Solubility of CO_2 in the Ionic Liquid [bmim][PF_6]

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New experimental results are presented for the solubility of carbon dioxide in the ionic liquid 1-*N*-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) for temperatures from (293 to 393) K and pressures up to about 9.7 MPa. Solubility pressures are correlated by means of the extended Henry's law.

Introduction

Ionic liquids are discussed as new solvents in transition metal catalysis, such as hydroformylation, hydrogenation, and oxidation. Several unique properties of ionic liquids, mainly their negligible vapor pressure and their capability of catalyst dissolution, provide great promise. Numerous types of reactions have been carried out in ionic liquids so far.[1,2] For some reactions, quantitative and systematic solubility measurements of carbon dioxide in the particular ionic liquids are of basic interest. Furthermore, separation and product recovery techniques in such systems need to be explored.[3]

The solubility of carbon dioxide in [bmim][PF_6] has been measured for temperatures ranging from (293 to 393) K and for pressures up to about 9.7 MPa, and it has been compared with very limited experimental information found in the literature.

Experimental Section

Apparatus and Measuring Technique. A detailed description of the experimental equipment and procedure is available in previous publications (cf., e.g., ref 4). Therefore, only the basic experimental technique and experimental uncertainties are given here.

In an experiment, a thermostated high-pressure cell (material = Hastelloy C4; volume = about 30 cm^3) with two sapphire windows is partially filled with a known amount of the particular solvent. A known amount of gas is added to the cell from a storage tank. Step by step, more solvent is added to the cell by a calibrated high-pressure displacer, until the gas is completely dissolved in the liquid phase. The amount of solvent charged to the cell is only slightly above the minimum amount needed to dissolve the gas completely. After equilibration, very small amounts of the liquid mixture are withdrawn stepwise from the cell until the first very small stable bubbles appear. That pressure is the equilibrium pressure to dissolve the charged amount of the gas in the charged amount of solvent at the fixed temperature.

The mass of carbon dioxide filled into the cell is determined volumetrically (for masses up to about 1.1 g)—by means of the equation of state given by Span and Wagner[5]—or by direct weighing (for masses from about 1.1 g up to about 6.3 g). Uncertainties amount up to about ±0.008 g. The volume of the solvent needed to dissolve the gas is determined in each experiment. The mass of the solvent (from about 32 to about 40 g) is calculated with a relative uncertainty of 0.7% maximum, from its volume and known density (from ref 6 and from separate measurements with a vibrating tube densimeter (Anton Paar GmbH, Graz, Austria; $\rho(T = 297.65\text{ K}) = (1.3653 \pm 0.0001)\text{ kg/dm}^3$; $\rho(T = 312.65\text{ K}) = (1.3536 \pm 0.0001)\text{ kg/dm}^3$), which match the literature data[6] to within the uncertainty given by those authors).

Two pressure transducers (WIKA GmbH, Klingenberg, Germany) for pressures ranging to 2.5 MPa and to 10 MPa, respectively, were used to determine the solubility pressure. Before and after each series of measurements, the transducers were calibrated against a high-precision pressure gauge (Desgranges & Huot, Aubervilliers, France). The maximum uncertainty in the pressure measurement is 0.1% of each transducer's maximum reading. The temperature is determined with two calibrated platinum resistance thermometers placed in the heating jacket of the cell with an uncertainty below ±0.1 K.

Substances and Sample Pretreatment. Carbon dioxide (≥99.995 mol %) was purchased from Messer-Griesheim, Ludwigshafen, Germany. It was used without further purification. [bmim][PF_6] ($C_8H_{15}F_6PN_2$, puriss, ≥99 mass %, from Solvent Innovation GmbH, Cologne, Germany) was degassed and dried under vacuum ($p < 0.1$ Pa) for 48 h at a temperature of approximately 75 °C. We filled the slightly yellowish and odorless ionic liquid into the glass buret (the same which is used later as sample container[4] to avoid any further contact with air and humidity), put it into a heatable ultrasonic bath, and connected the buret to a vacuum pump. During the first hours of this procedure, a vigorous degassing of large bubbles was observed; later it calmed down significantly until no further outgassing could be observed. The water content was less than 0.1 mass %, as measured by Karl Fischer analysis before and after the measurements.

The ionic liquid sample was collected after the measurement and reconditioned for further use. It is noteworthy to mention that some decomposition was observed after treatment at 393 K. During a solubility measurement (which took not more than approximately 2 h) and when the sample was released from the cell, the sample did not undergo any change. Only after some days at normal

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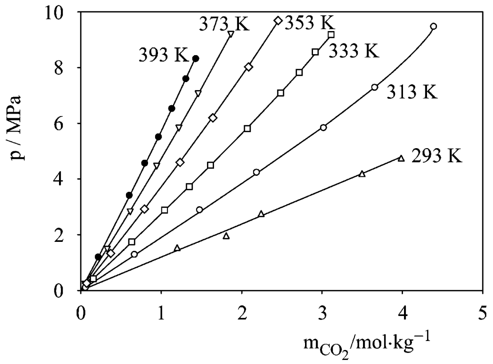

Figure 1. Total pressure above solutions of (CO_2 + [bmim][PF_6]): (△, ○, □, ◇, ▽, ●) experimental results, this work; (—) correlation, this work.

Table 1. Solubility of Carbon Dioxide in [bmim][PF_6]

T = 293.15 K		T = 313.15 K		T = 333.15 K	
m_{CO_2} mol/kg	p MPa	m_{CO_2} mol/kg	p MPa	m_{CO_2} mol/kg	p MPa
1.199	1.533	0.0557	0.105	0.1554	0.424
1.809	1.967	0.6674	1.292	0.6344	1.746
2.244	2.755	1.478	2.893	1.043	2.885
3.497	4.190	2.187	4.242	1.350	3.730
3.985	4.752	3.018	5.844	1.614	4.492
		3.656	7.293	2.073	5.807
		4.391	9.480	2.488	7.091
				2.719	7.822
				2.917	8.562
				3.116	9.184
T = 353.15 K		T = 373.15 K		T = 393.15 K	
m_{CO_2} mol/kg	p MPa	m_{CO_2} mol/kg	p MPa	m_{CO_2} mol/kg	p MPa
0.0734	0.266	0.0510	0.229	0.2179	1.199
0.3710	1.329	0.3286	1.486	0.6023	3.416
0.7914	2.915	0.6153	2.827	0.7959	4.571
1.234	4.592	0.9427	4.467	0.9649	5.513
1.641	6.194	1.221	5.830	1.132	6.526
2.088	8.025	1.459	7.055	1.307	7.597
2.453	9.685	1.867	9.191	1.430	8.324

laboratory conditions did a slow degradation process start in those samples, changing the color of the ionic liquid to brownish-yellow, and the characteristic odor of hydrogen fluoride became apparent. However, the samples subjected to 373 K and lower did not show this and could be reused after drying and degassing. It is reported in the literature that small traces of water[7] or free acid (when an anion metathesis reaction is involved in the preparation process[8]) cause decomposition with generation of hydrogen fluoride. In this context, future studies should be on completely halide-free ionic liquids.[9]

Experimental Results. The solubility of carbon dioxide in [bmim][PF_6] was measured at temperatures from (293 to 393) K in 20 K intervals. The results are given in Table 1. The total pressure above those solutions is plotted versus the stoichiometric molality of the gas in Figure 1. Throughout the paper, molality (i.e., number of moles per kilogram of the ionic liquid) is used for describing the solute concentration.

As can be seen from Figure 1, in the pressure region investigated in the present work, the solubility pressure practically linearly increases with increasing amount of the gas in the liquid. This is the typical behavior for a purely physical solubility.

Modeling

Due to the negligible vapor pressure of [bmim][PF_6] (see, e.g., ref 10), the gaseous phase is assumed to consist of pure carbon dioxide. Applying the vapor−liquid equilibrium condition to carbon dioxide results in the extended Henry's law:

$$k_{H,CO_2}(T,p)a_{CO_2}(T,m_{CO_2}) = f_{CO_2}(T,p) \tag{1}$$

$k_{H,CO_2}(T,p)$ is Henry's constant of CO_2 in [bmim][PF_6] (based on the molality scale). It is expressed as

$$k_{H,CO_2}(T,p) = k_{H,CO_2}(T)\exp\left(\frac{v^{\infty}_{CO_2}p}{RT}\right) \tag{2}$$

where $k_{H,CO_2}(T)$ is Henry's constant of CO_2 in [bmim][PF_6] at the vapor pressure of the solvent, that is, at zero pressure, and $v^{\infty}_{CO_2}$ is the partial molar volume of CO_2, infinitely diluted in pure [bmim][PF_6].

$a_{CO_2}(T,m_{CO_2})$ is the activity of CO_2 in the liquid:

$$a_{CO_2} = \frac{m_{CO_2}}{m^\circ}\gamma^*_{CO_2} \tag{3}$$

where m° = 1 mol/kg. The activity coefficient of CO_2 is calculated from the virial expansion proposed by Pitzer[11] to describe the excess Gibbs energy of an aqueous solution, which—applied to the ionic liquid solution—leads to

$$\ln\gamma^*_{CO_2} = 2\frac{m_{CO_2}}{m^\circ}\beta^{(0)}_{CO_2,CO_2} + 3\left(\frac{m_{CO_2}}{m^\circ}\right)^2\tau_{CO_2,CO_2,CO_2} \tag{4}$$

$\beta^{(0)}_{CO_2,CO_2}$ and τ_{CO_2,CO_2,CO_2} are parameters describing binary and ternary interactions between CO_2 molecules in the ionic liquid.

$f_{CO_2}(T,p)$ is the fugacity of pure carbon dioxide at equilibrium temperature and pressure. It is the product of the total pressure and the fugacity coefficient:

$$f_{CO_2}(T,p) = p\phi_{CO_2}(T,p) \tag{5}$$

$f_{CO_2}(T,p)$ is calculated from the equation of state proposed by Span and Wagner.[5]

By means of the usual extrapolation procedure, $k_{H,CO_2}(T)$ is evaluated from the new experimental results for the solubility pressure of CO_2 in [bmim][PF_6]:

$$k_{H,CO_2}(T) = \lim_{p\to p^s_{[bmim][PF_6]}=0}\left[\frac{f_{CO_2}(T,p)}{m_{CO_2}/m^\circ}\right] \tag{6}$$

In Figure 2, the calculated values for $f_{CO_2}/(m_{CO_2}/m^\circ)$ (for preset temperature) are plotted versus the total pressure above CO_2 + [bmim][PF_6]. Extrapolations were done by linear regression. Henry's constants resulting from the extrapolations are given in Table 2. Additionally, the standard deviations (between the experimental values and the linear fit) are given in Table 2. The final results for the Henry's constant (at zero pressure) of CO_2 in [bmim][PF_6] (on the molality scale) are correlated by

$$\ln(k_H/\text{MPa}) = 14.858 - 3205/(T/\text{K}) - 0.012755(T/\text{K}) \tag{7}$$

with an average deviation of 0.7% and a maximum deviation of 1.2%. Figure 3 shows the Henry's constant (and standard deviations) resulting from the extrapolations

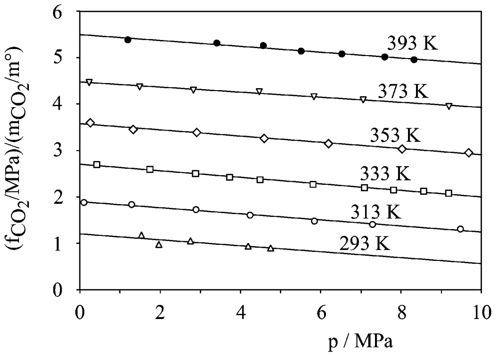

Figure 2. Influence of the total pressure on the ratio of CO_2-fugacity (in gaseous phase) to CO_2-molality (in liquid phase): (△, ○, □, ◇, ▽, ●) experimental results, this work; (—) linear fit.

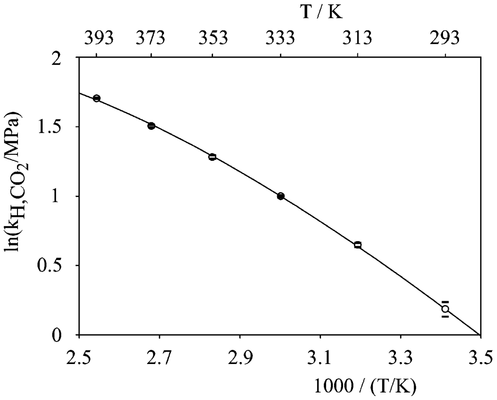

Figure 3. Henry's constant of CO_2 in [bmim][PF_6]: (○) extrapolated experimental results (and standard deviations), this work; (—) correlation, this work.

Table 2. Henry's Constant of Carbon Dioxide in [bmim][PF_6] (on the molality scale)

T/K	k_H/MPa	standard deviation $\Delta_s k_H$/MPa
293.15	1.20	0.06
313.15	1.89	0.03
333.15	2.70	0.02
353.15	3.57	0.02
373.15	4.47	0.02
393.15	5.49	0.03

plotted versus the inverse absolute temperature, as well as the correlation curve (eq 7).

The new solubility pressure data for the system CO_2 + [bmim][PF_6] might be described through $v^{\infty}_{CO_2}$ and the interaction parameters $\beta^{(0)}_{CO_2,CO_2}$ and τ_{CO_2,CO_2,CO_2}. However, $v^{\infty}_{CO_2}$ and $\beta^{(0)}_{CO_2,CO_2}$ turned out to be sufficient to describe the experimental total pressures with an average relative deviation of about 1%.

$$v^{\infty}_{CO_2}/(\mathrm{cm^3/mol}) = -192 + 0.469(T/\mathrm{K}) \qquad (8)$$

$$\beta^{(0)}_{CO_2,CO_2} = -0.0225 \qquad (9)$$

In the temperature range under consideration, negative numbers for the partial molar volume of CO_2 at infinite dilution in pure [bmim][PF_6] result from eq 8, which may be attributed to large differences in the molecular size of both components. Figure 1 shows the very good agreement between the experimental data and the correlation for the total pressure.

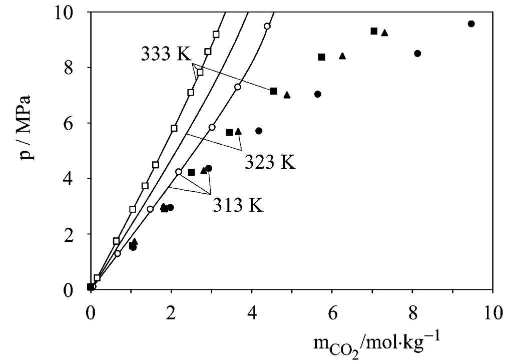

Figure 4. Comparison of experimental (and correlated/predicted) pressures above solutions of (CO_2 + [bmim][PF_6]) with literature data: (●, ▲, ■) Blanchard et al.;[12] (○, □) this work; (—) correlation (at 313 and 333 K)/prediction (at 323 K), this work.

Thermodynamic properties of solution (of CO_2 in [bmim][PF_6]) can be calculated from the correlation of Henry's constant given above applying well-known thermodynamic relations, for example:

$$\Delta_{sol}G = RT\ln(k_H(T,p)/p°) \qquad (10)$$

$$\Delta_{sol}H = R\left(\frac{\partial \ln(k_H(T,p)/p°)}{\partial(1/T)}\right)_p \qquad (11)$$

$$\Delta_{sol}S = (\Delta_{sol}H - \Delta_{sol}G)/T \qquad (12)$$

$$\Delta_{sol}C_p = \left(\frac{\partial \Delta_{sol}H}{\partial T}\right)_p \qquad (13)$$

At standard temperature and pressure ($T° = 298.15$ K, $p° = 0.1$ MPa) the following numbers (on the molality scale) result from the aforementioned equations: $\Delta_{sol}G° = 6.46$ kJ/mol, $\Delta_{sol}H° = -17.24$ kJ/mol, $\Delta_{sol}S° = -79.5$ J/(mol K), and $\Delta_{sol}C^{\circ}_p = 63.2$ J/(mol K).

Comparison with Literature Data

Blanchard et al.[12] reported some solubility data for carbon dioxide in (practically water-free) [bmim][PF_6]. Those solubilities were measured at (313, 323, and 333) K with a static vapor−liquid apparatus. As can be seen from Figure 4, the data reported by those authors considerably differ from the new data. Applying the usual extrapolation procedure to that data in order to determine the (zero pressure) Henry's constant of CO_2 in the ionic liquid (cf. eq 6) leads to the following numerical values (and standard deviations from the linear fit) at (313, 323, and 333) K: (1.58 ± 0.05), (1.70 ± 0.04), and (1.64 ± 0.08) MPa, respectively, which are well below the ones determined in the present work (about 16, 25, and 39%, respectively).

According to Scovazzo et al.,[13,14] 0.08 (0.051) moles of carbon dioxide dissolve in 1 L of [bmim][PF_6] at 300.65 K (333.15 K) and $p_{CO_2} = 1$ atm. Converting these data to Henry's constant (on the molality scale) results in 1.72 MPa (2.65 MPa) at 300.65 K (333.15 K), which is about 20% above (about 1.5% below) the Henry's constant reported in the present work.

Conclusions

New experimental results for the solubility of carbon dioxide in the ionic liquid [bmim][PF_6] are presented for temperatures from (293 to 393) K and pressures up to about 9.7 MPa, showing purely physical solubility. Solubility pressures were correlated with an average relative uncertainty of about 1% by means of the extended

Henry's law. The new experimental data considerably differ from the very scarce data found in the literature.[12−14]

List of Symbols

a = activity
C_p = molar heat capacity at constant pressure
f = fugacity
G = free molar enthalpy
H = molar enthalpy
k_H = Henry's constant of CO_2 in [bmim][PF_6] (on the molality scale)
m = molality
p = pressure
R = universal gas constant
S = molar entropy
T = absolute temperature
v^∞ = (partial) molar volume of CO_2 infinitely diluted in [bmim][PF_6]

Greek Letters

$\beta^{(0)}$ = binary interaction parameter in Pitzer's equation
γ_i^* = activity coefficient of component i normalized to infinite dilution in pure [bmim][PF_6] (on the molality scale)
Δ_s = characterizes a standard deviation
$\Delta_{sol}X$ = characterizes a thermodynamic property of solution (on the molality scale) (here $X = G, H, S, C_p$)
$\Delta_{sol}X(T,p) = X^\infty_{CO_2,[bmim][PF_6]}(T,p,m_{CO_2} = m°)_{liq} - X_{CO_2}(T,p°)_{pure\ ideal\ gas}$
ρ = density
τ = third virial coefficient in Pitzer's equation
ϕ = fugacity coefficient

Superscripts

s = saturation
° = standard state ($T° = 298.15$ K, $p° = 0.1$ MPa, $m° = 1$ mol/kg)

Note Added after ASAP Posting. This article was released ASAP on 4/5/2003. Data were corrected in equations 7 and 11 and in the paragraph following equation 13. The paper was reposted on 4/18/2003.

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