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Effect of Water Content on the Solubility of CO_2 in the Ionic Liquid [bmim][PF_6]

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The solubility of CO_2 in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) and the liquid-phase molar volume were determined, in a precision high-pressure PVT apparatus, for water mass fraction of [bmim][PF_6] ranging from 0.0067 % to 1.6 % and over temperature and pressure ranges of (40 to 60) °C and (1 to 25) MPa. The deviation in solubility, at the same temperature and pressure, with different water mass fractions was not more than 15 %, and the average is 6.7 %. Solubility pressures were correlated with an average relative uncertainty of about 1 % by means of the extended Henry's law for all water mass fractions investigated at less than 6 MPa.

Introduction

Ionic liquids (IL), holding great potential as replacements for traditional organic solvents, have attracted more and more attention due to their lack of volatility and other unique characteristics.[1−5] However, separation and recovery of IL is one of the major challenges in future industry applications. Distillation, liquid−liquid extraction, and supercritical fluid extraction are known feasible separation methods. Distillation, a reasonable option owing to no appreciable vapor pressure of IL, would not be prudent for thermally labile or low-volatility products. Cross-contamination between the phases presents a problem for liquid−liquid extraction.[6,7] Comparatively, supercritical fluid extraction with CO_2 can be used to separate both volatile and relatively nonvolatile organic compounds from ionic liquids without any IL contamination.[8,9] Knowledge of the phase behavior of the CO_2 + IL systems, which is a crucial aspect of this methodology, has been the focus of much research in recent years.[10−24]

Several research groups studied the effect of water content on the solubility of CO_2 in some IL. Blanchard et al.[10] reported solubility data of CO_2 in [bmim][PF_6] with two different water mass fractions (0.15 % and 2.3 %). Those data were measured at 40 °C and less than 10 MPa. They concluded that drying of IL samples prior to use was crucial as a small amount of water in the IL had a dramatic effect on the phase behavior with CO_2. Aki et al.[22] reported solubility data of CO_2 in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonylimide) ([bmim]-[Tf_2N]) with two different water mass fractions (0.045 % and 1.35 %). Those solubilities were measured at 25 °C and less than 7 MPa. They concluded that the presence of water had essentially no effect on the solubility of CO_2 in [bmim][Tf_2N]. Baltus et al.[23] studied the solubility of CO_2 in several ionic liquids at 25 °C with pressures at or less than 0.1 MPa. The data, which were measured with a quartz crystal microbalance, indicated that humidity had a small effect on the solubility of CO_2 in [bmim][Tf_2N] and 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonylimide) ([C_8mim][Tf_2N]). Scovazzo et al.[24] measured the Henry's constants of CO_2 + [bmim][PF_6] and CO_2 + 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonylimide) ([emim][Tf_2N]) for both dry and water-saturated ionic liquids at 30 °C and less than 0.1 MPa. The results indicated that moisture had a small effect on the solubilities. To sum up, there are different conclusions about the effect of water content on the solubility of CO_2 in ionic liquids, and no systematical exploration has been carried out.

It is almost inevitable for ionic liquid [bmim][PF_6] to absorb moisture in industrial processes due to its hydroscopic property. The question arises as how the water content affects the phase behavior. In this work, phase behavior data are reported for the system of CO_2 + [bmim][PF_6] within water mass fraction of [bmim][PF_6], temperature and pressure ranges of (0.0067 to 1.6) %, (40 to 60) °C, and (1−25) MPa, respectively.

Experimental Section

Materials. CO_2 with a purity of 99.995 % was supplied by Beijing Analytical Instrument Factory. 1-Methylimidazole (99 % purity) and potassium hexafluorophosphate (98 % purity) were used as received from Fluka. 1-Bromobutane was analysis reagent grade and produced by Beijing Chemical Reagent Factory. [bmim][PF_6] was synthesized and characterized following procedures reported elsewhere.[25,26] Five samples of [bmim][PF_6] with different water mass fractions were prepared by different pretreatment. [bmim][PF_6] with water mass fraction of 0.0067 % was obtained by contacting the sample with water mass fraction 0.15 % with 3 Å molecular sieve, 0.15 % by vacuum-drying at 80 °C for 48 h, 0.89 % by injection of quantitative water into the sample with water mass fraction 0.15 %, 1.6 % by centrifugal separation between wet IL and water at ambient temperature 16 °C, and 2.2 % by separatory funnel separation between wet IL and water at ambient temperature 24 °C. It is noteworthy to mention that sample with water mass fraction of 2.2 % is not a true solution and, therefore, was not included as a part of this study. Water mass fraction of this sample declined to 1.1 % after 40 min and 2000 revolution/min centrifugal separation at ambient temperature 24 °C. All the water concentrations were measured by Karl Fischer analysis. Sample density measurements were performed at 40 °C, and ambient pressure with AP PAAR density meter DMA 48. The results were shown in Table 1.

Apparatus and Procedure. The main apparatus is a Ruska PVT 2730−601 device, which is shown schematically in Figure 1. The model 2730 PVT system is a high precision instrument

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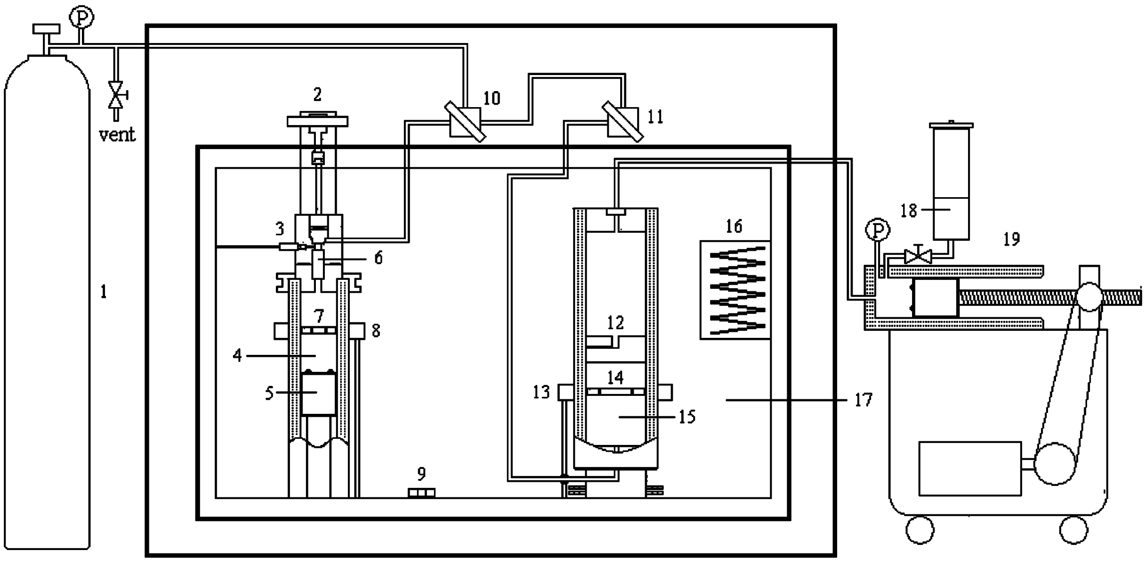

Figure 1. Schematic diagram of Ruska PVT 2730-601: 1, CO_2 reservoir; 2, pump cell shutoff valve; 3, temperature and pressure transducer; 4, pump cell; 5, pump piston; 6, sapphire tube; 7 and 14, stirring magnet; 8 and 13, stirring collar; 9, oven RTD; 10, charging valve; 11, floating piston cell shutoff valve; 12, floating piston; 15, floating piston cell; 16, heater; 17, thermostat; 18, hydraulic oil; 19, digital positive placement pump.

Table 1. Densities of [bmim][PF$_6$] (1) with Different Water (2) Mass Fractions w_2 at 40 °C and Ambient Pressure

pretreatment	w_2	$\rho/(g\cdot cm^{-3})$
3 Å molecular sieve	0.0067 %	1.3587
vacuum-drying	0.15 %	1.3576
water injection	0.89 %	1.3473
centrifugal separation	1.6 %	1.3355

used to perform volumetric and phase behavior studies. The system is based on a unique dual-cell arrangement where the main cell volume is varied by the vertical movement of a dynamically sealed piston driven by a computer-controlled stepping motor. The second cell contains a floating piston operated by an external pump. The cells are connected by small-bore tubing through a sapphire sight glass at the top of the main cell and placed in a constant-temperature bath. This configuration allows phase volume measurements to be made by positioning the phase boundary at a reference point in the sight glass. The computer then automatically calculates the volumes above and below the reference point. The maximum pressure accessible with this apparatus is 68.9 MPa. The resolutions of pressure, volume, and temperature in the system are 0.007 MPa, 0.01 mL, and 0.1 °C, respectively.

A static method, one of the commonly used techniques,[8,10,20,22] was used to determine the solubility of CO_2 in [bmim][PF$_6$] with different water concentrations. In a typical experiment, known amounts of CO_2 and [bmim][PF$_6$] were metered into the main cell while the sample within was vigorously stirred to ensure equilibrium. Up and down stirring mode of the PVT apparatus was helpful to reach equilibrium quickly. The criterion of reaching phase equilibrium was invariable whole volume over 40 min in the constant pressure mode. Subsequently, the liquid-phase volume was determined at constant pressure. The composition of the IL-rich liquid phase was calculated on the basis of material balance, along with the assumption of a pure CO_2 vapor phase. This assumption was verified by experiments done by many researchers.[8−11,14] In addition, water in [bmim]-[PF$_6$] can hardly enter CO_2-rich phase due to strong hygroscopicity of [bmim][PF$_6$] and very low solubility of water in CO_2, even at high pressures.[27] For example, the water mass fraction of sample was merely reduced to 1.5 % from 1.6 % after experiments at 60 °C and (1 to 9) MPa. The estimated uncertainties in the calculated liquid-phase mole fractions and liquid molar volumes are ± 0.001 and ± 0.1 mL/mol, respectively, based on propagation of random errors in the measurements of the pressures, volumes, and temperatures.

Results and Discussion

The phase behavior of CO_2 + [bmim][PF$_6$] systems with different water contents was determined by the static method. The results are presented in Table 2, which give a systematical knowledge about how pressure, temperature, and water content affect the solubility of CO_2 in [bmim][PF$_6$] as well as the liquid molar volume.

The solubility of CO_2 in [bmim][PF$_6$] with water mass fraction of 0.15 % is illustrated in Figure 2 where the mole fraction of CO_2 in the IL-rich phase is plotted as a function of pressure. As can be seen from Figure 2, the solubility increased dramatically with increasing pressure at pressure < 10 MPa, increased slowly and then more at > 10 MPa, and increased very little at > 15 MPa. As expected, the solubility decreased with an increase in temperature, but the temperature dependence is quite small over the temperature and pressure range studied.

Figure 3 shows the $P-x$ diagram of CO_2 + [bmim][PF$_6$] systems with different water contents at 50 °C, from which can be seen that the mole fraction of CO_2 decreased regularly with an increase in water mass fraction at the same temperature and pressure. Also, this figure indicates that influence of water content on the solubility is not so significant throughout the temperature and pressure range investigated, which can be clearer for mole fraction CO_2 calculated on a basis of water free (i.e., the formula $x_{CO_2} = n_{CO_2}/(n_{CO_2} + n_{IL} + n_{H_2O})$ turned into $x_{CO_2} = n_{CO_2}/(n_{CO_2} + n_{IL})$). The deviation in solubility, at the same temperature and pressure, with different water mass fraction investigated was not more than 15 %, and the average is 6.7 %. On the water free basis, the average deviation reduced to 3.9 %. Figure 4 was provided for contrast, in which mole fraction CO_2 was calculated with the latter formula.

The solubility pressures were correlated by means of the extended Henry's law[20] for all water mass fractions investigated at pressures less than 6 MPa. It should be noticed that solubility must be on the molality scale for better linearity. Henry's constants resulting from the correlations were given in Table

Table 2. Mole Fraction Solubility of CO_2 (2) x_2 in [bmim][PF_6] (1) with Different Water (3) Mass Fractions w_3 and Liquid Molar Volumes V_m at (40, 50, and 60) °C

		$t = 40$ °C		$t = 50$ °C		$t = 60$ °C	
w_3	P/MPa	x_2	V_m/mL·mol^{-1}	x_2	V_m/mL·mol^{-1}	x_2	V_m/mL·mol^{-1}
0.0067 %	1	0.129	187.2	0.112	192.7	0.099	195.3
	2	0.215	169.7	0.200	176.2	0.179	178.8
	3	0.288	156.3	0.271	162.7	0.243	168.3
	4	0.356	144.7	0.331	151.1	0.301	157.7
	5	0.412	136.8	0.383	141.9	0.350	148.5
	6	0.456	129.9	0.425	135.9	0.391	140.8
	7	0.490	124.3	0.465	128.3	0.426	135.0
	8	0.510	121.4	0.492	123.6	0.454	130.3
	9	0.529	117.2	0.514	120.3	0.478	125.8
0.15 %	1	0.131	183.0	0.110	183.6	0.094	196.5
	2	0.232	165.2	0.197	168.4	0.171	183.1
	3	0.312	151.4	0.268	157.9	0.235	171.0
	4	0.376	139.8	0.324	150.3	0.290	161.2
	5	0.427	131.0	0.374	141.9	0.335	153.2
	6	0.469	123.8	0.416	134.7	0.375	146.0
	7	0.503	118.2	0.451	128.4	0.408	139.9
	8	0.525	115.3	0.479	123.5	0.436	135.1
	9	0.554	109.1	0.499	120.3	0.460	131.3
	10	0.571	105.4	0.519	117.5	0.481	127.7
	12	0.626	92.3	0.553	110.3	0.510	121.8
	15	0.641	90.2	0.570	107.1	0.541	115.7
	20	0.648	88.2	0.590	103.2	0.564	111.1
	25	0.658	86.2	0.606	99.9	0.580	107.7
0.89 %	1	0.116	169.6	0.096	171.5	0.082	179.2
	2	0.205	156.4	0.174	159.5	0.152	167.9
	3	0.278	145.1	0.240	149.4	0.211	158.4
	4	0.339	135.6	0.296	140.9	0.262	150.5
	5	0.390	127.9	0.345	133.5	0.307	143.4
	6	0.432	121.5	0.386	127.2	0.346	137.2
	7	0.466	116.5	0.421	122.0	0.379	132.1
	8	0.492	112.4	0.448	117.7	0.407	127.9
	9	0.504	110.8	0.467	114.8	0.429	124.6
1.6 %	1	0.126	151.8	0.108	155.1	0.083	161.5
	2	0.215	139.0	0.183	144.9	0.161	149.3
	3	0.280	130.3	0.246	136.5	0.220	140.7
	4	0.338	122.7	0.297	129.5	0.274	133.1
	5	0.386	116.6	0.343	123.4	0.320	126.8
	6	0.426	112.4	0.380	118.5	0.358	121.5
	7	0.455	108.3	0.410	114.9	0.390	117.3
	8	0.467	107.5	0.429	112.9	0.417	113.5
	9	0.473	107.5	0.452	109.9	0.441	110.5

[a] x_2, mole fraction CO_2 in the liquid phase; $x_2 = n_2/(n_1 + n_2 + n_3)$. w_3, water mass fraction of the [bmim][PF_6] + water mixture; $w_3 = m_3/(m_1 + m_3)$. V_m, liquid molar volumes; $V_m = V_{liquid}/(n_1 + n_2 + n_3)$.

3. From Table 3, one can concluded that the Henry's constant increased with an increase in temperature. However, there was no obvious regularity about the influence of water content on Henry's constant.

The solubility of CO_2 in [bmim][PF_6] has been reported by several research groups.[10,20,22,28] The results obtained at 40 °C in this work are compared with those reported by various research groups in Figure 5. Our results agree well with the values reported by Kamps et al.[20] over all the pressure range. From Figure 5, one can also conclude that the solubility results for CO_2 in [bmim][PF_6] from various research groups are not in good agreement. The discrepancy in the solubility measurements may be related to the instability of [PF_6] anion,[22] different experimental techniques, uncertainties, impurities, and so on.

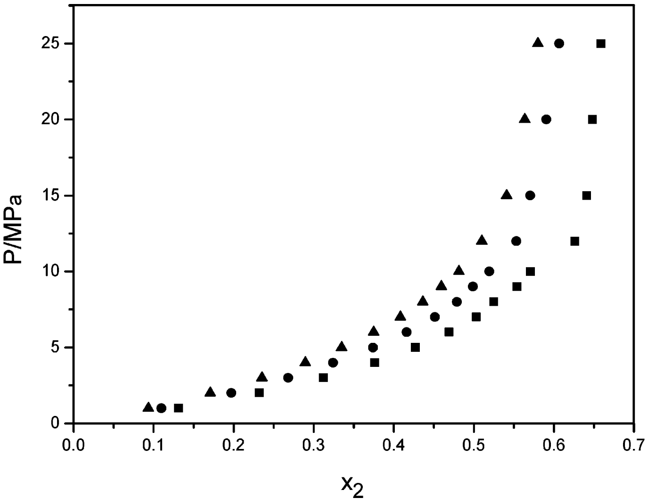

Figure 2. Solubility of CO_2 (2) in [bmim][PF_6] (1) with water mass fraction 0.15 %: ■, t = 40 °C; ●, t = 50 °C; ▲, t = 60 °C.

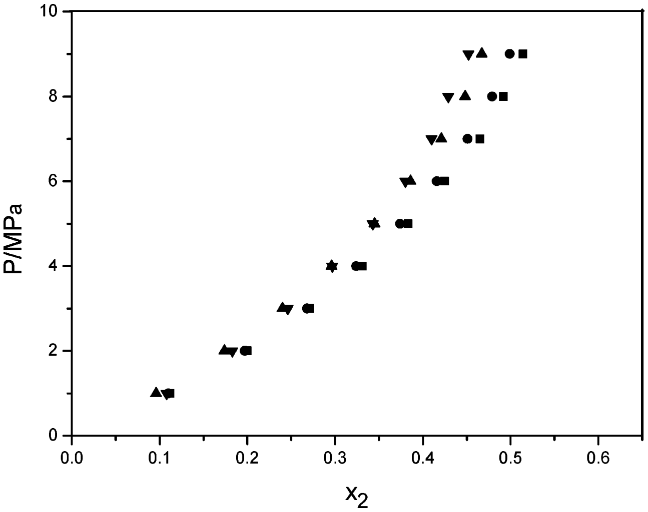

Figure 3. Solubility of CO_2 (2) in [bmim][PF_6] (1), calculated by the formula $x_{CO_2} = n_{CO_2}/(n_{CO_2} + n_{IL} + n_{H_2O})$, with different water mass fractions at 50 °C: ■, 0.0067 %; ●, 0.15 %; ▲, 0.89 %; ▼, 1.6 %.

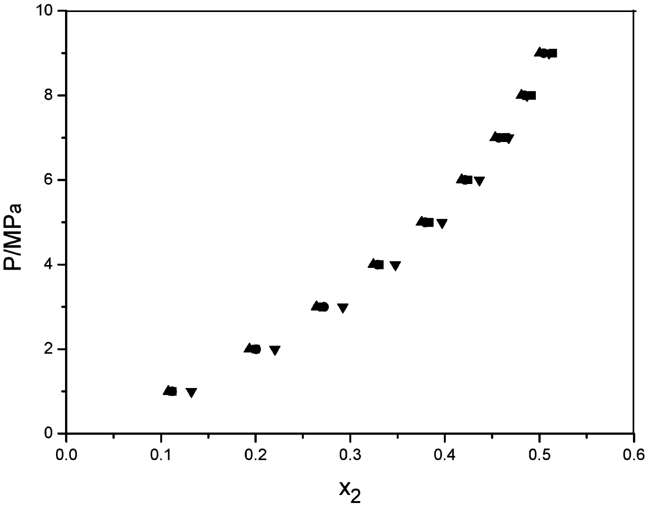

Figure 4. Solubility of CO_2 (2) in [bmim][PF_6] (1), calculated by the formula $x_{CO_2} = n_{CO_2}/(n_{CO_2} + n_{IL})$, with different water mass fractions at 50 °C: ■, 0.0067 %; ●, 0.15 %; ▲, 0.89 %; ▼, 1.6 %.

Another value measured in this work was the molar volume of the liquid phase, which can reflect liquid expansion. The volume of normal organic liquids will increase significantly by addition of CO_2. For example, a liquid composition of 0.74 mole fraction CO_2, for toluene + CO_2 system at 40 °C and 7 MPa, will give a 134 % increase in the volume of liquid phase. But lack of significant expansion of the liquid was found for CO_2 dissolved in [bmim][PF_6]. Simultaneously, molar volumes of the liquid phase decrease dramatically with increasing CO_2

Table 3. Henry's Constants of CO_2 (2) in [bmim][PF_6] (1) with Different Water (3) Mass Fractions w_3 at (40, 50, and 60) °C and Pressures Less than 6 MPa[a]

	Henry's constant/MPa·kg·mol^{-1}		
w_3	$t = 40$ °C	$t = 50$ °C	$t = 60$ °C
0.0067 %	2.05 ± 0.02	2.33 ± 0.02	2.71 ± 0.02
0.15 %	1.91 ± 0.02	2.36 ± 0.02	2.77 ± 0.02
0.89 %	1.96 ± 0.01	2.39 ± 0.01	2.84 ± 0.02
1.6 %	1.83 ± 0.03	2.21 ± 0.04	2.44 ± 0.03

[a] On the molality scale.

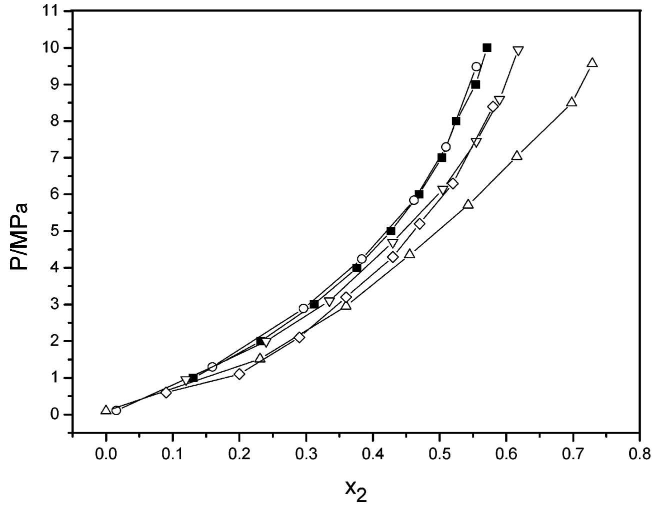

Figure 5. Comparison of the solubility of CO_2 (2) in [bmim][PF_6] (1) at 40 °C with literature data (water mass fraction = 0.15 %): ■, this work; ○, Kamps et al.;[20] △, Blanchard et al.;[10] ▽, Liu et al.;[28] ◇, Aki et al.[22]

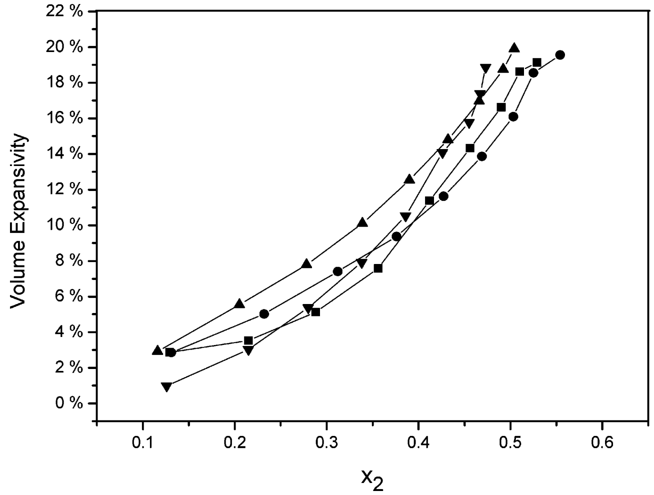

Figure 6. Liquid-phase volume expansivity, based on change in total volume as defined by eq 1, of the system CO_2 (2) + [bmim][PF_6] (1) with different water mass fractions at 40 °C: ■, 0.0067 %; ●, 0.15 %; ▲, 0.89 %; ▼, 1.6 %.

solubility, as can be seen from Table 2. The effect of water content on the volume expansion can be seen from Figure 6 and Figure 7. There are two definitions of liquid-phase volume expansion.[22] One definition is based on the change in absolute volume of the liquid:

$$\frac{\Delta V}{V} = \frac{V_L(T, P, x_1) - V_2(T, P_0)}{V_2(T, P_0)} \tag{1}$$

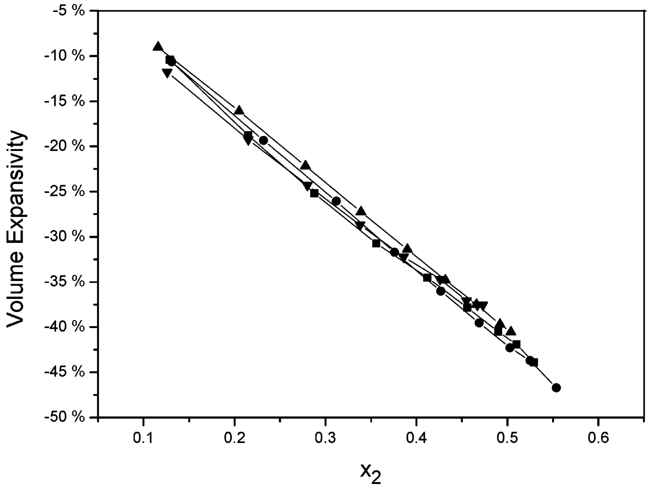

Figure 7. Liquid-phase volume expansivity, based on change in molar volume as defined by eq 2, of the system CO_2 (2) + [bmim][PF_6] (1) with different water mass fractions at 40 °C: ■, 0.0067 %; ●, 0.15 %; ▲, 0.89 %; ▼, 1.6 %.

where V_L is the total volume of the liquid mixture at a given temperature and pressure and V_2 is the volume of the liquid at the same temperature and ambient pressure. The other is based on the change in molar volume:

$$\frac{\Delta V_m}{V_m} = \frac{\tilde{V}_L(T, P, x_1) - \tilde{V}_2(T, P_0)}{\tilde{V}_2(T, P_0)} \tag{2}$$

where both $\tilde{V}_L$ and $\tilde{V}_2$ are corresponding molar volume. Volume expansivity in Figure 6 was calculated with eq 1 and in Figure 7 with eq 2. It should be noticed that mole number of water must be taken into account for molar volume, at 40 °C, and ambient pressure, calculated from density data in Table 1.

The unusual phase behavior of CO_2 + IL systems may be explained by the unique structure of ionic liquids. The phase behavior of CO_2 + IL is very different from that of normal organic liquids + CO_2 systems. Although large amounts of CO_2 dissolve in ionic liquids at low pressure, no mixture critical point appears even at extremely high pressures (such as 310 MPa).[10] Volume of IL-rich phase barely increases even when large amounts of CO_2 dissolve in the liquid phase. Henry's law,[20] equation of state,[14] and regular solution theory[24,29] used in modeling at present are difficult to explain these unusual phenomena. But they are easy to understand with a view to the unique structure of IL. IL were composed of organic cations asymmetric in space and anions, which resulted in very low melting points. Also, the asymmetry of the cations and the strong Coulombic forces between the ions dominated the phase behavior of CO_2 + IL systems. The asymmetry of the cations inevitably led to large but finite interspaces between ions, which was the cause that CO_2 could dissolve in IL largely but finitely. The strong Coulombic forces between the ions resulted in the extremely low solubility of IL in CO_2 and minor volume expansion of the liquid phase. Since the two phases can never become identical in composition and density even at extremely high pressures, a mixture critical point can never be reached. On the basis of this comprehension, a simple and effective model may be established to describe the phase behavior of CO_2 and IL.

Conclusions

The solubility of CO_2 in the IL [bmim][PF_6] and the liquid-phase molar volume were determined for water mass fraction of [bmim][PF_6] ranging from 0.0067 % to 1.6 % and within temperature and pressure ranges of (40 to 60) °C and (1 to 25)

MPa. The deviation in solubility, at the same temperature and pressure, with different water mass fraction was not more than 15 %, and the average is 6.7 %. Solubility pressures were correlated with an average relative uncertainty of about 1 % by means of the extended Henry's law for all water contents investigated at relatively low pressures.

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