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Solubility of room-temperature ionic liquid in supercritical CO_2 with and without organic compounds

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Ionic liquid can dramatically dissolve in supercritical (sc) CO_2 with polar organic compounds (ethanol, acetone) especially as the concentration of the compounds in $scCO_2$ exceeds 10 mol%, while the effect of a nonpolar organic compound (*n*-hexane) in $scCO_2$ on the solubility is very limited even when its concentration is as high as 30 mol%.

Minimizing energy consumption and pollution has become a major concern for the chemical industry. Utilization of green solvents to reduce the evaporation of organic solvents and/or improving the efficiency of the processes is an effective route. Room-temperature ionic liquids (ILs) and supercritical CO_2 ($scCO_2$) are among the most promising green solvents.

ILs have many unique properties.[1] For example, they have extremely low vapour pressure, and excellent solvent power for organic and inorganic compounds. Therefore, they can be used as environmentally benign solvents for a number of chemical processes, such as separations and reactions.[2] In recent years, supercritical (sc) science and technology have received much attention.[3] Supercritical fluids (SCFs) can be used in many processing applications, such as extraction and fractionation, chemical reactions, and material processing.[4] $scCO_2$ is the most attractive since it is nontoxic, nonflammable, inexpensive, readily available in large quantities, and has moderate critical temperature and pressure (31.1 °C and 7.38 MPa).

Both $scCO_2$ and ILs are environmentally benign solvents, and each of them has its own unique properties. Utilization of the binary mixtures is a new and interesting topic, which can combine the advantages of the two classes of solvents and may have additional features. Recently, Brennecke and co-workers performed elegant studies on the phase behavior of some $scCO_2$/IL systems.[5] They discovered that the unique feature of the phase behavior was that $scCO_2$ was soluble in the ILs, while the solubility of the ILs in $scCO_2$ was extremely low. It is well known that $scCO_2$ has a strong ability to dissolve organic solutes.[5] Therefore, some low-volatility organic compounds could be extracted from ILs completely using $scCO_2$ without cross-contamination. Based on this principle, researchers have successfully extracted organic compounds from ILs,[5,6] and separation of reactants and products from ILs has also been performed after reactions in ILs,[7] which make the reaction processes much cleaner.

It can be expected that many processes will be carried out in mixtures of the two clean solvents, which will not only eliminate pollution and cross-contamination, but also will improve the efficiency of many processes, such as improving the selectivity of reactions.[8] In scientific research and industrial applications, the $scCO_2$ phase contains other components (*e.g.* reactants, products, extracts), which may act as cosolvents to enhance the ability of $scCO_2$ to dissolve ILs significantly, and the amount of ILs in the CO_2-rich phase may be not negligible under some conditions. In this case the solubility of ILs in $scCO_2$ + organic compound mixtures is crucial for utilizing the binary solvents effectively and selecting conditions to avoid cross-contamination.

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The study of phase behavior is an important and long established field because it is key to many chemical processes. In this work, we conducted the first study on the effect of organic compounds in $scCO_2$ on the solubility of an IL in a $scCO_2$ phase, and the solubility of 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6])† in $scCO_2$, and in $scCO_2$ + ethanol, $scCO_2$ + acetone, and $scCO_2$ + *n*-hexane mixtures has been determined quantitatively.

The solubility was determined using a flow apparatus constructed in this work, which is illustrated schematically in Fig. 1‡. The data at different conditions are listed in Table 1, and the dependence of the solubility on temperature, pressure, and the concentration of the organic compounds in the $scCO_2$ phase is illustrated in Fig. 2. X_2 and X_3 in the table and figure are the

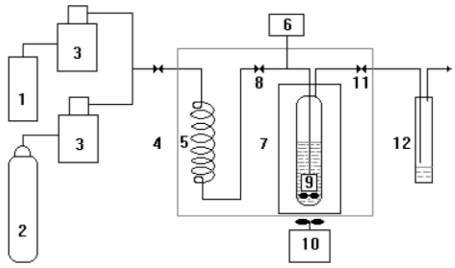

Fig. 1 Schematic diagram of the apparatus. 1: Organic solvent reservoir; 2: CO_2 reservoir; 3: Computer-controlled metering syringe pumps; 4: Constant temperature water bath; 5: Pre-heater; 6: Pressure gauge; 7: Optical cell; 8: Valve I; 9: Stainless steel filter; 10: magnetic stirrer; 11: Valve II; 12: Trap.

Table 1 Solubility of [BMIM][PF_6] (X_3) in $scCO_2$ with and without organic compounds (X_2)

T/°C	*P*/MPa	Cosolvent	X_2	$X_3 \times 10^6$
40.0	12.0	—	0.000	0.18
40.0	12.0	Ethanol	0.085	6.26
40.0	12.0	Ethanol	0.113	15.0
40.0	12.0	Ethanol	0.165	50.7
40.0	12.0	Ethanol	0.254	219.0
40.0	12.0	Ethanol	0.305	370.0
40.0	15.0	—	0.000	0.32
40.0	15.0	Ethanol	0.083	9.53
40.0	15.0	Ethanol	0.173	66.2
40.0	15.0	Ethanol	0.244	236.0
40.0	15.0	Ethanol	0.269	313.0
40.0	15.0	Ethanol	0.298	453.0
55.0	15.0	—	0.000	0.14
55.0	15.0	Ethanol	0.115	14.4
55.0	15.0	Ethanol	0.173	89.1
55.0	15.0	Ethanol	0.244	245.0
55.0	15.0	Ethanol	0.291	387.0
40.0	15.0	Acetone	0.093	4.50
40.0	15.0	Acetone	0.154	148.0
40.0	15.0	Acetone	0.236	586.0
40.0	15.0	*n*-Hexane	0.061	0.44
40.0	15.0	*n*-Hexane	0.100	0.55
40.0	15.0	*n*-Hexane	0.170	0.57
40.0	15.0	*n*-Hexane	0.288	1.38

mole fractions of the organic compounds and the IL in CO_2-rich phase, respectively.

Solubility of the IL in pure CO_2 is extremely low. For example, at 40.0 °C and 15.00 MPa, X_3 determined in this work is 3.2×10^{-7}. Brennecke and coworkers reported[5] that the mole fraction at 40.0 °C and 13.79 MPa was less than 5×10^{-7}. The results indicate that the data determined by the two laboratories are in agreement although the apparatuses used were different.

The effect of ethanol on the solubility of the IL is not considerable as X_2 is less than about 0.1, as can be seen from the data in Fig. 2. However, the solubility increases significantly as X_2 exceeds 0.1. At 40.0 °C and 15.0 MPa, the solubility of the IL increases about 3 orders with an increase of X_2 from 0.1 to 0.30. At the same temperature, the solubility increases slightly as pressure changes from 12.0 to 15.0 MPa, as is shown in Fig. 2.

The effect of acetone on the solubility is similar to that of ethanol, *i.e.*, the solubility varies very slowly with X_2 at $X_2 < 0.1$, and increases dramatically with an increase in X_2 as X_2 exceeds about 0.1. However, acetone has a more significant influence on the solubility than ethanol. At 40.0 °C and 15.00 MPa, X_3 can be 5.86×10^{-4} at $X_2 = 0.236$.

n-Hexane is a non-polar substance. Fig. 2 indicates that its effect on the solubility of the IL in $scCO_2$ is very limited.

Enhancement of the solubility by addition of ethanol and acetone results mainly from strong interaction of the two compounds with the IL due to their strong polarity. Ethanol is a typical polar compounds (dipole moment $\mu = 1.70$ D) that can form hydrogen bonds with electron donors or acceptors. It may hydrogen bond with N or F in the IL. The polarity of acetone is stronger ($\mu = 2.89$ D). However, it cannot hydrogen bond with the IL. The data in this work hint that polarity of the organic compounds is a dominant factor in influencing the solubility.

In summary, we conducted the first study on the solubility of an IL in $scCO_2$ + organic compound mixtures. It is demonstrated that the solubility of the [BMIM][PF_6] in $scCO_2$ + ethanol, $scCO_2$ + acetone is considerable and increases dramatically as the concentration of the organic compounds in $scCO_2$ exceeds 10 mol%, although the solubility is extremely low as the concentration of the organic compounds is lower. The effect of *n*-hexane in $scCO_2$ on the solubility is very limited even when its concentration is as high as 30 mol%. This work provides important information for fundamental research and applications related to $scCO_2$–IL binary systems. Specifically, the results remind researchers and engineers that the amount of an IL in $scCO_2$-rich phase may be significant and should be considered in the designs of experiments or industrial processes if the system contains enough polar organic compounds.

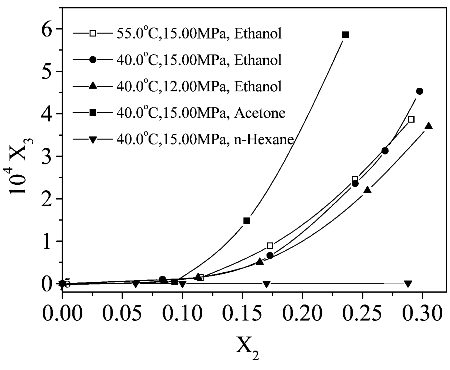

Fig. 2 Solubility (X_3) of [BMIM][PF_6] in $scCO_2$ + organic compound mixtures.

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Notes and references

† [BMIM][PF_6] was synthesized and characterized following the procedures reported by Huddleston *et al.*[9] The ionic liquid was dried under vacuum at 40 °C until the weight remained constant. Water concentration in the IL was 0.1 wt%, which was known from Karl Fischer analysis.

‡ The apparatus (Fig. 1) consisted mainly of a CO_2 cylinder, two computer-controlled metering syringe pumps, a constant-temperature water bath, a pressure gauge, a pre-heater, an optical cell of 55 ml, and a trap. The CO_2 and organic solvent were mixed in the pipe and the pre-heater. The mixed fluid entering the bottom of the optical cell was dispersed into to very small 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 the equilibrium.

In an 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 were compressed into the optical cell by opening needle valve I slowly. The ratio of CO_2 and the organic solvent and the flow rate were controlled by the flow rates of the two pumps. The needle valve II was opened to release the CO_2-rich phase slowly as the desired pressure was reached, and at least 150 g mixture of CO_2-rich phase was released without collecting the extracted sample. The flow rate of CO_2 was in the range of 50–100 ml min^{-1} (stp). The IL was precipitated in the trap after depressurization. The flow rate was slow enough for reaching equilibrium, 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 under fixed conditions, several samples were collected, and the solubility determined was independent of time. The solubilities of [BMIM][PF_6] were determined by both gravimetric analysis and UV–vis spectroscopy, and the results obtained from the two methods agreed within ±6%.

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