Solubilities and Thermodynamic Properties of Gases in the Ionic Liquid 1-*n*-Butyl-3-methylimidazolium Hexafluorophosphate

Jennifer L. Anthony, Edward J. Maginn,* and Joan F. Brennecke*

Department of Chemical Engineering, University of Notre Dame, Notre Dame, Indiana 46556

Received: March 6, 2002; In Final Form: May 6, 2002

This work presents the solubility of nine different gases in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate. The gases considered include carbon dioxide, ethylene, ethane, methane, argon, oxygen, carbon monoxide, hydrogen, and nitrogen. We also report the associated Henry's constants and enthalpies and entropies of absorption. We found carbon dioxide to have the highest solubility and strongest interactions with the ionic liquid, followed by ethylene and ethane. Argon and oxygen had very low solubilities and immeasurably weak interactions. Carbon monoxide, hydrogen, and nitrogen all had solubilities below the detection limit of our apparatus. Our results suggest that the mass transfer of gases into ionic liquids likely will be an important issue for reactions involving these gases. We also determined that ionic liquids show good potential for use as a gas-separation medium.

Introduction

Since volatile organic compounds (VOCs) have been found to be a major contributor to air pollution but are still frequently used in many chemical and industrial processes, much research has been dedicated to finding a solution to this problem. One promising solution has been found in the relatively new class of solvents referred to as ionic liquids. Room-temperature ionic liquids (ILs) is the term used to describe organic salts that are liquid in their pure state at ambient conditions. The reason these salts are generally being considered "green" solvents is their immeasurably low vapor pressure.[1,2] Without a vapor pressure, the means for solvent escape to the atmosphere is essentially eliminated.

The bulk of ionic liquid research has focused on the use of ILs as solvents for a variety of reactions and, more recently, the pure component properties for specific anion/cations pairs.[3−6] In addition to pure component properties, it is also important to consider mixture properties, particularly the phase behavior of ionic liquids with other compounds. Since phase behavior of ILs with solids, liquids, and gases will affect the attractiveness of using ILs in reactions, separations, and material processing, understanding that phase behavior is vitally important.

Specifically, a clear understanding of gas solubilities in ILs is important since many of the reaction studies in ILs, such as hydrogenations, hydroformylations, and oxidations, involve the reaction of permanent or condensable gases in the IL solutions.[3−5] If the gas has a low solubility in the IL, the mass transfer of the gas into the IL phase will likely be the rate-limiting factor. This limitation would require that efforts be made to increase the interfacial area and/or use high-pressure operations in order to reach the necessary concentration of gas in the IL. These efforts could affect the ability of ILs to realistically compete with conventional solvents.

In addition to its importance in reactions, understanding the solubility of compressed gases and supercritical fluids in ILs is required for assessing the feasibility of separating species from an IL mixture. Previous work from our laboratories has shown that supercritical CO_2 can successfully be used to extract a wide variety of solutes from an IL without any IL contaminating the CO_2 phase.[7,8] Theoretically, other compressed gases, such as C_2H_4 and C_2H_6, could also be used in IL extraction systems and will therefore require an understanding of their phase behavior with ILs.

Another potential application for ILs is to use them to separate gas mixtures.[9−11] Because the ILs are nonvolatile, they would not add any contamination to the gas stream. This quality gives ILs an innate advantage over traditional solvents used for absorbing gases. Whether used in conventional absorbers or in supported-liquid membrane systems, using ILs as a gas-separation medium will require knowledge of the pertinent gas solubilities.

Finally, an investigation of gas solubilities in ILs can be used to extract information about specific chemical and molecular interactions between the gas and the IL, such as hydrogen bonding and dipole−dipole, dipole−induced dipole, and dispersion forces. These simple probes can provide valuable information on the underlying solvent-behavior of ILs.

Thus far, very little information about gas solubilities in ILs is known. Most papers discussing reactions that involve a gas dissolved in an IL make no attempt to determine the gas concentration in the IL, although one recent publication on hydrogenation reactions does report hydrogen solubilities in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim][PF_6]$, or the common abbreviation $[bmim][PF_6]$) and 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (commonly abbreviated $[bmim][BF_4]$).[12] Recent publications from our group have presented solubilities of water vapor[13] and carbon dioxide[14] in several ILs. Bates et al. has synthesized an IL with an amine group on the cation, which they report significantly enhances the CO_2 solubility.[15] Sellin et al. suggest that the highly soluble CO_2 could possibly be used in reaction systems to enhance the transport of other permanent gases into the ionic liquids.[16] At a 5-day symposium on ionic liquids at the American Chemical Society National Meeting in San Diego in April 2001, a few solubility measurements were presented in oral and poster

* Corresponding author.

10.1021/jp020631a CCC: $22.00 © 2002 American Chemical Society
Published on Web 06/29/2002

presentations.[11,17] Overall, however, there is a considerable lack of available data on the phase behavior of ionic liquids and gases.

This work presents the solubilities and properties such as Henry's constants and enthalpies and entropies of dissolution for a series of nine gases in [bmim][PF_6]: carbon dioxide, ethylene, ethane, methane, hydrogen, carbon monoxide, oxygen, nitrogen, and argon. These particular gases were chosen for several reasons. Carbon dioxide solubility is important due to the possibility of using supercritical CO_2 to extract solutes from the ILs. Ethylene, hydrogen, carbon monoxide, and oxygen are reactants in several of the types of reactions studied in ILs, such as hydroformylations, hydrogenations, and oxidations. Considering methane, ethane, and ethylene enables the influence of hydrocarbon size and double versus single bonds to be studied. Nitrogen and argon serve as inert probes that assist in examining the solvent/solute interactions.

Experimental Section

Materials. The [bmim][PF_6] was obtained from Sachem and had a residual chloride of 3 ppm. The carbon dioxide was from Scott Specialty Gases, with a purity of 99.99%. The methane and ethane were both from Matheson Gas Products, with purities of 99.97% and 99.99%, respectively. The remaining gases were all purchased from Mittler Supply Co. with the following purities: ethylene, 99.5%; hydrogen, 99.999%; carbon monoxide, 99.97%; oxygen, 99.99%; nitrogen, 99.999%; and argon, 99.999%.

Apparatus and Measurements. The gas solubility measurements were made using a gravimetric microbalance (IGA 003, Hiden Analytical), the details of which are described elsewhere.[13] The microbalance consists of a sample pan and counterweight, which have been symmetrically configured to minimize buoyancy effects. The balance has a 1 μg stable resolution. A small sample of IL (about 75 mg) was added to the sample pan and the chamber was sealed. The sample was dried and degassed by evacuating the chamber to about 10^{-9} bar and heating to 75 °C. Once the weight remained constant for at least 30 min, the sample was considered to be free of volatile contaminants. Then the temperature-controlled chamber was pressurized with the gas of interest using the static gas mode on the apparatus; the sample weight subsequently increases as gas absorbed into the sample. The weight change was monitored until the weight did not change significantly for at least 15 min, after which the sample was deemed to have reached equilibrium, thus yielding a single point on the absorption isotherm. This process was repeated in steps up to a pressure of 13 bar. Depending on the gas, weight increases of up to 4 mg were seen. Following this, the process was reversed; the gas pressure above the sample was gradually reduced in a series of small desorption steps, during which the decrease in sample mass was recorded. Upon completion of this process, a complete absorption/desorption isotherm was obtained. The degree of hysteresis between the two isotherm branches gives an indication of the accuracy of each value. After the completion of an absorption/desorption loop, the sample was dried and degassed and the mass compared with the initial mass to confirm that the ionic liquid did not volatilize or decompose during the run. Even after performing multiple absorption/desorption experiments over many months, the sample exhibited no detectable loss in mass.

Two factors are critical in performing these experiments. The first factor is to carefully account for buoyancy effects in the system, even when a symmetric balance is used. We followed a procedure developed in previous work with this microbalance.[18] In particular, the density of the IL sample must be known accurately for this buoyancy correction. This is especially important for the low-solubility gases, as the buoyancy is a large percentage of the measured weight change. The temperature-dependent densities used for [bmim][PF_6] in these measurements are found from a linear fit of the data reported by Gu and Brennecke.[19] The densities of the bulk phase gas were calculated using the following equations of state: the ideal gas law for the low-pressure H_2O measurements;[13] equations of state developed by Wagner and co-workers for CO_2,[20] O_2,[21] N_2,[22] and Ar;[23] and the Benedict−Webb−Rubin equation of state[24,25] for C_2H_4, C_2H_6, CH_4, H_2, and CO.

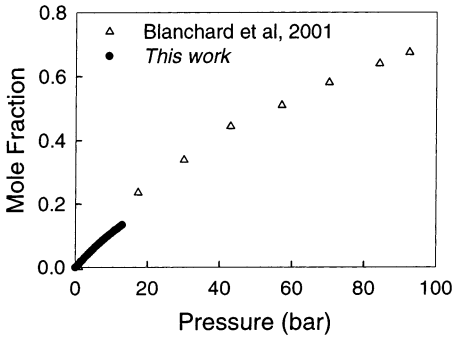

Figure 1. CO_2 solubility in [bmim][PF_6] at 50 °C.

The second factor is to ensure that sufficient time is allowed for the system to reach equilibrium. The ionic liquid sample used in this study is somewhat viscous, so the diffusion of gas into the liquid can be quite slow. This equilibrium time ranged from 90 to 180 min per point, depending on the gas and the sample temperature. A major advantage of using a microbalance for these measurements is that the weight change can be monitored as a function of time, which allows easy determination of the time necessary for equilibrium to be reached. The assurance of attaining equilibrium is important during the run as well as prior to the run to ensure the sample is sufficiently dried.

Results and Discussion

Solubilities. The absorption of the nine different gases into [bmim][PF_6] was measured up to a gas pressure of 13 bar at three temperatures: 10, 25, and 50 °C.

The solubilities of CO_2 in [bmim][PF_6] measured in this work are in qualitative agreement with previously published results from our laboratory at higher pressures, which were found using an entirely different technique.[14] Both sets of data at 50 °C are shown in Figure 1. We note that the method used here is more accurate than the one used previously. This is especially true for the lower pressure ($<$40 bar) measurements in the previous work.

The CO_2 solubilities in [bmim][PF_6] at the three temperatures are shown in Figure 2. As is typically expected with gas solubilities in liquids, the solubility decreases as temperature increases. These three curves exhibit a nonlinear trend as the CO_2 pressure is increased; the curves begin to flatten out, indicating that the IL is beginning to approach its maximum, pressure-independent capacity for CO_2. As seen in Figure 3, the C_2H_4 solubility in the IL at the three temperatures is linear with pressure. This trend is seen with all the gases examined here other than CO_2, so it is sufficient to just use Henry's constants to describe their behavior, rather than showing the individual isotherms. These Henry's constants are discussed in the next section. A comparison of the solubility of CO_2, C_2H_4,

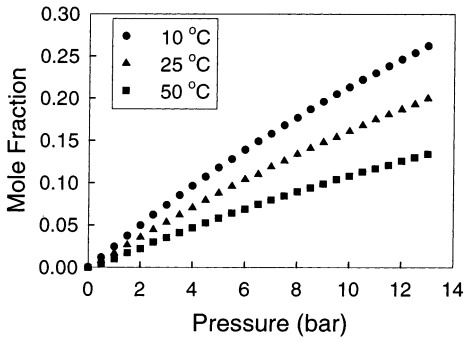

Figure 2. CO_2 solubility in [bmim][PF_6] at 10, 25, and 50 °C.

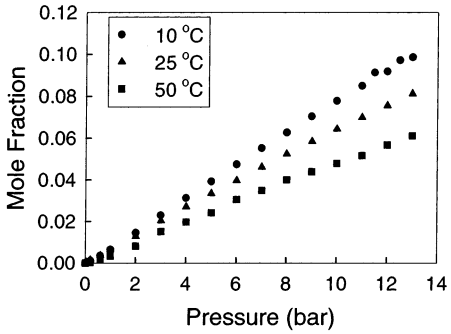

Figure 3. C_2H_4 solubility in [bmim][PF_6] at 10, 25, and 50 °C.

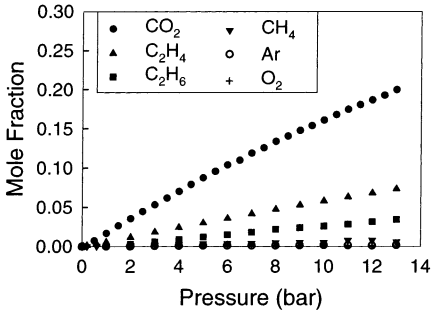

Figure 4. CO_2, C_2H_4, C_2H_6, CH_4, Ar, and O_2 solubility in [bmim][PF_6] at 25 °C.

C_2H_6, CH_4, O_2, and Ar in the IL at 25 °C is shown in Figure 4. Carbon dioxide has the largest solubility, followed by ethylene, ethane, and then methane. Oxygen and argon both have very low solubilities, almost falling along the *x*-axis in Figure 4. The low-molecular weight gases H_2, CO, and N_2 all had solubilities below the detection limit of the apparatus. These limits are discussed further in the following section on Henry's constants.

Henry's Law Constants. The solubility of a gas in a liquid is frequently described in terms of Henry's law, which is defined as

$$H_1(T,P) \equiv \lim_{x_1 \to 0} \frac{f_1^{\mathrm{L}}}{x_1} \approx \frac{P_1}{x_1} \qquad (1)$$

where $H_1(T,P)$ is the Henry's constant, x_1 is the mole fraction of gas dissolved in the liquid phase, f_1^{L} is the fugacity of vapor in the liquid phase, and P_1 is the pressure of the gas. Equation 1 implies that, for gases that behave nearly ideally, the solubility is linearly related to the pressure; this relation holds for the experimental measurements of C_2H_4, C_2H_6, CH_4, O_2, and Ar. Therefore, those Henry's constants were found by calculating the linear slope of the data. Since CO_2 was not linear for the entire pressure range, the Henry's constants were found by fitting a second-order polynomial to the data and calculating the limiting slope as the pressure (or solubility) approaches zero. All these values, along with our previously reported Henry's constants for water vapor in [bmim][PF_6], are shown in Table 1. The Henry's constants span a large range: from 0.07 bar for H_2O to 23 000 bar for O_2, both at 10 °C.

TABLE 1: Henry's Constants (bar) for Gases in [bmim][PF_6]

	10 °C	25 °C	50 °C
H_2O[13]	0.09 ± 0.02	0.17 ± 0.02	0.45 ± 0.05
CO_2	38.7 ± 0.4	53.4 ± 0.3	81.3 ± 0.5
C_2H_4	142 ± 14	173 ± 17	221 ± 22
C_2H_6	284 ± 47	355 ± 36	404 ± 41
CH_4	1480 ± 110	1690 ± 180	1310 ± 290
O_2	23 000 ± 15 000	8000 ± 5400	1550 ± 170
Ar	22 000 ± 10 000	8000 ± 3800	1340 ± 220
CO	nondetect (>20 000)	nondetect (>20 000)	nondetect (>20 000)
N_2	nondetect (>20 000)	nondetect (>20 000)	nondetect (>20 000)
H_2	nondetect (>1500)	nondetect (>1500)	nondetect (>1500)

As mentioned in the previous section, the microbalance measures the gas solubility on a mass basis, so the detection limit depends on the molecular weight of the gas. The low molecular weight gases H_2, CO, and N_2 all had solubilities below the detection limit of the apparatus. Using the lowest solubility measured (O_2 at 10 °C) as the minimum change in mass we can measure, we estimated the minimum Henry's constants that we could possibly measure for gases with molecular weights of 2 g/mol (H_2) and 28 g/mol (CO and N_2) to be 1500 bar and 20 000 bar, respectively. Therefore, we can report that the Henry's constants are greater than 20 000 bar for CO and N_2 and greater than 1500 bar for H_2.

Recently, Berger and co-workers[12] presented measurements for the Henry's constants for H_2 in [bmim][PF_6] and [bmim][BF_4] of 3.0×10^{-3} and 8.8×10^{-4} mol L^{-1} atm^{-1}, respectively. Converting their data to conform with the Henry's constant convention used in the present work, they find a Henry's constant of 5700 bar for H_2 in [bmim][PF_6]. This value is consistent with our measurements. Berger et al.[12] determined the H_2 solubility by measuring the pressure decrease in a closed vessel as the gas dissolved into the liquid at constant temperature. The 50 mL vessel, pressurized to 50 atm, contained just 10 mL of IL. For these conditions and the reported solubilities, the resulting pressure drop when the gas was absorbed into the liquid would only have been on the order of 0.005 atm. Thus, the values reported are probably only good order-of-magnitude estimates unless a highly accurate differential pressure transducer was employed. Unfortunately, the authors did not report the uncertainty of their Henry's constants, nor the accuracy of their pressure gauge.

There are several sources of uncertainty in our experiments. The uncertainties in measuring both the pressure and the mass are extremely small, about 0.06% and 0.0013%, respectively. The bulk of the error results from the uncertainty in achieving equilibrium and from fitting a curve to the data to calculate the Henry's constants (especially for the lower solubility gases). Most runs were allowed an equilibration time of 90 min at each pressure, which was found to be sufficient. The exceptions were CO_2 at 10 °C, which was allowed 180 min, and CH_4 at 25 °C, which was allowed 120 min. It should be noted that 90 min would have been sufficient to attain equilibrium for these runs as well, but the longer times were allowed merely as a check. The C_2H_4 runs at all temperatures were measured after 180 min per point, although equilibrium was reached after about 130

TABLE 2: Henry's Constants (bar) for Gases in Various Organic Solvents

	[bmim][PF_6]	heptane[28]	cyclohexane[28]	benzene[28]	ethanol[28]	acetone[28]
H_2O[13]	0.17		97[33]	10[33]	0.1[34]	0.3[34]
CO_2	53.4	84.3	133.3	104.1	159.2	54.7
C_2H_4	173	44.2[a]		82.2	166.0	92.9
C_2H_6	355	31.7	43.0	68.1	148.2	105.2
CH_4	1690	293.4	309.4	487.8	791.6	552.2
O_2	8000	467.8	811.9	1241.0	1734.7	1208.7
Ar	8000	407.4	684.6	1149.5	1626.1	1117.5
CO	nondetect (>20 000)	587.7	1022.5	1516.8	2092.2	1312.7
N_2	nondetect (>20 000)	748.3	1331.5	2271.4	2820.1	1878.1
H_2	nondetect (>1500)	1477.3	2446.3	3927.3	4902.0	3382.0

[a] For ethylene in hexane, not heptane.

min. The requirements for ensuring that equilibrium is achieved are the same as those described for the solubility of water vapor in a previous work.[13] The absorption and desorption branches of the isotherms serve as upper and lower bounds for the true equilibrium values, as discussed in a previous work.[13] Typically, the hysteresis between the absorption and desorption isotherms is less than 1 or 2%. However, for two of the ethane runs, this hysteresis was as large as 20%. To estimate the error bars for the linear fits of the data, we used a method in which lines were drawn so that at least 90% of the data points (including both absorption and desorption data) were contained within the range.

The uncertainty in the IL density measurements can also affect the uncertainty in the solubility measurements. The densities used for [bmim][PF_6] in these measurements were 1.3754 ± 0.0080 g/mL at 10 °C, 1.3634 ± 0.0080 g/mL at 25 °C, and 1.3434 ± 0.0080 g/mL at 50 °C.[19] The reported uncertainty for the densities used in this work was about 0.5%,[19] the effects of which yield Henry's constants within the range of the error due to deviation from equilibrium and from the linear fit. But if the uncertainty in density is greater than 0.5%, we see a significant increase in the uncertainty for the gases with Henry's constants greater than 2000 bar. For example, if the uncertainty in the density is 1%, then the uncertainty for the Henry's constant of a low-solubility gas such as oxygen is about 72%, whereas the uncertainty is only about 15% for the more soluble methane. Therefore, high-quality gravimetric solubility measurements of sparingly soluble gases require very accurate IL density data.

Along with the experimental uncertainty in measuring density, the water content in the IL can also affect the density. As described previously, the samples in our experiment were considered dry, due to the fact that no further mass decrease was observed during the heating and degassing process. In the work by Gu and Brennecke, the water content in the IL was reported as 0.15 wt %.[19] So if we subtract the mass of water and assume there is no volume change due to the presence of water, then the density of the dried IL at 25 °C would be 1.3614 g/cm^3 instead of 1.3634 g/cm^3. This change in density due to the presence of water is within their reported error and would have a negligible effect on the Henry's constants calculated from our experiments.

It is instructive to compare the gas solubilities in [bmim][PF_6] to those for gases dissolved in common polar and nonpolar solvents. These Henry's constants at 25 °C, listed in Table 2, show that, in general, the gases that are less soluble in the IL are less soluble in the other solvents as well. However, carbon dioxide is more soluble in the IL than the other solvents. Ethylene, ethane, methane, oxygen, and argon all have lower solubilities in the IL than in the other solvents.

As gas solubilities in liquids are governed by the interactions between the gas molecules and the solvent molecules, it is

TABLE 3: Polarizabilities (α), Dipole Moments (μ), and Quadrapole Moments (Q) of the Gases

	$\alpha \times 10^{24}$ (cm^3)[29]	$\mu \times 10^{18}$ (esu cm)[35]	$Q \times 10^{26}$ (esu cm^2)[35]
H_2O	1.48	1.84	0
CO_2	2.64	0	4.3
C_2H_4	4.252	0	1.5
C_2H_6	4.5	0	0.65
CH_4	2.6	0	0
O_2	1.60	0	0.39
Ar	1.64[36]	0	0
CO	1.95	0.112	2.5
N_2	1.74	0	1.5
H_2	0.81	0	0.662

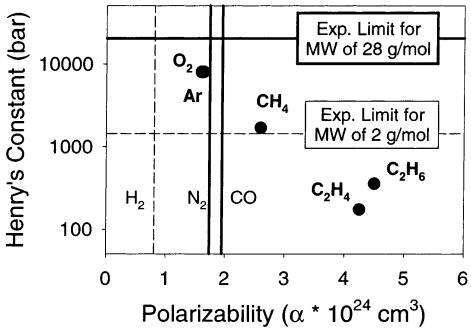

Figure 5. Solubility of gases in [bmim][PF_6] at 25 °C as a function of the gas polarizability.

informative to look at these gases in terms of their polarizabilities and dipole and quadrapole moments. The reported values for these properties for each of the gases investigated are listed in Table 3. We postulate that the high solubility of water in the IL is due to the large dipole moment of water and the possibility of hydrogen bonding. Kazarian and co-workers have used ATR−IR spectroscopy to confirm the presence of hydrogen bonding between water molecules and several IL anions, including $[PF_6]^-$.[26] The relatively high solubility of carbon dioxide is likely due to its large quadrapole moment. In another ATR−IR study of CO_2 in [bmim][PF_6] and [bmim][BF_4], Kazarian and co-workers concluded that although there was evidence of chemical interactions between the anion and the CO_2, those interactions were not large enough to be the sole factor leading to the high CO_2 solubility.[27] Gas solubility correlates reasonably well with polarizability for all the gases, except CO_2 and H_2O, as seen in Figure 5. This trend indicates that the solubility of these gases is governed by dispersion forces. Also shown in Figure 5 are vertical lines representing the polarizabilities for the nondetectable gases H_2, N_2, and CO and horizontal lines representing estimates of the solubility detection limits for the gases with molecular weights of 2 and 28 g/mol. If their solubilities were also governed by polarizability, we would predict Henry's constants of approximately

TABLE 4: Enthalpies (kJ/mol) and Entropies (J/mol K) of Absorption for the Gases in [bmim][PF_6] and Other Organic Solvents

	[bmim][PF_6]	heptane[28]	cyclohexane[28]	benzene[28]	ethanol[28]	acetone[28]
			Δh (kJ/mol)			
H_2O	-30 ± 4[13]		-9.6[33]	-21.6[33]	-40.0[b,34]	-38.0[34]
CO_2	-16.1 ± 2.2	-9.667	-5.556	-9.337	-12.795	-22.667
C_2H_4	-8.4 ± 3.7	-7.461[a]		-9.006		-9.077
C_2H_6	-6.5 ± 4.8	-11.162	-10.974	-9.211		-8.633
CH_4	2.1 ± 5.6	-0.066	-2.462	-1.277	-3.831	-2.821
O_2	51.1 ± 12.2		0.243	1.712	-1.218	0.126
Ar	52.9 ± 11.1	-1.223	-0.913	1.243	-0.385	1.930
CO	nondetect	3.785	5.192	6.360	3.730	4.538
N_2	nondetect		2.139	4.254	0.456	1.746
H_2	nondetect		0.846	2.659	0.352	0.247
			Δs (J/mol K)			
H_2O	-104 ± 14[13]		-70[33]	-92[33]	-124[b,34]	-114[34]
CO_2	-53.2 ± 6.9	-32.4	-18.5	-31.4	-42.9	-76.0
C_2H_4	-27.6 ± 12.2	-25.1[a]		-30.2		-30.5
C_2H_6	-21.2 ± 15.7	-37.4	-36.8	-30.9		-29.0
CH_4	0.7 ± 18	-12.7	-8.3	-4.3	-12.9	-9.5
O_2	169 ± 40		0.7	5.7	-4.1	0.4
Ar	175 ± 37	-4.2	-3.1	4.1	-1.3	6.4
CO	nondetect	12.7	17.4	21.3	12.5	15.2
N_2	nondetect		7.0	14.2	1.5	5.8
H_2	nondetect		2.7	8.9	1.1	0.8

[a] For ethylene in hexane, not heptane. [b] For water in methanol, not ethanol.

20 000, 6000, and 5000 bar, for H_2, N_2, and CO, respectively. This value for H_2 is consistent with the detection limit on our apparatus, but the predicted values for N_2 and CO are both within the detection limits of the apparatus, indicating that their solubilities are governed by more than just polarizability. An attempt was made to account for this as well as to include CO_2 and H_2O in the correlation by incorporating the effect of dipole and quadrapole moments. This correlation was less successful, indicating that other factors are important for these gases.

Enthalpies and Entropies of Dissolution. By considering the effect of temperature on the gas solubility, the enthalpy and entropy change upon absorption can be calculated as[13]

$$\Delta h_1 = \overline{h_1} - h_1^{\,\mathrm{ig}} = R\left(\frac{\partial \ln P}{\partial(1/T)}\right)_{x_1} \tag{2}$$

$$\Delta s_1 = \overline{s_1} - s_1^{\,\mathrm{ig}} = -R\left(\frac{\partial \ln P}{\partial \ln T}\right)_{x_1} \tag{3}$$

where $\overline{h_1}$ and $\overline{s_1}$ are the partial molar enthalpy and entropy of pure gas in solution, h_1^{ig} and s_1^{ig} are the enthalpy and entropy of the pure gas in the ideal gas phase, P is the partial pressure of the gas, T is the temperature of the system, and x_1 is the mole fraction of gas dissolved in the IL. The enthalpy yields information about the strength of interaction between the IL and gas, while the entropy indicates the level of ordering that takes place in the IL/gas mixture. Within the reported error, the calculated values of Δh_1 and Δs_1 are independent of composition (x_1) and equal to the values at infinite dilution, as found from the van't Hoff equations.[13]

The enthalpy and entropy values for the series of gases in the IL are listed in Table 4, along with those for the same gases in other common solvents.[28] Not surprisingly, water[13] and carbon dioxide exhibited significantly stronger molecular interactions and a higher degree of ordering than the other gases. Their enthalpy and entropy values were much higher than those for the gases in nonpolar solvents and very similar to the gases in small polar solvents such as ethanol and acetone. Ethylene and ethane also yielded significant enthalpy and entropy changes, similar to those seen for the gases in both polar and nonpolar solvents. Upon dissolution, methane shows essentially no interaction or ordering in the IL. Argon and oxygen both exhibited positive enthalpy and entropy changes, indicating that their solubility is driven by the increase of disorder in the system. Although this phenomenon is not unusual for gases with low solubilities in liquids[29] and is seen for several of the gases with low solubilities in the other organic solvents, the magnitude of the positive enthalpy and entropy changes are much greater for the gases in the IL than in the other solvents. One possible reason for these relatively large changes could be due to the high Coulombic attraction between the ions. Therefore, it takes more energy to insert the gas molecules into the IL than into the other solvents.

Implications. Reaction rates typically depend on the concentration of the reacting species with a positive power, which means that high reactant concentrations are required for high reaction rates. This means that high gas solubilities would be most desirable for reactions involving gases that occur in ILs. Unless the gas solubility in the IL is extremely high, the reaction rate is likely to be limited by the diffusion of the gas into the IL. There may be cases when the inherent reaction rate is slow enough to be the limiting factor, but generally the mass transfer of gas into the ILs will be a major concern. Mass transfer is particularly challenging for Ils, since they tend to be more viscous than conventional solvents[30,31] and therefore are likely to have lower diffusivities. To overcome the limitations, reactions would have to be run at high pressure and in efficient gas−liquid contacting equipment. These requirements increase the costs associated with the use of ILs and need to be overcome if ILs are to be used in practical applications.

Most of the reaction studies involving gases in ILs (e.g. hydrogenations, oxidations, and hydroformylations) did not discuss any influence of gas solubilities or whether the reaction was mass-transfer-limited. As [bmim][PF_6] is one of the most common ILs used in reaction studies and we have determined that many of the reactant gases (e.g., H_2, O_2, and CO) have low solubilities in the IL, we suspect that most of these reactions are indeed mass-transfer-limited. Observations by Suarez et al.[32] are consistent with our suspicions; they note that in the absence of stirring the consumption of hydrogen in their hydrogenation

reaction is completely stopped. These researchers point out, quite correctly, that one should hold gas solubility rather than the gas partial pressure constant when comparing reaction results in different ILs. Moreover, it is extremely difficult to compare results of reaction rates for reactions performed by different research groups when the reactions are mass-transfer-limited. This is because the rates depend solely on the quality of the interphase mass transfer, and all the researchers perform the reactions with different mixing conditions.

The nonvolatile nature of ionic liquids makes them well-suited for use as solvents for gas separations, as they cannot evaporate to cause contamination of the gas stream. This quality will be important whether these selective solvents are used in conventional absorbers or in supported liquid membranes. For conventional absorbers, the degree of separation that can be achieved depends entirely on the relative solubilities (ratio of Henry's constants) of the gases. Ionic liquids are also particularly promising for use in supported liquid membranes because they have the potential to be incredibly stable. Supported liquid membranes with conventional liquids eventually deteriorate, because the liquid slowly evaporates, which limits the minimum thickness of the membrane and thus the maximum net flux through the membrane. These problems could be eliminated with a nonvolatile liquid. In the absence of facilitated transport (e.g., complexation of CO_2 with amines to form carbamates), permeability of gases through supported liquid membranes depends on both the solubility and the diffusivity. The different solubilities of the various gases we measured in [bmim][PF_6] suggest that this IL could be used for a wide variety of industrially important gas separations. Both water vapor and CO_2 should be removed easily from natural gas, since the ratios of Henry's constants at 25 °C are ~9950 and 32, respectively. The high solubility of CO_2 compared to N_2 and O_2 suggests that it should be possible to scrub CO_2 from stack gases. We do not know if it would also be possible to remove H_2S, SO_x, or NO_x, since we have not yet performed measurements for those gases. Nonetheless, the possibility of using ILs for gas separations based upon the widely varying gas solubilities measured thus far seems quite promising.

Conclusions

Water and carbon dioxide exhibited the strongest interactions and the highest solubilities in [bmim][PF_6], followed by ethylene, ethane, and methane. Argon and oxygen both had very low solubilities and essentially no interactions with the IL. The high CO_2 and H_2O solubilities in [bmim][PF_6], relative to the other gases, bode well for the use of ILs in a gas-separation system. On the other hand, the solubilities in [bmim][PF_6] of the gases needed for hydrogenation reactions (H_2), oxidation reactions (O_2), and hydroformylation reactions (H_2 and CO) are extremely low and less than what is observed in conventional organic solvents. Overall, [bmim][PF_6] does not appear to be a very good industrial solvent for reactions involving permanent gases such as H_2, O_2, or CO, because these reactions would have to be carried out at extremely high pressures or they would be limited by interphase mass transfer. There would have to be significant independent factors favoring the IL solvent (such as higher selectivity) to warrant the use of the IL solvent.

Acknowledgment. We gratefully acknowledge financial support from the National Science Foundations (grant CTS99-87627). J.L.A. was supported by a NSF Graduate Research Traineeship (Grant No. 9452655) and a Bayer Predoctoral Fellowship.

Supporting Information Available: Tables S1−S8 give the pressure-dependent solubilities in terms of weight percent and mole fraction for each of the gases in [bmim][PF_6] at 10, 25, and 50 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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