ABSTRACT

The physical and electrochemical properties of a new series of room temperature molten salts (RTMS) based on the aliphatic onium cation and newly developed fluorinated anion, 2,2,2-trifluoro-N-(trifluoromethylsulfonyl) acetamide (TSAC), were investigated. The anion had an excellent ability to lower the melting point of small aliphatic onium salts. Almost all the cations, even the symmetric one, formed RTMS with the new anion in the temperature range of our experiments. The asymmetric structure of the new anion may be the cause the lowering of the melting point of the small onium salts. Not only the melting point but also the viscosity of these melts was decreased by about 20-30% compared with the corresponding salts containing bis(trifluoromethyl-sulfonyl)imide (TFSI). On the other hand, the electrochemical windows of the new RTMS based on aliphatic quaternary ammonium were not as wide as that of the corresponding TFSI melt. The reduction of the TSAC anion might determine the cathodic limit of the TSAC melts.

INTRODUCTION

Room temperature molten salts (RTMS) have attracted attention as a novel and safe electrolyte for electrochemical energy devices, such as the lithium battery, because of their various unique properties such as non-volatility and non-combustibility (1,2). We have studied the physical and electrochemical properties of RTMS based on aliphatic quaternary ammonium (AQA) and bis(trifluoromethylsulfonyl)imide (TFSI) systems because of their high cathodic stability compared with the imidazolium systems and their high chemical stability in air (3). In AQA-TFSI melts, the lithium deposition/stripping peak could be observed, however, AQA systems have several disadvantages as battery electrolytes. For example, they have a higher viscosity, lower conductivity and higher melting point than the imidazolium systems for the same molecular weight.

Though the TFSI anion has the ability to lower the melting point of even the symmetric aliphatic onium salts such as the trialkylsulfonium salts (4) and the tetraalkylammonium salts (5), the melting point of the small onium cations such as...
trimethylsulfonium and tetramethylammonium, which were expected to have a low viscosity due to their small molecular weights, were no longer below room temperature. In this study, we proposed new anionic species with an asymmetric structure (2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide, TSAC) to improve the melting point and the viscosity of the small aliphatic onium cations. The physical and electrochemical properties of these new RTMS were also reported and compared with the corresponding TFSI salts.

Scheme 1. Structure of the symmetric TFSI anion and the asymmetric TSAC Anion.

EXPERIMENTAL

The preparations of the RTMS based on the TSAC were followed by that of the EMI-TFSI melts in an aqueous solution (6). The water-insoluble TSAC salts were immediately segregated after mixing the two aqueous solutions, which contained equimolar amounts of K-TSAC, and various onium halides. The resulting RTIL was washed three times with H₂O. The RTIL was then extracted with CH₂Cl₂ and dried under vacuum (100 °C) for 24 h. These salts can be easily dehydrated below 50 ppm by vacuum drying. The calculated composition of the synthesized salt almost agreed with the elemental analysis result. Identification was carried out by ¹H-NMR and ¹³C-NMR. Details of the preparation of the TSAC salts and identification data (¹H-NMR, ¹³C-NMR, elemental analysis) will be published elsewhere. The melting points of the RTILs were measured by DSC (Perkin/Elmer, Pyris 1). The viscosity was measured using a Brookfield DV-III+ viscometer with a TC-501 circulating bath and programmable controller. The electrochemical measurements were carried out in a glove box equipped with a dry Ar ([H₂O]<5 ppm, [O₂]< 5 ppm) circulation system.

RESULTS AND DISCUSSION

The effect of asymmetric structure of cation on the melting points of AQA based melt.

The fluorinated anions, which can form an air stable RTMS with an aliphatic quaternary ammonium (AQA), are TFSI (7) and BF₄⁻ (8). As shown in Table 1, the melting points of the TFSI salt are about 40–100 °C lower than that of BF₄⁻. Considering that the melting point of the salts containing BF₄⁻ and AQA without a methoxy group (-OCH₃) are much higher than room temperature, the TFSI anion has an excellent ability to lower the AQA salts compared to BF₄⁻. However, the melting points of the AQA-TFSI salts steeply increased when the molecular weight of the cations were lower than 100 amu as shown in Figure 1. A cation smaller than the trimethylpropylammonium could not form a RTMS with TFSI. One of the purposes of this study is find a new anion
to form RTMS with the small AQA cations having no methoxy group. Such a melt might be an attractive candidate for a lithium battery electrolyte for the following reasons. 1. The viscosities of the new RTMS might be low compared with the TFSI melts because the molecular weights of both the anion and cation are small. Generally, the viscosity of RTMS decreased with the decreasing molecular weight of the ionic species. 2. The cathodic stability of RTMS based on TFSI and AQA without a methoxy group was higher than that of the aromatic melts such as the EMI systems (3).

Table 1 The melting point of various salts containing the quaternary ammonium (N'R1R2R3R4) and fluorinated anions. Data taken from refs. 3, 5 and 8.

| R1 | R2 | R3 | R4 | BF4⁻ | TFSI⁻ |
|----|----|----|----|------|-------|
| Me | Me | Me | Me | >300 | 130   |
| Et | Et | Et | Et | >300 | 105   |
| Hex| Hex| Hex| Hex| 87   | 6     |
| Me | Me | Me | Hex| 126  | 18    |
| Me | Me | Et | Bu | 158  |       |
| Me | Me | Et | Pr | -12  | -29   |
| Me | Me | Me | CH2OME| 46 | 4.5   |
| Me | Me | Et | CH2OME| -16| -29   |

Me: methyl, Et: ethyl, Pr: propyl, Bu: butyl, Hex: hexyl

As shown in Figure 1, there might be two methods to lower the melting points of the AQA salts. One is the use of a larger cation instead of a small one. The other is the selection of an asymmetric cation instead of a symmetric cation. Considering that the viscosity of the RTMS based on large cations was much higher than that of the small one, the latter method is much more preferable than the former one since the viscosity of the RTMS containing a large cation or anion must be very high. For example, the viscosity of the tetrapentylammonium-TFSI melts was 430 mPas at 25 °C (5), which was about 7 times greater than that of trimethylpropylammonium-TFSI (3).

![Figure 1](image_url) - The melting point of aliphatic quaternary ammonium salts. These data taken from refs. 3 and 5.
The effect of asymmetric structure of anion on the melting points and the viscosity of the AQA based melt.

Melting points. As already stated above, the asymmetric structure might be an effective way to lower the melting point of AQA based melt. We then expected that the asymmetric anion as shown in scheme 1 also forms low melting AQA based melts. The synthesis of RTMS based on TSAC is almost the same as that of the TFSI melts. The melting point was taken from the DSC chart as shown in Figure 2. At first, the temperature was set at −150°C for 10 minutes. The temperature was then increased at the rate of 10 °C / min. The melting point was taken as the highest temperature of the endothermic peak.

![DSC results for TMPA-TFSI and TMPA-TSAC](image)

**Figure 2.** The DSC results for TMPA-TFSI and TMPA-TSAC.

Table 2 shows the melting point and the viscosity of the TSAC salts and that of TFSI. The TSAC anion forms the RTMS with various cations, which have a low molecular weight (MW<100) except for the tetramethyl-ammonium salt. The melting points of the TSAC salts were 70~100°C lower compared with the corresponding TFSI salts. These facts indicated that the asymmetry of the anionic species caused effectively the decrease in the melting point of the salts containing poor charge dispersible cations such as the aliphatic onium cation as we expected. It was interesting that the symmetric AQA such as the tetraethylammonium forms a RTMS with the TSAC anion.

**Viscosity.** The viscosity of TSAC melts is lower than that of the corresponding TFSI melts as we expected. This might be the result of the decrease in the molecular weight of the anion. However, the viscosity of the TSAC melts with the small cations such as trimethylethylammonium was higher than those containing the larger cations.
such as trimethylpropylammonium. If the viscosity was decreased due to the decreasing molecular weight of the cation, the trimethylethylammonium-TSAC melts showed the lowest viscosity. This implies that the optimum value of the cationic species existed. For the small cation, the distance between the cation and anion might be in the range more influenced by the electrostatic interactions such as the Coulombic force.

Comparison of the melting points of the AQA salts

Recently, MacFarlane et al. reported that the melting points of the AQA salts containing a dicyanamide (NC-N'-CN, DCA) anion were much lower than that of the TFSI salts containing the same cations (9). However, N,N-dimethyl-pyrrolidinium (Pll) could not form a RTMS with DCA at room temperature. On the other hand, the melting point of Pll-TSAC was below room temperature (Table 3). Through the amide structure such as TFSI, DCA might possess the ability to reduce the melting point of the AQA-based melt compared to BF₄ and PF₆, and a further lowering of the melting point of the AQA salts can be achieved by introducing an asymmetrical structure into the amide anion. However, it is necessary to continue these investigations into the physical properties of the TSAC salts concerning the effect of anion asymmetry since the melting point of EMI-TSAC was unexpectedly higher than that of EMI-TFSI.

Table 2 Physical properties of the TSAC salts at 25°C comparing with the TFSI salts

| Cation                  | MW | TFSI m.p. / °C | η / mPas | TSAC m.p. / °C | η / mPas |
|-------------------------|----|---------------|---------|---------------|---------|
| (CH₃)₃N⁺                 | 74 | 130           | -       | 64            | -       |
| (CH₃)₃N⁺(C₂H₅)          | 88 | 105           | -       | -10           | 51      |
| (CH₃)₃N⁺(propargyl)      | 98 | 45            | -       | b             | 65      |
| (CH₃)₃N⁺(allyl)          | 100| 41            | -       | -2.9          | 42      |
| (CH₃)₃N⁺(l-C₃H₆)         | 102| 129           | -       | 29            | 108     |
| (CH₃)₃N⁺(n-C₃H₇)         | 102| 19            | 72      | 10            | 45      |
| (CH₃)₃N⁺(n-C₆H₁₃)        | 144| 27            | 132     | b             | 119     |
| (CH₃)₃N⁺(n-C₈H₁₇)        | 172| 5             | 156     | b             | 151     |
| (C₂H₅)₄N⁺                | 130| 110           | -       | 23            | 80      |
| (C₂H₅)₃N⁺(CH₃)          | 116| 129           | -       | 20            | 61      |
| N,N-dimethylpyrrolidinium| 100| 105           | -       | 14            | 80      |
| tetraethylphosphonium     | 147| 118           | -       | 19            | 50      |
| trimethylsulfonium        | 77 | 44.5          | -       | 32            | 80      |
| EMI                      | 111| -12           | 34      | 2.6           | 24      |

a: the molecular weight of cation, b: tg only

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Table 3 Comparison of the melting point of TSAC salt with other salts

|       | TEA | P11 | EMI | TMS |
|-------|-----|-----|-----|-----|
| PF₆⁺  | >300| >300| 58  | 13  |
| BF₄⁻  | >300| >300| 15  | 217 |
| TFSI  | 105 | 105 | -3  | 44.5|
| DCA   | -   | 115 | -21 | -   |
| TSAC  | 20  | 14  | 2.6 | 32  |

TEA: tetraethylammonium, P11: N,N'-dimethylpyrrolidinium
EMI: 1-Ethyl-3-methylimidazolium, TMS: trimethylsulfonium

Conductivity of the TSAC melts

Table 4 shows that the conductivity data of the TSAC melts containing trimethylpropylammonium (TMPA) and EMI. The specific conductivities of the TSAC melts are 13~15% higher than that of the corresponding TFSI melts. The decrease in the viscosity and the increase in the concentration are the main causes of such an increase in the specific conductivity. However, for the TSAC melts, the Walden product, which was obtained by multiplying the viscosity and the molar conductivity, was smaller than that of the TFSI melts. This means that the conductivity of the TSAC melts are not as high as the expected value from the low viscosity of the TSAC melts. The static interaction between cations and the TSAC anion might be much greater than that of the TFSI anion.

Table 4 Physical properties of amide based RTMS at 25°C

|          | M.W. | Density / g mL⁻¹ | Conc. / mol dm⁻³ | Visc. / mPas | Cond. / mS cm⁻¹ | Molar cond. / S cm² mol⁻¹ | Walden product |
|----------|------|------------------|------------------|--------------|-----------------|---------------------------|----------------|
| TMPA-TFSI| 382.4| 1.44             | 3.75             | 69           | 3.30            | 0.88                      | 61             |
| TMPA-TSAC| 346.3| 1.38             | 3.98             | 45           | 4.34            | 1.09                      | 49             |
| EMI-TFSI | 391.3| 1.52             | 3.88             | 34           | 9.21            | 2.19                      | 74             |
| EMI-TSAC | 355.3| 1.46             | 4.11             | 25           | 9.78            | 2.38                      | 60             |
Figure 3. Linear sweep voltammogram of glassy carbon electrode in dry RTMS ([H2O]<30ppm).
TMPA: trimethyl-propylammonium, TEA: tetraethylammonium. Temperature: 25°C,
Scan rate: 50 mV sec⁻¹, Reference electrode: Pt immersed in EMI-TFSI containing 15 mM I₂ and
60 mM tetrapropylammoniumiodide. Potential was corrected with the redox potential of
ferrocene in each melts.

Electrochemical windows of the TSAC melts

As previously reported, the cathodic limit of the TFSI melts were significantly
depended on the cationic structure (3). On the other hand, the anodic limit potentials of
the TFSI melts were almost the same compared with the large difference in the cathodic
limit. From these observations, the reduction of cations might reflect the cathodic limit potential of RTMS. However, unexpected results were obtained for the TSAC melts. As
shown in Figure 3, the cathodic limit of the tetraethylammonium (TEA)-TSAC was
almost the same as that of EMI-TFSI. If the cathodic limit of RTMS is determined by the
reduction potential of a cation, the cathodic limit of TEA-TSAC might be shifted toward
more negative potentials. To confirm the reduction and the oxidation of the anionic
species without the influencing of cationic species, we were investigating the
cyclicvoltammogram of glassy carbon in acetonitrile solution containing 0.1 mol dm⁻³
Li-TFSI and K-TSAC. The results are shown in Figure 4. The anodic limit potential
observed in acetonitrile solutions containing Li-TFSI and K-TSAC were almost identical
with the anodic limit of TMPA-TFSI and TEA-TSAC, respectively. This fact shows that
the oxidation limit of the AQA melts might be determined by the anion oxidation. On the
other hand, a reduction peak was observed at -2.6 V vs Fc/Fc⁺ in the acetonitrile
containing K-TSAC. Considering that the concentration of the TSAC melts is over 3 mol
dm⁻³, the reduction peak might be the cause of the poor cathodic limit of the TSAC melts
containing AQA. The reduction peak must be derived from the reduction of the TSAC
anion since the reduction of potassium occurred at much more negative potentials than
the reduction peak around -2.6 V vs Fc/Fc⁺.
CONCLUSIONS

The TSAC anion has an excellent ability to lower the melting point and the viscosity of RTMS based on aliphatic onium salts compared with other fluorinated anions such as BF₄⁻ and TFSI. An asymmetrical structure of the TSAC anion might cause the improvement of the physical properties of onium salts. Especially, it was interesting that the relatively small symmetric cations such as tetraethylphosphonium and tetraethyammonium could form RTMS, which have not yet been reported. However, the electrochemical windows of RTMS based on the TSAC anions were narrower than that of the corresponding TFSI melts even the use of an aliphatic quaternary ammonium cation. The cathodic limits of the TSAC melts were determined not by the reduction of the cationic species but by the reduction of the TSAC anion.

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