

Anion Effects on Gas Solubility in Ionic Liquids

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This work presents the results of solubility measurements for a series of gases in 1-*n*-butyl-3-methyl imidazolium tetrafluoroborate and 1-*n*-butyl-3-methyl imidazolium bis(trifluoromethylsulfonyl) imide. The gases considered include benzene, carbon dioxide, nitrous oxide, ethylene, ethane, oxygen, and carbon monoxide. Carbon dioxide and oxygen solubilities are also reported in methyl-tributylammonium bis(trifluoromethylsulfonyl) imide, butyl-methyl pyrrolidinium bis(trifluoromethylsulfonyl) imide, and tri-isobutyl-methyl phosphonium *p*-toluenesulfonate. We report the associated Henry's constants and enthalpies and entropies of absorption. In general, benzene, followed by carbon dioxide and nitrous oxide, have the highest solubilities and strongest interactions with the ionic liquids, followed by ethylene and ethane. Oxygen had very low solubilities and weak interactions. Carbon monoxide had a solubility below the detection limit of our apparatus. Ionic liquids with the bis(trifluoromethylsulfonyl) imide anion had the largest affinity for CO₂, regardless of whether the cation was imidazolium, pyrrolidinium, or tetraalkylammonium. These results suggest that the nature of the anion has the most significant influence on the gas solubilities.

Introduction

Understanding gas solubilities in ionic liquids (ILs) is important for several reasons. First, 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^{1–3} where reactant solubility is key. Second, understanding the solubility of compressed gases and supercritical fluids in ILs is required for assessing the feasibility of possible applications for ionic liquids. Two examples of applications involving gas and ionic liquid systems that have been shown to have potential include supercritical fluid extraction to remove solutes from the IL phase^{4,5} or using ILs to separate gas mixtures.^{6,7} 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.

Our group was the first to report carbon dioxide solubility in several imidazolium and one pyridinium ionic liquids.^{4,8} We have also reported the following solubility measurements: water vapor in three ionic liquids;⁹ nine gases in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate, or [bmim][PF₆], at several temperatures;^{10,11} carbon dioxide, benzene, and methane in 1-*n*-butyl-3-methylimidazolium tetrafluoroborate, or [bmim][BF₄], at room temperature;¹² and carbon dioxide in 1-*n*-butyl-3-methyl imidazolium bis(trifluoromethylsulfonyl) imide, or [bmim][Tf₂N], at room temperature.¹³ In a recent study, we investigated, through experimental and computational methods, the characteristics of dialkyl and trialkylimidazolium ILs that lead to their high affinity for carbon dioxide.¹⁴

In addition to work conducted in our laboratory, several other researchers have reported some gas solubility measurements,

such as the solubility of carbon dioxide in various ionic liquids,^{15–23} hydrogen in nine imidazolium, one phosphonium, and two pyridinium ILs,²⁴ oxygen solubility in [bmim][BF₄]¹⁶ and [emim][Tf₂N],²⁵ sulfur dioxide in tetramethylguanidine lactate,²⁶ and fluoroform in [emim][PF₆].²⁷ Although gas solubilities in ionic liquids are beginning to emerge in the literature, there is still a need for data that aid in evaluating the potential of ionic liquids in various applications as well as elucidating the structural features that govern the solvating ability of ILs.

Here we present a systematic study of how the anions [BF₄] and [Tf₂N] affect the gas solubilities relative to [PF₆] with the [bmim] cation. A tetraalkylammonium and a dialkylpyrrolidinium IL with the [Tf₂N] anion are also considered, as well as one phosphonium salt. Solubility measurements are made as a function of both pressure and temperature. The gases considered include carbon dioxide, ethylene, ethane, nitrous oxide, benzene vapor, carbon monoxide, and oxygen. These particular gases were chosen for several reasons. Carbon dioxide solubility is important due to the possibility of using supercritical CO₂ 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 ethane and ethylene enables the influence of double versus single bonds to be studied. Carbon dioxide is interesting due to its implications in terms of gas separations. In addition to carbon dioxide, gases such as nitrous oxide, nitric oxide, and sulfur dioxide are typically present in flue gases, and their removal is an important separation issue. Benzene is important given the potential of ionic liquids for aromatic/aliphatic separation.

Experimental Section

Materials. Ionic Liquids. Two samples of 1-*n*-butyl-3-methylimidazolium tetrafluoroborate, [bmim][BF₄], were used. One was obtained from Dr. Tom Welton and co-workers at Imperial College, London. They report a chloride content of <1.4 ppm.²⁸ The other sample of [bmim][BF₄] used was

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synthesized and purified in our laboratory.²⁹ The final concentrations of bromide and ammonium in the [bmim][BF₄] were measured using an Oakton Ion 510 series pH/mV/Ion/°C meter with Cole-Palmer specific probes (27 502-05 for Br⁻ and 27 502-03 for NH₄⁺) and were found to be less than 8 ppm bromide and less than 18 ppm ammonium. Both samples were clear, colorless liquids.

The sample of 1-*n*-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide, [bmim][Tf₂N], was purchased from Covalent Associates (99+% electrochemical grade). Experiments were conducted on the sample following a purification process consisting of dissolving the IL in dichloromethane and washing with water to remove any acid or halide. The IL dissolved in dichloromethane was also contacted with activated carbon for over 24 h. We also used a sample of [bmim][Tf₂N] that was synthesized in our laboratory by standard methods³⁰ for comparison. It was determined that the Notre Dame [bmim][Tf₂N] sample had a halide content <10 ppm, using a bromide ion specific electrode (Cole-Parmer 27 502-05). The additional syntheses, purifications, and comparisons were deemed necessary since we observed the formation of small amounts of an unknown solid precipitate when the Covalent Associates [bmim]-[Tf₂N] sample was placed in contact with high-pressure CO₂ in unrelated experiments. The samples were all clear, colorless liquids.

Samples of methyl-tri-butylammonium bis(trifluoromethylsulfonyl) imide, [MeBu₃N][Tf₂N], and butyl-methyl pyrrolidinium bis(trifluoromethylsulfonyl) imide, [MeBuPyr][Tf₂N], were obtained from Dr. Pedi Neta at the National Institute of Standards of Technology (NIST) in Gaithersburg, MD. The samples were clear, colorless liquids and were used as received. The synthesis method and purities of starting materials are reported elsewhere.³¹

A sample of tri-isobutyl-methyl phosphonium *p*-toluenesulfonate, [iBu₃MeP][TOS], was obtained from Cytec. This sample was a brown liquid and contained significant impurities, most likely from starting materials. This sample was heated at 70 °C under vacuum for several days. Approximately 8 to 10 wt % of volatile material was removed before using the sample.

Gases. Carbon dioxide (CO₂) was from Scott Specialty Gases, with a purity of 99.99%. Ethane (C₂H₆) was from Matheson Gas Products, with a purity of 99.99%. The remaining gases were all purchased from Mittler Supply Company with the following purities: ethylene (C₂H₄) had a purity of 99.5%, carbon monoxide (CO) had a purity of 99.97%, oxygen (O₂) had a purity of 99.99%, and nitrous oxide (N₂O) had a purity of 99.0%. The benzene (C₆H₆) was purchased from Aldrich with a reported purity of 99.9+%; it was redistilled prior to use.

Apparatus and Measurements. The gas solubility measurements were made using a gravimetric microbalance (IGA 003, Hidden Analytical), the details of which are described elsewhere.^{7,9} 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 50 °C. Once the weight remained constant for at least 30 min, the sample was considered to be free of volatile impurities. Then the temperature-controlled chamber was pressurized with the gas or vapor of interest, and the weight change due to gas absorption was monitored. The sample was deemed to have reached equilibrium once the weight did not change for at least 15 min, thus yielding a single point on the

absorption isotherm. This process was repeated in steps up to a pressure of 13 bar for the permanent gases. For benzene, the maximum pressure was between 50% and 80% of the vapor pressure. Following these pressurization steps, 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 samples exhibited no detectable loss in mass.

It is extremely important 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.³² 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 the ILs in these measurements are found from a linear fit of the data measured in our laboratory.

The densities of the bulk phase gas were calculated using the following equations of state, the ideal gas law for N₂O and benzene vapor, equations of state developed by Wagner and co-workers for CO₂³³ and O₂,³⁴ and the Benedict-Webb-Rubin equation of state^{35,36} for C₂H₄, C₂H₆ and CO.

$$\begin{aligned} &[\text{bmim}][\text{BF}_4]^{29} \\ &\rho(\text{g/cm}^3) = [(-6.43 \times 10^{-4}) \times T(^{\circ}\text{C}) + 1.22] \\ &\quad \pm 0.001 \quad (1) \end{aligned}$$

$$\begin{aligned} &[\text{bmim}][\text{Tf}_2\text{N}]^{29} \\ &\rho(\text{g/cm}^3) = [(-9.15 \times 10^{-4}) \times T(^{\circ}\text{C}) + 1.46] \\ &\quad \pm 0.002 \quad (2) \end{aligned}$$

$$\begin{aligned} &[\text{MeBu}_3\text{N}][\text{Tf}_2\text{N}] \\ &\rho(\text{g/cm}^3) = [(-7.57 \times 10^{-4}) \times T(^{\circ}\text{C}) + 1.29] \\ &\quad \pm 0.004 \quad (3) \end{aligned}$$

$$\begin{aligned} &[\text{MeBuPyr}][\text{Tf}_2\text{N}] \\ &\rho(\text{g/cm}^3) = [(-1.04 \times 10^{-3}) \times T(^{\circ}\text{C}) + 1.42] \\ &\quad \pm 0.002 \quad (4) \end{aligned}$$

$$\begin{aligned} &[\text{iBu}_3\text{MeP}][\text{TOS}] \\ &\rho(\text{g/cm}^3) = [(-5.00 \times 10^{-5}) \times T(^{\circ}\text{C}) + 1.06] \\ &\quad \pm 0.002 \quad (5) \end{aligned}$$

It is also important to ensure that sufficient time is allowed for the system to reach equilibrium. The ionic liquids used in this study are 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 ionic liquid, the gas, and the sample temperature. Typically 90 min was sufficient, although occasionally experiments were allowed longer times as a precaution. The systems where times longer than 90 min were necessary are indicated. 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

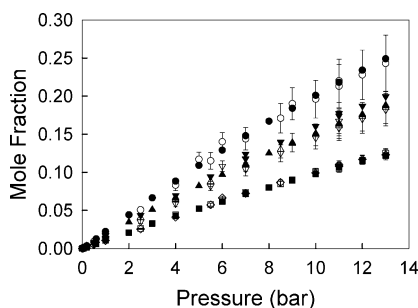


Figure 1. Solubility of CO₂ in [bmim][BF₄] at 10 °C using the Imperial College sample (●) and the Notre Dame sample (○), 25 °C using the Imperial College sample (▲)¹² and the Notre Dame sample (△, ▽, ▿), and 50 °C using the Imperial College sample (■) and the Notre Dame sample (□, ◇).

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

[bmim][BF₄]. The absorption of CO₂ and CO into [bmim]-[BF₄] was measured up to gas pressures of 13 bar at three temperatures: 10 °C, 25 °C, and 50 °C. The C₆H₆ solubility was measured up to approximately 80% of its vapor pressure for 10 °C and 25 °C and up to about 50% of its vapor pressure for 40 °C and 50 °C. All the data, along with uncertainties, are shown in tables in Supporting Information.

Three isotherms were collected for CO₂ in [bmim][BF₄] using the sample from Imperial College, as shown by the solid, black circles, upright triangles and squares in Figure 1. Error bars for each data point are included in the graph. The measurements were made using a 90 min equilibration time per point for the 10 °C isotherm and 180 min per point for the 25 °C and 50 °C isotherms. Although this sample was kept in an inert atmosphere, it was approximately one year old at the time of the experiments, and therefore there was some concern that degradation products may have formed.³⁷ Experiments were repeated using the fresh sample synthesized in our laboratory, as shown by the additional symbols in Figure 1. These measurements were made at 10 °C, 25 °C, and 50 °C using a 120 min equilibration time. Multiple measurements were collected for the 25 °C and 50 °C isotherms using a 90 min equilibration time and again for 25 °C using a 180 min equilibration time. In all cases, approximately 120 min would have been sufficient for equilibrium. The variation between the two different samples was within the 1–3% scatter seen when replicate experiments were conducted on the same sample, and therefore, it was assumed that no degradation products that could affect CO₂ solubility were present. The CO solubility was below the detection limit of the apparatus.

The benzene experiments were conducted with the Imperial College sample. 180 min were allowed for equilibration at all temperatures except 50 °C, where 90 min was sufficient. The 10 °C, 25 °C, and 50 °C data are plotted in Figure 2, along with the experimental uncertainty in the measurements. The 40 °C data were left off for clarity. This figure is plotted as mole fraction of benzene versus the ratio of the pressure of the benzene to its vapor pressure (P/P^{vap}). The vapor pressure of benzene, calculated using Antoine's equation,³⁸ is 0.061 bar at 10 °C, 0.126 bar at 25 °C, 0.244 bar at 40 °C, and 0.362 bar at 50 °C. Also plotted in Figure 2 as the large solid square is the liquid–liquid equilibrium value for [bmim][BF₄] in contact with a liquid benzene phase at 25 °C.¹² This value is equivalent to

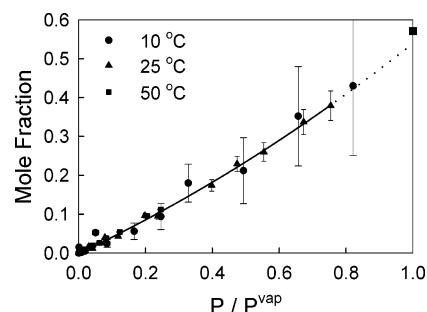


Figure 2. Solubility of C₆H₆ in [bmim][BF₄] at 10 °C, 25 °C, and 50 °C. The solid line is a fit through the experimental data, and the dotted line is an extrapolation to the liquid–liquid equilibrium value at 25 °C¹² (shown by the large filled square at $P/P^{\text{vap}} = 1$).

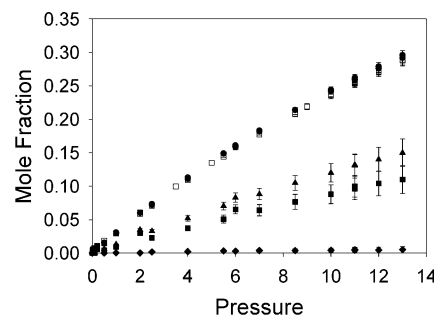


Figure 3. Solubility of CO₂ (●),¹³ N₂O (□), C₂H₄ (▲), C₂H₆ (■), and O₂ (◆) in [bmim][Tf₂N] at 25 °C.

the point when the pressure of benzene is equal to its vapor pressure; the vapor equilibrium data extrapolates quite nicely to this point.

[bmim][Tf₂N]. The absorption of CO₂, C₂H₄, C₂H₆, O₂, and N₂O into [bmim][Tf₂N] was measured up to a gas pressure of 13 bar at three temperatures: 10 °C, 25 °C, and 50 °C. These measurements were made using the ionic liquid sample from Covalent. All the experiments were conducted using a 90 min equilibration. This time was long enough for all runs except a slight hysteresis was seen between the CO₂ absorption and desorption isotherms at 10 °C, which is reflected by the larger uncertainties in the Henry's constants, as will be reported in the following section. N₂O experiments were repeated at all three temperatures allowing 180 min for equilibration, but they showed that 90 min was sufficient.

The solubility of N₂O was also measured at the three temperatures in the [bmim][Tf₂N] sample synthesized in our laboratory. Carbon dioxide solubility was measured at 10 °C and 25 °C in the Notre Dame sample, as well. Measurements of CO₂ in [bmim][Tf₂N] were also repeated on the sample several months later. In all cases, no significant differences were observed for solubilities measured in the Covalent sample versus the Notre Dame sample, nor were any differences seen using the same Notre Dame sample again after several months. All the data for the [bmim][Tf₂N] IL, along with uncertainties, are shown in tables in Supporting Information.

The 25 °C isotherms for the various gases in [bmim][Tf₂N] are plotted in Figure 3, along with the corresponding error bars. For clarity, only the data collected using the Covalent [bmim]-[Tf₂N] sample are shown. A representative comparison of the data collected using the Notre Dame sample is shown along with the Covalent sample data at 25 °C for CO₂ in Figure 4, along with uncertainties for all data points. This figure is discussed in the following section.

As shown in Figure 3, nitrous oxide and carbon dioxide have essentially the same solubility, which is significantly higher than

TABLE 1: Henry's Constants and Enthalpies and Entropies of Absorption for Various Gases in Several Ionic Liquids

ionic liquid	H (bar)			Δh (kJ/mol)	Δs (J/mol K)
	10 °C	25 °C	50 °C		
Water					
[bmim][PF ₆] ^a	0.08 ± 0.01	0.17 ± 0.01	0.45 ± 0.01	−31.9 ± 1.1	−104.5 ± 3.7
Benzene					
[bmim][BF ₄]	0.15 ± 0.04	0.32 ± 0.03 ^a	0.56 ± 0.03 (40 °C)	−34.7 ± 1.4	−110.8 ± 4.5
			0.86 ± 0.01 (50 °C)		
Carbon Dioxide					
[bmim][PF ₆] ^a	38.8 ± 0.2	53.4 ± 0.3	81.3 ± 0.8	−14.3 ± 0.2	−47.6 ± 0.7
[bmim][BF ₄]	41.8 ± 2.3	59.0 ± 2.6 ^a	88.6 ± 1.9	−13.9 ± 1.0	−45.6 ± 3.2
[bmim][Tf ₂ N]	25.3 ± 0.3	33.0 ± 0.3 ^a	48.7 ± 0.9	−12.5 ± 0.4	−41.3 ± 1.4
[MeBu ₃ N][Tf ₂ N]		43.5 ± 0.8			
[MeBuPyr][Tf ₂ N]	30.2 ± 2.6	38.6 ± 1.4	56.1 ± 1.0	−11.9 ± 1.1	−38.7 ± 3.5
[ⁱ Bu ₃ MeP][TOS]			90.5 ± 1.4		
Nitrous Oxide					
[bmim][Tf ₂ N]	25.7 ± 0.3	33.6 ± 0.3	49.5 ± 0.8	−12.5 ± 0.4	−41.5 ± 1.3
Ethylene					
[bmim][PF ₆] ^a	125 ± 4	144 ± 2	191 ± 6	−8.2 ± 0.9	−27.2 ± 2.9
[bmim][Tf ₂ N]	61 ± 5	70 ± 4	97 ± 8	−9.0 ± 2.1	−29.9 ± 6.9
Ethane					
[bmim][PF ₆] ^a	234 ± 36	336 ± 28	363 ± 29	−5.9 ± 2.9	−19.0 ± 9.4
[bmim][Tf ₂ N]	86 ± 10	97 ± 7	141 ± 15	−9.8 ± 2.9	−32.5 ± 9.6
Oxygen					
[bmim][PF ₆] ^a		7190 ± 4190	1200 ± 160		
[bmim][Tf ₂ N]	3700 ± 1450	1730 ± 560	1110 ± 240	20.6 ± 8.2	67.4 ± 26.9
[MeBu ₃ N][Tf ₂ N]	1160 ± 220	990 ± 240	1040 ± 700	5.0 ± 11.6	16.6 ± 39.3
[MeBuPyr][Tf ₂ N]	2420 ± 880	1830 ± 590	1210 ± 600	13.1 ± 12.5	43.5 ± 41.3
[ⁱ Bu ₃ MeP][TOS]			1660 ± 850 (70 °C)		
Argon					
[bmim][PF ₆] ^a		7310 ± 3690	1300 ± 560		
Carbon Monoxide					
[bmim][PF ₆] ^a	nondetect	nondetect	nondetect	undetermined	undetermined
[bmim][BF ₄]	nondetect	nondetect	nondetect	undetermined	undetermined
Nitrogen					
[bmim][PF ₆] ^a	nondetect	nondetect	nondetect	undetermined	undetermined
Hydrogen					
[bmim][PF ₆] ^a	nondetect	nondetect	nondetect	undetermined	undetermined

^a These data have been presented previously but the values and uncertainties of the Henry's law constants, enthalpies and entropies listed here are slightly different than the previously published values^{9–14} due to the improved analysis and error propagation technique used here.

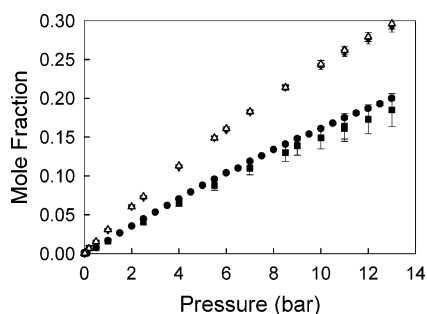


Figure 4. Solubility of CO₂ in the Covalent [bmim][Tf₂N] (▼)¹³, the Notre Dame [bmim][Tf₂N] (△), [bmim][PF₆] (●),¹⁰ and [bmim][BF₄] (■)¹² at 25 °C.

the other gases. Ethylene is the next most soluble followed by ethane. Oxygen is the lowest solubility gas shown on the graph. The gas solubilities at other temperatures exhibit the same trend as shown in Figure 3. This trend is also the same as seen with [bmim][BF₄] and [bmim][PF₆],¹⁰ but all the gases are more soluble in [bmim][Tf₂N].

Comparison of Isotherms for [bmim][Tf₂N], [bmim][BF₄] and [bmim][PF₆]. The 25 °C isotherms for CO₂ in the three ionic liquids are shown in Figure 4. For clarity, just one of the [bmim][BF₄] runs is shown. Both the [bmim][Tf₂N] isotherms for the Covalent sample and the Notre Dame sample are shown in the figure; there is no measurable difference between the two samples. In fact, the symbols are virtually superimposed upon each other.

The IL with the [Tf₂N] anion has a considerably higher affinity for CO₂ than either of the other two ILs. CO₂ has basically the same solubility in [bmim][BF₄] and [bmim][PF₆],¹⁰ although its solubility in [bmim][PF₆]¹⁰ is slightly greater at higher pressures. These same trends are also seen at the other temperatures. Molecular simulations of CO₂/IL mixtures show that CO₂ associates with the anion, positioning itself to maximize favorable interactions.¹⁴ For instance, with [bmim][PF₆] the linear CO₂ aligns itself tangent to the spherical anion to take advantage of interactions between the partial positive charge on the carbon of CO₂ with the partial negative on the fluorine atoms of the anion. The strength of these interactions with [Tf₂N] may simply be stronger, but this is not supported by the enthalpies of CO₂ absorption, which are shown in Table 1 and discussed below. An alternative explanation for the difference in CO₂ solubility between [bmim][Tf₂N] and either [bmim][BF₄] or [bmim][PF₆] may simply be the larger size of the [Tf₂N] anion. For instance, if the solubility of CO₂ in the ILs were dominated by nonspecific van der Waals interactions, then CO₂ would be more soluble in the IL with the smaller solubility parameter (δ), where the solubility parameter depends on the energy of vaporization and molar volume, $\delta = (\Delta U^{\text{vap}}/v)^{1/2}$. It is reasonable to assume that the heats of vaporization (ΔU^{vap}) of all three ILs are equally large. Then [Tf₂N] ILs, whose molar volumes (v) are much larger, would have δ values closer to that of CO₂ and would, therefore, dissolve CO₂ to a greater degree.

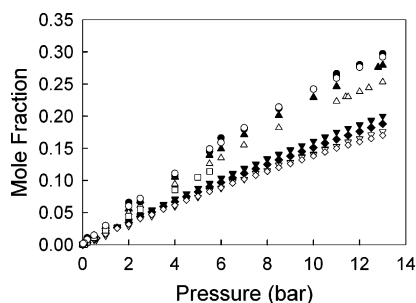


Figure 5. CO₂ solubility at 25 °C in [MeBu₃N][Tf₂N] (●), [bmim]-[Tf₂N] (○),¹³ [MeBu₃N][Tf₂N] (□), [emim][Tf₂N] (▲),¹⁴ [emmim][Tf₂N] (△),¹⁴ [bmim][PF₆] (▼),¹⁰ [bmmim][PF₆] (▽),¹⁴ [bmim][BF₄] (◆),¹² and [bmmim][BF₄] (◇).¹⁴

CO₂ solubility decreases as temperature increases in all three cases, as is typically expected with gas solubilities in liquids. The curves exhibit a nonlinear trend as the CO₂ pressure is increased; the curves begin to flatten out, indicating that the IL is beginning to approach its maximum, pressure-independent capacity for CO₂. Our group and others have observed that the CO₂ solubility approaches a maximum between 70 and 90 mol % CO₂ in the IL, and the system remains two-phase, even up to pressures of 3100 bar.^{8,20} This behavior is unusual when compared to other organic liquid–CO₂ mixtures, which typically reach a mixture critical point at pressures above which the system is single phase.^{8,20}

[MeBu₃N][Tf₂N], [MeBuPyrr][Tf₂N], and [iBu₃MeP][TOS]. In the previous sections, the experimental evidence suggested that the anion, particularly the [Tf₂N] anion, played a significant role in determining the solubility of gases in the ionic liquids. In this section, the effects different cations with the [Tf₂N] anion have on CO₂ and O₂ solubilities will be discussed. Specifically, we investigate how changing the cation to a tetraalkylammonium or pyrrolidinium affects CO₂ solubility. Figure 5 shows the previously presented CO₂ 25 °C isotherms, as well as isotherms for methyl-tributylammonium bis(trifluoromethylsulfonyl) imide ([MeBu₃N][Tf₂N]) and methyl-butyl pyrrolidinium bis(trifluoromethylsulfonyl) imide ([MeBuPyrr][Tf₂N]). For clarity, we have not included the uncertainties in the measurements on this graph, but they can be found in the tables in Supporting Information. Also shown in Figure 5 is the CO₂ absorption in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]),¹⁰ 1-*n*-butyl-2,3-dimethylimidazolium hexafluorophosphate ([bmmim][PF₆]),¹⁴ 1-*n*-butyl-2,3-dimethylimidazolium tetrafluoroborate ([bmmim][BF₄]),¹⁴ 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([emim][Tf₂N]),¹⁴ and 1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl) imide ([emmim][Tf₂N])¹⁴ from our previous work.

The absorption in [MeBu₃N][Tf₂N] was measured only at 25 °C, using a 90 min equilibration time. [MeBuPyrr][Tf₂N] was measured at 10, 25, and 50 °C, with 90 min equilibration times at all temperatures. The tri-isobutyl-methyl phosphonium *p*-toluenesulfonate ([iBu₃MeP][TOS]) absorption was measured at 50 °C, allowing 180 min equilibration time. The data for temperatures other than 25 °C are presented as Henry's law constants in Table 1, as discussed in the next section.

The most notable attribute seen in Figure 5 is that the ionic liquids with the [Tf₂N] anion show similar, high CO₂ solubility, regardless of the cation. Of the [Tf₂N]-based ILs, [MeBuPyrr]-[Tf₂N] and [bmim][Tf₂N] have the highest solubilities. These were closely followed by [emim][Tf₂N], [emmim][Tf₂N], and then [MeBu₃N][Tf₂N]. It appears that a longer alkyl chain on the cation, such as the butyl vs ethyl chain on the imidazolium cation, slightly increases the solubility. These differences are

minor, however, when compared to the effect of the anion. It is also interesting that the [iBu₃MeP][TOS] ionic liquid exhibits a CO₂ solubility comparable to [bmim][PF₆] and [bmim][BF₄]. But, as was pointed out earlier, this sample from Cytec probably contained significant impurities, even after the volatile compounds were removed. Since any effects these impurities may have on CO₂ solubility are unknown at this point, these data should be considered with caution.

Oxygen solubility was measured in [MeBu₃N][Tf₂N], [MeBuPyrr][Tf₂N], and [iBu₃MeP][TOS]. The solubility isotherms in [MeBu₃N][Tf₂N] and [iBu₃MeP][TOS] were measured using equilibration times of 90 min and 180 min, respectively. The isotherms in [MeBuPyrr][Tf₂N] were measured using an equilibration time of 90 min. Again, these solubilities are most efficiently discussed in terms of their Henry's constants.

Henry's Constants. A Henry's constant is the linear relationship between gas concentration and pressure. Therefore, Henry's constants can be found by calculating the slope of the isotherm in the limit of low solute concentrations. The lower solubility gases exhibit nearly linear behavior over the entire pressure range used in the experiments. However, in this work the Henry's constants for all the gases were found by fitting a second-order polynomial to the data and calculating the limiting slope as the pressure (or solubility) approaches zero.¹⁰

There are two sources of error in the Henry's Law constants. One source of error is due to uncertainty in the density, which affects the measured mass uptake via the buoyancy correction. Another source of error arises from uncertainty in the measured mass uptake, which is due to random error as well as hysteresis between absorption and desorption curves.

The error in the density, ρ , is due to the uncertainty in both the temperature, T , and the random error associated with the pycnometer measurement. To account for this, the uncertainties in the temperature, σ_T , and the measured density, σ_ρ , were calculated independently using a linear weighted least squares regression method.⁴⁰ The overall uncertainty in density was then taken as $\sigma_\rho' = \sqrt{\sigma_\rho^2 + (d\rho/dT(\sigma_T))^2}$.

The density uncertainty was propagated via buoyancy calculations to the mole fraction of gas absorbed into the liquid. The overall uncertainty in density provided upper and lower bounds on the buoyancy correction. These bounds in turn provided upper and lower bounds on the mole fraction absorbed.

To account for the random error and hysteresis, the following procedure was used.^{39,40} First the computed mole fraction versus pressure data were fit to a second-order polynomial, $X = \beta_1 P + \beta_2 P^2$. In this equation β_1 and β_2 are the best fit parameters to the curve, where β_1 is the reciprocal of the Henry's Law constant, X is the mole fraction of gas absorbed in the ionic liquid, and P is pressure. The error in X , β_1 , and β_2 can be determined by recasting the problem in vector-matrix notation as $\underline{X} = \underline{P}\underline{\beta}$, where \underline{P} is the matrix of pressure terms, $\underline{\beta}$ is the vector of the best fit parameters, and \underline{X} is the vector of best fit mole fraction. Using the normal equations, the problem is restated $\underline{P}^T \underline{P} \underline{\beta} = \underline{P}^T \underline{X}$, which is then rearranged to the form $\underline{\beta} = [\underline{P}^T \underline{P}]^{-1} \underline{P}^T \underline{X}$. This equation was solved iteratively for $\underline{\beta}$.

To quantify the error in the Henry's Law constant, the standard deviation is used to measure how the fit values of X vary with respect to their true values of X . The standard deviation is calculated:

$$\sigma_X = \sqrt{\frac{1}{N-2} \sum_{i=1}^N (X_i - \beta_1 P_i - \beta_2 P_i^2)^2}$$

The uncertainty in X is then used to calculate the uncertainty in β_1 and β_2 .

$$\sigma_{\beta_1(\beta_2)} = \sigma_X \sqrt{([P^T P]^{-1} P^T) * ([P^T P]^{-1} P^T)^T}$$

The Henry's Law constant and its uncertainty are taken as $H_1 = (1/\beta_1) \pm (1/\sigma_{\beta_1})$.

The Henry's constants for all the systems investigated are listed in Table 1, along with our recalculated values for [bmim]-[PF₆].¹⁰ We believe this method for calculating Henry's law constants and uncertainties is an improvement over the method we used in our previous publications.^{9–14} This is why the values for CO₂ and C₆H₆ in [bmim][BF₄] and CO₂ in [bmim][Tf₂N], all at 25 °C, as well as the values for all gases at all temperatures in [bmim][PF₆], are slightly different than those published previously.^{9,10,12–14} We have also repeated the data for these previously published systems in the tables in Supporting Information, where we include the new estimates of the uncertainty on each data point.

The benzene solubilities in [bmim][BF₄] are significantly larger than the solubility of the permanent gases in the various ILs and are comparable to the solubility of water in [bmim]-[PF₆].⁹ Henry's constants can be converted to infinite dilution activity coefficients (γ^∞) if the vapor pressure is known by the equation:

$$\gamma_1^\infty = \frac{H_1(T)}{P_1^{\text{sat}}} \quad (6)$$

For benzene, these activity coefficients are 2.5 ± 0.7 at 10 °C, 2.6 ± 0.2 at 25 °C, 2.3 ± 0.1 at 40 °C, and 2.4 ± 0.03 at 50 °C. The Henry's law constants depend on temperature, which is quantified by the associated enthalpy of absorption that is shown in Table 1. However, the temperature dependence of the Henry's law constant is roughly balanced by the temperature dependence of the vapor pressure so that the infinite dilution activity coefficient is essentially insensitive to temperature. Other researchers have measured γ^∞ for benzene in different ILs with the [Tf₂N] anion. At 50 °C, Heintz et al. report γ^∞ for benzene in [emim][Tf₂N] and [emim][Tf₂N] to be 1.179 and 1.100, respectively.⁴¹ Krummen et al. give γ^∞ values of 1.36 for [mmim][Tf₂N] (1,3-dimethylimidazolium bis(trifluoromethylsulfonyl) imide), 1.21 for [emim][Tf₂N], and 0.903 for [bmim][Tf₂N].⁴² The ILs with the [Tf₂N] anion have smaller deviations from ideality compared to [bmim][BF₄], indicating that the [Tf₂N] increases the ILs affinity for benzene relative to [BF₄]. One possible explanation for this, which was suggested earlier as an explanation of the differences in CO₂ solubility in ILs with different anions, is simply the difference in the size of the two anions. For instance, if the solubility of benzene in the ILs were dominated by nonspecific van der Waals interactions, then benzene would be more soluble in the IL with the smaller solubility parameter, $\delta = (\Delta U^{\text{vap}}/\nu)^{1/2}$. Assuming that the heat of vaporization (ΔH^{vap}) of both ILs is equally large, then [Tf₂N] ILs, whose molar volume (ν) is much larger, would have smaller values of δ and would, subsequently, dissolve benzene to a greater degree.

Carbon dioxide is also highly soluble in the ILs studied. The 10 °C Henry's constants are smaller than those at the other temperatures for all systems investigated, illustrating the typical temperature dependence of gas solubilities. The small differences between the Henry's constants for [bmim][PF₆] and [bmim][BF₄] again emphasize that a [PF₆] versus [BF₄] anion has little effect on the CO₂ solubility, whereas the significantly smaller

Henry's constants for [bmim][Tf₂N] show that the [Tf₂N] anion dramatically increases the CO₂ solubility. In fact, all the [Tf₂N] ILs, apparently regardless of the cation, exhibit comparable Henry's constants, ranging from 25 to 60 bar over the temperature range investigated. The [iBu₃MeP][TOS] values are slightly higher (i.e., lower solubility) than any of the other ILs. Yet, all the ionic liquids exhibit a relatively high affinity for CO₂ when compared to other gases.

Hussen-Borg et al. have recently reported CO₂ solubilities in [bmim][BF₄].¹⁶ At 30 °C, their Henry's constants range between 55 and 64 bar.¹⁶ These are consistent with the value reported here at 25 °C (59.0 ± 2.6 bar). At 50 °C, their Henry's constants range between 71 and 79 bar,¹⁶ which are somewhat lower than the 88.6 ± 1.9 bar reported here (i.e., they measured a slightly higher solubility). One possible explanation for this difference might be due to impurities in the ionic liquid samples; Hussen-Borg et al. report an overall purity of 97 mol % with a chloride content of 0.01 wt % and a water content of 700 ± 40 ppm.

Baltus and co-workers presented Henry's constants for CO₂ in several different ionic liquids.⁴³ They reported values of 52 ± 5 bar in [C₃mim][PF₆], 37 ± 7 bar in [C₃mim][Tf₂N], 37 ± 3 bar in [bmim][Tf₂N], 35 ± 5 bar in [C₆mim][Tf₂N], and 30 ± 1 bar in [C₈mim][Tf₂N], all at ambient temperature. These values are consistent with the Henry's constants reported here.

The solubility of nitrous oxide in [bmim][Tf₂N] is comparable to that of carbon dioxide. Ethylene and ethane both had significant solubilities in [bmim][Tf₂N], again exhibiting the same trend as was seen with [bmim][PF₆], but with higher overall solubilities. Oxygen had low solubility in all the ILs studied, but appeared to be somewhat more soluble in the tetraalkylammonium and pyrrolidinium salts than seen in the imidazolium-based ILs.

Hussen-Borg et al. report the Henry's constants for oxygen in [bmim][BF₄]; at 51 °C, their Henry's constants range between 326 and 355 bar.¹⁶ While O₂ was not measured in [bmim][BF₄] as part of the present work, Hussen-Borg's Henry's constants are smaller than what might be expected based on the Henry's constants in [bmim][PF₆] and [bmim][Tf₂N] reported here, which are an order of magnitude greater. We currently do not have an explanation for this potential discrepancy.

The approximate detection limit of our apparatus for CO is a Henry's constant on the order of 20 000 bar. This rough estimate of the detection limit was determined as part of our previous work,¹⁰ by assuming the lowest solubility measured was the minimum change in mass detectable by the apparatus. In our previous work,¹⁰ we calculated that hydrogen Henry's constants greater than 1500 bar could not be detected. Therefore, no attempts were made to measure H₂ solubility in either [bmim][BF₄] and [bmim][Tf₂N] due to the difficulty of measuring a low molecular weight gas gravimetrically. However, two other groups have reported Henry's constants for H₂ in these ILs. Berger and co-workers⁴⁴ presented measurements for the Henry's constants at room temperature for H₂ in [bmim][PF₆] and [bmim][BF₄] of 3.0×10^{-3} mol L⁻¹ atm⁻¹ and 8.8×10^{-4} mol L⁻¹ atm⁻¹, respectively. Converting their data to conform to the Henry's constant convention used in the present work, they find a Henry's constant of 5700 bar for H₂ in [bmim][PF₆] and 1900 bar for H₂ in [bmim][BF₄]. Since Berger et al. determined the hydrogen solubilities using a pressure drop method, they were likely measuring pressure decreases on the order of 0.005 atm (based on their reported setup of a 50 mL vessel at 50 atm containing 10 mL ionic liquid). Unfortunately, they do not report the accuracy of their pressure gauge or the

TABLE 2: Henry's Constants of Various Gases in Conventional Solvents at 25 °C

	heptane ⁴⁷	cyclohexane ⁴⁷	benzene ⁴⁷	ethanol ⁴⁷	acetone ⁴⁷
H ₂ O		97 ⁴⁸	10 ⁴⁸	0.1 ⁴⁹	0.3 ⁴⁹
CO ₂	84.3	133.3	104.1	159.2	54.7
C ₂ H ₄	44.2 ^a		82.2	166.0	92.9
C ₂ H ₆	31.7	43.0	68.1	148.2	105.2
CH ₄	293.4	309.4	487.8	791.6	552.2
O ₂	467.8	811.9	1241.0	1734.7	1208.7
Ar	407.4	684.6	1149.5	1626.1	1117.5
CO	587.7	1022.5	1516.8	2092.2	1312.7
N ₂	748.3	1331.5	2271.4	2820.1	1878.1
H ₂	1477.3	2446.3	3927.3	4902.0	3382.0

^a For ethylene in hexane, not heptane.

uncertainty in their measurements. A more recent work by Welton and co-workers reports hydrogen solubilities in several ionic liquids at 1 atm and either 293 or 298 K, measured using ¹H NMR spectroscopy.²⁴ They calculated Henry's constants based on their single solubility value of 6600 bar for [bmim]-[PF₆], 5800 bar for [bmim][BF₄], and 4500 bar for [bmim]-[Tf₂N]. The values from both works are consistent with our findings that hydrogen Henry's constants greater than 1500 bar are not detectable using the gravimetric microbalance. Welton and co-workers also report hydrogen Henry's constants of 3800 bar for [bmmim][Tf₂N], 3900 bar for [bupy][Tf₂N] (*N*-butylpyridinium bis(trifluoromethylsulfonyl)imide), 3700 bar for [bmpy]-[Tf₂N] (*N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide), 4900 bar for [bmim][SbF₆] (1-butyl-3-methylimidazolium hexafluoroantimonate), 4900 bar for [bmim][CF₃COO] (1-butyl-3-methylimidazolium trifluoroacetate), 5700 bar for [hmim][BF₄] (1-hexyl-3-methylimidazolium tetrafluoroborate), 6400 bar for [omim][BF₄] (1-octyl-3-methylimidazolium tetrafluoroborate), 4600 bar for [bmim][CF₃SO₃] (1-butyl-3-methylimidazolium triflate), and 700 bar for [P(C₆H₁₃)₃(C₁₄H₂₉)]-[PF₃(C₂F₅)₃] (tri-*n*-hexyl-*n*-tetradecyl phosphonium trifluoro tri(pentafluoroethane) phosphate).²⁴ Again, it is obvious that the anion can dramatically affect the gas solubility, as seen with the variety of anions with the [bmim] cation. It does appear that changing the cation can also have a large effect on the hydrogen solubility (e.g., changing from imidazolium to pyridinium or pyrrolidinium increases the solubility).

It is instructive to compare the gas solubilities in the ionic liquids to those for gases dissolved in common polar and nonpolar solvents, listed in Table 2 (at 25 °C). In general, the gases that are less soluble in the ILs are less soluble in the other solvents as well. However, carbon dioxide is more soluble on a mole fraction basis in the ILs than the other solvents. Ethylene, ethane, oxygen, and argon all have lower solubilities in the IL than in the other common solvents listed in Table 2.

Molecular Interactions. As gas solubilities in liquids are governed by the interactions between the gas molecules and the solvent molecules, it is informative to look at these gases in terms of their polarizabilities and dipole and quadrupole moments. The reported values for these properties for each of the gases investigated are listed in Table 3. The positive or negative sign associated with the quadrupole moment distinguishes between the two quadrupole structures: a plus sign for the (+ - - +) structure and a minus sign for the (- + + -) structure.

For most of the gases, solubilities in [bmim][Tf₂N], [bmim]-[BF₄], and [bmim][PF₆] correlate reasonably well with gas polarizability. We showed this previously for various gases in [bmim][PF₆]¹⁰ and the data for the additional ILs presented here follows the same trend. This trend indicates that the solubility of these gases is governed by nonspecific dispersion forces between the gas and IL.

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

	α * 10 ²⁴ (cm ³) ⁴⁶	μ * 10 ¹⁸ (esu * cm) ⁵⁰	Q * 10 ²⁶ (esu * cm ²) ⁵⁰
H ₂ O	1.48	1.84	0
C ₆ H ₆	10.6	0	+3.6
CO ₂	2.64	0	-4.3
N ₂ O	3.0 ⁵¹	0.166	-3.0
C ₂ H ₄	4.252 ⁵¹	0	+1.5
C ₂ H ₆	4.5	0	-0.65
CH ₄	2.6	0	0
O ₂	1.60 ⁵¹	0	-0.39
Ar	1.64	0	0
CO	1.95	0.112	-2.5
N ₂	1.74	0	-1.52
H ₂	0.81	0	+0.662

Outliers in this relationship between gas polarizability and solubility in the ILs are H₂O, CO₂, and N₂O. The high solubility of water in the ILs is likely due to the large dipole moment of water and the opportunities for 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 [PF₆].²⁸ The relatively high solubility of carbon dioxide and nitrous oxide is likely due to their large quadrupole moments, as well as specific interactions between the gas and the anion. In another ATR-IR study of CO₂ in [bmim][PF₆] and [bmim][BF₄], Kazarian and co-workers concluded that there was evidence of chemical interactions between the anion and the CO₂, although they say those interactions were probably not large enough to be the sole factor leading to the high CO₂ solubility.¹⁵ They conclude that they observed Lewis acid-base interactions where the anion acts as the Lewis base.¹⁵ Molecular simulations of CO₂ in [bmim][PF₆] and [bmmim][PF₆] also show that the CO₂ localizes around the anion.¹⁴

In our previous work,¹⁰ we could not detect the solubility of CO, H₂, or N₂ in [bmim][PF₆] and we were not able to find any measurable solubility of CO in [bmim][BF₄] in the current study. If their solubilities were also governed by polarizability, the correlation of Henry's constants with polarizability would predict Henry's constants for H₂, N₂, and CO of approximately 3000–20 000 bar, 1300–6000 bar, and 1100–5000 bar, in the three dialkylimidazolium ILs. These predicted values for H₂ are consistent with the detection limit on our apparatus and are in reasonable agreement with the reported Henry's constants of 5700 bar⁴⁴ and 6600 bar²⁴ for H₂ in [bmim][PF₆] and 4500 bar²⁴ for H₂ in [bmim][Tf₂N]. However, the predicted values for both N₂ and CO are within the detection limits of the apparatus, indicating that their solubilities are not governed solely by polarizability. Interestingly, N₂ and CO also have significant quadrupole moments, and yet CO had a sufficiently low solubility that it was below the detection limit of our apparatus. We currently do not have a reasonable explanation for this behavior.

Enthalpies and Entropies of Absorption. Enthalpies and entropies of absorption can be found by considering the temperature effects on gas solubilities. The enthalpy yields information about the strength of interaction between the liquid and dissolved gas, whereas the entropy indicates the level of ordering that takes place in the liquid/gas mixture. These properties can be determined from the following thermodynamic relations:

$$\Delta h = R \left(\frac{\partial \ln H}{\partial (1/T)} \right)_P \quad (7)$$

$$\Delta s = -R \left(\frac{\partial \ln H}{\partial \ln T} \right)_P \quad (8)$$

TABLE 4: Enthalpies and Entropies of Absorption for Various Gases in Conventional Solvents

	heptane ⁴⁷	cyclohexane ⁴⁷	benzene ⁴⁷	ethanol ⁴⁷	acetone ⁴⁷
Δh (kJ/mol)					
H ₂ O		−9.6 ⁴⁸	−21.6 ⁴⁸	−40.0 ^{b,49}	−38.0 ⁴⁹
CO ₂	−9.667	−5.556	−9.337	−12.795	−22.667
C ₂ H ₄	−7.461 ^a		−9.006		−9.077
C ₂ H ₆	−11.162	−10.974	−9.211		−8.633
CH ₄	−0.066	−2.462	−1.277	−3.831	−8.633
O ₂		0.243	1.712	−1.218	0.126
Ar	−1.223	−0.913	1.243	−0.385	1.930
CO	3.785	5.192	6.360	3.730	4.538
N ₂		2.139	4.254	0.456	1.746
H ₂		0.846	2.659	0.352	0.247
Δs (J/mol K)					
H ₂ O		−70 ⁴⁸	−92 ⁴⁸	−124 ^{b,49}	−114 ⁴⁹
CO ₂	−32.4	−18.5	−31.4	−42.9	−76.0
C ₂ H ₄	−25.1 ^a		−30.2		−30.5
C ₂ H ₆	−37.4	−36.8	−30.9		−29.0
CH ₄	−12.7	−8.3	−4.3	−12.9	−9.5
O ₂		0.7	5.7	−4.1	0.4
Ar	−4.2	−3.1	4.1	−1.3	6.4
CO	12.7	17.4	21.3	12.5	15.2
N ₂		7.0	14.2	1.5	5.8
H ₂		2.7	8.9	1.1	0.8

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

which give Δh and Δs at a specific pressure. The enthalpy and entropy values for the series of gases in the IL are listed in Table 1. The values of Δh and Δs are calculated from a linear fit of the data, as suggested by eqs 7 and 8. The uncertainty in these calculated values was found using a weighted least squares linear fit of the form $\ln H = a + b \cdot f(T)$, where $f(T) = 1/T$ for enthalpy and $f(T) = \ln T$ for entropy. The weight assigned to each data point was given by the previously determined uncertainties in the Henry's Law constant, $\sigma_{\beta_1}^2$. The weighted least squares calculation gives the uncertainties in a and b , from which the enthalpy and entropy are determined by the slope of the line, which is equivalent to the partial derivatives in the above equations. With only three temperatures, the uncertainty in the Δh and Δs values are, at times, quite large, so they should be viewed with caution. Nonetheless, we report Δh and Δs to allow some rough comparisons. However, we do not report values when we have only two temperatures. Within the reported error, the calculated values of Δh and Δs are independent of pressure and equal to the values at infinite dilution, as found from the van't Hoff equations.

Not surprisingly, water⁹ and benzene, followed by carbon dioxide and nitrous oxide, exhibited significantly stronger molecular interactions and a higher degree of ordering in the ILs than the other gases. Their enthalpy and entropy values are large and negative and very similar to the gases in small polar solvents such as ethanol and acetone (see Table 4). The enthalpies and entropies of absorption for CO₂ in [MeBuPyr][Tf₂N] are comparable to those measured in [bmim][Tf₂N]. Due to the overlap in error bars, it is difficult to draw conclusions about the effects of the anion (or cation) on the enthalpy or entropy. As mentioned above, since only three temperatures were examined, the experimental uncertainty is relatively large. However, it does appear that CO₂ interacts with the [BF₄] and [PF₆] ILs more strongly than with the [Tf₂N] ILs, despite having a higher solubility in the [Tf₂N] ILs.

Maurer and co-workers report values of −17.24 kJ/mol for the enthalpy and −79.5 J/mol K as the entropy of absorption of CO₂ in [bmim][PF₆].¹⁷ Hussen-Borg et al. found the enthalpy and entropy of CO₂ absorption into [bmim][BF₄] to range from

−6.3 to −10.2 kJ/mol and −55.5 to −67.8 J/mol K, respectively.¹⁶ These values are comparable to those reported here.

Ethylene and ethane also yielded significant enthalpy and entropy changes, similar to those seen for the gases in both polar and nonpolar solvents. Oxygen exhibited positive enthalpy and entropy changes, indicating that the solubility is driven by the increase of disorder in the system. The enthalpies and entropies for O₂ in [MeBu₃N][Tf₂N] and [MeBuPyr][Tf₂N] were also positive numbers, but smaller relative to the imidazolium ILs. This phenomenon is not unusual for gases with low solubilities in liquids⁴⁶ and is seen for several of the gases with low solubilities in the other organic solvents, listed in Table 2 and Table 3. It should be noted that Hussen-Borg et al. reported an increase in O₂ solubility with increasing temperature for O₂ absorption in [bmim][BF₄],¹⁶ consistent with the positive enthalpies and entropies reported here for O₂ dissolution in [Tf₂N] ILs.

Conclusions

The solubilities of a variety of gases in several different ionic liquids have been reported. Water and benzene were most soluble, followed by nitrous oxide and carbon dioxide, then ethylene, ethane and oxygen for the ionic liquids considered. Carbon monoxide solubility was below the detection limit of the apparatus. Gases with large dipole moments (e.g. water) or quadrupole moments (e.g. CO₂ and N₂O), as well as those with the opportunity for specific interactions (e.g., hydrogen bonding) have the highest solubilities in the ionic liquids, whereas the solubilities of the other nonpolar gases correlate well with their polarizability. However, carbon monoxide solubility does not follow this trend, indicating that dipole and quadrupole moments and polarizability cannot fully describe the behavior of the gases in the ILs. The anion appears to play the most significant role in determining the gas solubilities. The [Tf₂N] anion increases all gas solubilities relative to [BF₄] and [PF₆] ILs, whereas the [BF₄] anion has little effect on the solubility of these gases relative to [PF₆]. Changing the cation from imidazolium to quaternary ammonium or pyrrolidinium, all with the [Tf₂N] anion, made little difference in the CO₂ and O₂ solubility.

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Supporting Information Available: Solubility tables S1–S19. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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