High-pressure solubility of carbon dioxide in imidazolium-based ionic liquids with anions [PF$_6$] and [BF$_4$]

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(*Received 3 March 2009 • accepted 23 March 2009*)

Abstract−The solubility of carbon dioxide in three ionic liquids (ILs) under supercritical fluid condition was measured at pressures up to 32 MPa and at temperatures of 313.15, 323.15, and 333.15 K in a high-pressure view cell. The imidazolium-derivative ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF$_6$]), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF$_4$]), and 1-octyl-3-methylimidazolium tetrafluoroborate ([omim][BF$_4$]) were employed in this research. The effects of pressure, temperature, nature of anion and cation as well as the water content on the solubility of CO$_2$ in the ILs were investigated experimentally. The solubility of CO$_2$ in the IL was higher for the ILs with longer cationic alkyl group and for the ILs with lower anion polarity. The lower the water content or the lower the temperature as well as the higher the pressure, the higher was the solubility of CO$_2$.

Key words: Solubility, Carbon Dioxide, Ionic Liquid, Water Content, Anion, Cation

INTRODUCTION

Many ionic liquids (ILs) have been recognized as new green chemicals because of their useful and unique properties, such as negligible vapor pressure, non-toxicity (note that halide-containing ILs may have toxicity at high temperatures) and non-flammability, thermal stability, and good ionic conductivity [1]. Among them, room temperature ionic liquids (RTILs) which are organic salts are getting significant attention for a large variety of applications in many areas that span from pure sciences to industry, because their melting points are below room temperature [2]. Existing as a liquid over a wide temperature range, those compounds have generally been considered as an alternative to conventional organic solvents in a variety of reactions and separation processes [3]. Employing conventional solvents, the toxic volatile organic solvents vaporize after the reaction and escape into the atmosphere during the separation process, making a significant contamination to the environment. However, if nonvolatile IL solvents are used instead of volatile organic solvents, negative impacts on the environment or contamination of reaction products are prevented. The used IL solvents can then be recycled without vapor contamination. This is the main reason why ILs are considered as an environmentally friendly alternative to the harmful organic solvents [3]. Besides, ILs have very high polarity and good catalytic activity due to their ionic nature [4-6]. Another advantage of ILs is that they can dissolve both inorganic and organic compounds due to their high polarity and their organic functional

groups [1-3]. Moreover, ILs are normally synthesized quite easily, and their ionic nature offers many possibilities to create new compounds [1,2,4-6]. That unique opportunity, often denoted with the term "designer solvent," has paved the way for ILs into a wide variety of applications, such as catalysis, separations, and electrochemistry [2,3].

On the other hand, supercritical fluids as solvents are characterized by a unique property that allows tuning of the solubility by adjusting pressure and temperature. They have gas-like transport properties and dissolve materials like a liquid. For that particular reason, they can also be used in numerous applications, including extraction, fractionation, chemical reaction, polymerization, and materials processing. Among all the supercritical fluids, supercritical carbon dioxide (scCO$_2$) is the most attractive solvent due to its moderate critical condition (304.1 K and 7.38 MPa) and because it is non-toxic, nonflammable, and inexpensive. Therefore, scCO$_2$ has been considered as an environmentally friendly clean solvent.

Combining the above-mentioned advantages of scCO$_2$ and ILs may provide a clean synthesis process in which reaction and separation occur consecutively. Due to the strong electrostatic forces between cations and anions, scCO$_2$ dissolves well in ILs, but ILs actually do not dissolve in scCO$_2$ [7,8]. The organic products from a reaction in the IL-phase can, therefore, be extracted by supercritical CO$_2$, allowing only a small amount of cross-contamination between the IL and scCO$_2$ phases [9].

The solubility of CO$_2$ in ILs at pressures higher than atmospheric was investigated by many researchers [7,10-19]. In many cases, those experiments resorted to the IL [bmim][PF$_6$], since it was one of the first sufficiently air- and water-stable compounds that allowed

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successful and reproducible thermophysical investigations. Brennecke and co-workers [7,10] measured the CO_2 solubilities in several imidazolium-based ionic liquids using a high-pressure vapor-liquid phase equilibrium apparatus and correlated the solubility with the liquid molar volume using the "free volume" concept. In another study, Brennecke and co-workers [11] proved that the solubility of CO_2 in ILs increased as more hydrogen atoms were replaced by fluorine atoms, allowing higher solubilities of other gases in the IL-phase. Their experiments elucidated the effects of the anion and of the cation alkyl-chain length as well as the effect of temperature, and they compared their results with the literature data. Fu et al. [12] measured the solubility of CO_2 in ILs containing different amounts of water at high pressures up to 25 MPa. Peters and co-workers [13] investigated the high-pressure phase behavior of the binary system [omim][BF$_4$]+CO_2 in the pressure and temperature ranges of 0.1 to 100 MPa and 303 to 363 K, respectively, and observed a drastic increase in the pressure if the CO_2 mole fraction (solubility) became higher than 0.6.

Maurer and co-workers [14,15] measured the solubility of CO_2 in [bmim][PF$_6$] up to 9.8 MPa using a synthetic view-cell technique and correlated their results by means of an extended Henry's law. Chen et al. [16] measured the solubility of CO_2 in two different types of hydroxyl ammonium- and imidazolium-based ILs at pressures as high as 11 MPa. Kim et al. [17] measured the solubility of CO_2 in imidazolium-based ionic liquids up to about 1 MPa and analyzed it with group contribution theory. Shiflett and Yokozeki [18] employed a commercial gravimetric microbalance to measure the solubilities of CO_2 in both [bmim][BF$_4$] and [bmim][PF$_6$] up to 2 MPa and correlated the results with the Redlich-Kwong equation of state.

The solubility data are important in designing the synthesis-separation process using both IL and scCO$_2$. However, there is still a lack of CO_2 solubility data in ILs at pressures where CO_2 is already in the supercritical state. In the literature cited here [10-19], all solubility data were measured at low pressures of less than 10 MPa, except for the data by Muldoon et al. [11] who measured up to 13 MPa, by Gutkowski et al. [13] who even did experiments at 100 MPa, and by Fu et al. [12] who measured up to 25 MPa (only for [bmim][PF$_6$]). Therefore, in this study, the solubility of CO_2 in the three different ionic liquids [bmim][PF$_6$], [bmim][BF$_4$], and [omim][BF$_4$] is investigated up to obviously higher pressures of maximum 32 MPa. The effect of the water content in the IL on the solubility of CO_2 is discussed.

EXPERIMENTAL

1. Materials

The imidazolium-based ionic liquids [bmim][PF$_6$] (purity>99%, water content=12×10^{-4} in mass fraction, chloride content=0.79×10^{-4} in mass fraction), [bmim][BF$_4$] (purity>99%, water content=59×10^{-4} in mass fraction, chloride content=5.2×10^{-4} in mass fraction), and [omim][BF$_4$] (purity>99%, water content=10.5×10^{-4} in mass fraction, chloride content=1.01×10^{-4} in mass fraction) were purchased from C-Tri (Hwasung, Korea) and pretreated in the vacuum oven at 363.15 K for 12 h to remove water. The molecular structures of the above ionic liquids are shown in Fig. 1. CO_2 (99.5%) was purchased from Daedong Gastech (Daegu, Korea) and used
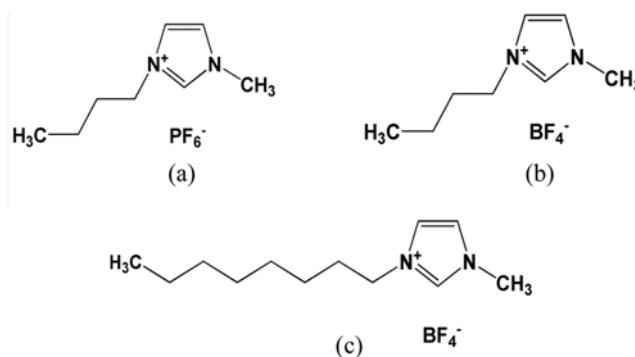

Fig. 1. The molecular structures of ionic liquids used in this study: (a) [bmim][PF$_6$], (b) [bmim][BF$_4$], and (c) [omim][BF$_4$].
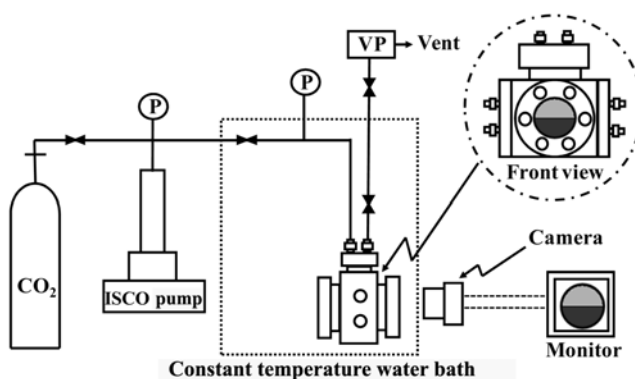

Fig. 2. A schematic diagram of the experimental equipment to measure the swelling and sorption behavior of ionic liquids in the presence of supercritical carbon dioxide (VP: vacuum pump, P: pressure sensor).

Table 1. The water (3) mass fraction ($w_3=m_3/(m_2+m_3)$) in the three ionic liquids (2) investigated here before and after the moisture removal treatment

Ionic liquids	Before/$10^4 w_3$	After/$10^4 w_3$
[bmim][PF$_6$]	7	1.7
[bmim][BF$_4$]	20	2.2
[omim][BF$_4$]	42	4.1

without further purification.

2. Measurement of CO_2 Solubility in ILs

The solubility of CO_2 in ILs was measured in a view-cell apparatus (Hanwool Model SC-6100) as shown in Fig. 2. Since the water content plays an important role, the IL samples were dried as described above. The water content before and after the drying process was measured by a Karl Fischer titrator (Barnstead International Aquametry I) and the results are given in Table 1. In all ILs, the initial water content was in the range from 7.0×10^{-4} to 42×10^{-4} in mass fraction and about 75 to 90% of water was removed after the drying step. However, a small amount of water (1.7×10^{-4} to 4.1×10^{-4} in mass fraction) still remained due to the strong polar nature of ILs.

To measure the CO_2 solubility, the view cell was evacuated and then filled with low-pressure CO_2. About 2.5 mL of IL was injected

into the view cell with a syringe. We obtained the weight of IL injected by measuring the weight of syringe before and after the injection with a balance (Mettler Toledo AG) to ±0.1 mg. The view cell was then placed in a constant temperature water bath controlled to ±0.1 K with a Lauda Immersion Thermostat B. The cell was kept at the same condition for 30 min to ensure the thermal equilibrium. High-pressure CO_2 was supplied to the view cell at a constant pressure controlled by an automatic syringe pump (ISCO Model 260D). The pressure in the cell was measured by a pressure gauge (Sensotec TJE/GM) to ±0.034 MPa. The amount of liquid CO_2 supplied to the cell was measured by the volume indicated on the syringe pump. The uncertainty of that measurement was about ±0.005 mL.

When the equilibrium was reached while stirring with a magnetic stirrer for 20 to 30 min, stirring was stopped to see the phase behavior at the new equilibrium. The liquid phase (i.e., the IL phase saturated with CO_2) and the vapor phase (i.e., the high-pressure CO_2 phase) in the view cell were recorded by a video camera connected to a 17 inch monitor on which the view was expanded by about 10 times [20]. The position of the phase boundary was measured on the monitor. The volume of each phase was then calculated using the calibration curve showing the volume of methanol injected with a precision syringe versus the height of the liquid level in the view cell. The liquid level on the monitor was measured at the equilibrium after every injection of 0.02 mL liquid CO_2. The amount of CO_2 injected is the difference between the volumes of CO_2 left in the ISCO syringe pump, before and after the injection, which was measured by the position sensor on the pump and shown on the pump monitor. The mass of CO_2 dissolved in the IL was obtained by subtracting the amount of CO_2 that remained in the vapor phase from the total amount of CO_2 supplied to the cell. The mass of CO_2 in the vapor phase was calculated by multiplying the volume of the vapor phase with the density of CO_2 at the corresponding pressure and temperature, which was obtained by CO2PAC program based on the Wagner and Schmidt equation of state [21]. As the ionic liquid is not soluble in CO_2, we assumed that there is no ionic liquid in the vapor phase [8].

At constant temperature, the pressure was then increased by 2.7 MPa for each step until it reached 31.5 MPa at maximum. The above-mentioned procedure to determine the phase volumes was repeated after each pressure increment. The same experiments were performed at three different temperatures of 313.15, 323.15, and 333.15 K. The overall experimental uncertainty was less than ±5%, including the reading error of the height of meniscus between IL and CO_2 phases.

RESULTS AND DISCUSSION

1. Effects of Pressure and Temperature on CO_2 Solubility in ILs

The solubility of CO_2 in ILs was measured at each stage of pressure with about 2.7 MPa increment at three different temperatures. The mole fraction solubility of CO_2 (x_1) is defined by the following equation:
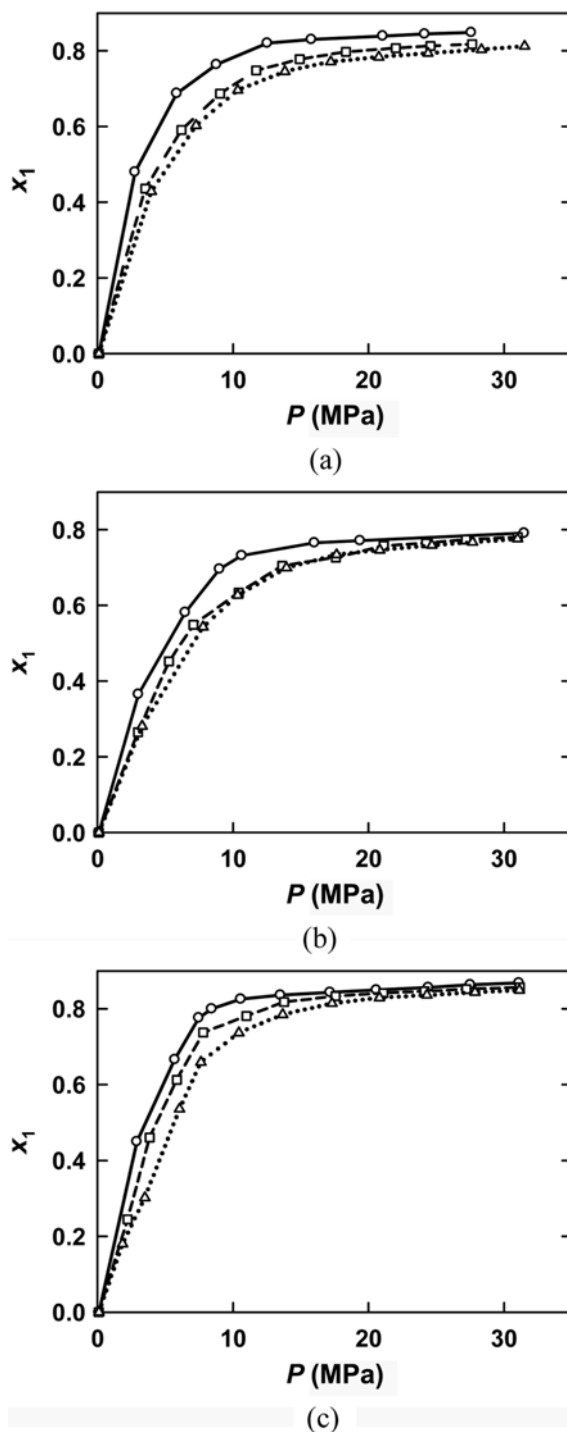
$$x_1 = \frac{n_1}{n_1 + n_2 + n_3} \tag{1}$$

Fig. 3. The mole fraction solubility of CO_2 (1) x_1 in IL (2) ([bmim][PF$_6$] (a), [bmim][BF$_4$] (b), and [omim][BF$_4$] (c)) with water mass fraction w_3 of 1.7×10^{-4}, 2.2×10^{-4}, and 4.1×10^{-4}, respectively: ◯ 313.15 K; ☐ 323.15 K; △ 333.15 K. The lines are the best fits to the data which are calculated by Sigma Plot, a graphics program.

where n_1, n_2, and n_3 are the numbers of moles of CO_2, IL, and water, respectively. However, we neglected the values of n_3 as they are very small compared to n_1 and n_2. The solubilities x_1 of CO_2 in [bmim][PF$_6$], [bmim][BF$_4$], and [omim][BF$_4$] increased rapidly to about 0.6 to 0.7 in mole fraction for pressures up to 9 to 10 MPa,

but towards higher pressures, the increasing rates slowed down and the solubility finally leveled off to about 0.8 in mole fraction above 15 MPa at all temperatures (Fig. 3). The fast solubility increase in the low-pressure range may be due to the Henry's sorption in the inter-ion space. The cations of ILs are normally bulkier than the corresponding anions and provide inter-ion spaces where CO_2 can squeeze in. As the openings between cation and anion of the IL are large, CO_2 molecules can easily enter into that space. However, these openings are continuously filled with CO_2 molecules with increasing pressure. Eventually, the spaces are filled up, leaving no more room for CO_2 molecules to get in. To let more CO_2 molecules enter into the IL, it is necessary for the inter-ion space to be expanded. As this expansion requires energy, only small amounts of CO_2 can penetrate into the IL. This is why ILs show that particular leveling-off solubility behavior. Blanchard et al. [10] also observed the same behavior and explained that it is due to the existence of "free volume" or "void space" available in the IL phase. They also mentioned that the almost linear CO_2 solubility as a function of pressure supports a space-filling mechanism. Therefore, the solubility of CO_2 in an IL depends on the interaction between CO_2 molecule and IL ion as well as on the free space in the IL available for CO_2 molecules to get in.

The solubility of CO_2 in the ILs at the same pressure decreases with increasing temperature for all three imidazolium-based ILs, which is in accordance with the observations reported in the literature [7,10,12,14,17,18]. A significant temperature effect on solubility was observed as the pressure increased up to about 10 MPa, but it became much less significant at high pressures about 30 MPa. In Fig. 3(b), the solubilities of CO_2 in [bmim][BF₄] at 323.15 and 333.15 K nearly overlap each other at pressures between 10 and 20 MPa, while the overlapping behavior is not observed for the other systems. Furthermore, the solubility difference in that pressure region is rather large between 313.15 and 323.15 K, but rather small between 323.15 and 333.15 K. In the literature [12,14], the solubility isotherms are shown nearly parallel to each other. Also, in our previous study [20], any overlapping of the volume change data between the three temperatures was observed throughout the pressure range investigated. So, the data at 323.15 K reported in Fig. 3(b) are presumed to be a little smaller (5 to 10%) than the corresponding values reported there. From Fig. 3, we can see that, at the same pressure, the solubility of CO_2 in these ILs became smaller at higher temperatures as shown in the literature [12,14]. This may be due to the decrease in the inter-ion space as the ions become active with the increased kinetic energy and are more irregularly distributed.

2. Effects of Cations and Anions on CO_2 Solubility in ILs

Ordinary inorganic salts, such as sodium chloride, have a strong inter-ion Coulombic force because the anion and the cation are small and thus the inter-ion distance is short. However, ILs (especially RTILs) have a weak inter-ion interaction force as their ion-sizes are large and the inter-ion distance is long. For all three ILs investigated, the positive charge of the nitrogen atom on the five-membered ring of the cation is not fixed but can be transferred indefinitely to and from between the two N atoms on the ring, thus weakening the ionic strength of the cation. Although the ionic strengths of ILs are smaller than those of inorganic salts, they are still much stronger than those of polar and nonpolar solvents. Fig. 4 illustrates this
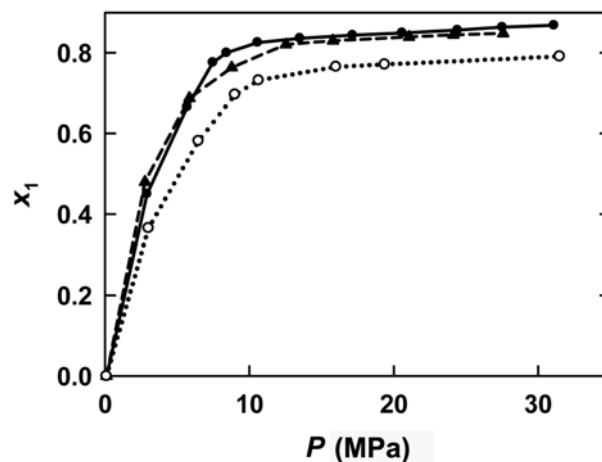

Fig. 4. Comparison of the mole fraction solubilities of CO_2 (1) x_1 in three ILs (2) with different water mass fractions w_3 at 313.15 K: ▲ [bmim][PF₆] with $w_3=1.7 \times 10^{-4}$; ○ [bmim][BF₄] $w_3=2.2 \times 10^{-4}$; ● [omim][BF₄] with $w_3=4.1 \times 10^{-4}$. The lines are the best fits to the data which are calculated by Sigma Plot, a graphics program.

cationic effect using [omim][BF₄], where the short butyl chain in the cation of [bmim][BF₄] is substituted with a longer octyl chain, which shows higher CO_2 solubility than [bmim][BF₄]. The difference in the solubility of CO_2 amounts to about 0.1 in mole fraction. This is because the longer alkyl group has a better affinity for CO_2 that increases the solubility of CO_2 in the IL. The experimental results shown in Fig. 4 coincide with the literature [7,17]. Aki et al. [7] reported an appreciable difference among the three imidazolium-based cations [bmim], [hmim] (i.e., 1-hexyl-3-methylimidazolium), and [omim], paired with the same anion, bis(trifluoromethylsulfonyl)imide (abbreviated as [Tf₂N]). They could prove the increase in CO_2 solubility with the increase in the length of the side-chain. An earlier paper from the same group [10], however, showed almost no difference in the solubility of CO_2 between [bmim][PF₆] and [omim][PF₆].

Fig. 4 also shows that substitution of the anion by a less polar one leads to an increase in the solubility. The solubility of CO_2 is higher in [bmim][PF₆] than in the corresponding IL [bmim][BF₄] that has a more polar anion. Because CO_2 is nonpolar, it prefers less polar ions. Occasionally, in this research, the solubility increase caused by replacing the cation from [bmim] to [omim] is similar to the increase in the solubility caused by substituting the anion from [BF₄] to [PF₆]. Aki et al. [7] showed that the anion has a significantly stronger impact on the gas solubility than the cation. At the same pressure (8 MPa) and temperature (313.15 K), the solubility difference between [NO₃] and [methide] anions is more than 40%, while that between [bmim] and [omim] cations is less than 10%. Their results showed that the solubility difference between [bmim][PF₆] and [bmim][BF₄] is about 13% at 8 MPa. In this study, that difference is about 14%, which is similar to that of Aki et al., while at 30 MPa it was reduced to 9%.

Cammarata et al. [22] suggested the following order of hydrogen bond basicity of the anion from the FTIR spectroscopic studies: [PF₆]<[BF₄]<[Tf₂N]<[NO₃]. However, Aki et al. [7] claimed that CO_2 solubility does not correlate with the hydrogen-bond basicity of the

anion, saying that the solubility of CO_2 in [bmim] cation-based ILs increases in the order of [NO$_3$]<[BF$_4$]<[PF$_6$]<[Tf$_2$N] at 313.15 K. They explained that behavior in terms of the acid/base interactions
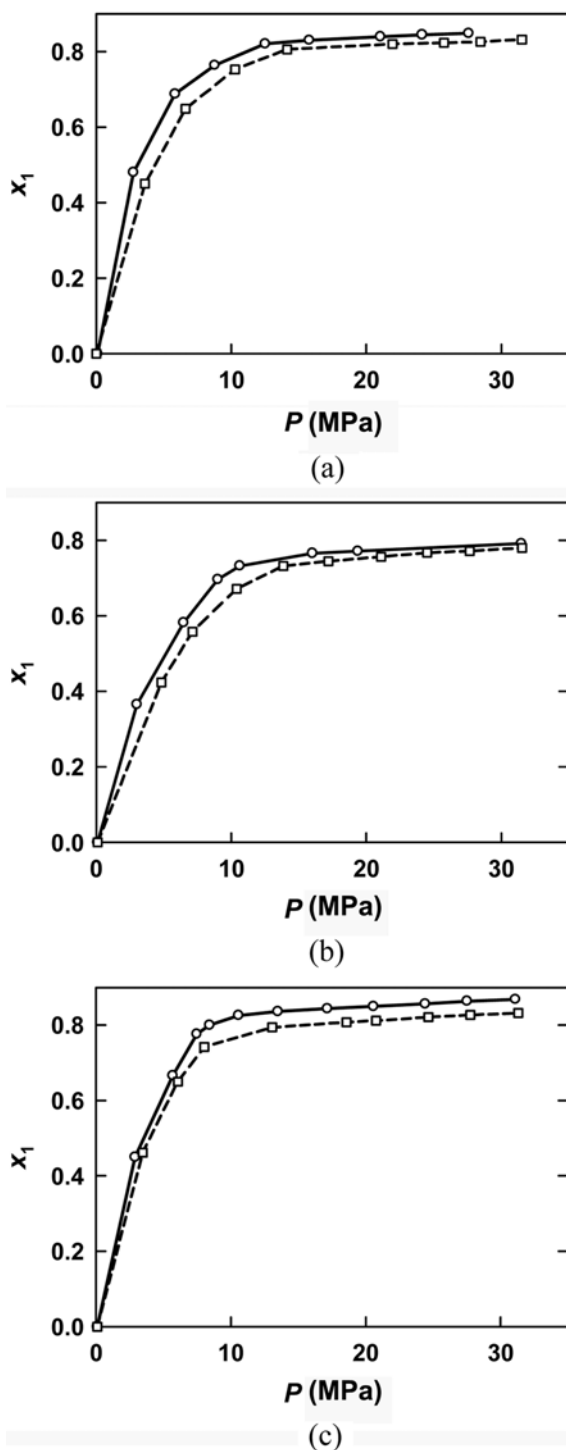

Fig. 5. The mole fraction solubility of CO_2 (1) x_1 in three ILs (2) with two different water (3) mass fractions w_3 at 313.15 K. For [bmim][PF$_6$] (a): ○ 1.7×10^{-4} and □ 7.0×10^{-4}; for [bmim][BF$_4$] (b): ○ 2.2×10^{-4} and □ 20×10^{-4}; for [omim][BF$_4$] (c): ○ 4.1×10^{-4} and □ 42×10^{-4}. The lines are the best fits to the data which are calculated by Sigma Plot, a graphics program.

of CO_2 with anions and of the molar volumes of the ILs. From ATR-IR spectroscopy, Kazarian et al. [23] showed that CO_2 forms weak Lewis acid-base complexes with the anions of the IL and that the axis of the O=C=O molecule is oriented towards the IL anion in perpendicular arrangement to P-F and B-F bonds, shielding the strong anion-cation interactions. They also showed that on pressurization with CO_2 the swelling of [bmim][PF$_6$] is larger than that of [bmim][BF$_4$] due to the weaker anion-cation interactions in [bmim][PF$_6$], resulting in a larger solubility of CO_2 in [bmim][PF$_6$]. Our results agree with Aki et al.'s and Kazarian et al.'s claims on the anion effect. The solubility of CO_2 for the [BF$_4$] IL is smaller than that for the [PF$_6$] IL, indicating that [PF$_6$] is less polar than [BF$_4$] and therefore more compatible with nonpolar CO_2.

3. Effects of Water Content on CO_2 Solubility in ILs

The solubility of CO_2 was measured for ILs (2) with different water (i.e., residual water) (3) contents (mass fractions) that were determined as follows:

$$w_3 = \frac{m_3}{m_2 + m_3} \tag{2}$$

where m_2 is the mass of the IL and m_3 is the mass of residual water in the IL. The water content w_3 of the IL before and after moisture removal treatment amounted to 1.7×10^{-4} and 7.0×10^{-4} for [bmim][PF$_6$], 2.2×10^{-4} and 20×10^{-4} for [bmim][BF$_4$], 4.1×10^{-4} and 42×10^{-4} for [omim][BF$_4$], respectively. Those ILs with higher water content showed lower solubility of CO_2 at 313.15 K (Fig. 5). The largest CO_2 solubility difference between the same ILs with different water contents was observed to be 7 to 8% at pressures near 8 to 10 MPa for all the ILs tested here. At higher pressures, that difference was about 2 to 3% for [bmim][PF$_6$], 1 to 2% for [bmim][BF$_4$], and 3 to 4% for [omim][BF$_4$]. The outcome of different water content on the gas solubility agrees with the findings reported by Fu et al. [14], who observed decreasing solubility of CO_2 in [bmim][PF$_6$], measured between 313.15 and 333.15 K and up to 25 MPa, with increasing water content. Fu et al. [12] reported that the decrease in the solubility was not so significant but less than 15% (with the average of 6.7%) when they increased the water content w_3 from 6.7×10^{-5} to 0.016 at the same pressure and temperature. Their solubility difference was reduced to 3.9% when calculated on a water-free basis. Since their pressure range was 1.0 to 9.0 MPa (except one series operated up to 25 MPa), they observed a smaller solubility reduction compared to us in that region. Aki et al. [7] also showed a visible but, however, small effect of water content on the solubility of CO_2 in [bmim][Tf$_2$N] at 298 K by using two IL samples, one with a water mass fraction of 4.5×10^{-4} and the other (water-saturated) containing 1.3 wt% (24.2 mol%) of water.

4. Comparison with Literature Values

The solubility data of CO_2 in [bmim][PF$_6$] measured in this study at a single temperature of 313.15 K were compared with those available from the literature (Fig. 6). We selected the solubility data at water content of 7.0×10^{-4} as the reference, so that we could make a relatively fair comparison with the data from literature that have similar degrees of water content w_3 in the range of 10×10^{-4} to 15×10^{-4}. Except for the data below 2 MPa, where we do not have the solubility, our results were similar, within about 10%, to the results of Blanchard et al. [10] who measured the solubility up to 9.6 MPa using the same IL, but with a water mass fraction w_3 of 15×10^{-4}.
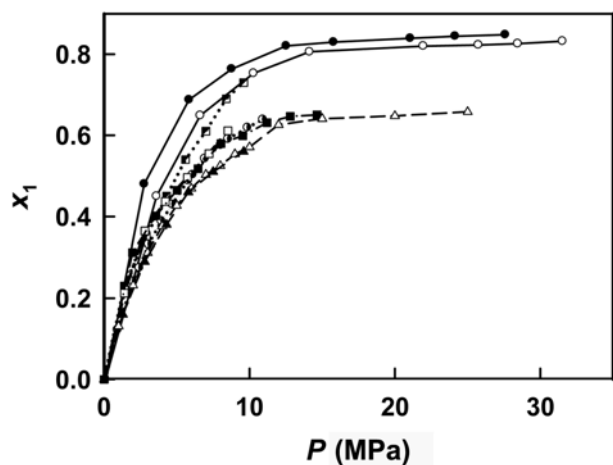
Fig. 6. Comparison of the mole fraction solubilities of CO$_2$ (1) x$_1$ in [bmim][PF$_6$] at 313.15 K with those from the literature. ● this work, w$_3$=1.7×10^{-4}; ○ this work, w$_3$=7.0×10^{-4}; ◨ Blanchard et al. [10], w$_3$=15×10^{-4}; ◑ Liu et al. [19], w$_3$= 10×10^{-4}; □ Aki et al. [7], w$_3$=3.0×10^{-4} (cleaned); ■ Aki et al. [7], w$_3$=2.3×10^{-4} (Sachem); △ Fu et al. [12], w$_3$=15×10^{-4}; ▲ Pérez-Salado Kamps et al. [14], w$_3$<10×10^{-4}. The lines are the best fits to the data which are calculated by Sigma Plot, a graphics program.

The solubility values measured by Fu et al. [12] (w$_3$=15×10^{-4}) and Pérez-Salado Kamps et al. [14] (w$_3$<10×10^{-4}) are a few to 5% smaller than ours at pressures less than 1 MPa, but the difference increases to about 25% at 25 MPa. Our data (w$_3$=7.0×10^{-4}) agree fairly well with the data reported by Liu et al. [19] (w$_3$=10×10^{-4}) as well as Aki et al. [7] (w$_3$=2.3×10^{-4}) at low pressures, but the deviation increases to 15% at 10 MPa. As discussed in the previous section, our solubility data in [bmim][PF$_6$] with w$_3$=1.7×10^{-4} are 2 to 8% larger than that in [bmim][PF$_6$] with w$_3$=7.0×10^{-4}, except for pressures lower than 3 MPa. So, we expect a smaller solubility for ILs with larger water content and it is impossible to explain our data with only water content.

Aki et al. [7] reported that the solubility of CO$_2$ in an IL may also be strongly affected by the impurities and degradation products, such as chloride ion remaining in the IL. In Fig. 6, their data for [bmim][PF$_6$] cleaned with water and dried under vacuum at 343.15 K for 48 h are about 5% larger than those of Fu et al. [12] and Pérez-Salado Kamps et al. [14], but are similar to Liu et al. [19]. However, in our experiments, a low-grade CO$_2$ (99.5%) was used and it is known that the main impurity is water. Contacting with IL during the solubility measurement, the water in the CO$_2$ must have been dissolved into the IL. However, our solubility was rather larger than that of Aki et al. [7], different from their report. This result requires us to find another reason for the higher solubility of CO$_2$ in the ILs.

The ILs used in this study have impurities less than 1% (see the above Materials section). Impurities other than water and chloride were not determined, but must have been the residues from the reaction. We neither washed any IL with water to remove water-soluble impurities nor used activated carbon to remove organic impurities as mentioned by Aki et al. [7]. We did not determine nature and amount of impurities except for water. However, we pretreated the ILs at 363.15 K under vacuum for 12 h until there was no further

decrease in the weight of IL. The colors of the new ILs were clear to yellowish clear. For the treated ILs, we could neither see any change in the color with the naked eye nor notice any change of smell. When the IL [bmim][PF$_6$] was treated at 423.15 K, the color turned to brownish yellow and released toxic fumes, probably of hydrogen chloride, hydrogen fluoride or both. The toxic gas must have been made by degradation of the IL, and hydrogen chloride, if any, must have been the one remaining in the IL. To avoid this degradation of the ILs, we kept them at temperatures less than 363.15 K throughout the entire experiments, while Aki et al. [7] treated the IL at 343.15 K, Pérez-Salado Kamps et al. [14] at 348.15 K, Fu et al. [12] at 353.15 K, and Liu et al. [19] at 313.15 K. Since our pretreatment temperature of ILs was the highest among the research on the solubility reported so far, we might have removed more impurities compared to the literature and thus obtained the highest solubility.

CONCLUSIONS

The solubility of CO$_2$ in three imidazolium-based ILs was measured at 313.15, 323.15, and 333.15 K and at pressures up to 32 MPa. As the pressure was increased, the solubility increased rapidly at low pressures, but this increase slowed down above the pressures of 8 to 10 MPa and finally leveled off at about 30 MPa. As temperature was increased by 20 K, the corresponding solubility decreased about 7 to 8% at pressures of 8 to 10 MPa and about 2 to 3% at 20 to 30 MPa, respectively. The solubility was also found to be dependent on the nature of cation and anion. The IL with longer alkyl-chain cation [omim] showed about 10% larger solubility than that of shorter alkyl-chain cation [bmim] due to the favorable interaction between CO$_2$ and alkyl side chain. Compared to the nature of cation and anion, the water content has a subordinate effect on gas solubility. When the anion was changed from [BF$_4$] to [PF$_6$], the solubility increased by about 10%. As the water content increased 4 to 10 times, the solubility of CO$_2$ at 313.15 K decreased 7 to 8% near 8 to 10 MPa and 2 to 3% at high pressures near 20 to 30 MPa, respectively. Our results may be worth following if the commercial IL and CO$_2$ are used in a commercial process without further purification. However, for sophisticated control of such processes it is recommended to purify the ILs and CO$_2$ before use.

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