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Room temperature ionic liquids based on small aliphatic ammonium cations and asymmetric amide anions

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The asymmetric amide anion (CF_3SO_2–N^-–$COCF_3$) has excellent abilities to lower both the melting points and viscosities of room temperature ionic liquids (RTILs) combining with small aliphatic ammonium cations that have not yet been reported to form RTILs.

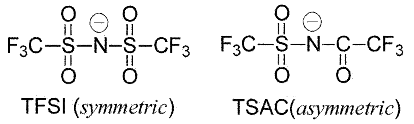
Room temperature ionic liquids (RTILs) have attracted much attention as novel solvents for green chemistry.[1] The most studied RTIL contains imidazolium cations such as 1-ethyl-3-ethylimidazolium (EMI). The reasons why the EMI systems are well studied are as follows. EMI forms low viscosity, low melting RTILs with various anions.[2] On the other hand, aliphatic quaternary ammonium (AQA) also seems to be useful for the cationic component of the RTIL since the salts containing AQA and the appropriate oxidation resistant anion such as ClO_4^-, BF_4^-, PF_6^- are sufficiently electrochemically stable to be used as the supporting electrolyte. If such AQA salts melted at room temperature and could be used as electrolytes, then volatile and flammable organic electrolytes could be eliminated in electrochemical devices such as the lithium battery. However, the AQA cation cannot form RTIL with various fluorinated anions that are able to form RTIL with EMI. To the best of our knowledge, BF_4^-[3] and bis(trifluoromethanesulfonyl)imide (TFSI)[4] are the only two fluorinated anions to form electrochemically stable RTILs. Furthermore, there is a limitation to reduce the viscosity of the AQA based RTIL compared with the imidazolium systems since the molecular weight of AQA cations could not be reduced to below some threshold value in both anions.[3,5] As the viscosity of RTILs generally decrease with decreasing molecular weight of the ion, a new anion to form a RTIL with small AQA cations might be required, especially in a practical application such as a lithium battery due to the expectation of reducing the viscosity. Recently, MacFarlane *et al.* have reported a new anion (dicyanamide (DCA)) that forms a RTIL with asymmetric and cyclic AQAs. The salts containing DCA show low melting point and low viscosity; however, the salt containing *N*,*N*-dimethylpyrrolidinium (P11) is a solid.[6]

Here, we would like to report that the asymmetric anion (2,2,2-trifluoro-*N*-(trifluoromethylsulfonyl)acetamide, TSAC)[7], as shown in Fig.1, has an excellent ability to decrease the melting point and the viscosity of its salts containing even a small aliphatic ammonium cation such as P11 which could not form a RTIL with TFSI, BF_4^-, and DCA.

The TSAC anion was prepared as the potassium salt according to ref. 7c except that the final product is not a sodium salt because of its hygroscopic nature.† A series of trimethylalkylammoniums, which as shown in Fig.2 were prepared as halides by mixing equimolar amounts of trimethylamine and the alkyl halide in water/acetone (50 : 50 vol%). *N*,*N*-dimethylpyrrolidinium iodide (P11-I), and 1-ethyl-3-methylimidazolium bromide (EMI-Br) was prepared following refs. 8 and 9, respectively. Tetramethylammonium iodide (TMA-I), trimethylethylammonium iodide (TMEA-I) and tetraethylammonium iodide (TEA-I) were purchased from Tokyo Kasei and recrystallised in acetone/ethanol before use. The TSAC salts containing small aliphatic ammonium cations were made by following the method of preparation of RTILs based on the TFSI anion.[9] The water-insoluble TSAC salts immediately separated after mixing the two aqueous solutions containing equimolar amounts of K-TSAC and a quaternary alkylammonium halide. The resulting RTIL was washed three times with H_2O. The RTIL was then extracted with CH_2Cl_2 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 ^{1}H-NMR and ^{13}C-NMR.§ The melting points of the RTILs were measured by DSC (Perkin/Elmer, Pyris 1) after the cooling of a few mg of a sample from 25 °C to -150 °C (40 °C min^{-1}). The viscosity was measured using a Brookfield DV-III + viscometer with a TC-501 circulating bath and programmable controller.

As already stated above, most of the AQA salts containing conventional fluorinated anions such as BF_4^-, PF_6^-, do not melt at room temperature, except for the salt containing dimethylethylmethoxymethylammonium and BF_4^-.[3] For large cations, tetraalkylammonium salts with a symmetric cation exhibit a high melting point (>100 °C). The TFSI anion has been known to lower the melting point of AQA salts. However, we previously reported that the melting point of a series of trimethylalkylammonium salts increased with decreasing molecular weight of the cations and exceeded rt when the molecular weight for the cation decreased below that of TMPA[5], as shown in Table 1. For the symmetric AQA cations, the melting point of the TFSI salts were about 70 °C lower compared to the corresponding salts with conventional fluorinated anions such as PF_6^-, BF_4^-. Though the RTIL could be obtained when the number of alkyl chain was greater than five, the viscosity of tetrapentylammonium(TPA)-TFSI was very high (>400 mPas at 25 °C).[10]

At first, we tried to prepare the TSAC salt with a series of asymmetric trimethylalkylammoniums together with symmetric AQAs that could not form the RTIL with TFSI. These results are shown in Table 1. Surprisingly, almost all of the cations except for TMA form RTILs with TSAC. Though TMA-TSAC did not melt at room temperature, the melting point was about 70 °C lower than the corresponding TFSI salt. It was quite



TFSI (*symmetric*) TSAC(*asymmetric*)

Fig. 1 Anionic structure used in this study.

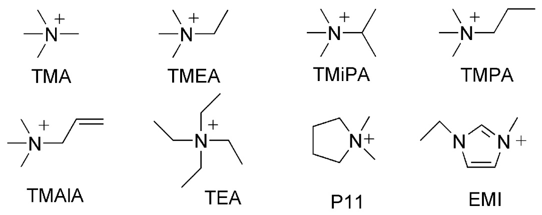


Fig. 2 Cationic structure used in this study.

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Table 1 Physical properties of TSAC salts at 25 °C

Cation	Anion	Molecular weight	Melting point/°C	Density/ g mL^{-1}	Concentration/ mol dm^{-3}	Viscosity/ mPa s	Ref.
TMA	TFSI	354	130				10
TMA	TSAC	318	64				
TEA	TFSI	410	105				10
TEA	TSAC	374	20	1.37	3.66	60	
TMEA	TSAC	332	15	1.40	4.22	51	
TMiPA	TSAC	346	21	1.41	4.08	90	
TMAlA	TSAC	344	−3.9	1.38	4.00	42	
TMPA	TSAC	346	10	1.38	3.99	45	
TMPA	TFSI	382	19	1.44	3.75	72	5
P11	PF$_6$	245	390 (decomp)				12
P11	BF$_4$	187	340 (decomp)				11
P11	DCA	166	115				6
P11	TFSI	380	105				8
P11	TSAC	344	24	1.43	4.16	80	
EMI	TSAC	355	−1.5	1.46	4.11	25	
EMI	TFSI	391	−15	1.52	3.88	34	9

interesting that the TEA as a second small symmetric AQA cation can also form RTIL with the TSAC anion. Since the molecular weight of the TEA is much smaller than the TPA, the viscosity of TEA-TSAC was about 7 times lower than that of TPA-TFSI. Not only the asymmetric cation but also a symmetric cation form low viscous RTIL with TSAC. The viscosity of the TMPA and EMI salt was reduced by changing the counter anion from TFSI to TSAC. These fact shows that the TSAC anion forms much lower melting point salts than AQA-TFSI salts and that because of both the smaller AQA cation and the asymmetric anion, AQA-TSAC has a low viscosity among the known AQA ionic liquids based on fluorinated anions.

To confirm the effect of TSAC, P11-TSAC was prepared. As we expected, only the TSAC salt formed a RTIL. Though the melting point of the P11 salt decreased about 200 °C by using a symmetric amide structure such as DCA or TFSI, a further decrease in the melting point of P11 could be observed. However, it is necessary to continue investigations into the physical properties of the TSAC salts concerning the effect of anion asymmetry since some unexpected results were obtained as follows. The melting point of EMI-TSAC was higher than that of EMI-TFSI. Also, the viscosity of TMiPA-TSAC was higher than that of TMEA-TSAC.

The electrochemical properties of RTILs based on TSAC and the preparation of RTIL based on another cationic species such as phosphonium or sulfonium are currently under investigation.

We are grateful to the Tokuyama Corp. for the supply of K-TSAC salt and some RTILs based on TSAC (TEA, TMiPA, EMI).

Notes and references

† Preparation of K-TSAC. In a 1 dm^3 three-necked flask fitted a cylindrical funnel and a thermometer were placed 69.4 g (0.466 mol) of trifluoromethanesulfonamide in 0.5 dm^3 of dry methanol. After addition of 52.3 g (0.466 mol) of potassium *t*-butoxide, the mixture was stirred at 60 °C for 3 h under nitrogen atmosphere. The reaction mixture was concentrated under reduced pressure to give the white solid. After addition of 0.25 dm^3 of dry diethyl ether, a solution of 97.8 g (0.466 mol) of trifluoroacetic anhydride in 0.25 dm^3 of dry diethyl ether was added dropwise at 0 °C and stirred at 0 °C for 2 h and then at rt for 4 h. The reaction mixture was filtered and washed with dry diethyl ether. The crystals were dried under reduced pressure to give 116.8 g (88.5% yield) of K-TSAC as colorless crystals. ^{13}C-NMR spectra of K-TSAC (100 MHz, acetone-d$_6$): δ 118 (q, CF$_3$-CO-), 121 (q, CF$_3$-SO$_2$-), 162 (q, C=O) ppm.

‡ Results of elemental analysis. Found: C, 26.5; H, 3.4; N, 8.9; F, 36.1%. Calcd for TMA-TSAC: C, 26.4; H, 3.8; N, 8.8; F, 35.8%. Found: C, 28.8; H, 4.0; N, 8.40; F, 34.6%. Calcd for TMEA-TSAC: C, 28.9; H, 4.3; N, 8.4; F, 34.3%. Found: C, 31.2; H, 4.1; N, 8.1; F, 33.8%. Calcd for TMAlA-TSAC: C, 31.4; H, 4.1; N, 8.1; F, 33.1%. Found: C, 31.1; H, 4.9; N, 8.2; F, 32.2%. Calcd for TMiPA-TSAC: C, 31.2; H, 4.7; N, 8.1; F, 32.9%. Found: C, 31.0; H, 4.8; N, 8.1; F, 33.5%. Calcd for TMPA-TSAC: C, 31.2; H, 4.7; N, 8.1; F, 32.9%. Found: C, 35.1; H, 6.4; N, 7.5; F, 30.9%. Calcd for TEA-TSAC: C, 35.3; H, 5.4; N, 7.5; F, 30.5%. Found: C, 31.2; H, 4.1; N, 8.2; F, 33.1%. Calcd for P11-TSAC: C, 31.4; H, 4.1; N, 8.1; F, 33.1%; Found: C, 30.3; H, 3.1; N, 11.8; F, 34.0%. Calcd for EMI-TSAC: C, 30.4; H, 3.1; N, 11.8; F, 32.1%.

§ Results of ^{1}H-NMR (400 MHz, acetone-d$_6$): TMA-TSAC: δ 3.40 (s, 4CH$_3$); TMEA-TSAC: 1.48 (br-t, CH$_3$), 3.32 (s,3CH$_3$), 3.64 (q, CH$_2$); TMAlA-TSAC: 3.33 (s, 3CH$_3$), 4.17 (d, CH$_2$), 5.75 (m, CH), 6.18 (s, CH), 6.20 (m, -CH=); TMiPA-TSAC: 1.52 (br-t, 2CH$_3$), 3.27 (s, 3CH$_3$), 3.89 (m, CH); TMPA-TSAC: 1.01 (t, CH$_3$), 1.95 (m, CH$_2$), 3.33 (s, 3CH$_3$), 3.50 (m, N-CH$_2$); TEA-TSAC: 1.38 (br-t, 4CH$_3$), 3.47 (q, 4CH$_2$); P11-TSAC: 2.34 (m, 2CH$_2$), 3.36 (s, 2CH$_3$), 3.73 (m, 2CH$_2$); EMI-TSAC: 1.56 (t, CH$_3$), 4.05 (s, N-CH$_3$), 4.39 (q, N-CH$_2$), 7.69 (s, CH), 7.77 (s, CH), 9.06 (s, N-CH-N) ppm. Results of ^{13}C-NMR (100 MHz, acetone-d$_6$): TMA-TSAC: δ 55.9 (t, CH$_3$); TMEA-TSAC: 8.67 (s, CH$_3$), 52.9 (t, 3CH$_3$), 62.8 (s, CH$_2$); TMAlA-TSAC: 53.1 (t, 3CH$_3$), 69.0 (s, N-CH$_2$), 126 (d, CH$_2$), 129 (s, CH); TMiPA-TSAC: 16.8 (s, 2CH$_3$), 51.2 (t, 3CH$_3$), 68.2 (s, CH); TMPA-TSAC: 10.7 (s, CH$_3$), 17.0 (s, CH$_2$), 53.6 (t, 3CH$_3$), 68.8 (s, N-CH$_2$); TEA-TSAC: 7.59 (s, 3CH$_2$), 53.0 (t, 3CH$_3$) P11-TSAC: 22.6 (s, 2CH$_2$), 52.4 (t, 2CH$_3$), 66.6 (t, 2N-CH$_2$); EMI-TSAC: 15.5 (s, CH$_3$), 36.5 (t, N-CH$_3$), 45.6 (t, N-CH$_2$), 125 (s, CH), 126 (s, CH), 137 (s, N-CH-N) ppm. The peaks derived from acetone-d$_6$ and TSAC were omitted because these peaks appeared at the same position in each TSAC salt.

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