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N,*N*-Dimethylpyrrolidinium hydroxide: a highly conductive solid material at ambient temperature

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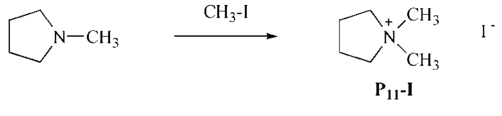
***N*,*N*-Dimethylpyrrolidinium hydroxide ($P_{11}OH \cdot 4H_2O$) was found to exhibit high ionic conductivity in the solid state (7×10^{-3} S cm^{-1} at 25 °C) and unusual thermal properties, and ^{2}H solid state NMR measurements indicate liquid-like mobility of the deuterium species in the solid state of $P_{11}OD \cdot 4.5D_2O$.**

New families of plastic crystal ionic compounds, involving the *N*-alkyl-*N*-methylpyrrolidinium cation along with, for example, the bis(trifluoromethylsulfonyl)amide anion, the hexafluorophosphate anion, or the heavy halide ions, have been synthesised and characterised in our group recently.[1,2] Some members of the family are molten at room temperature, and the highest conductivity for these room temperature molten salts was found to be 2×10^{-3} S cm^{-1} at 25 °C.[1] Many of these compounds also exhibit one or more thermal transitions prior to melting, and the final entropy of melting for some of these salts is near or less than 20 J K^{-1} mol^{-1}, behaviour which has previously been associated with the formation of plastic crystal phases.[3] Many of the compounds exhibit high ion conductivity in the solid state, in particular in the plastic phases. The origin of this ion mobility is thought to be related to lattice vacancies created in the solid state, an occurrence which is encouraged by the existence of a plastic phase but is not limited to this situation. In a recent example of the latter case we have shown[2a] that in the iodide and bromide salts of the ethylmethylimidazolium cation, solid state diffusion of the cation in the phase just below the melting point was more rapid than in the super-cooled liquid at the same temperature.

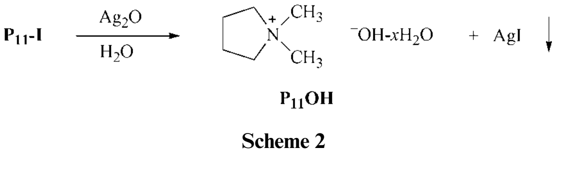
A member of this broad family of salts, *N*,*N*-dimethylpyrrolidinium hydroxide was investigated in this work as a possible alkaline component for use in preparation of solid alkaline electrolytes. Solid alkaline electrolytes can be used in several different electrochemical devices, such as alkaline fuel cells[4] and secondary air–metal hydride batteries.[5] Such alkaline electrochemical devices are reported[4,5] to be characterised by many advantages compared to their acid electrolyte analogues, such as high electrical efficiency, high energy density, high specific capacity, lack of memory effect and low toxicity. There were three reasons for choosing the pyrrolidinium cation as the basis for an organic hydroxide in this work: 1) the pyrrolidinium hydroxides may have better compatibility than inorganic hydroxides with organic or polymeric materials in preparation of solid alkaline electrolytes; 2) the alkylmethylpyrrolidinium cations of the hydroxides are expected to have good electrochemical stability, as the electrochemical window of stability is in excess of 5.5 V for pyrrolidinium bis(trifluoromethylsulfonyl)amide analogues;[1] 3) if pyrrolidinium hydroxide exhibits plastic crystal behaviour, as with other pyrrolidinium salts investigated in our previous work,[1,2] high conductivity is therefore expected.

N,*N*-Dimethylpyrrolidinium hydroxide was prepared by the reactions shown in Schemes 1 and 2. To investigate these compounds by solid state NMR, *N*,*N*-dimethylpyrrolidinium deuteroxide ($P_{11}OD$) was also synthesised *via* the same method as that of $P_{11}OH$, but using D_2O instead of H_2O in the reaction (Scheme 2). Further details of the preparation of P_{11}-I (Scheme 1) are described elsewhere.[1a] An example of the reaction in Scheme 2 is as follows: 9.00 g (0.0396 mol) P_{11}-I was dissolved in 15 g distilled water, and 4.70 g (0.0203 mol) silver oxide (Aldrich) was added into the solution; the mixture was stirred at room temperature for 4 h; the reaction mixture was filtered to remove silver iodide and residual silver oxide from the liquid, and the filtrate was distilled with water pump and vacuum pump at room temperature to remove water; the final product was dried under vacuum (~80 Torr) at 60 °C (boiling point of water under 80 Torr is 47 °C[6]) for at least two days and thereafter kept in a N_2 atmosphere dry box; 5.67 g of $P_{11}OH \cdot 4H_2O$ was obtained (yield 76%); ^{1}H-NMR (D_2O, δ/ppm relative to TMS): 3.55–3.49 (m, 4H), 3.15 (s, H^6), 2.28–2.21 (m, 4H); electrospray mass spectroscopy (MeOH, cone 20 V): ES$^+$ 99.7, 231.1, 275.2 *m*/*z*. The $P_{11}OH$ sample, after the vacuum treatment, was found to contain four crystal water molecules for each $P_{11}OH$ molecule by the traditional acid–base titration method,[7] and $P_{11}OD$ contained 4.5 crystal D_2O molecules for each $P_{11}OD$ molecule.

A Perkin-Elmer Differential Scanning Calorimeter (DSC) Model 7 was used to measure the thermal properties of $P_{11}OH \cdot 4H_2O$ and $P_{11}OD \cdot 4.5D_2O$ at a scanning rate of 10.0 °C per minute. All the samples were sealed in stainless steel DSC pans under a nitrogen atmosphere. Conductivity measurements were carried out in a locally made stainless steel conductance cell, which was sealed in an air-tight container under a nitrogen atmosphere. Conductances of the samples were obtained by measurement of the complex impedance of the cell between 20 Hz and 1 MHz using a HP4284A Impedance Meter, and determined from the first real axis intercept in the Nyuist plot of the impedance data. A Bruker AM-300 MHz NMR



Scheme 1



Scheme 2

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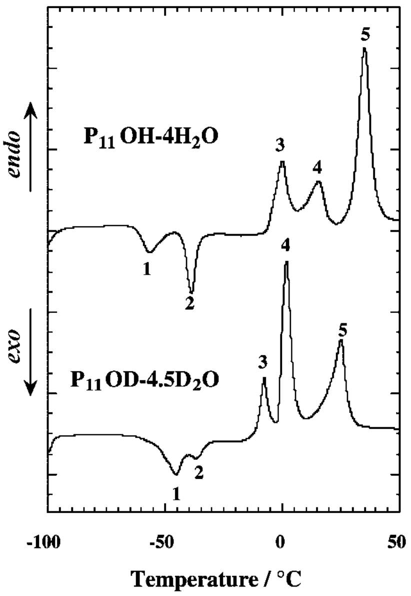

Fig. 1 Differential scanning calorimeter thermograms of *N*,*N*-dimethylpyrrolidinium hydroxide ($P_{11}OH{\cdot}4H_2O$) and *N*,*N*-dimethylpyrrolidinium deuteroxide ($P_{11}OD{\cdot}4.5D_2O$).

spectrometer was used in the measurements of the solid state NMR spectra in the case of the $P_{11}OD{\cdot}4.5D_2O$ sample.

Fig. 1 shows the DSC thermograms of $P_{11}OH{\cdot}4H_2O$ and $P_{11}OD{\cdot}4.5D_2O$, and the corresponding thermal property data for those compounds are presented in Table 1. It can be seen from Fig. 1 that $P_{11}OH{\cdot}4H_2O$ and $P_{11}OD{\cdot}4.5D_2O$ exhibit multiple crystallisation and solid–solid transitions below their melting temperatures. For $P_{11}OH{\cdot}4H_2O$, the exotherm at −62 °C (peak 1 in Fig. 1) is associated with the crystallisation from amorphous solid to ordered crystal, and this crystal phase is believed to be a metastable phase, as there is a subsequent stronger exotherm at −42 °C (peak 2 in Fig. 1) in which it transforms to the stable crystal phase. For $P_{11}OD{\cdot}4.5D_2O$, the crystallisation behaviour is very similar to that of $P_{11}OH{\cdot}4H_2O$, as we would expect. However, the two crystallisation peaks of $P_{11}OD{\cdot}4.5D_2O$ are closer and appear at higher temperatures than $P_{11}OH{\cdot}4H_2O$, as shown in Fig. 1. The different temperatures of crystallisation for $P_{11}OD{\cdot}4.5D_2O$ and $P_{11}OH{\cdot}4H_2O$ are expected due to the deuteration effect in the sample of $P_{11}OD{\cdot}4.5D_2O$. As an example of the deuteration effect, it has been reported[8] that deuterium oxide has a higher melting point (3.81 °C) and higher boiling point (101.4 °C) than normal water, and ΔS_f of D_2O (22.7 J K^{-1} mol^{-1}) is slightly larger than that of H_2O (22.0 J K^{-1} mol^{-1}). It was also reported[8] that solid–solid phase transitions often exhibit appreciable isotope effects, and an interesting example is that NH_4Br exhibits two solid–solid transitions at −38 °C and 138 °C respectively, while ND_4Br shows three solid–solid transitions at lower temperatures (−104 °C, −58 °C and 125 °C respectively). Therefore it is not surprising that the two solid–solid transition peaks and the melting peak of $P_{11}OD{\cdot}4.5D_2O$ appear at lower temperature (−11 °C, −2 °C and 18 °C respectively) than that of $P_{11}OH{\cdot}4H_2O$ (−6 °C, 6 °C and 30 °C) as shown in Fig. 1 and Table 1. These differences between $P_{11}OD{\cdot}4.5D_2O$ and $P_{11}OH{\cdot}4H_2O$ may also result from the fact that they have different amounts of crystal water molecules for each hydroxide molecule.

As shown in Fig. 1, samples of $P_{11}OH{\cdot}4H_2O$ and $P_{11}OD{\cdot}4.5D_2O$ exhibit two solid–solid transitions (peak 3 and peak 4 in Fig. 1) before melting. This phenomenon has been observed as typical of plastic crystal behaviour in the other pyrrolidinium based systems,[1,2] and has also been found in many plastic crystal compounds, for example, such as alkylammonium chlorides[9] and alkylammonium bromides.[10] It is noticeable (see Table 1) that the entropy of melting (ΔS_f) of $P_{11}OH{\cdot}4H_2O$ and $P_{11}OD{\cdot}4.5D_2O$ is larger than the value of 20 J K^{-1} mol^{-1}, in contrast to "normal" plastic crystals.[3] In our previous investigation on plastic crystals,[1,2] it was found that ΔS_f values for *N*-alkyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide were also larger than 20 J K^{-1} mol^{-1}, but ΔS_f values for the hexafluorophosphate with the same *N*-alkyl-*N*-methylpyrrolidinium cation were less than 20 J K^{-1} mol^{-1}. Comparing these previous results to the present work, it seems that the solid–solid transitions of $P_{11}OH{\cdot}4H_2O$ and $P_{11}OD{\cdot}4.5D_2O$ before melting are possibly due to orientational disordering[11] in plastic crystal phases in these compounds. The larger value of ΔS_f found in these compounds is probably associated with the additional configurational degrees of freedom associated with the anion, or associated with the crystal water molecules in the case of the $P_{11}OH{\cdot}4H_2O$ and $P_{11}OD{\cdot}4.5D_2O$ studied in this work.

On the other hand, however, it has been reported[12–14] that tetramethylammonium hydroxide presents several crystalline forms with different contents of crystal water ($Me_4NOH{\cdot}xH_2O$, $x = 1$, 2, 2.33, 4, 4.6, 5, 6.67, 8.75 and 10), and forms a complex phase diagram for the $Me_4NOH{\cdot}xH_2O$ system, with several eutectic/peritectic compositions. The compound structure of $P_{11}OH$ is quite similar to that of Me_4NOH, and it is therefore also possible that $P_{11}OH$ could form a complex system of compounds with different numbers of crystal waters for each $P_{11}OH$ molecule. Therefore the endothermic peaks for both $P_{11}OH$ and $P_{11}OD$ before melting (peak 3 and peak 4 in Fig. 1) may be associated with eutectic or peritectic transitions of the compounds. This hypothesis seems more likely valid for the $P_{11}OD$ sample, as the melting peak of $P_{11}OD$ (peak 5 for $P_{11}OD$ as shown in Fig. 1) is broader with lower leading edge slope than that of $P_{11}OH$.

Another property of plastic crystals is that[11] they readily deform (or creep) under an applied force (hence "plastic") below their melting point. The materials discussed in this work apparently have plastic properties, as they readily yield under pressure. These materials also appear to flow under their own weight despite being apparently in their solid state. The physical appearance of these materials is certainly not one of a liquid–solid mixture.

Conductivity as a function of temperature for $P_{11}OH{\cdot}4H_2O$ and $P_{11}OD{\cdot}4.5D_2O$ samples is presented in Fig. 2. (The arrows with numbers in Fig. 2 indicate the temperatures of the corresponding peaks shown in Fig. 1.) As shown in Fig. 2, conductivities of the two solid samples are as high as

Table 1 Some thermal properties of *N*,*N*-dimethylpyrrolidinium hydroxide ($P_{11}OH{\cdot}4H_2O$) and *N*,*N*-dimethylpyrrolidinium deuteroxide ($P_{11}OD{\cdot}4.5D_2O$) from the DSC measurements

	1		2		3		4		5	
Peak[a]	T^b /°C	ΔS	T/°C	ΔS	T/°C	ΔS	T/°C	ΔS	Mp/°C	ΔS_f
$P_{11}OH{\cdot}4H_2O$	−62	14	−42	20	−6	28	6	16	30	41
$P_{11}OD{\cdot}4.5D_2O$	−54	—	—	—	−11	9	−2	32	18	26

[a]Peak numbers in this table correspond to the numbers indicated in Fig. 1. [b]Temperatures of all peaks in this table were taken as the value of onset from Fig. 1 (±1 °C, including mp). ΔS = entropy of phase transition/J K^{-1} mol^{-1} (±5%); ΔS_f = entropy of fusion/J K^{-1} mol^{-1} (±5%).

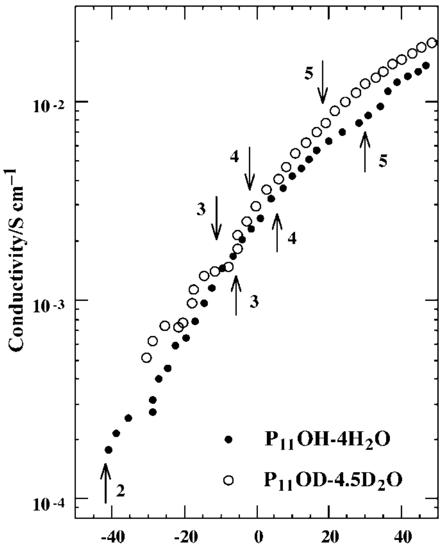

Fig. 2 Conductivity *versus* temperature for *N*,*N*-dimethylpyrrolidinium hydroxide ($P_{11}OH{\cdot}4H_2O$) and *N*,*N*-dimethylpyrrolidinium deuteroxide ($P_{11}OD{\cdot}4.5D_2O$) samples. (The arrows with numbers are used in this figure to indicate the position of the peaks shown in Fig. 1.)

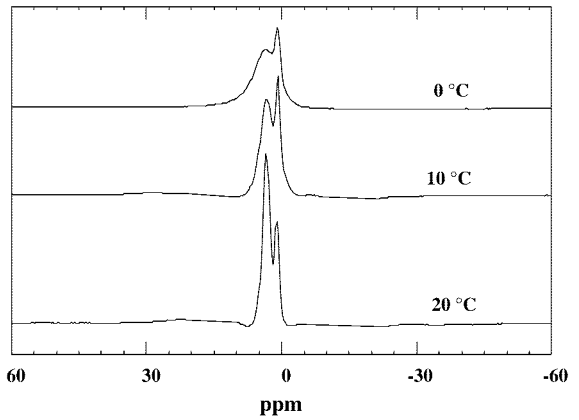

Fig. 3 ^2H static spectra of *N*,*N*-dimethylpyrrolidinium deuteroxide ($P_{11}OD{\cdot}4.5D_2O$) in solid state (10 °C and 0 °C) and liquid state (20 °C) at 46 MHz.

7×10^{-3} S cm^{-1} at temperatures just below their respective melting points. The conductivity of the $P_{11}OD{\cdot}4.5D_2O$ sample is slightly higher than that of $P_{11}OH{\cdot}4H_2O$, which is consistent with the thermograms in Fig. 1, since the solid–solid transition and melting peaks for $P_{11}OD{\cdot}4.5D_2O$ appear at lower temperatures than $P_{11}OH{\cdot}4H_2O$, hence $P_{11}OD{\cdot}4.5D_2O$ would be expected to present higher mobility than $P_{11}OH{\cdot}4H_2O$ at the same temperature. The most distinguishing behaviour for $P_{11}OH{\cdot}4H_2O$ and $P_{11}OD{\cdot}4.5D_2O$ samples in the conductivity measurements is that the conductivity of $P_{11}OD{\cdot}4.5D_2O$ increases smoothly in the temperature range of melting, whilst for $P_{11}OH{\cdot}4H_2O$ the conductivity curve presents a small step at the melting point. Usually conductivity of a solid ionic material increases very sharply when the sample melts. For example, it was found[1] that the conductivity of *N*-methyl-*N*-propylpyrrolidinium bis(trifluoromethylsulfonyl)amide increases from 7×10^{-5} S cm^{-1} to 9×10^{-4} S cm^{-1} during melting. We conclude from this that, like the methylethylimidazolium iodide and bromide salts mentioned above,[2a] the solid states of these hydroxide compounds possess some mechanism of ion transport that is almost as facile as that operative in the liquid state.

^2H static spectra of $P_{11}OD{\cdot}4.5D_2O$ at temperatures above and below the melting point (18 °C) are shown in Fig. 3, in which the $P_{11}OD{\cdot}4.5D_2O$ sample exhibits two sharp peaks both in the solid (10 °C) and liquid state (20 °C). By comparison of the chemical shifts of the two peaks in Fig. 3 (3.4 ppm and 1.1 ppm respectively) with that of D_2O (2.7 ppm) measured under the same conditions, the high field peak in Fig. 3 (3.4 ppm) is more likely associated with crystal D_2O in the $P_{11}OD{\cdot}4.5D_2O$. It should be pointed out that, as shown in Fig. 3, the spectrum of $P_{11}OD{\cdot}4.5D_2O$ at 10 °C does not present the typical quadrupolar splitting pattern, as expected for normal solid deuterium samples in the measurement of solid-state ^2H NMR.[15] Furthermore, the spectral pattern of $P_{11}OD{\cdot}4.5D_2O$ in the solid state is nearly the same as that of the sample in the liquid state. This ^2H NMR result indicates high, almost liquid-like, mobility of both OD^- and D_2O species in the solid sample prior to melting, in accord with the unusually high conductivity of the sample in the solid state. It is expected that this also reflects OH^- and H_2O mobility in $P_{11}OH{\cdot}4H_2O$ since $P_{11}OH{\cdot}4H_2O$ exhibits thermal properties and ionic conductivity similar to that of $P_{11}OD{\cdot}4.5D_2O$.

Further investigation of these compounds is currently under way to further elucidate the conduction mechanism in the alkaline compounds.

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