

High-Pressure Phase Behavior of Carbon Dioxide with Imidazolium-Based Ionic Liquids

Sudhir N. V. K. Aki, Berlyn R. Mellein, Eric M. Saurer, and Joan F. Brennecke*

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

Received: July 13, 2004; In Final Form: October 11, 2004

Previously we have shown that supercritical carbon dioxide can be used to extract organics from ionic liquids (ILs). Subsequently, ionic liquids/carbon dioxide biphasic solutions have been used for a variety of homogeneously catalyzed reactions. Therefore, an understanding of the phase behavior of carbon dioxide with ionic liquids is needed to design extraction and reaction processes necessary for these applications. We present measurements of the solubility of carbon dioxide in 10 different imidazolium-based ionic liquids at 25, 40, and 60 °C and pressures to 150 bar. As expected, the solubility increases with increasing pressure and decreases with increasing temperature for all the ILs investigated. To investigate the influence of the anion, seven of the ILs studied have 1-butyl-3-methylimidazolium ([bmim]) as the cation. The anions are dicyanamide ([DCA]), nitrate ([NO₃]), tetrafluoroborate ([BF₄]), hexafluorophosphate ([PF₆]), trifluoromethanesulfonate ([TfO]), bis(trifluoromethylsulfonyl)imide ([Tf₂N]), and tris(trifluoromethylsulfonyl)methide ([methide]). The other ILs considered in the study, chosen to investigate the influence of varying number and length of alkyl chains on the cation, include 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf₂N]), 2,3-dimethyl-1-hexylimidazolium bis(trifluoromethylsulfonyl)imide ([hmmim][Tf₂N]), and 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([omim][Tf₂N]). Results show that the solubility of carbon dioxide is strongly dependent on the choice of anion. In particular, CO₂ solubility is greater in ILs with anions, such as [Tf₂N] and [methide], which contain fluoroalkyl groups. Also, we observe that an increase in the alkyl chain length on the cation increases the CO₂ solubility marginally.

Introduction

The impetus for studying the phase behavior of carbon dioxide with ionic liquids (ILs) is threefold. First, we have shown that it is possible to recover a variety of solutes, including relatively low-volatility solutes, from ILs by extraction with CO₂.^{1–3} Obviously, phase behavior is important for this application. Second, a number of researchers have adopted the idea of IL/CO₂ biphasic systems for reaction/separation systems.^{4–23} In some cases the reaction is simply followed by extraction with supercritical CO₂, but in other cases the CO₂ plays an integral role in facilitating both the reaction and the separation or even acts as a reactant.^{4–23} Once again, understanding the phase behavior of CO₂ with various ILs is vital to designing and understanding these systems. Third, we and others have shown that ILs have potential uses in separating CO₂ from other gases, another application where CO₂ solubilities in ILs are important.^{24–26}

A number of high- and low-pressure CO₂/IL solubility studies have appeared in the literature. In our early work we established the general shape of the vapor/liquid equilibrium envelope for CO₂ with 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]).¹ Subsequently, we found similar behavior for four other ILs, reporting both solubilities and molar volumes.²⁷ While we were cognizant of the potential importance of water content of these hygroscopic solvents, we were not particularly aware, at that time, of a wide variety of other impurities and degradation products that may have been present in the IL

samples. Thus, the solubilities of CO₂ in [bmim][NO₃] and [bmim][PF₆] reported here are somewhat different than the values we reported earlier, as explained in much more detail below. Subsequently, two other groups have examined the CO₂/[bmim][PF₆] system at high pressures.^{28,29} In addition, Peters' group has reported values for CO₂ with 1-ethyl-3-methylimidazolium hexafluorophosphate and 1-hexyl-3-methylimidazolium hexafluorophosphate.^{30,31} Low-pressure CO₂ solubility measurements in ILs from our laboratory include [bmim]-[PF₆],^{32,33} [bmim][BF₄], [bmim][Tf₂N], methyltributylammonium bis(trifluoromethylsulfonyl)imide, hexyltributylammonium bis(trifluoromethylsulfonyl)imide, methylbutylpyrrolidinium bis(trifluoromethylsulfonyl)imide, and triisobutylmethylphosphonium *p*-toluenesulfonate.^{33–35} In addition, we have measured the CO₂ solubility in three pairs of dialkyl- and trialkylimidazolium ILs, where we complement the experimental measurements with molecular simulations.³⁶ From other groups, there are low-pressure CO₂ solubility measurements in a variety of ILs,^{25,26,37–39} including a specially designed IL containing an amine substituent.⁴⁰

The goal of this study is to systematically investigate the influence of anion, cation alkyl chain length, and additional alkyl substituents on the cation ring and on the solubility of CO₂ in ILs at pressures to 150 bar.

Experimental Section

The gas solubility measurements were carried out in a stoichiometric phase equilibrium apparatus, the details of which can be found elsewhere.^{41–43} The main components of the

* Corresponding author: Tel (574) 631-5847; Fax (574) 631-8366; e-mail: jfb@nd.edu.

TABLE 1: Ionic Liquids Used in the Current Study Indicating the Source of the ILs and Impurity Content in Each IL

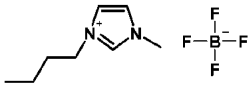
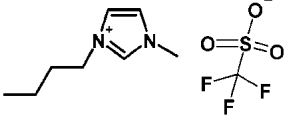
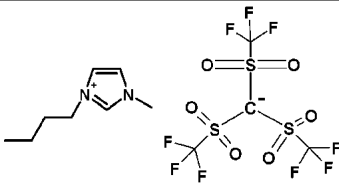
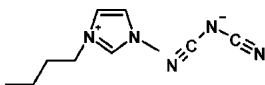
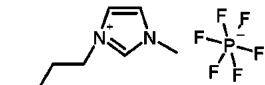
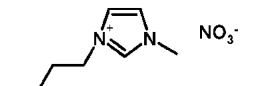
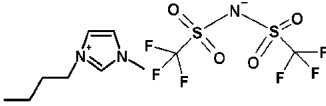
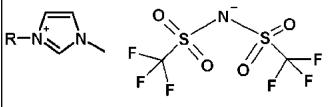
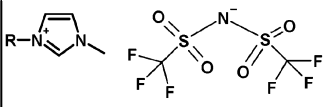
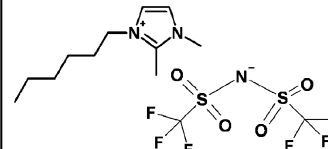
Ionic liquid	Structure	Short name	Source/Water content
1-butyl-3-methylimidazolium tetrafluoroborate		[bmim][BF ₄]	Synthesized in our laboratory; [H ₂ O] = 0.12 wt%; [Br] < 10 ppm; [NH ₄] = 18 ppm
1-butyl-3-methylimidazolium triflate		[bmim][TfO]	Synthesized in our laboratory; [H ₂ O] = 0.14 wt%; halide free synthesis
1-butyl-3-methylimidazolium methide		[bmim][methide]	Covalent Assoc. [H ₂ O] = 0.04 wt%; [Cl] = 18 ppm
1-butyl-3-methylimidazolium dicyanamide		[bmim][DCA]	Synthesized in our laboratory; [H ₂ O] = 0.21 wt%; [Br] = 293 ppm
1-butyl-3-methylimidazolium hexafluorophosphate		[bmim][PF ₆]	Sachem; Synthesized by our group; [H ₂ O] = 50 - 100 ppm; [Cl] < 10 ppm
1-butyl-3-methylimidazolium nitrate		[bmim][NO ₃]	Synthesized by our group; [H ₂ O] = 0.16 wt%; [Br] = 550 ppm; [Ag] = 20 ppm
1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide		[bmim][Tf ₂ N]	Covalent Assoc.; [H ₂ O] = 450 ppm, [Cl] = 18 ppm; Synthesized in our laboratory; [H ₂ O] = 450 ppm, [Br] < 10 ppm
1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; R = C ₆ H ₁₃		[hmim][Tf ₂ N]	Synthesized in our laboratory; [H ₂ O] = 160 ppm; [Br] < 10 ppm

TABLE 1 (Continued)

Ionic liquid	Structure	Short name	Source/Water content
1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide; R = C ₈ H ₁₇		[omim][Tf ₂ N]	Synthesized in our laboratory; [H ₂ O] = 110 ppm; [Br] < 10 ppm
2,3-dimethyl-1-hexylimidazolium bis(trifluoromethylsulfonyl) imide		[hmmim][Tf ₂ N]	Synthesized in our laboratory; [H ₂ O] = 105 ppm; [Br] < 10 ppm

apparatus are a feed pump to deliver CO₂, temperature and pressure indicators and controllers, a water bath to maintain the cell at constant temperature, a cathetometer to measure the volume of the liquid in the cell, two sapphire cells and cell holders (8 and 4 in. sapphire cells rated to a pressure of 340 bar), and an agitation system to stir the sample. The pressure was measured using Heise pressure gauges with an accuracy of ± 0.07 bar. The temperature was measured using either RTD probes or type T thermocouples with an accuracy of ± 1 K. In a typical experiment, the dry IL (1–2 g) was loaded in to the cell in a glovebox under a dry nitrogen atmosphere. The cell was then attached to the apparatus and placed in the constant temperature water bath until it reached thermal equilibrium. A known amount of CO₂ was added to the cell, and the liquid was stirred until equilibrium was attained (i.e., no further change in pressure). This procedure was repeated at several pressures to complete the isotherm. The solubility was measured at three temperatures, 25, 40, and 60 °C. The pressure was varied between 10 and 150 bar at 40 and 60 °C, whereas at 25 °C the pressure was varied between 10 and 60 bar to remain below the vapor pressure of CO₂ at this temperature. Some experiments were repeated several times at similar conditions to ascertain the reproducibility of the measurements. The reliability of these measurements was further verified by matching literature values of the solubility of CO₂ in toluene,⁴⁴ acetonitrile,⁴⁵ and methanol^{46,47} to within experimental uncertainty (about 2% for these cases). The error bars indicated in the results section were obtained from propagation of error calculations, the details of which are given elsewhere.⁴³ The measurement uncertainties used in the propagation of error calculations are temperature (± 1 K), pressure (± 0.07 bar), mass (± 0.0002 g), liquid volume (± 0.002 mL), gas volumes (± 0.05 mL) and line volumes (± 0.02 mL). This means that the uncertainty in the measurements is higher at low pressures, where the amount of gas absorbed is small. At intermediate pressures the error is smaller because the amount of gas absorbed with each increase in pressure is large. However, in ILs, where the solubility increase with increasing pressure becomes small again at the highest pressures, the error becomes larger again at the highest pressures.

Materials. Coleman instrument grade CO₂ was obtained from Mittler Supply Inc. The list of ILs used in the current study, including the source of the IL, water content, and halide content, is given in Table 1. Electrochemical grade (>99% purity) [bmim][methide] and [bmim][Tf₂N] were obtained from Covalent Associates, but [bmim][Tf₂N] was also prepared in our laboratory, as described below. [bmim][PF₆] was both purchased

from Sachem Inc. and prepared in our laboratory, as described below. All other ionic liquids were synthesized in our laboratory. The materials necessary for the synthesis of the ILs include 1-methylimidazole (616-47-7, Aldrich 99%, redistilled over KOH), 1,2-dimethylimidazole (1739-84-0, Aldrich 98%, redistilled over KOH), 1-butylimidazole (4316-42-1, Aldrich 98%, redistilled over KOH), 1-bromobutane (109-65-9, Aldrich 99%, washed with concentrated sulfuric acid and distilled over P₂O₅⁴⁸), 1-bromohexane (111-25-1, Aldrich 98%, washed with concentrated sulfuric acid and distilled over P₂O₅⁴⁸), 1-bromooctane (111-83-1, Aldrich 99.2%, washed with concentrated sulfuric acid and distilled over P₂O₅⁴⁸), ammonium tetrafluoroborate (13826-83-0, Aldrich 97+%, used without purification), methyl trifluoromethanesulfonate (333-27-7, Aldrich 99+%, used without purification), silver nitrate (7761-88-8, Aldrich 99+%, used without purification), sodium dicyanamide (1934-75-4, Aldrich 96%, used without purification), hexafluorophosphoric acid (16940-81-1, Aldrich 60 wt % solution in water, used without purification), and lithium bis(trifluoromethylsulfonyl)imide or LiTf₂N (90076-65-6, Aldrich 97%, 3M 98%, used without purification). Solvents used include deionized water from a Millipore purification unit and redistilled 99.9% grade dichloromethane obtained from Fisher Scientific.

All ILs, including those obtained from Sachem Inc. and Covalent Associates except for [bmim][methide], were washed with water to remove byproducts and any impurities as well as any degradation products. After obtaining a colorless clear IL (sometimes mixing with charcoal was necessary), each sample was dried under vacuum ($\sim 10^{-2}$ Torr) at 75 °C for at least 48 h. All ionic liquids synthesized in our laboratory were analyzed by proton NMR spectroscopy to ascertain the lack of any major impurities. The water content of the IL was determined from Karl Fischer titration (Aquastar V-200 Volumetric titrator, EM Science). The typical uncertainty in these measurements is $\pm 10\%$ of the reading, with a detection limit of 50 ppm. Halide (Cl⁻ and Br⁻) and ammonium ion contents were measured using an Oakton ion 510 series pH/mV/Ion/°C meter with Cole-Parmer ion specific probes (27502-13 for Cl⁻, 27502-05 for Br⁻, and 27502-03 for NH₄⁺), where the detection limit for all these probes is less than 10 ppm.

Synthesis. The synthesis of the ILs used in this study was accomplished as described below.

[bmim][Br], [hmim][Br], and [omim][Br]. These ILs, 1-butyl-3-methylimidazolium bromide ([bmim][Br]), 1-hexyl-3-methylimidazolium bromide ([hmim][Br]), and 1-octyl-3-methylimidazolium bromide ([omim][Br]), are precursors that are

needed to synthesize the desired compounds. 1-Methylimidazole was reacted with an excess of an alkyl halide (1-bromobutane, 1-bromohexane, or 1-bromooctane) in a round-bottom flask under a nitrogen atmosphere to produce the 1-alkyl-3-methylimidazolium halide ([bmim][Br], [hmim][Br], or [omim][Br]).

[hmim][Br]. This is another precursor IL, 2,3-dimethyl-1-hexylimidazolium bromide ([hmim][Br]), that is needed in the synthesis of [hmim][Tf₂N]. [hmim][Br] was synthesized in the same manner as [hmim][Br] with the exception that 1,2-dimethylimidazole was used instead of 1-methylimidazole.

[bmim][BF₄], [bmim][TfO], and [bmim][DCA]. The synthesis of these ILs has been described elsewhere.⁴⁹

[bmim][NO₃]. 1-Butyl-3-methylimidazolium bromide ([bmim][Br]) was reacted with an excess of silver nitrate (AgNO₃) in water. Silver bromide (AgBr) precipitates out of the solution so the solution ([bmim][NO₃] + AgNO₃) was filtered to remove AgBr and dried under vacuum to remove water. It was then titrated with a dilute solution of [bmim][Br] in dichloromethane (DCM) until no formation of AgBr was observed. The solution was filtered and dried under vacuum to remove all the solvents.

[bmim][PF₆]. [bmim][Cl] was reacted in water with aqueous hexafluorophosphoric acid, and the [bmim][PF₆] product formed as a separate phase. It was washed repeatedly with water until no acid was detected in the washwater.

[bmim][Tf₂N]. As mentioned previously, we purchased this IL from Covalent Associates. However, we were prompted to synthesize our own sample to check the high-pressure phase equilibrium results for two reasons. First, in unrelated experiments we observed the formation of a solid precipitate from the Covalent Associates sample, which raised the question of possible impurities. In addition, the IL unexpectedly became slightly colored during recovery of the IL from solvents. We synthesized two separate samples of this IL, ND1 and ND2. [bmim][Br] and LiTf₂N were mixed in water, and the solution was stirred at room temperature overnight, leading to the formation of the ionic liquid as a separate phase.

[hmim][Tf₂N]. [hmim][Br] was reacted with LiTf₂N in water at room temperature, leading to the formation of the [hmim][Tf₂N] as a separate phase.

[hmmim][Tf₂N]. [hmmim][Br] was reacted with LiTf₂N in water at room temperature, leading to the formation of [hmmim][Tf₂N] as a separate phase.

[omim][Tf₂N]. [omim][Br] was reacted with LiTf₂N in water at room temperature, leading to the formation of the [omim][Tf₂N] as a separate phase.

Results and Discussion

The dependence of CO₂ solubility on the choice of anion, on the length of the alkyl chain on the cation, and on the substitution at the C2 position was investigated. Furthermore, we discuss the influence of degradation products, impurities, and water on the solubility of CO₂ in ILs.

Solubility of CO₂ in [bmim][Tf₂N]. The solubility of CO₂ in [bmim][Tf₂N] at 25 °C and pressures to 60 bar is shown in Figure 1 along with other temperatures, which will be described below. The lines shown in the figure are to guide the eye only. CO₂ solubility increases with increasing pressure, reaching over 0.7 mole fraction at 60 bar. A complete listing of all of the data, for this system, as well as all of the other systems investigated here, can be found in the Supporting Information. The data shown are for two separate runs with the Covalent Associates sample as well as experiments with the two different samples (ND1 and ND2) synthesized in our laboratory. Although we had some concerns about the purity of the Covalent

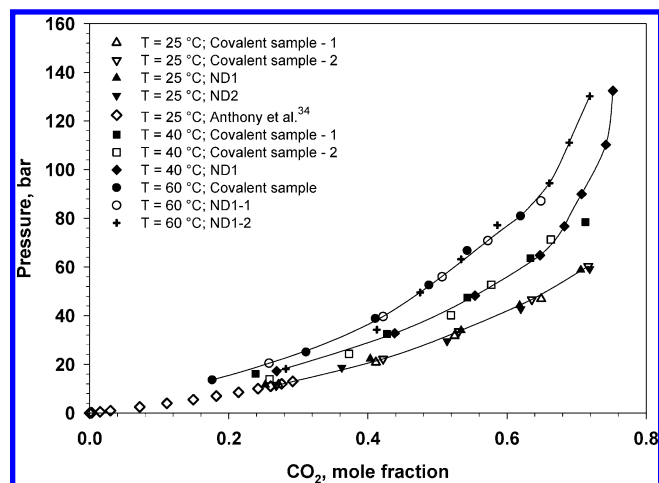


Figure 1. Effect of temperature on the solubility of CO₂ in [bmim][Tf₂N]. The results shown were obtained using samples from different sources.

Associates sample, it is clear that all of the data are entirely consistent within experimental uncertainty. The uncertainty values are not shown on most of the graphs for clarity, but they are listed for all systems in the Supporting Information. Uncertainties range from $\pm 3.8\%$ at low pressures to $\pm 0.96\%$ at higher pressures for this sample. The solubility measurements were obtained up to the vapor pressure of CO₂ at 25 °C so the solubility values reported are for gaseous CO₂ in the IL. Also shown on the graph are lower pressure measurements, obtained with a gravimetric microbalance by Anthony et al.³⁴ These values are in good agreement with those reported here. For example, Anthony et al.'s³⁴ solubility of 0.26 ± 0.01 mole fraction at 11 bar agrees very well with our measurement of 0.268 ± 0.014 mole fraction at 11.4 bar. Thus, we are convinced of the reliability of our measurements.

The solubilities of gases in liquids generally decrease with an increase in the temperature, and this is what we observe for CO₂ solubility in [bmim][Tf₂N], as shown in Figure 1 for temperatures between 25 and 60 °C. Multiple data sets, using all three [bmim][Tf₂N] samples, are included in the figure. The pressures for the supercritical temperatures extend to about 140 bar. In the Henry's law region (where the solubility is directly proportional to the pressure), the enthalpy and entropy change upon absorption can be calculated as^{50,51}

$$\Delta h_1 = \bar{h}_1 - h_1^{\text{ig}} = R \left(\frac{\partial \ln P}{\partial (1/T)} \right)_{x_1} \quad (1)$$

$$\Delta s_1 = \bar{s}_1 - s_1^{\text{ig}} = -R \left(\frac{\partial \ln P}{\partial \ln T} \right)_{x_1} \quad (2)$$

where \bar{h}_1 and \bar{s}_1 are the partial molar enthalpy and entropy of the gas solute 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 gives an indication of the strength of interaction between the IL and gas, and the entropy provides a measure of effect of the dissolved gas on the liquid structure. Of course, none of these measurements are in the Henry's law region. However, rough estimates from these data for [bmim][Tf₂N] give Δh between -13 and -16 kJ/mol, which is reasonably consistent with those calculated from lower pressure measurements.³⁴

It is also important to note the upward curvature of the isotherms. At the highest pressures further increase in pressure

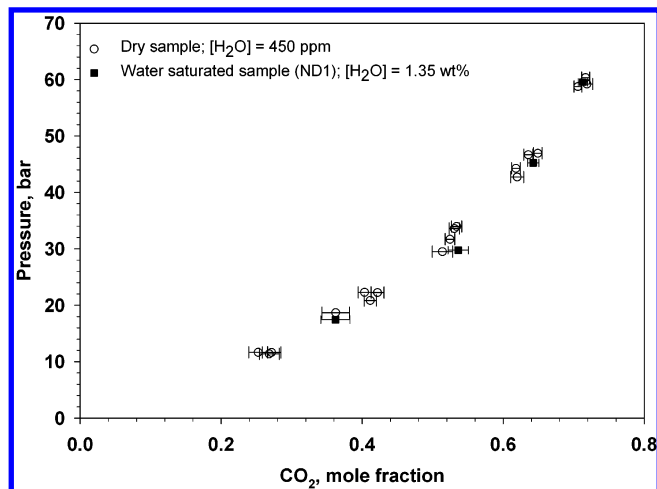


Figure 2. Effect of water content on the solubility of CO₂ in [bmim]-[Tf₂N] at 25 °C. The IL was saturated with water ([H₂O] = 1.35 wt %).

leads to very small increases in the CO₂ solubility, consistent with the observations reported in the literature.^{28,30,31}

Even though most ILs are water stable, they are highly hygroscopic in nature. Therefore, the solubility of CO₂ in water-saturated ILs will be important for practical applications. The effect of water on the solubility of CO₂ in [bmim][Tf₂N] at 25 °C is shown in Figure 2. We compare a dried sample (Covalent as well as ND samples; [H₂O] = 450 ppm) with one containing 1.35 wt % (13 500 ppm) or 24.2 mol % water, as determined by Karl Fischer titration. This is in agreement with the solubility limit of water in [bmim][Tf₂N].⁵² The presence of water had essentially no effect on the solubility of CO₂ in [bmim][Tf₂N], consistent with one previous observation.³⁸ One possible explanation is that any hydrogen bonding of the water with the [Tf₂N] anion does not eliminate [Tf₂N] anion/CO₂ interactions.³⁶

Effect of Anion on CO₂ Solubility. Solubility measurements,^{34,36} spectroscopic studies,⁵³ and molecular simulations³⁶ indicate that CO₂ solubility in ILs depends primarily on the strength of interaction of the CO₂ with the anion. Since the number of anions studied previously is rather limited, here we present the solubility of CO₂ in seven different ILs that differ only in the choice of anion. All of the ILs have the 1-butyl-3-methylimidazolium ([bmim]) cation, but the anions span a wide range of chemical types and basicity. The anions are [BF₄], [PF₆], [TfO], [NO₃], [Tf₂N], [methide], and [DCA] (see Table 1 for the structures).

The effect of the anion on the solubility of CO₂ in [bmim] ILs at 25 °C is shown in Figure 3. Also shown in the figure are low-pressure results for three of the ILs, [bmim][BF₄], [bmim][PF₆], and [bmim][Tf₂N], which were measured with a gravimetric microbalance^{32–35} and are consistent with the higher pressure results presented here. As mentioned previously, the results shown for [bmim][NO₃] and [bmim][PF₆] obtained in the current study are different from the results reported by our group several years ago.²⁷ We attribute this discrepancy, which is somewhat outside the error bars we report, to our ignorance of impurities and degradation products (as will be discussed in detail below for [bmim][PF₆]) in our early work on ILs.

The solubility of CO₂ increases with increasing pressure for all seven ILs, as expected. CO₂ is least soluble in the two ILs with nonfluorinated anions, [NO₃] and [DCA]. It has the highest solubility in ILs with anions containing fluoroalkyl groups, [TfO], [Tf₂N], and [methide]. The solubility in the two ILs with inorganic fluorinated anions, [BF₄] and [PF₆], lie in between

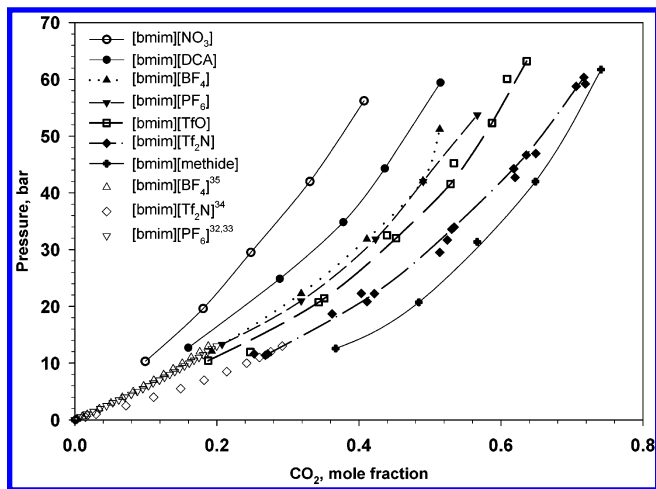


Figure 3. Effect of the anion and pressure on the solubility of CO₂ in [bmim] cation based ILs at 25 °C.

these two groups. It is common knowledge that fluoroalkyl groups are “CO₂-philic”, although the exact mechanism of this phenomenon is poorly understood.^{54–56} Nonetheless, researchers will frequently add fluoroalkyl ponytails to otherwise insoluble substrates in order to dissolve them in supercritical CO₂.^{57–63} Therefore, the relatively high solubility of CO₂ in [TfO], [Tf₂N], and [methide] may be due to favorable interactions between CO₂ and the fluoroalkyl substituents on the anion. In fact, CO₂ solubility increases with increasing number of CF₃ groups in the anion. For instance, at approximately 20 bar, the solubility of CO₂ in [bmim][methide] is 40% greater than in [bmim][TfO] at the same pressure.

CO₂ solubility does not correlate with the hydrogen bond basicity of the anion. We know the hydrogen bond basicity of four of the ILs investigated here, [bmim][BF₄], [bmim][PF₆], [bmim][TfO], and [bmim][Tf₂N], from spectroscopic studies using Kamlet–Taft probes⁶⁴ and a Cu²⁺ complex.⁶⁵ Both probes are consistent, yielding the following order of basicity: [TfO] > [BF₄] > [Tf₂N] > [PF₆]. The strength of hydrogen bonding between IL anions and water, as determined from FTIR spectroscopy,⁶⁶ yields a slightly different order for [bmim] ILs of interest here: [NO₃] > [TfO] > [Tf₂N] > [BF₄] > [PF₆]. From the data shown in Figure 3, it is clear that CO₂ solubility does not correlate with either of these measures of basicity or hydrogen-bond strength. Rather, at 25 °C, the solubility of CO₂ in [bmim] cation based ILs increases in the following order: [NO₃] < [DCA] < [BF₄] ~ [PF₆] < [TfO] < [Tf₂N] < [methide]. We believe this is because acid/base interactions of CO₂ with anions are only one mechanism of interaction. CO₂ interactions with fluorous alkyl chains may also be important. Another possible explanation is related to the molar volumes of the ILs. If one considers only nonpolar and induced dipole interactions (which is clearly a gross oversimplification for an ionic liquid), then the activity coefficient (and subsequently the solubility) of CO₂ in the ILs should be related to the difference in the solubility parameter (polarizability per volume) of the IL and the CO₂. If one assumes that the polarizability is similar for all the ILs, then the solubility parameter will be smaller (and CO₂ solubility higher) for ILs with larger molar volumes. This is, roughly, the trend that we observe. See Supporting Information for values of the IL molar volumes.

The solubility of CO₂ in the seven [bmim] ILs at two higher temperatures, 40 and 60 °C, is shown in Figures 4 and 5. As in the earlier graph, the lines are meant to guide the eye only. Of course, we are able to extend the measurements to higher

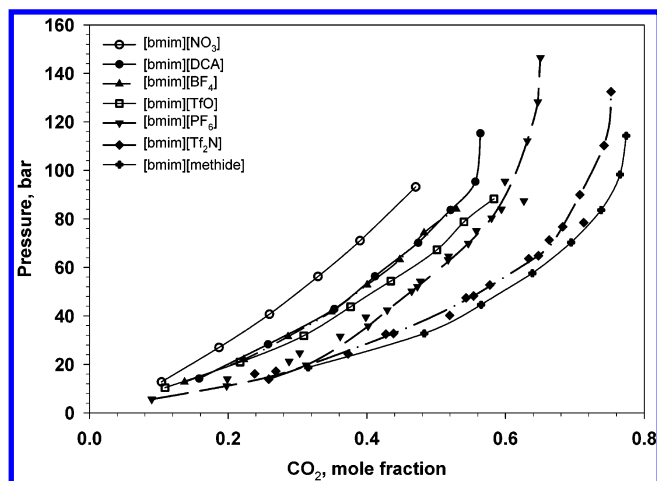


Figure 4. Effect of anion and pressure on the solubility of CO₂ in [bmim] cation based ILs at 40 °C.

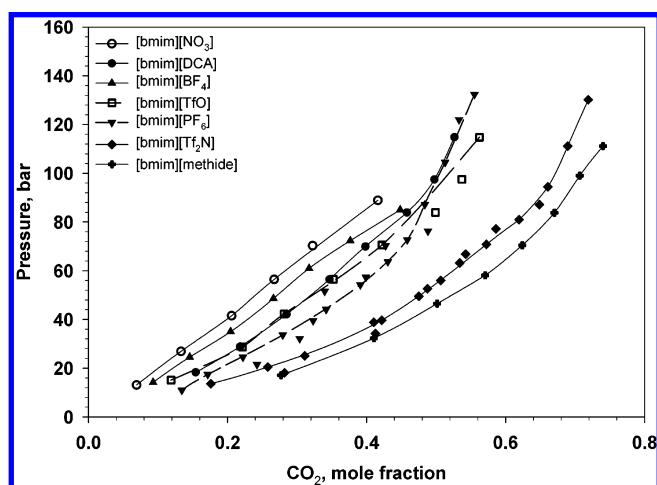


Figure 5. Effect of anion and pressure on the solubility of CO₂ in [bmim] cation based ILs at 60 °C.

pressures for these supercritical temperatures. From the data in Figures 3–5 (presented in tabular form in Supporting Information), it is clear that the enthalpies and entropies of dissolution are different for the different ILs. Of particular note is that the enthalpy for CO₂ dissolution in [bmim][BF₄] is significantly greater than [bmim][DCA] and [bmim][NO₃] so that at 60 °C the order of increasing CO₂ solubility has changed to [NO₃] < [BF₄] < [DCA] ~ [PF₆] ~ [TfO] < [Tf₂N] < [methide].

Effect of Cation Alkyl Chain Length. Another aspect of ILs that can affect the solubility of CO₂ is the substituents on the imidazolium ring. For example, the alkyl chain length and the substitution of CH₃ for H at the C2 position have dramatic influences on liquid–liquid phase behavior of ILs with alcohols.⁵² To study the influence of cation alkyl chain length, we compare the solubility of CO₂ in [bmim][Tf₂N], [hmim][Tf₂N], and [omim][Tf₂N] at 25, 40, and 60 °C. The results at 40 °C, including reproducible replicate runs for [hmim][Tf₂N], are shown in Figure 6. In general, the CO₂ solubility increases with an increase in the alkyl chain length at all pressures, with the increase being more apparent at higher pressures. For instance, at a pressure of 83.7 bar, the solubility increased from 0.72 ± 0.009 mole fraction for [hmim][Tf₂N] to 0.763 ± 0.007 mole fraction for [omim][Tf₂N]. Similar trends were observed at 25 and 60 °C. These results are consistent with previous reports for imidazolium-based ILs. Shariati and Peters found an increase in the solubility of CO₂ in [PF₆]-based ILs when the alkyl chain length was increased from ethyl to hexyl.^{30,31} Blanchard et al.

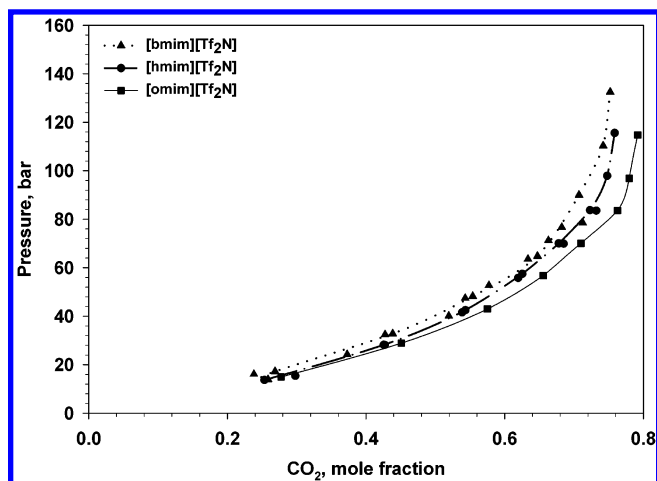


Figure 6. Effect of alkyl chain length on the cation on the solubility of CO₂ in [Tf₂N] anion based ILs at 40 °C. The alkyl chain length was varied between C4 and C8.

reported that CO₂ solubility increased when the alkyl chain length was increased from butyl to octyl for ILs with both [PF₆] and [BF₄] anions.²⁷ It should be noted that the densities of imidazolium-based ILs decrease with increasing alkyl chain length.^{67,68} Thus, one would anticipate greater free volume in the ILs with longer alkyl chains. In other words, we suspect that greater CO₂ solubility in ILs with longer cation alkyl chains can be explained by entropic rather than enthalpic arguments. Unfortunately, these measurements are at relatively high concentrations of CO₂ so one cannot obtain good estimates of the enthalpy and entropy of dissolution (according to eqs 1 and 2). From our low-pressure studies,^{32,51} we find that the solubility needs to be sufficiently below 10 mol % for eqs 1 and 2 to be valid.

Comparison of the solubility of CO₂ in [bmim][methide] and [omim][Tf₂N] indicates that the solubility is greater in [omim]-[Tf₂N] at all three temperatures. Thus, one can increase CO₂ solubility in ILs by increasing alkyl chain length on the cation as well as by adding expensive CF₃ groups to the anion.

Substitution at the C2 Position. A hydrogen at the C2 position (the carbon between the two nitrogens) in the imidazolium ring is known to be quite acidic, which is reflected in spectroscopic measures of the hydrogen bond donating ability (α) of ILs.⁶⁴ Recently, Cadena et al.³⁶ have shown that CO₂ prefers to interact with the anion and the interactions with the cation are secondary in nature, consistent with FTIR measurements.⁵³ The simulation work was further supported with experimental measurements of CO₂ solubility up to 13 bar, which were essentially independent of whether the substituent at the C2 position on the imidazolium ring was hydrogen or CH₃. We speculate that any dependence on the substituent at the C2 position will become more apparent at higher CO₂ concentrations, i.e., higher pressures. Therefore, we measured the solubility of CO₂ in [hmmim][Tf₂N] at 25, 40, and 60 °C and compared these results with those obtained with [hmim]-[Tf₂N], and the results are shown in Figures 7 and 8.

The solubility of CO₂ in [hmmim][Tf₂N] at 25, 40, and 60 °C and pressures to 120 bar is shown in Figure 7. Not surprisingly, the phase behavior for the system [hmmim][Tf₂N]/CO₂ binary system is similar to the others reported herein. Solubility increases with increasing pressure and decreases with increasing temperature. Moreover, the isotherms are concave up, indicating “diminishing returns”; i.e., at the higher pressures an increase in pressure results in smaller increases in solubility. The one unusual feature of this graph is the crossing of the 40

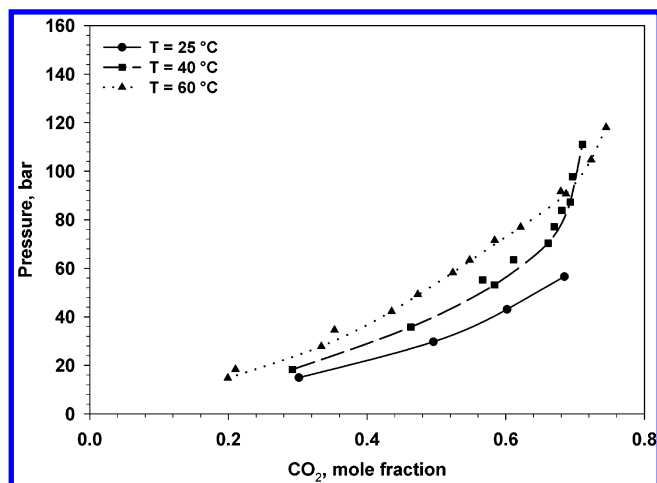


Figure 7. Effect of temperature and pressure on solubility of CO₂ in [hmmim][Tf₂N].

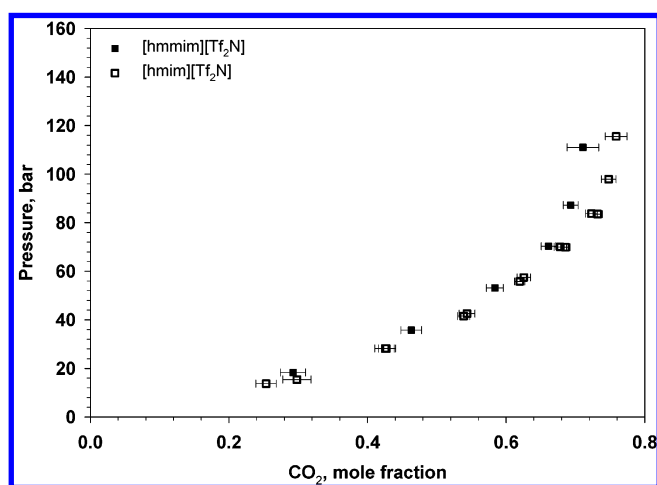


Figure 8. Effect of C2 substitution on the solubility of CO₂ at 40 °C in [Tf₂N] anion based ILs.

and 60 °C isotherms at the highest pressures, which was not observed for any of the other systems. The graph includes replicate runs so we are relatively confident of the trend.

To further understand the effect of C2 substitution on the solubility of CO₂, the solubility in [hmmim][Tf₂N] and [hmim][Tf₂N] at 40 °C is compared in Figure 8. At lower pressures replacing the protic hydrogen at the C2 position with a CH₃ group has very little effect on the solubility of CO₂, consistent with the previous low-pressure study.³⁶ However, at the highest pressures the two curves do diverge, with the [hmim][Tf₂N] having a somewhat higher capacity for CO₂ than [hmmim][Tf₂N]. For instance, at 97.8 bar the solubility in [hmim][Tf₂N] is 0.75, but just 0.7 mole fraction in [hmmim][Tf₂N], which is a statistically significant difference. A similar trend was observed at 25 °C, but at 60 °C the differences were quite small. Our interpretation of these results is that in both [hmim][Tf₂N] and [hmmim][Tf₂N] the preferred location for the CO₂ is in close proximity to the anion. However, as the amount of CO₂ increases (with increasing pressure), some CO₂ will adopt a secondary location, closer to C2 of the imidazolium ring, in the case of [hmim][Tf₂N]. Thus, the total capacity for CO₂ is slightly higher for [hmim][Tf₂N] than [hmmim][Tf₂N]. It should be noted that the molecular simulations^{36,69} show that the reason for the slightly favorable secondary location is not direct CO₂ interaction with the acidic hydrogen. Rather, in the case of [hmim][Tf₂N] the partial positive charge on N3 (the nitrogen with the methyl substituent) is greater than in [hmmim][Tf₂N], and it is

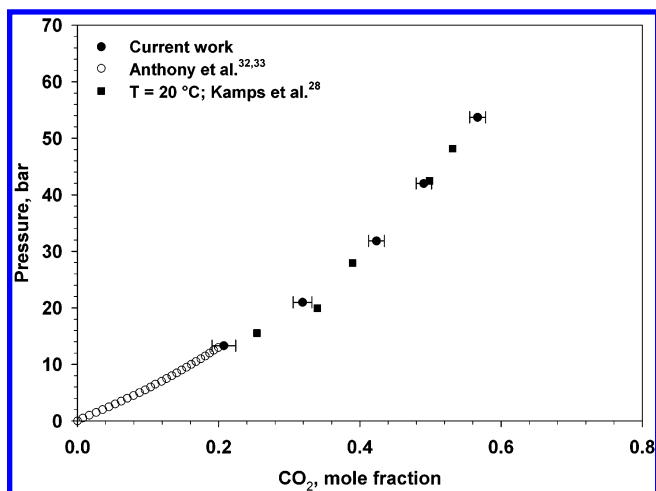


Figure 9. Comparison of the solubility of CO₂ in [bmim][PF₆] at 25 °C with literature values.

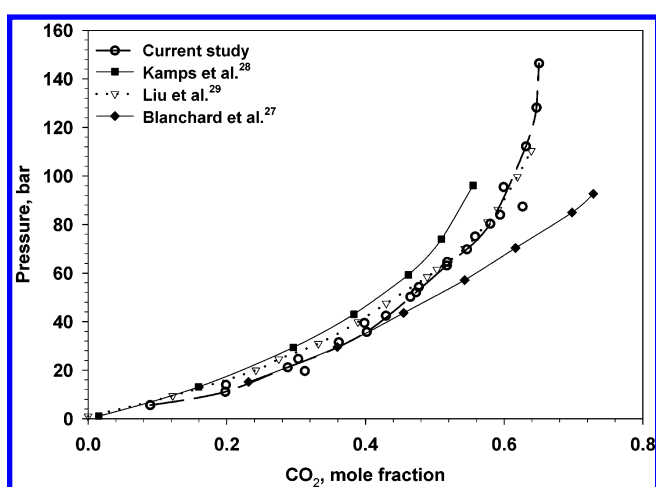


Figure 10. Comparison of the solubility of CO₂ in [bmim][PF₆] at 40 °C with literature values.

actually the favorable interaction of the CO₂ with the partial positive charge on N3 that accounts for the differences between [hmim][Tf₂N] and [hmmim][Tf₂N].

Solubility of CO₂ in [bmim][PF₆]. The phase behavior for the system [bmim][PF₆]/CO₂ has been widely reported by several research groups.^{27–29} We have previously reported the solubility of CO₂ in [bmim][PF₆] at 40, 50, and 60 °C up to 100 bar.²⁷ We have also reported the solubility at 25 °C up to 13 bar.^{32,33} A comparison of all the data available in the literature indicates a certain degree of discrepancy in the solubility measurements. To understand this discrepancy, we measured the solubility in [bmim][PF₆] in the current study, and we report the new results and discuss the possible reasons for the observed discrepancy.

The solubility of CO₂ in [bmim][PF₆] at 25 °C obtained in the current study is shown in Figure 9, and these results agree remarkably well with the low-pressure (<13 bar) points reported by Anthony et al.^{32,33} The results also agree remarkably well with those reported by Kamps et al.,²⁸ which is somewhat surprising since the Kamps et al. data are at 20 °C, where one would expect the solubility to be a little higher.

The results obtained at 40 °C in this study are compared with those reported by various research groups in Figure 10. While the agreement at low pressures seems to be reasonable for all the data sets, the differences at higher pressures are significant. First, the data we report in the current study at pressures above

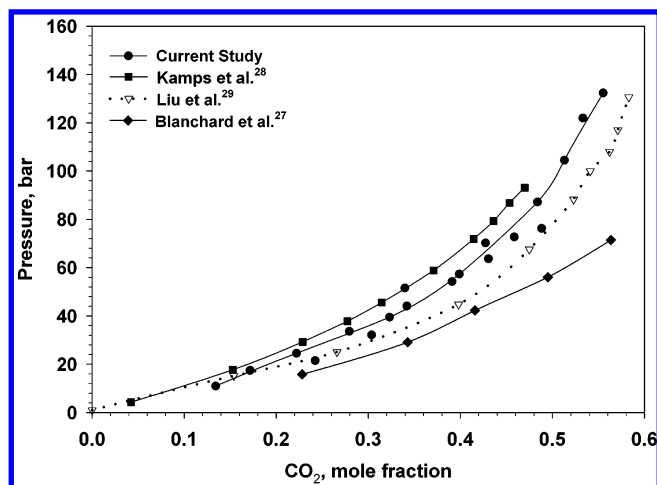


Figure 11. Comparison of the solubility of CO₂ in [bmim][PF₆] at 60 °C with literature values.

about 40 bar are significantly different than the values that our group reported previously.²⁷ As mentioned above, we were not cognizant of all the various impurities and degradation products that were undoubtedly present in the sample used in those early experiments. We simply took the sample and dried it before use. The results from the current study should be chosen over those reported in our early work. A comparison with the data reported by Kamps et al.²⁸ indicates good agreement at low pressures, but at higher pressures they report a slightly lower CO₂ solubility than we do here. For example, at approximately 43 bar we measured the solubility to be 0.43 mole fraction in the current study, while Kamps et al.²⁸ found the CO₂ solubility to be 0.38 mole fraction. However, our current results agree well with the values reported by Liu et al.²⁹ at all pressures. From these results one can conclude that the solubility results for CO₂ in [bmim][PF₆] from various research groups are not in good agreement.

The disagreement is further accentuated in Figure 11, which shows the CO₂ solubility data from various groups at 60 °C. Once again, the early results from our group²⁷ clearly overestimate the solubility and should be disregarded. As at 40 °C, Kamps et al.²⁸ report lower CO₂ solubility values at this temperature than we report in the current study. However, at this temperature, Liu et al.²⁹ report significantly higher solubility than we report in the current study.

We do not believe that the discrepancies highlighted in Figures 10 and 11 can be explained by differences in experimental technique or uncertainties in the various measurements. We believe that much more likely causes are impurities and degradation products in the samples. We readily acknowledge that we were not cognizant of impurities, other than water, in the samples used in our early work. In addition, Hardacre et al.⁷⁰ have shown recently that both [PF₆] and [BF₄] anions are unstable, even at room temperature, in the presence of water. These anions degrade rapidly to form fluoride-based impurities, in a process that would not be detected by proton NMR. Since normal drying will usually leave at least a few hundred ppm of water in the samples, degradation may still be possible even if the ILs are stored under nitrogen in a drybox. Obviously, when our group first published the phase behavior of [bmim][PF₆]/CO₂²⁷ we were unaware of the stability issues concerning this IL. The only precaution taken was to dry the sample thoroughly before use. Thus, it could have had significant amounts of degradation products present. By contrast, the sample used in the current work was thoroughly washed with water several times to remove any water-soluble impurities or degradation

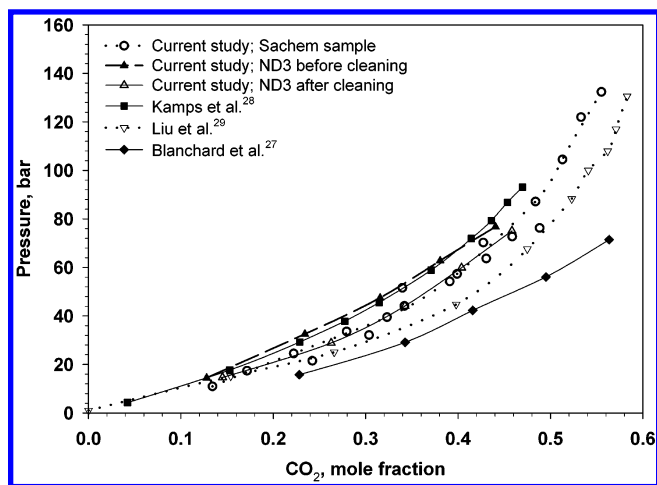


Figure 12. Effect of degradation products on the solubility of CO₂ in [bmim][PF₆] at 60 °C.

products and charcoal was used to remove organic impurities. As a further precaution, the sample was passed through an alumina column, and finally it was thoroughly dried at 70 °C under vacuum for at least 48 h to approximately 230 ppm water. The sample was used immediately to measure the solubility of CO₂. Even though the dried sample was stored in a drybox, the sample was purified as described if it was stored for more than a week in between measurements. The results shown thus far were obtained using samples that were subjected to this rigorous cleaning procedure immediately before each use.

Thus, we believe that some of the discrepancies between our current data and those presented by Kamps et al.²⁸ and Liu et al.²⁹ for [bmim][PF₆] may be due to impurities and degradation products. We tested this hypothesis by using various samples treated differently, and the results at 60 °C are shown in Figure 12. The results that we have shown thus far are for the sample obtained from Sachem Inc., which was cleaned rigorously before each use, as described above. As discussed previously, the solubilities measured in the current study for this sample were greater than those reported by Kamps et al.²⁸ The second sample is labeled “ND3 before cleaning”. This is a sample synthesized in our group that was dried and stored for more than 6 months in a drybox prior to use. Upon removal from the drybox, we further dried this sample to 300 ppm water (approximately equivalent to the Sachem sample when used) but did not subject it to any type of cleaning. As shown in Figure 12, the solubility of CO₂ in this sample is less than in our rigorously cleaned Sachem sample and in remarkably good agreement with the solubilities reported by Kamps et al.²⁸ at all pressures. We then took the ND3 sample and cleaned and dried it thoroughly as described above. The CO₂ solubility was measured again in this thoroughly cleaned sample, “ND3 after cleaning”, and the CO₂ solubility increased. In fact, the results for this cleaned sample are in agreement with the results we have presented in this study for the cleaned Sachem sample. Similar trends were observed at 40 °C. In summary, we believe the discrepancy observed in the literature regarding the solubility of CO₂ in [bmim][PF₆] might be due to the presence of impurities and degradation products in the IL. Because of these difficulties, especially with degradation of the [PF₆] and [BF₄] anions, we do not recommend further investigations with ILs of those two types.

Molar Volumes and Volume Expansion. Another parameter that was measured in this study was the molar volume of the IL and IL/CO₂ mixtures, and these data are included in the Supporting Information. Addition of CO₂ to normal organic liquids generally leads to a significant increase in the volume

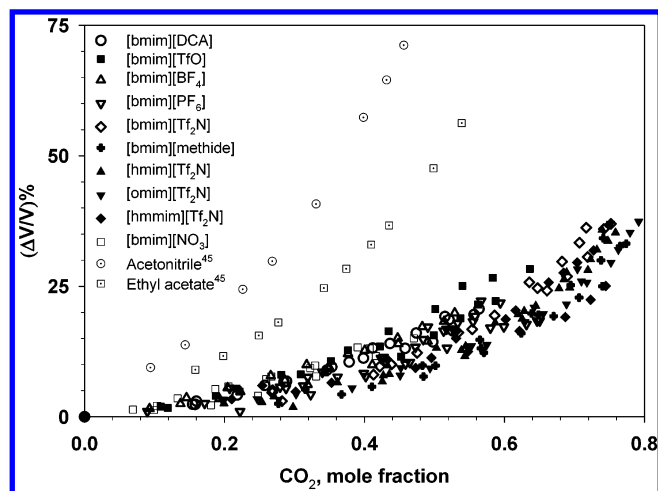


Figure 13. Volume expansivity based on change in total volume of the liquid upon addition of CO₂ as defined by eq 3 for various ILs and comparison with organic solvents.

of the liquid phase. This increase in liquid volume is accompanied by a decrease in mixture solvent strength, and this is why CO₂ is an effective antisolvent in the gas antisolvent process.^{71,72} The classical definition of volume expansion is based on the change in the absolute volume of the liquid.⁷³

$$\frac{\Delta V}{V} \% = \frac{V_L(T, P, x_1) - V_2(T, P_0)}{V_2(T, P_0)} \times 100 \quad (3)$$

where V_L is total volume of the liquid mixture at a given temperature and pressure and V_2 is the volume of the pure liquid at the same temperature and ambient pressure.

Using this classical definition, Badilla et al.⁷⁴ have shown that the volume expansion with added CO₂ is weakly dependent on the choice of the organic solvent, for the group of organic solvents they examined, and that the percent expansion can be very large. For example, an increase in the concentration of CO₂ from 0 to 0.92 in acetonitrile results in a volume expansion greater than 1100%.⁷⁴ This definition (eq 3) was used to calculate the percent volume expansion of all the ILs used in the current study, and the results are shown for the data at 25, 40, and 60 °C in Figure 13, where the data seem to collapse into a single curve at all temperatures for a particular compound. The most striking result is the difference in the volume expansion of the ILs in comparison with common organic solvents. The largest expansions observed are for the [methide] and [Tf₂N] ILs and for ones with longer alkyl chains because these are the ones with the greatest CO₂ solubility. We note that if the volume expansion is plotted as a function of weight fraction of CO₂, the differences between the ILs and common organic solvents are not as great (due to the molecular weight differences).

Badilla et al.⁷⁴ proposed a different definition for the volume expansion, based on the molar volume (eq 4), which shows dependence on the choice of solvent and gas.

$$\frac{\Delta V}{V} \% = \frac{\tilde{V}_L(T, P, x_1) - \tilde{V}_2(T, P_0)}{\tilde{V}_2(T, P_0)} \times 100 \quad (4)$$

In this definition, the percent volume expansion is given by the change in the molar volume of the liquid phase upon addition of CO₂ compared to the molar volume of pure liquid at the same temperature and ambient pressure. Percent molar volume expansions calculated using eq 4 are shown in Figure 14 for

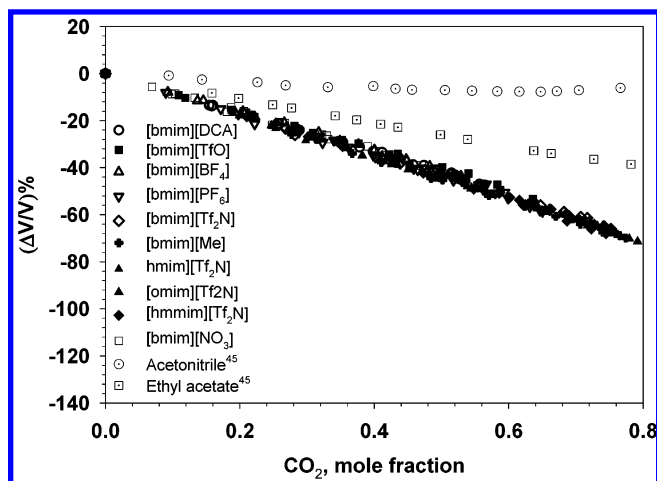


Figure 14. Volume expansivity based on change in molar volume of the liquid upon addition of CO₂ as defined by eq 4 for various ILs and comparison with organic solvents.

IL/CO₂ systems at all three temperatures as well as for two organic solvents. Even for the organic solvent systems, the molar volume initially decreases. This is due to the fact that initially the volume does not increase very much even though significant amounts of CO₂ dissolve in the liquid phase; i.e., the density increases. Further addition of CO₂ to organic solvents leads to very large increases in the molar volume of the liquid phase and, hence, a positive percent molar volume expansion for some cases. For organics the degree of percent volume expansion is very different for compounds of different molecular weights. The percent molar volume expansion of all of the ILs continues to decrease with further addition of CO₂. Moreover, the percent molar volume expansion appears to be independent of the choice of IL even though the molecular weights of the ILs differ by a factor of 2. These results indicate that the ionic liquids do not expand substantially upon dissolution of large amounts of CO₂.

The results can have a profound effect on our understanding of these solvent systems. Since the volume of the ILs does not change significantly upon dissolution of large amounts of CO₂, one might speculate that the solvent strength of these mixtures will decrease only marginally when CO₂ is added. Previously, we reported the solvent strength of IL/CO₂ systems according to Kamlet–Taft parameters.⁷⁵ We found that the addition of CO₂ decreased the solvent strength of ILs to a very small extent. Particularly, CO₂ did not reduce the polarity/polarizability of the mixture, and it was unable to disrupt the hydrogen-bonding interactions between the dye molecules and ILs. One possible explanation for this behavior is that the ILs do not expand upon addition of CO₂. The results presented in this paper support this argument.

Conclusions

We report the solubility of carbon dioxide in 10 different imidazolium-based ILs as a function of both temperature and pressure to evaluate the dependence on the choice of anion and substituents on cation ring. As expected, the solubility decreased with increasing temperature and increased with increasing pressure for all the ILs investigated. The increase in solubility with increasing pressure became quite small at the highest pressures investigated (about 150 bar) for all the ILs. The solubility depends strongly on the choice of anion, with CO₂ solubility being highest in the ILs with fluoroalkyl groups in the anion ([methide] and [Tf₂N]) and lowest in the ILs with nonfluorinated inorganic anions ([NO₃] and [DCA]). The

addition of over 1 wt % water to [bmim][Tf₂N] did not affect the CO₂ solubility.

The choice of alkyl groups on the cation affected the CO₂ solubility to a smaller extent. Increasing the alkyl chain length from butyl to octyl increased the CO₂ solubility. Replacement of the C2 hydrogen with a CH₃ group decreases the solubility marginally at low pressures, but this decrease became more apparent at high pressures.

It was also shown that the solubility of CO₂ in [bmim][PF₆] appears to depend on the presence of degradation products and impurities in the IL, and these are the likely explanations for discrepancies between various different sets of data in the literature for this compound. Removal of these impurities is important in obtaining consistent solubility results.

Finally, measurements of the molar volumes of the liquid phase in all of the experiments show that all of the ionic liquids expand a relatively small amount when CO₂ is added.

Acknowledgment. The financial support from the donors of the Petroleum Research Fund, administered by American Chemical Society, and the State of Indiana 21st Century Research and Technology Fund (#909010455) is greatly appreciated. We also acknowledge the generous contribution of [bmim][methide] from Covalent Associates. Finally, we thank Dr. Mark J. Muldoon for synthesis of the [bmim][DCA] sample and Mr. Jacob M Crosthwaite for the synthesis of the [bmim][NO₃], [hmim][Br], [hmim][Tf₂N], and [omim][Tf₂N] ILs.

Supporting Information Available: Tables of VLE data for [bmim][NO₃], [bmim][BF₄], [bmim][DCA], [bmim][TfO], [bmim][methide], [bmim][PF₆], [bmim][Tf₂N], [hmim][Tf₂N], [hmmim][Tf₂N], and [omim][Tf₂N] ILs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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