480 *J. Chem. Eng. Data* **2003,** *48,* 480−485

Solubilities of Oxygen and Carbon Dioxide in Butyl Methyl Imidazolium Tetrafluoroborate as a Function of Temperature and at Pressures Close to Atmospheric Pressure†

Pascale Husson-Borg,* Vladimir Majer, and Margarida F. Costa Gomes

Laboratoire de Thermodynamique des Solutions et des Polymères, UMR 6003, Université Blaise Pascal/CNRS,
24 avenue des Landais, 63 177 Aubière, France

The measurements of the solubility of carbon dioxide and oxygen in a commonly used room temperature ionic liquid, butyl methyl imidazolium tetrafluoroborate ([bmim][BF_4]), are reported as a function of temperature between 303 K and 343 K and at pressures close to atmospheric. A new experimental apparatus, based on a saturation method, is presented. The solubility is expressed in terms of molarities, mole fractions, and Henry's law coefficients. From their variation with temperature, the partial molar thermodynamic functions of solvation such as the standard Gibbs energy, the enthalpy, and the entropy are calculated. The precision of the experimental data, considered as the average absolute deviation of the Henry's law coefficients from appropriate smoothing equations, is 4% for oxygen and 3% for carbon dioxide.

Introduction

Room temperature ionic liquids (ILs) are organic salts composed of bulky univalent ions. They present low melting points (generally below 253 K) and high thermal stability, and they are liquid over a large range of temperature. During the past few years, these compounds have been attracting more and more attention and are now often referred to as a new generation of "green solvents".[1,2] This great interest is mainly due to their negligible vapor pressure but also to the fact that they are nonflammable, easy to recycle, and generally considered as nontoxic.

Many recent publications have focused on the use of ILs in catalysis,[3−6] organic synthesis,[7,8] and electrochemistry[9,10] and as alternatives to volatile organic solvents in separations.[11] This new class of substances seems to have the potential to replace many organic solvents, and their synthesis is relatively well described. Nevertheless, there is a lack of thermophysical and thermodynamic data, which are sometimes affected by the presence of impurities. For example, many reactions—hydrogenations or oxidations—involve the presence of a gas, but only very few data are available on the solubility or the vapor−liquid equilibrium of gases (or low molecular mass solutes) in ILs.

Anthony *et al.*[12] have studied the vapor−liquid equilibrium of water with butyl methyl imidazolium hexafluorophosphate ([bmim][PF_6]), octyl methyl imidazolium hexafluorophosphate ([C_8mim][PF_6]), and octyl methyl imidazolium tetrafluoroborate ([C_8mim][BF_4]), by means of a gravimetric microbalance. The Henry's law coefficients were found to be very low, from 3.3 kPa at 283.15 K for water in [C_8mim][BF_4] to 45 kPa at 323.15 K for water in [bmim][PF_6], which means that water is highly soluble in these ILs. With the same type of experimental apparatus, they[13] have also studied the solubility of different gaseous solutes in [bmim][PF_6] at pressures varying from atmospheric to 1.3 MPa. Carbon dioxide was found to have the highest solubility (Henry's law coefficient 5.34 MPa at 298.15 K) followed by ethylene and ethane. Argon and oxygen had very low solubilities (Henry's law coefficients about 800 MPa at 298.15 K). Finally, gases such as carbon monoxide, hydrogen, and nitrogen had solubilities in the IL too low to be detected by their method.

Berger *et al.*[14] have reported the solubility of hydrogen in [bmim][BF_4] and in [bmim][PF_6] in connection with catalytic hydrogenations in ILs. Their experimental method was based on the measurement of a pressure drop (at total pressures below 5 MPa), at constant temperature and constant volume. It was found that hydrogen was four times more soluble in [bmim][BF_4] (Henry's law coefficient 160 MPa) than in [bmim][PF_6] (Henry's law coefficient 600 MPa).

The success of the use of ILs as reaction media is determined by the development of appropriate separation processes. Supercritical carbon dioxide extraction appears as a very promising technique[15,16] where knowledge of vapor−liquid equilibria data is crucial. Some studies on the solubility of carbon dioxide in ILs at high pressures are already reported in the literature. Blanchard *et al.*[17] have studied the high-pressure behavior of carbon dioxide with six imidazolium or pyridinium based ILs. The experimental results showed that large amounts of carbon dioxide dissolved in the IL phase (mole fraction of carbon dioxide: 0.8 at 9 MPa and at 308 K). These results were confirmed by Muthukumaran and Gupta[18] on the binary system hexyl methyl imidazolium hexafluorophosphate ([C_6mim][PF_6]) + carbon dioxide.

In the present work, we were interested in obtaining original data on the solubility of carbon dioxide and oxygen in [bmim][BF_4], which is a commercially available and commonly used IL. The choice of the gaseous solutes was determined by their frequent use in industrial mixtures, their expected different solubilities in [bmim][BF_4], and the

---

[†] This contribution will be part of a special print edition containing papers presented at the Workshop on Ionic Liquids at the 17th IUPAC Conference on Chemical Thermodynamics, Rostock, Germany, July 28 to August 2, 2002.

* To whom correspondence should be adressed (e-mail: pascale.husson@univ-bpclermont.fr)

10.1021/je0256277 CCC: $25.00

availability of data on their solubilities in other ILs.[13] This study was performed at pressures close to atmospheric and as a function of temperature from 303 K to 343 K, allowing the calculation of the Gibbs energy, the enthalpy, and the entropy of solvation via the Henry's law coefficients. Furthermore, solubility measurements often constitute an important source of information about the properties and structure of solutions, namely about the solute−solvent molecular interactions.

Our experimental approach is based on an isochoric saturation method.[19] Known amounts of dry gas and degassed solvent are equilibrated at constant volume and constant temperature, with the determination of the equilibrium pressure allowing the calculation of the solubility. This approach has the advantage of requiring only the use of an accurate manometer instead of a special manostatic system. Furthermore, the amount of gas and liquid solvent can be considerably reduced as well as the overall volume of the experimental apparatus. This allows for considerable practical improvements such as the use of relatively small liquid thermostats and the possibility to work over a larger temperature range. The main disadvantages of such an experimental method are the need for accurately measuring the volumes of both the liquid and vapor phases in equilibrium and for knowing the saturation properties of the pure solvent (this last point is surmounted in the study of IL samples, as their volatility is negligible in the temperature ranges covered). The precision and accuracy of the experimental technique were determined previously with a different apparatus by measuring the solubility of xenon in hexane as a function of temperature.[19] The present experimental arrangement, very similar to the one described by Bonifacio et al.,[19] was optimized for the use of viscous nonvolatile solvents. Due to this fact, no appropriate standard system was found to check this particular arrangement, but it is believed that the accuracy of the present results is not different from the one reported previously.[19]

Experimental Procedure

Materials. The carbon dioxide used was from AGA/Linde Gaz with a mole fraction purity of 99.995%. The oxygen used was from AGA/Linde Gaz with a mole fraction purity of 99.999%. Both gases were used as received from the manufacturer.

The [bmim][BF$_4$] was purchased from Sigma Aldrich with a minimum mole fraction purity of 97%. Before using it, the chloride and water contents were measured, as these impurities seem to influence significantly the thermodynamic and thermophysical properties of the IL.[20] As [bmim][BF$_4$] was synthesized from butyl methyl imidazolium chloride, Cl$^-$ can remain in the IL sample. The quantity of this anion, measured following the Mohr method, was of a weight fraction of 0.01%. The water content was measured by Karl−Fisher titration. A value of (8500 ± 80) ppm was found in the purchased sample. This value was lowered to (700 ± 40) ppm after treating the IL for 24 h at 343 K under vacuum.

Procedures. The experimental apparatus is schematically represented in Figure 1.

The equilibrium cell (EC) allows working with a quantity of IL varying from (2 to 5) mL. This new simpler design of the cell[19] is more convenient for viscous solvents (like the IL used). It allows, by means of good agitation, an appropriate gas/liquid contact. The cell constitutes, together with the precise pressure transducer and the calibrated gas bulb (VB), the equilibration section of the apparatus. The temperature of a 45 L water thermostated bath is maintained constant within 0.01 K by means of a PID temperature controller and is accurately measured with a 25 Ω platinum resistance thermometer (primary standard from Rosemount, USA; calibration traceable to NIST, USA).

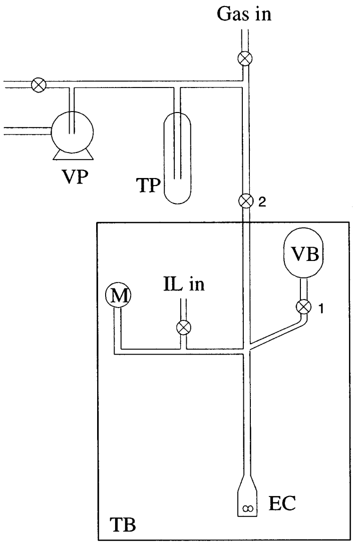

Figure 1. Solubility apparatus: VP, vacuum pump; TP, trap; VB, vapor phase bulb; M, precise manometer; EC, equilibrium cell; TB, thermostated bath.

The solubility determination starts with the introduction of a known quantity of solute in the calibrated gas bulb (VB). The exact amount of gas is determined by measuring its pressure by means of the transducer (M) (precision manometer, Druck RPT 200S, (10 to 1800) mbar, precision 0.01% full scale) at constant temperature, correcting for gas imperfection. The volume of the gas bulb was previously calibrated at 303.15 K and is (120.6 ± 0.4) cm^3, and appropriate corrections are considered for the thermal expansion.[21] The gas is then isolated from the rest of the apparatus by closing stopcock 1.

The solvent is introduced in the equilibrium cell by means of a previously calibrated micropipet of volume (2.00 ± 0.04) cm^3 to (4.99 ± 0.02) cm^3, at 301.15 K. The IL is degassed and dried during 24 h under vacuum at 343 K. At this stage, the vapor pressure of the pure solvent can be measured. It was checked that, as expected, this pressure was too low to be detected by our manometer.

The equilibrium process starts by bringing into contact the solute and the solvent (by closing stopcock 2 and opening stopcock 1). The total volume of the equilibrium section was previously calibrated by gas expansions from the gas bulb (V_{tot} = (158.68 ± 0.09) cm^3, at 303.81 K). The pressure during the dissolution process is recorded every 10 s in a computer until equilibrium is attained (a constant value is reached). The pressure is considered to be stabilized when it varies by less than 1 Pa. The equilibrium pressure and temperature are then recorded.

The determination of solubility at different temperatures is simply done by changing the liquid thermostat set point and waiting for a new thermodynamic equilibrium. With a single loading it is thus possible to make measurements over a large temperature range, (303.15 to 343.15) K in this study. For each system, several runs were performed in order to check the reproducibility of the results, by both increasing and decreasing the temperature. The sample of

IL can be reused after each measurement by treating it for 24 h at 343 K under vacuum.

Results and Discussion

Data Reduction. The total amount of solute (n_2^{tot}) was obtained from the initial pVT measurement:

$$n_2^{\text{tot}} = \frac{pV_{\text{VB}}}{Z_2(p,T)RT} \tag{1}$$

where V_{VB} is the volume of the gas bulb (previously calibrated), p is the pressure of the gas, R is the universal gas constant taken as 8.314 51 J·mol^{-1}·K^{-1},[22] T is the temperature, and Z_2 is the compressibility factor expressed as

$$Z_2 = 1 + \frac{pB_{22}}{RT} \tag{2}$$

where B_{22} is the second virial coefficient for the pure gas.

For the case of nonvolatile solvents, the total amount of substance can be considered equal to the quantity of solvent in the liquid phase after equilibrium: $n_1^{\text{tot}} = n_1^{\text{liq}}$.

The quantity of solute present in the vapor phase (n_2^{vap}) is then calculated according to

$$n_2^{\text{vap}} = \frac{p(V_{\text{tot}} - V_{\text{liq}})}{Z_2(p,T)RT} \tag{3}$$

where V_{tot} is the total volume of the equilibration section and V_{liq} is the volume of solvent.

The amount of solute dissolved can be calculated as

$$n_2^{\text{liq}} = n_2^{\text{tot}} - n_2^{\text{vap}} \tag{4}$$

and the solubility, expressed as a molarity, can be directly calculated from

$$c = \frac{n_2^{\text{liq}}}{V_{\text{IL}}} \tag{5}$$

where V_{IL} is the volume of IL introduced, which is equal to V_{liq}.

The mole fraction of the solute in the liquid phase can then be calculated according to

$$x_2 = \frac{n_2^{\text{liq}}}{n_1^{\text{liq}} + n_2^{\text{liq}}} \tag{6}$$

Finally, the solubility can be expressed in terms of the Henry's law coefficient defined as[23]

$$H_{2,1}(p,T) \equiv \lim_{x_2 \to 0} \frac{f_2(p,T,x_2)}{x_2} \tag{7}$$

where $f_2(p,T,x_2)$ is the fugacity of component 2 and x_2 is its mole fraction in the liquid phase. At equilibrium, the fugacities of each component in the liquid phase and in the vapor phase are equal. We can thus write[24]

$$f_2^{\text{liq}}(p,T,x_2) = f_2^{\text{vap}}(p,T,y_2) = \phi_2(p,T,y_2)y_2p \tag{8}$$

where $\phi_2(p,T,y_2)$ is the fugacity coefficient of component 2. In our particular case, as the IL has negligible vapor pressure

$$\phi_2(p,T,y_2)y_2p = \phi_2(p,T)p \tag{9}$$

The fugacity coefficient of component 2 can be expressed as

$$\phi_2(p,T) = \exp\left[\frac{pB_{22}(T)}{RT}\right] \tag{10}$$

For very low concentrations of the solute in an IL, it holds that

$$H_{2,1}(p,T) = \lim_{x_2 \to 0} \frac{f_2(p,T,y_2)}{x_2} = \lim_{x_2 \to 0} \frac{\phi_2(p,T)p}{x_2} \approx \frac{\phi_2(p,T)p}{x_2} \tag{11}$$

Standard Thermodynamic Properties of Solvation. The standard Gibbs energy of solvation $\Delta G_2^{\text{o}}(T)$ corresponds to the change in the molar Gibbs energy when the solute is transferred, at temperature T, from the pure perfect gas state at standard pressure, $p° = 101\,325$ Pa, to the standard state of infinite dilution in a solution. (The standard state adopted for the solute is unit activity in a hypothetical solution of unit mole fraction referenced to infinite dilution.) This thermodynamic function is related to the Henry's law coefficient as[25]

$$\Delta G_2^{\text{o}}(p,T) = G°(p,T) - G^{\text{ig}}(p°,T) = RT \ln\left(\frac{H_{21}(p,T)}{p°}\right) \tag{12}$$

From the variation of the solubility with temperature, the standard enthalpy and entropy of solvation can be determined. They correspond to the change in the molar enthalpy and entropy of the solute between the two states previously defined and can be calculated[25] from the partial derivatives of the Henry's law coefficients with respect to temperature:

$$\Delta H_2^{\text{o}}(p,T) = -T^2\left[\frac{\partial(\Delta G_2^{\text{o}}(p,T)/T)}{\partial T}\right]_p = R\left(\frac{\partial \ln(H_{21}(p,T))}{\partial(1/T)}\right)_p \tag{13}$$

$$\Delta S_2^{\text{o}}(p,T) = -\left(\frac{\partial \Delta G_2^{\text{o}}(p,T)}{\partial T}\right)_p = -R\left[\ln\left(\frac{H_{21}(p,T)}{p°}\right) + T\left(\frac{\partial \ln H_{21}(p,T)}{\partial T}\right)_p\right] \tag{14}$$

Experimental Results. Typical experimental curves for the variation of the pressure of the gas solute with time are presented in Figure 2 for one filling of IL. At zero time, for $T = 303.15$ K, the gas and the IL are put in contact and the decrease of pressure is due to the solubilization of the solute. Equilibrium is generally reached after 8 h for the systems considered in this work. When increasing temperature, an increase in the pressure is observed, resulting from the variation of the temperature and also, but to a lesser extent, from the change of the gas solubility. At higher temperatures, only about 2 h is necessary to stabilize the pressure and reach the thermodynamic equilibrium.

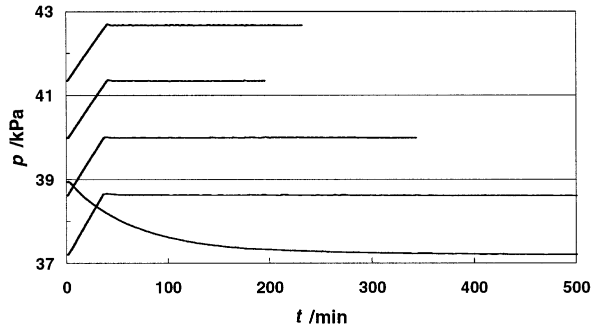

Figure 2. Example of equilibrium curves of pressure as a function of time for the solubilization of carbon dioxide in [bmim][BF$_4$] between 303 and 343 K.

Table 1. Values for the Equilibrium Pressure (p), Molarity (c), Mole Fraction of the Solutes in the Liquid Phase (x_2), and Henry's Law Coefficients (H_{21}) between (303 and 343) K

p/kPa	10^2c/mol·L^{-1}	10^3x_2	H_{21}/MPa
Carbon Dioxide + [bmim][BF$_4$]			
T = 303.72 K			
17.73	1.58	2.95	6.0
37.21	3.11	5.81	6.4
39.14	3.49	6.52	6.0
72.60	7.20	13.3	5.5
77.24	6.84	12.7	6.1
T = 313.89 K			
18.40	1.44	2.71	6.8
38.60	2.89	5.43	7.1
40.65	3.16	5.94	6.8
75.60	6.54	12.2	6.2
T = 324.12 K			
19.06	1.34	2.55	7.5
39.99	2.69	5.08	7.9
42.12	2.95	5.59	7.5
78.47	5.85	11.0	7.1
T = 334.38 K			
19.70	1.27	2.43	8.1
41.34	2.56	4.89	8.5
43.55	2.82	5.36	8.1
81.88	5.15	9.77	8.4
T = 344.49 K			
20.33	1.23	2.36	8.6
42.67	2.47	4.74	9.0
44.97	2.67	5.11	8.8
84.43	5.09	9.71	8.7
Oxygen + [bmim][BF$_4$]			
T = 314.09 K			
19.88	0.28	0.54	36.8
T = 324.19 K			
20.50	0.33	0.63	32.6
82.65	1.23	2.33	35.5
T = 334.31 K			
21.11	0.41	0.78	27.1
85.09	1.50	2.87	29.6
T = 344.54 K			
21.72	0.49	0.95	22.9
87.54	1.82	3.50	25.0

The solubilities of oxygen and carbon dioxide in [bmim][BF$_4$] at temperatures ranging from 303.15 K to 343.15 K and at pressures ranging from 0.015 MPa to 0.1 MPa are presented in Table 1. The solubility results are given in terms of molarities, mole fractions of solute, and Henry's law coefficients. The relative atomic masses were taken from the IUPAC tables.[26] The values of the second virial coefficients for oxygen and carbon dioxide were taken from the compilation of Dymond and Smith.[27] The density of [bmim][BF$_4$] was given[28] by

$$\rho_{[\mathrm{bmim}][\mathrm{BF_4}]}/\mathrm{g{\cdot}cm^{-3}} = 1.1811 - 7.6229 \times 10^{-4}(T/\mathrm{K} - 333.15) \qquad (15)$$

It is observed that carbon dioxide is 1 order of magnitude more soluble in the IL than oxygen. Furthermore, the solubility decreases with temperature in the case of carbon dioxide and slightly increases in the case of oxygen. The same behavior was observed in other ILs.[13] Finally, for carbon dioxide, at each temperature and for the pressure range studied, the Henry's law coefficients do not vary more than 5%, so they can be considered as independent of the pressure. Even though few data are available, it seems that the variation of Henry's law coeffcicient with pressure is slightly bigger in the case of oxygen.

The experimental data were fit to an equation of the type[29]

$$\ln(H_{21}(T)/\mathrm{Pa}) = \sum_{i=0}^{n} B_i (T/\mathrm{K})^{-i} \qquad (16)$$

The coefficients B_i found for carbon dioxide are $B_0 = 13.110$, $B_1 = 2.7513 \times 10^3$, and $B_2 = -6.0597 \times 10^5$ with an average absolute deviation (AAD) of 2.8%. For oxygen, $B_0 = -12.62$, $B_1 = 1.8025 \times 10^4$, and $B_2 = -2.6958 \times 10^6$ were calculated with an AAD of 3.7%. The AAD from these smoothing equations can be taken as a measure of the imprecision of the experimental data. These deviations can be compared with the statistical error estimation of 1% for carbon dioxide and 5% for oxygen obtained from the propagation of the experimental uncertainties in pressure (±20 Pa) and temperature (±0.01 K), as the errors affecting the volumes (±0.04 cm^3 for the micropipet, ±0.09 cm^3 for V_{tot}, and ±0.4 cm^3 for V_{VB}) are systematic and will only affect the accuracy.

There are other sources of uncertainties that are caused, namely, by the impurities in the IL samples (which influence the density and the solubility itself) and by the simplifications introduced during the calculations. These errors are negligible and will not be considered. For example, the presence of water in the IL causes a maximum change of 0.01% on the density, which will affect the Henry's law coefficient by 0.01%. This error is the same order of magnitude as the direct effect on solubility, which will be of the order 0.02% of the Henry's law coefficient for oxygen and 0.01% for carbon dioxide. Furthermore, the fugacity coefficient varies between 0.995 and 1 for oxygen and 0.998 and 1 for carbon dioxide in the temperature range studied. The correction of the pressure corresponds thus to a variation on the Henry's law coefficient that is lower than 0.5%. As the precision of our measurements is lower than this latter value, it is unnecessary to consider the fugacity coefficient. It seems realistic to consider that the accuracy of the measurement is that estimated by the statistic errors propagation.

Figure 3 shows the variation of the solubility for carbon dioxide (Figure 3a) and oxygen (Figure 3b) with pressure. As expected, in both cases the mole fraction of solute in the liquid phase (x_2) increases with pressure. For carbon dioxide, a systematic study of the solubility between (0.015 and 0.1) MPa at each temperature was performed. The liquid mole fraction, for the temperature range studied, appears as a linear function of the pressure, which seems to confirm the validity of Henry's law[13] for the given solubility range. No systematic study was done for oxygen, where at most two pressures were measured at each

Table 2. Gibbs Energy, Enthalpy, and Entropy of Solvation for Carbon Dioxide (2) and Oxygen (2) in [bmim][BF$_4$] (1) at Several Discrete Temperatures between (305 and 345) K

	carbon dioxide + [bmim][BF$_4$]			oxygen + [bmim][BF$_4$]		
T/K	ΔG_2^o/kJ·mol^{-1}	ΔH_2^o/kJ·mol^{-1}	ΔS_2^o/J·K^{-1}·mol^{-1}	ΔG_2^o/kJ·mol^{-1}	ΔH_2^o/kJ·mol^{-1}	ΔS_2^o/J·K^{-1}·mol^{-1}
305	10.4	−10.2	−67.8	15.1	2.9	−40.1
315	11.0	−9.1	−63.9	15.5	7.6	−25.1
325	11.7	−8.1	−60.9	15.6	11.9	−11.4
335	12.2	−7.2	−58.1	15.7	16.1	+1.1
345	12.8	−6.3	−55.5	15.6	19.9	12.5

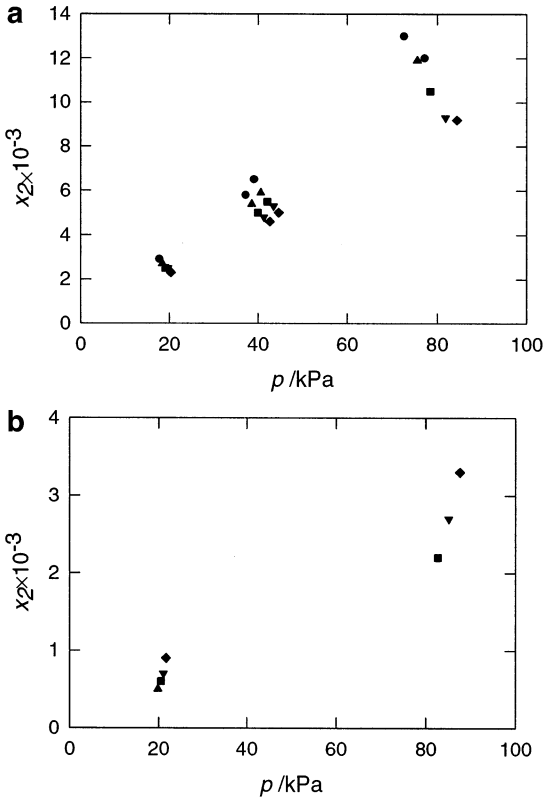

Figure 3. Mole fractions of solute in the liquid phase as a function of pressure. (a) Carbon dioxide + [bmim][BF$_4$]: (●) T = 303.15 K; (▲) T = 313.15 K; (■) T = 323.15 K; (▼) T = 333.15 K; (◆) T = 343.15 K. (b) Oxygen + [bmim][BF$_4$]: (▲) T = 313.15 K; (■) T = 323.15 K; (▼) T = 333.15 K; (◆) T = 343.15 K.

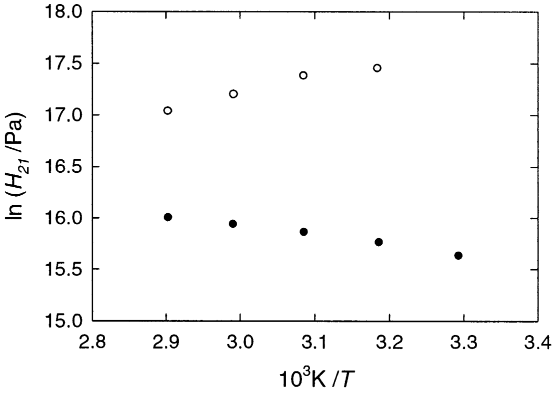

Figure 4. Logarithms of Henry's law coefficients as a function of the inverse temperature: (●) carbon dioxide; (○) oxygen.

temperature. As the solubility of oxygen is 1 order of magnitude smaller than that of carbon dioxide, Henry's law should also be followed.

Figure 4 shows the variation of ln $H_{21}(T)$ with the inverse of the temperature. An average value of the Henry's law coefficient was calculated from the experimental data at each temperature. First, the higher values obtained for oxygen reflect its lower solubility in the IL. Furthermore, the decrease of the Henry's law coefficient with temperature for oxygen corresponds to an increase of the solubility of this solute in the IL whereas the solubility for carbon dioxide in the IL decreases.

From the values of the Henry's law coefficients at different temperatures, the standard Gibbs energy ($\Delta G_2^o(T)$) was obtained using eq 12. The derived thermodynamic properties of solvation (ΔH_2^o and ΔS_2^o) were calculated from the dependence of the Henry's law coefficient on temperature according to eqs 13 and 14. The calculated values are presented in Table 2 at several discrete temperatures between (305 and 345) K.

For oxygen, the standard Gibbs energy first increases with temperature, reaches a maximum, and then decreases. This corresponds to a change in the sign in the standard entropy, as can be observed in Table 2. For carbon dioxide, in the studied temperature range, the standard Gibbs energy of solvation increases with temperature, which indicates negative values for the standard entropy, as apparent from Table 2.

According to eq 13, the standard enthalpy of solvation is proportional to the partial derivative of ln $H_{21}(T)$ with respect to the inverse temperature at constant pressure. As can be observed in Figure 4, this latter derivative is negative for carbon dioxide. This is in agreement with the negative standard enthalpy of solvation for carbon dioxide presented in Table 2. In an analogous way, for oxygen, ln $H_{21}(T)$ increases with the inverse temperature and possibly exhibits an extreme at low temperatures. This corresponds to positive values of ΔH_2^o which increase with temperature.

The behavior of the solutes in [bmim][BF$_4$] is similar to that found in [bmim][PF$_6$].[13] The solubility of carbon dioxide is of the same order of magnitude, and it decreases with temperature in both solvents. In the case of oxygen, the solubility is greater in [bmim][BF$_4$] than in [bmim][PF$_6$], and in both cases it slightly decreases with temperature. The solubilities of these gases in common hydrocarbons (both aliphatic like *n*-heptane and aromatic like benzene)[30] are of the same order of magnitude as that of those in the IL studied in this work. Their aqueous solubilities are much lower (2 orders of magnitude for oxygen[31] and 1 order of magnitude for carbon dioxide[32]).

Conclusion

A new apparatus for the measurement of gas solubilities in ILs has been assembled. This experimental technique is based on a saturation method, and the measurements are performed at constant volume. The solubilities, expressed as Henry's law coefficients, were measured between (303 and 343) K with precisions of 3% for carbon dioxide in [bmim][BF$_4$] and 4% for oxygen in [bmim][BF$_4$]. The accuracy of the present data was difficult to estimate, since no literature is available for comparisons. However, it can be considered as better than 1% for carbon dioxide and 5% for oxygen, which are the values calculated with the statistical errors estimation. Further improvements on the experimental apparatus could reduce these values. Carbon dioxide was found to be 1 order of magnitude more soluble in the IL than oxygen. Furthermore, solubility decreases with temperature in the case of carbon dioxide and it slightly increases in the case of oxygen. Similar results were obtained in [bmim][PF$_6$]. From the Henry's law coefficient and its variation with temperature, the standard thermodynamic properties of solvation, like the Gibbs energy, enthalpy, and entropy of solvation, were calculated. This work constitutes the first step to a future interpretation of the solute−solvent interactions involved in such systems.

Literature Cited

(1) Holbrey, J. D.; Seddon, K. R. Ionic Liquids. *Clean Products Processes* **1999**, *1*, 223−236.
(2) Cull, S. G.; Holbrey, J. D.; Vargas-Mora, V.; Seddon, K. R.; Lye, G. J. Room-Temperature Ionic Liquids as Replacements for Organic Solvents in Multiphase Bioprocess Operations. *Biotechnol. Bioeng.* **2000**, *69*, 227−233.
(3) Olivier, H. Recent Developments in the Use of Nonaqueous Ionic Liquids for Two-phase Catalysis. *J. Mol. Catal. A: Chem.* **1999**, *146*, 285−289.
(4) Sheldon, R. Catalytic Reactions in Ionic Liquids. *Chem. Commun.* **2001**, 2399−2407.
(5) Wasserscheid, P.; Keim, W. Ionic Liquids—New “Solutions” for Transition Metal Catalysis. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772−3789.
(6) Gordon, C. New Developments in Catalysis Using Ionic Liquids. *Appl. Catal. A: Gen.* **2001**, *222*, 101−117.
(7) Welton, T. Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. *Chem. Rev.* **1999**, *99*, 2071−2083.
(8) Chauvin, Y.; Olivier-Bourbigou, H. Nonaqueous Ionic Liquids as Reaction Solvents. *Chemtech* **1995**, 26−30.
(9) Suarez, P. A.; Selbach, V. M.; Dullius, J. E. L.; Einloft, S.; Piatnicki, C. M. S.; Azambuja, D. S.; de Souza, R. F.; Dupont, J. Enlarged Electrochemical Window in Dialkyl-imidazolium Cation Based Room-temperature Air and Water-stable Molten Salts. *Electrochim. Acta* **1997**, *42*, 2533−2535.
(10) Wadhawan, J. D.; Schroder, U.; Neudeck, A.; Wilkins, S. J.; Compton, R. G.; Marken, F.; Consorti, C. S.; de Souza, R. F.; Dupont, J. Ionic Liquid Modified Electrodes. Unusual Partioning and Diffusion Effects of Fe(CN)$_6^{4-/3-}$ in Droplet and Thin Layer Deposits of 1-methyl-3-(2,6-(S)-dimethylocten-2-yl)-imidazolium Tetrafluoroborate. *J. Electroanal. Chem.* **2000**, *493*, 75−83.
(11) Huddleston, J. G.; Willauer, H. D.; Swatloski, R. P.; Visser, A. E.; Rogers, R. D. Room-Temperature Ionic Liquids as Novel Media for ′Clean′ Liquid−Liquid Extraction. *Chem. Commun.* **1998**, 1765−1766.
(12) Anthony, J. L.; Maginn, E. J.; Brennecke, J. F. Solution Thermodynamics of Imidazolium-Based Ionic Liquids and Water. *J. Phys. Chem. B* **2001**, *105*, 10942−10949.
(13) Anthony, J. L.; Maginn, E. J.; Brennecke, J. F. Solubilities and Thermodynamic Properties of Gases in the Ionic Liquid 1-*n*-Butyl-3-methylimidazolium Hexafluorophosphate. *J. Phys. Chem. B* **2002**, *106*, 7315−7320.
(14) Berger, A.; de Souza, R. F.; Delgado, M. R.; Dupont, J. Ionic Liquid-Phase Asymmetric Catalytic Hydrogenation: Hydrogen Concentration Effects on Enantioselectivity. *Tetrahedron: Asymmetry* **2001**, *12*, 1825−1828.
(15) Liu, F.; Abrams, M. B.; Baker, R. T.; Tumas, W. Phase-Separable Catalysis Using Room-Temperature Ionic Liquids and Supercritical Carbon Dioxide. *Chem. Commun.* **2001**, *5*, 433−434.
(16) Blanchard, L. A.; Hancu, D.; Beckman, E. J.; Brennecke, J. F. Green Processing Using Ionic Liquids and CO$_2$. *Nature* **1999**, *399*, 28−29.
(17) Blanchard, L. A.; Gu, Z.; Brennecke, J. F. High-Pressure Phase Behavior of Ionic Liquids/CO$_2$ Systems. *J. Phys. Chem. B* **2001**, *105*, 2437−2444.
(18) Muthukumaran, P.; Gupta, R. A. Phase Equilibria of Mixtures Containing Ionic Liquids, Carbon Dioxide and Naphthalene. *Abstract of the 9th International Conference on Properties and Phase Equilibria for Products and Process Design*, Kurashiki, Japan, 2001.
(19) Bonifacio, R. P.; Costa Gomes, M. F.; Filipe, E. J. M. Solubility of Xenon in *n*-hexane between 257 and 333K. *Fluid Phase Equilib.* **2001**, *4822*, 1−11.
(20) Seddon, K. R. Personal communication.
(21) Perry, R. H.; Green, D. W. *Perry's Chemical Engineers' Handbook*, 7th ed.; McGraw-Hill: New York, 1997.
(22) *IUPAC Quantities, Units and Symbols in Physical Chemistry*; Blackwell: Oxford, 1988.
(23) Smith, J. M.; Van Ness, H. C.; Abbott, M. M. *Introduction to Chemical Engineering Thermodynamics*, 5th ed.; McGraw-Hill: New York, 1996.
(24) Rettich, T. R.; Handa, P. Y.; Battino, R.; Wilhelm, E. Solubility of Gases in Liquids. 13. High-precision Determination of Henry's Constants for Methane and Ethane in Liquid Water at 275 to 328 K. *J. Phys. Chem.* **1981**, *85*, 3230−3237.
(25) Benson, B. B.; Krause, D., Jr. A Thermodynamic Treatment of Dilute Solutions of Gases in Liquids. *J. Solution Chem.* **1989**, *18*, 803−821.
(26) IUPAC Commission on Atomic Weights and Isotopic Abundances. Atomic Weights of the Elements 1985. *Pure Appl. Chem.* **1986**, *58*, 1677−1692.
(27) Dymond, J. H.; Smith, E. B. *The Virial Coefficients of Pure Gases and Mixtures*; Clarendon Press: Oxford, 1980.
(28) Seddon, K. R.; Torres, M. J. In *Clean Solvents*; Moens, L., Abrahams, M. A., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 2001; p 819.
(29) Krause, D., Jr.; Benson, B. B. The solubility and Isotopic Fractionation of Gases in Dilute Aqueous Solution. IIa. Solubilities of Noble Gases. *J. Solution Chem.* **1989**, *18*, 823−873.
(30) Wilhelm, E.; Battino, R. Thermodynamic Functions of the Solubilities of Gases in Liquids at 25 °C. *Chem. Rev.* **1973**, *73*, 1−9.
(31) Rettich, T. R.; Battino, R.; Wilhelm, E. Solubility of Gases in Liquids. 22. High-precision Determination of Henry's Law Constants of Oxygen in Liquid Water from $T = 274$ K to $T = 328$ K. *J. Chem. Thermodyn.* **2000**, *32*, 1145−1156.
(32) Carroll, J. J.; Slupsky, J. D.; Mather, A. E. The Solubility of Carbon Dioxide in Water at Low Pressure. *J. Phys. Chem. Ref. Data* **1991**, *20*, 1201−1209.

Received for review October 22, 2002. Accepted January 1, 2003.

JE0256277