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CO_2 as a Separation Switch for Ionic Liquid/Organic Mixtures

Aaron M. Scurto, Sudhir N. V. K. Aki, and Joan F. Brennecke*

Department of Chemical Engineering, University of Notre Dame, Notre Dame, Indiana 46556

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Room-temperature ionic liquids (ILs) have been the subject of intense focus due to their lack of volatility and their demonstrated usefulness as solvents for extractions and reactions.[1−4] However, a challenge that may impede successful commercialization is the development of methods to separate ILs from organic and inorganic species. Evaporation may not be possible for high-boiling or thermally labile compounds, and liquid−liquid extraction presents further downstream separation issues due to finite IL solubility in the aqueous or organic extract phase. Moreover, one may wish to avoid the use of conventional volatile organic solvents for liquid extraction entirely. Recently, Blanchard and Brennecke[5] and Blanchard et al.[6] have shown that another environmentally benign solvent, supercritical carbon dioxide, can be used to extract successfully even relatively nonvolatile compounds from ILs without any extraction of the ILs themselves. Blanchard et al.[6,7] have also shown that many ILs dissolve a considerable amount of CO_2. Subsequently, a number of researchers have adopted the use of CO_2/IL biphasic reaction/separation systems.[8−11]

Here we present a new way that CO_2 can be used to separate ILs from organic compounds, which is a complement to supercritical extraction.[5,6] We demonstrate that solutions of methanol and the IL, 3-butyl-1-methyl-imidazolium hexafluorophosphate ([C_4mim][PF_6]), can be induced to form three phases in the presence of CO_2. The lower liquid phase is rich in IL. In addition, we show that with increased pressure the upper liquid layer, which is rich in methanol, can be induced to merge with the CO_2-rich gas phase. The phase that is formed is completely free of the ionic liquid; that is, all the IL has been forced out of the methanol into the IL-rich phase at the bottom of the container. This interesting phase behavior has mechanistic and practical implications for both reaction and separation systems using ILs.

Methanol and [C_4mim][PF_6] are completely miscible in all proportions at ambient conditions. However, if a pressure of CO_2 is placed upon a mixture of the IL and methanol, a second liquid phase appears, as shown schematically in Figure 1. The most-dense liquid is rich in IL (labeled L_1), the next phase is rich in methanol (L_2), and the third vapor phase (V) is mostly CO_2 with some methanol. At a given temperature and initial loading of methanol and IL, the applied CO_2 pressure at which the second liquid phase appears is called the lower critical endpoint (LCEP). At pressures above the LCEP, the methanol-rich phase expands significantly with increased CO_2 pressure, while the IL-rich phase expands relatively little; this is similar to the binary phase behavior of the individual liquids with CO_2. Eventually the increased CO_2 pressure induces another critical point, that is, the K-point. The K-point is the point at which one of the liquid phases (the methanol-rich one in this case, L_2) merges with the vapor (fluid) phase ($L_1 - L_2 = V$). At the K-point the last traces of IL that had remained in the methanol-rich liquid phase are expelled, and the resulting supercritical CO_2/methanol phase (SCF) contains no detectable IL. This was determined by venting the entire supercritical fluid phase from the experiment with the 9 mol % IL sample at 40 °C into a collection solvent of HPLC-grade methanol. This sample was analyzed by UV−visible absorption spectroscopy, ascertaining that there was no IL present with a detection limit of 5×10^{-7} mole fraction. However, if the temperature is below the critical temperature of CO_2, then there is no critical phase transition (K-point).

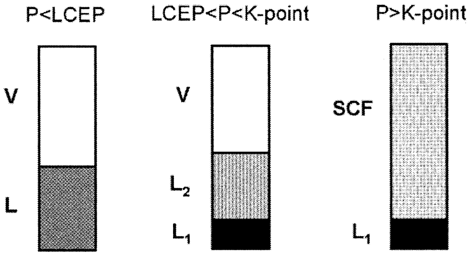

Figure 1. Schematic of [C_4mim][PF_6]/methanol phase behavior with increasing CO_2 pressure.

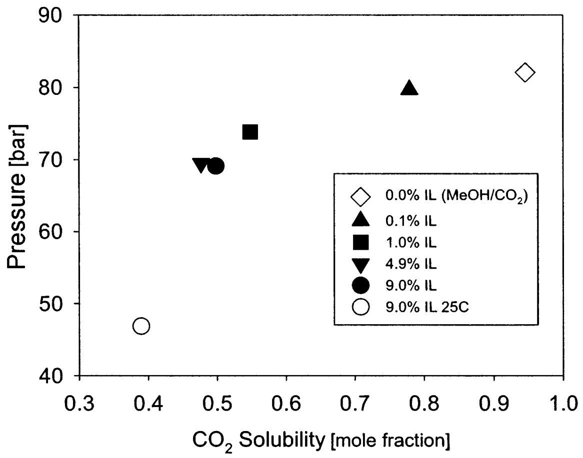

Figure 2. Lower critical endpoint of mixtures of [C_4mim][PF_6], methanol, and CO_2 at 25 and 40 °C illustrating changes in pressure, temperature, initial IL concentration, and solubility of CO_2.

Figure 2 shows the LCEP pressures at 40 and 25 °C for several different initial concentrations of IL in methanol, ranging from 0.1 to 9 mol %. At 40 °C, the LCEP occurs at increasingly higher pressures (which corresponds to increasing CO_2 solubility) with decreasing initial concentration of the IL; for example at an initial concentration of 1 mol % IL, *P* at the LCEP is 73.84 bar while at 9 mol %, *P* at the LCEP is 69.12 bar. Maintaining an initial concentration of 9 mol % IL, the pressure of the LCEP substantially decreases from approximately 69 to 47 bar by decreasing the temperature from 40 to 25 °C. Table 1 lists the experimental data for the lower critical endpoints and the K-points for the system studied. The concentrations, expressed as mole fraction of each

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* To whom correspondence should be addressed. E-mail: jfb@nd.edu.

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Table 1. Lower Critical Endpoints and K-points for $[C_4mim][PF_6]$, Methanol, and CO_2

initial loading IL mole %	T [°C]	lower critical endpoint ($L_1 = L_2 - V$) P [bar]	x_{CO2}	x_{IL}	x_{MeOH}	K-point P [bar]
0.1	40	79.69	0.7795	0.0002	0.2203	82.15
1.0	40	73.84	0.5486	0.0046	0.4468	82.01
4.9	40	69.49	0.4771	0.0258	0.4972	81.82
9.0	40	69.12	0.4989	0.0452	0.4558	82.16
9.0	25	46.89	0.3899	0.0551	0.5550	−
49.3	40	−	−	−	−	−

species in phase L, are those found at this phase transition. The measurements were made with a stirred, thermostated, high-pressure viewcell 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]

Previously, we have found that the solubility of IL in pure CO_2 is below detection limits, even at elevated pressures.[6] Despite the fact that there are strong interactions between CO_2 and ILs that result in high CO_2 solubility in the IL liquid phase,[13] nonpolar supercritical CO_2 is simply not capable of solvating ions. Conversely, methanol, which is polar and protic, possesses the ability to solvate ions. As CO_2 dissolves in the IL/methanol mixture, the solution expands substantially and the mixed solvent (methanol + CO_2) is no longer a good solvent for the organic salt. The pressure at which phase separation occurs depends on initial IL loading and temperature. Specifically, the pressure and solubility of CO_2 at the LCEP increases as the initial concentration of IL is decreased at a particular temperature. Obviously, the limiting behavior of the LCEP as the concentration of the IL tends to zero should be the mixture critical point of methanol and CO_2. This is confirmed by our measurement of the methanol/CO_2 critical point, which is shown in Figure 2.

Another major finding in this work is that the K-point pressure in the IL/methanol/CO_2 systems is identical to the methanol/CO_2 mixture critical point temperature and pressure, within experimental accuracy. This is entirely consistent with our measurements, described above, that show no IL in the supercritical CO_2/methanol phase.

The simple explanation for our observations is that the dissolution of CO_2 in a methanol/IL mixture reduces the solvent strength of the methanol to such an extent that it is no longer able to dissolve ionic species. This conclusion is supported by the dielectric constant measurements of Roskar et al.,[14] who have studied CO_2/methanol mixtures at 35 °C. They found that the dielectric constant depends primarily on the CO_2 mole fraction and is reduced from 37.5 for pure methanol to 4.9 at a CO_2 mole fraction of 0.733. The solutions tested here split into two liquid phases when the CO_2 mole fraction ranged from about 0.48 to 0.78. In the absence of IL, this would correspond to dielectric constants ranging from about 14 to 4. For comparison, the dielectric constants of ethyl acetate, diethyl ether, and hexane, three solvents that apparently dissolve very little $[C_4mim][PF_6]$ (because they are used commonly to extract products from IL reaction mixtures) are 6.0, 4.3, and 1.89, respectively.[15]

However, when the concentration of IL is high (e.g., 49.3 mol % initial loading of IL) we observe no LCEP and, thus, no K-point. Although these initial loadings do not contain very much methanol (50 mol % IL is about 90 wt % IL or 84 vol % IL), the vapor space was sufficiently small to eliminate the possibility that most of the methanol had been extracted into the CO_2-rich gas phase. Thus, when the IL content in the liquid is high, apparently it is not possible to induce a liquid/liquid-phase split by the addition of CO_2. Using spectroscopic probes, several researchers[16−20] have found the polarity of $[C_4mim][PF_6]$ to be similar to short-chain alcohols such as 2-propanol, which has a dielectric constant of 19.9. Baker et al.[21] and Aki and Brennecke[22] have found that the polarity index of $[C_4mim][PF_6]$ with added CO_2 only decreases about 10−15%, even when large amounts (up to 0.7 mole fraction) of CO_2 are present. This suggests that it may not be possible to reduce the dielectric constant of IL-rich mixtures enough to induce a phase split. Ultimately, a wide variety of molecular interactions, including specific chemical interactions, such as the Lewis acid−base interaction between the $[PF_6]$ anion and CO_2 observed by Kazarian et al.,[23] may be needed to fully understand the observed phase behavior.

The results presented here have two major implications. First, we have shown that it is possible to separate ILs from organics even when the IL is quite dilute. Application of CO_2 pressure induces the formation of an additional liquid phase that is rich in IL. The “cleaned” organic phase could simply be decanted off. Second, these results show that organic/IL/CO_2 mixture phase behavior can be quite complex. Thus, when performing reactions in IL/CO_2 biphasic systems with larger amounts of organic reactant and products, researchers should be particularly concerned about the possible formation of additional liquid phases that might contain only part of the components necessary for the desired reaction.

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