

Solubility of the Single Gases Carbon Monoxide and Oxygen in the Ionic Liquid [hmim][Tf₂N][†]

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Experimental data for the solubility of the two single gases carbon monoxide and oxygen in the ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([hmim][Tf₂N]) are reported for temperatures between (293.25 and 413.2) K. The maximum pressure (the maximum gas molality) was 9.8 MPa (0.27 mol·kg⁻¹) for carbon monoxide and 9.1 MPa (0.31 mol·kg⁻¹) for oxygen. The experiments were performed using a high-pressure view-cell technique operating on the synthetic method. Oxygen shows a slightly higher solubility than carbon monoxide under all conditions investigated, but the solubility generally remains very low. Both gases become less soluble in [hmim][Tf₂N] with increasing temperature; however, the effect is not very pronounced and becomes ambiguous for carbon monoxide above 373 K. An extension of Henry's law is employed in correlating the solubility pressures. The final results for the Henry's constant (at zero pressure) of carbon monoxide and oxygen in [hmim][Tf₂N] (on the molality scale) are represented within the experimental uncertainty (1 % for both gases) by $\ln(k_{\text{H,CO}}^0/\text{MPa}) = 5.3954 - 364.2/(T/\text{K}) - 0.002356 (T/\text{K})$ and $\ln(k_{\text{H,O}_2}^0/\text{MPa}) = 5.7618 - 505.1/(T/\text{K}) - 0.002802 (T/\text{K})$, respectively.

Introduction

During recent years, researchers have shown that ionic liquids are suitable solvents for performing reactions with reactant gases.¹ Carbon monoxide is involved in hydroformylation, whereas oxygen is the agent in oxidation. Knowing the solubility of a reactant gas in the ionic liquid is a precondition for the implementation of such reactions, and it is also known from various sources that the solubility of those gases in ionic liquids is very low compared with, for example, carbon dioxide.^{2,3} In previous investigations, our equipment proved particularly suitable for determining the solubility of sparingly soluble gases over the entire operational pressure and temperature range between about (293 and 413) K and up to 10 MPa maintaining high accuracy.^{4–7} Because experiments on hydrogen solubility in the ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([hmim][Tf₂N]) were successful as well⁸ (hydrogen usually exhibits extremely low solubility^{6,7}), we proceeded with solubility investigations of carbon monoxide and oxygen. In this work, we present the new experimental data for the solubility of carbon monoxide and oxygen in [hmim][Tf₂N] that were recorded as solubility isotherms at temperatures from about (293 to 413) K in intervals of 40 K using our high-pressure view-cell apparatus. The maximum pressure (the maximum gas molality) amounts to 9.8 MPa (0.27 mol·kg⁻¹) for carbon monoxide and 9.1 MPa (0.31 mol·kg⁻¹) for oxygen. We determined the corresponding Henry's constant of the gas by employing the classical method that was described in preceding papers.^{9,10}

[†] The experimental results for the solubility of carbon monoxide in [hmim][Tf₂N] were presented at the Conference "THERMO International 2006 (16th Symposium on Thermophysical Properties, 19th International Conference on Chemical Thermodynamics, 61st Calorimetry Conference)", held in Boulder, Colorado, July 30–August 04, 2006.

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Table 1. Experimental Results for the Solubility of Gas G (G is Carbon Monoxide) in the Ionic Liquid IL (IL is [hmim][Tf₂N])

<i>T</i>	<i>m_G</i>	<i>p</i>	<i>f_G/m_G</i>	<i>V/l_{m,IL}</i>
K	mol·kg ⁻¹	MPa	MPa/(mol·kg ⁻¹)	cm ³ ·kg ⁻¹
293.3 ± 0.1	0.04527 ± 0.00015	1.459 ± 0.017	32.1 ± 0.4	726.9 ± 3.7
	0.09535 ± 0.00033	3.119 ± 0.031	32.4 ± 0.3	728.3 ± 3.7
	0.15435 ± 0.00049	5.092 ± 0.036	32.4 ± 0.3	729.3 ± 3.7
	0.19349 ± 0.00074	6.431 ± 0.044	32.6 ± 0.3	730.9 ± 3.7
	0.23353 ± 0.00084	7.833 ± 0.047	32.8 ± 0.2	733.0 ± 3.7
333.2 ± 0.1	0.27090 ± 0.00093	9.261 ± 0.050	33.4 ± 0.2 ^a	732.5 ± 3.7
	0.04655 ± 0.00015	1.578 ± 0.018	33.9 ± 0.4	746.1 ± 3.8
	0.10545 ± 0.00035	3.627 ± 0.032	34.4 ± 0.3	747.8 ± 3.8
	0.14188 ± 0.00045	4.912 ± 0.035	34.6 ± 0.3	748.6 ± 3.8
	0.17901 ± 0.00068	6.236 ± 0.043	34.8 ± 0.3	750.6 ± 3.8
373.25 ± 0.1	0.21679 ± 0.00077	7.622 ± 0.046	35.2 ± 0.2	751.3 ± 3.8
	0.26027 ± 0.00088	9.284 ± 0.050	35.8 ± 0.2 ^a	752.6 ± 3.8
	0.04192 ± 0.00014	1.464 ± 0.017	35.0 ± 0.4	766.3 ± 3.8
	0.07389 ± 0.00026	2.581 ± 0.029	35.1 ± 0.4	767.4 ± 3.8
	0.12079 ± 0.00038	4.252 ± 0.033	35.4 ± 0.3	768.7 ± 3.8
413.15 ± 0.1	0.16667 ± 0.00063	5.867 ± 0.042	35.6 ± 0.3	770.0 ± 3.8
	0.20381 ± 0.00072	7.249 ± 0.045	36.1 ± 0.3	771.8 ± 3.9
	0.26123 ± 0.00086	9.390 ± 0.050	36.6 ± 0.2 ^a	772.8 ± 3.9
	0.05691 ± 0.00018	1.971 ± 0.019	34.8 ± 0.3	788.3 ± 3.9
	0.08904 ± 0.00029	3.104 ± 0.030	35.2 ± 0.4	789.2 ± 3.9
413.15 ± 0.1	0.12097 ± 0.00038	4.221 ± 0.033	35.3 ± 0.3	789.8 ± 3.9
	0.17755 ± 0.00064	6.231 ± 0.042	35.7 ± 0.3	791.8 ± 4.0
	0.23359 ± 0.00078	8.265 ± 0.047	36.3 ± 0.2	793.1 ± 4.0
	0.27495 ± 0.00089	9.785 ± 0.051	36.7 ± 0.2 ^a	794.8 ± 4.0

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

Experimental Section and Results

Apparatus and Method. The gas solubility apparatus was the very same as and the experimental procedures remained similar to those of previous investigations.^{9,10} Therefore, we restrict to the workflow and amend the specific differences that result from the particular systems investigated.

The procedure consists of measuring the pressure that is required to dissolve a precisely known amount of gas in an also precisely known amount of solvent that fills a high-pressure

Table 2. Experimental Results for the Solubility of Gas G (G is Oxygen) in the Ionic Liquid IL (IL is [hmim][Tf₂N])

<i>T</i>	<i>m_G</i>	<i>p</i>	<i>f_G/m_G</i>	<i>V/m_{IL}</i>
K	mol·kg ⁻¹	MPa	MPa/ (mol·kg ⁻¹)	cm ³ ·kg ⁻¹
293.25 ± 0.1	0.06362 ± 0.00026	1.618 ± 0.019	25.1 ± 0.3	725.9 ± 3.7
	0.09961 ± 0.00034	2.563 ± 0.029	25.3 ± 0.3	726.8 ± 3.7
	0.13556 ± 0.00044	3.523 ± 0.031	25.4 ± 0.2	728.8 ± 3.7
	0.17874 ± 0.00056	4.692 ± 0.034	25.4 ± 0.2	729.8 ± 3.7
	0.23595 ± 0.00102	6.322 ± 0.046	25.7 ± 0.2	731.2 ± 3.7
333.15 ± 0.1	0.28916 ± 0.00114	7.877 ± 0.049	25.9 ± 0.2	732.5 ± 3.7
	0.05388 ± 0.00023	1.502 ± 0.019	27.7 ± 0.4	746.5 ± 3.8
	0.10779 ± 0.00036	3.031 ± 0.030	27.8 ± 0.3	747.9 ± 3.8
	0.16431 ± 0.00051	4.667 ± 0.034	28.0 ± 0.2	749.3 ± 3.8
	0.21729 ± 0.00093	6.273 ± 0.046	28.3 ± 0.2	750.1 ± 3.8
373.2 ± 0.1	0.26086 ± 0.00102	7.553 ± 0.048	28.3 ± 0.2	751.4 ± 3.8
	0.30504 ± 0.00113	8.998 ± 0.051	28.7 ± 0.2	752.7 ± 3.8
	0.04991 ± 0.00021	1.451 ± 0.019	29.0 ± 0.4	765.8 ± 3.8
	0.09934 ± 0.00033	2.915 ± 0.029	29.2 ± 0.3	770.1 ± 3.9
	0.14885 ± 0.00046	4.383 ± 0.033	29.3 ± 0.2	771.8 ± 3.9
413.2 ± 0.1	0.19867 ± 0.00085	5.908 ± 0.045	29.6 ± 0.3	772.5 ± 3.9
	0.25033 ± 0.00096	7.505 ± 0.048	29.8 ± 0.2	773.1 ± 3.9
	0.30139 ± 0.00108	9.104 ± 0.051	30.0 ± 0.2	774.8 ± 3.9
	0.02456 ± 0.00015	0.724 ± 0.017	29.5 ± 0.7	788.8 ± 3.9
	0.09139 ± 0.00030	2.716 ± 0.029	29.7 ± 0.3	791.2 ± 4.0
	0.14773 ± 0.00072	4.412 ± 0.041	29.9 ± 0.3	792.5 ± 4.0
	0.20434 ± 0.00083	6.129 ± 0.044	30.1 ± 0.2	791.9 ± 4.0

view cell. The mass of the gas introduced to the cell was volumetrically determined, that is, from the known volume of the cell (approximately 29.7 cm³) and the density, which was calculated from readings of temperature and pressure via the software package ThermoFluids.¹¹ The calculations resort to implemented approved equations of state; that for carbon monoxide was adopted from the work of Lemmon and Span,¹² and that for oxygen was adopted from the work of Schmidt and Wagner.¹³ The mass of the solvent (i.e., the ionic liquid [hmim][Tf₂N]) in the cell was calculated from the volume displacement in a calibrated spindle press, which is used for transferring the solvent to the cell, and the solvent density.¹⁰ The temperature was measured using two calibrated platinum resistance thermometers with an uncertainty of less than ± 0.1 K. When the cell was charged with carbon monoxide, the pressure was recorded with three pressure transducers suitable for a maximum pressure of (0.25, 0.6, and 1.6) MPa. In the experiments with oxygen, two pressure transducers suitable for a maximum pressure of (0.6 and 2.5) MPa were employed. The corresponding solubility pressure was measured in both series with two pressure transducers suitable up to (2.5 and 10) MPa, respectively. All pressure transducers were from WIKA GmbH, Klingenberg, Germany. They were calibrated against a high-precision pressure balance (Desgranges & Huot, Aubervilliers, France) before and after each measurement series. The maximum uncertainty in the solubility pressure measurement results from the intrinsic uncertainty of the pressure transducers (i.e., 0.1 % of the transducer's full scale) and an additional contribution of about ± 0.01 MPa from a small temperature drift inside the isolated (high-pressure) tubes filled with the solvent, which connect the view cell to the pressure transducers. Several test runs verified that particular drift.

Materials and Sample Pretreatment. Carbon monoxide (3.7, mole fraction ≥ 0.9997) and oxygen (4.5, mole fraction ≥ 0.99995) were purchased from Messer Griesheim GmbH, Krefeld, Germany. Both gases were used without further purification. The ionic liquid [hmim][Tf₂N] (C₁₂H₁₉N₃F₆O₄S₂, high purity, mass fraction ≥ 0.99, slightly yellowish liquid, relative molar mass *M* = 447.42) was from Merck KGaA, Darmstadt, Germany. Initially, the ionic liquid was degassed and dried under vacuum over a period of two days to remove traces of water and other volatile impurities. ¹H, ¹³C, and ¹⁹F

NMR spectroscopic investigations were carried out with a Bruker Avance 600 MHz spectrometer (Bruker AXS GmbH, Karlsruhe, Germany), proving that the impurities of that sample were below 0.01 mol fraction. The water content of the sample was less than 0.00016 g·g⁻¹, as determined by Karl Fischer titration analysis after the completion of the measurement series. A glass burette served as a sample container so that the ionic liquid could be handled and introduced to the apparatus always under vacuum, and any moisture intrusion from the laboratory air was blocked. The ionic liquid was collected after each measurement and reconditioned (i.e., degassed and dried under vacuum) for further use.

No degradation was observed for [hmim][Tf₂N] during the experiments with carbon monoxide, and repeated NMR measurements of samples containing the processed material gave no indication of degradation. During an experiment with oxygen at 413 K, however, we observed a decomposition after exposure of the ionic liquid to the gas at approximately 7 MPa for 14 h. The gas molality, *m_G*, for that experiment was ~ 0.24 mol·kg⁻¹. This observation was made by chance because the equilibrium state required no more than 2 h under those conditions. The color of the ionic liquid visibly changed to orange after the elongated period; nevertheless, we decided to finish that solubility experiment as usual. The resulting solubility pressure amounted to ~ 2 MPa instead of ~ 7.2 MPa, as normally expected. However, all other experiments at *T* = 413 K could be successfully conducted, provided that the ionic liquid was exposed to oxygen for a maximum of 2 h, long enough to ensure equilibration but prior to the onset of decomposition. The experiments at lower temperatures were not affected by degradation of the ionic liquid, and the routine NMR measurements of these samples revealed no changes.

Experimental Results. Gas solubilities were determined at four temperatures (of about (293, 333, 373, and 413) K) at pressures up to approximately 10 MPa. The results are given in Tables 1 (for carbon monoxide) and 2 (for oxygen) as the pressure, *p*, that is required to dissolve the given amount of gas in 1 kg of the ionic liquid at a fixed temperature. The solubility pressure, *p*, is plotted versus the gas molality, *m_G* (i.e., the amount of substance (the number of moles) of the gas per kilogram of [hmim][Tf₂N]), at constant temperature, *T*, in Figure 1 (left diagram for carbon monoxide, right diagram for oxygen).

Within the temperature and pressure regions investigated during this study, the solubility pressure monotonously increases with increasing gas molality at given temperature for both systems. Figure 1 shows that the solubility isotherms of both gases develop a minor curvature of similar type toward increasing pressure. The temperature-induced solubility shift of carbon monoxide in [hmim][Tf₂N] is the least pronounced compared with that of all other gases investigated so far (i.e., carbon dioxide,¹⁰ hydrogen,⁸ methane,¹⁴ xenon,¹⁴ and tetrafluoromethane¹⁵). (See also the Discussion section below.) For both carbon monoxide and oxygen, the solubility decreases with increasing temperature, and the effect diminishes for higher temperatures. For carbon monoxide, the latter behavior of the isotherms at (373 and 413) K becomes indistinct, indicating a possible turnaround. The solubility isotherms manifest purely physical solubility behavior for both gases, which is also in accordance with prior investigations of the gas solubility in [hmim][Tf₂N].^{8,10,14,15} Carbon monoxide is less soluble in [hmim][Tf₂N] than is oxygen. For example, at *p* = 6 MPa and *T* = 293 K (413 K), about 0.181 (0.171) moles of carbon monoxide but about 0.225 (0.200) moles of oxygen dissolve in 1 kg of [hmim][Tf₂N]. Solution kinetics were observed to be

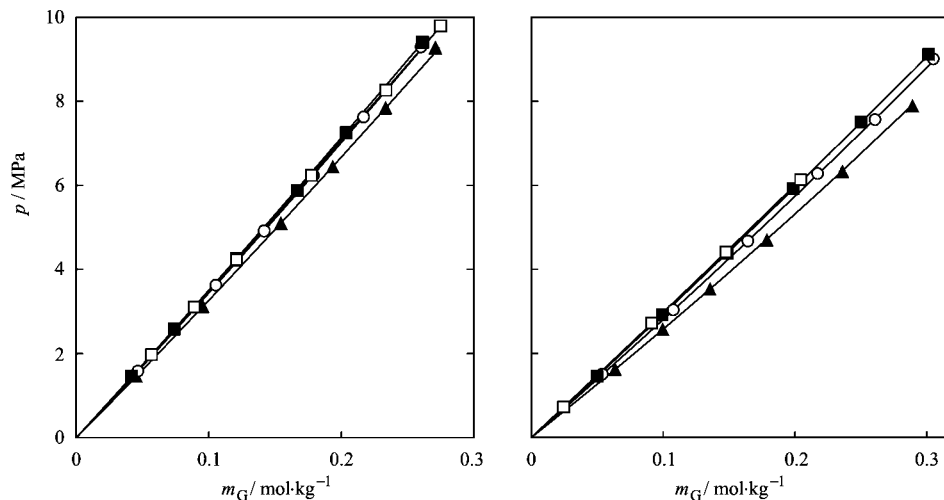


Figure 1. Total pressure above solutions of (gas G + [hmim][Tf₂N]): left diagram, G is CO; right diagram, G is O₂; (▲, ~ 293 K; ○, ~ 333 K; ■, ~ 373 K; □, ~ 413 K) experimental results; —, correlation.

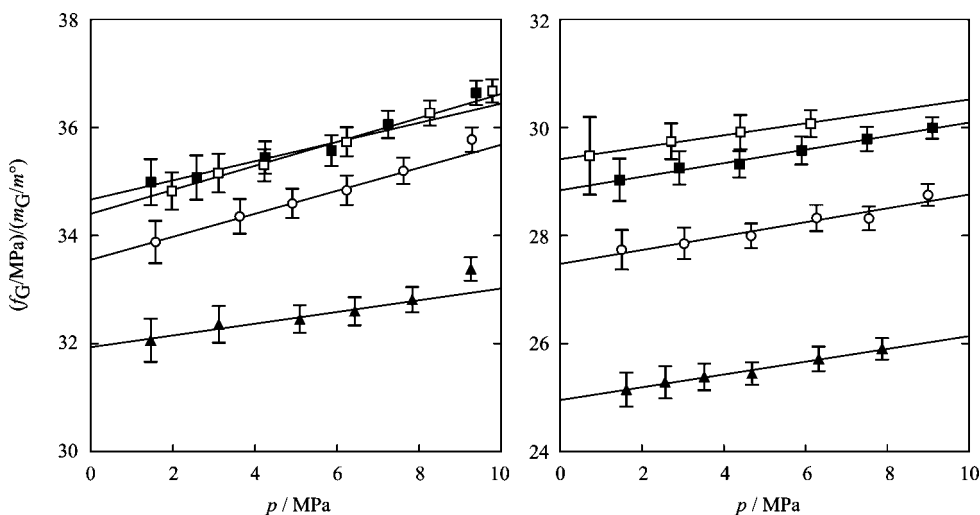


Figure 2. Influence of the total pressure on the ratio of the fugacity of gas G (in the gaseous phase) to the molality of that gas (in the ionic liquid [hmim][Tf₂N]): left diagram, G is CO; right diagram, G is O₂; (▲, ~ 293 K; ○, ~ 333 K; ■, ~ 373 K; □, ~ 413 K) experimental results (and estimated uncertainties); —, linear fit.

Table 3. Henry's Constant of the Gas G in [hmim][Tf₂N] (at Zero Pressure, on the Molality Scale)

gas G	T/K	$k_{H,G}^0$ /MPa
carbon monoxide	293.3	31.93 ± 0.32
	333.2	33.55 ± 0.32
	373.25	34.67 ± 0.38
	413.15	34.40 ± 0.34
oxygen	293.25	24.96 ± 0.28
	333.15	27.47 ± 0.29
	373.2	28.84 ± 0.31
	413.2	29.42 ± 0.37

almost identical for both carbon monoxide and oxygen. The state of equilibrium was accomplished after at least a minimum of 2 h at 293 K. Higher temperatures accelerated the gas absorption, but the 2 h equilibration period was maintained for all isotherms.

The experimental uncertainty for the absolute (relative) gas molality, Δm_G ($\Delta m_G/m_G$) (caused by the filling procedure), was estimated from a Gauss error propagation calculation and amounts at average to 0.00054 mol·kg⁻¹ (0.34 %) for the system (carbon monoxide + [hmim][Tf₂N]) and to 0.00063 mol·kg⁻¹ (0.39 %) for the system (oxygen + [hmim][Tf₂N]). (See Tables 1 and 2, respectively.) Similar to previous studies,^{8,10,14,15} the experimental uncertainty of the solubility pressure, p , is the sum

of two contributions: $\Delta p = \pm (\Delta p_{\text{sys}} + \Delta p_{\text{stat}})$. The first term accounts for the systematic uncertainties (i.e., pressure transducer's uncertainty (0.1 % of the transducer's full scale) + uncertainty resulting from the temperature drift (0.01 MPa)). The second term is a statistical one from a Gauss error propagation calculation (by applying the vapor–liquid equilibrium model described in the next section). It reflects the effect of the uncertainties of temperature and gas molality on the solubility pressure, p . The absolute (relative) uncertainty in the pressure, Δp ($\Delta p/p$), amounts in average to about 0.037 MPa (0.8 %) for the system (carbon monoxide + [hmim][Tf₂N]) and to about 0.036 MPa (0.9 %) for the system (oxygen + [hmim][Tf₂N]). (See Tables 1 and 2, respectively.)

Correlation of Gas Solubility

The correlation method applied here is congruent with that described in our previous work on the solubility of carbon dioxide.^{9,10} The principle with the main steps is given to guide the reader. Because the vapor pressure of [hmim][Tf₂N] is very low (cf. Zaitsau et al.¹⁶), it is neglected and the gaseous phase is assumed to consist completely of the pure gas component.

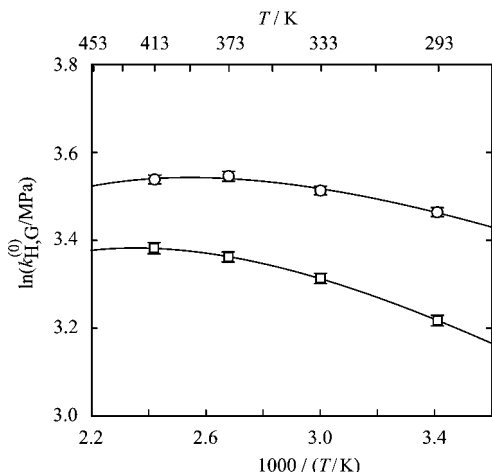


Figure 3. Henry's constant of gas G in [hmim][Tf₂N] (at zero pressure, on the molality scale) plotted against the (inverse) temperature: (O, G is CO; □, G is O₂), extrapolated experimental results (and estimated uncertainties); —, correlation.

Table 4. Results for the Molar Solution Properties, $\Delta_{\text{sol}}X_m$, under Standard Conditions ($T^\circ = 298.15$ K, $p^\circ = 0.1$ MPa) and on the Molality Scale from Henry's Constant

$\Delta_{\text{sol}}X_m^\circ$	carbon monoxide	oxygen
$\Delta_{\text{sol}}G_m^\circ/(\text{kJ}\cdot\text{mol}^{-1})$	14.314 ± 0.020	13.722 ± 0.029
$\Delta_{\text{sol}}H_m^\circ/(\text{kJ}\cdot\text{mol}^{-1})$	-1.29 ± 0.13	-2.13 ± 0.13
$\Delta_{\text{sol}}S_m^\circ/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	-52.3 ± 0.4	-53.2 ± 0.3
$\Delta_{\text{sol}}C_{p,m}^\circ/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	11.7 ± 0.9	13.9 ± 2.0

Consequently, the vapor–liquid equilibrium condition is applied to only that gas component. It results in the extended Henry's law

$$k_{\text{H,G}}(T, p) a_{\text{G}}(T, m_{\text{G}}) = f_{\text{G}}(T, p) \quad (1)$$

where $k_{\text{H,G}}(T, p)$ is Henry's constant on the molality scale of gas G in [hmim][Tf₂N] at temperature, T , and pressure, p , and $a_{\text{G}}(T, m_{\text{G}})$ is the activity of the gas in the liquid phase at temperature, T , and gas molality, m_{G} . The influence of pressure on that activity is neglected. The fugacity of the pure gas, f_{G} , in the vapor phase at equilibrium temperature and pressure is the product of the total pressure, p , and the fugacity coefficient, $\phi_{\text{G}}(T, p)$

$$f_{\text{G}}(T, p) = p\phi_{\text{G}}(T, p) \quad (2)$$

The fugacity coefficients, $\phi_{\text{G}}(T, p)$, of the two gases were calculated with ThermoFluids.¹¹

The influence of pressure on Henry's constant is expressed as

$$k_{\text{H,G}}(T, p) = k_{\text{H,G}}^{(0)}(T) \exp\left(\frac{V_{\text{m,G}}^{(\infty)} p}{RT}\right) \quad (3)$$

where $k_{\text{H,G}}^{(0)}(T)$ is the Henry's constant at zero pressure, $V_{\text{m,G}}^{(\infty)}$ is the partial molar volume of the gas at infinite dilution in the ionic liquid, and R is the universal gas constant.

Because the solubility of the gas in the ionic liquid is very low, the liquid mixture is treated as an ideal solution (cf. also Kumeřan et al.)¹⁷

$$a_{\text{G}} = \frac{m_{\text{G}}}{m^\circ} \quad (4)$$

where $m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$.

An extrapolation (with the temperature set constant) of the experimental results for the solubility pressure of the respective

gas in [hmim][Tf₂N] gives Henry's constant of the gas in [hmim][Tf₂N] at zero pressure $k_{\text{H,G}}^{(0)}(T)$

$$k_{\text{H,G}}^{(0)}(T) = \lim_{p \rightarrow 0} \left[\frac{f_{\text{G}}(T, p)}{m_{\text{G}}/m^\circ} \right] \quad (5)$$

The results for $f_{\text{G}}/(m_{\text{G}}/m^\circ)$ together with the estimated uncertainties are also given in Tables 1 and 2. For carbon monoxide, the $f_{\text{G}}/(m_{\text{G}}/m^\circ)$ values at the highest pressure do not fit a linear function and were thus disregarded. Figure 2 shows the extrapolation to zero pressure for both carbon monoxide and oxygen. Table 3 lists the numerical results for Henry's constant (at zero pressure and on the molality scale) after applying this procedure.

The order of magnitude for both zero-pressure Henry's constants (on the molality scale) is about 30 MPa. The estimated relative uncertainty for those Henry's constants amounts in average to 1 % for both gases.

Equations 6 and 7 describe Henry's constant as a function of temperature.

$$\ln(k_{\text{H,CO}}^{(0)}/\text{MPa}) = 5.3954 - 364.2/(T/\text{K}) - 0.002356(T/\text{K}) \quad (6)$$

$$\ln(k_{\text{H,O}_2}^{(0)}/\text{MPa}) = 5.7618 - 505.1/(T/\text{K}) - 0.002802(T/\text{K}) \quad (7)$$

The deviation between experimental and correlated values for Henry's constant remains within the experimental uncertainty given in Table 3. In Figure 3, both the data obtained from extrapolation to zero pressure and the correlation function for Henry's constant (eqs 6 and 7) are plotted versus the inverse absolute temperature.

Assuming the liquid mixture to behave like an ideal solution, the partial molar volume of the gas in the ionic liquid at infinite dilution, $V_{\text{m,G}}^{(\infty)}$, remains the only unknown parameter. That property might be determined from the volumetric data reported in Tables 1 and 2.¹⁷ However, when the solubility of a gas in [hmim][Tf₂N] is low, such an evaluation results in large uncertainties for $V_{\text{m,G}}^{(\infty)}$. Therefore, the calculation results for the gas solubility (that is, the gas molality at given temperature and solubility pressure) were fit to the experimental data by adjusting the numerical values for $V_{\text{m,G}}^{(\infty)}$ instead of evaluating it directly from experimental data. The curves in Figure 1 represent that correlation

$$V_{\text{m,CO}}^{(\infty)}/(\text{cm}^3 \cdot \text{mol}^{-1}) = -136 + 0.773(T/\text{K}) - 0.000949(T/\text{K})^2 \quad (8)$$

$$V_{\text{m,O}_2}^{(\infty)}/(\text{cm}^3 \cdot \text{mol}^{-1}) = 12.7 \quad (9)$$

The partial molar volume of carbon monoxide in [hmim][Tf₂N] is of the same order of magnitude as the partial molar volume of oxygen in that ionic liquid. It slightly increases from (about 9 to about 22) $\text{cm}^3 \cdot \text{mol}^{-1}$ when the temperature changes from (293 to 413) K. The uncertainty of these numerical values for $V_{\text{m,G}}^{(\infty)}$ is rather large. It was estimated, as previously described, to be $\pm 10 \text{ cm}^3 \cdot \text{mol}^{-1}$.¹⁷ The correlation results for the gas solubility agree with the data from the laboratory experiment within an average absolute (relative) deviation of about $0.00045 \text{ mol}\cdot\text{kg}^{-1}$ (0.26 %) for the system (carbon monoxide + [hmim][Tf₂N]) and of about $0.00038 \text{ mol}\cdot\text{kg}^{-1}$ (0.20 %) for the system (oxygen + [hmim][Tf₂N]).

The results for the partial molar volume, $V_{\text{m,G}}^{(\infty)}$, can be used together with the specific volumes, v_{IL} , of [hmim][Tf₂N], which

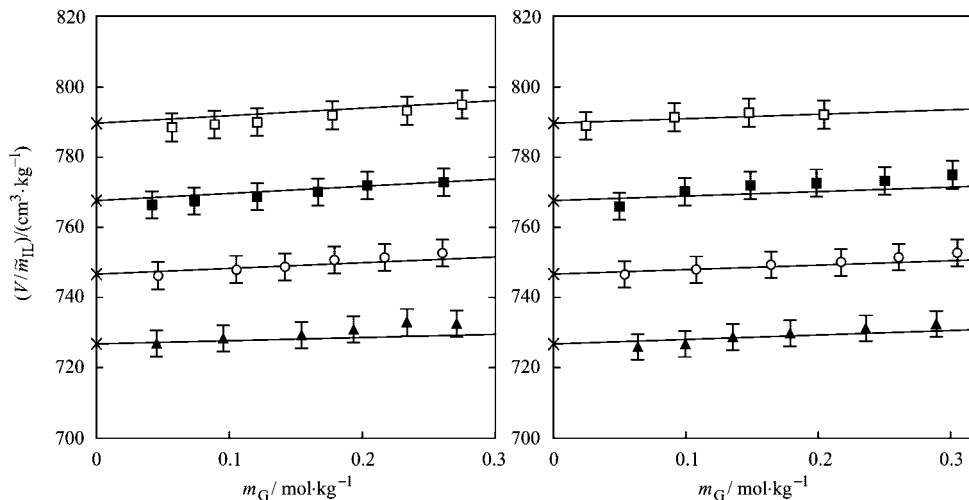


Figure 4. Volumetric data from the investigations of the system (gas G + [hmim][Tf₂N]): left diagram, G is CO; right diagram, G is O₂; (▲, ~ 293 K; ○, ~ 333 K; ■, ~ 373 K; □, ~ 413 K) experimental results and estimated uncertainties; —, calculation results; ×, specific volume of the pure ionic liquid [hmim][Tf₂N].^{10,17}

were previously reported,¹⁷ to calculate the ratio of the volume of the view cell (i.e., the volume of the equilibrated liquid mixture in that cell) and the mass of the ionic liquid in that liquid mixture, V/\tilde{m}_{IL} .¹⁷

$$\frac{V/\text{cm}^3}{\tilde{m}_{\text{IL}}/\text{g}} = \nu_{\text{IL}}/(\text{cm}^3 \cdot \text{g}^{-1}) + \frac{m_{\text{G}}}{1000 m^{\circ}} V_{\text{m,G}}^{(\infty)}/(\text{cm}^3 \cdot \text{mol}^{-1}) \quad (10)$$

The experimental results for V/\tilde{m}_{IL} (from Tables 1 and 2) are compared with the prediction results (i.e., the curves) in Figure 4. The slope of the curves given in Figure 4 represents the partial molar volume of the gas at infinite dilution, $V_{\text{m,G}}^{(\infty)}$. The deviations between both results are all within the experimental uncertainty of the volumetric data.

The partial molar volumes, $V_{\text{m,G}}^{(\infty)}$, can also be used (via eq 10) to estimate the relative volume expansion caused by the dissolved gas

$$\frac{\Delta V}{V} = \frac{m_{\text{G}} V_{\text{m,G}}^{(\infty)}/(\text{cm}^3 \cdot \text{mol}^{-1})}{m^{\circ} \nu_{\text{IL}}/(\text{cm}^3 \cdot \text{kg}^{-1})} \quad (11)$$

That volume expansion, however, is small. For example, at $p = 10$ MPa, it reaches for carbon monoxide (oxygen) only between 0.6 % (0.7 %) at 293 K and 0.8 % (0.5 %) at 413 K.

The knowledge of Henry's constant is the gateway for the calculation of various related (molar) solution thermodynamic properties, $\Delta_{\text{sol}}X_{\text{m}}$, where, for example, X can be replaced by G (the molar Gibbs energy), H (the molar enthalpy), S (the molar entropy), or C_p (the molar heat capacity at constant pressure).⁹ Table 4 gives the resulting values under standard conditions ($T^{\circ} = 298.15$ K, $p^{\circ} = 0.1$ MPa) and on the molality scale that result from the correlation equations given above.

Discussion

A plot of Henry's constant (at zero pressure and on the molality scale) versus the reciprocal temperature for the aforementioned seven gases in [hmim][Tf₂N] illustrates the different solubility behavior of those gases (cf. Figure 5). The correlation results from our experiments correspond to the curves. All curves shall meet in the critical point of the solvent,^{18,19} that is, the (nonvolatile) ionic liquid [hmim][Tf₂N]. However, the coordinates of that particular

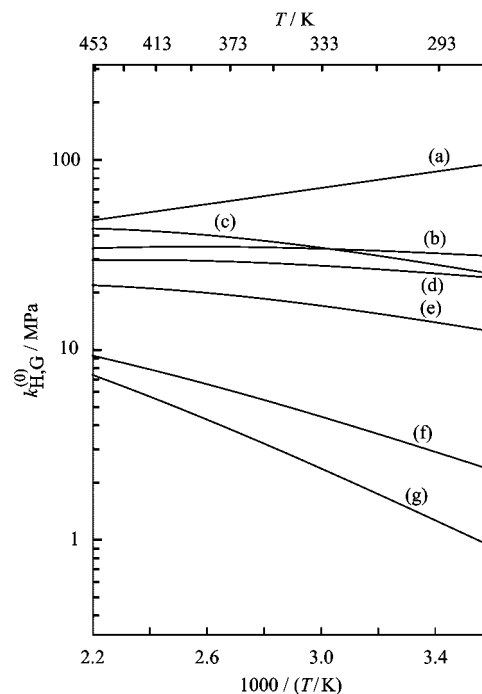


Figure 5. Correlation results for Henry's constant (at zero pressure, on the molality scale) of seven different gases in [hmim][Tf₂N]: (a) H₂, ref 8; (b) CO, this work; (c) CF₄, ref 15; (d) O₂, this work; (e) CH₄, ref 14; (f) Xe, ref 14; and (g) CO₂, ref 10.

point are rather speculative. It will definitely be located at much higher temperatures than those investigated here, but it is very likely that [hmim][Tf₂N] will already be thermally decomposed at these high temperatures.

Moreover, Figure 5 illustrates the solubility sequence (on a molality scale basis) within the investigated temperature and pressure ranges. Carbon dioxide has the largest solubility in [hmim][Tf₂N], followed by xenon, methane, oxygen, tetrafluoromethane, carbon monoxide, and ultimately hydrogen. A distinctly decreasing gas solubility with increasing temperature is found for carbon dioxide, xenon, methane, oxygen, and tetrafluoromethane, diminishing within this sequence, but a reversely increasing gas solubility with increasing temperature is found for hydrogen. Carbon monoxide, however, shows a rather weak temperature dependence of the gas solubility; it probably will turn into a hydrogen-like behavior at $T > 453$ K.

Similar solubility sequences were observed in previous studies with other ionic liquids.^{7,20}

Comparison with Literature Data

A communication by Hert et al. reports the solubility behavior of oxygen in [hmim][Tf₂N].²¹ An assessment of their results can resort only to a diagram given there, but oxygen solubility at 298.15 K and up to 1.3 MPa is found to be lower than the solubility of methane. That finding agrees with our results (cf. Figure 4).

Ohlin et al.²² published for Henry's constant of carbon monoxide in [hmim][Tf₂N] (transformed into the molality scale) at 295 K a value of 34 MPa (compared with 32.0 MPa from the present study) that was obtained from ¹³C NMR spectroscopy.

Conclusions

New experimental results are reported for the solubility of the single gases carbon monoxide and oxygen in the ionic liquid [hmim][Tf₂N] from about (293 to 413) K and up to approximately 10 MPa. Henry's law constants were determined from experimental solubility data, and solution thermodynamic properties for these two binary systems were in turn determined from Henry's law constants. Furthermore, the new experimental data for the gas solubility were correlated by an extension of Henry's law with an average relative deviation in the gas molality (at preset temperature and pressure) of 0.26 % for the system (carbon monoxide + [hmim][Tf₂N]) and of 0.20 % for the system (oxygen + [hmim][Tf₂N]).

Acknowledgment

We thank Dr. K. Massonne, BASF SE, Ludwigshafen, Germany, for purchasing the ionic liquid [hmim][Tf₂N] for these studies.

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Received for review October 15, 2008. Accepted December 31, 2008. We appreciate financial support by Deutsche Forschungsgemeinschaft (DFG), Bonn-Bad Godesberg, Germany.

JE8007556