Study on the Phase Behaviors, Viscosities, and Thermodynamic Properties of CO_2/[C_4mim][PF_6]/Methanol System at Elevated Pressures

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Abstract: An apparatus to determine the vapor–liquid equilibria of CO_2/ionic liquid (IL)/organic solvent multisystems and the viscosity of the liquid phase at elevated pressures has been constructed. The solubility of CO_2 in 3-butyl-1-methyl-imidazolium hexafluorophosphate ([C_4mim][PF_6]) and the viscosity of CO_2-saturated [C_4mim][PF_6] have been studied at 313.15, 323.15, and 333.15 K and at pressures up to 12.5 MPa. The phase behavior of CO_2/[C_4mim][PF_6]/methanol ternary mixture and the viscosity of the liquid phases at equilibrium condition have also been determined at 313.15 K and at 7.15 and 10.00 MPa. The partition coefficients of the components in the ternary system are calculated. Peng–Robinson equation of state and some thermodynamic functions are combined to calculate the fugacity coefficients of the components in the system. It demonstrates that the viscosity of the IL-rich phase decreases significantly with increasing pressure of CO_2, and the effect of temperature on the viscosity of CO_2/IL mixture is not noticeable at high pressure, although the viscosity of the CO_2-free IL decreases dramatically with increasing temperature. Compressed CO_2 may become an attractive reagent for reducing the viscosity of ILs in many applications. The mole fraction of methanol in the CO_2-rich phase is much lower than that in the IL-rich phase; this indicates that the interaction between the IL and methanol is stronger than that between CO_2 and methanol. The fugacity coefficient of CO_2 in IL-rich phase is larger than unity, while that of methanol is much small than unity, which further suggests that methanol–IL interaction is much stronger than CO_2–IL interaction. However, the CO_2–IL interaction is stronger than the CO_2–methanol interaction.

Keywords: carbon dioxide · ionic liquids · solubility · supercritical fluids · viscosity

Introduction

Room-temperature ionic liquids (ILs) are organic salts that are liquids at ambient conditions. ILs have many properties similar to conventional organic solvents, such as excellent solvating power to many solutes and a wide temperature range over which they are liquids. However, ILs have a unique advantage over traditional organic solvents. Typical ILs have vanishingly small vapor pressure, and therefore do not evaporate into the environment. This makes ILs potentially safer and more environmentally benign solvents than traditional organic solvents. The recognition of room-temperature ILs as neoteric green solvents has prompted a fast-growing literature.[1]

Supercritical fluids (SCFs) have many unique features. Their densities can be manipulated from gas-like to liquid-like by changing temperature and/or pressure. CO_2 is most widely used because it is inexpensive, nontoxic, nonflammable, readily available in large quantities, and has moderate critical temperature and pressure (31.1 and 73.8 bar). Moreover, it can be easily recaptured and recycled after use. In recent years, increasing numbers of scientists have begun to study supercritical science and technology related with CO_2.[2]

Both SC CO_2 and ILs are environmentally benign solvents, and each has their own unique properties. Combination of the advantages of these two classes of green solvents is a new and interesting topic. Recently, elegant researches on the solubility of compressed CO_2 in ILs have been carried out by Brennecke and co-workers.[3] They discovered that SC CO_2 was soluble in ILs, but the solubility of the ILs in SC CO_2 was negligible. The unusual phase behavior of CO_2/IL systems laid the foundation for the recovery of solutes from ILs without any cross-contamination. This principle has been used to extract solutes or products from ILs using CO_2.[3a, 4] Recently, catalytic reactions were carried out in an IL/compressed CO_2 system.[5]

CO_2–IL mixtures will be used widely after our understanding of their fundamental properties improves. This will not only eliminate the emission of toxic organic solvents, but

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also will optimize many processes. Phase behaviors and viscosity data of the related systems are basis for these applications. Obviously, many systems involved in practice are more complex than CO_2/IL binary systems. Recently, Scurto et al.[6] studied the phase transition of CO_2/methanol/[C_4mim][PF_6] system. They found that as methanol contained small amount of the IL, the methanol/IL mixture could be induced to form three phases in the presence of CO_2. However, there were only two phases in the system as the pressure of CO_2 was high enough, and the CO_2-rich phase was free of the IL. This shows a new way to separate ILs from organic compounds by using SC CO_2.

The effect of dissolved CO_2 on the viscosity of ILs, compositions of different phases in CO_2/IL/organic compound mixtures at equilibrium condition, and the thermodynamic parameters of the multicomponent systems are fundamental properties, which are of great importance to the combined applications of these two green solvents, SC CO_2 and ILs. In this work, the phase behaviors and viscosities of CO_2/[C_4mim][PF_6] binary mixture and CO_2/[C_4mim][PF_6]/methanol ternary mixture at different temperatures and pressures are studied. We focus on the 1) effect of dissolved CO_2 on the viscosities of the IL and the IL/methanol mixture; 2) the phase behavior of CO_2/IL/methanol ternary mixtures; 3) the intermolecular interaction and thermodynamic properties of the systems. We believe that this is the first work to determine the viscosities of the binary and more complex mixtures containing both CO_2 and ILs, and the partition coefficients and fugacity coefficients of the components in CO_2/IL/organic compound mixtures.

Results and Discussion

Solubility of CO_2 in [C_4mim][PF_6]: The solubility of CO_2 in [C_4mim][PF_6] was determined at 313.15, 323.15, 333.15 K and pressures up to 12.5 MPa. The results are listed in Table 1. Figure 1 compares the data of this work with those reported by other authors[3b] at 313.15 K. The data determined by the two laboratories agree reasonably considering that the methods used were different and the experiments were carried out at elevated pressures.

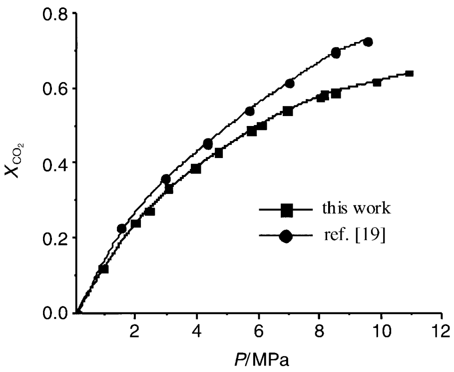

Figure 1. Comparison of CO_2 solubility in [C_4mim][PF_6] at 313.15 K determined by different authors.

Table 1. Solubility of CO_2 in [C_4mim][PF_6] (X_1) and viscosity (η) of the liquid phase.

T = 313.15 K			T = 323.15 K			T = 333.15 K		
P [MPa]	x_1	Vis. [cp]	P [MPa]	x_1	Vis. [cp]	P [MPa]	x_1	Vis. [cp]
0.10	0.0	92.3	0.10	0.0	60.4	0.10	0.0	44.1
0.93	0.122	50.8	0.57	0.061	48.0	1.50	0.154	39.4
1.98	0.242	43.8	1.54	0.176	41.5	2.48	0.266	36.4
2.43	0.275	40.6	2.38	0.266	38.3	4.43	0.398	33.0
3.06	0.332	38.5	3.83	0.369	34.8	6.69	0.475	31.2
3.95	0.389	36.0	5.08	0.433	33.0	8.74	0.523	29.7
4.70	0.430	34.3	6.71	0.494	31.3	9.90	0.541	29.3
5.78	0.489	32.7	7.29	0.518	31.2	10.69	0.562	29.0
6.09	0.503	32.0	8.25	0.542	30.0	11.58	0.571	28.5
6.94	0.543	31.5	10.20	0.586	29.1	12.93	0.583	28.0
8.02	0.576	30.5	11.58	0.604	28.5			
8.53	0.591	30.6						
9.87	0.619	29.5						
10.93	0.639	29.1						

Figure 2 shows the mole fraction of CO_2 in the liquid phase as a function of pressure at different temperatures. As expected, the solubility of CO_2 in the IL increases as pressure increases. It can be observed that the solubility is more sensitive to pressure at the lower pressures. This is because of the existence of "free volume" in the IL.[3b] More void space within the IL is occupied with increasing pressure, and therefore the solubility increases slowly in the higher pressure region.

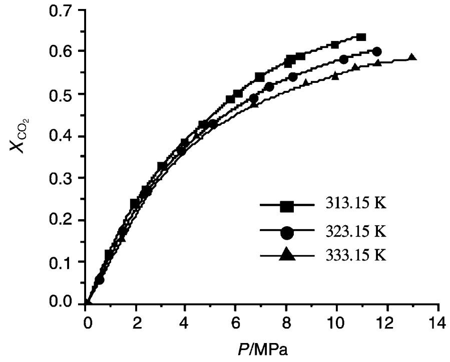

Figure 2. Solubility CO_2 in [C_4mim][PF_6] at different temperatures and pressures.

The temperature is known to have a considerable effect on the solubility of a gas in a liquid, and generally, one may expect that an increase in temperature will result in decrease in solubility. Figure 2 shows that the temperature effect on the solubility is quite small over the temperature and pressure range studied, although the solubility of CO_2 decreases with increasing temperature. In other words, the enthalpy of solution of CO_2 in the IL is small.

Viscosity of CO_2-saturated/[C_4mim][PF_6]: In order to verify the reliability of the viscometer, we first determined the viscosity of the gas-free IL at different temperatures. The results are illustrated in Figure 3 together with those reported in the literature, which were determined using a cone plate viscometer.[7] The results of this work agree with the literature values very well, as can also be seen from Figure 3.

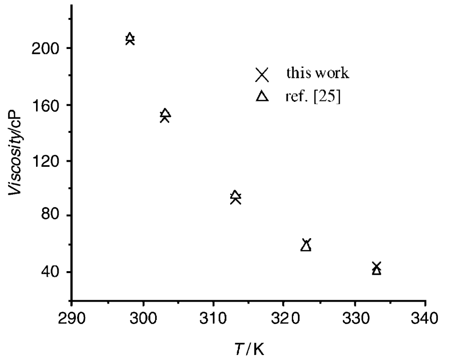

Figure 3. Comparison of [C$_4$mim][PF$_6$] viscosity determined in this work and reported by other authors.

The viscosity data of CO$_2$/[C$_4$mim][PF$_6$] mixtures at different conditions are listed in Table 1, and the dependence of the viscosity on pressure and temperature is shown in Figure 4. It can be seen that the viscosity of the liquid phase decreases dramatically with increasing pressure in the lower pressure range, and slowly at higher pressures. As discussed above, CO$_2$ solubility in the IL increases significantly with increasing pressure at the lower pressures. As a result, the viscosity is more sensitive to the pressure of CO$_2$. In contrast, the increase in pressure only slightly improves the solubility of CO$_2$ in the IL at the higher pressures. Therefore, the viscosity decreases slowly as pressure increases.

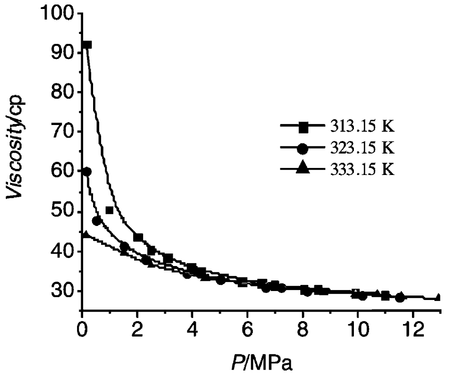

Figure 4. Dependence of viscosity of CO$_2$-saturated [C$_4$mim][PF$_6$] on pressure and temperature.

Figure 4 is also a comparison of the viscosity of CO$_2$-free and CO$_2$-saturated IL at different temperatures. In the absence of CO$_2$, the effect of temperature is significant, although the temperature range studied is small. It is interesting that the difference of viscosity at different temperatures becomes smaller as pressure increases; the difference is not noticeable as pressure is higher than about 4.0 MPa. There are two factors which influence the viscosity. First, the viscosity decreases with the increase in temperature. Second, the viscosity is reduced as the amount of CO$_2$ in the IL increases. At the lower pressures, the solubility of CO$_2$ in the IL is low, and the effect of temperature is dominant. Therefore, the difference of the viscosity at different temperatures is significant. At the higher pressures, however, the effect of the dissolved CO$_2$ on the viscosity is more significant, and the concentration of CO$_2$ in the liquid phase is larger at lower temperature. Therefore, the viscosity at different temperatures is nearly the same.

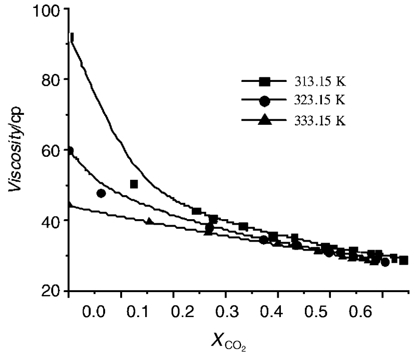

Figure 5. Dependence of the viscosity of CO$_2$/[C$_4$mim][PF$_6$] mixture on composition.

To get more evidence to support this argument, Figure 5 plots the viscosity of the liquid phase as a function of CO$_2$ mole fraction at various temperatures. The difference in viscosity at various temperatures becomes smaller and smaller with increasing mole fraction of CO$_2$. This further indicates that the dissolution of CO$_2$ in the IL can reduce the effect of temperature on the viscosity. However, the difference of the viscosities at different temperatures is still noticeable even at large CO$_2$ mole fraction. Therefore, the larger solubility at lower temperature is one of the reasons for the phenomenon that the viscosities at various temperatures are nearly the same as CO$_2$ pressure is high, as can be seen in Figure 4.

SC CO$_2$ has been used to extract solutes from ILs.[3a, 4] This principle can be used for a variety of applications, such as fractionation, recovery of reactants and products from the ILs after reaction processes. The unique advantage of this method is that cross-contamination is eliminated since the IL is not soluble in CO$_2$ and depressurization can remove CO$_2$ from the IL phase completely. Significant reduction of viscosity increases the mass transfer in the IL phase, which is favorable to enhancing extraction efficiency.

Recently, we studied the oxidation of *n*-hexene using molecular oxygen in [C$_4$mim][PF$_6$], SC CO$_2$, and in [C$_4$mim][PF$_6$]/CO$_2$ mixed solvent.[5b] The results indicated that in the IL/CO$_2$ mixed solvent, the selectivity of the reaction to the desired product is much higher than those in the pure IL. Reduction of viscosity of the IL may be one of the reasons for this positive result. Compressed CO$_2$ may become an attractive reagent for reducing the viscosity of ILs in many applications because it is environmentally benign, and the separation of CO$_2$ from ILs can be achieved simply by depressurization.

Seddon et al.[8] studied the effects of various organic solvents on the viscosity of [C$_4$mim][PF$_6$]. They discovered that the viscosity of the mixtures was dependent mainly on the mole fraction of the added solvents, and that the viscosity decreased with the mole fraction of the added solvents. In their study, the relationship between viscosity and mole fraction of organic solvents was correlated using the following equation with correlation coefficients >0.97:

$$\eta = \eta_s \exp(-x_{cs}/a) \quad (1)$$

where η_s is the viscosity of the pure ILs at fixed temperature, x_{cs} is the mole fraction of the added solvent and a is a constant. We tried to adopt this formula to correlate the data of this work, and found that this equation could not be used for CO_2/[C_4mim][PF_6] mixtures. It may results from the special interaction between CO_2 and the IL. Using ATR-IR spectroscopy, Kazarian et al.[9] have recently shown that CO_2 forms weak Lewis acid–Lewis base complexes with the anions of the IL. This may reduce the degree of association between the anions and the cations in the IL, which may cause great reduction in the viscosity.

Phase behavior of CO_2/[C_4mim][PF_6]/methanol ternary system: The phase behavior of CO_2/[C_4mim][PF_6]/methanol ternary system has been studied at 313.15 K and at 7.15 and 10.00 MPa, one of which is lower than the critical pressure of CO_2, and the other is above the critical pressure, so that the properties of CO_2 at the two pressures are different significantly. The results are listed in Tables 2 and 3.

Table 2. The phase equilibrium data, fugacity coefficients of the components, and the viscosity of the liquid phase of CO_2 (1)/methanol (2)/[C_4mim][PF_6] (3) ternary system at 313.15 K and 7.15 MPa.

x_1	x_2	x_3	y_1	y_2	η/cp	K_1	K_2	ϕ_1^l	ϕ_2^l	ϕ_1^v	ϕ_2^v
0.570	0.087	0.343	0.983	0.017	27.5	1.72	0.20	1.19	0.0411	0.689	0.210
0.489	0.194	0.317	0.979	0.021	27.6	2.00	0.11	1.38	0.0221	0.690	0.205
0.433	0.265	0.302	0.977	0.023	26.8	2.26	0.09	1.56	0.0175	0.690	0.202
0.403	0.360	0.237	0.975	0.025	26.1	2.41	0.07	1.67	0.0138	0.690	0.199
0.307	0.556	0.137	0.972	0.028	25.2	3.17	0.05	2.19	0.0097	0.691	0.194

Table 3. The phase equilibrium data, fugacity coefficients of the components the viscosity of the liquid phase of CO_2 (1)/methanol (2)/[C_4mim][PF_6](3) system at 313.15 K and 10.00 MPa.

x_1	x_2	x_3	y_1	y_2	η/cp	K_1	K_2	ϕ_1^l	ϕ_2^l	ϕ_1^v	ϕ_2^v
0.554	0.124	0.322	0.927	0.073	28.0	1.67	0.59	0.973	0.0144	0.581	0.0245
0.529	0.162	0.309	0.923	0.077	27.6	1.74	0.48	1.017	0.0113	0.583	0.0237
0.456	0.276	0.268	0.906	0.094	26.8	1.98	0.34	1.171	0.0072	0.589	0.0210
0.317	0.487	0.196	0.886	0.114	25.4	2.79	0.23	1.671	0.0044	0.598	0.0185

The liquid phase is composed of three components, [C_4mim][PF_6], CO_2, and methanol. Our experiments show that the concentration of the IL in the vapor phase is not detectable at the experimental conditions of this work. This is not surprising because the solubility of the IL in CO_2 is extremely low,[3a, b] and in our work the concentration of methanol in the vapor phase is relatively low. In other words, the methanol in the vapor phase cannot improve the solvent power of the CO_2 to dissolve the IL significantly. Therefore, it can be supposed that the vapor phase contains only CO_2 and methanol.

Figure 6a and b show the triangle phase diagrams of the ternary system at 313.15 K and at 7.15 and 10.00 MPa, respectively. As discussed, the CO_2-rich phase has two components, so the points are on the CO_2-methanol line, while the points of the IL-rich phase disperse in the ternary region. As expected, the mole fraction of methanol approaches the value in CO_2–methanol binary system[10] with increasing concentration of methanol in the liquid phase.

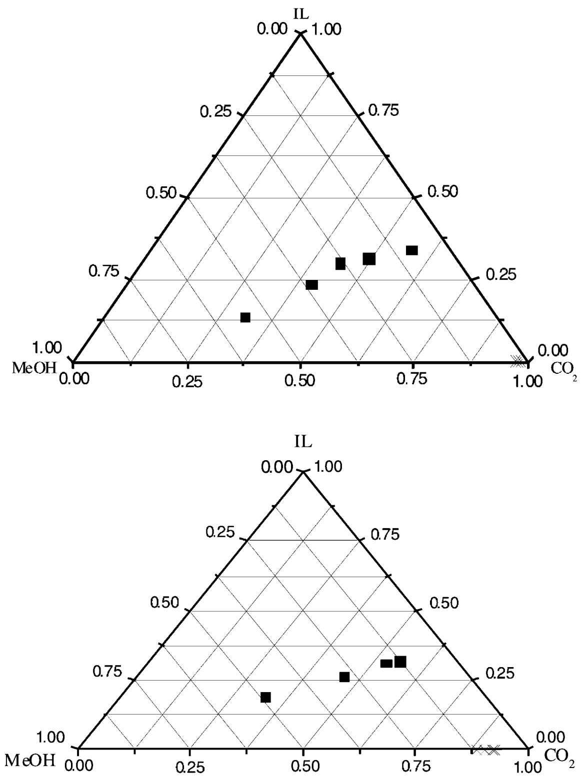

Figure 6. The phase diagram of CO_2/[C_4mim][PF_6]/methanol ternary system at 313.15 K and 7.15 MPa (a) and 10.00 MPa (b).

It can be observed that at 7.15 MPa methanol mole fraction in the vapor phase is not sensitive to the mole fraction of methanol in the liquid phase. This is understandable because the solvent power of CO_2 at this pressure is weak, and the concentration of methanol in the vapor phase is very low. The change in volume concentration of methanol cannot affect the mole fractions of the two components considerably because the concentration of CO_2 in the vapor phase is much higher. Comparing Figure 6a and 6b, it is clear that the mole fraction of methanol in the vapor phase at 10.00 is higher than that at 7.15 MPa. This is because the solvent power of CO_2 at higher pressure is much stronger than that at 7.15 MPa. The mole fraction of CO_2 in the liquid phase increases as the concentration of methanol decreases and the mole fraction of the IL increases, as is shown in Tables 2 and 3; this suggests that CO_2–IL interaction is stronger than CO_2–methanol interaction. Formation of weak Lewis acid–Lewis base complexes of CO_2 with the anions of the IL[9] may be the main reason.

Thermodynamics of the ternary system: The phase behavior of CO_2/[C_4mim][PF_6]/methanol system represents a liquid mixture in equilibrium with a gas or supercritical fluid mixture. Thus, an important thermodynamic parameter, the partition coefficient, K_i, the ratio of mole fraction of component i in the vapor phase (y_i) to that in the liquid phase (x_i), should be emphasized. K_i can be expressed by the following equation.

$$K_i = y_i/x_i \tag{2}$$

$$K_i = \frac{\phi_i^l}{\phi_i^v} \tag{3}$$

where ϕ_i^l and ϕ_i^v stand for the fugacity coefficient of component i in the liquid phase and in the vapor phase, respectively.

The K values of methanol and CO_2 in the ternary system at different conditions are calculated and listed in Tables 2 and 3. The partition coefficient of methanol K_2 is much smaller than unity, which indicates that the interaction between the methanol and [C_4mim][PF_6] is stronger than that between CO_2 and [C_4mim][PF_6]. At 10.00 MPa, CO_2 and methanol is miscible in the entire concentration range.[10] This means that the solvent power of CO_2 at this temperature and pressure is strong for methanol. Therefore, the smaller K_2 hints that the interaction between the IL and methanol is very strong. The K_2 at 7.15 MPa is much smaller than that at 10.00 MPa, as can be known from Table 3. This is easy to understand because the solvent power of CO_2 at this lower pressure is much weaker.

The fugacity coefficients of the components are basic thermodynamic parameters of the mixtures. They can be calculated using suitable equation of state (EOS) if their critical parameters and acentric factors are known. Unfortunately, the parameters of the IL are not known. However, it can be assumed, as discussed above, the vapor phase contains only methanol and CO_2. Therefore, their fugacity coefficients in the vapor phase can be calculated. In this work Peng-Robinson EOS[11] is used to calculated the fugacity coefficients of the methanol and CO_2 in the vapor phase, which can be expressed as:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)} \tag{4}$$

$$b = 0.077796\frac{RT_c}{P_c} \tag{5}$$

$$a = 0.457235\frac{R^2T_c^2}{P_c}\alpha \tag{6}$$

$$\alpha = [1+m(1-\sqrt{\frac{T}{T_c}})]^2 \tag{7}$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{8}$$

where T_c and P_c are the critical temperature and critical pressure, respectively. ω denotes the acentric factor. For a mixture, the van der Waals mixing rules are applied:

$$a = \sum_i\sum_j x_i x_j a_{ij} \tag{9}$$

$$b = \sum_i x_i b_i \tag{10}$$

$$a_{ij} = \sqrt{a_{ii}a_{jj}}(1-k_{ij}) \tag{11}$$

where the k_{ij} is the binary interaction coefficient. From the above equations, the fugacity coefficient of component i in a mixture can be expressed as

$$RT\ln\varphi_i = RT\ln\frac{V}{V-b_{mix}} + \frac{\sum_j x_j a_{ij}}{\sqrt{2}b_{mix}}\ln\frac{V+(1-\sqrt{2})b_{mix}}{V+(1+\sqrt{2})b_{mix}} + \frac{a_{mix}b_{mix}b_i}{(\sqrt{2}b_{mix})^3}\ln\frac{V+(1+\sqrt{2})b_{mix}}{V+(1-\sqrt{2})b_{mix}} - RT\ln\frac{PV}{RT} + \frac{b_iPV}{b_{mix}} - \frac{b_iRT}{b_{mix}} \tag{12}$$

Tables 2 and 3 list the fugacity coefficients of CO_2 and methanol in the vapor phase. The fugacity coefficients of the two components in the liquid phase can be calculated from Equation (3) and the fugacity coefficients in the vapor phase, and the data are listed in Tables 2 and 3. The fugacity coefficient of CO_2 in IL-rich phase is larger than unity, while that of methanol is much small than unity, which further demonstrates that methanol–IL interaction is much stronger than CO_2–IL interaction.

Viscosity of CO_2/[C_4mim][PF_6]/methanol mixture: The viscosity data of the liquid phase are given in Tables 2 and 3. The viscosity of the ternary system depends on temperature, pressure, and composition. At the fixed temperature and pressure, the composition is the main factor. The data in the table illustrate that the viscosity of the liquid phase is not sensitive to the composition in the concentration range studied. There are two main reasons for this. First, the viscosity of the liquid phase is much lower than that of the pure IL, as can be known by comparing the data in Tables 1–3. Second, both CO_2 and methanol can reduce the viscosity of the IL. The concentration of CO_2 in the liquid phase decreases with increasing mole fraction of methanol. Therefore, their effects on the viscosity compensate each other as the composition is varied.

Conclusion

The phase behaviors of CO_2/[C_4mim][PF_6] and CO_2/[C_4mim][PF_6]/methanol mixtures and the viscosity of the liquid phases at equilibrium conditions have been determined at different temperatures and pressures. Peng–Robinson equation of state is combined with other thermodynamic functions to calculate the fugacity coefficients of the components. The results indicate that the viscosity of the liquid phase decreases significantly with increasing pressure of CO_2, and the compressed CO_2 may become an attractive reagent for reducing the viscosity of ILs in many applications because it is environmentally benign, and CO_2 and ILs can be separated simply by depressurization. The mole fraction of methanol in the CO_2-rich phase is much lower than that in the IL-rich phase, which indicates that interaction between the IL and methanol is stronger than that between CO_2 and methanol. The fugacity coefficient of CO_2 in IL-rich phase is larger than unity, while that of methanol is much small than unity, which further proves that methanol–IL interaction is much stronger than CO_2–IL interaction. However, the CO_2–IL interaction is stronger than the CO_2–methanol interaction.

Experimental Section

Materials: CO_2 with a purity of 99.995 % was supplied by Beijing Analytical Instrument Factory. 1-Methylimidazole was purchased from Aldrich.

Hexafluorophosphoric acid was supplied by ACROS. Chlorobutane was produced by Beijing Chemical Reagent Plant, and was purified by distillation before use. $[C_4mim][PF_6]$ was synthesized in our laboratory following the procedures reported by other authors.[12] Prior to use, the ionic liquid was dried under vacuum at 40 °C until the weight remained constant. The resulting ionic liquid was examined by Fourier transform infrared spectroscopy and ^1H NMR, which indicated that pure $[C_4mim][PF_6]$ was obtained. Water concentration in the IL determined by Karl Fischer analysis was 0.1 wt%. Residual chloride in the IL was 0.002 mol L^{-1}, which was determined by the method reported by Seddon et al.[8]

Apparatus: The schematic diagram of the apparatus is shown in Figure 7a. It was composed mainly of a high-pressure view cell, liquid and gas sample bombs, a high-pressure syringe pump, a solenoid-operated circulating pump, a constant-temperature air bath, and a falling-ball viscometer.

Procedures: We only describe the experimental procedures for the study of the ternary system because those for the binary system are simpler. In a typical experiment, the air in the system was removed under vacuo. A suitable amount of $[C_4mim][PF_6]$ – methanol solution was added to the system. The air bath was maintained at desired temperature. CO_2 was charged into the system using the high-pressure pump until suitable pressure was reached. Then the solenoid operated circulation pump was started to circulate the vapor phase. In order to obtain the data at fixed pressure, the high-pressure pump was set at constant-pressure mode. To test whether equilibrium was reached or not, valve A was closed after the system had been equilibrated for a certain time so that the system was isolated. The system had reached equilibrium if the pressure kept unchanged with time. The circulation pump was stopped, and the viscosity of the liquid phase was determined. Valve B was opened to eliminate the pressure difference of the two sides, so that the liquid phase could enter the liquid sample bomb easily. The valves on the liquid and vapor sample bombs were closed and the sample bombs were removed for composition analysis. The masses of the sample bombs were determined by an electronic balance (Mettler MP1200) with a resolution of 0.001 g.

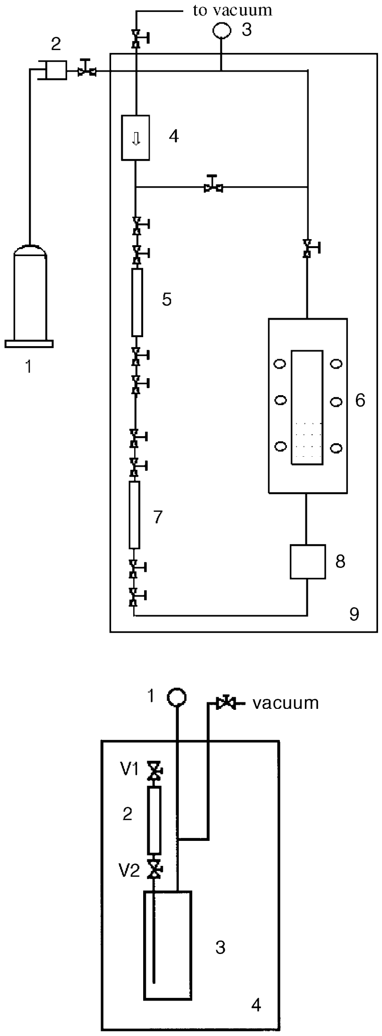

Figure 7. a) Schematic diagram of the apparatus for determination of phase behavior and viscosity of multi-component system. 1: CO_2 tank, 2: high-pressure syringe pump, 3: pressure gauge, 4: solenoid-operated circulating pump, 5: vapor phase sample bomb, 6: high-pressure view cell, 7: liquid phase sample bomb, 8: falling-ball viscometer, 9: constant-temperature air bath. b) Flashing apparatus for composition analysis of the liquid phase. 1: pressure gauge, 2: liquid sample bomb, 3: flashing chamber, 4: constant temperature water bath.

The composition of the liquid sample was determined by a flashing method using an apparatus shown schematically in Figure 7b. The sample bomb was connected to the flashing chamber, and the air in the chamber was evacuated. The constant temperature bath was maintained at 0 °C. The valve on the sample bomb was opened and the pressure of the flashing system was recorded. The moles of CO_2 could be calculated on the basis of the pressure, temperature, and volume of the flashing system. The methanol/IL solution in the flashing system was washed into a beaker using methanol, and the methanol in the beaker was removed under vacuum at 50 °C until the weight of the beaker was unchanged with time. The mass of IL was obtained by gravimetric method. With the amounts of CO_2 and IL, the mass of the methanol in the sample bomb was easily determined.

To analyze the composition of the vapor phase sample, we absorbed methanol with *N*,*N*-dimethylacetamide (DMA) by slowly releasing the CO_2 – methamol mixture through a cold trap with DMA. The composition of the DMA/methanol solution was measured by a gas chromatography (Agilent 4890D), the amount of the methanol could be obtained from the mass and the composition of the solution. The moles of CO_2 were known from the total mass of the sample and that of the methanol. To test the solubility of the IL in the vapor phase, the DMA/methanol solution was vaporized, and the mass of the IL was determined.

The viscosity of $CO_2/[C_4mim][PF_6]$/methanol mixture, η, could be calculated by the following equation:

$$\eta = K(\rho_0 - \rho)t \tag{13}$$

where ρ_0 and ρ stand for the density of the falling ball and the liquid phase, respectively. t denotes the falling time of the falling ball. K is the instrument parameter. The instrument parameter K is a key for determining the viscosity accurately. In this work, it was obtained by calibration using standard oils of different viscosities provided by National Standard Bureau of China.

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[1] a) J. J. Peng, Y. Q. Deng, *Tetrahedron Lett.* **2001**, *42*, 403; b) R. M. Lau, F. van Rantwijk, K. R. Seddon, R. A. Sheldon, *Org. Lett.* **2000**, *2*, 4189; c) S. T. Handy, X. L. Zhang, *Org. Lett.* **2001**, *3*, 233; d) A. J. Carmichael, M. J. Earle, J. D. Holbrey, P. B. McCormac, K. R. Seddon, *Org. Lett.* **1999**, *1*, 997; e) L. C. Branco, C. A. M. Afonso, *Tetrahedron* **2001**, *57*, 4405; f) J. N. Rosa, C. A. M. Afonso, A. G. Santos, *Tetrahedron* **2001**, *57*, 4189; g) L. J. Xu, W. P. Chen, J. L. Xiao, *Organometallics* **2000**, *19*, 1123; h) C. M. Gordon, A. McCluskey, *Chem. Commun.* **1999**, 1431; i) H. Olivier, *J. Mol. Catal. A: Chem.* **1999**, *146*, 285; j) C. W. Lee, *Tetrahedron Lett.* **1999**, *40*, 2461; k) V. Calo, A. Nacci, L. Lopez, N. Mannarini, *Tetrahedron Lett.* **2000**, *41*, 8973; l) M. H. Valkenberg, C. de Castro, W. F. Holderich, *Appl. Catal A* **2001**, *215*, 185; m) T. Welton, *Chem. Rev.* **1999**, *99*, 2071; n) P. Wasserscheid, W. Keim, *Angew. Chem.* **2000**, *112*, 3926; *Angew. Chem.*

Int. Ed. **2000**, *39*, 3772; o) S. A. Arnautov, *Synth. Met.* **1997**, *84*, 295; p) R. Sheldon, *Chem. Commun.* **2001**, 2399; q) P. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH, **2002**.

[2] a) M A. McHugh, V J. Ktukonis, *Supercritical Fluid Extraction*, 2nd ed., Boston, Butterworth-Heinemann, **1994**; b) C. A. Eckert, B. L. Knutson, P. G. Debenedetti, *Nature* **1996**, *383*, 313; c) R. A. Brown, P. Pollet, E. McKoon, C. A. Eckert, C. L. Liotta, P. G. Jessop, *J. Am. Chem. Soc.* **2001**, *123*, 1254; d) F. Loeker, W. Leitner, *Chem. Eur. J.* **2000**, *6*, 2011; e) X. G. Zhang, B. X Han, Z. S Hou, J. L. Zhang, Z. M. Liu, T. Jiang, J. He, H. P. Li, *Chem. Eur. J.* **2002**, *8*, 5107; f) H. P. Li, B. X. Han, J. Liu, L. Gao, Z. S. Hou, T. Jiang, Z. M. Liu, X. G. Zhang, J. He, *Chem. Eur. J.* **2002**, *8*, 5593; g) M. G. Hitzler, M. Poliakoff, *Chem. Commun.* **1997**, 1667; h) K. P. Johnston, K. L. Harrison, M. J. Clarke, S. M. Howdle, *Science* **1996**, *271*, 624; i) J. F. Brennecke, J. E. Chateauneuf, *Chem. Rev.* **1999**, *99*, 433; j) A. Baiker, *Chem. Rev.* **1999**, *99*, 453; k) P. G. Jessop, T. Ikariya, R. Noyori, *Chem. Rev.* **1999**, *99*, 475; l) J. A. Darr, M. Poliakoff, *Chem. Rev.* **1999**, *99*, 495; m) J. L. Kendall, D. A. Canelas, J. L. Young, J. M. DeSimone, *Chem. Rev.* **1999**, *99*, 543; n) P. E. Savage, *Chem. Rev.* **1999**, *99*, 603.

[3] a) L. A. Blanchard, D. Hancu, E. J. Beckman, J. F. Brennecke, *Nature* **1999**, *399*, 28; b) L. A. Blanchard, Z. Y. Gu, J. F. Brennecke, *J. Phys. Chem. B* **2001**, *105*, 2437; c) J. L. Anthony, E. J. Maginn, J. F. Brennecke, *J. Phys. Chem. B* **2002**, *106*, 7315.

[4] a) F. C. Liu, M. B. Abrams, R. T. Backer, W. Tumas, *Chem. Commun.* **2001**, 433; b) R. A. Brown, P. Pollet, E. McKoon, C. A. Eckert, C. L. Liotta, P. G. Jessop, *J. Am. Chem. Soc.* **2001**, *123*, 1254; c) M. F. Sellin, P. B. Webb, D. J. Cole-Hamilton, *Chem. Commun.* **2001**, 781; d) L. A. Blanchard, J. F. Brennecke, *Ind. Eng. Chem. Res.* **2001**, *40*, 287.

[5] a) A. Bosmann, G. Francio, E. Janssen, M. Solinas, W. Leitner, P. Wasserscheild, *Angew. Chem.* **2001**, *113*, 2769; *Angew. Chem. Int. Ed.* **2001**, *40*, 2697; b) Z. S. Hou, B. X. Han, L. Gao, T. Jiang, Z. M. Liu, Y. H. Chang, X. G. Zhang, J. He, *New J. Chem.* **2002**, *26*, 1246.

[6] A. M. Scurto, S. N. V. K. Aki, J. F. Brennecke, *J. Am. Chem. Soc.* **2002**, *124*, 10276.

[7] S. N. Baker, G. A. Baker, M. A. Kane, F. V. Bright, *J. Phys. Chem. B* **2001**, *105*, 9663.

[8] K. R. Seddon, A. Stark, M.-J. Torres, *Pure Appl. Chem.* **2000**, *72*, 2275.

[9] S. G. Kazarian, B. J. Briscoe, T. Welton, *Chem. Commun*. **2000**, 2047.

[10] C. J. Chang, C.-Y. Day, C.-M. Ko, K.-L. Chiu, *Fluid Phase Equilib.* **1997**, *131*, 243.

[11] D. Y.Peng, D. B. Robindon, *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59.

[12] J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser, R. D. Rogers, *Chem. Commun.* **1998**, 1765.

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