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High-pressure CO_2-induced reduction of the melting temperature of ionic liquids†

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An *in situ* ATR-IR spectroscopic study has shown that high-pressure CO_2 reduces melting temperature of ionic liquids such as [C_{16}mim][PF_6].

Ionic liquids are finding increasing interest as solvents for a range of applications including organic synthesis,[1] separations,[2] and electrochemistry.[3] It has recently been shown to be possible to combine chemical reactions in ionic liquids with separation routes utilising binary ionic liquids/supercritical CO_2 systems.[1b,4,5] Prior to this it had also been shown that CO_2 is soluble in some ionic liquids (*e.g.* $N(C_6H_{13})_4PF_6$).[6]

One unique feature of ionic liquids compared with conventional solvents is the potential to influence their properties by alteration of the cation or anion. For example, the presence of long alkyl chain substituents can result in the formation of liquid crystalline phases either on melting or on addition of solvents. The generation of low melting liquid crystalline salts based on the 1,3-dialkylimidazolium cation has been reported by a number of authors.[7] Such salts are distinguished from many other ionic liquid crystalline materials by generally low melting points, combined with notably high mesophase ranges. The possibility of reducing the melting temperature of these salts even further under high-pressure CO_2 opens an additional opportunity for chemical reactions and processes utilising ionic liquids with long alkyl chains.

We have investigated the effect of CO_2 pressure on the phase behaviour of 1-hexadecyl-3-methylimidazolium hexafluorophosphate ([C_{16}mim][PF_6]), as monitored using ATR-IR spectroscopy. This salt has been shown to form a smectic A liquid crystalline phase on melting at 75 °C, and finally melts to an isotropic liquid only at 125 °C.[7c] *In situ* spectroscopic study of a solid–liquid phase transition *via* transmission IR spectroscopy would be challenging due to light scattering of the solid and due to flow and absorbance of the liquid. Recently we have developed high-pressure *in situ* ATR-IR spectroscopy, which is ideally suited to the study of melting phenomena. In this approach the evanescent wave probes a solid or liquid sample subjected to high-pressure gas.[8] ATR-IR spectroscopy has also been used to study molecular states of water in room temperature ionic liquids.[9] Fig. 1(a) and 2(a) show the IR spectrum of crystalline [C_{16}mim][PF_6] at room temperature in the $\nu(PF_6)$ and ν(CH) regions.

The $\nu(PF_6)$ region in particular displays relatively complex splitting, suggesting that the octahedral geometry of the $[PF_6]^-$ anion is slightly perturbed in the crystalline form. It should be noted that in the crystal structure of the analogous salt [C_{12}mim][PF_6] slight deviations from the pure octahedral structure were indeed observed.[7c] It is also possible that the splitting arises from a general low site symmetry of the $[PF_6]^-$ anion. Such behaviour is well known in highly symmetrical molecules and ions even in the absence of strong interactions with neighbouring species. As the temperature was raised, the IR bands broadened slightly, but showed no significant change in position or intensity until the temperature reached 75 °C, the melting point of the salt. At this temperature it forms a smectic A liquid crystalline phase,[7c] and clear changes are observed in the IR spectrum (Fig. 1(b)). The splitting in the $\nu(PF_6)$ band has now disappeared, and is replaced by a single band at 825 cm^{-1}. In general, all bands in this region have become smoother as they lost the sharp structure characteristic of the crystalline phase. Fig. 2(b) shows that the aliphatic $\nu(CH_2)$ stretching modes below 3000 cm^{-1} are shifted slightly to higher wavenumber, and the aromatic ν(CH) modes broaden and shift to lower wavenumber. An overall decrease in intensity was also observed in this spectral region. The shift to higher wavenumber for the $\nu(CH_2)_s$ and $\nu(CH_2)_{as}$ peaks at 2850 and 2920 cm^{-1}, respectively, on conformational melting of the alkyl chain has been previously noted in long alkyl chain substituted ammonium salts.[10]

Exposure of the salt to high pressures of CO_2 causes a depression of the melting temperature, along with spectroscopic changes consistent with the formation of a liquid crystalline phase. Melting point depression by CO_2 has been noted previously for tetrahexylammonium hexafluorophosphate and nitrate,[6] although in the former system the CO_2 contained added water. No *in situ* spectroscopic investigations of the salt structure were reported in these studies, however. Depression of the melting temperature of [C_{16}mim][PF_6] has been observed in our work using carefully dried CO_2. Fig.1(c) and 2(c) show

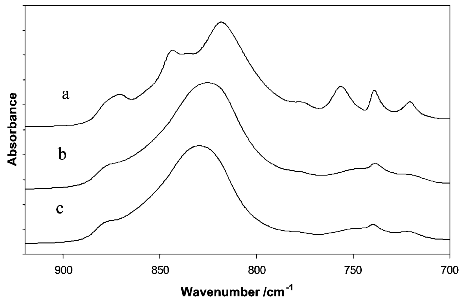

Fig. 1 ATR-IR spectra of [C_{16}mim][PF_6] in the $\nu(PF_6)$ region: (a) solid sample at room temperature; (b) melt at 75 °C (liquid crystalline phase); (c) subjected to 70 bar of CO_2 at 50 °C.

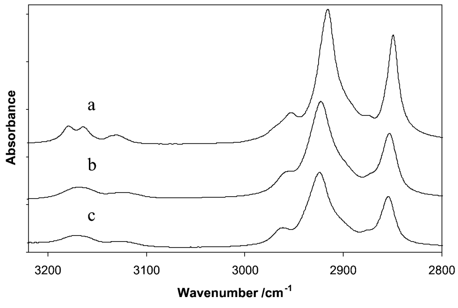

Fig. 2 ATR-IR spectra of [C_{16}mim][PF_6] in the region of aromatic ν(CH) and aliphatic $\nu(CH_2)$: (a) solid sample at room temperature; (b) melt at 75 °C (liquid crystalline phase); (c) subjected to 70 bar of CO_2 at 50 °C.

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† Electronic supplementary information (ESI) available: Fig. S1: ATR-IR spectrum of [C_{16}mim][PF_6] after it has been subjected to solution of ferrocene in CO_2 at 50 °C and pressure of *ca.* 110 bar. See http://www.rsc.org/suppdata/cc/b2/b202759c/

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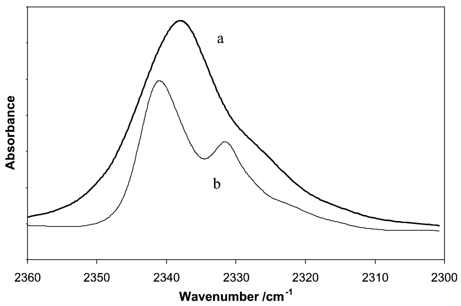

Fig. 3 ATR-IR spectra of CO_2 dissolved in [C_{16}mim][PF_6] in the ν_3 region at 50 °C and CO_2 pressure of 70 bar (a) and 50 bar (b).

parts of the IR spectrum of [C_{16}mim][PF_6] at 50 °C after the addition of 70 bar CO_2 (the salt was heated to 50 °C and subjected to high-pressure CO_2 of *ca.* 70 bar).

The similarities between Fig. 1(b) and (c), and between Fig. 2(b) and (c) are clear, suggesting that a smectic A structure is formed even in the presence of CO_2. The broadening and the shift of all spectral bands of the salt suggest the formation of a liquid crystalline phase under these conditions. Thus it is clear, as is the case for some polymers, that high pressures of CO_2 may be used to decrease the melting point of ionic liquid crystals. It also appears that the $\nu(PF_6)$ band in molten [C_{16}mim][PF_6] is shifted *ca.* 7 cm^{-1} to higher wavenumber in the presence of CO_2. Behaviour of this type has been noted previously[5] on pressurisation of liquid [C_4mim][PF_6] with CO_2, although the magnitude of the shift was smaller in this case. The phenomenon was assigned to a weak Lewis acid–base type interaction between the anion and CO_2, with the P–F bonds perpendicular to the O=C=O axis thereby reducing the rather stronger interactions between the P–F bonds and the cations. It should be noted that the changes in the $\nu(PF_6)$ spectral region have been observed at somewhat lower pressures than the changes in the ν(CH) region of the cation, suggesting that the CO_2 molecules cause distortion in the crystalline arrangements in the vicinity of the anions first. This is consistent with the proposal of the weak interaction between CO_2 and anions in room temperature ionic liquids.[5] The CO_2-induced reduction in the melting temperature of ionic liquids may have important implications, since it would allow the use of these ionic liquids as solvents at milder temperatures and facilitate separation processes using the combination of these two classes of environmentally benign solvents. For example, in some preliminary experiments [C_{16}mim][PF_6] has been pressurised by a supercritical CO_2 solution containing dissolved ferrocene. Once the salt melted, the IR bands of the ferrocene were observed in the spectrum of the melt along with the bands of the dissolved CO_2. After depressurisation of the system, the CO_2 left the melt, resulting in solidification with the ferrocene molecules remaining trapped in the salt (see Fig. S1 in ESI†). The initial data on impregnation of ferrocene molecules into an ionic salt from supercritical CO_2 solution demonstrates that the methodology outlined in the paper will provide a means to prepare new materials based on ionic salts that have melting temperatures above ambient.

One of the other observations was made when the sample of [C_{16}mim][PF_6] was subjected to the lower pressure (*ca.* 50 bar) of CO_2 at 50 °C or was cooled down to 20 °C under a CO_2 pressure of 70 bar. The spectrum measured in the ν_3 region of CO_2 is shown in Fig. 3. Two bands at 2341 cm^{-1} and 2331 cm^{-1} (Fig. 3) for the ν_3 mode of CO_2 dissolved in [C_{16}mim][PF_6] indicates that a large concentration of CO_2 is maintained within the salt lattice even in the solid state, since no evidence of melting was observed from the IR spectrum of the salt under these conditions (50 bar, 50 °C). The presence of the two bands for antisymmetric stretching mode of CO_2 suggests that the CO_2 molecules exist in more than one environment. Indeed, the only other possible explanation would involve the presence of the combinational $(\nu_3 + \nu_2) - \nu_2$ 'hot-band'.[11] However, it is known that the 'hot band' is always separated from the main band by 12 cm^{-1} and has much smaller relative absorbance compared to the ν_3 band. Once the pressure of CO_2 increased to 70 bar the ν_3 band of CO_2 becomes a single band with the shoulder corresponding to the 'hot-band'. Thus, it has been demonstrated, for the first time, that the CO_2 molecules may reside in two different sites of the solid ionic crystals, apparently in the vicinity of anions and hydrocarbon tails in the cation.

Furthermore, the pattern and position of the bands observed for [C_{16}mim][PF_6] under 50 bar of CO_2 are different again from those in either the liquid state or in the virgin crystalline state. For example, a small shift of the $\nu(CH_2)$ bands to lower wavenumber was observed under these conditions. This indicates that the presence of dissolved CO_2 can cause considerable rearrangement in the crystalline lattice of solid [C_{16}mim][PF_6], but to a different degree from the situation observed in the melt.

Thus, the *in situ* ATR-IR spectra of [C_{16}mim][PF_6] provide a direct indication that high-pressure CO_2 reduces the melting temperature of this salt. The data presented here indicate that 70 bar of CO_2 reduces the melting temperature of [C_{16}mim][PF_6] from 75 to 50 °C. The amount of CO_2 dissolved in melt was estimated from the absorbance of the antisymmetric stretching band of CO_2 following the procedure described in our related paper.[5] This provided an estimate of CO_2 solubility under these conditions (70 bar and 50 °C) as *ca.* 0.55 mol fraction. It should be noted that at 40 °C the melting has not been observed even at pressures as high as 170 bar; apparently due to the effect of compression of the solid salt on the dissolution of CO_2 molecules. We have also measured the IR spectra of salt subjected to high-pressure argon (up to 150 bar) and found no reduction of the melting temperature of the salt. This is also consistent with our proposal that CO_2 disrupts cation–anion and tail–tail interactions rather than simply playing an 'impurity' role in the mechanism of induced melting.

Preliminary results for other analogous ionic liquids with the melting temperatures higher than room temperature have shown that the reduction in melting point by high-pressure CO_2 is not unique to [C_{16}mim][PF_6]. Such reductions in the melting temperature of ionic liquids may allow their use as solvents at milder temperatures.

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