

Solubility of CO₂, CH₄, C₂H₆, C₂H₄, O₂, and N₂ in 1-Hexyl-3-methylpyridinium Bis(trifluoromethylsulfonyl)imide: Comparison to Other Ionic Liquids

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ABSTRACT

The solubilities of gases in ionic liquids are important in evaluating ionic liquids as solvents for reactions involving permanent gases, as gas storage media, and as solvents for gas separations. Gas solubilities are also important in developing methods to separate solutes from ionic liquid solutions. Here we describe our measurements of the solubilities of CO₂, CH₄, C₂H₆, C₂H₄, O₂, and N₂ in 1-hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide and compare these results to our previous investigations. In addition, focus is placed on efforts to tailor ionic liquids to enhance the solubilities of some gases, with particular emphasis on carbon dioxide.

Introduction

Ionic liquids (ILs) are salts with low melting points, frequently below room temperature. The most common ILs are based on imidazolium, pyridinium, quaternary ammonium, or quaternary phosphonium cations, but there is growing interest in many other classes of salts. Even with commonly available starting materials, a tremendous diversity in chemical and physical properties, as well as phase behavior with other compounds, can be achieved. This tunability is one of the most attractive

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features of ILs. The IL can be designed for a particular application by judicious choice of cation, anion, and functional groups. For instance, viscosities at room temperature can be tuned from <50 cP to >10000 cP. They can be designed to be completely miscible with water (hydrophilic) or to form two phases with water (hydrophobic). Some react with other compounds (e.g., inclusion of amine functionality allows reaction with CO₂¹ and SO₂, while numerous groups could be used to complex metals) or are relatively inert.

Despite this diversity, most ILs share some common properties. Most ILs exhibit extremely low volatility (i.e., vapor pressure less than 10⁻⁹ bar²) over normal operating temperatures. This can translate to a reduced fire hazard. In addition, most ILs show good thermal stability (473–673 K before noticeable decomposition³) and, thus, exist as liquids over a rather wide temperature range. This affords the possibility of using liquids under many different processing conditions without fear of vapor emissions.

The focus of this Account is the solubilities of gases in ILs. There are four main reasons for growing interest in gas solubilities in ILs: (1) use of ILs as solvents for reactions involving permanent gases, (2) gas storage applications, (3) gas separation applications, and (4) use of gases to separate solutes from IL solutions.

(1) Use of ILs as solvents for reactions involving permanent gases. A primary motivation for understanding gas solubilities in ILs stems from the many successful demonstrations of ILs as solvents for reactions.⁴ ILs are particularly attractive for homogeneously catalyzed reactions, since typical organometallic catalysts are effectively “immobilized” in the IL, reducing loss of precious metals. Hydrogenation, oxidation, and hydroformylation reactions, among others, involve the reaction of substrates with permanent gases. If the reactant gas is highly soluble in the IL, this can reduce mass transfer resistances that are frequently limiting in liquid phase reactions involving gases.

(2) Gas storage applications. A second motivation for understanding gas solubilities in ILs is the possibility of using ILs as liquid absorbents for the storage of gases. Air Products has developed ILs for the storage and delivery of highly toxic gases such as AsH₃, PH₃, and BF₃.⁵ ILs have also been investigated for hydrogen storage applications.⁶

(3) Gas separation applications. The third reason for understanding gas solubilities in ILs is the possibility of using ILs to separate gases.⁷ Selectivities for various gases of interest are greater in ILs than in many common liquids. In addition, ILs would not contaminate the gas stream in even small amounts because they are nonvolatile. High thermal stability means they could be used at higher temperatures than is possible with conventional absorption solvents. ILs could be used in a conventional absorber/stripper configuration or in a supported liquid

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membrane configuration, without loss of liquid and subsequent degradation of membrane performance with time.

(4) Use of gases to separate solutes from IL solutions. A fourth motivation is the potential of using compressed gases or supercritical fluids to separate species from an IL mixture. It is possible to recover a wide variety of solutes from ILs using supercritical CO₂ extraction without cross-contamination.^{8,9} Alternatively, separation of ILs from conventional organic liquids and water can be achieved using lower pressure CO₂, which induces liquid/liquid phase separation.¹⁰ Clearly, the phase behavior of the gases with the IL is important for these applications.

The organization of this Account is as follows. In the Results and Discussion section, we present new data on the solubilities of CO₂, CH₄, C₂H₆, C₂H₄, O₂, and N₂ in 1-hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide ([hmpy][Tf₂N]). Then we show how solubilities change when the pyridinium cation is replaced with an imidazolium cation, as well as the influence of changing the identity of the anion. This is followed by a discussion of our extensive efforts to increase the solubility of CO₂ in ILs. We briefly discuss the work that has been done on correlating, modeling, and simulating gas solubilities in ILs, and we mention the importance of the solubilities of mixtures of gases in ILs. The experimental and data analysis details can be found in the Supporting Information.

Results and Discussion

Solubilities of CO₂, CH₄, C₂H₆, C₂H₄, O₂, and N₂ in [hmpy][Tf₂N]. In order to demonstrate the wide range of solubilities of different gases, 1-hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide ([hmpy][Tf₂N]) is selected as an example. We will then compare the solubilities of several of the gases in [hmpy][Tf₂N] to their solubilities in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf₂N]) and other ILs. A list of all of the ILs described in this paper can be found in Table 1, along with the abbreviations used and the chemical structures. Although imidazolium-based ILs are among the most widely used at present, we are interested in pyridinium ILs because many of them are fully and readily biodegradable, while imidazolium-based ILs are not.¹¹

The experimental results for the solubilities of various gases in [hmpy][Tf₂N] are listed in Table 2 as Henry's law constants (K_H) at multiple temperatures. All Henry's law constants are calculated on a mole fraction basis. A large value of the Henry's law constant corresponds to low solubility, while a small value of K_H indicates high gas solubility. Thus, the gases are listed from highest solubility to lowest solubility. The uncertainty in the measurements is greater for the low solubility gases, where the mass uptake is smaller. The solubility data used to determine these values of Henry's law constants are shown in tabular form in the Supporting Information.

Figure 1 presents the solubilities (mole fraction) of gases in [hmpy][Tf₂N] at 298.15 K. As expected, the gas solubility increased with pressure. From this figure (and from Table 2), it is clear that SO₂ has the highest solubility (notice the break in the y-axis), followed by CO₂, which is also quite soluble in this IL. The light hydrocarbons are less soluble in [hmpy][Tf₂N] than SO₂ and CO₂. Their solubilities in [hmpy][Tf₂N] decrease in the following order: C₂H₄, C₂H₆, and CH₄. The lowest solubility gases able to be measured were O₂ and N₂. H₂ has sufficiently low solubility in the IL that we were not able to determine its solubility with the gravimetric microbalance. The absorption and desorption points shown on the graph are virtually indistinguishable, indicating equilibrium and reversibility.

Clearly, there are very large differences in the solubilities of the various gases in [hmpy][Tf₂N]. Neither oxygen nor hydrogen exhibit significant solubility, so mass transfer may be limiting for many oxidation and hydrogenation reactions. The high solubility of CO₂ relative to N₂ and CH₄ means that this IL may be capable of separating CO₂ from flue gas and natural gas. The high SO₂ solubility means that it could be removed, along with the CO₂, from postcombustion flue gas.

Comparison with Other Ionic Liquids. Also shown in Table 2 are the solubilities of many of the same gases in [hmim][Tf₂N]. The values for the imidazolium- and pyridinium-based ILs are virtually identical, suggesting that gas solubility in these particular ILs is controlled primarily by interactions with the anion, consistent with previous investigations.¹²

The solubilities of SO₂, CO₂, C₂H₄, and C₂H₆ clearly decrease with increasing temperature in [hmpy][Tf₂N] and [hmim][Tf₂N]. The solubilities of CH₄ and O₂ show much less temperature dependence. Where gas solubility was measured at three or more temperatures, the partial molar enthalpy (ΔH) and entropy (ΔS) of gas dissolution were calculated. Decreasing solubility with increasing temperature yields a negative value of the ΔH . All of the partial molar enthalpies are relatively small, as shown in Table 3, indicating physical absorption. Chemical complexation would yield much larger values. As expected, the values for CH₄ and O₂ are small, indicating little temperature dependence of the solubility. The ΔH for C₂H₆ in [hmpy][Tf₂N] is comparable to that of Costa Gomes for C₂H₆ in [hmim][Tf₂N]: $\Delta H \sim -10 \text{ kJ/mol}$.¹³ The ΔS values give an indication of the degree of ordering in the solution associated with the gas dissolution. As expected, more ordering occurs with SO₂ and CO₂ than with gases such as CH₄ and O₂. The ΔS values of a particular gas (e.g., CO₂) in different ILs are not sufficiently different to warrant further analysis.

The interactions between CO₂ and ILs include dispersion, dipole/induced dipole, and electrostatic forces. The partial molar enthalpies of CO₂ dissolution in [hmpy][Tf₂N] and [hmim][Tf₂N] are similar to those of polar solvents that physically absorb CO₂, where the interactions are dispersion and dipole/induced dipole but

Table 1. Structures, Names, and Abbreviation of ILs

Structure	Name	Abbreviation
	1-hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide	[hmpy][Tf ₂ N]
	1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[hmim][Tf ₂ N]
	1-hexyl-3-methylimidazolium hexafluorophosphate	[hmim][PF ₆]
	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[bmim][Tf ₂ N]
	choline bis(trifluoromethylsulfonyl)imide	[choline][Tf ₂ N]
	N,N,N,N-trimethylbutylammonium bis(trifluoromethylsulfonyl)imide	[N ₄₁₁₁][Tf ₂ N]
	1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[omim][Tf ₂ N]
	1-hexyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide	[hmmim][Tf ₂ N]
	1-methyl-3-(3,3,4,4,5,5,6,6,6-nonafluorohexy)imidazolium bis(trifluoromethylsulfonyl)imide	[C ₆ H ₄ F ₉ mim][Tf ₂ N]
	1-methyl-3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)imidazolium bis(trifluoromethylsulfonyl)imide	[C ₈ H ₄ F ₁₃ mim][Tf ₂ N]
	1-butyl-3-methylimidazolium nitrate	[bmim][NO ₃]
	1-butyl-3-methylimidazolium dicyanamide	[bmim][DCA]
	1-butyl-3-methylimidazolium tetrafluoroborate	[bmim][BF ₄]
	1-butyl-3-methylimidazolium hexafluorophosphate	[bmim][PF ₆]
	1-butyl-3-methylimidazolium trifluoromethanesulfonate	[bmim][TfO]
	1-butyl-3-methylimidazolium methide	[bmim][methide]
	1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate	[hmim][eFAP]

Table 1. Continued

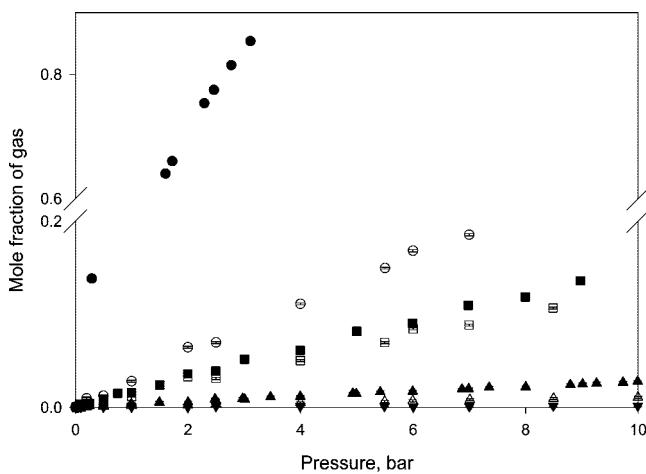
Structure	Name	Abbreviation
	1-hexyl-3-methylimidazolium tris(heptafluoropropyl)trifluorophosphate	[hmim][pFAP]
	1-pentyl-3-methylimidazolium tris(nonafluorobutyl)trifluorophosphate	[p ₅ mim][bFAP]
	1-butyl-3-methylimidazolium trifluoroacetate	[bmim][TFA]
	1-butyl-3-methylimidazolium pentadecafluoroctanoate	[bmim] [C ₇ F ₁₅ CO ₂]
	1-butyl-nicotinic acid butyl ester bis(trifluoromethylsulfonyl)imide	[b ₂ -Nic] [Tf ₂ N]
	PEG-5 cocomonium methylsulfate	Ecoeng 500
	1-butyl-3-methylimidazolium 2-(2-methoxyethoxy)ethylsulfate	Ecoeng 41 M
	tetrabutylammonium docusate	[N ₄₄₄₄][doc]
	1-hexyl-3-methylimidazolium saccharinate	[hmim][SAC]
	1-hexyl-3-methylimidazolium acesulfumate	[hmim][ACE]
	(1-methylimidazole)(triethylamine) boronium bis(trifluoromethylsulfonyl)imide	[Et ₃ NBH ₂ mim] [Tf ₂ N]
	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[emim][Tf ₂ N]
	1-ethyl-3-methylimidazolium bis(methylsulfonyl)imide	[emim][Nmes ₂]

not electrostatic, as shown in Figure 2. The ΔH values for CO₂ absorption into nonpolar solvents such as cyclohexane and heptane tend to be smaller, since molecular interactions are limited to dispersion forces. ΔH values

for compounds that afford the possibility of chemical complexation, such as monoethanolamine (MEA) and monodiethanolamine (MDEA), are much larger. Heat of absorption plays an important role in determining the

Table 2. Henry's Law Constants for Various Gases in Several ILs

ionic liquid	H (bar)				
	283 K	298 K	313 K	323 K	333 K
[hmPy][Tf ₂ N] ¹⁶			Sulfur Dioxide		
[hmPy][Tf ₂ N] ¹⁶		1.64 ± 0.01	2.29 ± 0.02		4.09 ± 0.06
[bmim][PF ₆] ¹⁵	38.8 ± 0.2	53.4 ± 0.3			
[bmim][BF ₄] ¹⁵	41.8 ± 2.3	59.0 ± 2.6			
[bmim][Tf ₂ N] ¹⁵	25.3 ± 0.3	33.0 ± 0.3			
[hmim][Tf ₂ N] ^{16,17}	24.2 ± 0.1	31.6 ± 0.2			
[hmPy][Tf ₂ N] ^{16,17}	25.4 ± 0.1	32.8 ± 0.2			
[hmim][eFAP] ¹⁷		25.2 ± 0.1			42.0 ± 0.1
[hmim][pFAP] ¹⁷		21.6 ± 0.1			36.0 ± 0.3
[p ₅ mim][bFAP] ¹⁷		20.2 ± 0.1			32.9 ± 0.2
[C ₆ H ₄ F ₉ mim][Tf ₂ N] ¹⁷		28.4 ± 0.1			48.5 ± 0.4
[C ₈ H ₄ F ₁₃ mim][Tf ₂ N] ¹⁷		27.3 ± 0.2			44.7 ± 0.5 ^a
[hmim][SAC] ¹⁷					132.2 ± 19.7
[hmim][ACE] ¹⁷					113.1 ± 16.9
[Et ₃ NBH ₂ mim][T ₂ N] ¹⁷		33.1 ± 1.2			
[bmim][PF ₆] ¹⁵	125 ± 4	144 ± 2		191 ± 6	
[bmim][Tf ₂ N] ¹⁵	61 ± 5	70 ± 4		97 ± 8	
[hmPy][Tf ₂ N]		58 ± 1	75 ± 1		96 ± 2
[bmim][PF ₆] ¹⁵	234 ± 36	336 ± 28		363 ± 29	
[bmim][Tf ₂ N] ¹⁵	86 ± 10	97 ± 7		141 ± 15	
[hmPy][Tf ₂ N]		72 ± 2	91 ± 2		118 ± 3
[hmPy][Tf ₂ N]			Methane		
[hmim][Tf ₂ N]		300 ± 30	442 ± 125		371 ± 63
[hmPy][Tf ₂ N]		329 ± 23	380 ± 31		359 ± 28
[bmim][PF ₆] ¹⁵			Oxygen		
[bmim][Tf ₂ N] ¹⁵	7190 ± 4190	1200 ± 160			
[bmim][Tf ₂ N] ¹⁵	3700 ± 1450	1730 ± 560	1110 ± 240		
[hmPy][Tf ₂ N]	593 ± 350		459 ± 100 ^c		
[hmPy][Tf ₂ N]	422 ± 220 ^b	463 ± 104	715 ± 210	545 ± 123	
[hmPy][Tf ₂ N]			Nitrogen		
[hmPy][Tf ₂ N]		3390 ± 2310			

^a Estimated density from 25 °C. ^b Data at 293 K. ^c Data at 303 K.**FIGURE 1.** Solubility of various gases in [hmPy][Tf₂N] at 298.15 K: (●) SO₂; (○) CO₂; (■) C₂H₄; (□) C₂H₆; (▲) CH₄; (△) O₂; (▼) N₂.

total heat load and in deciding between pressure swing and temperature swing in absorption/desorption separation processes.

A comparison can be made for the solubilities of various gases in common solvents¹⁴ and in these ILs. As shown in Figure 3 for 298.15 K and 1 bar gas pressure, CO₂ solubility in the ILs is higher than that in any of the

Table 3. Enthalpies and Entropies of Gas Dissolution

ionic liquid	gas	ΔH , kJ mol ⁻¹	ΔS , J mol ⁻¹ K ⁻¹
[hmPy][Tf ₂ N]	CO ₂ ¹⁶	-11.5 ± 0.1	-38.1 ± 0.5
	CH ₄	-5.6 ± 4.6	-17.7 ± 14.7
	C ₂ H ₆	-11.5 ± 0.8	-36.3 ± 2.5
	C ₂ H ₄	-12.1 ± 0.6	-38.5 ± 1.8
	O ₂	-5.8 ± 8.3	-19.1 ± 27.0
	SO ₂ ¹⁶	-20.0 ± 0.4	-64.0 ± 1.1
[hmim][Tf ₂ N]	CO ₂ ¹⁶	-11.8 ± 0.3	-48.2 ± 0.9
	CH ₄	-2.1 ± 2.5	-6.4 ± 7.9

molecular solvents,¹⁴ including polar solvents such as acetone. The nonpolar solvents tend to have higher hydrocarbon solubilities than the CO₂ solubility, while the polar solvents, such as methanol and ethanol, have similar CO₂ and hydrocarbon solubilities. This suggests that, for the separation of hydrocarbons from CO₂ mixed gas streams, ILs would have better selectivities than any of the conventional molecular solvents. Notice all solvents, including ILs, have relatively poor N₂ and O₂ solubilities. Yet, higher CO₂ solubility suggests better CO₂/N₂ or CO₂/O₂ selectivity for the ILs. This graph emphasizes the potential use of ILs for gas separations.

As shown above for [hmPy][Tf₂N] and [hmim][Tf₂N], there is very little difference in the solubilities of various gases in ILs with different cations and the same anion.

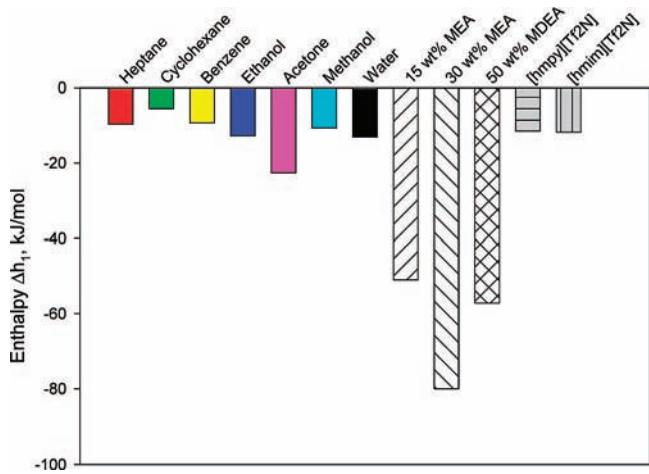


FIGURE 2. Comparison of the heat of absorption/reaction for CO₂ in various solvents.

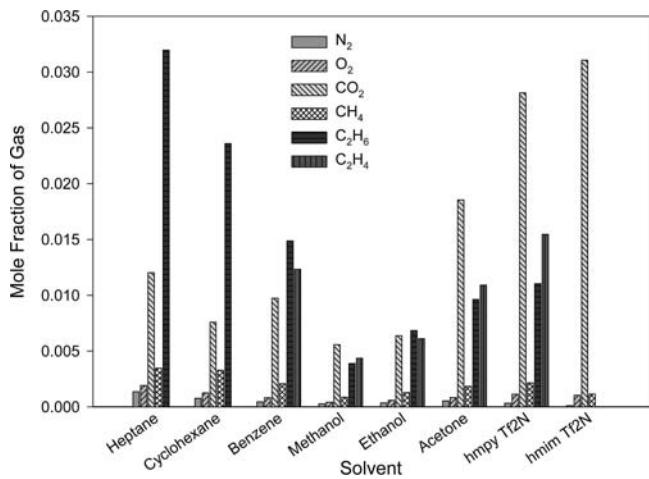


FIGURE 3. Solubility of CO₂ in various solvents at a partial pressure of 1 atm and a temperature of 298.15 K.

This suggests that the primary interaction involving CO₂ and the IL, for the ILs investigated here, occurs between the anion and the gas. This is borne out by direct comparison of the Henry's Law constants of four gases in [bmim][PF₆] and [bmim][Tf₂N] shown in Table 2.¹⁵ CO₂, C₂H₄, C₂H₆, and O₂ all are significantly more soluble in [bmim][Tf₂N] at low pressures than in [bmim][PF₆]. The solubility is O₂ < C₂H₆ < C₂H₄ < CO₂ for both ILs, but the absolute values are significantly higher in [bmim][Tf₂N] than in [bmim][PF₆].

Enhancing the Solubility of CO₂ in ILs. Since a primary motivation for our work has been exploring ILs for separation of CO₂ from mixed gas streams, we have investigated ways to further increase the solubility of CO₂ in ILs. Below we concentrate on CO₂ solubility and compare different cation types, alkyl substitution on the cation, fluorination of alkyl chains on the cation, different anion types, degree of fluorination of the anion, and various attempts to increase CO₂ solubility without fluorination.

Cation Type. The data in Table 2 have already been used to show that the solubilities of CO₂ in imidazolium and pyridinium [Tf₂N]⁻ compounds at low pressure are virtually identical.¹⁶ We have also considered tetraalkyl-

ammonium cations.¹⁷ The [choline]⁺ cation lowered CO₂ solubility compared to the [hmim]⁺ cation, whereas the solubility of CO₂ in [N₄₁₁₁][Tf₂N] is similar to that in [hmim][Tf₂N]. Strong hydrogen bonding of the [Tf₂N]⁻ anion with the [choline]⁺ cation may make the anion less available for interaction with CO₂. In these ILs, the primary interaction of the CO₂ appears to be with the anion. This is supported by molecular simulations^{18,19} and Fourier transform infrared spectroscopy (FTIR).¹² ILs can be designed to have cations that can more strongly interact with CO₂, especially those developed to chemically complex with the gas.¹

Alkyl Substitution on the Cation. To study the influence of cation alkyl chain length, one can compare the solubility of CO₂ in [bmim][Tf₂N], [hmim][Tf₂N], and [omim][Tf₂N].²⁰ The solubility increases slightly with increasing chain length, with the effect becoming more apparent as pressure increases. This trend is also observed for ILs containing the [BF₄]⁻ and [PF₆]⁻ anions.^{8,21} The slight increase in solubility with increasing alkyl chain length is likely due to greater free volume in the IL.

In imidazolium ILs, the C2 hydrogen (the hydrogen connected to the carbon atom between the two nitrogens in the imidazolium ring) is known to be acidic and, therefore, potentially interacts with the oxygen atoms on the CO₂. By adding a methyl group to the C2 position, any contributions from the C2-H/oxygen interactions would be eliminated. Replacement of the hydrogen with a methyl has very little effect on the solubility of CO₂ at pressures below 80 bar.²⁰ At higher pressures, [hmim][Tf₂N] shows a slightly higher solubility than [hmim][Tf₂N]. These results are consistent with the anion-CO₂ interaction being dominant and are supported by molecular simulations that show the secondary location some CO₂ molecules adopt at higher pressures is actually closer to the partial positive on N3 (nitrogen with the methyl substituent) instead of the acidic C2 hydrogen.^{18,19} Overall, though, the effect of alkyl chain length and alkyl substitution has a very minor effect on CO₂ solubility.

Fluorination of the Cation. Fluoroalkyl chains are frequently added to substrates to increase their solubility in supercritical CO₂.²² Therefore, we have examined ILs with partially fluorinated alkyl chains on the cation. [hmim][Tf₂N]^{16,20,23,24} can be directly compared to [C₆H₄F₉mim][Tf₂N],¹⁷ and as seen in Figure 4, fluorinating the last four carbons of the alkyl chain does increase the CO₂ solubility. The Henry's law constant at 298.15 K (Table 2) for [C₆H₄F₉mim][Tf₂N] is 28.4 ± 0.1 bar compared to 31.6 ± 0.2 bar for [hmim][Tf₂N]. However, this increase in the solubility of CO₂ was less than expected based on a reported Henry's law constant of 4.5 ± 1 bar at 298.15 K,²⁵ later revised to 6 ± 1 bar,²⁶ for the analogous IL, [C₈H₄F₁₃mim][Tf₂N]. After graciously receiving a sample of [C₈H₄F₁₃mim][Tf₂N] used by Prof. Baltus' group, we determined that the Henry's law constant for [C₈H₄F₁₃mim][Tf₂N] is 27.3 ± 0.2 bar at 298.15 K (Table 2). As expected, the CO₂ solubility was higher in the IL with the longer fluoroalkyl chain, [C₈H₄F₁₃mim][Tf₂N],

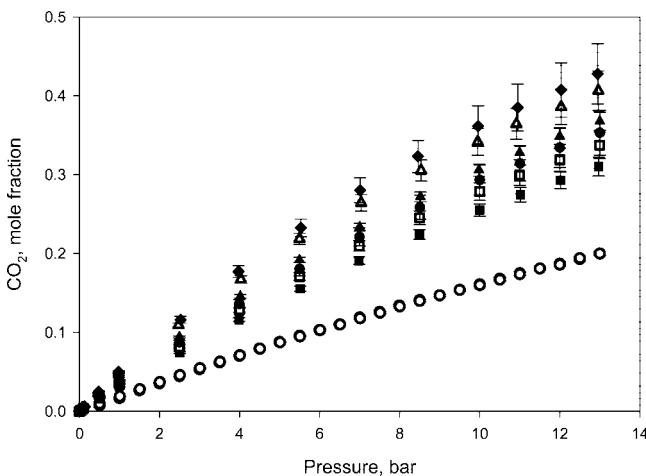


FIGURE 4. Solubility of CO₂ at 298.15 K: (○) [bmim][PF₆]; (■) [hmim][Tf₂N]; (□) [C₆H₄F₉mim][Tf₂N]; (●) [C₈H₄F₁₃mim][Tf₂N]; (▲) [hmim][eFAP]; (△) [hmim][pFAP]; (◆) [p₅mim][bFAP].

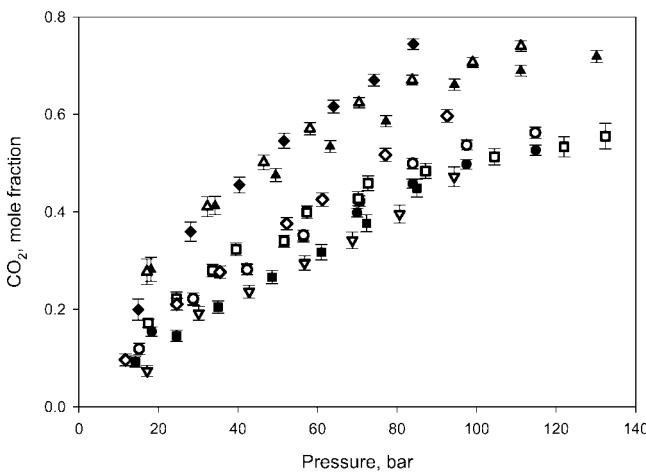


FIGURE 5. Solubility of CO₂ at 333.15 K in various [bmim]⁺-based ILs: (▽) [NO₃]⁻; (●) [DCA]⁻; (■) [BF₄]⁻; (□) [PF₆]⁻; (◇) [TFA]⁻; (○) [TfO]⁻; (▲) [Tf₂N]⁻; (△) [methide]⁻; (◆) [C₇F₁₅CO₂]⁻.

than in [C₆H₄F₉mim][Tf₂N]. However, the solubility was significantly less than that reported by Baltus et al.²⁶ Nonetheless, increasing the fluorination on the alkyl chain on the cation does lead to increased CO₂ solubility.

Effect of Anion. Above we showed that the solubilities of all the gases studied were higher in [bmim][Tf₂N] than in [bmim][PF₆]. In a more extensive study of the solubility of CO₂ in [bmim]⁺-based ILs, we found that the solubility of CO₂ did not correspond to the basicity of the anion but instead showed increasing solubility in the following order: [NO₃]⁻ < [DCA]⁻ < [BF₄]⁻ ~ [PF₆]⁻ < [TfO]⁻ < [TFA]⁻ < [Tf₂N]⁻ < [methide]⁻ < [C₇F₁₅CO₂]⁻.^{17,20} These results are shown at 333.15 K in Figure 5. We believe that this may be due to a stronger interaction of CO₂ with the fluorous alkyl chains than acid/base interactions. Further support of this hypothesis was provided by Pringle et al., who found greater CO₂ solubility in [emim][Tf₂N] than in the nonfluorinated version of the anion, [emim][Nmes₂].²⁷

Effect of Fluorination of the Anion. As mentioned above, fluorination is a proven method of increasing the CO₂-philicity of compounds. We have already presented results for the following ILs with fluorinated anions:

[bmim][PF₆], [bmim][BF₄], [bmim][Tf₂N], [hmim][Tf₂N], and [bmim][methide]. We have also tested three fluoroalkylphosphonates: [hmim][eFAP], [hmim][pFAP], and [p₅mim][bFAP].¹⁷ Although the cations differ, the effect of cation alkyl chain length on CO₂ solubility is minor and not enough to mask the anion effect. Replacing three of the fluorine atoms of [PF₆]⁻ with fluoroalkyl groups of varying length increases the CO₂ solubility significantly. From Figure 4, we see that the solubility increases as the fluorinated alkyl chain length increases. Also shown on the graph is the solubility of CO₂ in [hmim][Tf₂N], which is the IUPAC standard IL.^{16,17,20,23,24}

The results confirm that an increase in the length of the fluoroalkyl chain increases the CO₂ solubility. The Henry's law constants for [hmim][eFAP], [hmim][pFAP], and [p₅mim][bFAP] are shown in Table 2. Of all the ILs studied, the CO₂ solubility is highest in [p₅mim][bFAP], with a Henry's law constant at 298.15 K of 20.2 bar. Continually increasing the amount of fluorination is unlikely to lead to proportionate increases in CO₂-philicity. Computational results suggest an optimum number of fluorine atoms for maximum CO₂-philicity.²⁸

Enhancing CO₂ Solubility without Additional Fluorination. In designing CO₂-philic polymers, surfactants, and ligands, researchers have used nonfluorinated functional groups due to the cost and potential environmental implications of their fluorinated counterparts.^{22,29} Carbonyl, esters, and ether groups are known to enhance a molecule's CO₂-philicity. We have examined a number of ILs that include these functional groups and tested them for CO₂ solubility.

[b₂-Nic][Tf₂N] is a pyridinium-based IL with a butyl ester group. Unfortunately, this functional group did not dramatically improve the solubility of CO₂ in the IL compared to [hmim][Tf₂N].¹⁷ The [Tf₂N]⁻ anion appears to be the dominant factor. At higher pressures, [b₂-Nic][Tf₂N] does have slightly higher CO₂ solubility compared to [hmim][Tf₂N], which may be due to secondary interactions between CO₂ and the cation. This behavior is similar to what we have reported earlier for [hmim][Tf₂N] and [hmim][Tf₂N] systems.¹⁸ The addition of ether groups is believed to improve CO₂-philicity by increasing the flexibility of alkyl chains, leading to increased free volume.^{22,29} The ether oxygen has also been shown to interact with the carbon of CO₂.³⁰ We investigated two commercially available ILs possessing ether groups, Ecoeng 500 and Ecoeng 41M.¹⁷ The solubility of CO₂ in these ILs is as good, but not better than, that in [hmim][Tf₂N]. The addition of ether groups affects key physical properties (i.e., Ecoeng 500 viscosity at 333.15 K = 300 cP).³¹ However, Ecoeng 500 is composed of ions of known toxicity³² and that are not likely to be as environmentally persistent as fluorinated ILs, while maintaining good capacity for CO₂.

Additionally, we measured the solubility of CO₂ in another nonfluorous IL, [N₄₄₄₄][doc], containing ester functional groups. [N₄₄₄₄][doc] also contains an anion of known low toxicity³³ and has good affinity for CO₂, but it is highly viscous (12100 cP at 298.15 K).³¹ Finally, the

solubility of CO₂ was measured with the low pressure apparatus in three other ILs: [hmim][SAC],³⁴ [hmim][ACE],³⁴ and [Et₃NBH₂mim][Tf₂N].³⁵ The [SAC]⁻ and [ACE]⁻ anions contain sulfonyl groups, as does [Tf₂N]⁻. They also contain carbonyl groups adjacent to the nitrogen that may be particularly nucleophilic, providing the opportunity to interact with the carbon in CO₂. However, they do not contain fluoroalkyl groups. From the Henry's law constants in Table 2, it is clear that the sulfonyl and carbonyl functionality is not sufficient to enhance CO₂ solubility, leading one to conclude that it is the fluoroalkyl groups in [Tf₂N]⁻ that play a key role in dissolution of CO₂. [Et₃NBH₂mim][Tf₂N] was tested to see if it may act as a hydride, reacting with the CO₂ to produce formate.¹⁷ Clearly, this did not occur, since the CO₂ solubility in this compound is virtually the same as that in [hmim][Tf₂N].

Another way of increasing the solubility of CO₂ in ILs is to append functional groups to the IL with which the CO₂ can react. This idea was set forth by Davis and co-workers,¹ who showed that appending a free amine and exposure to CO₂ can result in the formation of a carbamate, with subsequent high uptake of CO₂. Zhang and co-workers have shown that amino acid-based ILs can serve the same purpose.³⁶ There are a variety of issues that must be considered in selecting a physically absorbing versus a chemically complexing IL for CO₂ capture. For instance, there may be significant changes in physical properties (e.g., viscosity) with chemical complexation. In addition, one may expect higher heats of absorption and desorption when the CO₂ reacts with the IL.

Modeling and Simulation of Gas Solubility. There have been a number of attempts to correlate or model the solubilities of gases in liquids. For instance, using a conventional Peng–Robinson equation of state and effectively fitting the critical properties and acentric factor of the IL, Peters and co-workers³⁷ were able to obtain a reasonable representation of the 1-ethyl-3-methylimidazolium hexafluorophosphate/CF₃H system. Economou and co-workers³⁸ have successfully fit the parameters in the truncated perturbed chain polar statistical associating fluid theory (tPC-PSAFT) to model 1-alkyl-3-methylimidazolium hexafluorophosphate and tetrafluoroborate IL phase behavior with CO₂. Qin and Prausnitz³⁹ correlated the Henry's law constants for a variety of gases in several different ILs with a perturbed-hard-sphere theory. Noble and co-workers have correlated some data with a Regular Solution Theory model.⁴⁰ All of these models have rather limited applicability, due to either the large number of parameters fit to the experimental data or the gross simplicity of the model or correlation.

While molecular simulations of ILs and IL mixtures are becoming more prevalent, very few of these studies attempt to perform calculations of gas solubilities in ILs. The first such study⁴¹ estimated the Henry's law constants of water, CO₂, C₂H₆, C₂H₄, CH₄, O₂, and N₂ in [bmim][PF₆] using the test particle insertion method, where they determined that the statistics were not sufficiently robust to obtain reliable estimates. Subsequently, the groups of Liu,⁴² Padua,⁴³ and Maurer⁴⁴ presented molecular simula-

tions using particle insertion and Gibbs ensemble Monte Carlo techniques. While correct trends can be captured, we look forward to the publication of more accurate estimates of gas solubilities in ILs.

Gas Mixtures. All of the discussion above has focused on the solubility of individual gases. When ILs are used in many of the applications listed in the Introduction, especially for gas separations, gas mixtures will be present. Thus, the solubility of gas mixtures in ILs is really the key issue. While some gases may behave ideally, this is seldom the case. In fact, there is evidence to suggest, for instance, that the presence of CO₂ in a mixture can enhance the solubilities of less soluble gases in the IL.^{23,45} This could have a detrimental effect, such as lowering selectivities for gas separations, or could be beneficial, such as enhancing the solubility of reactants. Whatever the case, one should be aware that the solubilities of pure gases in ILs are just a first indication of the potential of ILs for reactions, separations, and storage.

Conclusions

Since the solubilities of gases in ionic liquids are important in evaluating ILs for a variety of applications, including as solvents for reactions involving permanent gases, as gas storage media, and as solvents for gas separations, understanding what controls the solubility is vitally important. To investigate this, we present the solubilities of CO₂, CH₄, C₂H₆, C₂H₄, O₂, and N₂ in 1-hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide and compare the results to the solubility of these gases in other ionic liquids. Gases, especially carbon dioxide, interact strongly with the anion of many common ILs, with the cation and substituents playing secondary roles. The use of fluoroalkyl chains, as well as some nonfluorinated substituents, can increase carbon dioxide solubility several fold. In general, the selectivity for carbon dioxide over nitrogen and small hydrocarbons is better with ILs than with many conventional polar and nonpolar solvents. Moreover, the solubilities of gases in ILs can be tuned for specific applications.

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Supporting Information Available: Experimental details and information on data analysis, and tables of the experimental solubility data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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