Room Temperature Molten Salts Based on Tetraalkylammonium Cations and Bis(trifluoromethylsulfonyl)imide

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Symmetric and aliphatic tetralkylammonium cations (QA) form room temperature molten salts (RTMS) with bis(trifluoromethylsulfonyl)imide (TFSI). Tetrapentylammonium (TPA) is the smallest cation to form RTMS with TFSI. The viscosity and the specific conductivity of TPA-TFSI at 25 °C are 430 mPa·s and 0.154 $\mathrm{mS \cdot cm^{-1}}$, respectively. This is the first report of the preparation of RTMS based on symmetric QA.

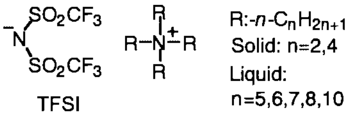
Room temperature molten salts (RTMS) have unique properties such as involatility, incombustibility, and relatively high conductivity. From this, RTMS have been studied as an attractive candidate for novel and safe electrolytes.[1,2] These research have been developed with the use of 1-ethyl-3-methylimidazolium (EMI) and chloroaluminate ($AlCl_4^-$) system due to its high ionic conductivity and low melting point.

Recently, moisture and air stable RTMS with fluorine contained anions, such as BF_4^-, $CF_3SO_3^-$, bis(trifluoromethylsulfonyl)imide (TFSI)[3–6] also have much attention to novel electrolyte for electrochemical devices. In both cases, EMI have been essential cation to form highly conductive RTMS. However, the electrochemical stability of EMI might not be enough high to perform Li electrochemistry because the cathodic limit is 0.5 V vs Li/Li^+.[1,6] Therefore some additives such as $C_6H_5SO_2Cl$, H_2O are used to expand cathodic limit of EMI.

In view of the electrochemical stability, aliphatic quaternary ammonium (QA) might be more preferable due to its cathodic stability comparing aromatic cation such as EMI. We have reported the new air and moisture stable RTMS based on trimethylpropylammonium (TMPA) and TFSI. The cathodic limit of such alipahtic quaternary ammonium (QA)-based melt was 1.0 V negatively shifted comparing with EMI-TFSI.[7] However, the viscosity of the melt was about twice as large as EMI-TFSI. In the case of aliphatic QA, the kind of anions is quite poor comparing with imidazolium systems. In particular, air and moisture stable RTMS have been known only one anion such as triethylhexylboride (B_{2226})[8] beside TFSI and hydrate systems such as tetraalkylammonium benzoate hydrate[9]. The B_{2226} and TFSI anions could form RTMS with asymmetric QA as reported so far. On the other hand, the symmetric QA-based RTMS have not been reported to the best of our knowledge beside hydrates.

Recently, we reported the new RTMS based on symmetric trialkylsulfonium such as triethylsulfonium (TES) and TFSI.[10] However, the cathodic limit of TES-TFSI was almost the same as that of EMI-TFSI. To prepare a QA-based RTMS for electrochemical devices with low melting point and low viscosity, we believe that the kind of cations and anions must be enriched to elucidate the principle of molecular design of such novel RTMS.

In this study, we tried to prepare symmetric QA-based RTMS which have not been reported yet. TFSI and seven tetraalkylammonium cations as shown in Scheme 1 were used. As a result, symmetric QA cation could form RTMS with TFSI. The smallest cation to form RTMS with TFSI was tetrapentylammonium (TPA). The physical properties such as melting point, viscosity, conductivity, density of QA-based RTMS were investigated.



Scheme 1. Structures of newly developed TFSI salts containing symmetric QA. TEA (n=2): Tetraethylammonium; TBA (n=4): Tetrabutylammonium; TPA (n=5): Tetrapentyllammonium; THA (n=6): Tetrahexylammonium; ThpA (n=7): Tetraheptylammonium; TOA (n=8): Tetraoctylammonium; TDA (n=10): Tetradecylammonium. TFSI: bis(trifluoromethylsulfonyl)-imide.

The preparation of symmetric QA-based RTMS was basically followed by the preparation of QA-TFSI melts.[7] Seven tetraalkylammonium bromides purchased from Tokyo Kasei, TEA-Br, TBA-Br, TPA-Br, THA-Br, THpA-Br, TOA-Br, TDA-Br, were recrystallized from ethyl acetate–cyclohexane solutions. Li-TFSI was used as received (Fluka). Symmetric QA-based RTMS was easily obtained by the mixing of two aqueous solutions, which contain the same concentration of Li-TFSI, and the respective tetraalkylammonium bromide. The resulting RTMS was washed with H_2O several times until no residual byproduct (LiBr) was detected with the use of $AgNO_3$. Then the RTMS was extracted with CH_2Cl_2 and dried under vacuum (100 °C) for 24 h. The yield of the symmetric QA-TFSI systems were shown in Table 1. The measurements of conductivity (TOA, CV-40M), viscosity (Yamco, VM-100) and the electrochemical measurement (ALS, model 600A) were performed in a globe box ($[O_2] < 1$ ppm, $[H_2O] < 1$ ppm). The calculated composition of the synthesized salt was almost agreed with the result of the elemental analysis operated by Sumika Chemical Analysis Service.[11] The melting point of RTMS was measured by DSC (Perkin/Elmer, Pyris 1). The melting point was obtained from the highest temperature of endothermic peaks appeared in a heating process from –150 °C to 60 °C.

The melting points of QA-based salts were shown in Figure 1. The melting point of TFSI-based QA salts were markedly decreased with the use of TFSI anion from that of the QA bromide as a source material except for tetrabutylammonium. The melting point of TFSI-based QA salts decreased below room temperature (25 °C) when a number of carbons in alkyl group in QA were larger than five. The melting point of THA-TFSI was the lowest (–6.8 °C) of all the QA-based salts as reported so far. However, it has not been clarified the reason why the melting point of TFSI salts has a minimum value at THA and increased with increasing molecular weight of cations

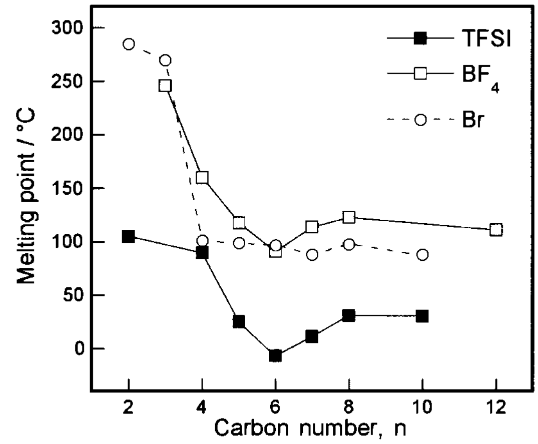


Figure 1. The relationship between melting points of various symmetric quatemary ammonium salts and the carbon number of alkyl group (-nC_nH_{2n+1}). The melting points of BF_4 and Br salts were taken from the Fluka reagent catalog.[12]

Table 1. Properties of symmetric quatemary ammonium salts based on TFSI anion at 25 °C

Cation	Yield /%	m.p. /°C	Density /g cm^{-3}	C^a /mol dm^{-3}	η^b /mPa s	Λ^c /S $cm^2 mol^{-1}$
TEA	90	105	——	——	——	——
TBA	92	91	——	——	——	——
TPA^d	96	25.2	1.16	2.01	430	0.076
THA	98	-6.8	1.11	1.75	435	0.061
THpA	99	11.2	1.10	1.59	453	0.042
TOA^d	98	31.2	1.06	1.41	$>500^e$	0.031
TDA^d	97	30.8	1.04	1.21	$>500^e$	0.015

[a] Concentration. [b] Viscosity. [c] Molar conductivity. [d] Supercooled liquid. [e] Detection limit of a viscometer used in this study.

from THA to TDA. However it should be noted that the relationships between the melting point of QA-BF_4 salts and a number of cation shown in Figure 1 was almost the same tendency as that of QA-TFSI salts. Furthermore the other QA-salts such as QA-NO_3, QA-ClO_4, also exhibit the same relationships and the minimum melting point at corresponding tetrahexylammonium salt.[12] However, further investigation on the relationships between melting point and ionic structure must be necessary to elucidate why TFSI anion strongly lowered the melting point of QA salts particularly in the case of small symmetric QA such as TEA. We need more detailed study such as X-ray diffraction study of these salts to explain why TFSI anion lowered the melting point of QA salts in view of the physical interaction between cation and anion because the electrostatic force between cation and anion might be governed the physical properties of RTMS.

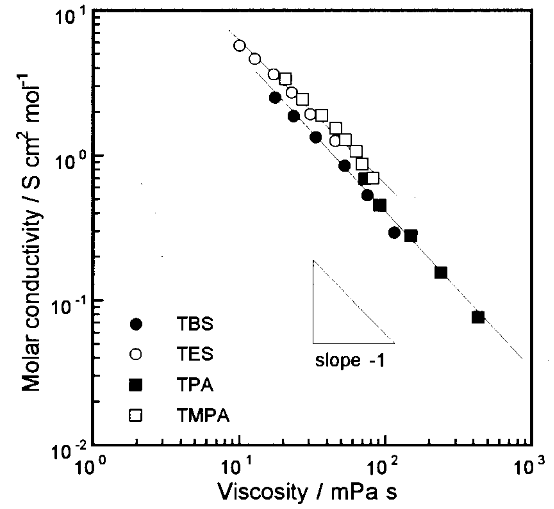


Figure 2. The relationship between viscosity and molar conductivity of RTMS based on TFSI at various temperature. TBS: Tributylsulfonium, TES: Triethylsulfonium. TPA: Tetrapentylammonium, TMPA: Trimethylpropylammonium,

The viscosity and the conductivity of symmetric QA-based melt were monotonically changed with the temperature. The molar conductivity of QA-based melt was increased with decreasing molecular weight of the melt. On the other hand, the viscosity was increased with increasing molecular weight of the melt as shown in Table 1. Figure 2 shows the relationship between the molar conductivity and the viscosity at various temperatures of TFSI-based melts. The figure indicates that the Walden's products are almost constant. Therefore Walden's rule seems to be valid for the TFSI-based melts. However, at the same viscosity, the molar conductivity of RTMS based on smaller cations such as TES, TMPA is higher than that of RTMS based on bulky cations such as TBS and TPA. This fact suggests that the diffusion of ions might be interfered with the large cations which have long alkyl chains entangled between cations.

In conclusion, we have succeeded in the synthesis of RTMS based on symmetric ammonium cation with the use of TFSI. The melting point of symmetric QA-based melt, which was dramatically lowered, with the use of TFSI anion, exhibits complicated correlation with a number of carbons of alkyl group in QA. On the other hand, density, viscosity, conductivity of symmetric QA-TFSI was changed monotonously with increasing a number of carbons of alkyl group in QA.

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11 Results of elemental analysis. Found: C, 29.3 ; H, 4.9 ; N, 6.8 ; F, 27.7%. Calcd for TEA-TFSI: C, 29.3; H, 4.9; N, 6.8; F, 27.8%. Found: C, 41.2; H, 6.9; N, 5.2; F, 22.2%. Calcd for TBA-TFSI: C, 41.4; H, 6.9; N, 5.4; F, 21.8%. Found: C, 45.6; H, 7.6; N, 4.7; F, 19.4%. Calcd for TPA-TFSI: C, 45.7; H, 7.7; N, 4.8; F, 19.7%. Found: C, 49.2; H, 8.2; N, 4.3; F, 18.4%. Calcd for THA-TFSI: C, 49.2; H, 8.3; N, 4.4; F, 18.0%. Found: C, 52.1; H, 8.7; N, 3.9; F, 16.6%. Calcd for THpA-TFSI: C, 52.2; H, 8.8; N, 4.1; F, 16.6%. Found: C, 54.7; H, 9.2; N, 3.6; F, 16.2%. Calcd for TOA-TFSI: C, 54.7; H, 9.2; N, 3.8; F, 15.3%. Found: C, 58.6; H, 9.8; N, 3.2; F, 13.4%. Calcd for TDA-TFSI: C, 58.7; H, 9.9; N, 3.3; F, 13.3%.
12 Fluka reagent catalog.