gas only slightly depends on the amount of dissolved gas. Nevertheless, it is determined in each experiment from the displacement of the spindle press and the solvent's density ρ, which was determined in previous work.[2]

The initial pressure of hydrogen in the cell was measured with two pressure transducers (WIKA GmbH, Klingenberg, Germany) with ranges up to 0.25 and 1.6 MPa, respectively. The maximum uncertainty in that pressure measurement is 0.1 % of each transducer's full range. Two additional pressure transducers (WIKA GmbH, Klingenberg, Germany) with ranges of 2.5 MPa and 10 MPa, respectively, were used to determine the solubility pressure. The maximum systematic uncertainty in that pressure measurement results from the uncertainty of the pressure transducers (0.1 % of each transducer's full scale) and a contribution of ± 0.02 MPa caused by a small temperature drift in the isolated tubes filled with the ionic liquid, which connect the cell with the pressure transducers. The contribution from that temperature drift was determined in test runs. All pressure transducers were calibrated against a high-precision pressure gauge (Desgranges & Huot, Aubervilliers, France) before and after each series of measurements. The temperature is determined with two calibrated platinum resistance thermometers with an uncertainty below ± 0.1 K.

Substances and Sample Pretreatment. Hydrogen (mole fraction ≥ 99.999 %) was purchased from Messer-Griesheim,

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Table 1. Experimental Results for the Solubility of Hydrogen in [bmim][PF$_6$]

T	m_{H_2}	p	f_{H_2}/m_{H_2}
K	mol·kg^{-1}	MPa	MPa/(mol·kg^{-1})
313.05 ± 0.1	0.01425 ± 0.00008	1.695 ± 0.032	120.04 ± 2.33
	0.01720 ± 0.00008	2.016 ± 0.032	118.56 ± 1.96
	0.02865 ± 0.00010	3.372 ± 0.042	119.97 ± 1.52
	0.03807 ± 0.00012	4.422 ± 0.044	119.09 ± 1.21
	0.04731 ± 0.00013	5.518 ± 0.046	120.32 ± 1.03
	0.05689 ± 0.00015	6.650 ± 0.049	121.35 ± 0.91
	0.06774 ± 0.00018	7.935± 0.052	122.50 ± 0.82
	0.07775 ± 0.00049	9.085 ± 0.088	122.99 ± 1.36
333.15 ± 0.1	0.01179 ± 0.00007	1.231 ± 0.030	105.15 ± 2.64
	0.02173 ± 0.00009	2.288 ± 0.032	106.57 ± 1.51
	0.03171 ± 0.00010	3.329 ± 0.041	106.90 ± 1.33
	0.04293 ± 0.00012	4.502 ± 0.043	107.45 ± 1.05
	0.05411 ± 0.00015	5.679 ± 0.046	108.24 ± 0.89
	0.06507 ± 0.00017	6.875 ± 0.048	109.66 ± 0.79
	0.07549 ± 0.00019	7.974 ± 0.050	110.29 ± 0.71
	0.08541 ± 0.00021	9.014 ± 0.053	110.84 ± 0.67
353.1 ± 0.1	0.01541 ± 0.00007	1.456 ± 0.030	95.23 ± 1.98
	0.02751 ± 0.00009	2.643 ± 0.039	97.43 ± 1.45
	0.03959 ± 0.00012	3.758 ± 0.041	96.82 ± 1.07
	0.05191 ± 0.00014	4.926 ± 0.044	97.37 ± 0.88
	0.06323 ± 0.00017	6.040 ± 0.046	98.58 ± 0.77
	0.07387 ± 0.00045	7.045 ± 0.073	98.95 ± 1.14
	0.08488 ± 0.00046	8.115 ± 0.074	99.76 ± 1.01
	0.09564 ± 0.00047	9.100 ± 0.075	99.79 ± 0.92
373.15 ± 0.1	0.01251 ± 0.00007	1.084 ± 0.029	87.16 ± 2.33
	0.02482 ± 0.00009	2.147 ± 0.030	87.44 ± 1.25
	0.03711 ± 0.00011	3.200 ± 0.040	87.64 ± 1.10
	0.04957 ± 0.00013	4.258 ± 0.042	87.75 ± 0.88
	0.06306 ± 0.00042	5.378 ± 0.067	87.62 ± 1.21
	0.07685 ± 0.00044	6.596 ± 0.068	88.72 ± 1.01
	0.09102 ± 0.00045	7.721 ± 0.069	88.19 ± 0.87
	0.10607 ± 0.00047	9.021 ± 0.071	89.00 ± 0.77

Ludwigshafen, Germany. It was used without further purification. [bmim][PF$_6$] ($C_8H_{15}F_6PN_2$, puriss., mass fraction ≥ 99 %) was supplied by Solvent Innovation GmbH, Cologne, Germany. It was degassed and dried under vacuum as described previously.[1] Its water mass fraction was less than 0.05 %, as determined by Karl Fischer 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.

Experimental Results. The solubility of hydrogen in [bmim][PF$_6$] was measured at temperatures from 313 K to 373 K in 20 K intervals. Attempts were also made to measure that solubility at 293 K, but due to the combination of rather high viscosity of the solvent and extremely low gas solubility, the reproducibility of those measurements was not satisfactory; therefore, no results are reported here. Experiments at higher temperatures than 373 K were not carried out since in previous work[1] a degradation of [bmim][PF$_6$] was observed at least at temperatures above 393 K. Recent investigations showed a seriously poor hydrolysis stability of some fluorine-containing anions such as [PF$_6$]$^-$ that can liberate HF during thermal treatment.[7] The new experimental results are given in Table 1. Figure 1 shows the new 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 [bmim][PF$_6$]). Gas molality is easily converted to mole fraction when the molar mass of the solvent is known. The relative molar mass of [bmim][PF$_6$] is 284.18.

As can be seen from Figure 1, the solubility pressure nearly linearly increases with increasing molality of hydrogen in the liquid phase. This behavior was expected from previous investigations on the solubility of carbon monoxide, which is somewhat better soluble, and carbon dioxide, which is much better soluble in [bmim][PF$_6$]. The behavior is typical "physical" gas solubility in particular when the gas is sparsely soluble.

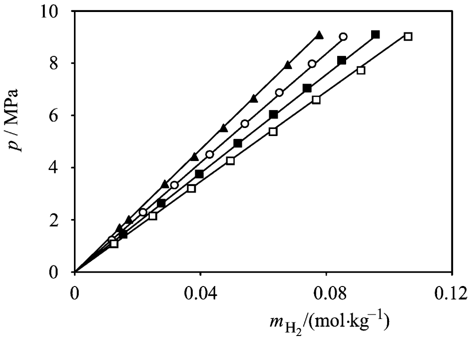

Figure 1. Total pressure above solutions of (H_2 + [bmim][PF$_6$]): ▲, 313.05 K; ○, 333.15 K; ■, 353.1 K; □, 373.15 K experimental results, this work; —, correlation, this work.

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 at average (at maximum) about 0.4 % (0.7 %). The relative uncertainty in the pressure decreases from about 2.6 % at low pressures to about 0.6 % at the higher pressures. It is worthwhile to mention that the solubility of hydrogen increases by about 36 % when the temperature increases from 313 K to 373 K. Thus, this system is one of the few examples where at around room temperature the gas solubility increases with increasing temperature.

Modeling

As is well-known, the vapor pressure of [bmim][PF$_6$] is negligibly small. For example, Kabo et al.[8] give the vapor pressure of [bmim][PF$_6$] at 298.15 K as $p^s \approx 10^{-11}$ Pa. Therefore, here the gaseous phase is regarded as pure hydrogen, and the vapor−liquid equilibrium condition results in the extended Henry's law for hydrogen:

$$k_{H,H_2}(T,p)\cdot a_{H_2}(T,m_{H_2}) = f_{H_2}(T,p) \tag{1}$$

$k_{H,H_2}(T,p)$ is Henry's constant of hydrogen in [bmim][PF$_6$] (based on the molality scale), $a_{H_2}(T,m_{H_2})$ is the activity of hydrogen in the liquid, and $f_{H_2}(T,p)$ is the fugacity of hydrogen in the vapor phase.

Equation 2 gives an expression for the influence of pressure on the Henry's constant of hydrogen in [bmim][PF$_6$]:

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

where $k^{(0)}_{H,H_2}(T)$ is Henry's constant of hydrogen in [bmim][PF$_6$] at zero pressure, $v^{\infty}_{H_2}$ is the partial molar volume of hydrogen at infinite dilution in [bmim][PF$_6$], and R is the universal gas constant.

The activity of hydrogen in the liquid is

$$a_{H_2} = \frac{m_{H_2}}{m^\circ}\gamma^*_{H_2} \tag{3}$$

where $m^\circ = 1$ mol·kg^{-1}. For example, Pitzer's virial expansion for the excess Gibbs energy[9] may be used for calculating the activity coefficient of hydrogen, $\gamma^*_{H_2}$ (cf. also ref 1). $\gamma^*_{H_2}$ is normalized to infinite dilution in pure [bmim][PF$_6$] and is based

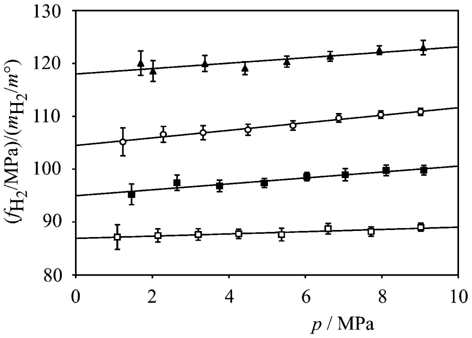

Figure 2. Influence of the total pressure on the ratio of H_2 fugacity (in the gaseous phase) to H_2 molality (in the liquid phase): ▲, 313.05 K; ○, 333.15 K; ■, 353.1 K; □, 373.15 K experimental results (and estimated uncertainties), this work; —, linear fit.

Table 2. Henry's Constant of Hydrogen in [bmim][PF$_6$][a]

T/K	$k^{(0)}_{H,H_2}$/MPa
313.05	118.0 ± 1.3
333.15	104.5 ± 1.1
353.10	95.0 ± 1.1
373.15	86.9 ± 1.1

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

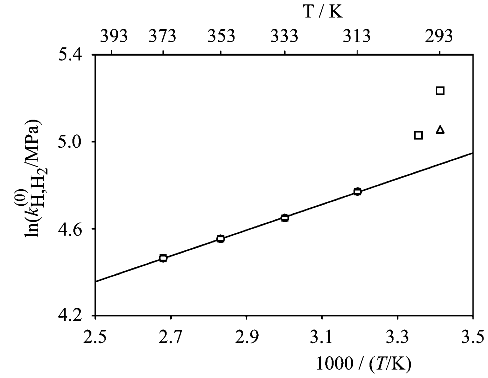

Figure 3. Henry's constant of H_2 in [bmim][PF$_6$] (at zero pressure, on the molality scale): ○, extrapolated experimental results (and estimated uncertainties), this work; △ experimental, ref 10; □, experimental, ref 12; —, correlation, this work.

on the molality scale. However, in the course of the estimation of the model parameters, the assumption that the liquid mixture is an ideal solution (i.e., $\gamma^*_{H_2} = 1$) proved to be a good approximation (i.e., due to the very low solubility of hydrogen in the ionic liquid, it was not necessary to account for interactions between the gas molecules in that liquid, and all interaction parameters in Pitzer's equation were set to zero). Furthermore, it was not necessary to consider an influence of temperature on $v^\infty_{H_2}$.

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 $\phi_{H_2}(T,p)$:

$$f_{H_2}(T,p) = p\phi_{H_2}(T,p) \tag{4}$$

$\phi_{H_2}(T,p)$ is calculated from the virial equation of state, truncated after the second virial coefficient, resulting in

$$\phi_{H_2}(T,p) = \exp\left[\frac{B_{H_2,H_2}p}{RT}\right] \tag{5}$$

The second virial coefficient of hydrogen B_{H_2,H_2} is calculated from a correlation based on experimental data recommended by Hayden and O'Connell:[6]

$$\frac{B_{H_2,H_2}}{\mathrm{cm^3 \cdot mol^{-1}}} = 19.08 - 65.39\left(\frac{43.6}{T/K}\right)^{1.37} \tag{6}$$

As, within the investigated temperature range, the second virial coefficient of hydrogen is positive and small, the fugacity coefficient of hydrogen is larger than one but does not deviate much from one (by about 5 % at maximum).

Henry's constant of hydrogen in [bmim][PF$_6$] 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 [bmim][PF$_6$]:

$$k^{(0)}_{H,H_2}(T) = \lim_{p \to p^s_{[\mathrm{bmim}][\mathrm{PF_6}]} = 0}\left[\frac{f_{H_2}(T,p)}{(m_{H_2}/m^\circ)}\right] \tag{7}$$

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. As can be seen from that figure, a linear regression was sufficient for a reliable extrapolation.

Table 2 lists the numerical values for Henry's constants resulting from the extrapolations. The estimated relative uncertainty of these numbers is 1.2 %. The final results for the Henry's constant (at zero pressure) of hydrogen in [bmim][PF$_6$] (on the molality scale) are correlated within the estimated uncertainty range by

$$\ln(k^{(0)}_{H,H_2}(T)/\mathrm{MPa}) = 2.8785 + 591.4/(T/\mathrm{K}) \tag{8}$$

Figure 3 shows the Henry's constant (at zero pressure) and its estimated uncertainty plotted versus the inverse absolute temperature together with the correlation curve (eq 8). As can be seen from Table 2 and Figure 3, Henry's constant of hydrogen in [bmim][PF$_6$] (at zero pressure) decreases from about 117.6 MPa at 313.15 K to about 86.8 MPa at 373.15 K.

Like in the previous investigation on the solubility of carbon monoxide in the same solvent, the new experimental results for the solubility pressure data for the system (H_2 + [bmim][PF$_6$]) were correlated with the results for the Henry's constant given in eq 8, and the partial molar volume of hydrogen in [bmim][PF$_6$], $v^\infty_{H_2}$. The correlation resulted in

$$v^\infty_{H_2} = 13.7\ \mathrm{cm^3 \cdot mol^{-1}} \tag{9}$$

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 0.039 MPa (0.7 %).

The knowledge of Henry's constant allows the calculation of some interesting solution thermodynamic properties, $\Delta_{sol}X$, of H_2 in [bmim][PF$_6$] (cf. ref 1), where, for example, $X = G$ (the molar Gibbs energy), H (the molar enthalpy), or S (the molar entropy). 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:

$$\Delta_{sol}G^\circ = (17.762 \pm 0.030)\ \mathrm{kJ \cdot mol^{-1}} \tag{10}$$

$$\Delta_{sol}H^\circ = (4.92 \pm 0.40)\ \mathrm{kJ \cdot mol^{-1}} \tag{11}$$

$$\Delta_{sol}S^\circ = (-43.1 \pm 1.3)\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}} \tag{12}$$

Comparison with Literature Data

Berger et al.[10] presented some experimental data for the solubility of hydrogen in [bmim][PF_6] at room temperature and at pressures of about (5, 50, and 100) atm. According to their results, the numerical value for Henry's constant at room temperature (after conversion to the molality scale) is 157 MPa, which is 17 % larger than the value following from eq 8 (at 293 K: 133.9 MPa) (see also Figure 3).

Anthony et al.[11] gravimetrically measured the solubility of several gases in [bmim][PF_6] at temperatures from 283 K to 323 K. The solubility of hydrogen in [bmim][PF_6] was below the detection limit of their experimental arrangement. From that detection limit, they concluded that the Henry's constant of H_2 in [bmim][PF_6] (on the molality scale) is above 42.6 MPa, which is consistent with but remarkably lower than the results from the present work $\{k^{(0)}_{H,H_2}(283\ K) = 143.8\ MPa;\ k^{(0)}_{H,H_2}(323\ K) = 111.0\ MPa$, cf. eq 8$\}$.

Dyson et al.[12] determined the solubility of hydrogen in several ionic liquids at 293 K and 298 K using high-pressure ^{1}H NMR spectroscopy. According to these authors, at those temperatures, Henry's constant $k^{(0)}_{H,H_2}$ of H_2 in [bmim][PF_6] (on the molality scale) amounts to 187.6 MPa and 152.9 MPa, respectively, which is about 40 % and 18 % larger than the numbers reported here {133.9 MPa and 129.4 MPa, from eq 8} (see also Figure 3).

Conclusions

New experimental results for the solubility of hydrogen in the ionic liquid [bmim][PF_6] are presented for temperatures from (313 to 373) K and pressures up to 9.1 MPa. The solubility of hydrogen in [bmim][PF_6] is rather low (i.e., it is lower than the solubility of carbon dioxide and carbon monoxide in that ionic liquid, which were investigated in previous work by Pérez-Salado Kamps et al.[1] and Kumełan et al.[2]). The solubility of hydrogen in [bmim][PF_6] increases with rising temperature. For example, the Henry's constant on the molality scale (at zero pressure) decreases from 117.6 MPa to 86.8 MPa when the temperature rises from 313.15 K to 373.15 K. The new experimental results for the solubility pressure were correlated with an average relative deviation of about 0.7 % (with gas molality and temperature preset) by means of the extended Henry's law.

Acknowledgment

This paper is dedicated to the memory of the late Prof. Rahoma Sadeg Mohamed, Campinas, Brazil.

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