COMMUNICATION

ChemComm
www.rsc.org/chemcomm

# Carbon dioxide induced separation of ionic liquids and water

**Aaron M. Scurto, Sudhir N. V. K. Aki and Joan F. Brennecke***
*Department of Chemical Engineering, University of Notre Dame, Notre Dame, IN, USA.*
*E-mail: jfb@nd.edu; Fax: 01 574 631-8366; Tel: 01 574 631-5847*

***Received (in Corvallis, OR, USA) 18th November 2002, Accepted 17th January 2003***
***First published as an Advance Article on the web 29th January 2003***

DOI: 10.1039/b211376g

**Both hydrophobic and hydrophilic room-temperature ionic liquids can be separated from aqueous solutions with relatively low-pressure gaseous carbon dioxide.**

Room-temperature ionic liquids (ILs) are being aggressively investigated for use as replacement solvents for a variety of reactions and extractions.[1–4] One of their major advantages is their lack of volatility which would make them attractive for industrial implementation. However, successful commercialization may be frustrated by difficulties in separating ILs from organic and inorganic solutions. Since the ILs are non-volatile, evaporation or distillation of the other components in the mixture is an attractive option. However, this may not be practical for high-boiling or thermally labile compounds or when the IL is the minor component in the mixture. 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[5,6] that supercritical carbon dioxide, which is usually considered to be an environmentally benign solvent, can be used to extract even relatively non-volatile compounds from ILs without any extraction of the ILs themselves. We found that many ILs dissolve a considerable amount of $CO_2$.[5,7] Subsequently, a number of researchers have adopted the use of $CO_2$/IL biphasic reaction/separation systems.[8–14] Rogers and coworkers[15] have shown that a large number of compounds can be extracted from hydrophobic ILs (ones that are not completely miscible with water) with water. However, this may present further downstream separation issues due to finite IL solubility in the aqueous phase.

Recently, we have shown that relatively low-pressure gaseous $CO_2$ can be used to separate ILs from organic mixtures.[16] The dissolved $CO_2$ induces a phase separation, with the most likely mechanism being the expansion of the organic liquid phase by the $CO_2$, which decreases the dielectric constant, forcing a significant amount of the IL into a separate liquid phase. This type of separation would be most useful when the IL is the minor component of the mixture and is, thus, a complement to supercritical fluid extraction.[5,6]

Here we show that the introduction of gaseous or liquid $CO_2$ can also cause the separation of both ‘hydrophobic’ and hydrophilic ILs from *aqueous* solutions. We demonstrate that solutions of water and ILs can be induced to form three phases in the presence of $CO_2$. One liquid phase is rich in IL, one is rich in water and the vapor phase is mostly $CO_2$ with a small amount of dissolved water. This interesting phase behavior has mechanistic and practical implications for both reaction and separation systems using ILs with water.

In this communication, mixtures of water and the hydrophilic ILs, 1-butyl-3-methylimidazolium tetrafluoroborate ($[C_4mim][BF_4]$) and 1-butyl-3-methylimidazolium trifluoromethanesulfonate ($[C_4mim][CF_3SO_3]$), and the ‘hydrophobic’ ILs 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim][PF_6]$) and 1-propyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonylimide) ($[PDmim][NTf_2]$) are shown to phase split in the presence of gaseous $CO_2$.

Water and the hydrophilic ILs are completely miscible in all proportions at ambient conditions. Whereas, the ‘hydrophobic’ ILs (*e.g.* $[C_4mim][PF_6]$ and $[PDmim][NTf_2]$) have only a slight solubility in water (see Table 1). However, if a pressure of $CO_2$ is placed upon a mixture of the IL and water, a second liquid phase can appear, as shown schematically in Fig. 1. The most-dense liquid is rich in IL (labeled $L_1$), the next phase is rich in water ($L_2$) and the third vapor phase (V) is mostly $CO_2$ (with a small amount of dissolved water). At a given temperature and initial concentration of IL in water, the applied $CO_2$ pressure at which the second liquid phase appears, is called the lower critical endpoint (LCEP).

Table 2 illustrates the conditions at which the LCEP forms for each of the IL/water mixtures investigated. As expected the LCEP depends on the temperature and the concentration of IL. 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.[18]

In this study we were particularly interested in determining whether ILs could be separated from water using $CO_2$ at ambient temperatures. Therefore, experiments were conducted between 15 and 25 °C. 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 phase splits is below 5.2 MPa. For example, $[C_4mim][PF_6]$ can be separated from a IL saturated aqueous solution at 20 °C and at a $CO_2$ pressure of 4.93 MPa. Similarly, $[PDmim][NTf_2]$ can be

**Table 1** Solubility of ILs in water at ambient conditions

| Ionic liquid | Abbreviation | Solubility in water [mole %] |
|---|---|---|
| 1-Butyl-3-methylimidazolium hexafluorophosphate | $[C_4mim][PF_6]$ | 0.129[17] |
| 1-Propyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonylimide) | $[PDmim][NTf_2]$ | 0.047[a] |
| 1-Butyl-3-methylimidazolium tetrafluoroborate | $[C_4mim][BF_4]$ | miscible |
| 1-Butyl-3-methylimidazolium trifluoromethanesulfonate | $[C_4mim][CF_3SO_3]$ | miscible |

[a] Solubility was determined as per the procedure described by Anthony *et al.*[17]

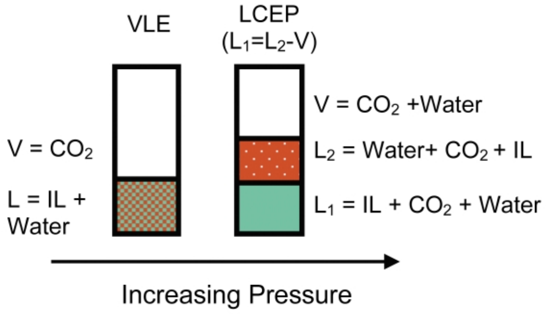

**Fig. 1** Phase behavior of IL/water/$CO_2$ mixture at increasing pressure at near-ambient temperatures.

**Table 2** 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 $H_2O$[a] [mole %] |
|---|---|---|---|---|
| $[C_4mim][PF_6]$ | 0.1 | 20 | 4.93 | 2.4 |
| $[PDmim][NTf_2]$ | 0.047 | 25 | 3.15 | 1.6 |
| $[C_4mim][BF_4]$ | 24.6 | 25 | — | |
| | 9.3 | 25 | 5.11 | 2.1 |
| | 1.58 | 20 | 5.53 | 2.53 |
| | 0.2 | 25 | — | |
| | 0.1 | 25 | — | |
| $[C_4mim][CF_3SO_2]$ | 9.36 | 15.8 | 4.94 | 2.6 |
| $[C_4mim][Cl]$ | 9.29 | 25 | — | |

[a] Interpolated $CO_2$ solubility in pure $H_2O$ at the conditions of the LCEP of the ternary mixture from the experimental data of Wiebe[22] and Houghton *et al.*[23]

recovered from water saturated with this IL at even lower pressure of $CO_2$, just 3.15 MPa. On the other hand, it is more difficult to remove hydrophilic ILs from water. For example, hydrophilic ILs at very low concentrations cannot be removed from water using $CO_2$ at ambient temperatures. Specifically, $[C_4mim][BF_4]$ can be separated from water at ambient temperatures 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 (*i.e.*, 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 from water using $CO_2$ than hydrophilic ILs.

All the pressures at which we were successful in achieving phase separation are below the saturation (vapor) pressure of pure $CO_2$ at room temperature. $CO_2$ is usually sold in cylinders at its vapor pressure, thus practical laboratory separations could be performed with no special heating or pumping systems to induce separation. Interestingly, at a IL loading of 24.6 mole% of $[C_4mim][BF_4]$ in water, a phase split does not appear. It should be noted that 24.6 mole% of IL in water is 80.4 weight percent IL so this is a situation in which it might be easier to remove the water by supercritical fluid extraction.[5,6] Also, at low concentrations of the $[C_4mim][BF_4]$, such as 0.1 and 0.2 mole%, phase separation is not observed at moderate temperatures and pressures, *i.e.* 15 °C to 25 °C and below the vapor pressure of pure $CO_2$, which is between 5.07 and 6.41 MPa for this temperature range. This represents the limit of using *vapor* $CO_2$ to induce phase split. Higher pressure liquid $CO_2$ could be used to increase the solubility of $CO_2$ but at the cost of high pressure requirements. It should be noted that even though much of the IL is separated from water at the LCEP, there will still be some finite amount of IL in the water rich phase. The concentration of IL in the water rich phase and the pressure at which most of the IL is removed from the water is currently under investigation.

The mechanism for this phase behavior seems much different than for organic solutions containing ILs.[16] For organic solutions, $CO_2$ solubility is high, resulting in a large volume expansion and the concomitant dramatic reduction in the dielectric constant of the mixture, which forces the IL from solution. As a result, with organic solutions, ethane (which has high solubility in many organics) is also effective at inducing a phase split. However, as seen in Table 2, the solubility of $CO_2$ in pure water at the pressures of the observed LCEP is very low, roughly 0.02 mole fraction, which does not result in any noticeable volume expansion. 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 $[C_4mim][PF_6]$ in water at 20 °C. The solubilities of these gases in water are also low, estimated at 0.00145 and 0.00085 mole fraction, respectively,[19,20] at the highest pressures investigated. Thus, with aqueous solutions containing ILs, we have so far found that only $CO_2$ is capable of causing a phase separation.

A possible explanation for the observed phase behavior might be the chemical interactions between water and $CO_2$. $CO_2$ reacts with water to form carbonic acid and its dissociation products, thus lowering the pH. The pH of the water/$CO_2$ system at 25 °C to 40 °C and 7.0 MPa is about 2.8.[21] Perhaps this change in pH contributes to the changes in solution equilibrium between the IL and water that lead to the separation of ILs from water using $CO_2$. The observed behavior could also be due to a slight decrease in dielectric constant upon addition of $CO_2$. We tested these possibilities by adding HCl and acetone to a $[C_4mim][PF_6]$ saturated water solution to decrease pH and dielectric constant, respectively. Neither addition led to a phase separation, indicating that the observed behavior is not due solely to either of these effects.

This unusual phase behavior has a number of practical implications for designing processes with ILs. Since aqueous waste streams are the most likely avenue for ILs to enter the environment, IL contamination of aqueous streams is a major issue. Removing water from aqueous solutions dilute in IL using distillation would be a very energy intensive process. Anthony *et al.*[17] found that activated carbon can remove $[C_4min][PF_6]$ from water but not very efficiently. In this work we have shown that one can use relatively low pressure $CO_2$, an environmentally benign solvent, for the removal of several different ILs from aqueous solutions.

This work was funded by the NSF under grant number CTS99-87627. We would like to thank Covalent Associates for their generous gift of the $[PDmim][NTf_2]$ sample.

## Notes and references

1 T. Welton, *Chem. Rev.*, 1999, **99**, 2071–2083.
2 P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3773–3789.
3 J. F. Brennecke and E. J. Maginn, *AICHE J.*, 2001, **47**, 2384–2389.
4 K. R. Seddon, *J. Chem. Technol. Biotechnol.*, 1997, **68**, 351–356.
5 L. A. Blanchard, D. Hancu, E. J. Beckman and J. F. Brennecke, *Nature*, 1999, **399**, 28–29.
6 L. A. Blanchard and J. F. Brennecke, *Ind. Eng. Chem. Res.*, 2001, **40**, 287–292.
7 L. A. Blanchard, Z. Y. Gu and J. F. Brennecke, *J. Phys. Chem. B*, 2001, **105**, 2437–2444.
8 A. Bosmann, G. Franciò, E. Janssen, M. Solinas, W. Leitner and P. Wasserscheid, *Angew. Chem., Int. Ed.*, 2001, **40**, 2697–2699.
9 M. F. Sellin, P. B. Webb and D. J. Cole-Hamilton, *Chem. Commun.*, 2001, 781–782.
10 F. C. Liu, M. B. Abrams, R. T. Baker and W. Tumas, *Chem. Commun.*, 2001, 433–434.
11 R. A. Brown, P. Pollet, E. McKoon, C. A. Eckert, C. L. Liotta and P. G. Jessop, *J. Am. Chem. Soc.*, 2001, **123**, 1254–1255.
12 M. T. Reetz, W. Wiesenhofer, G. Franciò and W. Leitner, *Chem. Commun.*, 2002, 992–993.
13 P. Lozano, T. de Diego, D. Carrie, M. Vaultier and J. L. Iborra, *Chem. Commun.*, 2002, 692–693.
14 J. A. Laszlo and D. L. Compton, *Biotechnol. Bioeng.*, 2001, **75**, 181–186.
15 J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser and R. D. Rogers, *Chem. Commun.*, 1998, 1765–1766.
16 A. M. Scurto, S. Aki and J. F. Brennecke, *J. Am. Chem. Soc.*, 2002, **124**, 10276–10277.
17 J. L. Anthony, E. J. Maginn and J. F. Brennecke, *J. Phys. Chem. B*, 2001, **105**, 10942–10949.
18 A. M. Scurto, PhD Dissertation, The University of Notre Dame, Notre Dame, IN-46556, USA, 2002.
19 R. Crovetto, R. Fernandez-Prini and M. L. Japas, *Ber. Bunsen-Ges. Phys. Chem. Chem. Phys.*, 1984, **88**, 484–488.
20 R. Wiebe, V. L. Gaddy and C. Heins, *Ind. Eng. Chem.*, 1932, **24**, 927.
21 K. L. Toews, R. M. Shroll, C. M. Wai and N. G. Smart, *Anal. Chem.*, 1995, **67**, 4040–4043.
22 R. Wiebe, *Chem. Rev.*, 1941, **29**, 475–481.
23 G. Houghton, A. M. McLean and P. D. Ritchie, *Chem. Eng. Sci.*, 1957, **6**, 132–137.