Combining ionic liquids and supercritical fluids: *in situ* ATR-IR study of CO_2 dissolved in two ionic liquids at high pressures†

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Received (in Cambridge, UK) 10th July 2000, Accepted 5th September 2000
First published as an Advance Article on the web 2nd October 2000

An *in situ* ATR (attenuated total reflectance)-IR study of CO_2 dissolved in two ionic liquids at high pressures has demonstrated the effects of the anionic species of the ionic liquids on the molecular state of the dissolved CO_2.

In the search for alternatives to conventional solvents partly driven by the need for 'green' chemistry and sustainable technology, but primarily because of the potential for novel synthetic routes, a number of media have been explored recently. These include supercritical fluids (SCF) and room-temperature ionic liquids (IL).[1] One of the challenges that exist in the use of ionic liquids is that it is often difficult to separate products from reactants, catalyst or solvent. Distillation of the solvent cannot be applied for separation because of the low vapour pressure of ionic liquids. The possibility of combining chemical reactions in IL with separations using SCF is of potential value.

Very recent work has demonstrated that supercritical (sc) CO_2 is highly soluble in certain ionic liquids while these ionic liquids are not measurably soluble in the $scCO_2$ phase.[2] This observation indicates that there is a potentially useful opportunity to separate $scCO_2$-soluble products from ionic liquids using SCF/liquid extraction. The 'tunable' solvent power of the supercritical fluid, owing to its variable (with pressure or temperature) solvent density may be utilised for extraction and separation of the products of chemical processing in ionic liquids (without, for example, removing catalyst from IL). Synthetic procedures and catalytic processes using IL media have been recently summarised[3] and the applications of SCF solvents for extraction, and in particular the role of spectroscopy in monitoring these processes, have also been reviewed.[4] The preliminary data showed that naphthalene could be extracted from an ionic liquid into $scCO_2$ phase.[2] However, the same authors later indicated that the presence of water in the IL had a significant effect on CO_2 solubility.[5] In this work the authors also speculated about the origins of the high solubility of CO_2 in ionic liquids, and the role of different anions.

A molecular-level insight into the state of CO_2 dissolved in IL is needed to elucidate the fundamental origin of this phenomenon. Here, we report an *in situ* ATR-IR study of CO_2 dissolved in two ionic liquids at high pressures. The advantage of a very shallow penetration (few microns) of the IR light in ATR-IR spectroscopy has been utilised to measure the spectrum of CO_2 dissolved in two ionic liquids. Ionic liquids based on the 1-alkyl-3-methylimidazolium cation in conjunction with either $[PF_6]^-$ or $[BF_4]^-$ {$[bmim][PF_6]$ **I** and $[bmim][BF_4]$ **II**}, were synthesised by established procedures.[3] ATR-IR spectroscopy overcomes some of the limitations inherent to other techniques when the objective is to gain spectra of molecules dissolved in highly absorbing media. It would be very difficult, if not impossible, to measure the IR spectrum of the bending mode of CO_2 dissolved in ionic liquids using transmission spectroscopy because of the strong absorbance of these ionic liquids in the important region of the bending mode of CO_2. The current ATR-IR method uses a modified commercial diamond ATR accessory (Specac, Ltd., UK) and a miniature high-pressure flow cell.[6] Diamond's ability to withstand high pressure was used to measure the spectra of CO_2 dissolved in IL at various pressures and temperatures. IR spectra were measured using an Equinox-55 FTIR spectrometer (Bruker) with DTGS and MCT detectors; resolution was 2 cm^{-1}. The cell was pressurised with CO_2 up to 200 bar at room temperature, equilibrated for periods from several hours to a few days, and the spectra were measured. The temperature of the cell could readily be varied from room temperature to 200 °C (for a schematic view of the cell see ESI†).

The IR spectrum of CO_2 dissolved in two ILs shows the bands corresponding to antisymmetric (not illustrated) and bending modes of CO_2. There was no difference in position of the bands corresponding to the ν_3 antisymmetric stretching modes of CO_2 dissolved in **I** and **II**. Both bands appear with the peak maximum at *ca.* 2338 cm^{-1} with the shoulder on the low-wavenumber side of the band. The position of this band of CO_2 dissolved in IL is very close to that of CO_2 dissolved in glassy polymers, such as PMMA[7] rather than the CO_2 incorporated in halogen salts of alkali metals[8] where the bands are observed in the region of 2150–2200 cm^{-1}. The absorbance of the ν_3 band is 0.35 for CO_2 dissolved in **I** at 68 bar and 40 °C. *In situ* ATR-IR spectroscopy provides a direct but approximate measurement of the solubility of CO_2 in IL; the effective pathlength for this band is *ca.* 1.5 μm, and using the same molar absorptivity for CO_2 as for CO_2 dissolved in water at high pressures[9] the solubility of CO_2 in **I** at these conditions is *ca.* 0.6 mol fraction (2 M). The absorbance of the ν_3 band of CO_2 dissolved in **II** is approximately 40% lower indicating the lower solubility of CO_2 in **II**.

Fig. 1 shows the normalised spectra of CO_2 in the ν_2 region in **I** and **II** at 68 bar and 40 °C. There are two important

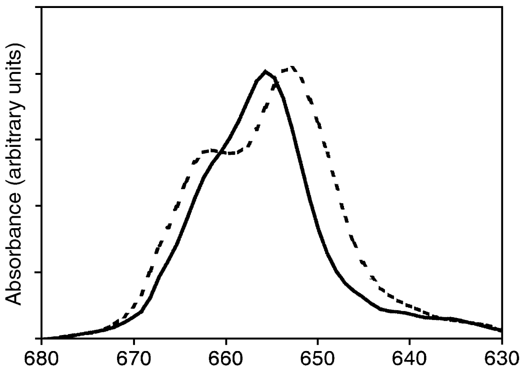

Fig. 1 ATR-IR spectra of CO_2 in the ν_2 mode region: spectrum of CO_2 dissolved in **II** (- - - -) and **I** (———). The absorbance scales of these spectra have been normalized to the absorbance of the stronger band (the maximum absorbance for **I** was *ca.* 0.2).

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† Electronic supplementary information (ESI) available: schematic view of the miniature high-pressure flow cell. See http://www.rsc.org/suppdata/cc/b0/b005514j/

observations: (i) the band is split into a doublet comprising of two bands; (ii) the magnitude of the splitting is different for CO_2 dissolved in **I** compared with **II**; the bands are strongly overlapped in **I** while the bands are distinct in **II**. The splitting of the bending mode of CO_2 indicates that the double degeneracy has been removed. This occurs due to a small bending of the CO_2 molecule. The angle of the bending is, probably, just a few degrees since we did not detect the appearance of the band corresponding to the symmetric stretching mode of CO_2. By analogy with the reported specific interaction between CO_2 and Lewis bases, which also results in the splitting of the bending mode,[7] it is reasonable to speculate that the splitting of the bending mode of CO_2 dissolved in ionic liquids indicates an interaction of CO_2 with a negatively charged fluorinated anion in **I** and **II**. These anions could act as weak Lewis bases, and CO_2 appears to be a useful probe to sense the extent of their basicity. The width of the ν_2 mode, measured as an effective average width of the split band (the average width represents the width of the doublet at the half-maximum of the absorbance) is an estimate of the strength of the interaction of CO_2 with the Lewis bases: the width increases with the increase of the strength of the interaction.[7] The observation of the striking differences in the band widths for CO_2 dissolved in **I** and **II** suggests that $[BF_4]^-$ is a stronger Lewis base in its interaction with CO_2 than $[PF_6]^-$. The average width of ν_2 for CO_2 dissolved in **II** reaches 19 cm^{-1}, the ν_2 width of CO_2 in **I** is just 15 cm^{-1}. The degree of the splitting also indicates that CO_2 molecules are more strongly bent and interactive with **II** than with **I** as was observed previously for CO_2 dissolved in organic solvents and supported by *ab initio* calculations.[10] Thus $[BF_4]^-$ acts as a stronger Lewis base towards CO_2 than $[PF_6]^-$. This conclusion contradicts the proposal by Brennecke and coworkers[5] that the strength of the interaction between CO_2 with $[PF_6]^-$, in ionic liquids, should be stronger than with $[BF_4]^-$. The current spectroscopic data provide strong evidence that the trend is the opposite, the $[BF_4]^-$ anion interacting more strongly with CO_2 than $[PF_6]^-$. This could also be a result of the strength of interaction decreasing with the increase of anion size. Thus, the strength of these interactions cannot be solely responsible for the solubility of CO_2 in these ionic liquids, and, presumably, a free volume contribution in the IL plays a significant role.[5] The strength of anion–cation interaction in the IL affects the available free volume, and one would anticipate that a weaker interacting anion leads to more free volume being available.

The spectroscopic ATR-IR method also facilitates the estimation of the swelling of ionic liquids subjected to high-pressure CO_2. The bands corresponding to the vibrations of the ionic liquids decrease in intensity as the pressure of CO_2 increases which would indicate that the evanescent wave in ATR spectroscopy probes a smaller number of ions in the vicinity of the ATR crystal due to the swelling of the liquid. This indicates that the interaction of CO_2 molecules with anions in ionic liquids facilitates swelling by decreasing anion–cation interactions for ions that are already largely mobile at room temperature in ionic liquids compared to other salts. The swelling of **I** is greater than of **II** presumably due to the weaker anion–cation interactions in **I**; it was noted earlier that the estimated solubility of CO_2 in **II** was *ca.* 40% less than for **I**, consistent with the differences in swelling. We have also observed a small (a few cm^{-1}) shift to the high-frequency region of the some of the bands corresponding to the stretching ν_3 modes of anions in **I** and **II** (relative to the bands of these ionic liquids in absence of dissolved CO_2) which also indicates that CO_2 interacts with the anions in these ILs. This shift also indicates a weakening of the interactions of the anions with their environment as CO_2 molecules weakly interact with the anions and act as a 'shield' reducing stronger interactions. The interactions between the CO_2 molecule and anion are probably of Lewis acid–base type, with the axis of the O=C=O molecule orienting towards the anion in perpendicular arrangement to P–F or B–F bonds. If the interaction of the CO_2 molecule with the cation in IL was *via* the CO_2 oxygen atom one would expect the ν_3 band to appear in a higher frequency range (2345–2360 cm^{-1}), the appearance of the ν_1 band and no splitting of the bending mode ν_2. This was observed in a number of studies on CO_2 adsorption in zeolites.[11] The influence of the negative charge density of the oxygen atoms in some zeolite networks reduces the ν_3 frequency,[11] which is consistent with the current proposal for the origin of the CO_2/anion interactions. The variation of the temperature of the **I**/CO_2 system in the range 40–60 °C shows that the absorbance bands of CO_2 dissolved in IL decrease in intensity as temperature increases; the interaction between CO_2 and **I** is exothermic which is typical for Lewis acid–base type interactions.

These data for the CO_2 interactions with IL is remarkably similar to those observed for CO_2 interactions with polymers.[7] There it was shown that the bending mode ν_2 of dissolved CO_2 is a very informative probe in elucidating its interactions with electron-donating functional groups in polymers. It is significant that the splitting of the bending mode of CO_2 in **II** exceeded any of the corresponding splittings observed for CO_2 in the polymers,[7] and the splitting for both **I** and **II** is significantly larger than that observed in fluorine-containing polymers indicative of the role of the negative charge in IL. There is a report implying that $[BF_4]^-$ is a stronger Lewis base than $[PF_6]^-$ based on the measurements of the coordinating ability of these anions.[12] Our spectroscopic assignment of the strength of interaction between CO_2 and anions in the two ionic liquids is also consistent with recent work[13] on the interactions between methanol and various anions where it was shown that $[BF_4]^-$ is a stronger proton acceptor relative to $[PF_6]^-$. Preliminary results for ionic liquids containing anions that are stronger bases, compared to [bmim]$[PF_6]$ and [bmim]$[BF_4]$, *e.g.* $[CF_3CO_2]^-$, has shown that the bending mode of CO_2 dissolved in this ionic liquid is split even further reflecting the greater basicity of this anion.

In summary, these spectroscopic data provide a first direct indication of the effect of an anion in the weak Lewis acid–base interactions with CO_2 molecules, and also provides a way to study phase partition behaviour of supercritical CO_2/IL systems, and hence to facilitate the design and optimisation of IL/SCF synthetic and separation routes.

We are particularly grateful to the RSC for a Journals Grant for International Authors in 1997. We thank EPSRC for support, Dr P. Turner (Bruker), Dr D. Coombs (Specac, Ltd.), Dr L. Lancaster, Dr C. J. Lawrence and Mr N. M. B. Flichy (Imperial College) for their support.

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