

Room-Temperature Molten Salts Based on the Quaternary Ammonium Ion

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The properties of a family of novel quaternary ammonium salts based on the bis(trifluoromethylsulfonyl)imide and triflate anions are reported. Binary phase diagrams for some of their mixtures and their electrochemical windows of stability are also reported. The highest conductivity observed in the pure salt systems at 25 °C was $7 \times 10^{-4} \text{ S cm}^{-1}$. An electrochemical window of stability of up to 5 V was measured on graphite electrodes. The effect of salt structure and solvent on conductivity of the salts is also discussed.

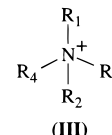
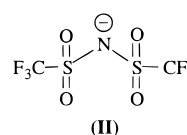
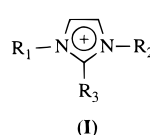
Introduction

The number of families of molten salts exhibiting room-temperature liquid behavior is quite limited. Excluding the hydrate salts, few purely inorganic systems form stable molten salts at room temperature. Molten organic salts, such as the quaternary ammonium and imidazolium salts, have been investigated for several reasons. They have been used as an effective tool in electrolyte solution chemistry^{1–3} and molten salt chemistry,^{4–7} as well as being excellent ionic media with negligible vapor pressure for organic reactions and instrumental analysis.^{8–11} In recent years, room-temperature molten salts have also been investigated as potential candidate electrolytes for use in batteries, photoelectrochemical cells, electroplating, and capacitors.^{12–16}

Room-temperature molten salt systems were reported in 1951 by Hurley and Wier.¹⁷ In their work, fused mixtures of ethylpyridinium bromide and metallic chlorides were studied, and it was found that mixtures of ethylpyridinium bromide and aluminum chloride had a sharp minimum in their liquidus behavior (−40 °C) at 67 mol % AlCl_3 . Jones and Blomgren⁶ studied similar systems, using quaternary ammonium chlorides mixed with aluminum chloride; a mixture of trimethylphenylammonium chloride and aluminum chloride at 67 mol % AlCl_3 showed an even lower liquidus point (−75 °C). The room-temperature conductivity of the systems studied was in the range 10^{-3} – $10^{-4} \text{ S cm}^{-1}$, and their electrochemical window of stability was $\sim 3 \text{ V}$.

Molten salts based on the imidazolium cation (I) have recently received special attention. Wilkes et al.¹² used dialkylimidazolium chlorides mixed with aluminum chloride to prepare room-temperature ionic liquids. The 1-methyl-3-ethylimidazolium chloride–aluminum chloride mixture, which melts at 30 °C, has an electrochemical window similar to that of the ammonium chloride–aluminum chloride system mentioned above. Similar work was reported by Matsunaga et al.,¹⁸ who have studied the ionic conductivity of 1-methyl-3-ethylimidazolium chloride–aluminum chloride mixtures at different compositions, as well as the effect of adding LiCl , NaCl , and KCl on the conductivity. Vestergaard et al.¹³ studied the 1,4-dimethyl-1,2,4-triazolium chloride–aluminum chloride system

and reported that the mixtures were liquid at room temperature when the AlCl_3 content was more than 50 mol %.



Molten salts based solely on the imidazolium cation (I) have been reported recently,^{19–21} the anions utilized including a range of perfluorinated ions. In the work of Wilkes et al.¹⁹ and Fuller et al.,²⁰ the 1-methyl-3-ethylimidazolium cation was used, in a combination with a variety of different anions, to prepare single-component molten salts. The 1-methyl-3-ethylimidazolium salts were reported with a melting point of 58–60 °C for the hexafluorophosphate (PF_6^-), 15 °C for the tetrafluoroborate (BF_4^-), and −45 °C for the acetate (CH_3COO^-) salts. A series of imidazolium molten salts were synthesized and characterized by Bonhote et al.²¹ These salts contained the imidazolium cation with different alkyl groups (methyl, ethyl, butyl, methoxyethyl, trifluoroethyl) in the 1, 2, and 3 positions of the imidazole ring and anions, including CF_3COO^- , CF_3SO_3^- , $\text{C}_4\text{F}_9\text{SO}_3^-$, and the bis(trifluoromethylsulfonyl)imide ion (II) ($(\text{CF}_3\text{SO}_2)_2\text{N}^-$).²² This latter anion, in particular, appeared to depress the melting point of salts in the imidazolium family. Most of the salts melt below room temperature, and some have a glass transition in the region of −30 to −50 °C. A conductivity around $10^{-3} \text{ S cm}^{-1}$ at room temperature and an electrochemical window over 4 V were reported for the 1-methyl-3-ethylimidazolium salt of the $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ anion.²¹

Molten salts have long been known in the family of quaternary ammonium salts; however, the melting point only approaches room temperature when the size of the quaternary ammonium cation (III) is large, for example, where the total number of carbons in the structure is > 20 . The properties of a large group of the molten salts of the quaternary ammonium cation were reported by Gordon and Subba Rao.²³ In their work, 64 quaternary ammonium salts with different alkyl groups and three different anions (Br^- , ClO_4^- , and BPh_4^-) were synthesized. For these quaternary ammonium salts, temperatures, heats, and entropies of solid–solid transition and fusion were measured, along with phase diagrams for a number of salt–salt and salt–solvent systems. It was found that 13 of the 64 quaternary ammonium salts appeared to freeze below room

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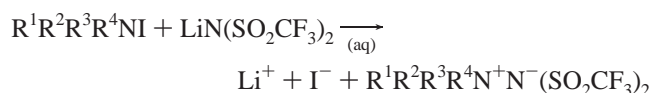
temperature; an additional seven salts were investigated less thoroughly but also probably melted near or below room temperature. All of the salts exhibiting low melting points had a total number of carbon atoms around 20 in the four dissimilar alkyl groups; the anions were ClO_4^- or Br^- . It was suggested in their work that reduction of symmetry in the cations was an effective means of lowering the freezing point of the quaternary ammonium salts. For example, tetrapentylammonium bromide has a melting point of 101 °C, while butyl–pentyl–octyl–propylammonium bromide, which has the same number of carbon atoms in the cation, melts below room temperature.

Attempts to prepare molten salts involving small (carbon number < 12) low symmetry ammonium cations have never previously succeeded. In recent reports from our laboratories,^{14,15} the synthesis of 16 novel tetraalkylammonium bis-(trifluoromethylsulfonyl)imide salts with the structure $(\text{C}_n\text{H}_{2n+1})_4\text{N}^+\text{N}^-(\text{SO}_2\text{CF}_3)_2$ ($n = 1, 2, 3, 4$), $(\text{C}_2\text{H}_5)_2(i\text{-C}_3\text{H}_7)_2\text{N}^+\text{N}^-(\text{SO}_2\text{CF}_3)_2$, $(\text{C}_2\text{H}_5)(\text{CH}_3)(i\text{-C}_3\text{H}_7)_2\text{N}^+\text{N}^-(\text{SO}_2\text{CF}_3)_2$, $(\text{C}_7\text{H}_{15})(i\text{-C}_3\text{H}_7)_2(\text{C}_2\text{H}_5)\text{N}^+\text{N}^-(\text{SO}_2\text{CF}_3)_2$, and $(\text{C}_m\text{H}_{2m+1})(\text{C}_n\text{H}_{2n+1})_3\text{N}^+\text{N}^-(\text{SO}_2\text{CF}_3)_2$ ($m = 6, 7, 8$; $n = 1, 2, 4$) were reported. The symmetrical tetraalkylammonium imide salts in the family exhibited much lower melting points than that of corresponding tetraalkylammonium halides, while the imide salts having lower symmetry ammonium cations were stable liquids at room temperature and had glass transitions in the region of –60 to –80 °C.

In this work, the properties of this family of novel imide salts have been investigated, including their phase equilibria for salt–salt binary systems, their electrochemical window of stability, and their conductivity in both pure salt and salt–solvent systems. The effects of salt structure and solvent on conductivity are also discussed.

Experimental Section

The imide salts were prepared as described in detail elsewhere.¹⁴ Briefly, they were obtained by reaction of the corresponding alkylammonium iodide with the salt $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ in water at room temperature.



The desired salts, all being hydrophobic to some extent, separate from the aqueous phase either as a distinct liquid layer or as a precipitate. These were recovered, purified, and characterized structurally as described in ref 14. Microanalyses of selected examples confirmed the structure of the product. In most cases the corresponding ammonium halide is not commercially available; these were made by standard preparative routes.¹³ The triflate salts discussed were prepared by the same reaction, using $\text{LiOSO}_2\text{CF}_3$ as the source of the anion. Each sample was dried under vacuum at room temperature for at least 3 days before measurement of thermal or electrical properties. Water content of the dried samples was determined as <0.1% (w/w) by Karl Fischer titration.

Conductance measurements were carried out in a locally designed multisample conductance cell consisting of a block of aluminum, into which sample compartments were machined. The cell constants of the embedded electrodes in each compartment were determined by calibration before and after each sample measurement with 0.01 M KCl solution at 25 °C. Conductivities were obtained in the first instance by measurement of the complex impedance of the cell between 20 Hz and

1 MHz using a HP4284A impedance meter. The conductance of the sample was determined from the first real axis touchdown point in the Cole–Cole plot of the impedance data. Examination of the impedance vs frequency plot showed that this touchdown corresponded to a range of frequencies from 5 to 50 kHz. Further comparative measurements are made using a Wayne Kerr B221 conductance bridge (fixed frequency = 1592 Hz), the slightly lower frequency of this bridge producing a small (~5%) systematic underestimate of the true conductivity.

Densities of the liquid samples were determined by weighing a measured volume of the material. The Ostwald method²⁴ was used in viscosity measurements of the liquid salts; glycerol (viscosity 954 mPa s at 25 °C), cyclohexanol (57.5 mPa s), 1,2-propylene glycol (40.4 mPa s), diethylene glycol (30.2 mPa s), ethanolamine (21.1 mPa s), ethylene glycol (16.1 mPa s), and glycerol–water solution (60 wt % glycerol, 8.82 mPa s) were used as standards.

A ML 400 MacLab/4e with Echem v1.3.1 software was used for the electrochemical measurements. Glassy carbon was used as the working and counter electrodes, and the quasi-reference electrode was a silver wire (effectively forming a Ag/Ag^+ reference electrode in the melt). The scanning rate used was 100 mV/s. Before each measurement, the samples were bubbled with dry, high-purity N_2 for more than 20 min to remove dissolved O_2 . The instrumental sign convention adopted was positive potentials with negative currents correspond to anodic.

A Perkin-Elmer model 7 differential scanning calorimeter was used to measure the thermal properties at a heating rate of 10.0 °C/min. Two standard samples, *p*-nitrotoluene (mp 51.6 °C) and acetic acid (mp 16.6 °C), were used for the calibration of temperature in the DSC over the temperature range from –20 to 150 °C. A standard sample of cyclohexane (crystal–crystal transition temperature –87.06 °C and mp 6.54 °C) was used for the range from –120 to 30 °C. Overall reproducibility of the DSC measured transition temperatures was found from repeated measurements to be ± 2 °C in T_g and ± 1 °C in T_m . Before the DSC measurement, all salt mixture samples were heated to their molten state twice to ensure that they were mixed with each other completely. All samples were dried under vacuum at room temperature for at least 3 days prior to measurement of thermal properties.

Results and Discussion

The imide salts prepared and their properties are summarized in Table 1. In each case an abbreviation for the ammonium ion is developed by subscripting the number of carbons in each of the four alkyl substituents.

The effect of the imide ion in destabilizing the crystalline state is immediately obvious in the first six salts in Table 1. All of these contain highly symmetrical ammonium ions. Their imide salts have melting points around 100 °C below those of their respective halide salts, for example, N_{2222}I , mp > 300 °C, N_{2222}Im , mp = 109 °C, and N_{4444}I , mp = 148 °C, N_{4444}Im , mp = 96 °C. However, it is apparent that the introduction of the imide ion is insufficient to lower the melting point to room temperature in these cases of symmetrical ammonium ions. To achieve yet further reduction in the melting point, two hypotheses were investigated: (i) that binary and ternary mixtures of the salts may contain low melting eutectics and (ii) that lowering the symmetry of the quaternary ammonium ion may further destabilize the crystalline state and depress the melting point. These are further discussed below.

Binary Systems. Many binary salt mixture systems have one or more eutectic points.²⁵ Based on DSC thermograms,

TABLE 1: Properties of Quaternary Ammonium Imide Salts

| acronym | structure | mp/°C (±1 °C) | T_g /°C (±2 °C) | density (20 °C)/gcm ⁻³ | V_m / cm ³ mol ⁻¹ | viscosity/mPas (±5%, 25 °C) | $\sigma/10^{-4}$ S cm ⁻¹ (±5%, 25 °C) | $\Lambda/10^{-1}$ S cm ² mol ⁻¹ |
|------------------------|--|------------------|----------------------|--------------------------------------|--|--------------------------------|---|---|
| N ₁₁₁₁ | (CH ₃) ₄ N ⁺ N ⁻ (SO ₂ CF ₃) ₂ | 133 | | | | | | |
| N ₂₂₂₂ | (C ₂ H ₅) ₄ N ⁺ N ⁻ (SO ₂ CF ₃) ₂ | 109 | | | | | | |
| N ₃₃₃₃ | (<i>n</i> -C ₃ H ₇) ₄ N ⁺ N ⁻ (SO ₂ CF ₃) ₂ | 105 | | | | | | |
| N ₄₄₄₄ | (<i>n</i> -C ₄ H ₉) ₄ N ⁺ N ⁻ (SO ₂ CF ₃) ₂ | 96 | | | | | | |
| N _{223'3'} | (CH ₃ CH ₂) ₂ (<i>i</i> -C ₃ H ₇) ₂ N ⁺ N ⁻ (SO ₂ CF ₃) ₂ | 148 | | | | | | |
| N _{123'3'} | (CH ₃)(CH ₃ CH ₂)(<i>i</i> -C ₃ H ₇) ₂ N ⁺ N ⁻ (SO ₂ CF ₃) ₂ | 140 | | | | | | |
| N ₆₁₁₁ | (<i>n</i> -C ₆ H ₁₃)(CH ₃) ₃ N ⁺ N ⁻ (SO ₂ CF ₃) ₂ | | -74 | 1.33 | 320 | 153 | 4.3 | 1.4 |
| N ₇₁₁₁ | (<i>n</i> -C ₇ H ₁₅)(CH ₃) ₃ N ⁺ N ⁻ (SO ₂ CF ₃) ₂ | | -73 | 1.28 | 342 | 153 | 4.0 | 1.4 |
| N ₈₁₁₁ | (<i>n</i> -C ₈ H ₁₇)(CH ₃) ₃ N ⁺ N ⁻ (SO ₂ CF ₃) ₂ | | -73 | 1.27 | 356 | 181 | 3.5 | 1.3 |
| N ₆₂₂₂ | (<i>n</i> -C ₆ H ₁₃)(C ₂ H ₅) ₃ N ⁺ N ⁻ (SO ₂ CF ₃) ₂ | 20 | -81 | 1.27 | 367 | 167 | 6.7 | 2.5 |
| N ₇₂₂₂ | (<i>n</i> -C ₇ H ₁₅)(C ₂ H ₅) ₃ N ⁺ N ⁻ (SO ₂ CF ₃) ₂ | | -79 | 1.26 | 380 | 75.5 | 5.1 | 1.9 |
| N ₈₂₂₂ | (<i>n</i> -C ₈ H ₁₇)(C ₂ H ₅) ₃ N ⁺ N ⁻ (SO ₂ CF ₃) ₂ | | -74 | 1.25 | 395 | 202 | 3.3 | 1.3 |
| N ₆₄₄₄ | (<i>n</i> -C ₆ H ₁₃)(<i>n</i> -C ₄ H ₉) ₃ N ⁺ N ⁻ (SO ₂ CF ₃) ₂ | 26 | -68 | 1.15 | 480 | 595 | 1.6 | 0.8 |
| N ₇₄₄₄ | (<i>n</i> -C ₇ H ₁₅)(<i>n</i> -C ₄ H ₉) ₃ N ⁺ N ⁻ (SO ₂ CF ₃) ₂ | | -67 | 1.17 | 482 | 606 | 1.6 | 0.8 |
| N ₈₄₄₄ | (<i>n</i> -C ₈ H ₁₇)(<i>n</i> -C ₄ H ₉) ₃ N ⁺ N ⁻ (SO ₂ CF ₃) ₂ | | -63 | 1.12 | 516 | 574 | 1.3 | 0.7 |
| N _{723'3'} | (<i>n</i> -C ₇ H ₁₅)(C ₂ H ₅)(<i>i</i> -C ₃ H ₇) ₂ N ⁺ N ⁻ (SO ₂ CF ₃) ₂ | | -82 | 1.27 | 400 | 362 | 3.1 | 1.2 |
| N ₇₄₄₄ trif | (C ₇ H ₁₅)(C ₄ H ₉) ₃ N ⁺ O ⁻ SO ₂ CF ₃ | | -55 | | | | | |
| N ₈₄₄₄ trif | (C ₈ H ₁₇)(C ₄ H ₉) ₃ N ⁺ O ⁻ SO ₂ CF ₃ | | -57 | 1.02 | 422 | 2.03 × 10 ³ | 0.17 | 0.07 |

Temperature / °C

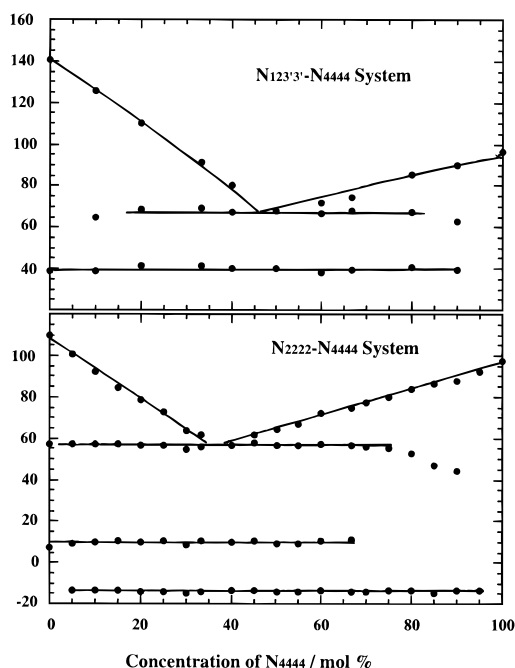


Figure 1. Solid-liquid phase diagrams for mixed quaternary ammonium salt systems.

solid-liquid phase diagrams for various binary mixtures of the ammonium salts prepared in this work were constructed, as shown in Figure 1. In the N_{123'3'}-N₄₄₄₄ system, a eutectic point at 68 °C was observed at approximately 50 mol %. It was also observed that the N_{123'3'} salt has a solid-solid transition at about 40 °C, which appears at N_{123'3'} concentrations from 100 to 10 mol % in the binary. In the N₂₂₂₂-N₄₄₄₄ system, there is a eutectic point at 56 °C at 40 mol % N₄₄₄₄. This binary also indicates that N₂₂₂₂ has two solid-solid transitions, one at 7 °C and the other at 57 °C. The first solid-solid transition (7 °C) was observed at N₂₂₂₂ concentrations from 100 to 33 mol % in the binary, while the second solid-solid transition is overlapped by the eutectic transition. There is a further thermal event at about -14 °C in the N₂₂₂₂-N₄₄₄₄ mixtures, which was observed at N₄₄₄₄ concentrations from 5 to 95 mol % as shown in Figure 1, which is not observed in either of the pure phases. This may indicate the existence of a peritectoid transition involving a compound forming near the middle of the phase diagram.

Solid-liquid phase behavior for some ternary salt systems has also been investigated. The eutectic composition of the N₂₂₂₂-N₄₄₄₄ binary system (abbreviated as EB) i.e., N₄₄₄₄[40 mol %]-N₂₂₂₂[20 mol %], was used to mix with a third salt component. In the EB-N₁₁₁₁ and EB-N₃₃₃₃ mixtures, these having a common anion, the lowest liquidus points observed were 42 °C at an N₁₁₁₁ concentration of 20 mol % in the EB-N₁₁₁₁ system and 45 °C at an N₃₃₃₃ concentration of 20 mol % in the EB-N₃₃₃₃ system. To introduce a different anion, tetrabutylammonium *p*-toluenesulfonate (*n*-Bu)₄NOSO₂C₆H₄-CH₃ (BS) was chosen as an additional component since the melting point of BS is relatively low (72 °C). This produced a lowest liquidus point of 34 °C at a BS concentration of 60 mol % in the EB-BS system.

In the binary N₄₄₄₄-(*n*-Bu)₄NBF₄ system (not shown), the effect of mixing different anions with a common cation was examined. The lowest melting point observed in this system was 55 °C at 50 mol % N₄₄₄₄. Three other related binary systems were studied, and the lowest melting point observed was always at the 50 mol % composition in each system: at 66 °C for N₄₄₄₄-(*n*-Bu)₄NPF₆, 65 °C for N₄₄₄₄-(*n*-Bu)₄NClO₄, and 40 °C for N₄₄₄₄-(*n*-Bu)₄NSO₃CF₃. Using the ternary eutectic composition of the N₂₂₂₂-N₄₄₄₄-N₃₃₃₃ system (EBP, N₄₄₄₄[32 mol %]-N₂₂₂₂[48 mol %]-N₃₃₃₃[20 mol %]) and BS as the fourth salt, a cut across the phase diagram of the quaternary system was obtained and a lowest liquidus point at 38 °C at 60 mol % EBP observed.

It can be seen from the above results that, for the salt systems investigated, the effect on melting point of introducing a different salt into the system seems to be largely independent of whether it is the cation or anion of the component salts that are in common. However, the binary systems exhibit the deepest eutectics as compared with the subsequent lowering of liquidus temperatures in the ternary and quaternary systems. The temperature difference between the eutectic point and the lower of the melting points of the component salts in the binary systems is as high as 30-50 °C.

Ionic conductivity as a function of temperature in the binary N₄₄₄₄(40 mol %)-N₂₂₂₂(60 mol %) mixture at its eutectic composition and the ternary N₄₄₄₄(32 mol %)-N₂₂₂₂(48 mol %)-N₃₃₃₃(20 mol %) mixture at its lowest liquidus point composition is shown in Figure 4. As the melting point of the N₄₄₄₄(40 mol %)-N₂₂₂₂(60 mol %) system is 56 °C, conductivity of this system at 45 °C is quite low (only 10⁻⁵ S cm⁻¹). However, conductivities of the two systems in the molten state are in the region of 10⁻³ S cm⁻¹. Figure 3 indicates that the

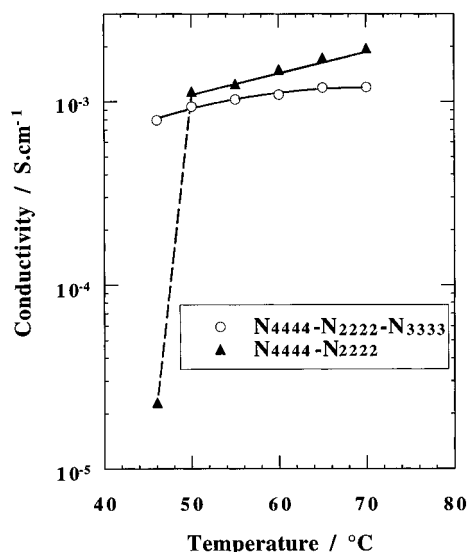


Figure 2. Ionic conductivity as a function of temperature of tetraalkylammonium imide salt mixtures: N_{4444} (32 mol %)- N_{2222} (48 mol %)- N_{3333} (20 mol %), N_{4444} (40 mol %)- N_{2222} (60 mol %). The sudden drop in conductivity at low temperatures in the N_{4444} - N_{2222} system indicates freezing of the sample.

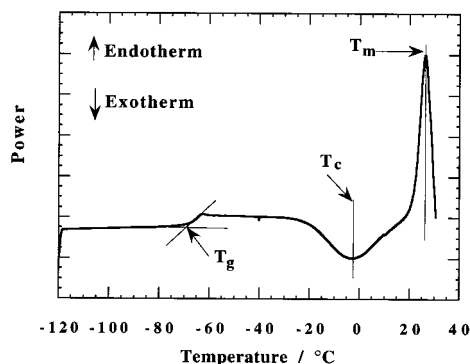


Figure 3. DSC trace for the tributylhexylammonium imide N_{6444} molten salt after quenching into the glassy state. The glass transition temperature is obtained as indicated. The trace also shows an exotherm corresponding to crystallization during warming at T_c and the subsequent melting of this crystalline phase at T_m .

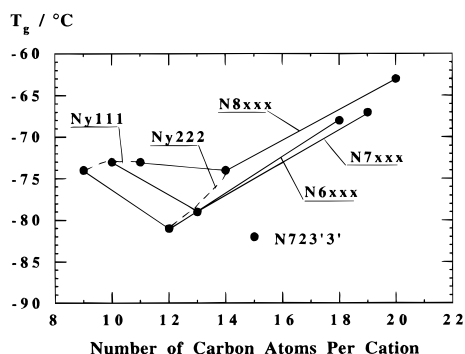


Figure 4. Glass transition temperatures as a function of the total number of carbons in the cation. The lines indicate sequences wherein $x = 1, 2$, and 4 or $y = 6$ and 7 .

conductivity of the ternary system in the temperature range 50–75 °C is slightly lower than that of the binary. This result correlates with the average size of cations in the ternary system being larger than that in the binary.

Low Symmetry Cations. Since all of the simple symmetrical quaternary ammonium imide salts investigated had melting points well above room temperature, a series of lower

symmetry ammonium cations were investigated to test the hypothesis that such cations would destabilize the solid state with respect to the liquid state and hence lower the melting point. The compounds prepared and their density, molar volume (V_m), viscosity, conductivity (σ), and molar conductivity ($=\sigma V_m$) are listed in Table 1. In all cases the melting point was lowered to room temperature or below, and in many of the compounds listed, no crystallization or melting events were obtained in the temperature interval -100 °C to room temperature. A DSC thermogram for N_{6444} is shown in Figure 3 as an example of a range of these behaviors. In this case the sample appears to have quenched, without crystallization, to a glassy state. On warming in the DSC, a glass transition is observed, as indicated, at -68 °C. The sample then crystallizes at -2 °C on continued warming, as is commonly observed in “marginal glass formers”. The sample subsequently melts at the point marked T_m . The approximate equivalence of the areas of the crystallization and melting peaks indicates that the total enthalpies of the transitions involved are approximately the same and therefore that the sample as quenched was substantially free of crystallization. In those samples where no crystallization or melting transitions were observed (Table 1), the DSC thermogram showed only the glass transition event. This does not unambiguously indicate that the compound exhibits no melting point; simply, that under the conditions of cooling and heating rate used here, no crystallization was observed. It remains possible that some of the systems are trapped in an undercooled state, even at room temperature; however, samples maintained at room temperature for more than 2 years have to date shown no tendency to crystallize, and samples of N_{6222} held at -4 °C ($=24$ °C undercooling) for 100 h have also showed no evidence of crystallization. The noncrystallizing salts exhibited glass transition temperatures which were in the region of -80 to -60 °C.

The glass transition temperatures trend generally upward as the cation becomes larger; however, there are some interesting variations in this trend as shown in Figure 4. In each N_{xxxx} series there is a sharp minimum at the N_{y222} compound. The low value for N_{7233} , which is somewhat of an outlier compared to these other trends, suggests that the true minimum may lie in the region of the propyl and isopropyl groups. From the perspective of the configurational entropy model of viscous liquids and the glass transition, the existence of the minimum in T_g in the region of this alkyl group size must reflect the additional degrees of rotational freedom introduced on moving from $-Me$ to $-Et$ or $-Pr$. The longer alkyl chain substituents introduce still further internal degrees of freedom, but this effect is countered by the increasing molar size of the cation, producing fewer cations per unit volume. Hence, the configurational entropy per unit volume of the molten salts containing these larger cations eventually decreases with increasing alkyl chain length. There may be an additional effect, also forcing T_g up as the cation becomes larger relative to the anion, associated with the flexibility of the imide anion, as discussed further below.

Conductivity data for the low symmetry imide salts are presented in Figure 5 as a function of temperature. The conductivities of the pure liquid salts at 25 °C lie in the region 0.1 – 0.7 mS cm^{-1} , the highest value of which is 7×10^{-4} S cm^{-1} for N_{6222} . It is interesting to compare conductivity data of the imide salts with their viscosity data in Table 1, where it can be seen, as expected, that higher conductivity is generally associated with lower viscosity. It is also interesting to correlate conductivity with T_g data as shown in Figure 5; the order of conductivity values (from high to low) for the imide salts is

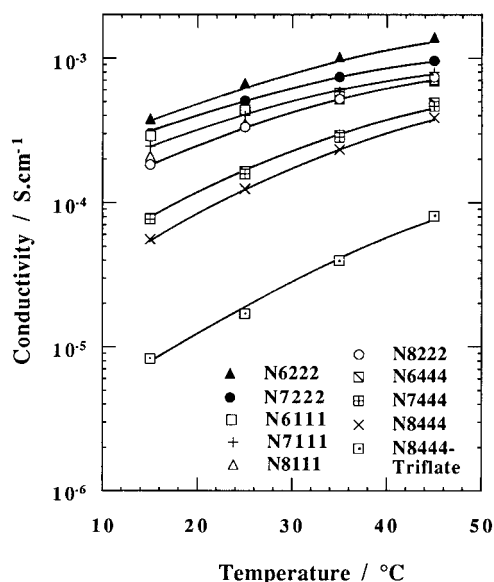


Figure 5. Conductivity of the low symmetry quaternary ammonium imide salts as a function of temperature. The N_{8444} triflate is included for comparison.

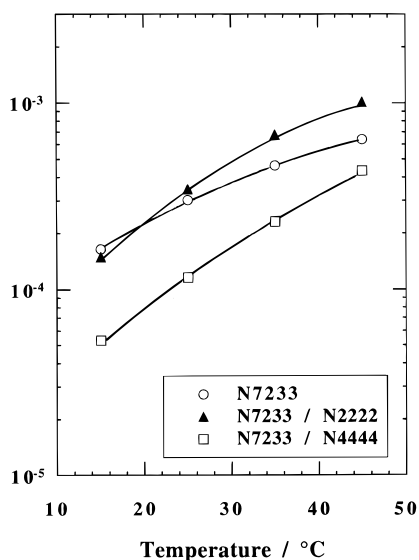


Figure 6. Conductivity of N_{7233} and its mixtures, N_{7233}/N_{2222} (1 mol:1 mol) and N_{7233}/N_{4444} (1 mol:1 mol).

concordant with the order of the T_g data (from low to high). N_{7233} , which is the only exception in the above comparison, has the lowest T_g (-82°C) of the imide salts studied but has room-temperature viscosity more than double that of N_{6222} and, thereby, lower conductivity.

Figure 6 shows a comparison between the conductivity of N_{7233} and its mixtures with N_{2222} and N_{4444} . It was found that N_{7233} had better compatibility with N_{2222} than with N_{4444} , the N_{7233}/N_{2222} mixture (1 mol:1 mol) at 25°C being a clear solution while the N_{7233}/N_{4444} mixture (1 mol:1 mol) at 25°C was a turbid gel. It is therefore not surprising that the N_{7233} – N_{4444} system in Figure 6 has the lower conductivity. It is interesting, however, that the conductivity of the N_{7233} – N_{2222} system is higher than that of N_{7233} itself, especially at higher temperatures, as shown in Figure 6. This may be due to an optimum combination of cation size (N_{2222}) in a low-viscosity medium.

Anion Effect. It was hypothesized that, since the triflate anion, $-\text{OSO}_2\text{CF}_3$, is smaller than the imide anion, $-\text{N}(\text{SO}_2\text{CF}_3)_2$, the triflate anion should have the higher mobility. Thus,

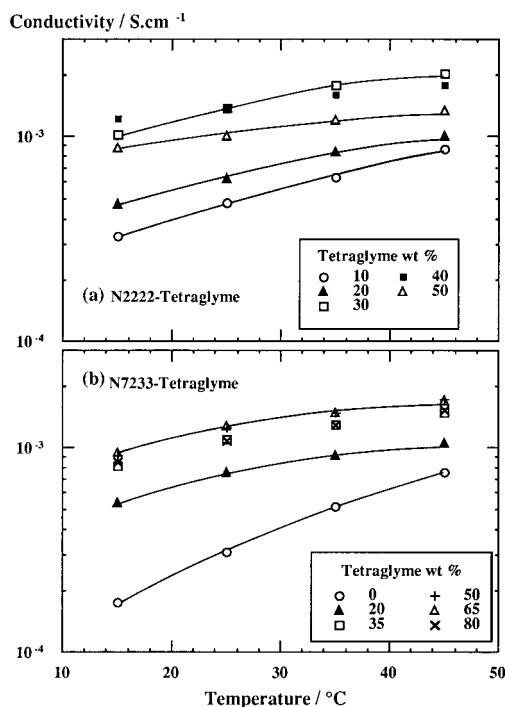


Figure 7. Conductivity of (a) N_{2222} –tetraglyme and (b) N_{3327} –tetraglyme systems as a function of temperature.

several quaternary ammonium triflate salts were prepared for comparison.¹⁴ The properties of two of these are also listed in Table 1. Contrary to our original hypothesis, it was found that the T_g of the two triflate salts, $(\text{C}_7\text{H}_{15})(\text{C}_4\text{H}_9)_3\text{N}-\text{OSO}_2\text{CF}_3$ and $(\text{C}_8\text{H}_{17})(\text{C}_4\text{H}_9)_3\text{N}-\text{OSO}_2\text{CF}_3$, were higher than those of the corresponding imide salts. A comparison of the conductivities of N_{8444} imide and N_{8444} triflate is shown in Figure 5, where the difference in T_g is reflected in an almost order of magnitude difference in conductivity. The imide ion has been described as a plasticizing anion by Armand et al.²⁶ due to its ability to depress the glass transition in polymer electrolytes. On the other hand, the imide anion may be more weakly associated with the cation than the triflate anion. The negative charge is delocalized more widely over the two trifluoromethylsulfonyl groups in the imide ion as indicated by the crystal structure of related compounds.²⁷ The ammonium imide salt would therefore dissociate more easily and be more mobile than the corresponding triflate. That the viscosity of N_{8444} triflate is almost 4 times that of N_{8444} imide (Table 1) is likely to be a result of both effects.

Tetraglyme–Molten Salt Mixtures. To obtain a liquid electrolyte system at room temperature with the symmetric ammonium imide salts prepared in this work, several organic solvents have been used to mix with the imide salts. It was found that the high boiling point ether, tetraethylene glycol dimethyl ether (tetraglyme, boiling point 275°C), is miscible with N_{2222} up to 70 wt % N_{2222} at room temperature. When the concentration of N_{2222} is 80 wt % or higher in tetraglyme solution, the mixture becomes a transparent, gellike material at room temperature.

Figure 7a presents the conductivity as a function of temperature for the N_{2222} –tetraglyme mixtures. For the systems of higher tetraglyme concentration (30, 40, and 50 wt %), the conductivities are around $10^{-3} \text{ S cm}^{-1}$ from 15 to 45°C . The limitation in the investigation of the N_{2222} –tetraglyme system as an ambient-temperature liquid electrolyte is that the solubility limit of N_{2222} in tetraglyme is 70 wt %. However, using asymmetric ammonium cations in place of N_{2222} , it was possible

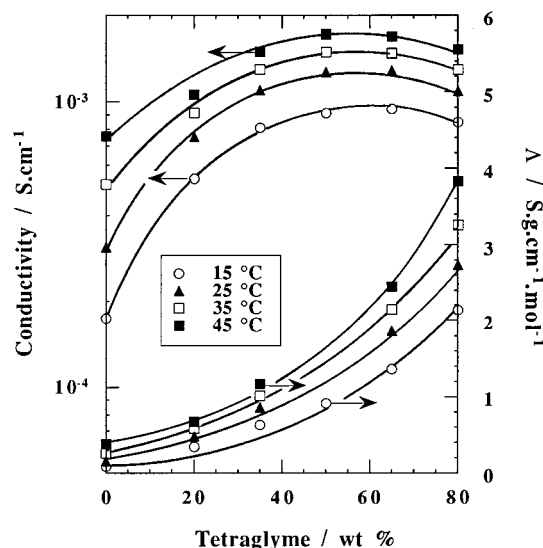


Figure 8. Conductivity and molar conductivity of the N_{7233} -tetraglyme system as a function of tetraglyme concentration. The nonstandard units for molar conductivity result from the concentration units used in its calculation.

to investigate the salt-tetraglyme system across the entire concentration range, as all of these salts are miscible with tetraglyme. Figure 7b shows the conductivity of N_{7233} -tetraglyme solutions as a function of temperature. The room-temperature conductivity of N_{7233} -tetraglyme is $10^{-3} \text{ S cm}^{-1}$ at a tetraglyme concentration $\geq 35 \text{ wt } \%$. The introduction of tetraglyme into the liquid salt leads to a decrease in the viscosity of the system, hence increasing the mobility of the ions. The viscosities of tetraglyme, N_{2222} -40 wt % tetraglyme, and N_{7233} -40 wt % tetraglyme at 25°C were found to be 3.5, 13, and 17 mPa s, respectively.

The conductivities of the N_{7233} -tetraglyme mixtures as a function of composition at various temperatures are shown in Figure 8, which indicates that there is a maximum value in conductivity as a function of tetraglyme concentration. With increasing tetraglyme concentration, the salt concentration decreases, thereby resulting in fewer charge carriers, and the conductivity trends in Figure 8 therefore exhibit maxima. The first-order effect of salt concentration on conductivity is removed by plotting the molar conductivity versus tetraglyme concentration as also shown in Figure 8. (In this case molar conductivity is calculated from $\Lambda = \sigma/c$, where c is the salt concentration in mol g^{-1} .) The molar conductivity increases steadily with tetraglyme content, increasing by approximately an order of magnitude in the range 0–80 wt % tetraglyme. Interestingly, the extent of the increase in molar conductivity is less than expected from the changes observed in viscosity. For example, the viscosity decreases by approximately a factor of 20 at 25°C on addition of 40 wt % tetraglyme to N_{7233} while the molar conductivity rises by only a factor of 6. It would appear from this that the effect of tetraglyme is primarily to disrupt and disperse ionic aggregates, thereby lowering the viscosity, while conduction perhaps retains some of its molten salt characteristics even at 40% tetraglyme.

Electrochemical Stability. The electrochemical stability of electrolytes is of vital importance in many of the electrochemical roles in which they find application. The results below indicate that the molten salts prepared here show some of the largest electrochemical windows measured thus far. Cyclic voltammetry measurements for the quaternary ammonium imide salts which are liquid at room temperature were carried out over

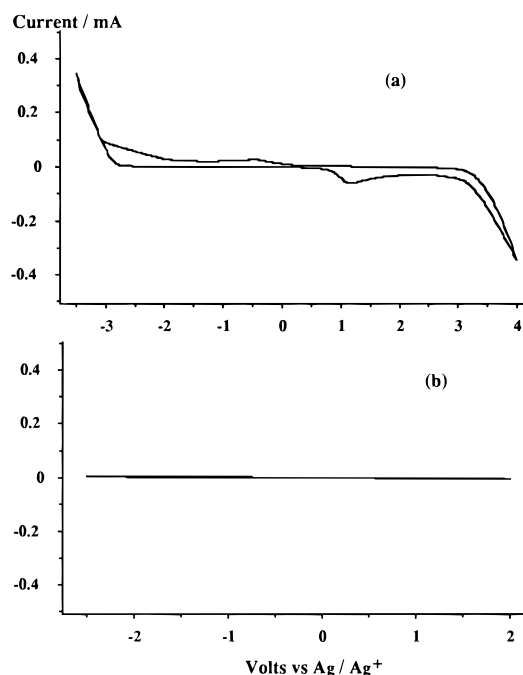


Figure 9. Cyclic voltammograms for N_{6222} over various voltage ranges. Glassy carbon working and counter electrodes. Scan rate, 100 mV/s ; $T = 25^\circ\text{C}$.

various voltage ranges. Figure 9a shows the cyclic voltammogram for N_{6222} in the voltage range from -3.5 to 4 V vs Ag/Ag^+ , in which a number of reduction and oxidation peaks are observed. The result of the same measurement for N_{6222} , but in the voltage range from -2.5 to 2 V , is shown in Figure 9b. From this it is clear that N_{6222} exhibits good electrochemical stability from -2.5 to 2 V . The peaks between -2.5 and 2 V in Figure 9a are the result of the reduction of some species at potentials more negative than -2.5 V and the oxidation in the voltage range more positive than 2 V . Similar results were obtained for the other imide salts; all exhibit an electrochemical window of at least $\sim 4.5 \text{ V}$, which is wider than that of the alkyl imidazolium bis(trifluoromethylsulfonyl)imide salts,²¹ thus suggesting that the alkylammonium cation has greater electrochemical stability than a comparable imidazolium ion. In similar cyclic voltammetry measurements for N_{8222} and N_{8444} at room temperature, an electrochemical window of $\sim 5.0 \text{ V}$ was observed. This even wider electrochemical window may result from the higher purity of these samples, since the intermediates in the preparation of N_{8222} and N_{8444} can be purified by recrystallization.

The cyclic voltammogram for a carbon electrode in the N_{4444} -(40 mol %)- N_{2222} (20 mol %) mixture is shown in Figure 10a. As the melting point of the mixture is 56°C , the cyclic voltammetry measurement was carried out at 90°C to ensure the system was in a molten state. In Figure 10a, an electrochemical window of 5 V is indicated, which is 1 V wider than for comparable dialkylimidazolium bis(trifluoromethylsulfonyl)imide salt systems.²¹ The small peaks appearing between 2 and 3 V are thought to be due to some anionic impurities; if this were the case, the electrochemical window for this system may be even greater.

Figure 10b shows the cyclic voltammetry result for the N_{2222} -tetraglyme(40 wt %) system. This system exhibits a 4.5 V electrochemical window, which indicates that, while tetraglyme has good electrochemical stability under the experimental conditions, it nonetheless limits the anodic stability of the system. Other solvents, such as CH_3CN , mixed with the imide

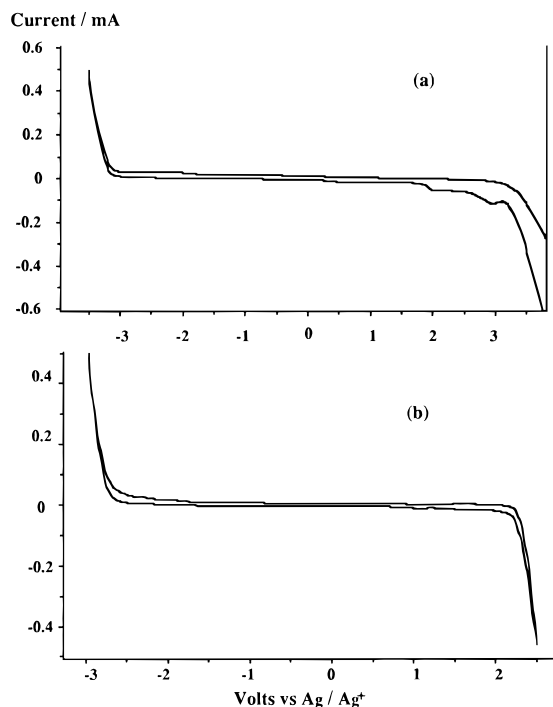


Figure 10. Cyclic voltammograms for the N_{4444} (40 mol %)- N_{2222} (20 mol %) system (a) without and (b) with 40% added tetraglyme. Glassy carbon working and counter electrodes. Scan rate, 100 mV/s; $T = 90^\circ\text{C}$ for (a) and 25°C for (b).

salts have also been studied in this work and show similar effects, particularly in reducing the anodic stability of the mixture as compared to that of the molten salt.

Conclusions

This investigation has shown that molten salts in the quaternary ammonium family can be prepared with a total number of carbons in the cation < 20 . The salts are characterized by having a low symmetry ammonium cation, a sufficient degree of asymmetry being provided by having one longer carbon chain, of carbon number in the region 6–8, with the remaining alkyl chains being identical and as small as $-\text{CH}_3$. The anions involved were the bis(trifluoromethylsulfonyl)imide and triflate ions.

Many of the molten salts in the family are glass formers, exhibiting glass transition temperatures in the range -80 to -60°C . Despite its larger size, the imide anion produced a significantly lower glass transition temperature, and lower viscosities, than did the triflate ion, confirming earlier descriptions of this ion as a “plasticizing” anion. The conductivities of the molten salts were in the region of 10^{-4} to $10^{-3} \text{ S cm}^{-1}$ at room temperature, the highest conductivity being observed for the imide salt of the N_{6222} cation. The corresponding triflate

salt was almost 1 order of magnitude less conductive. The increase in conductivity upon addition of tetraglyme was surprisingly less than that expected by the decrease in the viscosity of the mixture compared to that of the pure salt.

The electrochemical window of stability of the molten salts were observed to be in excess of 4.5 V at room temperature on a graphite electrode.

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