Separation of Ionic Liquids from Organic and Aqueous Solutions using Supercritical Fluids: Dependence of Recovery on the Pressure

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Room temperature ionic liquids (ILs) have received immense interest in both pure and applied chemistry due to their large liquidus range and negligible vapor pressure. We used gaseous and supercritical carbon dioxide to separate ILs from organic and aqueous solutions. The pressure at which the separation occurs was found to be dependent on the initial concentration of the IL, solvent, temperature and the gas used. ILs can be separated from organic solutions using either high-pressure carbon dioxide or ethane, whereas high-pressure nitrogen cannot induce the phase separation. Carbon dioxide was able to induce the separation of ILs from water at ambient temperatures. It was also found that neither high-pressure nitrogen nor ethane was able to induce the separation of ILs from water.

INTRODUCTION

Room temperature ionic liquids (ILs) are organic salts existing in a liquid state at ambient conditions. ILs have received tremendous recent interest due to their large liquidus range and negligible vapor pressure[1-4]. Designer ILs can be synthesized from a large number of possible cations and anions for a given application. However, the separation and recovery of ILs from process streams is a major challenge for the development of industrial processes that will use these interesting new solvents. Due to their non-volatile nature, ILs can be separated from the other components in the mixture by distillation of the minor components. However, in the presence of high-boiling or thermally labile compounds or when the IL is the minor component in the mixture, distillation may not be an economical option. Liquid-liquid extraction is a viable option, but if one aims to eliminate the use of volatile organic solvents, then the choice of extraction solvent is seriously limited. Previously, our group has shown that supercritical carbon dioxide can be used to extract both volatile and relatively non-volatile compounds from ILs without any extraction of the ILs themselves[5,6]. We found that several ILs dissolve significant amounts of CO_2[5,7]. Upon commercialization of processes using ILs, the ILs will inevitably come in contact with both organic and aqueous process streams, indicating the necessity for the development of a variety of environmentally benign separation processes for the recovery of ILs.
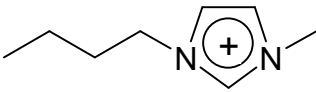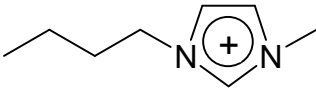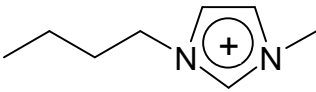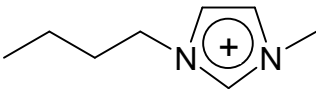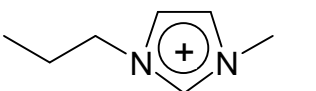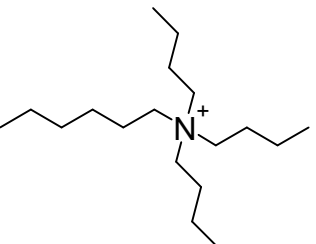
Recently, we have shown that relatively low pressure gaseous carbon dioxide can cause a phase separation in methanol and aqueous solutions containing ILs[8,9]. For example, we have demonstrated that solutions of methanol and the IL, 1-butyl-3-methyl-imidazolium hexafluorophosphate, can form three phases in the presence of CO_2 and the lower critical end point was dependent on the initial concentration of IL[8]. IL/water/CO_2 systems also exhibited similar behavior[9]. In this report, we present the effect of organic solvent and the type of IL used on the pressure at which the phase separation occurs. We will present our

findings of the effect of temperature on the lower critical end point for 1-butyl-3-methyl-imidazolium tetrafluoroborate/water/CO_2 systems.

MATERIALS AND METHODS

The various ILs used in the current study along with the abbreviation used in this report are shown in Table 1.

Table 1: Structures of the ILs and the nomenclature used in the current study.

Ionic Liquid	Cation	Anion	Abbreviation
1-butyl-3-methyl-imidazolium hexafluorophosphate		PF_6^-	[C$_4$mim][PF$_6$]
1-butyl-3-methyl-imidazolium tetrafluoroborate		BF_4^-	[C$_4$mim][BF$_4$]
1-butyl-3-methyl-imidazolium trifluoromethanesulfonate		$CF_3SO_3^-$	[C$_4$mim][CF$_3$SO$_3$]
1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl imide)		$N(CF_3SO_2)_2^-$	[C$_4$mim][NTf$_2$]
1-propyl-2,3-dimethyl-imidazolium bis(trifluoromethylsulfonyl imide)		$N(CF_3SO_2)_2^-$	[PDmim][NTf$_2$]
Hexyl tributyl ammonium bis(trifluoromethylsulfonyl imide)		$N(CF_3SO_2)_2^-$	[C$_6$(C$_4$)$_3$N][NTf$_2$]

[C$_4$mim][BF$_4$] and [C$_4$mim][CF$_3$SO$_3$] were synthesized as per the literature procedures[10,11], [C$_4$mim][PF$_6$] was purchased from Sachem Inc., TX, U.S.A., [C$_4$mim][NTf$_2$] and [PDMim][NTf$_2$] were obtained from Covalent Associates, MA, U.S.A., and [C$_6$(C$_4$)$_3$N][NTf$_2$] was provided by Dr. P. Neta at NIST, U.S.A. Coleman Instrument grade carbon dioxide and nitrogen (99.999%) purchased from Mittler Supply, Inc., IN, U.S.A., and ethane (99.99%) from Matheson Gas Products were used. Methanol (99.8%), acetophenone (99%) and acetonitrile (99.8%) purchased from Sigma-Aldrich Co., U.S.A., were used as received. Deionized water was used to make aqueous solutions. ILs were dried at 70 °C under vacuum for 48 hours and were stored in a dessicator prior to use.
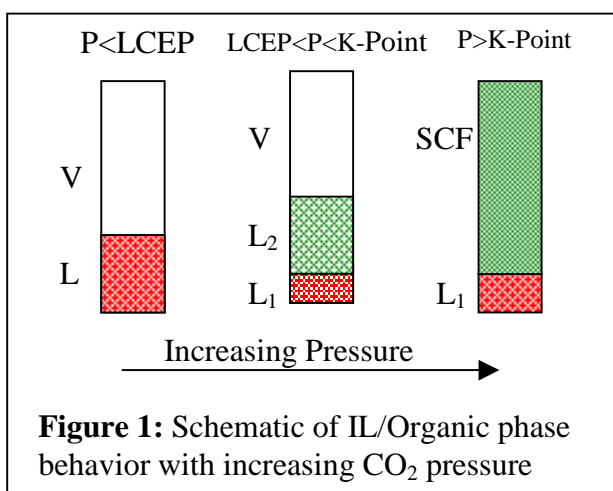
The experimental measurements were made with a stirred, thermostatted, high-pressure, view-cell, where known amounts of CO_2 can be accurately metered into the cell. A detailed description of the apparatus and procedure can be found elsewhere[12].

RESULTS

In this report, the IL/organic/CO_2 and IL/water/CO_2 phase behavior is presented. The phase behavior of $[C_4mim][PF_6]$/methanol/N_2 and $[C_4mim][PF_6]$/methanol/ethane is also presented. We demonstrate the ability of carbon dioxide to separate ILs from various solvents including, methanol, acetonitrile, acetophenone and water.

IL/Organic/CO_2 System

Previously, we have shown that $[C_4mim][PF_6]$ can be separated from methanol using high pressure CO_2 up to a concentration of 9 mole% IL in methanol[8]. Here we demonstrate that ILs can be separated from acetonitrile and acetophenone using CO_2. Specifically, when CO_2 pressure is applied up on a solution of IL/organic, a second liquid phase appears, as shown schematically in Figure 1. The most dense phase is rich in IL (L_1), the next phase is rich in organic (L_2), and the top vapor phase (V) is rich in CO_2 with some organic. The lower critical end point (LCEP) at a given temperature is defined as the pressure at which the second liquid layer first appears. At this phase transition point, the liquid phase turns cloudy and therefore the LCEP can be determined by visual observation. Upon further increase in the CO_2 pressure, the organic rich phase, L_2, expands significantly. Comparatively, the IL-rich phase, L_1, did not expand to the same extent as L_2; this behavior is similar to the binary phase behavior of the individual liquids with CO_2. A further increase in CO_2 pressure induces another critical point, K-point, which is defined as the point at which one of the liquid phases (in this case, the organic rich phase, L_2) merges with the vapor (fluid) phase ($L_1 - L_2 = V$). At the K-point, the supercritical CO_2/organic phase contains no detectable IL. The K-point is absent if the separation is performed below the critical temperature of CO_2.

The effect of initial concentration of IL in various organic solvents on the LCEP pressure and the K-point at 40 °C is shown in Table 2. The concentrations, expressed as mole fraction of each species in phase L, are those found at the phase transition. As shown in the Table 2, we chose three solvents representing three distinct classes: methanol, a protic solvent, acetonitrile, an aprotic solvent with a high dielectric constant and acetophenone, a hydrogen bond accepting solvent with a very high boiling point (b.p. 202 °C). As the results indicate, ILs can be separated from these solvents at relatively mild temperatures and pressures. The separation of ILs from these three distinct solvents upon addition of CO_2 indicates the versatility of this novel separation technique. For example, this technique can even be used to recover ILs from a very high boiling solvent such as acetophenone.

Figure 1: Schematic of IL/Organic phase behavior with increasing CO_2 pressure

Table 2: Lower Critical Endpoints and K-points for the systems studied at 40 °C.

Organic solvent	IL	Initial IL concentration, mole %	Lower Critical Endpoint ($L_1 = L_2$-V)				K-point, MPa
			P, MPa	x_{CO2}	x_{IL}	$x_{organic}$	
Methanol		0					8.21
Methanol	[C$_4$mim][PF$_6$]	0.1	7.97	0.7795	0.0002	0.2203	8.22
Methanol	[C$_4$mim][PF$_6$]	1.01	7.38	0.5486	0.0046	0.4468	8.2
Methanol	[C$_4$mim][PF$_6$]	4.9	6.95	0.4771	0.0258	0.4972	8.18
Methanol	[C$_4$mim][PF$_6$]	9.03	6.91	0.4989	0.0452	0.4558	8.22
Methanol	[C$_4$mim][PF$_6$]	34.4	6.97	0.5939	0.1397	0.2664	8.22
Acetophenone		0					8.51
Acetophenone	[C$_4$mim][PF$_6$]	0.107	8.23	0.9257	7.95E-5	0.0742	8.5
Acetophenone	[C$_4$mim][PF$_6$]	0.988	8.05	0.8689	0.0013	0.1298	8.5
Acetophenone	[C$_4$mim][PF$_6$]	11.01	7.94	0.7036	0.0326	0.2638	8.45
Acetonitrile		0					8.21
Acetonitrile	[C$_4$mim][PF$_6$]	0.103	7.71	0.9173	8.53E-5	0.0826	8.21
Acetonitrile	[C$_4$mim][PF$_6$]	0.993	7.19	0.8181	0.0018	0.1801	8.21
Acetonitrile	[C$_4$mim][PF$_6$]	9.88	7.01	0.6428	0.0353	0.3219	8.21
Acetonitrile	[C$_4$mim][PF$_6$]	28.87	7.74	0.7545	0.0709	0.1746	8.21
Acetonitrile	[C$_4$mim][NTf$_2$]	0.996	7.47	0.8679	0.0013	0.1308	8.21
Acetonitrile	[C$_6$(C$_4$)$_3$N][NTf$_2$]	0.999	7.55	0.8751	0.0012	0.1237	8.21

The effect of initial concentration of [C$_4$mim][PF$_6$] in each of the three solvents on the pressure at the LCEP is shown in Figure 2. An increase in the initial concentration of IL from 0.1 mole % to 10 mole % decreased the pressure at the LCEP. For example, the pressure at the LCEP for the system with an initial concentration of 0.1 mole % [C$_4$mim][PF$_6$] in acetonitrile is 7.71 MPa while at 10 mole % it is 7.01 MPa. A further increase in the initial IL concentration was found to increase the pressure of the LCEP. A dramatic increase in the pressure at the LCEP from 7.01 MPa to 7.74 MPa was observed as the initial concentration of [C$_4$mim][PF$_6$] in acetonitrile was increased from 9.88 mole % to 28.87 mole %.

In all cases, the pressure at the K-point was found to be independent of the initial IL concentration and it was

Figure 2: Effect of [C$_4$mim][PF$_6$] concentration on the pressure at the LCEP in various solvents at 40 °C
▲ Acetophenone ■ Acetonitrile ● Methanol

found to be same as the mixture critical point for the binary system, organic/CO$_2$, indicating that most of the IL has been removed from the organic rich phase at this point. This behavior was found to be the case with all three organic solvents studied.
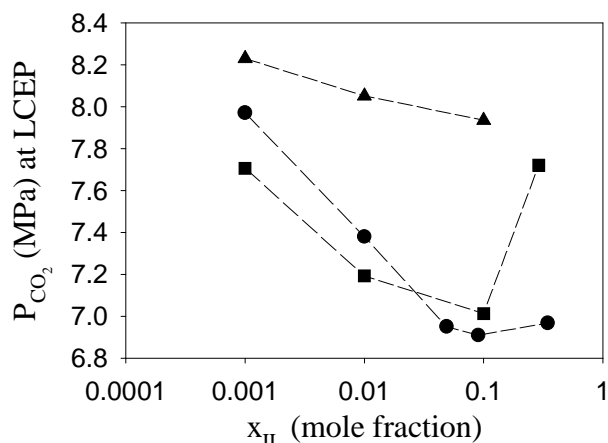
The pressure at the LCEP was found to be dependent on the type of IL used. By changing the anion from [PF$_6$] to [NTf$_2$] with the cation being [C$_4$mim] increased the pressure at the LCEP from 7.2 MPa to 7.47 MPa. The cation had a marginal effect on the pressure at the LCEP as seen by changing the cation from [C$_4$mim] to [C$_6$(C$_4$)$_3$N] with the anion being [NTf$_2$]. The initial concentration of IL was fixed at 1 mole % in acetonitrile and the IL used had no effect on the K-point.

Finally, the ability of different gases to induce phase separation was investigated. High-pressure ethane was able to separate [C$_4$mim][PF$_6$] from methanol 40 °C and at an initial concentration of 10 mole % and the pressure at the LCEP was 4.97 MPa. Application of high-pressure nitrogen to pressures up to 8.35 MPa did not yield a phase separation. These results indicate that the observed behavior was not due simply to the pressure applied but rather due to some interactions between the solvent and the gases used. One possible explanation for the observed behavior is the reduction of the solvent strength upon dissolution of CO$_2$ to such an extent that the solvent is no longer able to dissolve the ionic species.

IL/Water/CO$_2$ System

Hydrophobic ([C$_4$mim][PF$_6$] and [PDmim][NTf$_2$]) and hydrophilic ([C$_4$mim][BF$_4$], [C$_4$mim][CF$_3$SO$_3$] and [C$_4$mim][Cl]) ILs can be separated from aqueous solutions by addition of gaseous or liquid CO$_2$. We found that the LCEP is dependent on the concentration of IL, temperature and the type of IL used. The temperature and the pressure at the LCEP for each of the IL/water mixtures studied is shown in Table 3 [9]. The results indicate that ILs can be separated from water using CO$_2$ close to ambient temperatures and the pressure required to achieve each of the

Table 3: Lower critical endpoints of IL/water systems with CO$_2$

Ionic Liquid	IL Concentration in Water [mole %]	T, °C	Pressure [MPa]	CO$_2$ Solubility in H$_2$O^a [mole %]
[C$_4$mim][PF$_6$]	0.1	20	4.93	2.4
[PDmim][NTf$_2$]	0.047	25	3.15	1.6
[C$_4$mim][BF$_4$]	24.6	25	-	
	9.3	25	5.11	2.1
	1.58	20	5.53	2.53
	0.2	25	-	
	0.1	25	-	
[C$_4$mim][CF$_3$SO$_3$]	9.36	15.8	4.94	2.6
[C$_4$mim][Cl]	9.29	25	-	

^{a} Interpolated CO$_2$ solubility in pure H$_2$O at the conditions of the LCEP of the ternary mixture from the experimental data of Wiebe[13] and Houghton *et al.*[14]

separations is below 5.2 MPa. For example, at a CO$_2$ pressure of 4.93 MPa, one can separate [C$_4$mim][PF$_6$] from a IL saturated aqueous solution at 20 °C. It is more difficult to remove hydrophilic ILs from water. We were unable to separate hydrophilic ILs at very low concentrations from water using CO$_2$ at ambient temperatures. Specifically, the separation of [C$_4$mim][BF$_4$] from water at ambient temperatures is possible when the concentration of the IL is between 1.58 and 9.3 mole %, but no separation is observed for lower concentrations, even when the pressure is increased to 6.41 MPa, which is the vapor pressure of pure CO$_2$ at 25 °C; further increases in pressure result in the formation of a liquid CO$_2$ phase. From these results one can conclude that it is easier to separate hydrophobic ILs than hydrophilic ILs from water using CO$_2$. Interestingly, neither ethane (to its vapor pressure of 3.7 MPa) nor

nitrogen (to 8.2 MPa) was capable of separating the IL from a 0.1 mole % solution of [C$_4$mim][PF$_6$] in water at 20 °C.

The effect of temperature on the pressure at the LCEP for the system 10.3 mole % [C$_4$mim][BF$_4$] in water is shown in Figure 3. For this system, the LCEP was found to be very sensitive to temperature. A 5 °C increase in the temperature increased the pressure at the LCEP from 6.3 MPa to 29.38 MPa.

CONCLUSIONS

We have developed a green separation technique for the recovery of ILs from organic and aqueous solutions. Vapor or supercritical carbon dioxide can be used for this purpose. We have shown the applicability of this technique for a wide variety of ILs and types of organic solvents. Due to the cost and concerns about introduction of ILs into aquatic environment, these types of separations may be very important.

Figure 3: Effect of temperature on the pressure at the LCEP for the system 10.3 mole % [C4mim][BF$_4$]/Water/CO$_2$

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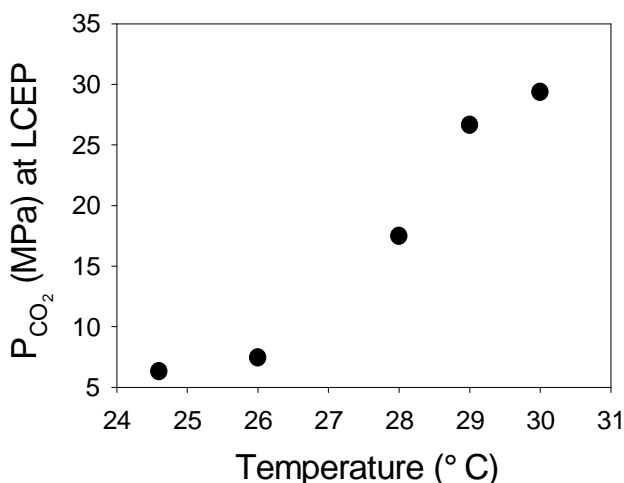[14]   HOUGHTON, G.; MCLEAN, A. M.; RITCHIE, P. D. *Chem. Eng. Sci.*, *7*, **1957**, 40-50.