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A series of N-methyl-N-alkylpyrrolidinium nonafluoro-1-butanesulfonate salts were synthesised and characterised. The thermophysical characteristics of this family of salts have been investigated with respect to potential use as ionic liquids and solid electrolytes. N-Methyl-N-butylpyrrolidinium nonafluoro-1-butanesulfonate (p1,4NfO) has the lowest melting point of the family, at 94 °C. Electrochemical analysis of p1,4 NfO in the liquid state shows an electrochemical window of ~ 6 V. All compounds exhibit one or more solid–solid transitions at sub-ambient temperatures, indicating the existence of plastic crystal phases.

Introduction

The search for new materials with combinations of advantageous properties with respect to electrolyte applications coincides with a large expansion in the range and diversity of molten salts (or ionic liquids if their melting point is below 100 °C) that have recently been identified. Properties such as negligible vapour pressure, thermal stability, electrochemical stability and, importantly, ionic conductivity are recognised as critical characteristics if these materials are to not only match current electrolytes, but to surpass them. Ionic materials having several solid phases, some of which exhibit distinctly higher conductivity than the low temperature phase, often also display plastic material properties as described by Timmermans. The ionic conductivity of such solid electrolytes is thought to be intimately linked with the nature and degree of molecular rotational motions within the crystal lattice. These temperature dependent crystal lattice alterations and phase changes can be observed using differential scanning calorimetry.

The pyrrolidinium cation (1) has gained attention as an ionic liquid and plastic crystal former with anions such as tetrafluoroborate, hexafluorophosphate and bis(trifluoromethanesulfonfyl)amide. These low melting salts exhibit high ionic conductivity in both solid and liquid phases and have received attention for use as electrolytes in a range of applications including lithium batteries. In the battery application the pyrrolidinium cation coupled with the fluorinated anion in particular provide stable cycling of Li metal in the ionic liquid, an observation which may enable a safe lithium metal battery technology. Some of the plastic phases are also able to act as hosts for dopant ions such as Li, where the Li ion in this case can show fast-ion conduction properties. It has, therefore, become of interest to identify these useful electrochemical and transport properties in a range of related compounds.

The nonafluoro-1-butanesulfonate anion (nonaflate, 2) belongs to an expanding group of fluorinated anions including tetrafluoroborate, hexafluorophosphate and bis(trifluoromethanesulfonfyl)amide. The nonaflate anion is far more stable than the very common tetrafluoroborate and hexafluorophosphate anions. For example, hexafluorophosphate salts have been shown to be susceptible to hydrolysis even under relatively mild conditions. Warming an aqueous solution of a PF₆ salt results in considerable formation of HF over several hours. Nonaflate salts of organic cations were first prepared as a by-product from the reaction between nonafluoro-1-butanesulfonyl fluoride, 4-(dimethylmethoxysilyl)-butylamine and an amine such as; pyridine, triethylamine, 1-methylimidazole, 1-methylmorpholine and 1-methylpyrrolidine. A number of imidazolium nonaflate salts have previously been prepared, by the metathesis of 1-alkyl-3-methylimidazolium bromide and the readily available potassium salt of nonafluorobutanesulfonic acid. Wasserscheid and Hilgers have also described the synthesis of perfluoroalkylsulfonate salts with many different cations.

N-methyl-N-alkylpyrrolidinium cation (1)  Nonafluoro-1-butanesulfonate anion (nonaflate, 2)
Table 1  Thermal properties of pyrrolidinium nonaflate salts

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abbrev.</th>
<th>$T_p$ °C</th>
<th>$T_m$ °C</th>
<th>$T_s$ °C</th>
<th>$T_u$ °C</th>
<th>$T_u$ °C</th>
<th>$T_u$ °C</th>
<th>$q_A$I K⁻¹ mol⁻¹</th>
<th>$T_{dec}$ °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N,N$-Dimethylpyrrolidinium nonaflate</td>
<td>p1,2NfO</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>24</td>
<td>198</td>
<td>26</td>
<td>360</td>
</tr>
<tr>
<td>$N$-Ethyl-$N$-methylpyrrolidinium nonaflate</td>
<td>p1,3NfO</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>45</td>
<td>182</td>
<td>26</td>
<td>360</td>
</tr>
<tr>
<td>$N$-Propyl-$N$-methylpyrrolidinium nonaflate</td>
<td>p1,4NfO</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>85</td>
<td>140</td>
<td>23</td>
<td>350</td>
</tr>
<tr>
<td>$N$-Butyl-$N$-methylpyrrolidinium nonaflate</td>
<td>p1,5NfO</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>47</td>
<td>116</td>
<td>34</td>
<td>350</td>
</tr>
<tr>
<td>$N$-Pentyl-$N$-methylpyrrolidinium nonaflate</td>
<td>p1,6NfO</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>60</td>
<td>120</td>
<td>30</td>
<td>350</td>
</tr>
<tr>
<td>$N$-Hexyl-$N$-methylpyrrolidinium nonaflate</td>
<td>p1,7NfO</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>45</td>
<td>109</td>
<td>24</td>
<td>350</td>
</tr>
<tr>
<td>1-Ethyl-3-methylimidazolium nonaflate</td>
<td>emiNfO</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>60</td>
<td>130</td>
<td>29</td>
<td>350</td>
</tr>
<tr>
<td>1-Butyl-3-methylimidazolium nonaflate</td>
<td>bmiNfO</td>
<td>20b</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>45</td>
<td>116</td>
<td>34</td>
<td>350</td>
</tr>
</tbody>
</table>

$a$ Peak has shoulder.  $b$ See Bonhote et al.  $c$ Notes: all transitions quoted for peak temperatures.  $d$ $T_p$ = Glass transition (onset), $T_m$ = Temperature of crystallization (peak), $T_u$ = Solid–solid transition (peak), $T_{dec}$ = Decomposition temperature.

Alkali-metal nonaflate salts have been used in a wide variety of applications including; oil and water-proofing of textiles, fireproofing agents and organic electrolytes for batteries.

More recently, nonaflate ionic liquids have been used as fireproofing agents and organic electrolytes for batteries.

This paper describes the synthesis and characterisation of a novel series of $N$-alkyl-$N$-alkylpyrrolidinium nonaflates ($p_{1,x}$NfO). Thermophysical and electrochemical analyses were used to evaluate the compounds for potential use in a variety of electrolyte applications. For simplicity, the nomenclature of the prepared compounds has been abbreviated (see Table 1). The cation nomenclature is abbreviated to $p_{1,x}$, where $p$ indicates the pyrrolidinium cation, the subscript 1 indicates the $N$-methyl substituent and the $x$ indicates the carbon number of the $N$-alkyl substituent. The anion is abbreviated to NfO as used in previous publications. For example the $N$-methyl-$N$-butylpyrrolidinium nonaflate is denoted $p_{1,4}$NfO.

**Results and discussion:**

**Thermal analysis—melting point**

Fig. 1 displays melting point data as a function of alkyl chain length for the current series of nonaflates and also a number of other pyrrolidinium salts (PF$_6$, BF$_4$ and Nf$_2$). The melting points of the nonaflate salts decrease with increasing alkyl chain length up to $p_{1,4}$ NfO. This trend is also apparent for the other salts displayed, with the exception of a ‘dip’ in the tetrafluoroborate series.

For the nonaflate series, the $N$-methyl derivative ($p_{1,2}$NfO) and $N$-ethyl derivative ($p_{1,3}$NfO) melt at 198 °C and 176 °C respectively. The downward trend continues with a substantial drop in melting point for the $N$-propyl ($p_{1,4}$NfO) and $N$-butyl ($p_{1,5}$NfO) derivatives, which melt at 109 °C and 94 °C respectively. This relatively large drop in melting point (67 °C) between $p_{1,2}$NfO and $p_{1,3}$NfO is not unique to pyrrolidinium nonaflate salts. Significant melting point depressions between the $N$-ethyl and $N$-propyl derivatives are also found in pyrrolidinium hexafluorophosphates, $p_{1,2}$PF$_6$ (mp 200 °C) and $p_{1,3}$PF$_6$ (mp 113 °C), pyrrolidinium tetrafluoroborates, $p_{1,2}$BF$_4$ (mp 280 °C) and $p_{1,3}$BF$_4$ (mp 64 °C) and pyrrolidinium bis(trifluoromethanesulfonamides), $p_{1,2}$ TFSA (mp 86 °C) and $p_{1,3}$ TFSA (mp 12 °C). The melting points of the $p_{1,x}$NfO series therefore are only low enough to produce a sub 100 °C melting point in one case. The temperature range around 100 °C is of significant interest in some electrochemical applications. Nonetheless, mixing of cations, and in particular addition of a lithium salt to produce a typical lithium battery electrolyte will further lower the melting points.

**Thermal analysis—phase behavior**

Differential scanning calorimetry (DSC) traces from −120 °C to 60 °C and 60 °C to the melting point have been compiled in Fig. 2. All of the thermal data are summarised in Table 1. Employing phase nomenclature, as used previously, multiple solid phases are numbered sequentially from the highest temperature crystalline phase to the lowest temperature phase. The nonaflate salts were heated to 20 °C above the melting point then quenched and held at −100 °C before heating began. In Fig. 2 all the pyrrolidinium nonaflate salts exhibit multiple transitions below 60 °C and only a melting transition above 60 °C. All the salts in the series are in Phase 1 up to at least 90 °C, which may be important for solid electrolyte applications at moderate temperatures. Both the $N$-methyl and $N$-ethyl derivatives have two solid–solid transitions quite close together. The $N$-methyl derivative has two broad transitions between −1 °C and 24 °C, while $N$-ethyl has two quite sharp transitions at −59 °C and −51 °C. The $N$-propyl and $N$-butyl derivatives also have at least two solid–solid transitions but also display exothermic crystallisation at −22 °C and −4 °C respectively. The $N$-butyl, pentyl and hexyl (not shown)
The bis(trifluoromethane)sulfonamide \(18\) (38–43 J \(K^{-1} mol^{-1}\)) has quite sharp melting points compared to the other salts in the series.

The multiple phases seen in this series of salts are likely to arise from rotational motions of one or both of the ions. As observed in other compounds exhibiting this behavior, the increasing complexity of the rotator motions involved (e.g. uniaxial vs isotropic), with respect to either or both the ions present, generates a number of distinct rotator phases.\(^{13,18}\)

Each phase has entropy closer to the liquid state as the complexity approaches that of isotropic motion of both ions. This behavior makes these compounds very interesting from the point of view of ion conductors, in particular doped ion conductors.

The melting transitions for the series of nonaflates have entropy \(\Delta S_f\) values between 24 and 34 J \(K^{-1} mol^{-1}\). The \(\Delta S_f\) values are calculated by integration of the melting enthalpy \(\Delta H_f\) and the relationship \(\Delta S_f = \Delta H_f/T_m\).\(^{15}\)

Timmermans observed that materials which have entropies fit the plastic crystal definition as outlined by Timmermans.\(^{15}\) These values are sufficiently low to suggest that the nonaflate series are somewhat higher than the record low entropies for pyrrolidinium tetrafluoroborate salts (5–17 J \(K^{-1} mol^{-1}\)) often have sub-melting phases with special properties; these phases are also known as plastic crystal phases.\(^{14}\) The entropies of fusion for the nonaflate series are thermally stable, showing virtually no weight loss between 30 \(^\circ\)C and 350 \(^\circ\)C.

This thermal stability is at least as good as 1,3-dialkylimidazolium triflates\(^{23,30}\) and superior (~50 \(^\circ\)C higher) than other pyrrolidinium alkylsulfonate ionic liquids, i.e. mesylates and tosylates.\(^{31}\) The greater thermal stability of perfluoroalkylsulfonates compared to non-fluorinated alkylsulfonates is an advantage for higher temperature applications, or at least brief excursions to high operating temperatures.

### Cyclic voltammetry

Cyclic voltamograms are shown in Fig. 4A, B and C for \(p_{1,4}NfO\) cycled on a Pt working electrode at 150 \(^\circ\)C. Fig. 4A shows that the sample is completely stable between ~2.0 V and +2.3 V vs. \(Ag/Ag^+\). The lack of any oxidative or reductive processes in this potential range indicates not only electrochemical stability of the solvent but also an absence of impurities that would normally be reactive in this range.

Fig. 4B shows an extended cyclic voltammogram, which indicates an electrochemical window approaching 6.0 V. Oxidation processes at ~+2.75 V are followed by a corresponding reduction event at around ~1.59 V in the reverse scan. Reduction processes at around ~3.0 V are followed by a corresponding oxidation process around +1.0 V. The large potential differences between these melt breakdown processes and their corresponding reverse reactions indicate the strongly irreversible nature of the reactions involved.

Fig. 4C shows the result of extending the potential range to +5.0 V. The oxidation process resolves into a well-defined peak indicating a diffusion or kinetic limit to the process. Given the appearance of a corresponding reduction peak (commencing at ~1.0 V) and the fact that the reaction involves solvent molecules it is likely that the limit is imposed by reaction kinetics, possibly due to the formation of a solid passivating film. The peak from the corresponding reduction process
increases proportionately. Also of note is the similarity in appearance of the cyclic voltammograms for p1,4NfO and that of p1,4TFSA. The oxidation/reduction processes occur at almost identical potentials and behave in the same manner indicating similar reaction mechanisms are occurring in both materials.

Conductivity

Fig. 5 shows the conductivity behavior of p1,4NfO versus temperature. The phase I conductivity is quite low and relatively constant, over the temperature range 25 °C to 80 °C, having a conductivity of around $10^{-8} \text{ S cm}^{-1}$ at 25°C. Approaching the melt, conductivity increases to $5 \times 10^{-3} \text{ S cm}^{-1}$ in the liquid state. The DSC traces (Fig. 2) indicate the presence of plastic crystal phase I over a wide temperature range for these materials, particularly in the case of p1,2NfO (>200 °C), although that of p1,4NfO (~100 °C) is still appreciable. The presence of sufficient rotational disorder in these substances at room temperature to exhibit appreciable conductivity in the solid state makes them interesting candidates for lithium doping. Increases in conductivity of up to four orders of magnitude have been reported in p1,1TFSA and p1,2TFSA by doping with Li-TFSA; these materials are thought to conduct by a fast ion conduction mechanism. However, the highest conductivity was exhibited by a 30 mol% p1,2TFSA Li–TFSA binary system which melted at 30 °C. It was proposed that for the higher melting p1,xNfO series, a high melting solid displaying fast ion conduction might be obtained. This is being further investigated.

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Conclusions

The synthesis and characterisation of a series of N-methyl-N-alkyl-pyrrolidinium nonaflate salts has been described. The thermal and electrochemical properties have been assessed with regard to potential use in electrolyte applications. The combination of two plastic crystal forming ions has produced a series of salts with multiple solid phases below the melting point. All of the salts are in plastic phase I at ambient temperature, which may be important for their potential use in electrochemical devices. The nonaflate salts display remarkable thermal and electrochemical stability, with thermal decomposition temperatures approaching 350 °C and an electrochemical window of approximately 6 V (vs. Ag/Ag⁺). Ionic liquid applications for these pyrrolidinium nonaflate salts are possible at temperatures around 100 °C.

Experimental

Synthesis

N-Methylpyrrolidinium, iodomethane, bromoethane, bromopropane, bromobutane, bromopentane and bromohexane were obtained from Aldrich (all > 99%) and used as received. Potassium nonaflate (Fluka > 97%) was recrystallised from water before use. The six nonaflate salts were prepared by a three-step process (see Scheme 1, in which the alkylmethylpyrrolidinium halide was initially prepared from literature methods18,32 and then metathesised with potassium nonaflate in water.

N-N-Dimethylpyrrolidinium nonafluorobutanesulfonate (p1,1NfO). Potassium nonafluorobutanesulfonate (KNfO, 7.5 g, 22.2 mmol) was dissolved in 50 mL of water at 70 °C. An aqueous solution of N,N-dimethylpyrrolidinium iodide (p1,1I, 5 g, 22.0 mmol) was added and the mixture stirred at 70 °C for 2–3 hours. The solution was cooled and then extracted with dichloromethane. The organic layer was washed three times with water and then evaporated to dryness using a rotary evaporator. The white solid product was dried under vacuum.

N-Methyl-N-ethylpyrrolidinium nonafluorobutanesulfonate (p1,2NfO). Same procedure as for p1,1NfO. KNfO (7.6 g, 22.6 mmol) and p1,2Br (4 g, 20.6 mmol) afforded the title compound as a white solid (7.2 g, 85%). IR vmax/cm⁻¹ : 3418, 1353, 1258, 1133, 1058, 1057, 1005, 975, 908, 871, 803, 750, 736, 656. 1H nmr δH (300 MHz; CDCl3) 1.38–1.48 (3H, t, CH3), 2.21–2.32 (4H, m, CH2), 3.10 (3H, s, N-CH3), 3.50–3.60 (2H, m, N-CH2). ES-MS: ES⁺ m/z 114 p1,2⁺. ES⁻ m/z 299 NfO⁻.

N-Methyl-N-propylpyrrolidinium nonafluorobutanesulfonate (p1,3NfO). Same procedure as for p1,1NfO. KNfO (11.6 g, 34.3 mmol) and p1,3Br (4 g, 19.2 mmol) afforded the title compound as a white solid (7.7 g, 94%). IR vmax/cm⁻¹ : 3518, 1352, 1260, 1135, 1058, 1059, 1006, 972, 907, 870, 802, 750, 698, 656. 1H nmr δH (300 MHz; CDCl3) 0.95–0.99 (3H, t, CH3), 1.83–1.97 (2H, m, CH2), 2.25–2.34 (4H, m, CH2), 3.22 (3H, s, N-CH3), 3.45–3.50 (2H, m, N-CH2). ES-MS: ES⁺ m/z 128 p1,3⁺. ES⁻ m/z 299 NfO⁻.

N-Methyl-N-butylpyrrolidinium nonafluorobutanesulfonate (p1,4NfO). Same procedure as for p1,1NfO. KNfO (6.70 g, 19.8 mmol) and p1,4Br (4 g, 18.0 mmol) afforded the title compound as a white solid (7.3 g, 92%). IR vmax/cm⁻¹ : 3518, 1352, 1260, 1135, 1058, 1057, 1005, 987, 908, 871, 803, 736, 656. 1H nmr δH (300 MHz; CDCl3) 0.92–0.97 (3H, t, CH3), 1.34–1.46 (2H, m, CH2), 1.81–1.92 (2H, m, CH2), 2.25–2.31 (4H, m, CH2), 3.22 (3H, s, N-CH3), 3.49–3.55 (2H, m, N-CH2), 3.66–3.72 (4H, m, N-CH2) ES-MS: ES⁺ m/z 142 p1,4⁺. ES⁻ m/z 299 NfO⁻.

N-Methyl-N-pentylpyrrolidinium nonafluorobutanesulfonate (p1,5NfO). Same procedure as for p1,1NfO. KNfO (7.6 g, 19.8 mmol) and p1,5Br (4.23 g, 18.0 mmol) afforded the title compound as a white solid (7.85 g, 93%). IR vmax/cm⁻¹ : 3518, 1352, 1260, 1135, 1058, 1057, 1005, 987, 908, 871, 803, 751, 736, 656. 1H nmr δH (300 MHz; CDCl3) 0.95–0.99 (3H, t, CH3), 1.38–1.48 (3H, t, CH3), 1.34–1.46 (4H, m, CH2), 1.81–1.92 (2H, m, CH2), 2.25–2.31 (4H, m, CH2), 3.22 (3H, s, N-CH3), 3.49–3.55 (2H, m, N-CH2), 3.66–3.72 (4H, m, N-CH2) ES-MS: ES⁺ m/z 156 p1,5⁺. ES⁻ m/z 299 NfO⁻.

N-Methyl-N-hexylpyrrolidinium nonafluorobutanesulfonate (p1,6NfO). Same procedure as for p1,1NfO. KNfO (6.70 g, 19.8 mmol) and p1,6Br (4.48 g, 18.0 mmol) afforded the title compound as a white solid (7.85 g, 93%). IR vmax/cm⁻¹ : 3518, 1352, 1260, 1135, 1057, 1057, 1005, 975, 908, 871, 803, 750, 736, 656. 1H nmr δH (300 MHz; CDCl3) 0.92–0.97 (3H, t, CH3), 1.38–1.48 (4H, m, CH2), 1.81–1.92 (4H, m, CH2), 2.25–2.31 (4H, m, CH2), 3.22 (3H, s, N-CH3), 3.49–3.55 (2H, m, N-CH2), 3.66–3.72 (4H, m, N-CH2) ES-MS: ES⁺ m/z 158 p1,6⁺. ES⁻ m/z 299 NfO⁻.

Scheme 1 Two-step process involves alkylation of N-methylpyrrolidine followed by metathesis with potassium nonaflate.
N-CH₃), 3.66–3.72 (4H, m, N-CH₂). ES-MS: ES⁺ m/z 170 p₁,6⁻. ES⁻ m/z 299 NIO⁻.

**Analysis**

Infrared spectra were obtained in the range of 4000–650 cm⁻¹ on a Perkin-Elmer 1600 series FTIR spectrometer using KBr discs.¹H NMR spectra were recorded on a Bruker DPX 300 spectrometer for solutions in CDCCl₃. Positive and Negative ion electrospray mass spectra (ESMS) were recorded with a Micromass Platform electrospray mass spectrometer for samples dissolved in methanol. Thermal analysis and temperature dependent phase behavior was studied in the range −100 °C to 300 °C by differential scanning calorimetry under N₂ at a rate of 10 °C min⁻¹ (Perkin Elmer DSC7). Thermal scans below room temperature were calibrated with the cyclohexane solid–solid transition and melting point at −87.0 °C and 6.5 °C respectively.

Thermal scans above room temperature were calibrated with the indium melting point at 156.6 °C. Transition temperatures were recorded at the peak maximum of the thermal transition. Thermogravimetric analysis was conducted using a STA1500 (Rheometric Scientific) in a flowing dry nitrogen atmosphere (50 ml min⁻¹) between 30 °C and 500 °C with a heating rate of 10 °C per minute. The instrument was calibrated using four melting points (indium, tin, lead and zinc) and aluminium pans were used in all experiments. Electrochemistry was carried out in an argon drybox using a Maclab potentiostat, and Maclab software. Electrodes consisted of a platinum working electrode (polished, 0.05 μm Al₂O₃), a platinum coiled wire counter electrode and a silver wire pseudo reference electrode. All samples dissolved in methanol. Thermal analysis and temperature dependent phase behavior was studied in the range −100 °C to 300 °C by differential scanning calorimetry under N₂ at a rate of 10 °C min⁻¹ (Perkin Elmer DSC7). Thermal scans below room temperature were calibrated with the cyclohexane solid–solid transition and melting point at −87.0 °C and 6.5 °C respectively.

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**References**