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Aust. J. Chem. 2004, 57, 139-144

Design of Ionic Liquids for Electrochemical Applications

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Zwitterionic liquids composed of a tethered cation and anion were synthesized and their thermal properties and ionic conductivity were investigated as novel ionic liquids especially for electrochemical applications. We prepared nine zwitterions in this study. In addition, this paper includes 36 kinds of zwitterions already reported in order to discuss the relationship between the zwitterion structure and their properties. Most zwitterions melt above 100°C; their melting points are generally higher than that of simple ionic liquids. When an equimolar amount of lithium salt (LiTFSI, LiBETI, LiCF₃SO₃, LiBF₄, or LiClO₄) was added to the zwitterion, the mixture showed only a glass transition temperature T_g . The T_g values of the zwitterionic liquid/salt mixture showed the lowest value of -37° C when mixed with LiTFSI. This mixture also showed the highest ionic conductivity of 8.9×10^{-4} S cm⁻¹ at 100°C. There is a good relationship between T_g and the ionic conductivity of the zwitterionic liquid/lithium salt mixtures.

Manuscript received: 12 September 2003. Final version: 24 October 2003.

Recently, ionic liquids,^[1,2] molten salts at room temperature, have attracted the attention of many researchers because they have excellent properties such as high ion content, liquidity over a wide temperature range, low viscosity, non-volatility, non-flammability, and high ionic conductivity. Current topics are divided into two categories, (a) as neoteric solvents as environmentally benign reaction media,^[3–7] and (b) as electrolyte solutions for battery applications in, for example, lithium ion batteries,^[8–11] fuel cells,^[12–14] solar cells,^[15–17] and capacitors.^[18–20]

Most electrochemical systems require target carrier ions such as lithium cations, protons, or iodide anions for constructing corresponding cells. Therefore the matrix, which predominantly transports these target ions, is required for electrochemical applications. Although ionic liquids show excellent ionic conductivities of over 10^{-2} S cm⁻¹ at room temperature, this derives from the component ions themselves.^[21–23] These ions are mostly useless as target ions. Even when target ions were added to the ionic liquid, the ionic liquid component ions can also migrate along the potential gradient. Further, addition of other salts induced increase in both T_g and viscosity, and accordingly ionic conductivity was considerably reduced.

We have been trying to design ionic liquids in which the component ions cannot migrate along the potential gradient.^[24–26] One candidate is the zwitterion structure in which both cation and anion are tethered.^[24] Since a zwitterion includes both a cation and anion, it is expected to not migrate with the potential gradient. There are some reports on zwitterions as ion conductive matrices.^[24,27–29] They showed ionic conductivity of $10^{-5}-10^{-7} \,\mathrm{S \, cm^{-1}}$ at room temperature when alkali metal salts were added. Of course, their ionic conductivity depends on the structure and properties of both cation and anion in the zwitterion and also of the added salts. Although there are major efforts underway investigating ion-conductive poly(zwitterion)s, the analysis of the properties of monomeric zwitterions is far less developed.

In this paper, we discuss the relation between structure of the zwitterion and both thermal properties and ionic conductivity after adding alkali metal salts.

We prepared nine kinds of zwitterions in this study. In addition, this paper includes 36 kinds of zwitterions already reported in order to investigate the relationship between the zwitterion structure and their properties. Table 1 summarizes melting points $T_{\rm m}$ of previously prepared zwitterions having a sulfonate group as the anion.

Most melt above 100° C, suggesting an increase in $T_{\rm m}$ after tethering of the cation and anion. This difference would be based on the decrease in the degree of motional freedom of each ion by tethering. Some of them decomposed before melting, i.e. zwitterions 1 and 2. Of the cases having sulfonate as the counter-anion, 4 and 11 showed relatively low $T_{\rm m}$ values as compared with the other zwitterions.

Figure 1 shows the differential scanning calorimetry (DSC) charts of zwitterions 9. For the first heating process, only melting was observed. The second heating for zwitterion 9 showed a glass transition temperature T_g , crystallization point T_c , and melting point T_m of 22, 91, and 177°C, respectively. Since they were still solid at room temperature,

 Table 1. Melting points of sulfonate-containing zwitterions

Table 2. Melting points of carboxylate-containing zwitterions

No.	Structure	$T_{\rm m} [^{\circ} \rm C]$	Ref.
1		271.1 ^A	[30]
2	$\searrow_{N} \bigoplus \bigoplus_{SO_3} \bigoplus$	284.7 ^A	[30]
3		293.5 ^A	[30]
4		146.9	[30]
5		169–170	[31]
6		274.3	[30]
7		279.1 ^A	[30]
8		216.5	[30]
9		178	This work ^B
10		175	This work ^B
11		158	This work ^B
12		190	[33]
13	$\sim N \xrightarrow{\Theta} SO_3$	240	[33]
14		227	[33]
15		248	[33]
16		224	[33]

^A Decomposition temperature. ^B However these compounds have already been reported.^[32]

it appears necessary to analyze the controllable factors for lowering the $T_{\rm m}$ of these zwitterions.

The effect of the anion on the thermal properties of the zwitterions is another interesting variable. Table 2 summarizes the $T_{\rm m}$ values of zwitterions having carboxylate as the counter-anion. In order to analyze the effect of anion structure

No.	Structure	$T_{\rm m} \ [^{\circ}{\rm C}]$	Ref.
17		250	This work
18		171	This work
19		165	This work
20		130	This work
21		134	This work
22		168	This work
23		212 ^A	[34]

^A Decomposition temperature.



Fig. 1. DSC charts of zwitterion 9. (a) 1st heating; (b) 2nd heating.

points

of

dicyanoethenolate-containing

Table

4. Melting

points

of

Table

3. Melting

zwitterions			zwitterions			
No.	Structure	$T_{\rm m}$ [°C]	Ref.	No.	Structure	$T_{\rm m} [^{\circ}{\rm C}]$
24		186–187	[35]	35		186.9
25		113	[35]	36		148.4
26		201–202	[36]	37		70
27		174	[36]	38		94–95
28		168–170	[36]	39		143–144
29		173–174	[36]	40		115
30		242–246	[35]	41		136–137
31		213–217	[35]	42		144–145
32		239–240	[35]	43		129.9
33		>300	[35]	44		118–119
34		183–185	[35]	45		111.4

141

Ref.

[30]

[30]

[36]

[35]

[35]

[35]

[35]

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[35]

[35]

dicyanoethenolate-containing

on the $T_{\rm m}$ of zwitterions, zwitterions having sulfonate and carboxylate were compared. The $T_{\rm m}$ values of 9 and 18 were almost the same. Although zwitterion 19 possessed a lower $T_{\rm m}$ than that of 10, the carboxylate group cannot be concluded to be more suitable for lowering the $T_{\rm m}$ of the zwitterions. From Table 2, it is shown that zwitterions having longer spacer length between the cation and anion showed lower T_m values, within the range of spacer length studied. This is likely the result of compensation of the increase in the flexibility of ions by decrease in the ion density.

Tables 3 and 4 summarize the $T_{\rm m}$ values of zwitterions composed of an onium cation and dicyanoethenolate anion. Zwitterions having the dicyanoethenolate anion showed lower $T_{\rm m}$ values than that of zwitterions having sulfonate anion. For instance, 1 and 2 decomposed before melting at 271 and 285°C, respectively, whereas zwitterions 35 and 36 showed $T_{\rm m}$ values of 187 and 148°C, respectively. In addition, the $T_{\rm m}$ of 6 was 274°C, whereas that of zwitterion 29 was 174°C. Since the negative charge is delocalized by the electron-withdrawing effect of the cyano groups, the

Table 5. Thermal behaviour of zwitterion 10with an equimolar amount of LiX

	$T_{\rm m} \ [^{\circ}{\rm C}]$	$T_{\rm g} [^{\circ}{\rm C}]$
Neat 10 (2nd heating)	175	18
+ LiTFSI	_	-37
+ LiBETI	-	-5
+ LiCF ₃ SO ₃	_	19
$+ LiBF_4$	_	5
+ LiClO ₄	_	24

interaction force between cation and dicyanoethenolate anion is weaker than that in the case of the sulfonate anion. Therefore, the dicyanoethenolate structure is effective in lowering the T_m values of the zwitterions. However, the starting material, dicyanoketene cyclic acetal, is produced from highly toxic reagents such as potassium cyanide. Currently we are trying to prepare new zwitterions using another anion structure such as the bis(trifluoromethane)sulfonylimide (TFSI) anion. Table 5 shows the thermal behaviour of zwitterion 10 containing an equimolar amount of lithium salts. Five kinds of lithium salt (LiTFSI, lithium bis(perfluoroethylsulfonyl)imide (LiBETI), LiCF₃SO₃, LiBF₄, and LiClO₄) were used in order to compare the effect of added salt species on thermal behaviour. Zwitterion 10 showed a Tg at 18°C on second heating without salt addition. When lithium salts were added to this zwitterion, their mixtures also showed only glass transition regardless of the added salt species. The T_g of zwitterion 10 after mixing with an equimolar amount of LiTFSI was -37° C (see Fig. 2). This was the lowest T_{g} among the mixtures of zwitterion 10 with five lithium salts. LiTFSI also produces the lowest T_g for an analogous zwitterion (with a three-carbon chain).^[38] It is known that the TFSI anion has plasticizing effect when it was added to polyether matrix.^[39] This ability seems to be effective for lowering T_g in the case of zwitterions. The analysis of this effect is still under investigation.

Figure 3 shows temperature dependence of the ionic conductivity for zwitterion 10 with and without an equimolar amount of lithium salt. Neat 10 showed low ionic conductivity of approximately 10⁻⁶ S cm⁻¹ even at 200°C because there are no mobile ions in the system. On the other hand, 10 mixed with an equimolar amount of lithium salt showed much higher ionic conductivity than that of the neat zwitterion. Among these lithium salts, the zwitterion mixture including LiTFSI showed the highest ionic conductivity of $8.9 \times 10^{-4} \,\mathrm{S \, cm^{-1}}$ at 100°C, reflecting the lowest $T_{\rm g}$ of -37° C. This result agrees with that of zwitterion 9, including various lithium salts.^[24] In addition, we will report that there is a good relation between the ionic conductivity and T_g for various zwitterions including lithium salts.^[37b] As shown in Fig. 3, the ionic conductivity of zwitterions with and without lithium salts was measured over a wide temperature range. It has already been confirmed that the zwitterion including an equimolar amount of LiTFSI decomposed at around 300°C before volatilizing.^[38] Therefore, these zwitterionic liquids can work as non-volatile solvents and be able to dissolve salts. It is quite an important feature for the electrochemical



Fig. 2. DSC charts of zwitterion 10 with an equimolar amount of LiTFSI.



Fig. 3. Temperature dependence of the ionic conductivity for zwitterion 10 with an equimolar amount of LiX.

applications. Currently we are investigating electrochemical properties of zwitterionic liquids in detail.

To conclude, we have synthesized some zwitterions and investigated their thermal properties. We focussed especially on the effect of lithium salt addition on both their thermal properties and the ionic conductivity. The $T_{\rm m}$ values of the zwitterions was lowered by increasing the spacer length between the cation and anion. Zwitterions with a dicyanoethenolate anion had lower $T_{\rm m}$ values than that of other anion species. Anion structures with delocalized negative charge should be effective for further lowering the $T_{\rm m}$ of the zwitterions. Addition of lithium salts (LiTFSI, LiBETI, LiBF₄, LiCF₃SO₃, and LiClO₄) made the zwitterion **10** amorphous. LiTFSI was effective in producing the lowest $T_{\rm g}$ of zwitterion **10** at -37° C. It also showed the highest ionic conductivity of 8.9×10^{-4} S cm⁻¹ at 100°C.



Scheme 1. Synthesis of sulfonate-containing zwitterions.



Scheme 2. Synthesis of carboxylate-containing zwitterions.



Scheme 3. Synthesis of dicyanoethenolate-containing zwitterions.

Experimental

Materials

N-Ethylimidazole, 1,3-propanesultone, and 1,4-butanesultone were purchased from Tokyo Kasei. *N*-Methylimidazole and *N*-butylimidazole were purchased from Aldrich. LiTFSI and LiBETI were a gift from the Sumitomo 3M corporation. All reagents were used without further purification.

Synthesis of Zwitterions

Schemes 1–3 show the synthetic routes of zwitterions with different anion structure. The synthesis of zwitterions has been described in detail elsewhere.^[30,35,36] Here we added the synthesis of **8** as a reference. *N*-Methylimidazole (4.4 g, 0.54 mmol) was dissolved in acetone (80 mL), and then 1,3-propane sultone (6.6 g, 0.54 mmol) was added to the solution. The solution was stirred under dry nitrogen at room temperature for 3 d. The insoluble zwitterion was separated by filtration. It was further recrystallized from ethanol (yield 47%).

Methods

Structures were confirmed by ¹H NMR spectroscopy (JEOL α -500 NMR spectrometer). Ionic conductivity of the obtained compounds was measured with complex-impedance method using an impedance analyzer (Solartron 1260, Schlumberger). Dynamic ionic conductivity measurement system was developed in our laboratory.^[40] The conductivity measurements were performed in dry nitrogen gas atmosphere in the temperature range of +30 to +200°C. The DSC measurement was performed with a DSC-6200 (Seiko) at a heating rate of 10°C min⁻¹ and temperature range -120 to +300°C.

Acknowledgments

The present study was supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan (#14205136). The present study was carried out under the 21st Century COE program, Future Nano Materials.

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