

초임계이산화탄소의 존재 하에서 이온성액체의 부피팽창

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(2008년 12월 14일 접수; 2008년 12월 18일 수정본 접수; 2008년 12월 22일 채택)

Volume Expansion of Ionic Liquids in the Presence of Supercritical Carbon Dioxide

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(Received for review December 14, 2008; Revision received December 18, 2008; Accepted December 22, 2008)

요 약

초임계이산화탄소의 존재 하에서 세 가지 이온성액체(IL)의 부피팽창을 압력 32 MPa까지, 온도 313.15에서 333.15 K까지 뷰셀(view cell) 내에서 측정하였다. 이미다졸유도체 이온성액체인 육불화 1-부틸-3-메틸이미다졸([bmim][PF₆]), 사불화 1-부틸-3-메틸이미다졸([bmim][BF₄]), 사불화 1-옥틸-3-메틸이미다졸([omim][BF₄])을 연구에 사용하여, 압력, 온도, 양이온과 음이온의 성질, 그리고 수분 함량이 CO₂의 흡수에 의한 이온성액체의 부피팽창에 미치는 영향을 실험적으로 조사하였다. 부피팽창은 긴 양이온 알킬그룹을 가지고 있는 이온성액체 및 음이온 극성이 작은 이온성액체에서 크게 나타났다. 수분함량이 적을수록, 온도가 낮을수록, 그리고 압력이 높을수록 이온성액체상의 부피는 더 크게 나타났다.

주제어 : 이온성액체, 부피팽창, 초임계이산화탄소, 수분함량, 양이온, 음이온

Abstract : The volume expansion of three ionic liquids (ILs) in the presence of supercritical carbon dioxide has been measured at pressures up to 32 MPa and at temperatures from 313.15 to 333.15 K in a high-pressure view cell. The imidazolium-derivative ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]), and 1-octyl-3-methylimidazolium tetrafluoroborate ([omim][BF₄]) were employed in this research. The effects of pressure, temperature, nature of anion and cation as well as the water content on the volume expansion of ILs by absorbing CO₂ were investigated experimentally. The volume expansion was higher for the ILs with longer cationic alkyl group and for the ILs with lower anion polarity. The lower the water content, the lower the temperature, or the higher the pressure, the higher was the expansion of IL phase.

Key words : Ionic liquid, Volume expansion, Supercritical carbon dioxide, Water content, Anion, Cation

Introduction

Due to their useful properties, ILs have been considered as new green chemicals. ILs have negligible vapor pressure, non-toxicity and non-flammability, thermal stability, and good ionic

conductivity[1]. Room temperature ionic liquids (RTILs) are ILs that have melting points below the room temperature because they are weak organic salts and have been spotlighted as alternative solvents for the last two decades[2]. RTILs are attracted in many applications that span from pure sciences to industry. Existing as a liquid over a wide temperature range, those compounds have

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generally been considered as alternative solvents to conventional organic solvents in a variety of reactions and separation processes[3]. Toxic conventional volatile organic solvents vaporize after the reaction and escape into the atmosphere during the separation process, contaminating the environment significantly. Nonvolatile IL solvents, however, can prevent the negative effects on the environment since they can be regenerated and recycled without vapor contamination, making them environmentally friendly alternatives to the harmful organic solvents[3]. The very high polarity and good catalytic activity of ILs make them dissolve both inorganic and organic compounds due to their ionic nature[4-6], which, in turn, offers a lot of possibilities to create new compounds [1,2,4-6].

Supercritical fluids have unique characteristic property of tunable solvent strength obtained by adjusting pressure and temperature. They also have gas-like transport properties and liquid-like solubility, allowing numerous applications such as extraction, fractionation, chemical reaction, polymerization, and materials processing. Among all the supercritical fluids, supercritical carbon dioxide (scCO₂) is the most attractive solvent due to its mild critical condition (304.1 K and 7.38 bar), and as it is nontoxic, nonflammable, and inexpensive. Therefore, scCO₂ has also been considered as an environmentally friendly clean solvent.

We can apply this new set of clean solvents to a synthesis process by combining those advantages of scCO₂ and ILs, in which reaction and separation occur consecutively. Due to the strong electrostatic forces between cations and anions, scCO₂ dissolves and swells well the IL phase, while ILs basically do not dissolve in scCO₂[7,8]. The organic products from a reaction in the IL-phase can, therefore, be extracted by supercritical CO₂, allowing only a small amount of cross-contamination between the IL and scCO₂ phases[9]. To establish such a one-pot process, we need to know the solubility of CO₂ in ILs and the ternary phase equilibrium of a ternary IL/CO₂/organic compound system. As it is difficult to measure the amount of CO₂ in the IL phase, the majority of the previous research have measured the amount of CO₂ remaining in the fluid phase. The initial and final volumes of the fluid phase can be determined by the total internal cell volume subtracted by the volume of the IL phase. As increasing the pressure, the more CO₂ penetrates into the IL phase with increasing the volume of the phase. Therefore, the knowledge of the volume expansion (or swelling) of the IL phase is necessary to calculate the sorption and phase equilibrium of the IL and CO₂ phases. The volume expansion of the IL phase has been measured by many researchers at various temperatures and pressures[7,10-15].

Brennecke and co-workers[7,10] measured the CO₂ solubility in several imidazolium-based ILs and their volume expansivity using a high-pressure vapor-liquid phase equilibrium apparatus and correlated the solubility with the liquid molar volume using the

“free volume” concept. Fu et al.[11] measured the solubility of CO₂ as well as the volume expansivity of ILs containing different amounts of water at high pressures up to 25 MPa. Maurer and co-workers[12,13] measured the volume expansivity of ILs as well as the solubility of CO₂ in [bmim][PF₆] up to 9.8 MPa using a synthetic view-cell technique and correlated their results by means of an extended Henry’s law. Gu and Brennecke[14] measured the volume expansivities and isothermal compressibilities of imidazolium and pyridinium-based ionic liquids at pressures up to 206.9 MPa. In our previous study[15], we measured the volume expansion of [bmim][PF₆] in the presence of CO₂ as well as the phase equilibrium of ternary systems consisting of IL-CO₂-organic compound at pressures up to 33 MPa and temperatures between 313.15 and 343.15 K. Since we did not measure the volume of the vapor phase, our previous volume expansion data could not be used to calculate the amount of sorption.

Though the binary and ternary phase equilibrium data are of great importance in designing the synthesis/separation process using both IL and scCO₂, we still lack of reliable and accurate CO₂ solubility data in ILs at very high pressures[10-15]. Most solubility and volume expansion data were measured at low pressures less than 10 MPa, except for some studies including the one by Fu et al.[11] who measured up to 25 MPa (only for [bmim][PF₆]). Therefore, in this study, the volume expansions of three ILs ([bmim][PF₆], [bmim][BF₄], and [omim][BF₄]) are investigated up to explicitly higher pressures of maximum 32 MPa. The influence of types of IL as well as the water content on the volume expansion of IL is discussed.

Experimental

Materials

The imidazolium-based ionic liquids [bmim][PF₆] (purity > 99 %, water content = 12×10^{-4} in mass fraction, chloride content

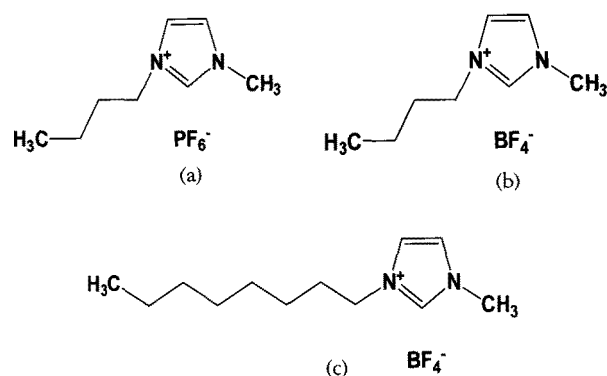


Figure 1. The molecular structures of ionic liquids used in this study: (a) [bmim][PF₆], (b) [bmim][BF₄], and (c) [omim][BF₄].

Table 1. Water contents in the three ionic liquids investigated in this study before and after the moisture removal treatment

Ionic liquids	Before (mass ppm)	After (mass ppm)	Moisture Removal (%)
[bmim][PF ₆]	700	170	76
[bmim][BF ₄]	2000	220	89
[omim][BF ₄]	4200	410	90

= 0.79×10^{-4} in mass fraction), [bmim][BF₄] (purity > 99 %, water content = 59×10^{-4} in mass fraction, chloride content = 5.2×10^{-4} in mass fraction), and [omim][BF₄] (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). Figure 1 shows the molecular formulas of these ILs. They were pretreated in the vacuum oven at 363.15 K for 12 hr to remove water. The percentage of moisture removal from the ILs was ranged from 76 to 90% (Table 1). CO₂ (99.5 %) was purchased from Daedong Gastech (Daegu, Korea) and used without further purification.

Measurement of Volume Expansion of ILs

The volume expansions of ILs due to the CO₂ sorption were measured in a view-cell apparatus (Hanwool Model SC-6100) shown in Figure 2. Since water with polar nature can play an important role in the sorption of CO₂ and the expansion of the IL phase, the IL samples were dried as described above. The water contents before and after the drying process were 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 700 to 4200 ppm and about 75 to 90% of water was removed after the drying step. However, a small amount of water (170 to 410 ppm) still remained in the ILs due to their

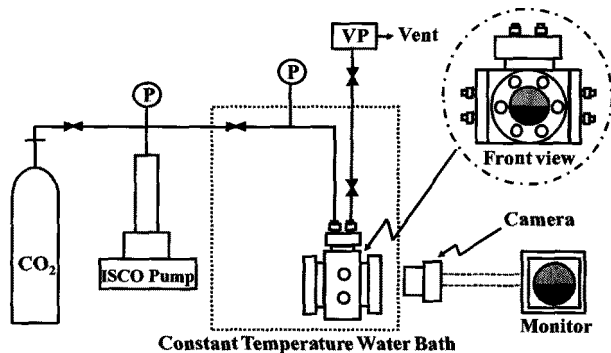


Figure 2. A schematic diagram of the experimental equipment to measure the volume expansion of ionic liquids in the presence of supercritical carbon dioxide (VP: vacuum pump, P: pressure transducer).

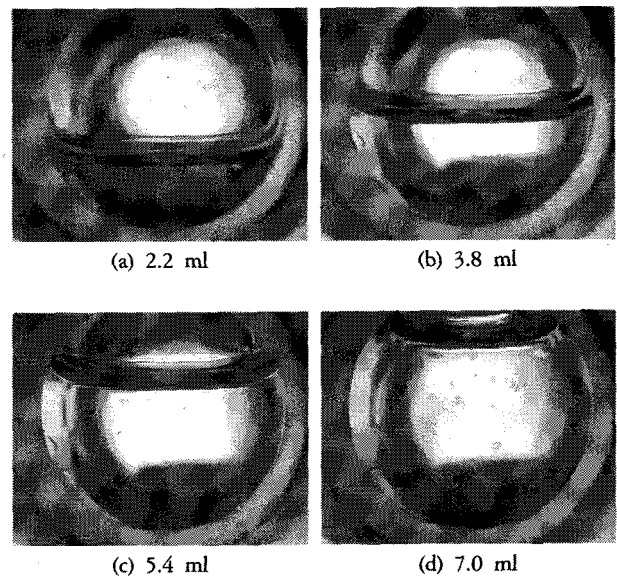


Figure 3. Gas-liquid boundaries (i.e., menisci) that were formed by injecting (a) 2.2 ml, (b) 3.8 ml, (c) 5.4 ml, and (d) 7.0 ml of methanol. The bottommost curve in each meniscus was considered as the true interface of liquid and gas (or liquid level).

strong polar nature.

Before measuring the volume expansion of IL, a calibration chart was made to show the relationship between the height of the liquid level and the amount of liquid in the cell. It was done by injecting incrementally a known volume (0.2 mL) of methanol with a precision syringe and measuring the corresponding height of the liquid level in the view cell. The injected amount of methanol was obtained from the difference of the weights of the syringe before and after the injection measured to ± 0.0001 g on a chemical balance (Mettler Toledo AG204). All the methanol samples in the view cell were video-taped and the height of the liquid phase was measured on a 17 inch monitor where the view was expanded about 10 times to reduce the error in reading the liquid levels. Among all the 26 samples only four are shown consecutively in Figure 3 with an interval of 1.6 ml. The position of the phase boundary appears thick covering 11 ~ 13% of the diameter of the visible window. As methanol is adhesive to the wall making a meniscus concave-downward on the window, we have selected the bottommost curve as the true interface between the liquid and gas phases (or liquid level).

To measure the volume expansion of IL, the view cell was evacuated and then filled with low-pressure CO₂. A predetermined amount of IL (about 2.5 ml) 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. 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

Table 2. Volume expansions of [bmim][PF₆] ($\Delta V/V$) with water content of 170 ppm caused by absorbing CO₂ with water at various pressures and temperatures

<i>T</i> (K)	<i>P</i> (MPa)	$\Delta V/V$ (%)
313.15	0.101	0.0
	2.77	7.0
	5.85	17.3
	8.78	24.0
	12.53	26.0
	15.79	26.4
	21.06	27.2
	24.14	28.0
	27.59	28.4
	323.15	0.101
3.52		7.0
6.19		14.6
9.03		22.0
11.71		24.0
14.92		25.0
18.33		25.8
22.02		26.4
24.58		27.0
27.64		27.6
333.15	0.101	0.0
	3.96	6.5
	7.27	14.5
	10.35	19.3
	13.83	22.1
	17.22	23.4
	20.76	24.7
	24.40	25.4
	28.33	26.7
	31.52	27.2

same condition for 30 min to ensure the thermal equilibrium. High-pressure CO₂ was supplied to the view cell at a constant pressure controlled by an automatic syringe pump (ISCO 260D). The pressure in the cell was measured by a pressure gauge (Sensotec TJE/GM) to ± 34 kPa.

When the equilibrium was reached after 20 to 30 min of stirring with a magnetic stirrer, stirring was stopped to see the phase behavior at the new equilibrium. The liquid phase (i.e., the IL phase saturated with CO₂) and the vapor phase (i.e., the high-pressure CO₂ phase) in the view cell were recorded by a video camera connected to a 17 inch monitor as described above. The position of the phase boundary was measured from the monitor with uncertainty of $\pm 2\%$, depending on the angle of view because the sapphire window is located about 1.5 cm inside of the edge of the window cap. The volume of each phase was then calculated using the calibration chart made previously as shown above. The liquid level on the monitor was measured at the equilibrium after each injection of 0.02 ml liquid CO₂.

At a constant temperature, the pressure was then increased by 2.7 MPa in each step until it reaches 31.5 MPa at the maximum.

Table 3. Volume expansions of [bmim][BF₄] ($\Delta V/V$) with water content of 220 ppm caused by absorbing CO₂ with water at various pressures and temperatures

<i>T</i> (K)	<i>P</i> (MPa)	$\Delta V/V$ (%)	
313.15	0.101	0.0	
	3.01	9.3	
	6.48	21.0	
	9.01	26.0	
	10.65	28.0	
	16.02	29.5	
	19.38	31.2	
	31.50	33.6	
	323.15	0.101	0.0
		2.98	7.1
5.28		14.9	
7.08		19.6	
10.41		25.5	
13.64		26.7	
17.6		28.2	
21.13		29.4	
24.26		30.6	
27.19		31.4	
31.00	32.2		
333.15	0.101	0.0	
	3.29	7.5	
	7.79	16.7	
	10.34	21.7	
	13.95	24.0	
	17.65	26.3	
	20.84	28.0	
	24.68	28.5	
	27.68	29.5	
	31.00	30.0	

The above-mentioned procedure to determine the phase volumes was repeated after each pressure increment. Similar experiments were performed at three different temperatures of 313.15, 323.15, and 333.15 K. The overall experimental uncertainty was less than $\pm 5\%$, including the reading error of the height of meniscus between IL and CO₂ phases.

Results and Discussion

Effects of pressure and temperature

The volume expansion of IL(2) caused by the sorption of CO₂(1) was measured at each pressure after increment of about 2.7 MPa at three different temperatures (see Tables 2–4). The volume expansion of IL is defined as[16]:

$$\frac{\Delta V}{V} = \frac{V_L(T, P, x) - V_2(T, P_0)}{V_2(T, P_0)} \quad (1)$$

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

Table 4. Volume expansions of [omim][BF₄] ($\Delta V/V$) with water content of 410 ppm caused by absorbing CO₂ with water at various pressures and temperatures

<i>T</i> (K)	<i>P</i> (MPa)	$\Delta V/V$ (%)
313.15	0.101	0.0
	2.91	7.5
	5.70	17.5
	7.48	25.0
	8.42	27.5
	10.57	31.8
	13.49	33.0
	17.16	34.5
	20.58	35.3
	24.42	36.5
	27.52	36.6
323.15	0.101	0.0
	2.23	3.5
	3.85	8.0
	5.85	15.0
	7.81	21.3
	11.0	27.5
	13.77	30.0
	17.57	32.3
	21.09	33.5
	24.13	34.0
	27.23	34.8
333.15	0.101	0.0
	1.85	2.0
	3.49	5.0
	6.06	12.5
	7.63	16.3
	10.43	22.5
	13.67	27.0
	17.32	30.0
	20.80	31.3
	24.31	32.5
	27.86	33.0
31.14	33.8	

temperature and atmospheric pressure. The volume expansion of IL ($\Delta V/V$) increased rapidly to about 20 ~ 30% at pressures up to 8 ~ 10 MPa for all three ILs ([bmim][PF₆], [bmim][BF₄], and [omim][BF₄]), but above these pressures the volume expansion rate was much reduced but still in appreciable amount even above 30 MPa at all temperatures (Figure 4). The steep increase in volume with increasing pressure at low-pressures may be due to the sorption into the inter-ion space. As the openings, called "free volume," between bulky cation and relatively small anion of the IL are large, CO₂ molecules can easily enter that space, until they are filled up with CO₂ molecules as pressure increases. This process is closely related to the solubility behavior[7,17-19]. To allow more CO₂ molecules in the IL the inter-ion space must be expanded but this process requires energy. After then, only small

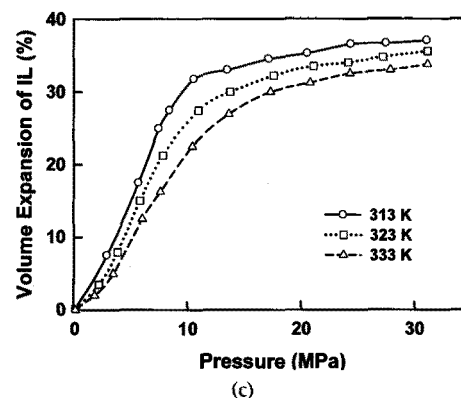
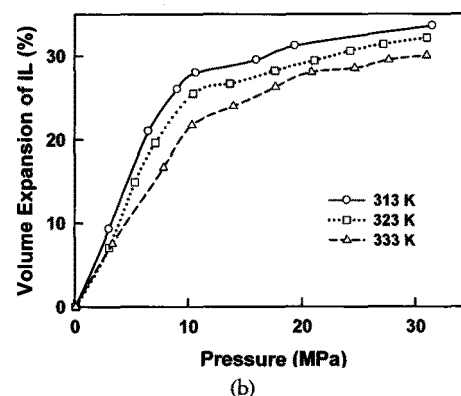
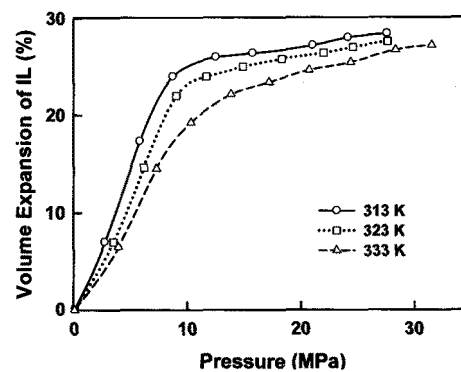


Figure 4. Volume changes of ILs caused by absorbing CO₂ at three different temperatures: (a)[bmim][PF₆] with 170 ppm of water content, (b)[bmim][BF₄] with 220 ppm, and (c)[omim][BF₄] with 410 ppm.

amount of CO₂ can penetrate into the free-volume.

At a given pressure, the volume expansion of IL at a higher temperature is smaller than that at a lower temperature for all three imidazolium-based ILs (Figure 4). This may be due to the decrease in the attractive interaction between the ions and CO₂ molecules, caused by the increase in their kinetic energy with temperature. For each IL, the difference in the volume expansions at 313.15 and 333.15 K was largest (25 ~ 30%) near 10 MPa, while it was reduced to 6 ~ 10% at 30 MPa. At 10 MPa and 313.15 K the values of the volume expansions of [bmim][PF₆], [bmim][BF₄], and

[omim][BF₄] are 25.1, 28.3, and 31.3%, respectively. The details of this result will be discussed below.

Effects of cations and anions

Ordinary inorganic salts, such as NaCl and KCl, have a strong inter-ion Coulombic force because the anion and the cation are small and thus have a high ionic density. On the contrary, ILs have a weak inter-ion interaction force as their ions are bulky and thus have a lower ionic density. Furthermore, the positive charge of the cation is evenly distributed on the two N atoms of the imidazolium ring. Therefore, the ionic strength of the cation is further weakened, lowering the melting point to below room temperature.

In Figures 4 and 5, [omim][BF₄] that has cation [omim]⁺ with a longer linear CO₂-philic hydrocarbon chain than [bmim]⁺ showed the largest volume expansion and thus the highest CO₂ solubility among the three. These results coincide with the literature[7,17-19]. Aki et al.[7] and Shin et al.[19] showed an increase in solubility when a longer alkyl chain is substituted onto an N atom of the imidazolium cation. For ILs with the same anion [BF₄]⁻, we can assume the higher solubility of CO₂ results in the larger volume of IL because the anion dominates the interactions with CO₂, with the cation playing the secondary role[3]. The two ILs, [bmim][PF₆] and [bmim][BF₄], have the same cation but have different anions. Anion [PF₆]⁻ in the former IL is less polar and thus more CO₂-philic than anion [BF₄]⁻ in the latter, resulting in a higher CO₂ solubility. Our companion study[17] has verified this cation and anion effects on solubility by showing that the solubilities of CO₂ in the three ILs at 313.15 K and 10 MPa are 0.72, 0.78, and 0.81 in mole fraction for [bmim][BF₄], [bmim][PF₆], and [omim][BF₄], respectively. However, the volume expansion data of the two ILs showed the reverse of what we had expected based on the solubility (Figure 5). The volume expansion of [bmim][PF₆] was 25.1%, which is smaller than 28.3% of [bmim][BF₄]. Aki et al.[7] showed that the anion has a significantly stronger impact on the gas solubility than the cation and that the solubility of CO₂

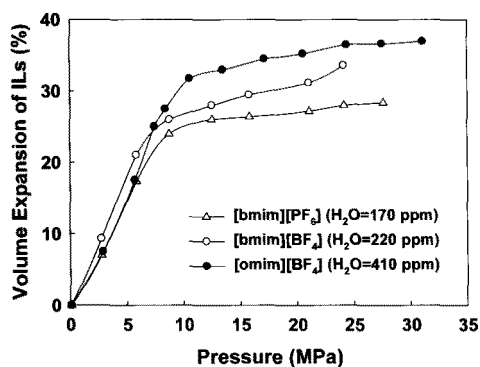


Figure 5. Comparison of the volume expansions of three ILs at 313.15 K.

Table 5. Volume expansions of ILs ([bmim][PF₆], [bmim][BF₄], and [omim][BF₄]) with a high water content(*w*₃) caused by absorbing CO₂ at 313.15 K

<i>W</i> ₃ (ppm)	<i>P</i> (MPa)	$\Delta V/V$ (%)	
700	[bmim][PF ₆]		
		0.101	0.0
		3.62	8.1
		6.62	15.9
		10.29	22.7
		14.13	25.0
		21.95	27.3
		25.75	27.7
		28.45	28.4
		31.53	28.7
2000	[bmim][BF ₄]		
		0.101	0.0
		4.82	12.0
		7.14	20.0
		10.39	25.0
		13.85	27.6
		17.20	28.2
		21.11	29.9
		24.50	30.9
		27.65	31.2
	31.54	31.6	
4200	[omim][BF ₄]		
		0.101	0.0
		3.47	8.0
		6.06	17.0
		8.03	22.0
		13.07	29.7
		18.59	32.3
		20.76	32.6
		24.66	33.2
		27.77	33.5
	31.33	34.3	

in [bmim] cation-based ILs increases in the order of [NO₃] < [BF₄] < [PF₆] < [Tf₂N] at 313.15 K. From ATR-IR spectroscopy, Kazarian et al.[20] showed that [BF₄]⁻ acts as a stronger Lewis base towards CO₂ than [PF₆]⁻, which contradicts to the data of Blanchard et al.[10] as well as our data[17]. They concluded that, in addition to the strength of the interaction of CO₂ with anion, the free volume contribution in the IL plays a significant role. Actually, as [PF₆]⁻ anion is bulkier than [BF₄]⁻, [bmim][PF₆] has more free space between the anion and the cation than [bmim][BF₄]. By acknowledging this difference we can explain the above volume expansion behavior (shown in Figure 5) that this free space may be used to admit the CO₂ molecules without its volume expansion and that the stronger interaction between [bmim]⁺ and [BF₄]⁻ breaks and the gaps are expanded as more CO₂ molecules attach on the fluorine atoms of the anion[20]. The interaction between CO₂ molecules and the anion is stronger for [PF₆]⁻ than [BF₄]⁻ since larger molecules normally have a stronger

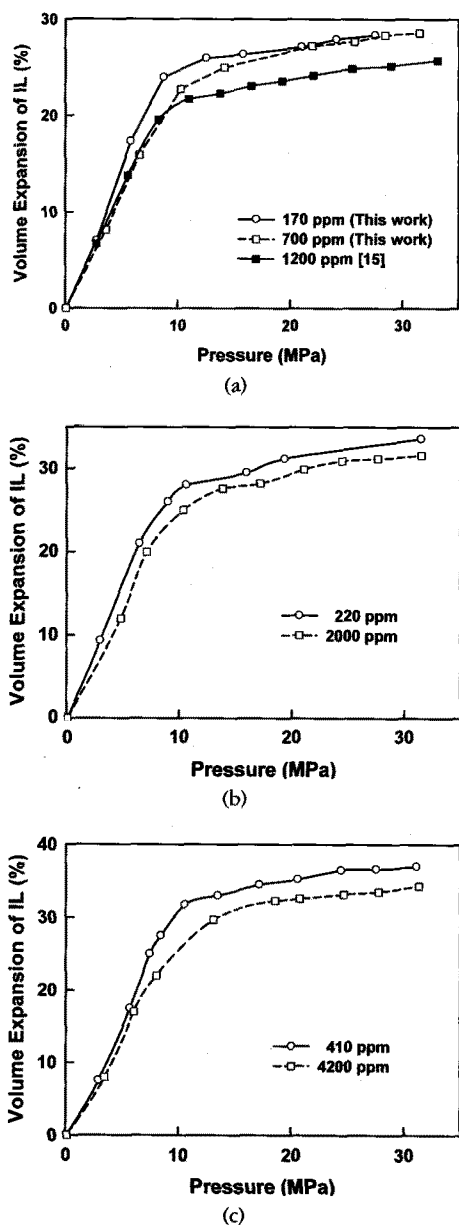


Figure 6. Volume expansions of ILs with two different water contents caused by absorbing CO₂ at 313.15 K: (a) [bmim][PF₆], (b) [bmim][BF₄], and (c) [omim][BF₄].

dispersion force.

Effects of water content

The water(3) content in IL(2) is defined as follows:

$$w_3 = \frac{m_3}{m_2 + m_3} \quad (2)$$

where m_2 is the mass of IL and m_3 is the mass of water in IL. The water content of IL before treatment and the one after moisture removal treatment are obtained to be 1.7×10^{-4} and 7.0×10^{-4} for

[bmim][PF₆]; 2.2×10^{-4} and 20×10^{-4} for [bmim][BF₄]; 4.1×10^{-4} and 42×10^{-4} for [omim][BF₄], respectively (see Tables 2–5). Those ILs with lower water content showed higher solubility of CO₂ at 313.15 K (Figure 6). The largest difference in volume expansion of IL between the same ILs with different water contents was observed to be about 10 ~ 15% at pressures 8 ~ 10 MPa for all the ILs tested here. At higher pressures, that difference is reduced to about 8% at 30 MPa, except for [bmim][PF₆] that shows only 1 ~ 2%. When an IL has higher water content, those water molecules may occupy more “inter-ion” space which CO₂ molecules can take otherwise. This agrees with the results by our companion study[17] and by Fu et al.[11] who observed smaller CO₂ solubility for IL with higher water content. The volume expansion of [bmim][PF₆] with 700 ppm is similar to that of our previous study with 1200 ppm[17] up to about 10 MPa. Our previous study done with a Jerguson gauge a few years ago shows 10 ~ 15% smaller volume expansion than this study. The reason for this discrepancy may be because in the precious study the vapor-liquid contact surface and time were not good enough (as relatively large CO₂ bubbles slowly passed through the long IL column) and because the IL must have been saturated with water as CO₂ with high water content (<0.5%) was continuously supplied for several hours. As discussed above, an IL with 5 times higher water content had about 1 ~ 10% smaller volume expansion for [bmim][PF₆]. If the IL was saturated with water, the volume expansion could have been further reduced. Two other ILs with about 10 times higher water content showed 10 ~ 20% smaller volume expansion.

Conclusions

The volume expansion of three imidazolium-based ILs were measured at the three temperatures of 313.15, 323.15, and 333.15 K and at pressures up to 32 MPa. As the pressure was increased, the volume of IL increased rapidly at low pressures but this increase slowed down above the pressure range of 8 to 10 MPa and finally leveled off at about 30 MPa. As temperature was raised by 20 K, the corresponding volume expansion decreased about 25 ~ 30 % at pressures of 8 to 10 MPa and about 6 ~ 10 % at 30 MPa. The volume expansion of IL was also found to be dependent upon the nature of cation and anion. The IL with longer alkyl-chain cation [omim] showed an about 11 % larger solubility than that of shorter alkyl-chain cation [bmim] due to the favorable interaction between CO₂ and alkyl side chain. When the anion [BF₄]⁻ was replaced by [PF₆]⁻, the volume expansion unexpectedly decreased by about 11 %. This decrease may be due to the larger free volume of [bmim][PF₆] than [bmim][BF₄]. As the water content increased by 4 ~ 10 times, the solubility of CO₂ at 313.15 K dropped 10 ~ 15% near the pressure of 8 to 10 MPa and 1 ~ 8% at high pressures near 30 MPa. Our results are necessary in calculating the solubility of CO₂ in ILs that

may be worth in designing the commercial process using IL as a solvent.

Acknowledgement

This research was supported by the grant (RTI04-01-04) from the Regional Technology Innovation Program of the Ministry of Knowledge Economy.

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