Phase Equilibrium of Ionic Liquid/Organic/CO_2 Systems

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The volume change and sorption of CO_2 of ionic liquids(ILs) were measured in a high pressure view cell under supercritical fluid condition. Imidazolium-based ILs such as 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]), 1-butyl-3-methyl-imidazolium 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 phase equilibrium of IL/organic/CO2 systems was also investigated. In addition to the above ILs, 1-octyl-3-methylimidazolium hexafluorophosphate ([omim][PF_6]) was employed in the research. Methanol and dimethyl carbonate were selected as organic compounds of interest. The lower critical endpoint (LCEP) and K-point pressures were measured. The LCEP pressure decreased with increasing the amount of organic compound and increased with increasing water content. We found some the condition that we do not see the LECP anymore. The variation of volume of liquid phases upon pressure and temperature as well as the ratio of IL/organic was measured and discussed.

INTRODUCTION

Supercritical carbon dioxide and ILs have attracted a lot of attention as environmentally friendly clean solvents. ILs, especially room temperature ionic liquids (RTILs), are organic salts that have a melting point of lower than the room temperature. Because it exists as a liquid at room temperature, it has generally been considered as an alternative to the conventional organic solvent for reaction and separation. Most organic solvents are volatile, toxic and flammable. Toxic organic solvents vaporize and diffuse into the atmosphere in the separation process after the reaction, making a significant contamination to the environments. However, RTIL is nonvolatile, nontoxic, and nonflammable and is also thermally stable with a good ionic conductivity. As it doesn’t vaporize during the separation process, it is considered as an environmentally safe alternative to the organic solvents. Since RTIL is a highly polar material, it dissolves the inorganic and organic compounds and exists as a liquid over a wide range of temperature. RTIL can therefore be used in the wide variety of chemistry such as catalysts, separations, and electrochemistry [1-2].

Supercritical CO_2 dissolves well in ILs. ILs melt at very low temperatures as they are consisted of an organic cation and an inorganic anion with much different sizes. The strong electrostatic force between the cation and anion that are unbalanced in their sizes dictates the phase behavior of the CO_2/IL system. Larger cations provide more space between them, where CO_2 can dissolve into so that the volume of the liquid phase increases [3-5]. However, ILs do not dissolve in CO_2 due to the strong electrostatic force between ions. Because the composition and density of these two phases cannot become identical even at very high pressure, the mixture critical point cannot be reached.

It is possible to extract the CO_2-soluble organic compounds from IL without being contaminated with the IL. This enables us separate a mixture of an organic compound and an IL using supercritical CO_2. IL can also be used as solvent in the chemical reaction due to the easy separation of the products from the solvent. This principle can, in turn, be used in recovering the IL from the organic solvents. This kind of separation was achieved above the LCEP pressure, where a liquid phase was separated into two liquid phases (Figure 1). They reported that LCEP was heavily influenced by the types of organic compound and IL, temperature, and the initial composition of IL in the organic liquid mixture. When the pressure increased further, the lighter liquid phase – the methanol-rich phase (L_2) – was incorporated with the CO_2-rich phase (V) at the K-point [6]. As the pressure increased, the distribution coefficient also increased. Wu et al.[7] showed that, as pressure increases, the concentrations of IL and CO_2 increase but the concentration of organic liquid decreases in the heavier liquid phase L_1 separated at LCEP (40℃), while the concentrations for IL and organic compound decrease but the concentration of CO_2 increases in the L_2 phase.

In this study the soption of CO_2 in ILs as well as the ternary phase equilibrium of IL/organic compound/supercritical CO_2 has been investigated. Four ILs, [bmim][PF_6], [bmim][BF_4], [bmim][PF_6], and [omim][BF_4] and methanol and dimethyl carbonate (DMC) were selected as ILs and organic compounds.

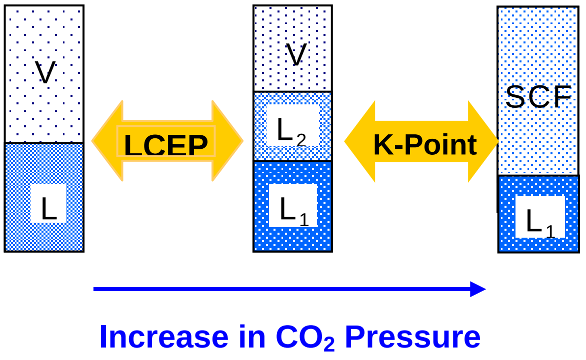


Figure 1: Effect of pressure on the phase behavior of a ternary system consisted of an IL, an organic compound and carbon dioxide.

EXPERIMENTAL

Materials

ILs, [bmim][PF_6] (purity > 99 %, moisture content = 1,200 ppm, chloride content = 79 ppm), [bmim][BF_4] (purity > 99 %, moisture content = 5,900 ppm, chloride content = 520 ppm), [omim][PF_6] (> 98 %, moisture content = 1,110 ppm, chloride content = 89 ppm), and [omim][BF_4] (> 98 %, moisture content = 1,050 ppm, chloride content = 101 ppm) were purchased from C-Tri. The moisture content was reduced to about 700 ppm by evacuating the vessel containing IL. Supercritical CO_2 with a purity of 99.5 % was purchased from Daedong Gastech and used without further purification. Methanol(>99.8 %) and DMC(>99%) were purchased from Aldrich Chemical and used without further purification.

Measurement of Sorption of CO_2 in ILs

The solubility of CO_2 in ILs was measured in a view-cell apparatus (Hanwool Model SC-6100) as shown in Figure 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). To measure the CO_2 solubility, about 2.5 mL of IL was injected into the view cell with a syringe. The view cell was then placed in a constant temperature water bath controlled to ± 0.1 K with a Lauda Immersion Thermostat B. High-pressure CO_2 was supplied to the view cell by an automatic syringe pump (ISCO Model 260D). The pressure in the cell was measured by a pressure gauge (Sensotec TJE/GM). 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 level on the monitor was measured at the equilibrium after every injection of 0.02 mL liquid CO_2. 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.

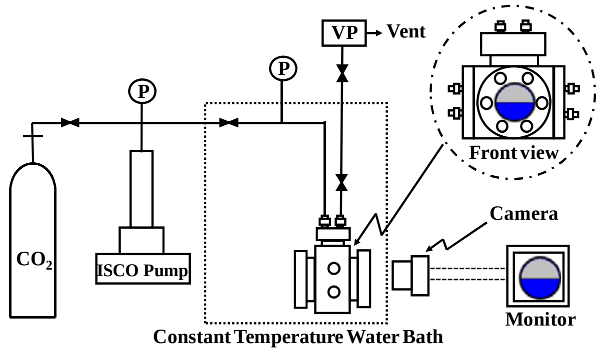


Figure 2: A schematic diagram of the experimental equipment to measure the swelling and sorption behavior of ILs in the presence of supercritical carbon dioxide (VP: vacuum pump, P: pressure sensor).

Phase Equilibria of the Ternary IL/Organic Compound/Supercritical CO_2 System

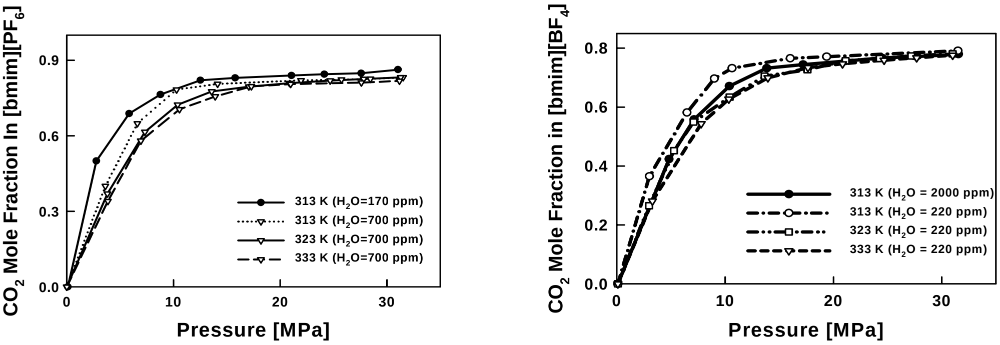
An apparatus for the phase equilibria of IL/organic liquid/supercritical CO_2 was set up with a view cell. A vial with a known amount of moisture-stripped IL was placed at the center of the view cell. Then, the view cell was capped and placed in a water bath maintained at 313.15 K (±0.1 K). A high pressure syringe pump (ISCO Model 260D) was used to supply CO_2 into the view cell and the pressure in the view cell was monitored by a pressure gauge (Sensotec THE/GM) with an accuracy of ±0.034 MPa. At a fixed temperature of 313.15 K, the volume and the phase behavior of the mixture was measured at equilibrium. Then, the pressure was increased by 2 MPa below the LCEP (about 7 MPa). When approaching the LCEP, we used a very small pressure interval of 0.014 MPa. After the LCEP, the pressure interval was 0.34 MPa. Near the K-point, the pressure interval was reduced to 0.014 MPa. Once the K-point was located, the pressure was increased by 0.068 MPa, while the three-phase behavior in the view cell was monitored at each pressure. Typical equilibration time was less than 30 minutes. The phase behavior in the vial was taken by a camera and viewed on a 17 inch monitor. The volume of each phase was measured using the graduations made on the vial as references. The uncertainty of this calibration is ±2%.

The composition of each phase was measured using an apparatus shown in Figure 4. A variable volume view cell was used to sample each phase. IL and organic liquid were placed into the cell. When CO_2 was added to the cell, the liquid phase was separated into two liquid phases at LCEP and the L_2 and vapor phases merged into one at the K-point. At each stage, the pressure in the cell was kept constant while sampling the phase by moving the piston forward using the automatic syringe pump. The samples collected in the sample vessels were analyzed by NMR and GC to see the composition of each phase.

RESULTS AND DISCUSSION

Binary Phase Equilibrium of IL/Supercritical CO_2 System

The increasing rates of solubility of CO_2 in [bmim][PF_6] and the volume change of IL was large at pressures lower than 10 MPa but was leveled off at higher pressures (Figure 3). When the solubility of CO_2 was higher than 0.8 mol%, the IL volume increasing rate was small, which indicates that the inter-ion space was almost filled-up with CO_2 molecules at that solubility and further energy is necessary for the accompanying CO_2 molecules to expand the inter-ion space. The smaller volume change at higher temperatures may be due to the decrease in the inter-ion space as the ions became active and more irregularly distributed. The solubility of CO_2 in IL with the moisture content of 170 ppm was higher than that of 700 ppm, which reveals that water molecules favorably fill the inter-ion space and expel CO_2 molecules that were already in the space.



(a) (b)

Figure 3: Solubility of CO_2 in [bmim][PF_6] (a) and [bmim][BF_4] (b).

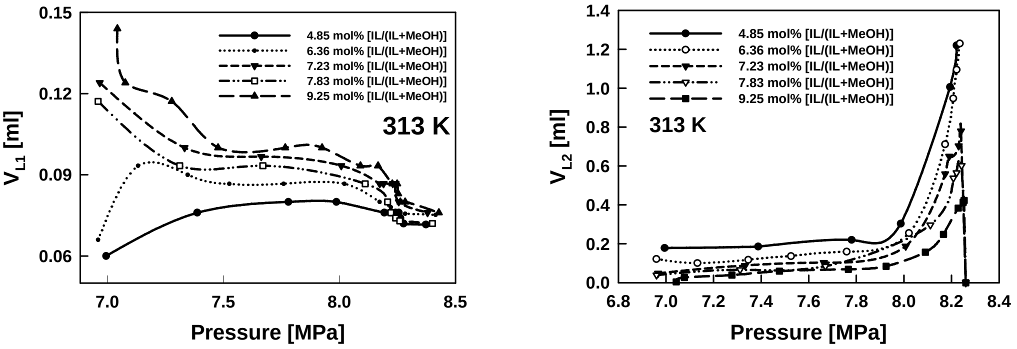
Ternary Phase Equilibrium of IL/Organic/Supercritical CO_2 System

Effect of the Amount of Organic (Methanol) in IL

The phase behavior was observed at a fixed amount (0.25 ml) of [bmim][PF_6], while the amount of methanol was varied. The volume of the liquid phase (L) increased with pressure as CO_2 dissolved more in IL until the LCEP was reached. After the LCEP the L-phase was suddenly divided into the heavier L_1-phase and the lighter L_2-phase. When the initial concentration of IL in the mixture of methanol and IL was lower than 7 mol%, the volume of L_1 was smaller than that of L_2 near the LCEP and the volumes of both L_1 and L_2 phases increased with pressure until it reached the K-point (Figure 4). When the initial concentration of IL was higher than 7 mol%, however, the volume of L_1 was larger than that of L_2 at the LCEP. The volume of L_1 decreased but the volume of L_2 increased with pressure up to the K-point. Another characteristic behavior of the L_2-phase is that, when the initial concentration of IL was lower than 7 mol%, the volume of the L_2 phase decreased until it was absorbed into the V-phase at the K-point. At the initial IL concentration higher than 7 mol%, the L_2 phase increased rapidly and absorbed the V-phase at the K-point, as shown in Figure 5. As the initial concentration of IL increased, the LCEP appeared at the higher pressure, while the K-point turned up almost at the same pressure (Figure 6). The LCEP of [bmim][BF_4] was found to be about 0.9–1.0 MPa higher than that of [bmim][PF_6]. Although both [BF_4] and [PF_6] are inorganic anions, the more polar [BF_4] has larger interactive force with methanol than [PF_6], resulting in the higher LCEP. For [bmim][PF_6], the LCEP was observed up to 17.7 mol% of the initial concentration of IL. But, for [bmim][BF_4], the limit was reduced to 6.8 mol%.

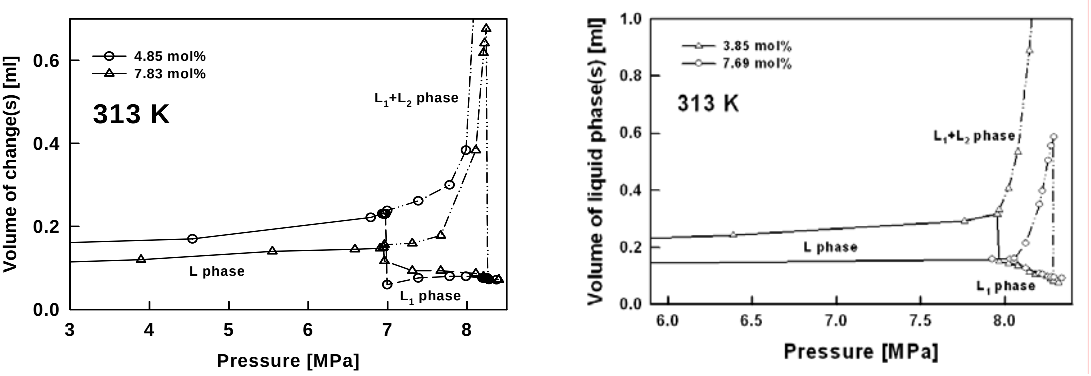
Effect of the Amount of Organic (DMC) in IL

With an fixed amount of [bmim][PF_6], the volume of the L-phase increased with increasing pressure by absorbing CO_2 and the L-phase was separated into the L_1 and L_2 phases just after the the LCEP, regardless of the amount of DMC. The volume of L_1-phase decreased nearly linearly, while the volume of L_2-phase increased monotonically. For the initial concentration of IL of 17.53 mol%, the volume of L_2-phase increased with pressure but disappeared near the K-point, while, for 21.83 mol% and above, the volume of



(a) (b)

Figure 4: Variations of the volume of L_1 phase (a) and L_2 phase (b) of [bmim][PF_6]/methanol /CO_2 system.



(a) (b)

Figure 5: Variations of the volumes of L, $L_{1,}$ and L_1+L_2 phases for the IL/methanol/CO_2 system with two different initial IL concentrations at 313 K. (a) [bmim][PF_6] with water content of 700 ppm and (b) [omim][PF_6] with water content of 300 ppm.

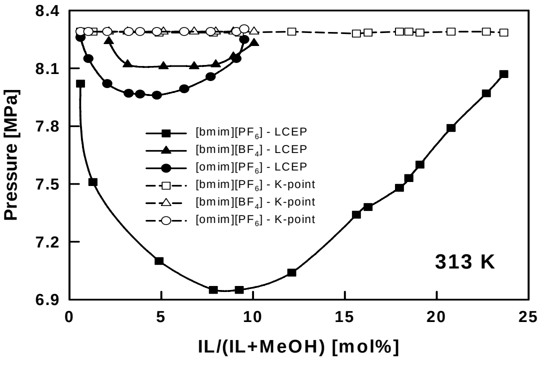


Figure 6: The LCEP and K-point pressures with the initial concentration of IL for the IL/methanol/CO_2 system (Moisture content in [bmim][PF_6] = 170 ppm, in [bmim][BF_4] = 220 ppm, and in [omim] [PF_6] = 300 ppm).

the L_2 phase decreased and disappeared near the K-point. For DMC, similarly to methanol, the LCEP pressure was higher but the K-point pressure was lower for the higher initial concentration of IL.

Effect of the Moisture Content in IL

When the amount of moisture in the IL was higher than 1.0 wt%, the L-phase was never separated. For the moisture content of 1.0 wt%, the L-phase volume increased with increasing pressure, but suddenly decreased with time a pressure. The LCEP was not observed, either. For ILs with lower moisture content, the LCEP was observed. For the initial concentration of IL of 9.25 mol%, the more the moisture content, the higher was the LCEP pressure.

Effect of the Initial Concentration of IL

The concentrations of IL and methanol in the L_1- and L_2-phases just after the phase separation increased but that of CO_2 decreased as the initial concentration of IL increased. This observation explains that the amount of penetrating CO_2 decreases with increasing IL concentration and the effect of organic is better than that of IL in dissolving CO_2 into the liquid phase. Increasing the IL concentration raises the LCEP pressure due to the small amount of organic compound.

CONCLUSIONS

The solubility of 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 of CO_2 in IL increased rapidly at low pressures but slowed down above the pressures of 8 to 10 MPa and finally leveled off at about 30 MPa. The IL with longer alkyl-chain cation [omim] showed a higher solubility than that of shorter alkyl-chain cation [bmim]. IL with anion [BF_4] has a lower solubility than Il with [PF_6]. Increasing water content decreased the solubility. The LCEP pressure increased but the K-point pressure remained the same with increasing the initial concentration of IL or the moisture content in IL. In case of very high moisture content, LCEP was not observed. The pressure difference between LCEP and K-point was 1.2 MPa for [bmim][PF_6], but only 0.2 MPa for [bmim][BF_4]. At higher initial concentration of IL, the concentrations of IL and methanol for both L_1 and L_2 phases were higher but that of CO_2 was lower. At certain pressure the LCEP and K-point merged and thereafter no LCEP was formed.

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