Equilibrium of Supercritical Fluid-Ionic Liquid-Organic Compound Ternary Phases

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ABSTRACT

Binary phase equilibria of supercritical CO_2 (scCO_2) and ionic liquid has been measured by Kamps et al. Ternary phase equilibria of supercritical fluid/organic liquid/ionic liquid systems have been measured in the literature. In this research we measured the phase equilibrium of binary and ternary systems using a high pressure view cell. Two ionic liquids such as 1-butyl-3-methyl imidazolium hexafluorophosphate ([bmim][PF$_6$]) and 1-butyl-3-methyl imidazolium tetrafluoroborate ([bmim][BF$_4$]) and an organic compound, methanol, have been used. The increase in the amount of organic compound at fixed amount of ionic liquid lowers the LCEP pressure. The K-point pressure was not changed by the type of ionic liquid, the amount of organic compound, or the amount of moisture content.

INTRODUCTION

ScCO$_2$ and ionic liquids have attracted a lot of attention worldwide as environmentally friendly clean solvents. Room temperature ionic liquid (RTIL) is an organic salt that has 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. RTIL is nonvolatile, nontoxic, and nonflammable and is also thermally stable with a good ionic conductivity. 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].

ScCO$_2$ is the most attractive supercritical fluid in the industry as it is nontoxic, nonflammable, inexpensive and has a mild critical point (31.1^{o}C and 7.38 bar) [3,4]. ScCO$_2$ dissolves well in ionic liquids, while ionic liquids do not dissolve in scCO$_2$ 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 [5,6]. The solubility of scCO$_2$ in ionic liquid follows Henry's law at low pressures, but the increasing tendency of the solubility decreases at pressures higher than 10 MPa. The solubility of CO_2 decreases with increasing temperature or the moisture content of ionic liquid increases [6,7].

Due to the properties of CO_2 and the ionic liquid mentioned above, it is possible to extract the CO_2-soluble organic compounds from ionic liquid without being contaminated with the solvent (ionic liquid). This enables us separate a mixture of an organic compound and an ionic liquid using scCO$_2$. Ionic liquid can also be used as solvent in the chemical reaction due to the easy separation of the products from the solvent. Brennecke et al. [8] reported that they separated a mixture of [bmim][PF$_6$] and methanol using scCO$_2$ at 298.15 and 313.15 K. 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 ionic liquid, temperature, and the initial composition of ionic liquid 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. In the case of the same ionic liquid, the K-point pressure was the same for different types of organic liquid and for different amount of initial concentration of ionic liquid in the organic liquid.
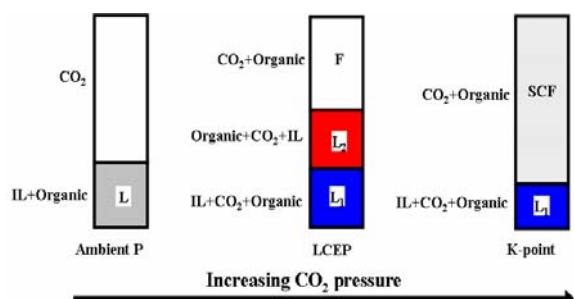
Figure 1: Effect of pressure on the phase behavior of a ternary system consisted of of an ionic liquid, an organic compound and carbon dioxide.
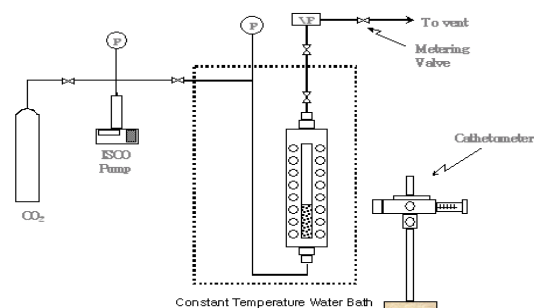

Figure 2: Schematic diagram of the experimental equipment to measure the volume change of ionic liquid in the presence of $scCO_2$.

Wu et al.[9] showed that, as pressure increases, the concentrations of ionic liquid and CO_2 increase but the concentration of organic liquid decreases in the heavier liquid phase L_1 separated at LCEP ($40^{\circ}C$), while the concentrations for ionic liquid and organic compound decrease but the concentration of CO_2 increases in the L_2 phase. They also found that the concentration of organic compound increases but the concentration of CO_2 decreases in the fluid phase (V) when the pressure increases above LCEP and suggested that this kind of separation behavior is related to the distribution coefficient of ionic liquid.

In this study the binary phase equilibrium of ionic liquid/$scCO_2$ system as well as the ternary phase equilibrium of ionic liquid/organic compound/$scCO_2$ has been investigated. Two ionic liquids, [bmim][PF_6] and [bmim][BF_4], were selected. Methanol and dimethyl carbonate (DMC) were selected as our goal is to efficiently synthesize DMC from methanol. For the binary system, the volume and the concentration of ionic liquid have been measured and discussed. For the ternary system, the concentration and the volume of each phase has been measured at the fixed initial concentration of ionic liquid. LCEP and K-point pressures have also been measured. The effects of the amount of ionic liquid as well as the moisture content have been measured and discussed.

MATERIALS AND METHODS

Materials

Ionic liquids, [bmim][PF_6] (> 99 %, moisture content = 1,200 ppm, chloride content = 79 ppm) and [bmim][BF_4] (> 99 %, moisture content = 5,900 ppm, chloride content = 520 ppm), were purchased from C-Tri. $ScCO_2$ (purity of 99 %) was obtained from Daedong Gastech. Methanol (>99 %) and DMC(>99%) were purchased from Aldrich Chemical.

Phase Equilibria of the binary IL/$scCO_2$ system

To measure the volume change of the ionic liquid in the IL/CO_2 system, an apparatus was made with Jerguson Gauge (Figure 2). Firstly, 25 ml of [bmim][PF_6] was put into the Jerguson Gauge. To remove the moisture in the IL, the cell was evacuated using a vacuum pump (Ulvac GVD-050A) for 4 hours. Then, the cell was placed in the constant temperature water bath, in which temperature is controlled to ±0.1 K by Lauda Immersion Thermostat B. After 2 hours, CO_2 was supplied at a constant pressure by the computer-controlled high pressure syringe pump (ISCO Model 260D). To maximize the mass transfer and thus to reduce the equilibration time, CO_2 was bubbled from the bottom of the cell. A metering valve (Hoke Milli-Mite) at the exit of the cell was kept open to control the pressure and the flow rate of CO_2 until the equilibrium is attained. It took about 30 minutes to get the equilibrium at each pressure. A cathetometer (Gaertner Scientific M911) was used to measure the liquid level height with the accuracy to ±0.05 mm. Measuring was repeated for different pressures and temperatures. The

solubility of CO_2 in ionic liquid was measured in a view cell apparatus, similar to the one shown in Figure 3. After removing the moisture in ionic liquid by applying vacuum, the view cell was maintained in a constant temperature water bath. Other procedures for measuring the solubility and the volume are similar to that for the ternary phase equilibrium shown below. Each measurement took about 40 minutes.

Phase Equilibria of the Ternary IL/Organic Compound/ScCO$_2$ System

An apparatus to measure the phase equilibria of IL/organic liquid/scCO$_2$ was built as in Figure 3. A view cell (Hanwool Model SC-6100) is the main equipment where the phase equilibrium occurs. 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 ($\pm$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 $\pm$5 psi (34 kPa).
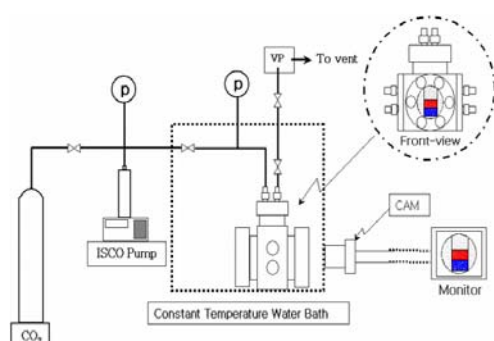

Figure 3: Schematic diagram of an apparatus to measure the phase equilibrium of an ionic liquid/ organic compound/CO$_2$ ternary system.
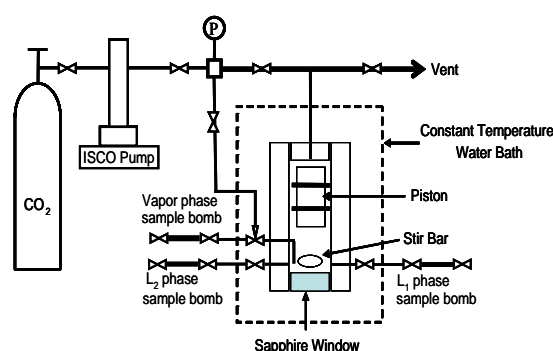
Figure 4: Schematic diagram of an apparatus to analyze the phase equilibrium of an ionic liquid/organic compound/CO$_2$ ternary system.

At a fixed temperature of 313.15 K, the volume and the phase behavior of the mixture were measured at equilibrium. Then, the pressure was increased by 2 MPa below the LCEP (about 7 MPa). When approaching the LCEP, the pressure interval was greatly reduced to 14 kPa. After the LCEP, the pressure interval was elevated to 340 kPa but was reduced to 68 kPa when the volume change of L$_2$ phase became large. Near the K-point of about 8.2 MPa, the pressure interval was even reduced to 14 kPa to avoid passing by the K-point. Once the K-point was located, the pressure was increased by 68 kPa up to 8.5 PMa, 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 pictured with a camera and viewed on a 17 inch monitor to see the phases 10 times enlarged. The volume of each phase was measured with the graduations made on the vial as references. 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. Ionic liquid 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 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

Binary Phase Equilibrium of IL/ScCO$_2$ 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 (Figures 5, 6). When the solubility of CO_2 was higher than 0.7 mol%, the IL volume increasing rate was small, which indicates that the inter-ion spaces 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.
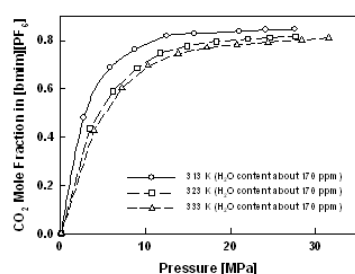

Figure 5: The solubility data of CO_2 in [bmim][PF_6] with H_2O content of 170 ppm at three different temperatures.
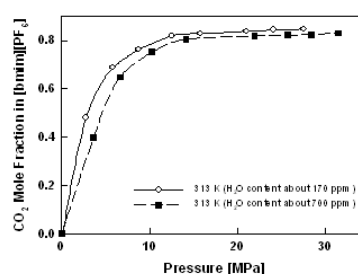

Figure 6: A solubility data of CO_2 in [bmim][PF_6] with a small and a large amount of moisture content at 313 K.

Ternary Phase Equilibrium of IL/Organic/ScCO$_2$ System

A) *Effect of the Amount of Organic (Methanol) in IL*

The phase behavior was observed at a fixed amount (0.025 ml) of [bmim][PF_6], while the amount of methanol was varied (Figures 7, 8). The volume of the liquid (L) phase 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 6.36 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. When the initial concentration of IL was higher than 7.23 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. Moreover, when the initial concentration of IL was lower than 7.5 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 7.5 mol%, the L_2 phase increased rapidly and absorbed the V-phase at the K-point, as shown in Figure 8.
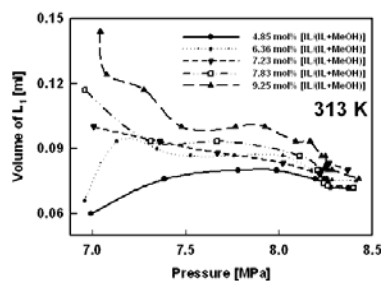

Figure 7: Variation of the volume of L_1 phase with pressure for the [bmim][PF_6]/methanol/CO_2 system with different initial IL concentrations (IL/(IL+MeOH)) above their LCEP at 313 K.
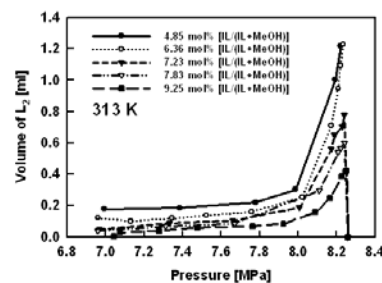

Figure 8: Variation of the Volume of L2 phase with pressure for the [bmim][PF_6]/methanol/CO_2 system with different initial IL concentrations (IL/(IL+MeOH)) above their LCEP at 313 K.

(Moisture content in [bmim][PF$_6$] ≒ 700 ppm)   (Moisture content in [bmim][PF$_6$] ≒ 700 ppm).

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 9). 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%.
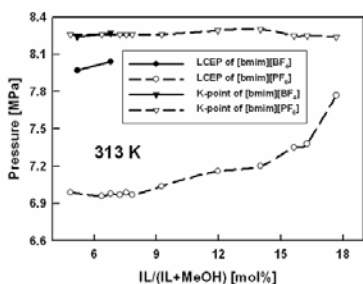

Figure 9: Variations of the LCEP and K-point pressures with the initial concentration of IL for the [bmim][PF$_6$]/methanol/CO$_2$ system at 313 K. (Moisture content in [bmim][PF$_6$] ≒ 700 ppm, in [bmim][BF4] ≒ 200 ppm)
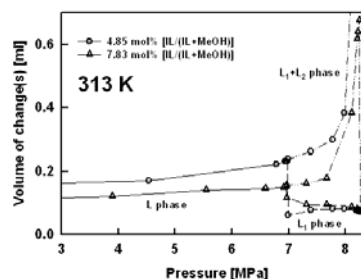
Figure 10: Variation of the volumes of L, L1, and L1+L2 phases with pressure for the [bmim][PF$_6$]/methanol/CO$_2$ system with two different initial IL concentrations (IL/(IL+MeOH)) at 313 K. (Moisture content in [bmim][PF$_6$] ≒ 700 ppm)

B) Effect of the Moisture Content in IL

When the amount of moisture in the ionic liquid 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 at certain 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.

C) 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 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 (1.0 wt%), 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. The solubility of CO$_2$ in IL decreased as the moisture content and temperature increased.

ACKNOWLEDGMENT

REFERENCES

[1] KIM, H., S., KIM, Y., J., NICE, Vol. 21, **2003**, p.200

[2] DUPONT, J., R., SOUZA, F., De, SUAREZ, P., A., Z., Chem. Rev., Vol.102, **2002**, p. 3667

[3] CARTER, C., A., G., BARKER, R., T., NOLAN, S,. P., TUMAS, W., Chem. Commun., **2000**, p. 314

[4] ZHANG, J., L., HAN, B., X., LIU, J., C., ZHANG, X., G., LIU Z., M., HE, J., Chem. Commun., Vol. 24, **2001**, p. 2724

[5] WU, W., Z., ZHANG, J., M., HAN, B., X., CHEN, J., W., LIU, Z., M., JIANG, T., HE, J., LI, W., J., Chem. Commun., Vol. 26, **2003**, p. 1412

[6] FU, D., FU, B., SUN, X., W., PU, J., J., ZHAO, S., Q., J. Chem. Eng. Data., Vol. 51, **2006**, p. 371

[7] KAMPS, A., P., S., TUMA, D., XIA, J., MAURER, G., J. Chem. Eng. Data., Vol. 48, **2003**, p. 746

[8] AKI, S., N., V., SCURTO, A., M., BRENNECKE, J., F., Ind. Eng. Chem. Res., Vol.45, **2006**, p. 5574

[9] ZHANG, Z., M., WU, W., Z., LIU, Z., M., HAN, B., X., GAO, H., X., JIANG, T., Phys. Chem. Chem. Phys., Vol. 6, **2004**, p.2352