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Phase equilibria for separation of high boiling point organics from ionic liquids by supercritical CO_2 or C_3H_8

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ABSTRACT

Application of room temperature ionic liquids (RTILs) as reaction media, catalysts and solvents, will encounter a problem of organics separation from RTILs systems. The utilization of supercritical fluids (SCFs) to separate high boiling point organics needs quantitative phase equibliria data and modeling. The phase equilibria and modeling for separating high boiling point organics from RTILs by supercritical (SC) CO_2 and C_3H_8 have been studied thereof to take their advantage of low critical temperature. The long-term stability of 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) and 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([bmim][CF_3SO_3]) has been observed in SC CO_2 and C_3H_8, which for [bmim][PF_6] is below 120 °C while [bmim][CF_3SO_3] can stay stable at 120 °C over 72 h. The solubility of CO_2 and volume expansivity in [bmim][CF_3SO_3] at 40, 50 and 60 °C and pressure of 1–20 MPa were measured, as well the solving behavior has been determined for C_3H_8–[bmim][CF_3SO_3] system under conditions of 100, 110 and 120 °C, 1–9 MPa. C_3H_8 give a much lower dissolving molarity in [bmim][CF_3SO_3] than CO_2 under the same pressure and reduced temperature. The ternary phase equilibria of CO_2–[bmim][CF_3SO_3]–DBT, C_3H_8–[bmim][CF_3SO_3]–DBT, CO_2–[bmim][CF_3SO_3]–naphthalene and C_3H_8–[bmim][CF_3SO_3]–naphthalene are determined in a wide pressure and molality of solute in this ionic liquid (IL) at given temperature 323 and 393 K, respectively. Modified Chrastil's association model was extended to ternary system with the equation $c_A/m_A = d^k \exp((a/T) + b)$ giving a good correlation. The error between experimental data and the calculated concentration of solute in SCF phase for CO_2–[bmim][CF_3SO_3]–DBT, C_3H_8–[bmim][CF_3SO_3]–DBT, CO_2–[bmim][CF_3SO_3]–naphthalene and C_3H_8–[bmim][CF_3SO_3]–naphthalene are 5.0, 6.0, 7.9 and 9.4%, respectively. Extraction of naphthalene from [bmim][CF_3SO_3] is calculated in continuous and batch processes. Batch SCF extraction may be applied to separate high boiling point organics from ILs. As long time and recycle solvent to feed ratio are necessary for using SC CO_2, C_3H_8 could be a good alternative since it shows nearly a magnitude higher solving power than SC CO_2.

1. Introduction

One aspect concerned in ionic liquids (ILs) applications such as solvent, catalysts or reaction media is the separation of solutes, reactants or products. There are challenges in high boiling point organics separation because the long-term (>10 h) stability of ILs are generally below 200 °C [1]. Apparently distillation is not applicable. Although liquid–liquid extraction is known as a feasible separation method, cross-contamination between the phases is a problem [2,3]. In addition, liquid extraction is not suitable for thermal liable compounds because the solvent recovery needs a higher temperature. Comparatively, SCF extraction with CO_2 have been introduced to extract both volatile and relatively non-volatile organic compounds from ILs without any IL contamination [4–6], showing a bright promise. Knowledge of the phase behavior of these systems is a crucial aspect of this methodology and has been the focus of many researches in recent years. Many investigations have been carried out on the phase behavior of the binary systems "SC CO_2 + ILs" [7–24]. But the SCF-liquid equilibrium data of the ternary systems "SC CO_2 + ILs + organics" [25–29], which are more useful for the prospective extraction applications, were rarely reported. Scurto et al. [25,26] reported that the solution of 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) and methanol could be induced to form three phases in the presence of CO_2 and investigated the effects of temperature, pressure and initial IL concentration on the liquid–liquid phase split. Najdanovic-Visak et al. [27] studied the liquid–liquid phase behavior of the system "l-butyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide ([bmim][NTf_2]) + 1-butanol + water" and the CO_2-induced phase changes. Zhang et al. [28] investigated the phase behavior of the ternary system "CO_2 + 1-N-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) + water" by a static method at 278–298 K

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and pressure up to 16 MPa. They calculated the distribution coefficients of [bmim][BF_4] between IL-rich phase and water-rich phase and discussed the separation of IL and water. Liu et al. [29] studied the phase behavior of the ternary system "SC CO_2 + [bmim][PF_6] + methanol" and the viscosity of the liquid phases at 313 K and the pressure of 7.15 and 10.00 MPa, and calculated the fugacity coefficients of the components in the system by the Peng–Robinson state equation and some thermodynamic functions. In all, most involved ILs are [bmim][BF_4] and [bmim][PF_6] and almost all system used SC CO_2. Few investigations have been carried out for the phase equilibria of the ternary systems involving high boiling point organics, and even fewer paid particular attention to the quantitative concentration distribution of organics between SC CO_2 and ILs.

As is known, propane is another wide used SCF in petrochemical industry because of its high solving power, for example, petroleum residuum deasphalting. Propane has a moderately higher critical temperature 369.83 K and lower critical pressure 4.248 MPa, compared to CO_2 which is 304.13 K and 7.375 MPa. [bmim][CF_3SO_3] is believed to be more stable than [bmim][PF_6] [1]. In this work, phase equilibria experiments and modeling of naphthalene and dibenzothiophene (DBT)–[bmim][CF_3SO_3]–CO_2 or C_3H_8 were conducted. And the feasibility of extracting organics from IL by SC propane will be discussed comparing with SC carbon dioxide.

2. Experimental

2.1. Chemicals

CO_2 with a purity of 99.995% and C_3H_8 over 99% were supplied by Beijing Analytical Instrument Factory. Naphthalene, DBT and 1-chlorobutane were AR grade and produced by Beijing Chemical Reagent Factory. Potassium hexafluorophosphate (98% purity) was used as received from Fluka. [bmim][PF_6] was synthesized and characterized by the procedures reported elsewhere [31,32]. [bmim][CF_3SO_3] was synthesized according the following procedure: about 30 mL 1,1,1-trichloroethane was added into a flask firstly, 17.23 g $CF_3SO_3CH_3$ was also added slowly under Ar to prevent it from hydrolysis, and then 12.42 gram 1-butyl-3-methyl imdazolium was added slowly into the flask droply and refluxed 2 h at mild temperature. When the reaction was completed, 26.9 g [bmim][CF_3SO_3] was gained through separation and vacuum distillation.

2.2. Apparatus and procedures

Two main experiments were carried out. One is the detection of phase equilibrium of binary system of SC solvent in IL. The methods have been described elsewhere [24]. The RUSKA-2370 Hg free PVT was applied for the measurement of SCF–IL phase equilibrium. In a typical experiment, given amounts of CO_2 and [bmim][PF_6] were metered into the main cell where the samples were vigorously stirred to ensure equilibrium quickly. The criterion of reaching phase equilibrium is the whole volume keep invariable over 40 min in constant pressure mode. Subsequently, the liquid phase volume was determined at constant pressure. The composition of the IL-rich liquid phase was calculated on the basis of material balance, along with the assumption of a pure CO_2 vapor phase based on the low solubility of ionic liquid in CO_2.

Another apparatus is a micro-SFE system with high pressure UV online detector system [30]. The phase equilibrium system consists of an ISCO syringe pump, a preheater, and an equilibrium cell. The detection system consists of an ISCO syringe pump, a preheater, a sample injector, a six-way valve, an UV–vis detector, a chromatography workstation, an accumulator and a counterbalance valve.

In a typical experiment, the IL solution of naphthalene or DBT with given composition was added quantitatively into the equilibrium cell and then SC CO_2 was pumped into it very slowly. After the mixture reached equilibrium at the present temperature and pressure, the CO_2-rich fluid in the quantitative tube of the six-way valve was injected into the detection system by switching it. The concentration of solute (g/L) in SC-rich phase was then determined by online ultraviolet detector. Since scarcely any ILs dissolved in the SC-rich phase [4–6,10], the phase can be considered as a mixture of CO_2 and solute. So the equilibrium naphthalene molality in the liquid phase was attained as $m_A = n_B/ms_A$ (mol/kg) where ms_A is the mass of IL.

3. Solubility of CO_2 and C_3H_8 in [bmim][CF_3SO_3]

3.1. Long-term stability of [bmim][PF_6] and [bmim][CF_3SO_3] in SC solvents

The long-term stability of [bmim][PF_6] and [bmim][CF_3SO_3] was observed under high pressure with SC solvent in the PVT and compared to the one without SC solvent. The phenomena of IL decomposing is the color darken and with solid precipitation and gas production. The data are shown in Table 1. Generally speaking, the temperature is the most significant parameter, while pressure does not show obvious influence. Compared with [bmim][PF_6] which can keep stable 8 h at 120 °C, [bmim][CF_3SO_3] is more stable and may be used under 120 °C without significant decomposition.

3.2. Solubility and liquid phase volume expansivity of CO_2 in [bmim][CF_3SO_3]

The solubility and liquid phase volume expansivity of CO_2 in [bmim][CF_3SO_3] at 40, 50 and 60 °C, pressure of 1–20 MPa were measured. The density of CO_2 was calculated by the state equation of Huang et al. [33] and the density of propane was calculated by the BWR state equation (abbreviated as BRWS) modified by Starling [34]. According to Fig. 1, the solubility of CO_2 in [bmim][CF_3SO_3] changes with temperature and pressure in the same tendency with the solubility of CO_2 in [bmim][PF_6]. When the pressure is higher than 9 MPa, CO_2 is more soluble in [bmim][PF_6]. While the pressure is lower than 9 MPa, the solubility of CO_2 is higher in [bmim][CF_3SO_3].

Liquid phase volume expansivity has two definitions [30]. One is based on the change of total volume of liquid phase:

$$\frac{\Delta V}{V} = \frac{V_L(T,P,x_1) - V_2(T,P_0)}{V_2(T,P_0)} \quad (1)$$

where V_L is the total volume of the liquid mixture under temperature T and pressure P. V_2 is the volume of liquid under the same temperature and 1 atm.

Another definition is based on the change of molar volume:

$$\frac{\Delta V_m}{V_m} = \frac{\tilde{V}_L(T,P,x_1) - \tilde{V}_2(T,P_0)}{\tilde{V}_2(T,P_0)} \quad (2)$$

$\tilde{V}_L$ and $\tilde{V}_2$ are molar volumes under different conditions.

Table 1
Thermal stability of ionic liquid [bmim][PF_6] and [bmim][CF_3SO_3].

System	Temperature	Pressure	Thermal stability (h)
[bmim][PF_6]–CO_2	80 °C	10 MPa	>72
[bmim][PF_6]–CO_2	90 °C	10 MPa	48
[bmim][PF_6]–C_3H_8	100 °C	5 MPa	30
[bmim][PF_6]	120 °C	0.1 MPa	8
[bmim][CF_3SO_3]	120 °C	0.1 MPa	>72
[bmim][CF_3SO_3]–CO_2	120 °C	10 MPa	>72
[bmim][CF_3SO_3]–C_3H_8	120 °C	5 MPa	>72

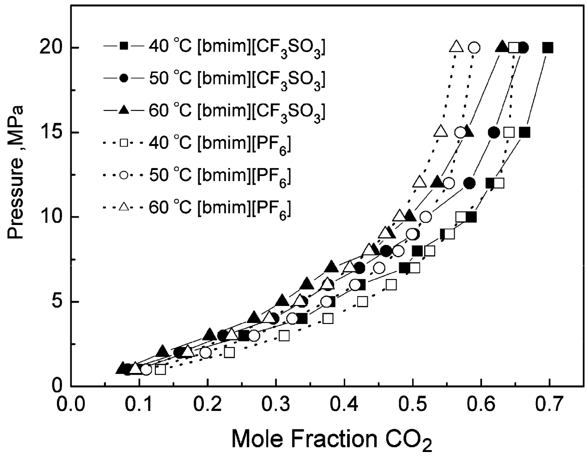
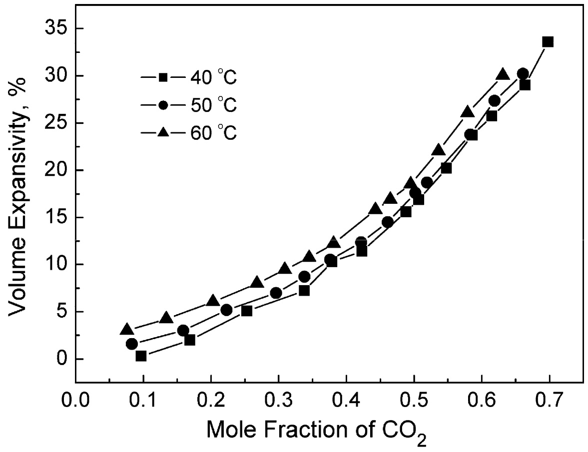
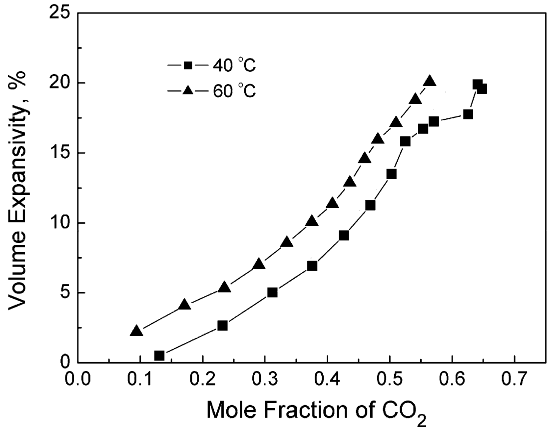


Fig. 1. Comparison of the solubility of CO_2 in [bmim][CF_3SO_3] with that of CO_2 in [bmim][PF_6] at 40–60 °C.

The liquid phase volume expansivity of CO_2–[bmim][CF_3SO_3] system is shown in Figs. 2 and 3, which are calculated by Eqs. (1) and (2), respectively. According to Figs. 2 and 3, the liquid phase expansivity of CO_2–[bmim][CF_3SO_3] system has a similar varying tendency to the expansivity of CO_2–[bmim][PF_6] system. Volume of IL-rich phase barely increases even when large amounts of CO_2 dissolve in the liquid phase, while the molar volume decreases linearly when CO_2 dissolved in IL.

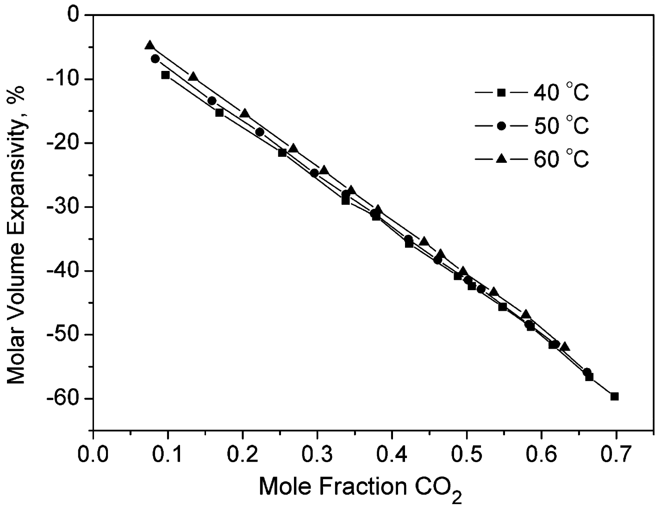


(a) CO_2–[bmim][CF_3SO_3]

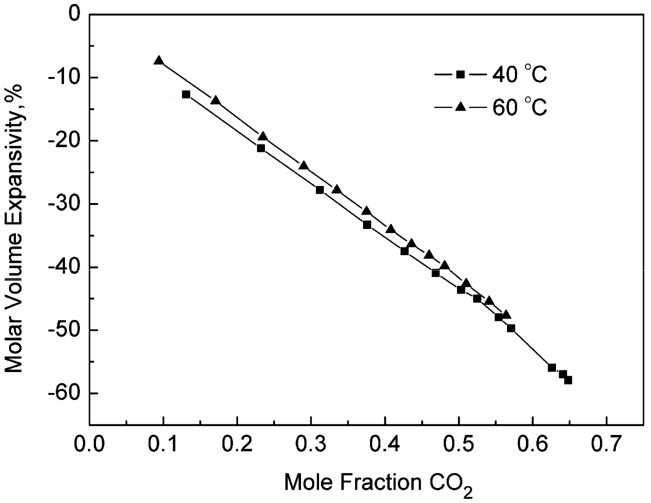


(b) CO_2-[bmim][PF_6]

Fig. 2. Liquid phase volume expansivity of the systems CO_2–[bmim][CF_3SO_3] and CO_2–[bmim][PF_6] at various temperatures.



(a) CO_2–[bmim][CF_3SO_3]



(b) CO_2-[bmim][PF_6]

Fig. 3. Liquid phase molar volume expansivity of the systems CO_2–[bmim][CF_3SO_3] and CO_2–[bmim][PF_6] at various temperatures.

3.3. The solubility and liquid phase volume expansivity of propane in [bmim][CF_3SO_3]

The solubility of propane in [bmim][CF_3SO_3] are measured under 100–120 °C, 1–9 MPa in similar reduced temperature and pressure with CO_2–[bmim][CF_3SO_3] system. The data for the two systems were compared in Fig. 4, which shows that the solubility of propane in [bmim][CF_3SO_3] is much lower than the solubility of CO_2 under the same conditions. For example, when the reduced pressure is 1.5, the solubility of propane in mole fraction is about 0.1, but that for carbon dioxide is higher to 0.6. The higher solubility of CO_2 in [bmim][CF_3SO_3] is mainly due to the lewis acid–base interaction between the carbon dioxide and the anion of the ionic liquid ([CF_3SO_3]$^-$) [35]. This kind of interaction does not exist in the propane–[bmim][CF_3SO_3] system. Higher solubility of CO_2 in IL may facilitate the interaction between CO_2 and organics in the SCF exaction process. This is an advantage of CO_2 in the SC extraction process compared to propane.

The liquid phase volume expansivity C_3H_8–[bmim][CF_3SO_3] system is calculate by Eqs. (1) and (2) and shown in Figs. 5 and 6,

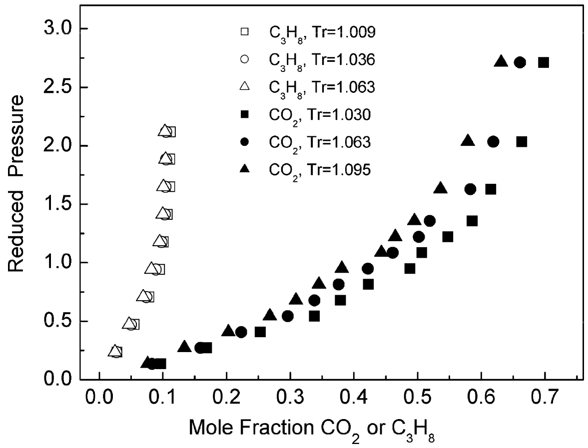


Fig. 4. Comparison of the solubility of CO_2 in [bmim][CF_3SO_3] with that of C_3H_8 in [bmim][CF_3SO_3] at the same reduced pressures and approximate reduced temperatures.

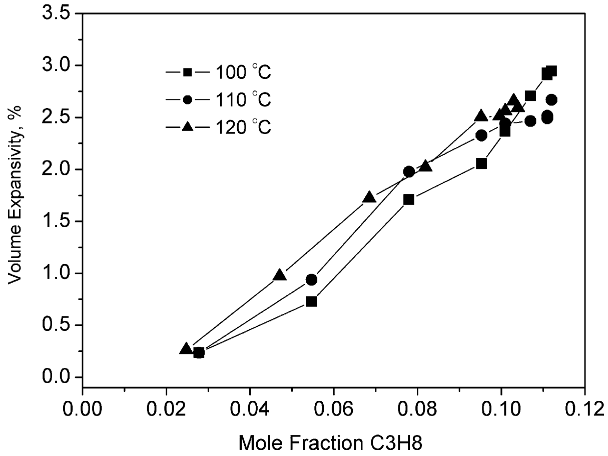


Fig. 5. Liquid phase volume expansivity of the system C_3H_8–[bmim][CF_3SO_3] at various temperatures.

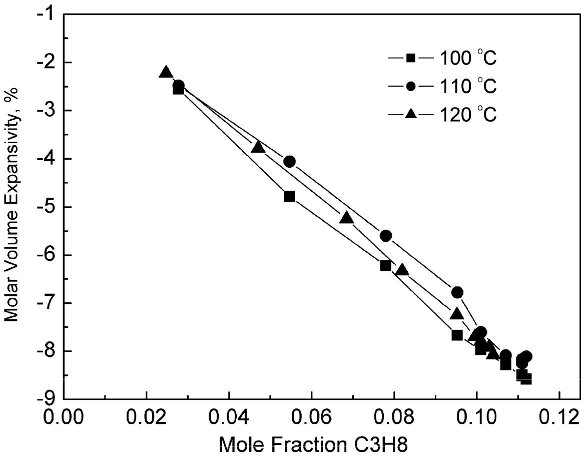


Fig. 6. Liquid phase molar volume expansivity of the system C_3H_8–[bmim][CF_3SO_3] at various temperatures.

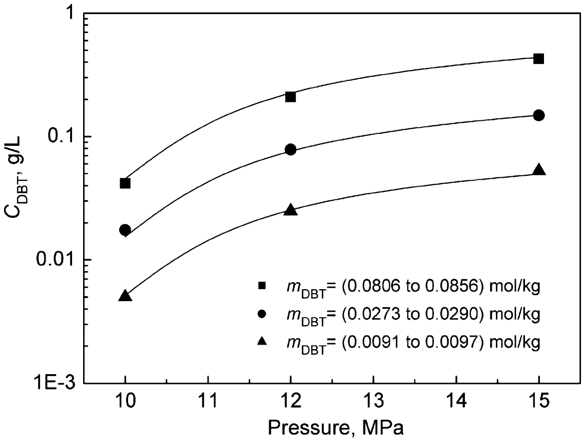


Fig. 7. Concentration of DBT in the CO_2-rich phase at indicated DBT molality in the liquid phase as a function of pressure at 323 K (the curves were calculated by Chrastil's association model).

respectively. Comparing to Figs. 2 and 3, the expansivity of C_3H_8–[bmim][CF_3SO_3] has a much mild change trend to the expansivity of CO_2–[bmim][CF_3SO_3] system due to C_3H_8 lower solubility in [bmim][CF_3SO_3].

4. Phase equilibria of SC–Organics–ILs

4.1. High-pressure state equilibrium of CO_2(propane)–[bmim][CF_3SO_3]–DBT ternary system

The conditions for ternary phase equilibria of CO_2–[bmim][CF_3SO_3]–DBT, C_3H_8–[bmim][CF_3SO_3]–DBT, CO_2–[bmim][CF_3SO_3]–naphthalene and C_3H_8–[bmim][CF_3SO_3]–naphthalene are listed in Table 2. The temperature for two CO_2 systems was kept at 323 K by adjusting the pressure and solute molality, while that for two C_3H_8 system is 393 K at the about the same reduced temperature.

The variation tendency of concentration of DBT in the CO_2-rich phase for CO_2–[bmim][CF_3SO_3]–DBT system is shown in Fig. 7. Under the constant temperature and pressure, the weight molalities of DBT in the CO_2-rich phase and in the [bmim][CF_3SO_3]-rich phase follow a double logarithmic correlation, as shown in Fig. 8. The variation tendency of concentration of DBT in the propane-rich phase is shown in Fig. 9. Under the constant temperature and pressure, the relation between molalities of DBT in the propane-rich phase and in the [bmim][CF_3SO_3]-rich phase is shown in Fig. 10.

The variation tendency of concentration of naphthalene in the CO_2-rich phase is shown in Fig. 11. Under the constant temperature and pressure, the relationship between the weight molalities of naphthalene in the CO_2-rich phase and in the [bmim][CF_3SO_3]-

Table 2
Phase Equilibria conditions for 4 ternary systems and correlation results of modified Chrastil model.

System	Range of conditions			Regressed parameter		AAD %
	T (K)	P (MPa)	Solute molarity (mol/kg)	k	$((a/T)+b)$	
CO_2–[bmim][CF_3SO_3]–DBT	323	10–15	0.0091–0.0856	3.9421	−24.138	5.0
C_3H_8–[bmim][CF_3SO_3]–DBT	393	4.61–8.64	0.0074–0.0288	2.3415	−10.343	6.0
CO_2–[bmim][CF_3SO_3]–naphthalene	323	8–15	0.044–0.210	2.9706	−16.967	7.9
C_3H_8–[bmim][CF_3SO_3]	393	4.61–8.64	0.031–0.094	1.8316	−7.0113	9.4

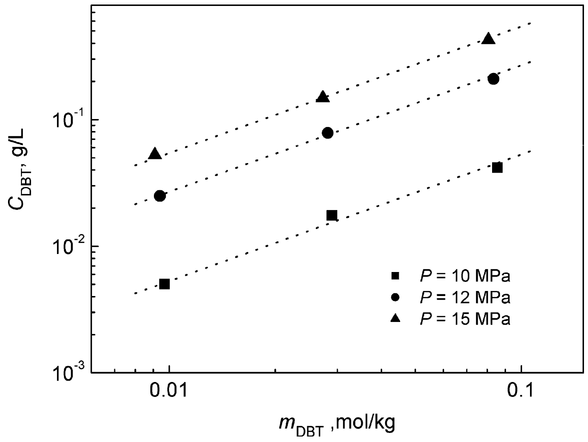


Fig. 8. Concentration of DBT in the CO_2-rich phase as a function of DBT molality in the liquid phase at 323 K and various pressures (the lines were calculated by Chrastil's association model).

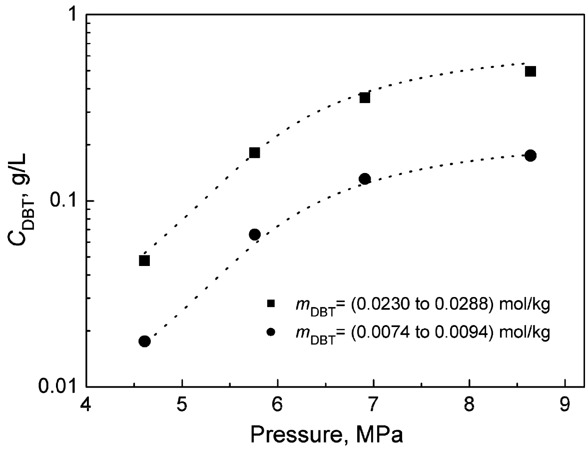


Fig. 9. Concentration of DBT in the C_3H_8-rich phase at indicated DBT molality m_{DBT} in the liquid phase as a function of pressure at 393 K (the lines were calculated by Chrastil's association model).

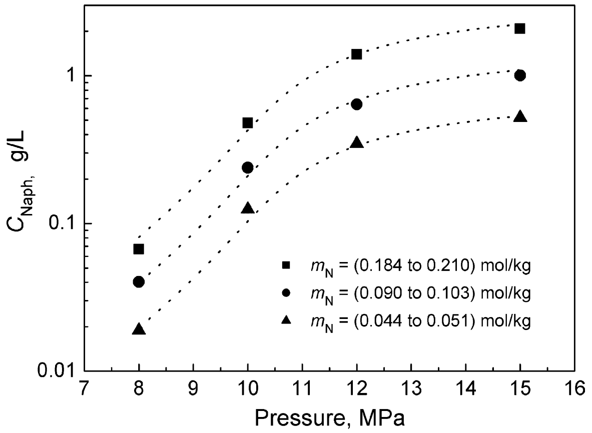


Fig. 11. Concentration of naphthalene in the CO_2-rich phase at indicated naphthalene molality in the liquid phase as a function of pressure at 323 K (the lines were calculated by Chrastil's association model).

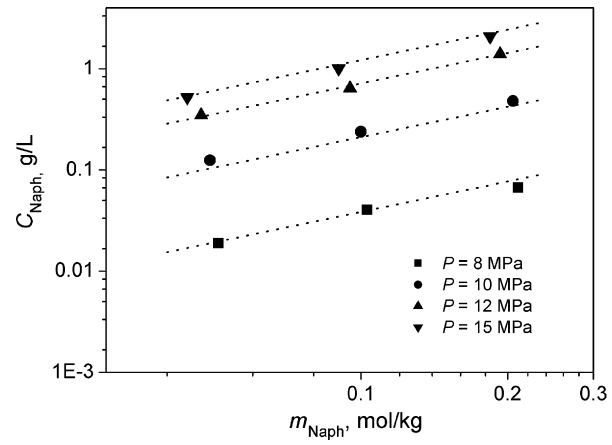


Fig. 12. Concentration of naphthalene c_N in the CO_2-rich phase as a function of naphthalene molality in the liquid phase at 323 K and various pressures (the lines were calculated by Chrastil's association model).

rich phase also follows a double logarithmic correlation, as shown in Fig. 12. The variation tendency of concentration of naphthalene in the propane-rich phase at 393K is shown in Fig. 13. Under the constant temperature and pressure, the relation between weight molalities of naphthalene in the propane-rich phase and in the [bmim][CF_3SO_3]-rich phase is shown in Fig. 14.

According to above data, systems of CO_2–[bmim][CF_3SO_3]–DBT, C_3H_8–[bmim][CF_3SO_3]–DBT, CO_2–[bmim][CF_3SO_3]–naphthalene and C_3H_8–[bmim][CF_3SO_3]–naphthalene have a similar variation

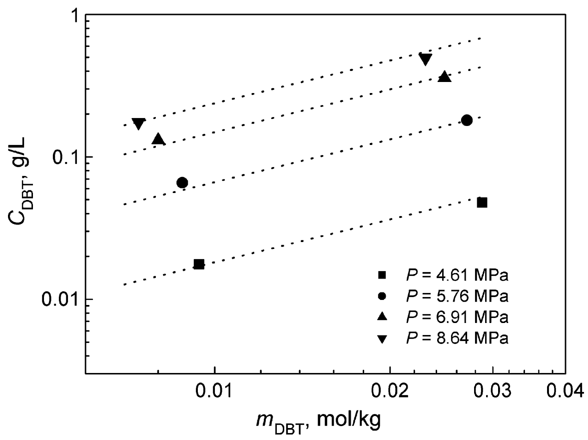


Fig. 10. Concentration of DBT in the C_3H_8-rich phase as a function of DBT molality in the liquid phase at 393 K and various pressures (the lines were calculated by Chrastil's association model).

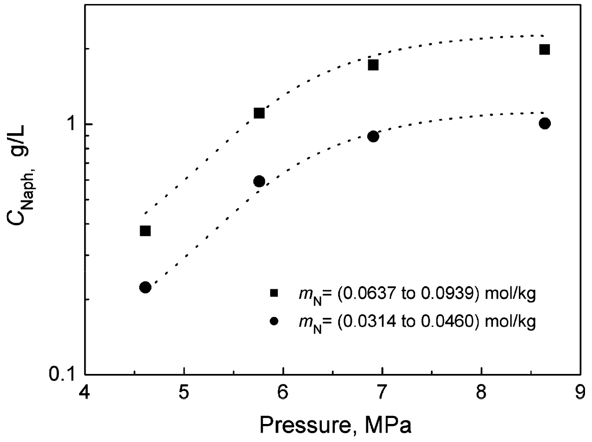


Fig. 13. Concentration of naphthalene in the C_3H_8-rich phase at indicated naphthalene molality in the liquid phase as a function of pressure at 393 K (the lines were calculated by Chrastil's association model).

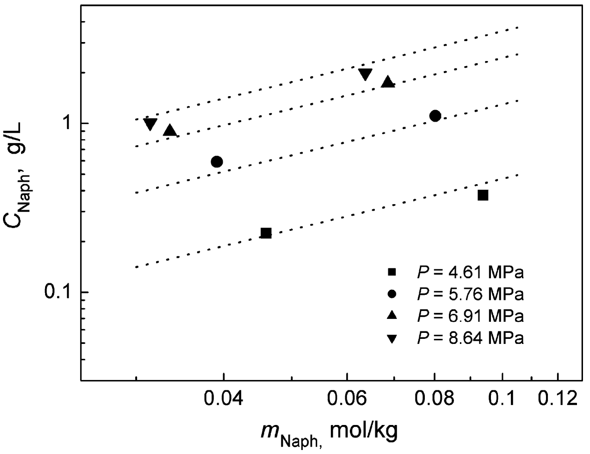


Fig. 14. Concentration of naphthalene in the C_3H_8-rich phase as a function of naphthalene molality in the liquid phase at 393 K and various pressures (the curves were calculated by Chrastil's association model).

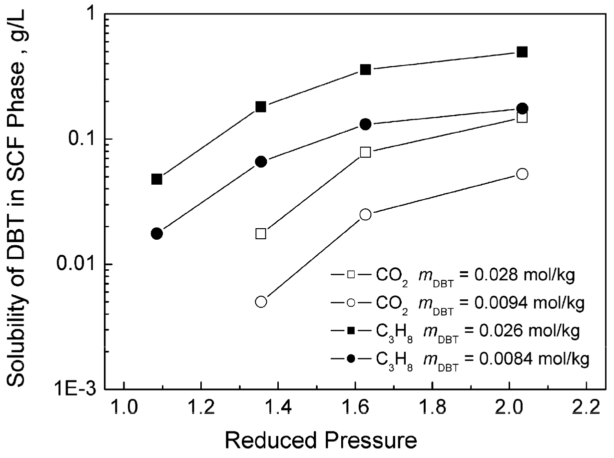


Fig. 15. Comparison of DBT dissolving from [bmim][CF_3SO_3] between SC C_3H_8 and SC CO_2 at reduced temperature T_r = 1.062 and various reduced pressures.

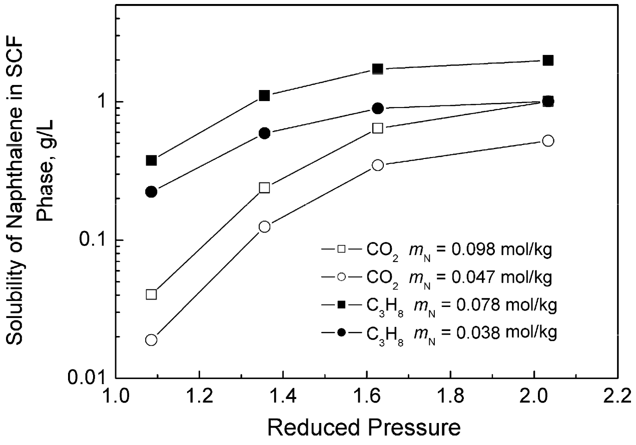


Fig. 16. Comparison of naphthalene dissolvability from [bmim][CF_3SO_3] between supercritical propane and SC CO_2 at reduced temperature T_r = 1.062 and various reduced pressures.

trend to CO_2–[bmim][PF_6]–naphthalene ternary system. Generally, the concentration of organics in SC phase increases with the increase of its concentration in the IL liquid phase, which follows double logarithmic correlations. As well, the distribution of organics increases when the pressure increases [30].

4.2. Modified Chrastil association model for ternary system

In our previous work, the Chrastil association model for ternary system of naphthalene–IL–CO_2 have been derived as following:

$$\frac{c_B}{m_B} = d^{k''} \exp\left(\frac{a''}{T + b''}\right) \tag{3}$$

where k'', a'', b'' are all constants for a given system, m_B is the solute molality in the IL liquid phase, c_B is the solubility of organics in SC phase in g/L, and d is the density of supercritical fluid in g/mL.

The densities of CO_2 were calculated with Huang's accurate EOS [36] for carbon dioxide. The parameters regressed for naphthalene-[bmimPF$_6$]-CO_2 are k'' = 2.7552, a'' = 1470.9, b'' = −10.752, respectively and show good agreement over wide conditions. For the naphthalene molality in the liquid phase ranging from 0.0169 to 0.378 mol/kg, and within temperature and pressure ranges of 313–333 K and 8–20 MPa, they give a mean relative deviation 14.9% [30].

The regressed parameters are also shown in Table 2. The calculated results are shown in Figs. 7–14 as lines. The error between experimental data and the calculated concentration of solute in SC phase for CO_2–[bmim][CF_3SO_3]–DBT, C_3H_8–[bmim][CF_3SO_3]–DBT, CO_2–[bmim][CF_3SO_3]–naphthalene and C_3H_8–[bmim][CF_3SO_3]–naphthalene are 5.0, 6.0, 7.9 and 9.4%, respectively. The parameters regressed are considered reasonable for the wide range of conditions. The association solvent numbers k is smaller for C_3H_8 than CO_2 for the same solute and IL, which represent solvent molecule number to solve a solute. The parameter $(a/T) + b$ represents the total association energy. C_3H_8 system shows a lower number under higher temperature, which means high temperature favoring disassociation.

4.3. Comparison of dissolvability of SC CO_2 and SC propane to the organics in ionic liquid

Comparison of dissolvability of SC CO_2 and SC propane to the DBT or naphthalene in [bmim][CF_3SO_3] is shown in Figs. 15 and 16. According to Fig. 15, the solubility of DBT in SC C_3H_8 is 3.3–13.1 times higher than that in SC CO_2, under the same reduced temperature and pressure and DBT concentration in liquid phase. As in Fig. 16, the solubility of naphthalene in SC propane is 1.9–11.8 times higher than that SC CO_2, under the same reduced temperature and pressure and naphthalene in liquid phase concentration.

Because propane has a much lower critical pressure (4.248 MPa) than carbon dioxide does (7.375 MPa), the practical operation pressure of propane can be much lower than carbon dioxide. So even under a mild condition (such as 8.6 MPa), SC C_3H_8 has an obviously higher dissolvability than SC CO_2 does under a very high pressure (15 MPa).

5. Analysis of extraction process

To understand the extraction applicability, the extraction of organics is simulated in batch and continuous way using SC CO_2 and propane as solvent, respectively.

5.1. Batch extraction

The process of batch extraction: IL is pumped into extractor in batch and solvent is pumped into extractor continuously from the bottom. The extracted organics are separated from the solvent and collected by the separator on the top of extractor. After the extraction, ionic liquid are separated from solvent and collected by the separator.

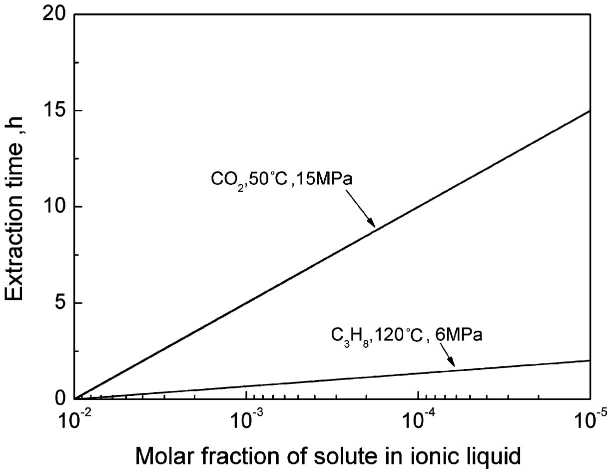


Fig. 17. Extraction time as a function of outlet solute molar fraction in IL.

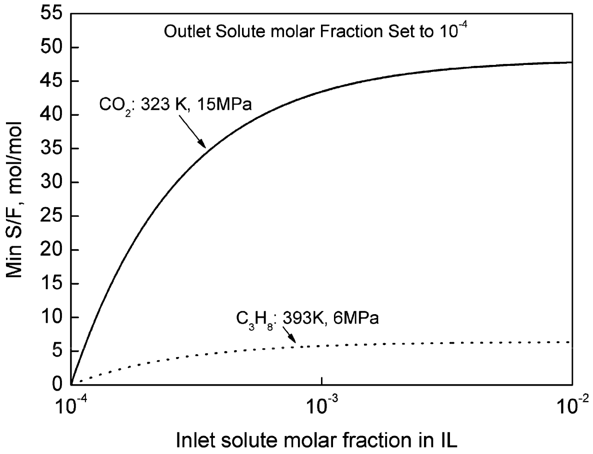


Fig. 18. Minimum Solvent to IL flow rate molar ratio as a function of organics concentration in IL feed.

Because ILs show very low solubility in SC liquid [4,5]and the equilibrium is easy to achieve in the process of SCF extraction, extraction process can be simulated by equilibrium mode. The operation equation can be deduced by material balance easily:

$$y\rho_{\mathrm{SCF}}Q_{\mathrm{SCF}}dt = -n_{\mathrm{IL}}^{0}d\left(\frac{x}{1-x}\right) \qquad (4)$$

y, solubility of organics in SCF (molarity); x, solubility of organics in IL (molarity); ρ_{SCF}, molarity concentration of SCF (mol L^{-1}); Q_{SCF}, volume flow of SCF (L h^{-1}); n_{IL}, moles of IL in extractor; where equilibrium equation is:

$$\ln y = a + b\ln x \qquad (5)$$

Considering SCF as diluted solution, the extraction solubility of naphthalene–SCF system by Eq. (4) was analyzed and the following correlations for extraction time were acquired.

$$t = \frac{n_{\mathrm{IL}}^{0}}{a(1-b)\rho_{\mathrm{SCF}}Q_{\mathrm{SCF}}}(x_0^{1-b} - x_{\mathrm{end}}^{1-b})(b \neq 1) \qquad (6)$$

$$t = \frac{n_{\mathrm{IL}}^{0}}{a\rho_{\mathrm{SCF}}Q_{\mathrm{SCF}}}(\ln x_0 - \ln x_{\mathrm{end}})(b = 1) \qquad (7)$$

So the extraction of high boiling-point organics from IL is suitable to perform under lower temperature and appropriated pressure. The higher concentration of high boiling-point organics in IL, the higher the extraction solubility, the shorter the time is needed. Suppose the volume of extractor is 200 L, which is fed in 100 L [bmim][CF$_3$SO$_3$] with naphthalene mole fraction 0.01 and the extraction conditions for SC CO$_2$ are 322 K, 15 MPa. The circulation volume of liquid CO$_2$ (283 K) Q is set to 500 L h^{-1}, mass flow rate is 500 × 0.862 or 431 kg h^{-1}, molar flow rate is 9795 mol h^{-1}. The density of [bmim][PF$_6$] is: $\rho = a_0 + b_0 \times (T - 60)$, where $a_0 = 1.2799$, $b_0 = -8.00\mathrm{E}{-4}$, T is the temperature in °C. The moles of IL $n = (1278 \times 100)/288 = 443.8$ mol. The calculated extraction time in hour under different outlet concentrations is shown in Fig. 17. The lower concentration of organics in end extracted IL, the longer the extraction time is necessary. If the outlet concentration of organics needs to be very low, the extraction time would be doubled. When the concentration of naphthalene in outlet IL is 10^{-3}, 10^{-4} and 10^{-5}, respectively, the corresponding extraction time is 5, 10 and 15 h, and the corresponding circulation solvent to IL molar ratio S/F (mol/mol) are 110, 220 and 330, which are quite high numbers. In contrast, C$_3$H$_8$ needs shorter time and lower pressure than CO$_2$ to achieve the same end naphthalene concentration. When the extraction temperature is 393 K, the pressure is only 6 MPa. The IL feed quantity and the mole flow rate of C$_3$H$_8$ are taken the same number. The lower of end naphthalene concentration in IL is, the larger of the time gap is between two solvents. Only 2 h are needed for naphthalene in [bmim][CF$_3$SO$_3$] molar fraction to reach 10^{-5}. Circulation solvent ratio has a prominent effect on the energy consuming in extraction process. The smaller the ratio, the less energy consuming and high efficiency are. So C$_3$H$_8$ is a good alternative if ILs are stable enough around 100 °C to perform extraction to reduce the investment of facilities and increase efficiency. But Its higher critical temperature may be not suitable to some ILs with poor thermal stabilities. Regarding its safety issues, petrochemical industry can solve flammable and explosive problems.

5.2. Continuous countercurrent extraction

The difference between the continuous countercurrent extraction and batch extraction is that the IL and SCFs are continuous flows or not. So the collecting of extract and discharging of IL process can be performed continuously.

The operation equation of continuous countercurrent extraction under given pressure and temperature is:

$$y = \frac{\rho_{\mathrm{IL}}Q_{\mathrm{IL}}}{\rho_{\mathrm{SCF}}Q_{\mathrm{SCF}}}\left(\frac{x}{1-x} - \frac{x_{\mathrm{out}}}{1\text{-}x_{\mathrm{out}}}\right) \qquad (8)$$

where equilibrium equation is same as Eq. (5). Corresponding to a concentration of organic in outlet liquid phase is x, the correlation between the minimum solvent to IL flow rate molar ratio and

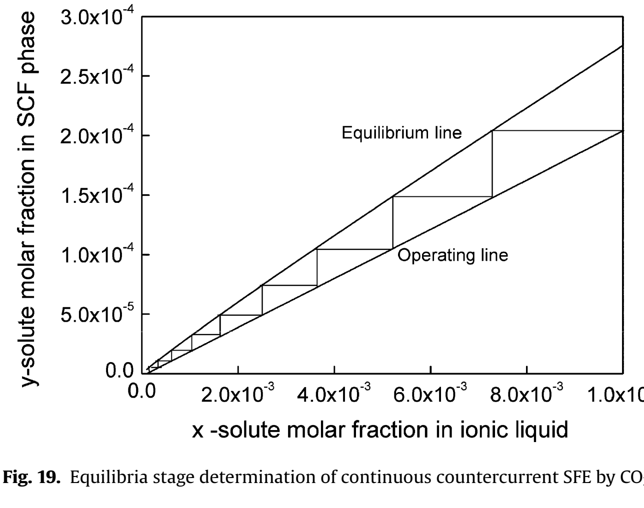


Fig. 19. Equilibria stage determination of continuous countercurrent SFE by CO$_2$.

the inlet concentration of organic in IL are shown in Fig. 18. The minimum solvent ratio goes up rapidly with rise of inlet organic concentration. Taking naphthalene/[bmim] [CF_3SO_3] as example also, when its molar fraction in outlet IL is required as 10^{-4}, SC CO_2 is used as extraction solvent under 323 K and 15 MPa, the minimum molar solvent to feed ratio S/F is calculated 47.8. If the operation was carried in S/F 1.3 times to the minimum number, then nine theoretical plates is necessary in the extraction column as shown in Fig. 19. While it is not a big number, from engineering point, it is very difficult or impossible to operate at very high solvent to feed ratio. If C_3H_8 is applied, a reasonable minimum S/F 6.34 is required only and continuous extraction becomes possible.

6. Conclusions

Pressure does not show obvious influence on long-term stability of two ILs [bmim][PF_6] and [bmim][CF_3SO_3] in SC CO_2 and C_3H_8. The long-term stability is mainly determined by temperature, which for [bmim][PF_6] is below 120 °C. While [bmim][CF_3SO_3] can be stable at 120 °C over 72 h.

C_3H_8 gives a much lower dissolving molarity in [bmim][CF_3SO_3] than CO_2 under the same reduced pressure and the same reduced temperature.

Modified Chrastil association model was extended to ternary system and deduced the equation $c_A/m_A = d^k \exp((a/T)+b))$ and give a good correlation for the error between the calculated concentration of solute in SC phase. The deviations for CO_2–[bmim] [CF_3SO_3]–DBT, C_3H_8–[bmim][CF_3SO_3]–DBT, CO_2–[bmim] [CF_3SO_3]–naphthalene and C_3H_8–[bmim][CF_3SO_3]–naphthalene are 5.0, 6.0, 7.9 and 9.4%, respectively.

Batch SCF extraction may be applied to separate high boiling points organics from ILs with reasonable operating conditions. Because long time and recycle solvent to feed ratio is necessary for using SC CO_2. SC C_3H_8 could be a good alternative to CO_2 since it shows a very higher solving power for DBT or naphthalene and needs much shorter extraction time. Continuous extraction generally needs very high CO_2 to feed IL ratio, thus may be not practical. However, continuous extraction of those organics form IL by C_3H_8 is possible.

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