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Effect of Organic Cosolvents on the Solubility of Ionic Liquids in Supercritical CO_2

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The solubilities of ionic liquids (ILs) 1-butyl-3- methylimidazolium hexafluorophosphate ([bmim][PF_6]) and 1-butyl-3- methylimidazolium tetrafluoroborate ([bmim][BF_4]) in supercritical (sc) CO_2 with and without organic cosolvents were determined at 40.0 °C and 15.0 MPa. The mole fraction of a cosolvent was up to 0.3. The solubilities of the ILs in sc CO_2 + polar cosolvent mixtures increased dramatically as the cosolvent concentration exceeded 10 mol %, but the solubility was extremely low when the concentration of the cosolvent was lower than 10 mol %. The effect of a cosolvent on the solubility of the ILs in sc CO_2 depends mainly on its polarity. The stronger the polarity of a cosolvent, the larger the effect. The ability of the mixed cosolvent to enhance the solubility is intermediate between the two pure cosolvents.

1. Introduction

Ionic liquids (ILs) have attracted much attention because of their lack of volatility and their usefulness as solvents for separations and reactions[1−6] and are considered to be greener solvents. Usually, organics dissolved in an IL can be separated from the IL by evaporation or liquid−liquid separation, but for high-boiling point or thermally labile compounds, traditional separation methods have some shortcomings.

Supercritical (sc) CO_2 can dissolve many organic compounds and has been used in different fields such as separations, reactions, and material preparation.[7−16] The combination of sc CO_2 and ILs in various applications is a new and interesting field.[17−22] Recently, Brennecke et al.[23,24] reported that the solubility of ILs in sc CO_2 was extremely low. Therefore, sc CO_2 can be used to extract low volatile compounds from ILs without cross contamination. It is well known that cosovlents can enhance the solubility of solutes in sc CO_2.[25−27] In practical applications, many compounds (e.g., reactants, products, and extracts) are involved in the systems, which may act as cosolvents to increase the solubility of ILs. There is no doubt that the study of the solubility of ILs in sc CO_2 with cosolvents is crucial for the effective utilization of the two green solvents because it is closely related to the separation efficiency and cross contamination of the separation process.

In our previous short communication,[28] we reported the solubility of [bmim][PF_6] in sc CO_2 with ethanol, acetone, and *n*-hexane cosolvents. The results demonstrated that polar cosolvents could enhance the solubility of ILs significantly, especially when their mole fraction was greater than 0.1. In this work, we study the solubility of [bmim][PF_6] in sc CO_2 with different mixed cosolvents. In addition, we study the effect of cosolvents on the solubility of hydrophilic [bmim][BF_4] in sc CO_2.

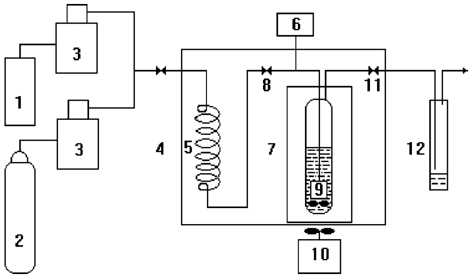

Figure 1. Schematic diagram of the apparatus. (1) Organic solvent reservoir, (2) CO_2 reservoir, (3) computer-controlled metering syringe pumps, (4) constant-temperature water bath, (5) preheater, (6) pressure gauge, (7) optical cell, (8) valve I, (9) stainless steel filter, (10) magnetic stirrer, (11) valve II, and (12) trap.

2. Experimental Section

Materials. CO_2 with a purity of 99.995% was supplied by Beijing Analytical Instrument Factory. 1-Methylimidazole (99% purity) was used as received from Acros Organics. 1-Chlorobutane, ethanol, acetone, and *n*-hexane were all analysis reagent grade and produced by Beijing Chemical Reagent Factory. [bmim][PF_6] and [bmim][BF_4] were synthesized and characterized following procedures reported elsewhere.[29,30] The ILs were dried under vacuum at 40 °C until the mass remained constant. The water concentration in the ILs after drying was (0.1 to 0.14) wt %, as measured by Karl Fischer analysis.

Apparatus and Procedures. A dynamic or flow method is one of the commonly used techniques to determine the solubility of solid or liquid solutes in sc CO_2 with or without cosolvents.[31−33] In this work, we used this method to determine the solubilities of the ILs in sc CO_2 with and without cosolvents. The apparatus is shown schematically in Figure 1. It consisted of a CO_2 cylinder, two computer-controlled metering syringe pumps, a constant-temperature water bath, a pressure gauge, a preheater, a 55-mL optical cell, and a trap. The CO_2 and organic solvent were mixed in the pipe and the preheater. The mixed fluid entering the bottom of the optical cell was dispersed into very small

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Table 1. Dipole Moments μ of the Cosolvents

cosolvent	acetonitrile	acetone	methanol	ethanol	*n*-hexane
μ/D	3.94	2.88	1.7	1.7	0

bubbles after passing the stainless steel filter (pore size 20 μm) in the IL, and the IL-rich phase was stirred by a magnetic stirrer. Experiments showed that this was very effective in facilitating equilibrium. The water bath was maintained within ±0.1 °C of the desired temperature by using a Haake D8 temperature controller. The pressure gauge was composed of a pressure transducer (Foxboro/ICT, model 93) and an indicator, which was accurate to ±0.025 MPa in the pressure range of (0 to 20) MPa. The flow rate of CO_2 was accurately controlled by the computer-controlled metering syringe pump, which was calibrated by a wet test meter. The flow rate of cosolvent was accurately controlled by another computer-controlled metering syringe pump, which was calibrated by using water as a medium.

In a typical experiment, a suitable amount of IL was loaded into the optical cell. The cell was placed in the constant-temperature water bath. The CO_2 and cosolvent or mixed cosolvent were compressed into the optical cell by opening needle valve 8 slowly. Needle valve 11 was opened to release the CO_2-rich phase slowly as the desired pressure was reached. The molar ratio of CO_2 to the cosolvent in the feed was fixed by controlling the flow rates of the two pumps. It can be known from the phase rule that the compositions of both the vapor phase and liquid phase are fixed after equilibrium has been reached because the molar ratio of CO_2 to cosolvent in the feed is fixed. In each experiment, enough of the mixture of the CO_2-rich phase was released, and the extracted sample was not collected unless equilibrium was reached. Equilibrium was confirmed by the fact that the volume of the liquid phase did not change with time. Therefore, the molar ratio of CO_2 to the cosolvent in the vapor phase was equal to that in the feed. After enough IL had been collected in the trap, the two needle valves (8 and 11) were closed. The amounts of CO_2 and the cosolvent were known from the flow rates of the pumps and the experimental time. The mass of the IL collected in the trap was determined gravimetrically using a balance with a resolution of 0.1 mg. In each experiment, at least 50 mg of an IL was collected. The mole fractions of each component in the vapor phase were calculated on the basis of the amount of each component. The flow rate of CO_2 was in the range of (50 to 120) $mL\cdot min^{-1}$ at 0 °C and 0.101 MPa. The flow rate was slow enough to maintain equilibrium during the experiment, which was verified by the fact that the solubility determined was independent of the flow rate. The reliability of the data was also confirmed by the fact that at fixed conditions several samples were collected and the solubility determined was independently of time. The solubilities of [bmim][PF_6] and [bmim][BF_4] were determined by both gravimetric analysis and UV−vis spectroscopy, and the results obtained from the two methods agreed within ±6%.

3. Results and Discussion

We selected different cosolvents, which are listed in Table 1, to investigate the effects of the properties of cosolvents on the solubility of the ILs in sc CO_2. CO_2 and the cosolvents are miscible under the experimental conditions used in this work. In the present paper, x_2 and x_3 are mole fractions of the cosolvents and the ILs in CO_2-rich phase, respectively. The solubility (x_3) of [bmim][PF_6] and [bmim][BF_4] under different conditions is given in Table 2.

Table 2. Mole Fraction Solubility of ILs x_3 in sc CO_2 with Cosolvents x_2 at 40.0 °C and 15.0 MPa

ILs	cosolvent	x_2	$10^4 x_3$
[bmim][PF_6]		0.00	0.0032
	acetonitrile	0.10	0.90
		0.15	7.00
		0.20	15.36
		0.25	119.3
	methanol	0.10	0.095
		0.15	0.363
		0.20	1.295
		0.24	4.23
	ethanol + *n*-hexane[a]	0.098	0.0020
		0.20	0.297
		0.26	0.389
		0.29	0.451
	acetone + *n*-hexane[a]	0.097	0.0068
		0.15	0.0637
		0.198	0.621
		0.25	1.23
	ethanol + acetone[a]	0.099	0.121
		0.15	0.727
		0.20	2.73
[bmim][BF_4]		0.00	0.0086
	ethanol	0.10	0.0173
		0.15	8.12
		0.20	20.5
		0.25	52.1
		0.30	85.9

[a] With a molar ratio of 1:1.

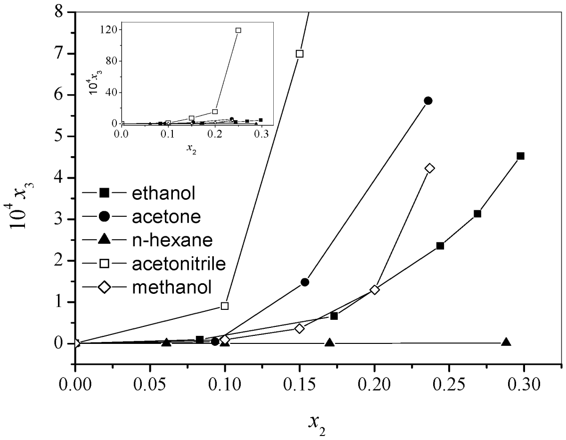

Figure 2. Solubility of [bmim][PF_6] x_3 in sc CO_2 with cosolvents x_2 at 15.0 MPa and 40.0 °C. The inset shows the large value of the solubility that is hidden.

Effect of Cosolvent Polarity on the Solubility of [bmim][PF$_6$]. The solubility of [bmim][PF_6] in sc CO_2 with different cosolvents is illustrated in Figure 2. The solubility of the IL in sc CO_2 with ethanol, acetone, and *n*-hexane cosolvents[28] is also shown in the Figure for comparison. Figure 2 contains two plots because of the large difference in solubility with different cosolvents. The effect of *n*-hexane on the solubility of the IL in sc CO_2 is very limited; even the molar fraction reaches 0.29. Methanol, ethanol, and acetone have intermediate-valued dipole moments, and they have a similar effect on the solubility. The solubility of the IL is not considerable as the mole fraction of the three cosolvents in CO_2 is less than about 0.1. However, the solubility increases dramatically as mole fraction of the cosolvents exceeds 0.1. At 40.0 °C and 15.0 MPa, the solubility of the IL increases by more than 3 orders of magnitude as the mole fraction of the cosolvents changes from 0.0 to 0.30.

Acetonitrile has the largest dipole moment. At the same mole fraction, the solubility of the IL in sc CO_2 with

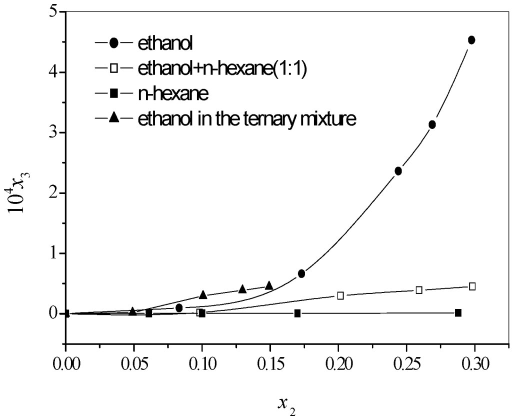

Figure 3. Solubility x_3 of [bmim][PF_6] in sc CO_2 + ethanol + n-hexane mixtures x_2 at 15.0 MPa and 40.0 °C.

acetonitrile is greater than that with other cosolvents. For instance, at the mole fraction of 0.25, the solubility of the IL in sc CO_2 with acetonitrile is 1.19×10^{-2}, and the solubility with other polar cosolvents is on the order of 10^{-3}.

Solubility enhancement by a polar cosolvent results mainly from the strong interaction of the cosolvent with the IL due to their strong polarity. Figure 2 shows that under the same conditions the ability of the cosolvents to enhance the solubility of the IL follows the order acetonitrile > acetone > methanol ≥ ethanol > n-hexane, which follows the same order of dipole moments of the cosolvents. This indicates that the polarity of the cosolvents is a dominant factor influencing the solubility. Methanol and ethanol not only are typical polar compounds (dipole moment $\mu = 1.70$ D) but also can form hydrogen bonds with electron donors or acceptors. They may hydrogen bond with N or F in the IL to strengthen the interaction of the compounds with the IL. Acetone and acetonitrile are stronger polar compounds (μ = 2.88 D and 3.94 D, respectively). However, they cannot hydrogen bond with the IL. The data in this work hint that the polarity of the organic compounds is more important than hydrogen bonding to the solubility enhancement.

The IL consists of a cation and an anion. The polarity of imidazolium ionic liquids has been studied by several authors.[34−37] Brennecke and co-workers[34] reported that these ILs are between acetonitrile and methanol in polarity. A recent study on [bmim][BF_4] using static fluorescence measurement indicated that the IL was as polar as 2-propanol.[37] Hence, the addition of polar cosolvents to sc CO_2 can greatly enhance the interaction of an IL molecule with the solvent, resulting in increased solubility of IL. n-Hexane, a nonpolar compound, has a weaker interaction with the IL. Therefore, the addition of n-hexane to sc CO_2 has little effect on the solubility of the IL.

Effect of Mixed Cosolvents on the Solubility of [bmim][PF_6]. The solubility of [bmim][PF_6] in sc CO_2 with mixed cosolvents ethanol + n-hexane, acetone + n-hexane, and ethanol + acetone (1:1 mol/mol) was determined, and the results are shown in Table 2 and Figures 3 to 5. The solubility of the IL in sc CO_2 with pure cosolvents is also given in the Figures for comparison.

The solubility of the IL in sc CO_2 with the ethanol + n-hexane mixed cosolvent is very low when the total mole fraction of the mixed cosolvents is below 0.1, but the solubility increase noticeably when the mole fraction is greater than 0.1. The solubility in sc CO_2 + ethanol + n-hexane is lower than in sc CO_2 + ethanol and higher than in sc CO_2 + n-hexane. n-Hexane has little effect on the solubility, so the solubility enhancement of the mixed cosolvent may result mainly from ethanol. To study the role of n-hexane in the mixed solvent for the solubility enhancement, Figure 3 also shows the solubility of the IL in sc CO_2 with the mixed solvent as a function of the ethanol mole fraction in the system (the curve marked by ethanol in the ternary mixture). The solubility with the mixed cosolvent is greater than that in sc CO_2 with pure ethanol, provided that the mole fraction of ethanol in the binary and ternary systems is the same, suggesting that nonpolar cosolvent n-hexane can also enhance the solubility when the polar cosolvent exists.

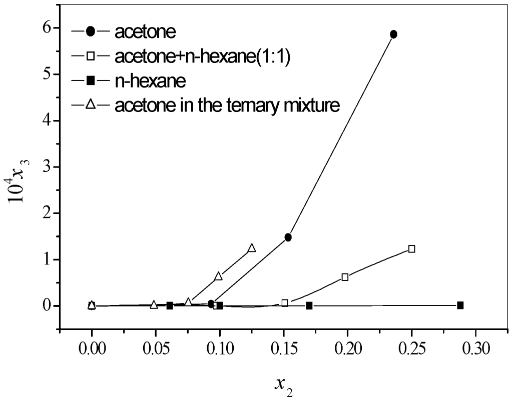

Figure 4. Solubility x_3 of [bmim][PF_6] in sc CO_2 + acetone + n-hexane mixtures x_2 at 15.0 MPa and 40.0 °C.

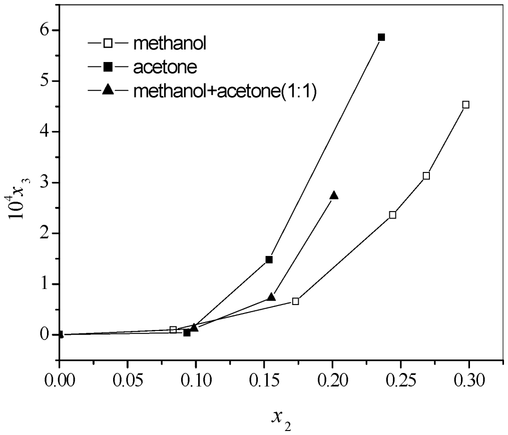

Figure 5. Solubility x_3 of [bmim][PF_6] in sc CO_2 + acetone + ethanol mixtures x_2 at 15.0 MPa and 40.0 °C.

The mixture of acetone + n-hexane (1:1 mol/mol) has a similar effect on the solubility of the IL in sc CO_2 with ethanol + n-hexane (1:1 mol/mol), which can be known from Figure 4. The solubility is very low at the beginning and increases significantly when the mole fraction of the mixed cosolvent is greater than about 0.15. The ability of the mixed cosolvent to enhance the solubility is also intermediate between that of the two pure cosolvents. The solubility is obviously greater than that in sc CO_2 with the ethanol + n-hexane (1:1 mol/mol) cosolvent under the same conditions, as can be known from Figures 3 and 4. Similarly, to study the role of n-hexane in the mixed solvent for the solubility enhancement, Figure 4 also shows the solubility of the IL in sc CO_2 with the mixed solvent as a function of the acetone mole fraction in the system. The solubility with the mixed cosolvent is greater than that in sc CO_2 with pure acetone, provided that the mole fraction of acetone is the same.

The solubility of the IL in the sc CO_2 with ethanol + acetone (1:1 mol/mol) cosolvent is shown in Figure 5. The solubility increases greatly when the mole fraction of the

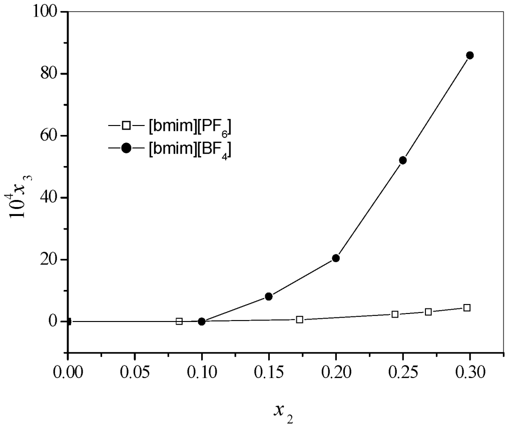

Figure 6. Solubility x_3 of [bmim][PF$_6$] and [bmim][BF$_4$] in sc CO$_2$ + ethanol x_2 mixtures at 15.0 MPa and 40.0 °C.

cosolvent is larger than 0.1. Similarly, the solubility in sc CO$_2$ with the mixed cosolvent is between those in sc CO$_2$ + ethanol and sc CO$_2$ + acetone.

Solubility of [bmim][BF$_4$]. The solubility of hydrophilic IL [bmim][BF$_4$] in sc CO$_2$ with ethanol was determined at 40.0 °C and 15.0 MPa, and the results are shown in Table 2 and illustrated in Figure 6. The solubility of [bmim][PF$_6$] in sc CO$_2$ with ethanol is also given in the Figure. The solubility of [bmim][BF$_4$] has a similar trend to that of [bmim][PF$_6$]. However, the solubility of [bmim][BF$_4$] in the sc CO$_2$ + ethanol mixture is much larger than that of [bmim][PF$_6$] under same conditions, as shown in Figure 6. The solubilities of [bmim][BF$_4$] and [bmim][PF$_6$] in pure sc CO$_2$ at 40.0 °C and 15.0 MPa are 8.6×10^{-7} and 3.2×10^{-7} in mole fraction, respectively. These results indicate that [bmim][BF$_4$] is more soluble than [bmim][PF$_6$] in sc CO$_2$ with or without ethanol. There are two main reasons for this. First, Kazarian et al.[38] reported that [BF$_4$]$^-$ and [PF$_6$]$^-$ are Lewis bases when CO$_2$ dissolves in the ILs at high pressures and [BF$_4$]$^-$ is a stronger Lewis base than [PF$_6$]$^-$ with the same cation of imidazolium. Furthermore, CO$_2$ is a molecule with a relatively large quadrupole moment, so the [BF$_4$]$^-$ anion interacts more strongly with CO$_2$ and ethanol than [PF$_6$]$^-$ does. Second, [bmim][PF$_6$] and [bmim][BF$_4$] have similar structures, but [bmim][BF$_4$] has lower molecular weight. Both factors are favorable to the dissolution of [bmim][BF$_4$].

4. Conclusions

The results of this work indicate that the solubility of [bmim][PF$_6$] and [bmim][BF$_4$] in sc CO$_2$ can be enhanced significantly by the existence of organic compounds in the systems. This work may provide valuable information for scientific research and the applications related to sc CO$_2$–IL binary systems. Specifically, the results remind researchers and engineers that the IL content in a sc CO$_2$-rich phase should be considered in the design of experiments or industrial processes if the system contains enough polar organic compounds.

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