Room temperature fast-ion conduction in imidazolium halide salts

Hayley A. Every,[a] Andrea G. Bishop,[b]† Douglas R. MacFarlane,[b] Greger Orädd[c] and Maria Forsyth*[a]

[a]School of Physics and Materials Engineering, PO Box 69M, Monash University, Victoria 3800, Australia. E-mail: maria.forsyth@spme.monash.edu.au
[b]School of Chemistry, PO Box 23, Monash University, Victoria 3800, Australia
[c]Department of Chemistry, Umeå University, SE-901 87 Umeå, Sweden

Fast-ion conduction has been observed in the iodide and bromide salts of 1-methyl-3-ethylimidazolium at ambient temperatures. The melting point of these two compounds is above 350 K and even at 273 K the ionic conductivity in the solid-state is greater than 10^{-3} S cm^{-1}. Cation diffusion coefficients have been measured using fringe field gradient and/or pulse field gradient ^{1}H NMR techniques, which indicated cation diffusion coefficients of the order of 10^{-10} m^2 s^{-1} in the solid-state. Remarkably, these values are up to an order of magnitude higher than the cation diffusion coefficient in the supercooled liquid at 293 K. The activation energy for diffusion in the solid-state is extremely small, as is typical of solid-state fast-ion conductors and indicates a change in transport mechanism from the melt to the crystal. The inability to detect an ^{127}I signal together with the modelling of the conductivity using the Nernst–Einstein equation suggests that the solid-state conduction is primarily due to cation diffusion. The solid-state fast-ion conduction is most likely related to vacancy diffusion along the cation layers in the crystal. The temperature dependence of the NMR signal intensity indicates that the number of mobile species is increasing with increasing temperature with an activation energy of approximately 20–30 kJ mol^{-1}.

Introduction

In solid materials, fast-ion conduction is a well-known phenomenon involving rapid ion transport through a largely immobile lattice. As a consequence of the high ionic mobilities, the conductivities of these materials can be of a similar magnitude, over appropriate temperature ranges, to molten salts or aqueous solutions of strong electrolytes.[1] A number of transport mechanisms that would facilitate ion motion in such materials have been recognised.[2,3] Self-diffusion of the host material generally involves a vacancy mechanism where the ions migrate from one lattice site to an adjacent vacant lattice site. Under certain circumstances, these vacancies may coalesce to form larger defects, such as dislocations, thus enabling ion transport to occur *via* pipe diffusion. Alternatively, ion diffusion may also occur *via* an interstitial process. Interstitials are the voids that are not normally occupied in a crystal lattice and may form 1-, 2- or 3-dimensional channels through which ions can migrate. This mechanism is favoured by small ions as the interstitial sites are typically smaller than lattice vacancies. The preferred mechanism for ion transport, however, is dependent on the structure and chemistry of the electrolyte.

For some fast-ion conductors, the transport mechanisms can also be associated with plastic crystal behaviour. Originally reported for organic compounds,[4,5] the soft, "plastic" nature exhibited by these materials is the result of dynamic orientational disorder in the crystal lattice, as molecular mobility and/or diffusion occurs well below the final melting point of the crystal.[6] In the case of ionic materials, the diffusion of ionic moieties can lead to sizeable ionic conductivities in the solid-state.[7,8] For inorganic plastic crystals, such as Li$_2$SO$_4$ or α-Na$_3$PO$_4$,[9–12] ionic conductivity has been linked in detail to a "paddle wheel" type mechanism, where the alkali metal cation diffuses as a direct result of anion rotations. For these salts, however, the plastic phases only occur at temperatures above 600 K. In previous work, we have shown that high conductivities can also be measured in ionic organic salts based on alkyl substituted pyrrolidinium salts with (CF$_3$SO$_2$)$_2$N$^-$, PF$_6^-$ and BF$_4^-$.[13] Furthermore, doping of these salts with a small ion such as lithium can lead to still higher values of conductivity in the plastic crystal phase.[14]

Recently, imidazolium salts have received considerable interest due to their high molten state ionic conductivities[15] and large electrochemical windows,[16] making them promising electrolytes for photo-electrochemical cells.[17] Their high conductivities most likely stem from weak interionic associations due to the delocalised charge on the imidazolium cation. In the solid-state, 1-methyl-3-ethylimidazolium iodide (MeEtImI) exhibits an alternating layered structure of cation and anion layers,[18] and one could envisage ionic transport along these layers. Previously we have discussed ionic conduction and diffusion in a family of imidazolium molten salts.[15] In this paper, we report on the solid-state transport properties of the MeEtImBr and MeEtImI salts. The solid-state conductivity reported here is amongst the highest known at ambient temperatures.

Experimental

Sample preparation

Preparation of the 1-methyl-3-ethylimidazolium halides involves reacting 1-methylimidazole with the appropriate ethyl halide as described elsewhere.[16,19,20] The bromide and iodide salts were investigated in this work. For simplicity, the name of each salt is abbreviated according to the main components, *e.g.* 1-methyl-3-ethylimidazolium iodide is referred to as MeEtImI. Samples were rigorously dried under vacuum prior to measurements.

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†*Current address*: Ångström Laboratory, Uppsala University, Box 538, SE-751 21 Uppsala, Sweden.

Thermal analysis

Thermal transitions were measured using a Perkin-Elmer differential scanning calorimeter (DSC-7) over the range 153 to 373 K scanned at 20 K min^{-1}. The head was cooled with either dry ice in ethanol or liquid nitrogen as required and calibrated with a cyclohexane standard. Reported values are reproducible to within ± 1 K.

Conductivity measurements

A micro-conductivity probe was constructed with 0.7 mm diameter platinum wire electrodes encased in a 50×10 mm glass tube. The wires were blackened by bulk electrolysis in a 50 mM solution of chloroplatinic acid in 2 M HCl at a current density of 200 mA cm^{-2} against a platinum wire anode (5–10 min per electrode). The cell constant was determined in aqueous KCl to be approximately 500 cm^{-1}. Conductivity, σ, was measured between 273 and 403 K *via* AC impedance over a range of 20 Hz to 1 MHz using a Hewlett-Packard 4282 Precision LCR meter and 100 kHz to 13 MHz using a Hewlett-Packard 4199 LF impedance analyser.

Diffusion measurements

Temperature dependent diffusion coefficients were measured using both the pulsed field gradient (PFG) and fringe field gradient (FFG) methods. Pulsed field gradient proton diffusion coefficients were measured on two Varian CMX Infinity spectrometers (100 and 400 MHz) equipped with a 2.3 and 9.4 T magnet respectively. The gradient strengths were either 0.477 or 0.954 T m^{-1} for the 100 MHz spectrometer and ranged from 0.028 to 11.3 T m^{-1} for the 400 MHz spectrometer. A stimulated-echo pulse sequence[21] was used ($\pi/2$–τ_1–$\pi/2$–τ_2–$\pi/2$–τ_1) with a $\pi/2$ pulse of either 5 or 6.5 μs for the two spectrometers respectively. For each experiment either the gradient strength or duration was varied while the other parameters were kept constant. The diffusion times ranged from 5 to 520 ms. The echo attenuation was fitted with eqn. (1)

$$A(g,\delta) = A(0)\exp\left[-\gamma^2 g^2 D\delta^2\left(\Delta - \frac{\delta}{3}\right)\right] \qquad (1)$$

where A is the echo amplitude, γ is the gyromagnetic ratio, g is the gradient strength, δ is the duration of the gradient pulse, Δ is the time between gradient pulses (diffusion time) and D is the diffusion coefficient. Measurements were made as a function of temperature between 293 and 353 K.

Fringe field gradient proton diffusion coefficients were measured using a Bruker CXP300 spectrometer. The probe was positioned in the fringe field at a distance of 24.5 cm from the centre of the magnet where the field strength is 2.7 T and the magnetic field gradient was found to be 46.8 T m^{-1}. Protons resonate at 116 MHz, at this position. Diffusion coefficients were measured using a spin-echo pulse sequence ($\pi/2$–τ–π–τ) with a $\pi/2$ pulse of 2.1 μs. The echo attenuation in this case was fitted with eqn. (2)

$$A(2\tau) = A(0)\exp\left(-\frac{2}{3}\gamma^2 g^2 D\tau^3\right) \qquad (2)$$

where the same definitions apply as described above. Measurements were made as a function of temperature over the range 273 to 403 K.

Results

Thermal analysis

MeEtImBr and MeEtImI are both solids at room temperature, melting at 352 and 351 K respectively. No glass transition temperatures are observed upon quenching these materials from the melt and conducting thermal analysis from 153 K. A
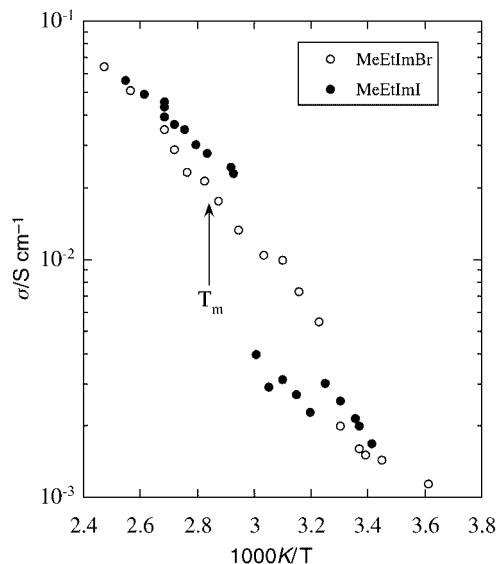

Fig. 1 Temperature dependent conductivity data for MeEtImBr and MeEtImI. As the materials change from solid to liquid, an obvious discontinuity in the data is observed.

solid–solid phase transition is observed at 242 K in MeEtImI with entropy change, $\Delta S = 1.4$ J K^{-1} mol^{-1}. The final melting event at 352 K has entropy of fusion, $\Delta S_f = 44$ J K^{-1} mol^{-1}.

Conductivity

The conductivities for the two salts are shown in Fig. 1. Measurements were made during cooling in isothermal steps from the melt. The solid-state conductivity is of the order of 10^{-3} S cm^{-1} at room temperature, which is comparable to some of the *liquid* state conductivities observed for other dialkylimidazolium salts.[15,19] This level of conductivity is also approximately one order of magnitude higher than similar crystalline organic salts of other anions such as PF$_6^-$ and bis(trifluoromethylsulfonyl)amide (TFSA).[13] An obvious discontinuity is observed in these conductivity data where the conduction mechanism appears to change from a solid-state diffusion process to a liquid-state process. For both salts, however, this transition occurs at a temperature slightly lower than the melting point due to supercooling. This will be discussed further in the context of the diffusion measurements.

Diffusion

Fig. 2 and 3 present the cation diffusion coefficients for MeEtImBr and MeEtImI obtained from ^{1}H NMR fringe field gradient (FFG) measurements. The cation diffusion coefficients for these salts exhibit two diffusion processes that are dependent on the thermal history of the sample. Measurements made upon cooling the salts show a steady decrease in diffusion with decreasing temperature, even below the DSC melting point of the material. Such behaviour is indicative of supercooling, and this was confirmed by inspection of the quenched material. Close inspection of the supercooled data reveals a slight curvature, implying a deviation from simple Arrhenius behaviour, as expected for the liquid between T_g and $2T_g$. Measurements made during heating of the crystallized sample resulted in higher diffusion coefficients than those measured in the supercooled liquid-state. In fact, the solid-state diffusion coefficients over this temperature region below the melting point are only slightly lower than the liquid-state value at the melting point. The slope of the solid-state line indicates a relatively low activation energy for the process. Furthermore, there is no significant change in the cation diffusivity as the solid melts, indicating that the cation is almost equally mobile
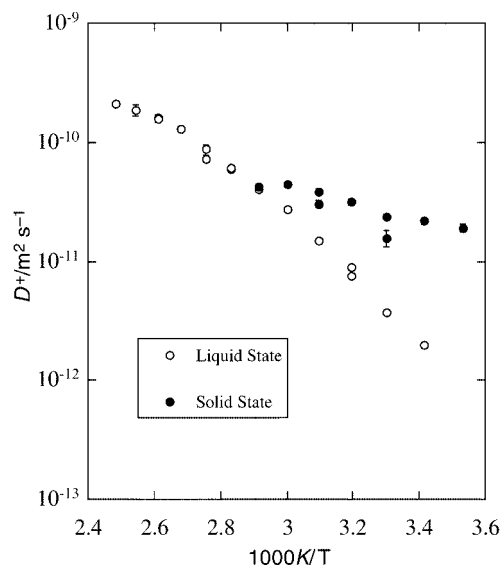
Fig. 2 Cation diffusion coefficients as a function of temperature for MeEtImBr. Data shown for both the liquid- and solid-states.
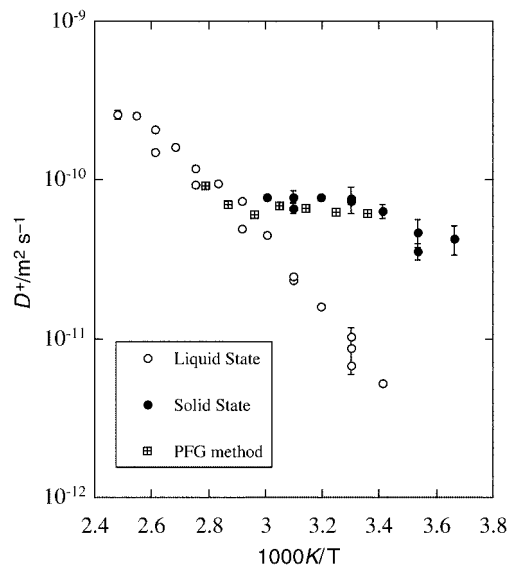

Fig. 3 Cation diffusion coefficients as a function of temperature for MeEtImI. Data shown for both the liquid- and solid-states. Results obtained from the PFG measurements are also shown for comparison.

in the solid and liquid states at the melting point. The one obvious change that does occur at the melting point is a change in activation energy (as observed from the change in slope) which suggests a change in the transport mechanism. No anion diffusion coefficients were obtained due to the inability to observe a bromide or iodide NMR signal in these samples. This is due to the fact that [127]I has a very large quadrupole moment and thus quadrupolar relaxation is dominant in these systems leading to linewidths typically of several kHz. Hence refocussing of the signal in the diffusion measurement is nearly impossible.

In measuring diffusion coefficients with the fringe field method, both diffusion and spin–spin (T_2) relaxation can contribute to the signal attenuation, particularly if T_2 is shorter than the τ values used in the experiment. Since T_2 in solids is often quite short, one might expect that these materials will also have small T_2 values. The pulsed field gradient method for measuring diffusion coefficients, however, does not suffer from the same T_2 interference and signal attenuation is solely due to diffusion. In order to confirm that these diffusion coefficients were not affected by T_2 relaxation, measurements were also conducted with the PFG diffusion technique. A comparison of these two diffusion techniques is also shown in Fig. 3 for MeEtImI. The diffusion results are very similar in the solid-state, confirming that the measurements from the fringe field method are indeed valid. It is also interesting to note that in the PFG measurements, supercooling was not observed probably due to the larger diameter of the sample tubes used. PFG measurements at elevated temperatures have also confirmed that the diffusion measured is indeed for the entire cation and not merely traces of other mobile proton impurities (*e.g.* water or acid). The spectra at higher temperatures are well enough resolved to allow an assignment of the peaks in accordance with the imidazole structure. All of these peaks lead to the same diffusion coefficient and there are no signs of another species in the spectra. As the temperature is decreased, the lines broaden and start to coalesce; however the basic spectrum characteristics are unchanged. This type of diffusion of large organic molecules has previously been found in molecular plastic crystals investigated using tracer diffusion and NMR techniques.[5]

Discussion

As outlined in the introduction, ion diffusion in crystalline solids typically occurs *via* discrete jumps.[2,3] In the liquid state,

however, diffusion involves the collective rearrangement of small sections of the material.[22] For MeEtImBr and MeEtImI, a step in the conductivity data is observed upon melting (Fig. 1), although the increase is only slight, σ changing by only a factor of 2 to 3. While this step corresponds to a change in the transport mechanism, it appears that ionic motion is still very significant in the solid-state for these two salts. This is further supported by the cation diffusion measurements for these salts (Fig. 2 and 3) which also indicate an almost liquid-like cation mobility in the solid-state. Unlike the conductivity data, however, there is no step increase in the diffusion coefficient at the melting point; in fact the diffusion process changes only its activation energy at the melting point. The cation diffusion coefficients in the solid-state are therefore almost the same as those observed above the melting point and actually greater than those observed in the supercooled state.

The diffusion measurements therefore imply little change in the cation mobility on melting, in contrast to the step increase in conductivity. Hence the mobility alone cannot account for conductivity behaviour through this transition. From the Nernst–Einstein equation [eqn. (3)], it can be seen that conductivity is dependent not only on the diffusion coefficients, D_+ and D_-, but also on the concentration of charge carriers, c_+ and c_-, involved in the conduction process:

$$\sigma = \frac{(D_+ c_+ + D_- c_-)q^2}{kT} \qquad (3)$$

where q is the ionic charge, k is the Boltzmann constant and T is temperature. Therefore, the lower absolute conductivity in the solid-state must be the result of fewer mobile charge carriers.

In the solid-state, two cation species can be hypothesized to exist: those that are involved in maintaining the crystal lattice and those that are able to diffuse through this matrix. The distinction between the two types may be only one of timescale, the mobile species perhaps only remaining so for short periods of time (but longer than the NMR probe timescale) corresponding to the brief presence nearby of a mobile vacancy. The immobile fraction is not detected in the NMR diffusion measurements as the resultant signal is too broad. Therefore, it is only the mobile cation component that can be observed.

The number of charge carriers available for conduction can therefore be analysed by monitoring the NMR signal intensity; if there is a change in the number of mobile charge carriers as
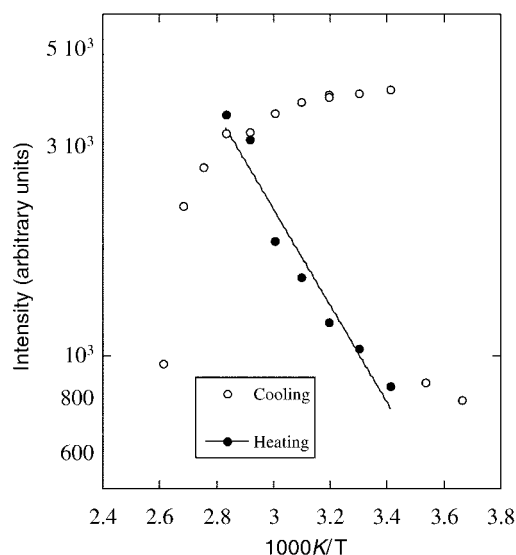
Fig. 4 Temperature dependence of NMR signal intensities measured upon cooling and heating for MeEtImBr. The line indicates the data fitted with eqn. (4).

the temperature increases, one would expect to observe a change in the signal intensity. The signal intensities for these two salts were measured upon heating and cooling of the samples, and the results are shown in Fig. 4 and Fig. 5. Upon cooling the samples from 403 K down to room temperature, the signal intensity showed a relatively small change with temperature, even below the expected melting point of the material, and this coincides with the steady decrease in diffusion coefficient observed (see Fig. 2 and 3) which suggests a supercooling of the sample. At a certain level of undercooling, the materials crystallise, as highlighted by a sudden decrease in signal intensity. This transition temperature occurred between 283 and 293 K, approximately 70 K below the DSC melting points of the materials. Subsequent heating of the sample resulted in a steady increase in signal intensity up to the melting point. Once the temperature had exceeded the melting point, the intensity then began to decrease slightly. The increase in signal intensity with temperature in the solid-state suggests that more cations are becoming mobile, thus increasing the
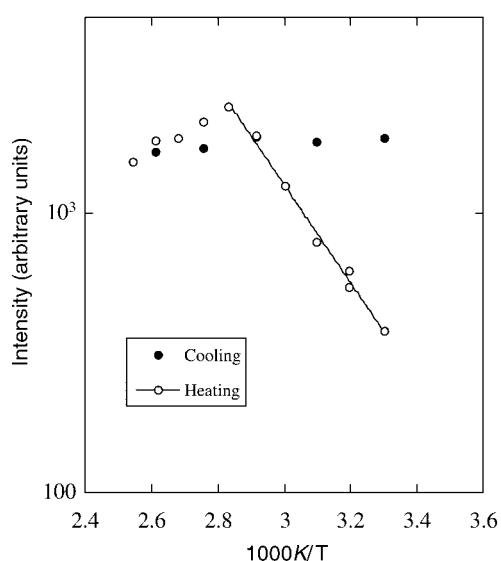

Fig. 5 Temperature dependence of NMR signal intensities measured upon cooling and heating for MeEtImI. The line indicates the data fitted with eqn. (4).

Table 1 Parameters for calculating ion concentration from eqn. (4)

Salt/MeEtImX	N/ions cm^{-3}	Q_v/kJ mol^{-1}
MeEtImBr	5.88×10^{24}	21.0 ± 2.2
MeEtImI	5.11×10^{26}	34.2 ± 1.9

concentration of available charge carriers. The origins of this are discussed further below.

In light of the NMR signal intensity results, it is possible to propose a model for ion transport in these materials. MeEtImBr and MeEtImI are isomorphous and the crystal structures appear to form alternating cation and anion layers that are held together by intermolecular hydrogen bonding.[18] One can envisage that the presence of vacancies in these layers would provide a suitable 2-dimensional pathway for ion diffusion. Thus a vacancy model would be most appropriate to describe the transport properties of these materials. The formation of vacancies is a temperature dependent process and can be calculated using eqn. (4):[23]

$$N_v = N \exp\left(\frac{-Q_v}{RT}\right) \qquad (4)$$

where N_v is the number of vacancies, N is the total number of atomic sites, Q_v is the activation energy (vibrational energy) for vacancy formation, R is the gas constant and T is temperature. As the data in Fig. 4 and 5 show a linear relationship when plotted as log (Intensity) *versus* $1/T$, it would seem that this equation is appropriate for modelling the increase in signal intensity. The concentration of mobile ions in the solid-state was determined by fitting the NMR signal intensity data with the vacancy formation equation using the parameters shown in Table 1. Lines indicating the fitting of eqn. (4) to the data are also shown in Fig. 4 and 5.

While these signal intensity data are representative of the change in the proportion of mobile cations in these materials, they do not indicate the concentration of *anions* that may contribute to the conductivity. As mentioned earlier, in the solid-state it is possible that the anion may be immobile, as indicated by the inability to detect an ^{127}I NMR signal. However, one cannot exclude the possibility that the anions are indeed mobile and that the lack of detection *via* NMR is due to experimental difficulty as a result of the large quadruple moment leading to efficient relaxation. For example, if T_1 and T_2 are very short, then a measurement would not be possible; typically even solutions of iodide compounds have relaxation times less than 1 ms.

In an attempt to establish the nature of conduction in these materials, two alternative assumptions may be made regarding the mobility of the ions; (i) both ions are diffusing at a similar rate, or alternatively (ii) only the cation (MeEtIm$^+$) is mobile. Based on these assumptions, solid-state conductivities were calculated from the diffusion coefficients and signal intensity data using the Nernst–Einstein equation [eqn. (3)]. Above the melting points, the concentration of mobile species was determined from the densities of the materials[15] and the diffusion coefficients of both species were taken to be the liquid-state values for the cation. A comparison of the calculated conductivities and the measured conductivities reveals some interesting behaviour (Fig. 6 and Fig. 7). The calculation assuming that both ions are mobile in the solid-state generally overestimates the conductivity in the solid-state. However, if it is assumed that only the cation is mobile, the calculated values are consistent, within the scatter of the measurements, with the measured conductivities. (Note that in the iodide case conductivity measurements just below the melting point are of the supercooled liquid). The trends quite clearly suggest, therefore, that the conductivity in the solid-state is the result of cation diffusion and that the charge carrier concentration
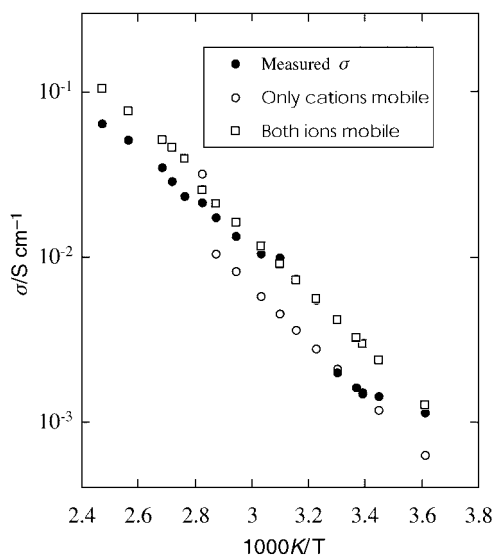
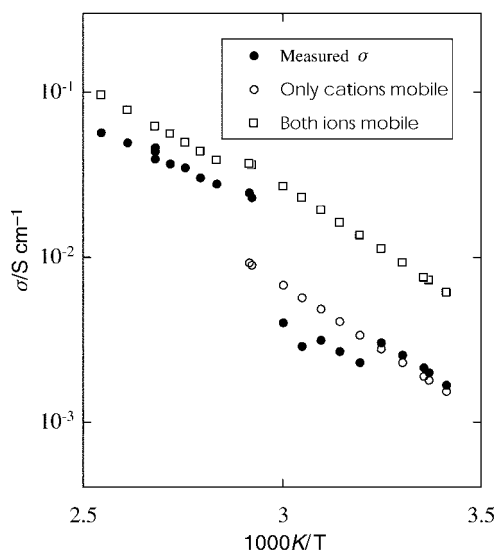**Fig. 6** A comparison of the measured and calculated conductivities for MeEtImBr.

Fig. 7 A comparison of the measured and calculated conductivities for MeEtImI.

Fig. 8 Extended crystal lattice for MeEtImI (the hydrogens have been removed for clarity) (a) viewed down the *a* axis, (b) viewed down the *b* axis. One of the MeEtIm cations has been removed to indicate the presence of a cation vacancy. The iodide ions are shown in a space fill view using the I⁻ van der Waals radius. The arrow indicates that another cation from a lower layer is capable of moving into the vacancy *via* a 180° rotation and simultaneous translation.

can be adequately estimated from the signal intensity in the fringe field NMR diffusion experiments. The anions in this case would seem to be relatively immobile and are therefore probably involved in maintaining the crystal lattice through which the cations are diffusing.

The differences between measured and calculated conductivity above the melting point are discussed in detail in another publication[15] and are most likely the result of ionic associations in the salt. Ion associations are expected in the molten state such that the actual number of ions contributing to the conductivity is only a fraction of the total number of ions in the melt.

In both cases, the lack of significant temperature dependence for diffusion in the solid state (Fig. 2 and 3) indicates that the activation barrier for the ionic motion or 'jump' is quite low (~ 10 kJ mol^{-1}). A view of the extended MeEtImI crystal lattice is given in Fig. 8 derived from data in reference 24. Given the almost planar shape of the imidazolium cation and the layered structure of the crystal it could be envisaged that anion and/or cation motion could occur through sliding of ions along the rows seen in Fig. 8a. However, a space-filled view of this structure indicates that such motions are severely hindered
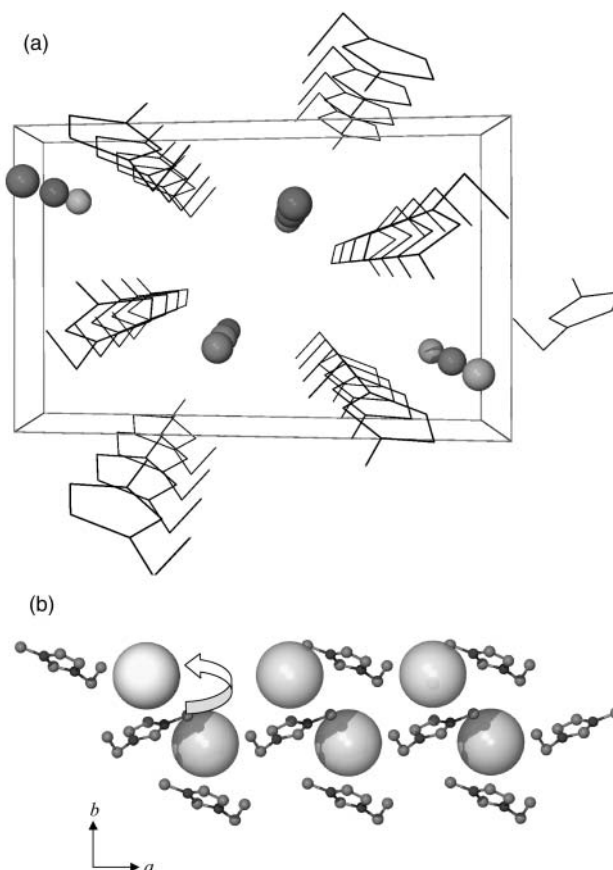
due to overlap of van der Waals radii during the motion. Fig. 8b shows a view along the *a*–*b* plane of the crystal in which it is possible that, in the presence of a vacancy defect, a sliding motion accompanied by a 180° rotation of the cation (as shown by the arrow) can also lead to facile cation motion from one site to a vacant neighbouring site. Such rotary motions can be thought of as being precursors to full rotations of the molecular cations on their lattice sites, a phenomenon suggested to lead to plastic crystal behaviour in some systems. Indeed such behaviour has previously been associated with the presence of vacancy defects in fast ion organic conductors[8] and molecular plastic crystals.[5]

Since it appears that cation motion could be relatively facile in this system *via* a vacancy diffusion mechanism, the temperature dependence of the conductivity in the solid-state can therefore be attributed predominantly to the temperature dependence of the mobile charge carrier concentration. The Arrhenius fits of the NMR intensity data confirm that the number of mobile cations increases with increasing temperature, suggesting vacancy formation with an activation energy of 21 kJ mol^{-1} in the case of MeEtImBr and 34 kJ mol^{-1} for MeEtImI. The mechanism of formation of these vacancies is not clear at present, especially given that this level of conductivity is not uniformly observed in related MeEtIm salts.[13] However, it is known that orientational and/or rotational disorder in organic solids can assist in vacancy formation. In the related pyrrolidinium family of compounds we have shown that plastic crystal behaviour, which is attributable to defect formation (including vacancies), is prevalent.[13] In these compounds the plastic phases are a

result of one or more solid–solid phase transitions. It is interesting to note that in the case of MeEtImI a solid–solid phase transition is seen at about 242 K, although the entropy of this transition is considerably smaller than that observed in the pyrrolidinium compounds Also, the final entropy of fusion of MeEtImI is more than twice the value recognized by Timmermans' criterion ($\Delta S_f < 20$ J K^{-1} mol^{-1}) for plastic crystal behaviour.[4] Although we have previously observed $\Delta S_f > 20$ J K^{-1} mol^{-1} in plastic crystal materials, the extra entropy of fusion in those cases has been suggested to result from the anion degrees of freedom (rotational and translational) that are activated in the melt. Since the halides in the present systems appear to be predominantly immobile in the solid-state then the translational degrees of freedom that become active in the melt would only partly account for the higher entropy of fusion as compared to Timmermans' criterion; the remainder must therefore be associated with the onset of full rotational and translational motions of the cations. The room temperature crystal structure data[18] also show no evidence of orientational disorder in MeEtImI. It thus appears that there is no direct evidence of wholesale rotatory motions in the higher temperature phase in these compounds. Nonetheless the comparison to the pyrrolidinium family of compounds confirms the feasibility of the rotatory motion of the mobile cation required for its movement into a vacant cation site.

Summary

High solid-state conductivities have been observed in the MeEtImBr and MeEtImI salts, with values of the order of 10^{-3} S cm^{-1}. Near the melting point, there is an abrupt change in the conduction mechanism and an associated sudden increase in conductivity. Cation diffusion in the solid-state was found to occur readily, and was faster than the diffusion observed in the supercooled liquid at any given temperature. This solid-state behaviour makes this family of materials one of the most conductive at room temperature and is consistent with the notion of fast-ion conductors; a vacancy diffusion process being responsible for ion transport. A change in the diffusion mechanism was also observed near the melting point, but this was not accompanied by a sudden increase in the cation diffusion coefficients nor a large step in conductivity. Through the use of the Nernst–Einstein equation, the conductivity was modelled from the diffusion coefficients. Although no anion diffusion coefficients were able to be measured, the conductivity was adequately predicted by assuming that only the cation is mobile and that the charge carrier concentration increases with temperature due to vacancy formation.

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