

High-pressure phase behavior of carbon dioxide in ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

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Abstract—Phase equilibrium data of carbon dioxide in the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf₂N]) are presented at high pressures up to about 30 MPa and at temperatures between 298.15 K and 343.15 K. The solubilities at a given temperature were determined by measuring the bubble point pressure of the ionic liquid solution with carbon dioxide dissolved using the high-pressure equilibrium apparatus equipped with a variable-volume view cell. Solubility results are reported for carbon dioxide concentrations ranging from 0.21 up to 0.80 mole fraction. Carbon dioxide gave very high solubilities in the ionic liquid at lower pressures, while the equilibrium pressure increased very steeply at higher concentrations of carbon dioxide. The solubility of carbon dioxide in the ionic liquid decreased with an increase in temperature.

Key words: Phase Behavior, Solubility, Ionic Liquid, Carbon Dioxide, 1-Butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide

INTRODUCTION

Ionic liquids are a class of organic salts that are liquid at or near room temperature. They are generally composed of a large asymmetric organic cation and either an organic or inorganic anion. Asymmetry of the cation is believed to be responsible for the low melting points of ionic liquids, while the nature of the anion is considered to be responsible for many of the physical properties of ionic liquids such as their miscibility with conventional solvents and hygroscopicity [Dzyuba and Bartsch, 2002]. A key feature of ionic liquids is that their physical properties can be tailored by judicious selection of cation, anion, and substituents [Brennecke and Maginn, 2001]. Unlike molecular liquids, ionic liquids have a number of advantages determined by the unique combination of their properties such as negligible vapor pressure at room temperature, a stable liquid range of over 300 K, and density being greater than that of water [Marsh et al., 2002]. Therefore, these fluids have been proposed as an attractive alternative to volatile organic compounds (VOCs) for "Green Processing," because they are nonvolatile, nonflammable, and thermally stable [Brennecke and Maginn, 2001; Seddon, 1997; Holbrey and Seddon, 1999; DeSimone, 2002]. Replacement of conventional solvents with ionic liquids would prevent the emission of VOCs, a major source of environmental pollution.

Ionic liquids have recently gained great attention in a variety of chemical processes. They are being used as solvents for homogeneous catalysis for a variety of organic reactions [Welton, 1999; Wasserscheid and Keim, 2000; Sheldon, 2001], media for gas and liquid separations [Blanchard et al., 1999; Visser et al., 2001], electrolytes [Quinn et al., 2002; Kim et al., 2004] for batteries and fuel cells, and thermal fluids [Wu, 2001]. A potential application of ionic liquids is for gas separation processes such as a supported liquid

membrane process using porous supports whose pores are impregnated with an ionic liquid solvent [Scovazzo et al., 2004]. The nonvolatility of ionic liquids would not cause any contamination to a gas stream, and thus this feature gives ionic liquids a big advantage over conventional solvents used for absorbing gases. To select an efficient ionic liquid for use as a gas separation medium, it is necessary to know the solubility of the gas in the ionic liquid phase.

Recently, Brennecke and coworkers presented some potential applications for ionic liquids using supercritical fluids. They reported that it is possible to extract a desired solute from an ionic liquid using a supercritical fluid without any contamination of the extracted solute with the ionic liquid solvent [Blanchard and Brennecke, 2001; Blanchard et al., 1999]. They also investigated the use of supercritical carbon dioxide for separating ionic liquids from their organic solvents [Scurto et al., 2002]. Such researches are composed of a complete understanding and designing of processes involving both ionic liquids and supercritical fluids. For this purpose, knowing the phase behavior of ionic liquids+supercritical fluids is most important. However, the amount of such data is insufficient in literature. Shariati and Peters [2003, 2005], Costantini et al. [2005], and Kroon et al. [2005] studied the high-pressure phase behavior of binary mixtures consisting of a supercritical fluid (fluoroform or carbon dioxide) and imidazolium-based ionic liquids (1-alkyl-3-methylimidazolium tetrafluoroborate and 1-alkyl-3-methylimidazolium hexafluorophosphate) in a wide range of solute concentration and at pressures up to about 100 MPa. Blanchard et al. [2001] presented the high-pressure phase behavior of carbon dioxide with six different imidazolium-based ionic liquids and showed the effect of systematically changing the anionic and cationic components of the ionic liquid on the carbon dioxide+ionic liquid phase behavior. Large quantities of carbon dioxide dissolved into the ionic liquid phase, but no appreciable amount of ionic liquid solubilized into the carbon dioxide phase.

The main objective of the work described in this article is to gain

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more insight into the phase behavior of ionic liquid+supercritical fluid systems. We measured the solubilities of carbon dioxide in the ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf₂N]), using a high-pressure equilibrium apparatus equipped with a variable-volume view cell. In our experiments, the determination of solubility was based on the measurement of bubble point pressure for a mixture of ionic liquid and carbon dioxide with a known composition at a constant temperature. The solubilities of carbon dioxide in the ionic liquid were measured as a function of temperature and pressure. A variable-volume view cell apparatus is well-known as a simple and quick way capable of measuring the phase equilibrium behavior of high-pressure compressible fluid mixtures [Lee et al., 2000a]. The bubble point pressure can be easily measured by changing the volume of the view cell containing the fluid mixture of a known composition and by observing the phase change through the window of the cell.

EXPERIMENTAL

Table 1. Physical properties of ionic liquid [bmim][Tf₂N]

Chemical name	1-butyl-3-methyl imidazolium bis(trifluoromethyl-sulfonyl)imide
CAS registry number	174899-83-3
Chemical formula	[C ₈ H ₁₅ N ₂ ⁺] [(CF ₃ SO ₂) ₂ N ⁻]
Molecular weight	419.36
Melting temperature ^a	-6 °C
Glass transition temperature ^a	-87 °C
Density ^b	1.437 g/cm ³ at 25 °C and 0.1 MPa
Viscosity ^c	63.5 mPa·s at 20 °C for dried sample
Electrolytic conductivity ^d	0.406 S·m ⁻¹ at 25 °C for dried sample
Water content ^e	100-1,000 ppm
Halogen content ^e	30-100 ppm

^aData from Dzyuba and Bartsch [2002]. ^bData from Gomes de Azevedo et al. [2005]. ^cData from Widegren et al. [2005a]. ^dData from Widegren et al. [2005b]. ^eData from C-TRI (www.c-tri.com).

1. Materials

The ionic liquid [bmim][Tf₂N] was purchased from C-TRI (Korea). The mass fraction purity of the ionic liquid was about 99%. Prior to use, the [bmim][Tf₂N] was dried under vacuum conditions at room temperature for several days. The chemical structure and physical properties of [bmim][Tf₂N] are shown in Fig. 1 and Table 1, respectively. Carbon dioxide (CO₂) used for the measurements was purchased from Myung Sin General Gas Co. (Korea), and had a high

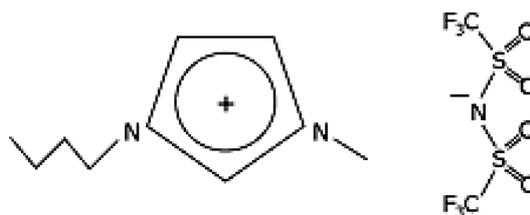


Fig. 1. Chemical structure of [bmim][Tf₂N].

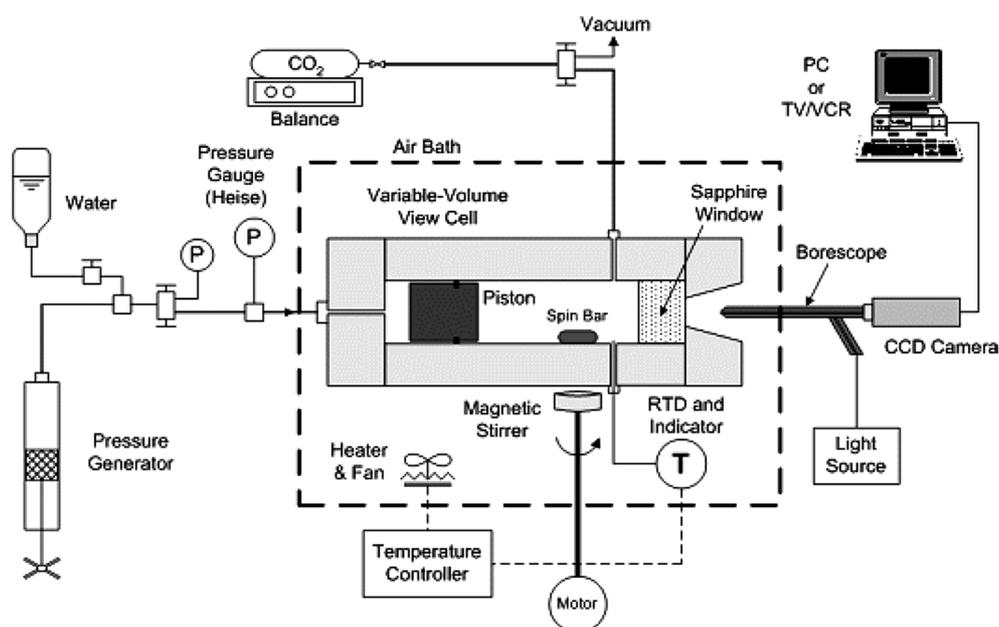


Fig. 2. A schematic diagram of experimental apparatus of measuring gas solubility in ionic liquid.

purity of 99.99%. The ionic liquid and CO₂ gas were used without further purification.

2. Apparatus

Fig. 2 shows a schematic diagram of the experimental high-pressure apparatus for measuring the bubble point and cloud point pressures of the CO₂+[bmim][Tf₂N] mixtures. The experimental apparatus used in this work is similar to that used by Lee et al. [2000a, b]. The heart of the system is the high-pressure variable-volume view cell. The cell has a dimension of 16 mm i.d.×70 mm o.d. and an internal working volume of about 31 cm³. A movable piston is placed inside the cell to change the cell volume. A pressure generator (High Pressure Equipment Co. model 50-6-15, 15,000 psi rating, 20 cm³ capacity) is used to pressurize water and thereby displace the piston. A change in the cell volume causes a change of the system pressure. A sapphire window (3/4" diameter×3/4" thick) is inserted into the view cell for visual observation of the interior of the cell. O-rings and back-up rings create seals between the end caps and the cell body, and between the piston and the inner wall of the cell.

The system pressure is measured with a high-precision pressure gauge (Dresser Heise model CC-12-G-A-02B, 50 MPa max. pressure, ±0.05 MPa accuracy) placed between the pressure generator and the view cell instead of being connected directly to the cell. The pressure is measured on the pressurizing fluid (water) side of the piston. The system temperature is measured by an RTD (Pt-100Ω) inserted into the interior of the cell. A temperature-controlled forced-convection air bath is used to keep the system temperature constant. A visual observation of the interior of the cell through the sapphire window is made by a borescope (Olympus model R080-044-000-50) and a CCD camera (WAT-202B) connected to a monitor. A cold light source (Olympus model ILK-5) is used to provide illumination inside the view cell. A magnetic stirring system is equipped under the cell body to mix the contents in the cell. A stirring bar in the cell is activated by a samarium-cobalt magnet located below the cell, and the magnet is driven by an electric motor and an RPM controller.

3. Methods

The solubilities of CO₂ in the ionic liquid phase were determined by measuring a bubble point pressure or cloud point pressure at various temperatures for a mixture of CO₂+[bmim][Tf₂N]. A certain amount of the [bmim][Tf₂N] ionic liquid was loaded into the cell by using a gas-tight syringe. The amount of the ionic liquid loaded was determined by using a sensitive balance (AND model HM-30) measurable to ±0.1 mg. After assembling a piston, o-rings and a sapphire window into the view cell, we placed the cell inside the air bath to keep the system temperature constant. To remove any entrapped air present in the cell and any dissolved gas in the ionic liquid phase, the cell was evacuated overnight with a vacuum pump. Once the vapor space of the system was fully evacuated, a certain amount of CO₂ was charged into the cell through the inlet line. The exact amount of CO₂ gas introduced into the cell was determined by weighing CO₂ sample cylinder before and after loading using a balance (Precisa model 1,212 M) with an accuracy of ±1 mg. To prevent any loss of CO₂ gas in the inlet line during loading, the CO₂ gas in the inlet line was recovered back into the CO₂ sample cylinder by dipping the cylinder in a dewar bottle filled with liquid nitrogen right after loading.

Temperature was fixed at desired values, and the pressure was varied until a phase change was visually observed for a mixture with a constant overall composition. To dissolve the CO₂ gas into the ionic liquid, the fluid in the cell was then continuously pressurized with the pressure generator. As the pressure generator pressurizes water, the compressed water moves the piston to the window side to decrease the cell volume and thus raise the pressure inside the cell. As the pressure increases, the CO₂ gas is dissolved into the ionic liquid phase and finally the fluid becomes a single homogeneous phase. At the same time the solution was well agitated by a stirring bar.

Once the system reached thermal equilibrium and the fluid was maintained at a homogeneous single phase, the pressure was then reduced very slowly until tiny CO₂ bubbles started to form from the single phase solution by moving the piston back to the water side. At a fixed composition and temperature, the bubble point pressure was defined as the initial pressure at which the first bubble was observed. For reproducing consistent measurements, every measurement was repeated at least twice at each temperature. The bubble point pressures at different temperatures and compositions were measured in the same way, changing the temperature of the solution up to about 343 K. For a solution with CO₂ concentrations higher than about 0.75, the cloud point behavior was observed rather than the bubble point behavior. At the cloud point the solution becomes cloudy due to the phase transition from a single to a liquid-liquid phases. In our experiments, the cloud point pressure was defined as the pressure at which it was no longer possible to visually observe the stirring bar in the cell. The bubble point or cloud point pressures at different temperatures and compositions were measured in the same way, thus creating pressure-temperature (P-T) isopleths.

RESULTS AND DISCUSSION

The solubility of carbon dioxide in [bmim][Tf₂N] was measured by using the high-pressure equilibrium apparatus. For systems with a fixed overall composition of CO₂ and [bmim][Tf₂N], bubble point or cloud point pressures were observed as a function of temperature. The experimental results are summarized in Table 2, and a P-T diagram of the experimental data is shown in Fig. 3. It is clear from Fig. 3 that bubble point or cloud point pressures increase as the system temperature of mixtures at fixed compositions increase. This means that the solubility of CO₂ in the ionic liquid decreases at higher temperatures. The slope of the bubble point pressure with respect to temperature, $(\partial P/\partial T)_x$, increased as the CO₂ composition increased. Table 2 also shows the results of phase change behavior observed during the experiments. A bubble point behavior was observed at the CO₂ mole fractions lower than about 0.7, while a cloud point behavior was observed at the CO₂ mole fractions higher than about 0.75.

When the mole fraction of CO₂ increased isothermally, the bubble point or cloud point pressure increased significantly. This can be more easily seen from a P-x diagram in which the bubble point or cloud point pressure is plotted against the mole fraction of CO₂ at various temperatures. This plot was obtained by fitting the bubble point or cloud point curves of Fig. 3 at different CO₂ mole fractions with polynomial equations and then determining the pressures corresponding to desired temperatures from the curve fits. The second-

Table 2. Experimental bubble point or cloud point data for various mole fractions of CO₂ in the CO₂+ [bmim][Tf₂N] system

Mole fraction of CO ₂	T [K]	P [MPa]	Phase behavior	Mole fraction of CO ₂	T [K]	P [MPa]	Phase behavior
0.2132	297.54	0.60	b*	0.7003	301.19	5.15	b
	303.87	0.73	b		303.87	5.55	b
	314.06	0.87	b		314.06	6.95	b
	324.19	1.01	b		324.19	8.60	b
	334.35	1.15	b		334.35	10.50	b
0.3760	344.51	1.29	b	0.7310	344.51	12.67	b
	300.26	1.64	b		299.63	5.45	b
	304.08	1.79	b		303.87	6.07	b
	314.06	2.14	b		314.06	7.95	b
	324.19	2.58	b		324.19	10.51	b
0.4965	334.35	3.00	b	0.7542	334.35	13.35	c**
	344.51	3.40	b		344.51	16.42	c
	299.11	2.45	b		298.69	5.65	b
	303.87	2.72	b		303.87	6.48	b
	314.06	3.40	b		314.06	8.99	c
0.5413	324.19	4.10	b	0.7739	324.19	11.94	c
	334.35	4.75	b		334.35	15.47	c
	344.51	5.34	b		344.51	18.45	c
	298.38	2.90	b		299.11	6.47	c
	304.18	3.30	b		303.97	7.81	c
0.6124	314.06	4.00	b	0.7902	314.26	12.34	c
	324.19	4.81	b		324.19	16.23	c
	334.35	5.58	b		334.35	20.01	c
	344.51	6.40	b		344.51	24.20	c
	298.69	3.75	b		299.21	8.45	c
0.6409	303.87	4.26	b	0.8041	303.87	10.45	c
	314.06	5.20	b		314.06	15.02	c
	324.19	6.27	b		324.19	19.75	c
	334.35	7.38	b		334.35	23.23	c
	344.51	8.51	b		344.51	27.14	c
0.6834	298.27	4.01	b	0.8041	298.69	11.80	c
	303.87	4.52	b		303.87	14.21	c
	314.06	5.54	b		314.16	18.95	c
	324.19	6.70	b		324.29	23.71	c
	334.35	8.13	b		334.35	27.61	c
0.6834	344.51	9.49	b	344.51	31.72	c	
	298.59	4.51	b				
	304.08	5.19	b				
	314.06	6.46	b				
	324.19	7.92	b				
	334.35	9.85	b				
	344.51	11.55	b				

*bubble point behavior observed.

**cloud point behavior observed.

order polynomial equation was used in this work, and the correlation coefficients of the curve fits, which expressed the goodness of the fits, were greater than 0.998 for all cases. Fig. 4 shows the results estimated by the polynomial interpolation of the bubble point pressures with the CO₂ mole fraction at several temperatures. The equilibrium pressures were reasonably low at lower concentrations of CO₂. However, when the CO₂ concentration further increased, the equilibrium pressures increased dramatically. As shown in Fig. 4 the solubility of CO₂ in the ionic liquid decreased with an isobaric

increase in temperature and the effect of temperature on CO₂ solubility was larger at higher mole fractions of CO₂.

The phase behavior of the CO₂+ [bmim][Tf₂N] system is unusual: CO₂ dissolves well in the [bmim][Tf₂N] at lower pressures, while the equilibrium pressures increase steeply at higher concentrations of CO₂. In general, a system in which a large amount of CO₂ dissolves in the liquid phase at low pressures gives a simple two-phase envelope with a mixture critical point at moderate pressures [Blanchard et al., 2001; Kroon et al., 2005]. However, the CO₂+ [bmim]

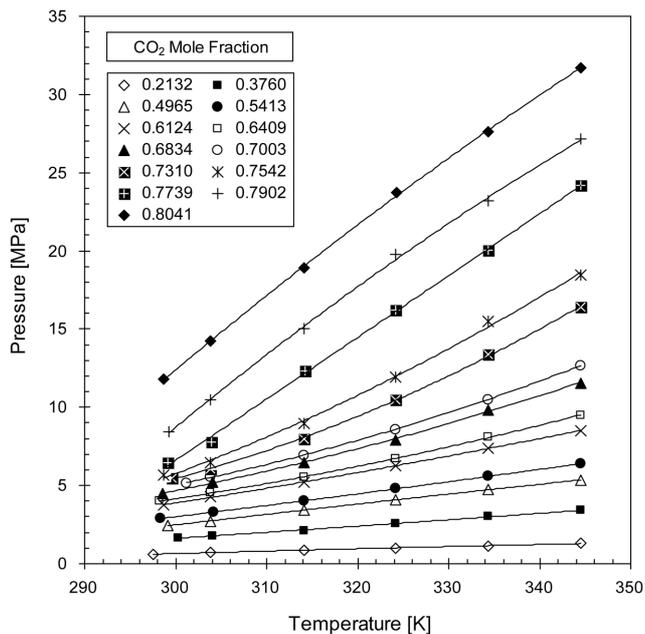


Fig. 3. P-T isopleths of the CO_2 + $[\text{bmim}][\text{Tf}_2\text{N}]$ mixtures at different mole fractions of CO_2 .

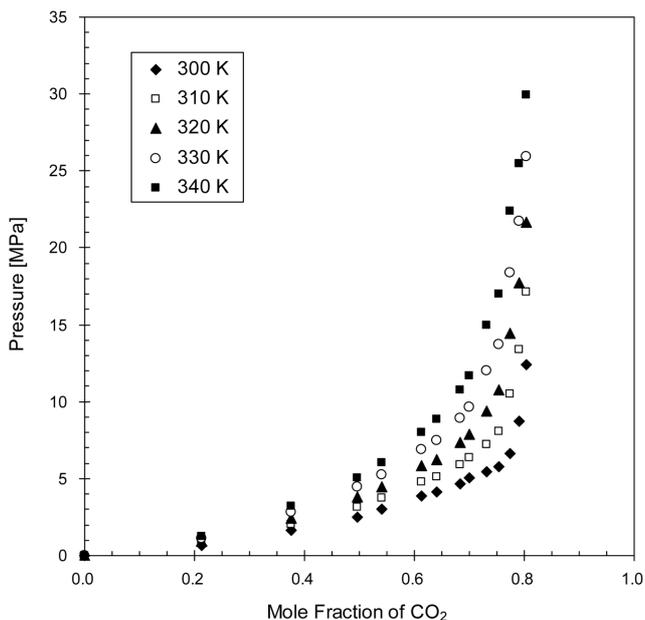


Fig. 4. Solubility of CO_2 in ionic liquid $[\text{bmim}][\text{Tf}_2\text{N}]$ as a function of pressure at various temperatures.

$[\text{Tf}_2\text{N}]$ system studied in this work illustrated almost vertical extension to a very high pressure of the two-phase boundary, instead of having a critical point at a moderate pressure. This kind of behavior has also been noticed for other CO_2 +ionic liquid systems [Shariati and Peters, 2003; Shariati and Peters, 2005; Costantini et al., 2005]. Our data were compared to the data published from others. Recently, Kroon et al. [2005] and Shariati et al. [2005] reported the phase behavior of the systems CO_2 + $[\text{bmim}][\text{BF}_4]$ and CO_2 + $[\text{bmim}][\text{PF}_6]$. Fig. 5 compares the phase equilibrium data for three binary systems: CO_2 + $[\text{bmim}][\text{Tf}_2\text{N}]$, CO_2 + $[\text{bmim}][\text{BF}_4]$ and CO_2 + $[\text{bmim}][\text{PF}_6]$ at

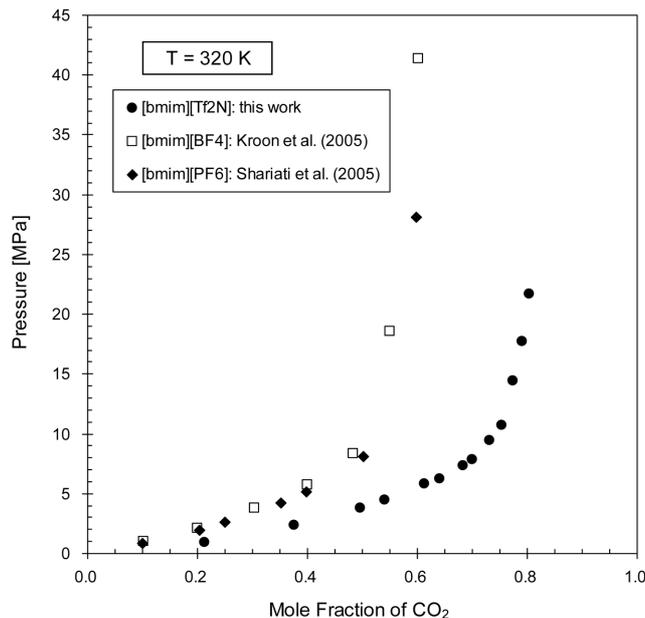


Fig. 5. Comparison of solubilities of CO_2 in the $[\text{bmim}]$ -based ionic liquids with different anions.

320 K. The data show the similarities in phase behavior; in all these binary systems the equilibrium pressure increased very sharply at high mole fractions of CO_2 .

Fig. 5 also shows the effect of anion on the solubility of CO_2 in three kinds of $[\text{bmim}]$ -based ionic liquids with different anions. The solubilities of CO_2 in $[\text{bmim}][\text{Tf}_2\text{N}]$ are higher than those in $[\text{bmim}][\text{BF}_4]$ and $[\text{bmim}][\text{PF}_6]$, compared at a given pressure. The solubilities of CO_2 in $[\text{bmim}][\text{BF}_4]$ and $[\text{bmim}][\text{PF}_6]$ are almost the same. The anion appears to play a significant role in determining the CO_2 solubility. Cadena et al. [2004] showed in their molecular simulations for CO_2 +ionic liquid mixtures that CO_2 associated with the anion, positioning itself to maximize favorable interactions. The strength of these interactions with $[\text{Tf}_2\text{N}]$ may simply be stronger than those with $[\text{BF}_4]$ and $[\text{PF}_6]$. The $[\text{Tf}_2\text{N}]$ anion increased the CO_2 solubility relative to the $[\text{BF}_4]$ and $[\text{PF}_6]$ anion ionic liquids, whereas the $[\text{BF}_4]$ anion has little effect on the CO_2 solubility relative to the $[\text{PF}_6]$ anion. In other words, CO_2 had a higher solubility in ionic liquid with the anion containing a fluoroalkyl group (CF_3) than in the two ionic liquids with inorganic fluorinated anions, $[\text{BF}_4]$ and $[\text{PF}_6]$. Therefore, the increase of the CO_2 solubility in $[\text{bmim}][\text{Tf}_2\text{N}]$ can be attributed to the fluoroalkyl group present in the anion $[\text{Tf}_2\text{N}]$. It is well-known that fluoroalkyl groups are CO_2 -philic, although the exact mechanism of this phenomenon is poorly understood. An alternative explanation for the difference in CO_2 solubility between $[\text{bmim}][\text{Tf}_2\text{N}]$ and either $[\text{bmim}][\text{BF}_4]$ or $[\text{bmim}][\text{PF}_6]$ may simply be the larger size of the $[\text{Tf}_2\text{N}]$ anion [Anthony et al., 2005].

CONCLUSIONS

The solubilities of CO_2 in the ionic liquid $[\text{bmim}][\text{Tf}_2\text{N}]$ were determined by measuring the bubble point or cloud point pressures of the binary system of CO_2 + $[\text{bmim}][\text{Tf}_2\text{N}]$ by using a high-pressure equilibrium apparatus equipped with a variable-volume view cell. The experimental results showed that CO_2 gave very high solu-

bilities in the ionic liquid at lower pressures, while the equilibrium pressure increased very steeply at higher concentrations of carbon dioxide. The solubility of carbon dioxide in the ionic liquid decreased with an increase in temperature. Further experimental investigation of obtaining the phase behavior of ionic liquids and supercritical fluids of interest for industrial process design is needed; more specifically, experimental measurements of the high-pressure solubilities of supercritical carbon dioxide in ionic liquids with different kinds of cation (length of the alkyl group) and anion can be carried out.

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