Solubility of CO_2 in the Ionic Liquids [bmim][CH_3SO_4] and [bmim][PF_6]

Jacek Kumełan, Álvaro Pérez-Salado Kamps, Dirk Tuma, and Gerd Maurer*

Chair of Applied Thermodynamics, University of Kaiserslautern, P.O. Box 30 49, D-67653 Kaiserslautern, Germany

A high-pressure view-cell technique based on the synthetic method was used to determine the solubility of carbon dioxide in the ionic liquid 1-*n*-butyl-3-methylimidazolium methyl sulfate ([bmim][CH_3SO_4]). The temperature ranged from 293.2 K to 413.1 K, the pressure and the carbon dioxide molality reached up to ∼10 MPa and ∼3.3 mol of CO_2•(kg of [bmim][CH_3SO_4])$^{-1}$, respectively. The (extended) Henry's law was successfully applied to correlate the solubility pressures. The final results for the Henry's constant (at zero pressure) of carbon dioxide in [bmim][CH_3SO_4] (on the molality scale) are correlated within the estimated uncertainty (± 1.3 %) by $\ln(k_{\mathrm{H,CO_2}}^{(0)}/\mathrm{MPa}) = 7.2738 - 1775/(T/\mathrm{K}) - 0.002033(T/\mathrm{K})$. Furthermore, some small corrections were applied to the experimental results for the solubility of carbon dioxide in the ionic liquid 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) reported in previous work. The corrected values for the Henry's constant of carbon dioxide in [bmim][PF_6] only slightly and systematically deviate (by about −2 % at given temperature) from the values reported previously.

Introduction

Continuing recent investigations on 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])[1−4] as well as on the solubility of the single gases carbon dioxide and hydrogen in the ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf_2N]),[5,6] this contribution presents new experimental data for the solubility of carbon dioxide in another (but halide-free) ionic liquid, namely, 1-*n*-butyl-3-methylimidazolium methyl sulfate ([bmim][CH_3SO_4]). Despite the proven poor hydrolytic stability of the [PF_6]$^-$ anion,[7] [bmim][PF_6] holds a prominent position in the application of ionic liquids. This is due to two major facts: that the production costs are low, enabling the disposability of bulk quantities, and that [bmim][PF_6] and its respective mixtures are still best-known at present. To overcome the problem of [PF_6]$^-$ decomposition, Holbrey et al.[8] proposed the introduction of halide-free alkyl sulfate ionic liquids as an alternative. If the new candidate meets the task-specific demands through suitable characteristics, for example, similar transport properties or similar solvation behavior, it will be, at any rate, a better choice. From those perspectives, we opted for [bmim][CH_3SO_4] to be the next ionic liquid in our experimental work. At present, no experimental information for the solubility of carbon dioxide in this ionic liquid is found in the open literature.

Series of isothermal measurements were performed at temperatures from 293.2 K to 413.1 K in ∼20 K intervals. The pressure ranged up to ∼9.8 MPa. The new experimental data were used to determine Henry's constant of carbon dioxide in [bmim][CH_3SO_4].

In addition, some small corrections were applied to the experimental results for the solubility of carbon dioxide in [bmim][PF_6] reported previously.[1] Mainly, the temperature values were revised. The corrected temperatures slightly deviate from the previously reported temperatures (by about +0.4 K at $T \approx 313$ K up to +1.9 K at $T \approx 393$ K). Therefore, the reevaluated numerical values for the Henry's constant of carbon dioxide in [bmim][PF_6] only slightly and systematically deviate (by about −2 %) from the values reported previously.

Table 1. Density of [bmim][CH_3SO_4] (experimental uncertainties: $\Delta T = \pm 0.1$ K, $\Delta\rho = \pm 0.0001$ kg·dm^{-3})

T/K	ρ/kg·dm^{-3}	T/K	ρ/kg·dm^{-3}
290.95	1.2149	301.00	1.2080
292.95	1.2135	303.00	1.2067
294.95	1.2121	305.00	1.2053
297.00	1.2107	307.05	1.2040
299.00	1.2094		

Experimental Section

Apparatus and Method. The apparatus and the measuring technique were the same as in previous work;[1−11] therefore, no descriptions are repeated here.

The mass of carbon dioxide filled into the cell is determined either volumetrically for small amounts of masses (i.e., from the exactly known volume of the cell; approximately 29.2 cm^3) and readings for temperature and pressure by means of the equation of state given by Span and Wagner[12] or gravimetrically for larger amounts of masses by weighing a condenser (from which the cell is charged) before and after the charging process on a high precision balance. Gravimetric uncertainties amount to ± 0.01 g. The amount of mass of the solvent filled into the cell (from about 30.3 g to about 34.4 g) is calculated from the volume displacement in a calibrated spindle press (from which the solvent is charged into the cell) and the solvent density with a relative uncertainty of about 0.14 %. The density of the solvent is known from separate measurements with a vibrating-tube densimeter (Anton Paar GmbH, Graz, Austria), cf. Table 1. Two calibrated platinum resistance thermometers were used to determine the temperature with an uncertainty below ± 0.1 K.

When carbon dioxide was volumetrically filled into the cell, the pressure was measured with two pressure transducers

---

* Corresponding author. Tel: +49 631 205 2410. Fax: +49 631 205 3835. E-mail: gmaurer@rhrk.uni-kl.de.

10.1021/je060190e CCC: $30.25

suitable for pressures ranging up to 2.5 MPa and 4 MPa, respectively. The respective solubility pressure was measured with a pressure transducer suitable for pressures up to 10 MPa. Commercially available pressure transducers (WIKA GmbH, Klingenberg, Germany) were used. The maximum systematic uncertainty in the solubility pressure measurement results from the uncertainty of the pressure transducers (0.1 % of the transducer's full scale) and an additional contribution of about ± 0.01 MPa caused by a small temperature drift in the isolated tubes filled with the ionic liquid, which connect the cell with the pressure transducers. That temperature drift contribution 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.

Table 2. Experimental Results for the Solubility of Carbon Dioxide in [bmim][CH_3SO_4]

T	m_{CO_2}	p	f_{CO_2}/m_{CO_2}
K	mol·kg^{-1}	MPa	MPa/(mol·kg^{-1})
293.2 ± 0.1	0.4927 ± 0.0066	0.908 ± 0.033	1.756 ± 0.067
	0.7996 ± 0.0068	1.457 ± 0.033	1.684 ± 0.041
	1.1827 ± 0.0070	2.139 ± 0.034	1.608 ± 0.027
	1.7123 ± 0.0074	3.031 ± 0.035	1.494 ± 0.018
	2.3837 ± 0.0079	4.120 ± 0.037	1.362 ± 0.013
313.25 ± 0.1	0.3512 ± 0.0013	0.933 ± 0.024	2.553 ± 0.066
	0.8968 ± 0.0027	2.359 ± 0.028	2.374 ± 0.029
	1.3614 ± 0.0042	3.428 ± 0.032	2.163 ± 0.022
	1.7429 ± 0.0052	4.368 ± 0.036	2.058 ± 0.018
	1.8459 ± 0.0075	4.583 ± 0.041	2.017 ± 0.020
	2.2724 ± 0.0079	5.670 ± 0.043	1.918 ± 0.016
	2.6464 ± 0.0082	6.643 ± 0.045	1.831 ± 0.014
	3.0728[a] ± 0.0086	7.962 ± 0.046	1.748 ± 0.011
	3.3042[a] ± 0.0088	9.357 ± 0.047	1.730 ± 0.010
333.1 ± 0.1	0.4928 ± 0.0068	1.756 ± 0.044	3.351 ± 0.096
	0.7157 ± 0.0069	2.506 ± 0.044	3.207 ± 0.065
	1.1303 ± 0.0071	4.008 ± 0.046	3.072 ± 0.040
	1.4214 ± 0.0073	5.029 ± 0.047	2.949 ± 0.031
	1.7426 ± 0.0075	6.230 ± 0.048	2.844 ± 0.025
	1.9743[a] ± 0.0076	7.284 ± 0.049	2.812 ± 0.022
	2.2077[a] ± 0.0079	8.177 ± 0.050	2.720 ± 0.019
	2.3597[a] ± 0.0080	8.944 ± 0.050	2.693 ± 0.018
353.1 ± 0.1	0.3787 ± 0.0068	1.780 ± 0.051	4.469 ± 0.152
	0.5064 ± 0.0068	2.393 ± 0.052	4.413 ± 0.112
	0.6901 ± 0.0069	3.262 ± 0.052	4.303 ± 0.081
	0.9486 ± 0.0071	4.467 ± 0.053	4.137 ± 0.058
	1.0896 ± 0.0071	5.169 ± 0.053	4.081 ± 0.050
	1.2207 ± 0.0072	5.879 ± 0.054	4.054 ± 0.044
	1.5194 ± 0.0073	7.495 ± 0.055	3.950 ± 0.035
	1.8775[a] ± 0.0077	9.428 ± 0.057	3.782 ± 0.028
373.1 ± 0.1	0.1871 ± 0.0009	1.114 ± 0.025	5.803 ± 0.135
	0.3764 ± 0.0013	2.232 ± 0.028	5.627 ± 0.073
	0.5553 ± 0.0069	3.286 ± 0.061	5.478 ± 0.122
	0.7274 ± 0.0070	4.387 ± 0.061	5.437 ± 0.092
	0.8853 ± 0.0071	5.336 ± 0.062	5.310 ± 0.075
	1.0931 ± 0.0072	6.652 ± 0.063	5.193 ± 0.060
	1.1729 ± 0.0073	7.170 ± 0.063	5.152 ± 0.055
	1.4200[a] ± 0.0074	8.942 ± 0.064	5.080 ± 0.045
393.1 ± 0.1	0.1351 ± 0.0008	0.973 ± 0.026	7.067 ± 0.190
	0.2728 ± 0.0010	1.960 ± 0.028	6.918 ± 0.101
	0.4188 ± 0.0014	3.041 ± 0.030	6.845 ± 0.071
	0.5606 ± 0.0017	4.076 ± 0.033	6.718 ± 0.058
	0.7124 ± 0.0021	5.226 ± 0.036	6.627 ± 0.050
	0.8661 ± 0.0027	6.412 ± 0.040	6.535 ± 0.046
	1.0307 ± 0.0031	7.729 ± 0.043	6.450 ± 0.041
	1.2148[a] ± 0.0036	9.246 ± 0.047	6.355 ± 0.037
413.1 ± 0.1	0.1316 ± 0.0007	1.113 ± 0.026	8.309 ± 0.202
	0.2640 ± 0.0010	2.258 ± 0.029	8.250 ± 0.109
	0.4020 ± 0.0013	3.431 ± 0.031	8.077 ± 0.078
	0.5412 ± 0.0017	4.655 ± 0.034	7.981 ± 0.064
	0.6890 ± 0.0020	5.993 ± 0.038	7.901 ± 0.055
	0.8430 ± 0.0026	7.380 ± 0.043	7.778 ± 0.051
	0.9649[a] ± 0.0029	8.585 ± 0.045	7.756 ± 0.047
	1.0927[a] ± 0.0033	9.805 ± 0.048	7.673 ± 0.044

[a] These experimental points were not taken into account for the extrapolation procedure to determine Henry's constant.

Materials and Sample Pretreatment. Carbon dioxide (mole fraction ≥ 0.99995) was purchased from Messer-Griesheim, Ludwigshafen, Germany. It was used without further purification. The ionic liquid [bmim][CH_3SO_4] ($C_9H_{18}N_2O_4S$, purum, mass fraction ≥ 0.98, dark yellow to brownish color) was supplied by Solvent Innovation GmbH, Cologne, Germany. In our laboratory, it was degassed and dried under vacuum for 2 days. The ionic liquid was collected after a measurement and reconditioned (i.e., degassed and dried under vacuum) for further use. [bmim][CH_3SO_4] and [bmim][PF_6] strongly resemble each other in their behavior during the particular procedures of the entire investigation, but no signs of degradation were observed for [bmim][CH_3SO_4]. Multiple use led to an intensification of the color, but we could prove by redoing measurements that it did not affect the experimental results for the gas solubility. After completion of the gas solubility measurements, the water content of the sample (<0.0005 mass fraction) was determined by Karl Fischer titration analysis.

Experimental Results. The solubility of carbon dioxide in [bmim][CH_3SO_4] was investigated at temperatures from 293.2 K to 413.1 K in about 20 K intervals. The new experimental results are given in Table 2. Figure 1 shows them plotted as the pressure required to dissolve carbon dioxide versus the gas molality m_{CO_2} {i.e., the amount of substance (the number of moles) of CO_2·(kg of [bmim][CH_3SO_4])$^{-1}$} at preset temperature. Gas molality is easily converted to mole fraction when the molar mass of the solvent is known. The relative molar mass of [bmim][CH_3SO_4] is 250.32.

As can be seen from Figure 1—within the temperature and pressure regions investigated here—the solubility pressure practically linearly increases with increasing gas molality at given temperature. This purely physical solubility behavior is in accordance with our previous investigations of the solubility of carbon dioxide in the pure ionic liquids [bmim][PF_6] and [hmim][Tf_2N].[1,5] Furthermore, the solubility of CO_2 in [bmim][CH_3SO_4] clearly decreases with rising temperature. For example, when pressure and temperature amount to 3 MPa and 293.2 K (413.1 K), about 1.7 (0.35) mol of carbon dioxide dissolves in 1 kg of [bmim][CH_3SO_4].

The experimental uncertainty for the gas molality Δm_{CO_2} (resulting from the filling procedure) is also given in Table 2. It was estimated from a Gauss error propagation calculation and amounts at average 0.0052 mol·kg^{-1} (0.55 %). The experimental uncertainty for the solubility pressure was calculated from $\Delta p = \pm$ (0.02 MPa + Δp^*). The first contribution accounts for the systematic uncertainties mentioned before {pressure transducer's uncertainty (0.01 MPa) + uncertainty resulting from the temperature drift (0.01 MPa)}. The second term considers the statistic uncertainties and is determined from a Gauss error propagation calculation (by applying the VLE model described in the next section). It reflects the effect of the uncertainties of temperature and gas molality on the solubility pressure. The absolute uncertainty in the pressure Δp amounts in average to 0.043 MPa. The relative uncertainty in the pressure amounts in average to 1.2 %. It decreases from (at maximum) 3.6 % at low pressures to (at minimum) 0.5 % at the highest pressures.

Correlation of the Gas Solubility

The correlation method was also described in detail before;[1] therefore, we restrict to a brief outline here. The vapor–liquid

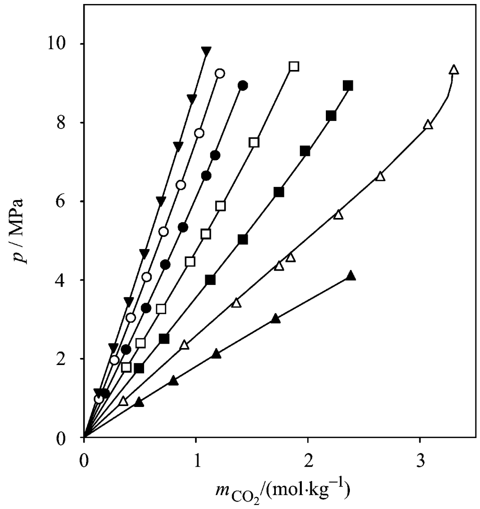

Figure 1. Total pressure above solutions of (CO_2 + [bmim][CH_3SO_4]): (▲, T = 293.2 K, △, T = 313.25 K; ■, T = 333.1 K; □, T = 353.1 K; ●, T = 373.1 K; ○, T = 393.1 K; ▼, T = 413.1 K) experimental results; —, correlation.

equilibrium condition results in the extended Henry's law for carbon dioxide:

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

$k_{H,CO_2}(T, p)$ is Henry's constant of carbon dioxide in [bmim][CH_3SO_4] at temperature T and pressure p (based on the molality scale). $a_{CO_2}(T, m_{CO_2})$ is the activity of carbon dioxide in the liquid. As usual, the influence of pressure on that activity is neglected. $f_{CO_2}(T, p)$ is the fugacity of carbon dioxide in the vapor phase. Following the assumption that the ionic liquid exhibits a negligibly small vapor pressure, the gaseous phase consists of (nearly) pure carbon dioxide.

Henry's constant of carbon dioxide in [bmim][CH_3SO_4] is expressed as

$$k_{H,CO_2}(T, p) = k^{(0)}_{H,CO_2}(T) \exp\left(\frac{V^{(\infty)}_{m,CO_2} p}{RT}\right) \tag{2}$$

where $k^{(0)}_{H,CO_2}(T)$ is Henry's constant of carbon dioxide in [bmim][CH_3SO_4] at zero pressure, and $V^{(\infty)}_{m,CO_2}$ is the partial molar volume of carbon dioxide at infinite dilution in [bmim][CH_3SO_4].

The activity of carbon dioxide in the ionic liquid (expressed on a molality scale basis) is

$$a_{CO_2} = \frac{m_{CO_2}}{m^\circ} \gamma_{CO_2} \tag{3}$$

where m° = 1 mol·kg^{-1}. Pitzer's virial expansion for the (molality scale based) excess Gibbs energy[13,14] is used for calculating the activity coefficient of carbon dioxide, γ_{CO_2}:

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

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

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

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

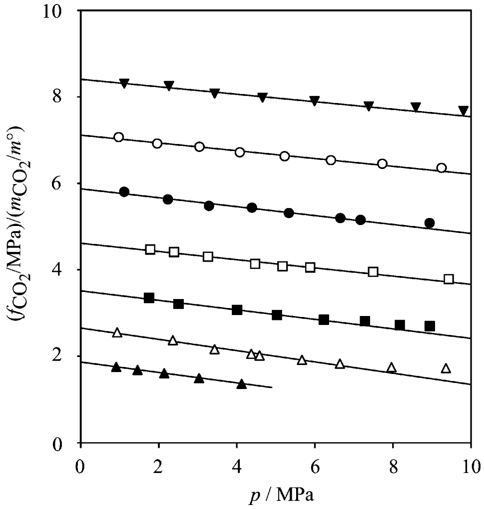

Figure 2. Influence of the total pressure on the ratio of CO_2 fugacity (in the gaseous phase) to CO_2 molality (in the ionic liquid [bmim][CH_3SO_4]): (▲, T = 293.2 K; △, T = 313.25 K; ■, T = 333.1 K; □, T = 353.1 K; ●, T = 373.1 K; ○, T = 393.1 K; ▼, T = 413.1 K) experimental results; —, linear fit.

Table 3. Henry's Constant of Carbon Dioxide in [bmim][CH_3SO_4] (at zero pressure, on the molality scale)

T / K	$k^{(0)}_{H,CO_2}$ / MPa	T / K	$k^{(0)}_{H,CO_2}$ / MPa
293.2	1.866 ± 0.031	373.1	5.873 ± 0.091
313.25	2.651 ± 0.022	393.1	7.115 ± 0.070
333.1	3.514 ± 0.050	413.1	8.407 ± 0.083
353.1	4.615 ± 0.062		

The equation of state by Span and Wagner[12] was used to calculate $\phi_{CO_2}(T, p)$. Henry's constant of carbon dioxide in [bmim][CH_3SO_4] at zero pressure $k^{(0)}_{H,CO_2}(T)$ is obtained by an extrapolation (at preset temperature) of the new experimental results for the solubility pressure of CO_2 in [bmim][CH_3SO_4]:

$$k^{(0)}_{H,CO_2}(T) = \lim_{p \to p^s_{[bmim][CH_3SO_4]} = 0} \left[\frac{f_{CO_2}(T, p)}{(m_{CO_2}/m^\circ)}\right] \tag{6}$$

The experimental results for $f_{CO_2}/(m_{CO_2}/m^\circ)$ as well as their experimental uncertainties are also given in Table 2. The extrapolation itself was done by a simple linear regression shown in Figure 2. Table 3 lists the numerical values for Henry's constants resulting from these extrapolations and their estimated absolute uncertainties. The estimated relative uncertainty amounts in average to 1.3 %. The final results for the Henry's constant (at zero pressure) of carbon dioxide in [bmim][CH_3SO_4] (on the molality scale) are correlated within the estimated uncertainty by

$$\ln(k^{(0)}_{H,CO_2}/\text{MPa}) = 7.2738 - 1775/(T/\text{K}) - 0.002033(T/\text{K}) \tag{7}$$

Figure 3 shows the Henry's constant (at zero pressure) plotted versus the inverse absolute temperature together with the correlation curve (eq 7). So, the new experimental results for the solubility pressure data for the system (CO_2 + [bmim][CH_3SO_4]) were correlated with the results for the Henry's constant {given here by eq 7}, the partial molar volume of carbon dioxide in [bmim][CH_3SO_4], $V^{(\infty)}_{m,CO_2}$, and the (molality scale based) Pitzer model for the Gibbs excess energy of the liquid solution using a single binary parameter $\beta^{(0)}_{CO_2,CO_2}$. The curves in Figure 1 originate from that correlation:

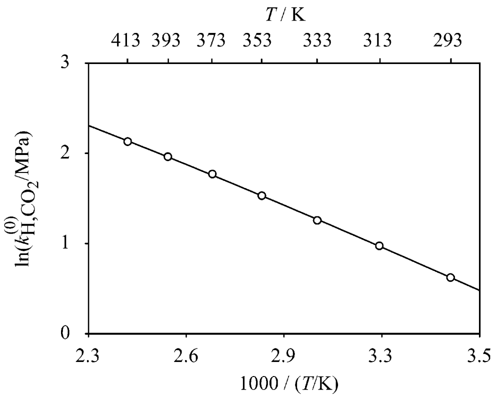

Figure 3. Henry's constant of CO_2 in [bmim][CH_3SO_4] (at zero pressure, on the molality scale): ○, extrapolated experimental results. The estimated experimental uncertainties are smaller than the symbols; —, correlation.

$$V^{(\infty)}_{m,CO_2}/(cm^3 \cdot mol^{-1}) = -742.49 + 4.4875(T/K) - 0.0059684(T/K)^2 \quad (8)$$

$$\beta^{(0)}_{CO_2,CO_2} = -0.3654 + \frac{81.26}{(T/K)} \quad (9)$$

The correlation results for the gas solubility (i.e., the gas molalities at given temperature and solubility pressure) agree with the experimental data with an average absolute (relative) deviation of about 0.009 mol·kg^{-1} (0.76 %). The maximum absolute (relative) deviation amounts to 0.042 mol·kg^{-1} (2.3 %). Moreover, Figure 1 illustrates that good agreement between experimental data and correlation results.

The knowledge of Henry's constant of CO_2 in [bmim][CH_3SO_4] allows for the calculation of related (molar) solution thermodynamic properties, $\Delta_{sol}X_m$, where, for example, $X = G$ (the Gibbs energy), H (the enthalpy), S (the entropy), or C_p (the heat capacity at constant pressure).[1] At standard temperature and pressure ($T^\circ = 298.15$ K, $p^\circ = 0.1$ MPa) the following numerical values (on the molality scale) result from the correlation equations given above:

$$\Delta_{sol}G_m{}^\circ = (7.485 \pm 0.036)\ kJ \cdot mol^{-1} \quad (10)$$

$$\Delta_{sol}H_m{}^\circ = (-13.28 \pm 0.31)\ kJ \cdot mol^{-1} \quad (11)$$

$$\Delta_{sol}S_m{}^\circ = (-69.6 \pm 0.9)\ J \cdot mol^{-1} \cdot K^{-1} \quad (12)$$

$$\Delta_{sol}C_{p,m}{}^\circ = (10.4 \pm 1.8)\ J \cdot mol^{-1} \cdot K^{-1} \quad (13)$$

Comparison with Literature Data

The present work is the first to give experimental information for the solubility (as well as for the influence of temperature on the solubility) of carbon dioxide in the ionic liquid [bmim][CH_3SO_4]. In Figure 4, the temperature dependent (zero pressure) Henry's constant of carbon dioxide in [bmim][CH_3SO_4] (based on the molality scale) is compared with the temperature dependent (zero pressure) Henry's constant of that particular gas in the two single ionic liquids [bmim][PF_6] and [hmim][Tf_2N], which were determined in previous work.[1,5] Note that some very small corrections were applied to the experimental data for the solubility of carbon dioxide in the ionic liquid [bmim][PF_6] from ref 1 (cf. Appendix). The (zero pressure) Henry's constant of carbon dioxide in [bmim][PF_6] differs from that in [hmim][Tf_2N] by only about −5 %, +15.1 %, and +11.7 % at 293 K, 353 K, and 413 K, respectively. Larger differences are observed between the (zero pressure) Henry's constants of carbon dioxide in [bmim][CH_3SO_4] and in [hmim][Tf_2N] {about +49.9 %, +51.3 %, and +54.4 % at 293 K, 353 K, and 413 K, respectively}. In other words, [hmim][Tf_2N] is the best solvent for carbon dioxide, followed by [bmim][PF_6], and ultimately [bmim][CH_3SO_4].

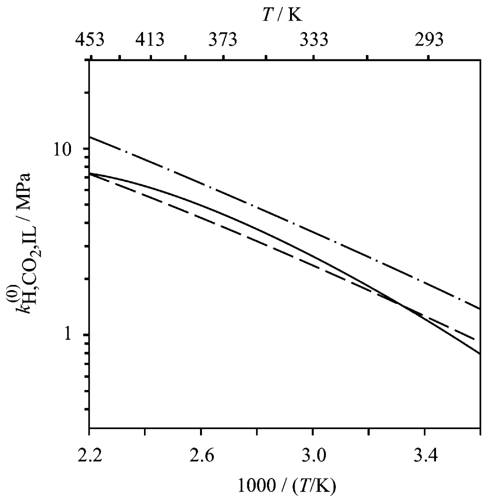

Figure 4. Correlation results for Henry's constant (at zero pressure, on the molality scale) of CO_2 in different ionic liquids {—, [bmim][PF_6]; − −, [hmim][Tf_2N]; − · −, [bmim][CH_3SO_4]}.

Conclusions

New experimental results for the solubility of carbon dioxide in the ionic liquid [bmim][CH_3SO_4] are presented for temperatures from about 293 K to 413 K and pressures up to about 10 MPa. Henry's law constants are determined from that solubility pressure data within an uncertainty of about ± 1.3 %. The gas solubility (i.e., the gas molality at given temperature and pressure) was correlated with an average relative deviation of about 0.76 % by means of the extended Henry's law.

Appendix

Corrected Experimental Results for the Solubility of CO_2 in [bmim][PF_6] from Our Previous Work.[1] The platinum resistance thermometers used in the work by Pérez-Salado Kamps et al.[1] were re-calibrated straight after those experimental results had been published, showing that a small correction had to be applied to the temperature values. The corrected temperatures are calculated from $T = T_{old} + \Delta T$, where $\Delta T =$ (0.4, 0.6, 0.9, 1.2, 1.55, and 1.9) K at $T_{old} =$ (293.15, 313.15, 333.15, 353.15, 373.15, and 393.15) K, respectively. During the experiment, when the amount of gas charged into the cell was small, this amount was determined volumetrically (i.e., from the known volume of the cell and readings for temperature and pressure) by means of an equation of state.[12] In that particular case, a small correction had to be applied to the gas molality as well. Furthermore, the mass of the ionic liquid solvent pressed into the cell has been recalculated by considering more and more precise density data for the ionic liquid (which were adopted from Kumełan et al.[2]). For better clarity, Table 4 lists the corrected experimental results for the solubility of carbon dioxide in [bmim][PF_6] together with the experimental uncertainty for the gas molality Δm_{CO_2} (resulting from the filling procedure), which was estimated from a Gauss error propagation calculation. It amounts at average 0.0059 mol·kg^{-1} (0.55 %). The experimental uncertainty for the solubility pressure was calculated from $\Delta p = \pm (\Delta_1 p + \Delta_2 p)$. The first contribution

Table 4. Experimental Results for the Solubility of Carbon Dioxide in [bmim][PF$_6$] from Ref 1 (after applying some small corrections, cf. text)

T	m_{CO_2}	p	f_{CO_2}/m_{CO_2}
K	mol·kg^{-1}	MPa	MPa/(mol·kg^{-1})
293.55	1.2096 ± 0.0063	1.533 ± 0.021	1.167 ± 0.017
	1.8251 ± 0.0070	1.967 ± 0.022	0.968 ± 0.012
	2.2629 ± 0.0071	2.755 ± 0.031	1.045 ± 0.012
	3.5274 ± 0.0085	4.190 ± 0.034	0.933 ± 0.008
	4.0203 ± 0.0090	4.752 ± 0.036	0.894 ± 0.007
313.75	0.0561 ± 0.0007	0.105 ± 0.014	1.861 ± 0.248
	0.6717 ± 0.0020	1.292 ± 0.017	1.821 ± 0.025
	1.4920 ± 0.0066	2.893 ± 0.034	1.709 ± 0.021
	2.2073 ± 0.0072	4.242 ± 0.036	1.589 ± 0.014
	3.0462 ± 0.0080	5.844 ± 0.039	1.464 ± 0.010
	3.6896 ± 0.0087	7.293 ± 0.041	1.393 ± 0.009
	4.4309 ± 0.0095	9.480 ± 0.044	1.301 ± 0.007
334.05	0.1569 ± 0.0059	0.424 ± 0.028	2.667 ± 0.204
	0.6403 ± 0.0061	1.746 ± 0.029	2.568 ± 0.049
	1.0528 ± 0.0063	2.885 ± 0.038	2.477 ± 0.036
	1.3622 ± 0.0066	3.730 ± 0.039	2.401 ± 0.027
	1.6299 ± 0.0068	4.492 ± 0.039	2.349 ± 0.023
	2.0919 ± 0.0071	5.807 ± 0.041	2.250 ± 0.018
	2.5100 ± 0.0075	7.091 ± 0.043	2.177 ± 0.015
	2.7433 ± 0.0078	7.822 ± 0.044	2.132 ± 0.013
	2.9424 ± 0.0079	8.562 ± 0.045	2.110 ± 0.012
	3.1442 ± 0.0082	9.184 ± 0.046	2.063 ± 0.012
354.35	0.0739 ± 0.0007	0.266 ± 0.015	3.568 ± 0.203
	0.3732 ± 0.0012	1.329 ± 0.017	3.431 ± 0.046
	0.7994 ± 0.0063	2.915 ± 0.043	3.357 ± 0.056
	1.2460 ± 0.0065	4.592 ± 0.044	3.231 ± 0.035
	1.6582 ± 0.0069	6.194 ± 0.045	3.122 ± 0.026
	2.1088 ± 0.0072	8.025 ± 0.047	3.007 ± 0.021
	2.4778 ± 0.0076	9.685 ± 0.049	2.932 ± 0.017
374.7	0.0513 ± 0.0006	0.229 ± 0.015	4.431 ± 0.303
	0.3303 ± 0.0011	1.486 ± 0.018	4.347 ± 0.054
	0.6185 ± 0.0018	2.827 ± 0.029	4.282 ± 0.045
	0.9523 ± 0.0064	4.467 ± 0.049	4.228 ± 0.054
	1.2328 ± 0.0066	5.830 ± 0.050	4.127 ± 0.042
	1.4734 ± 0.0068	7.055 ± 0.051	4.057 ± 0.035
	1.8856 ± 0.0071	9.191 ± 0.053	3.923 ± 0.027
395.05	0.2192 ± 0.0009	1.199 ± 0.017	5.348 ± 0.080
	0.6054 ± 0.0018	3.416 ± 0.030	5.287 ± 0.049
	0.8038 ± 0.0064	4.571 ± 0.055	5.212 ± 0.075
	0.9750 ± 0.0065	5.513 ± 0.056	5.090 ± 0.062
	1.1441 ± 0.0066	6.526 ± 0.056	5.035 ± 0.052
	1.3205 ± 0.0067	7.597 ± 0.057	4.975 ± 0.045
	1.4449 ± 0.0068	8.324 ± 0.058	4.913 ± 0.041

Table 5. Henry's Constant of Carbon Dioxide in [bmim][PF$_6$] (at zero pressure, on the molality scale) from Ref 1 (after applying some small corrections, cf. text)

T	$k_{H,CO_2}^{(0)}$	T	$k_{H,CO_2}^{(0)}$
K	MPa	K	MPa
293.55	1.193 ± 0.013	354.35	3.548 ± 0.040
313.75	1.877 ± 0.017	374.70	4.444 ± 0.048
334.05	2.675 ± 0.027	395.05	5.466 ± 0.064

accounts for systematic uncertainties {pressure transducer's uncertainty (0.0025 MPa for pressures up to 2.5 MPa and 0.01 MPa for higher pressures) + uncertainty resulting from the temperature drift (0.01 MPa)}. The second term is determined from a Gauss error propagation calculation and considers the uncertainties in temperature and gas molality. Consequently, the absolute uncertainty in the pressure Δp amounts in average to 0.038 MPa. The relative uncertainty in the pressure amounts in average to 1.6 % (0.9 % discarding the four experimental points, where the solubility pressure is below 0.5 MPa, and where the experimental uncertainty in that pressure ranges from about 5 % to about 13 %). The experimental results for $f_{CO_2}/(m_{CO_2}/m^\circ)$ as well as their experimental uncertainties are also given in Table 4.

Table 5 lists the numerical values for the revised Henry's constants resulting from the usual extrapolations and their estimated absolute uncertainties. The estimated relative uncertainty amounts in average to 1.1 %.

The final results for the Henry's constant (at zero pressure) of carbon dioxide in [bmim][PF$_6$] (on the molality scale) are correlated by

$$\ln(k_{H,CO_2}^{(0)}/\text{MPa}) = 14.559 - 3157/(T/\text{K}) - 0.012355(T/\text{K}) \tag{A1}$$

As expected, the corrected values for the Henry's constant of CO$_2$ in [bmim][PF$_6$] only very slightly and systematically deviate (by about −2 % at given temperature) from the values reported previously.[1]

The new correlation for the solubility pressure data resulted in the following equations for the partial molar volume of carbon dioxide in [bmim][PF$_6$], $V_{m,CO_2}^{(\infty)}$, and the Pitzer parameter $\beta_{CO_2,CO_2}^{(0)}$:

$$V_{m,CO_2}^{(\infty)}/(\text{cm}^3 \cdot \text{mol}^{-1}) = -188 + 0.463(T/\text{K}) \tag{A2}$$

$$\beta_{CO_2,CO_2}^{(0)} = -0.0219 \tag{A3}$$

The quality of the correlation is as good as in the previous work.[1]

The resulting solution thermodynamic properties (at T° = 298.15 K, p° = 0.1 MPa and on the molality scale) are as follows:

$$\Delta_{sol}G_m{}^\circ = (6.414 \pm 0.025)\ \text{kJ} \cdot \text{mol}^{-1} \tag{A4}$$

$$\Delta_{sol}H_m{}^\circ = (-17.14 \pm 0.20)\ \text{kJ} \cdot \text{mol}^{-1} \tag{A5}$$

$$\Delta_{sol}S_m{}^\circ = (-79.0 \pm 0.6)\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \tag{A6}$$

$$\Delta_{sol}C_{p,m}{}^\circ = (61.3 \pm 2.1)\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \tag{A7}$$

Acknowledgment

The authors thank Dr. K. Massonne, BASF AG, Ludwigshafen, Germany, for supplying the ionic liquid [bmim][CH$_3$SO$_4$].

Note Added after ASAP Publication. This paper was published ASAP on July 13, 2006. A typographical error was corrected in eq 5. The revised paper was reposted on July 17, 2006.

Literature Cited

(1) Pérez-Salado Kamps, Á.; Tuma, D.; Xia, J.; Maurer, G. Solubility of CO$_2$ in the ionic liquid [bmim][PF$_6$]. *J. Chem. Eng. Data* **2003**, *48*, 746−749.

(2) Kumełan, J.; Pérez-Salado Kamps, Á.; Tuma, D.; Maurer, G. Solubility of CO in the ionic liquid [bmim][PF$_6$]. *Fluid Phase Equilib.* **2005**, *228−229*, 207−211.

(3) Kumełan, J.; Pérez-Salado Kamps, Á.; Tuma, D.; Maurer, G. Solubility of H$_2$ in the ionic liquid [bmim][PF$_6$], *J. Chem. Eng. Data* **2006**, *51*, 11−14.

(4) Kumełan, J.; Pérez-Salado Kamps, Á.; Urukova, I.; Tuma, D.; Maurer, G. Solubility of oxygen in the ionic liquid [bmim][PF$_6$]: experimental and molecular simulation results. *J. Chem. Thermodyn.* **2005**, *37*, 595−602.

(5) Kumełan, J.; Pérez-Salado Kamps, Á.; Tuma, D.; Maurer, G. Solubility of CO$_2$ in the ionic liquid [hmim][Tf$_2$N]. *J. Chem. Thermodyn.* (in press).

(6) Kumełan, J.; Pérez-Salado Kamps, Á.; Tuma, D.; Maurer, G. Solubility of H$_2$ in the ionic liquid [hmim][Tf$_2$N]. *J. Chem. Eng. Data* **2006**, *51*, 1364−1367.

(7) Swatloski, R. P.; Holbrey, J. D.; Rogers, R. D. Ionic liquids are not always green: hydrolysis of 1-butyl-3-methylimidazolium hexafluorophosphate. *Green Chem.* **2003**, *5*, 361−363.

(8) Holbrey, J. D.; Reichert, W. M.; Swatloski, R. P.; Broker, G. A.; Pitner, W. R.; Seddon, K. R.; Rogers, R. D. Efficient, halide free synthesis of new, low cost ionic liquids: 1,3-dialkylimidazolium salts containing methyl- and ethyl-sulfate anions. *Green Chem.* **2002**, *4*, 407−413.

(9) Rumpf, B.; Maurer, G. Solubilities of hydrogen cyanide and sulfur dioxide in water at temperatures from 293.15 K to 413.15 K and pressures up to 2.5 MPa. *Fluid Phase Equilib*. **1992**, *81*, 241−260.

(10) Rumpf, B.; Maurer, G. An experimental and theoretical investigation on the solubility of carbon dioxide in aqueous solutions of strong electrolytes. *Ber. Bunsen-Ges. Phys. Chem*. **1993**, *97*, 85−97.

(11) Xia, J.; Jödecke, M.; Pérez-Salado Kamps, Á.; Maurer, G. Solubility of CO_2 in ($CH_3OH + H_2O$). *J. Chem. Eng. Data* **2005**, *49*, 1756−1759.

(12) Span, R.; Wagner, W. A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 1100 K at pressures up to 800 MPa. *J. Phys. Chem. Ref. Data* **1996**, *25*, 1509−1596.

(13) Pitzer, K. S. Thermodynamics of electrolytes. 1. Theoretical basis and general equations. *J. Phys. Chem*. **1973**, *77*, 268−277.

(14) Pitzer, K. S. Ion interaction approach: theory and data correlation. In *Activity Coefficients in Electrolyte Solutions*; Pitzer, K. S., Ed.; CRC Press: Boca Raton, FL, 1991; pp 75−155.

Received for review May 8, 2006. Accepted June 4, 2006. The authors appreciate financial support by Deutsche Forschungsgemeinschaft (DFG), Bonn-Bad Godesberg, Germany.

JE060190E