Effect of Methyl Groups onto Imidazolium Cation Ring on Liquid Crystallinity and Ionic Conductivity of Amphiphilic Ionic Liquids

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Phase transition behavior of imidazolium dodecylsulfonate was considerably affected by the introduction of methyl groups onto the imidazolium cation ring. Methyl group on the 2-position eliminated the liquid crystallinity. That on the 4-position was effective to suppress the crystallization.

Ionic liquids were prepared by coupling asymmetric organic cations and charge-delocalized anions.[1] Since these ionic liquids (ILs) show such excellent properties as high ionic conductivity, non-volatility, non-flammability, etc., ILs have been studied vigorously in wide variety of research fields.[2] Taking the possibility of functional design into account, it is important to analyze the effect of structure on their properties. For example, a proton on the 2-position of imidazolium ring has recently been revealed to have an important role to interact with anion through hydrogen bond.[3] It is also known that introduction of a methyl group on the 2-position of imidazolium ring elevated the melting point of the corresponding ILs.[3]

On the other hand, amphiphilic ionic liquids (AILs) such as salts containing long hydrocarbon chain or perfluorocarbon chain on the imidazolium cation show thermotropic liquid crystalline phase in the bulk.[4] These AILs provide phase-separated layers of polar ionic liquid domain and nonpolar alkyl chains. We have already reported that these AILs were effective to provide 1-[5] and 2-dimentional[6] ion conductive path by using self-assemble characteristics of these AILs. Such assembled AILs show dramatic change in the ionic conductivity through the phase transition. Since this transition can be used as switching devices, it is necessary to study the effect of their structures on the transition behavior. There are a lot of studies[4,7] on the phase transition and assembled structure of alkylpyridinium salts by changing alkyl chain length of cations. We focused on the methyl group substitution on the imidazolium cation ring expecting fine tuning of thermal behavior. In the present study, we prepare a series of methyl substituted imidazolium dodecylsulfonates, and analyze their phase transition behavior and ionic conductivity.

1,4-Dimethylimidazole was synthesized under Ar atmosphere as follows. 4-Methylimidazole was dissolved in THF and the resulting solution was added to a NaH/THF turbid mixture at 0 °C. After stirring the mixture for 2 h, it was refluxed over night. The mixture was cooled to 0 °C, and then methanesulfonic acid methyl ester was added and the mixture was further stirred for 2 h. The mixture was refluxed again for 1 day. Then precipitated CH_3SO_3Na was removed by filtration. The solution was concentrated in vacuo. The residue was purified by distillation under reduced pressure. 1,4,5-Trimethylimidazole was prepared according to the reported method.[8] 1-Methyl-, and 1,2-dimethylimidazole (Aldrich) were purified by distillation under reduced pressure before use. *N*,*N*′-Dimethylimidazolium iodides were obtained by the reaction of *N*-methylimidazoles and iodomethane in acetonitrile for 1 day at room temperature. The product was purified by recrystallization from ethylacetate/acetonitrile. Silver dodecylsulfonate was obtained by ion-exchange reaction between sodium dodecylsulfonate and silver nitrate in water. The white precipitate was corrected by the filtration and purified by the recrystallization from methanol. *N*,*N*′-Dimethylimidazolium dodecylsulfonates were obtained by ion-exchange reaction of *N*,*N*′-dimethylimidazolium iodides and silver dodecylsulfonate in dichloromethane at room temperature. The precipitated silver iodide was removed by filtration, solvent was removed in vacuo. The obtained white powder was purified by recrystallization from acetonitrile three times. The product was collected by filtration and dried in vacuo at 45 °C for 3 days.

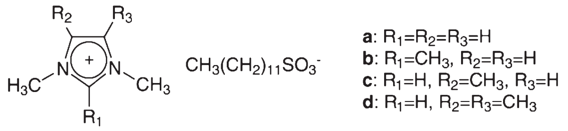

Figure 1. Structure of various methyl substituted imidazolium dodecylsulfonate.

Phase transition behavior was characterized by DSC measurement and polarized optical microscopic observation. Dynamic ionic conductivity was carried out by complex impedance method with comb-shaped gold electrode cell system.

First, we studied the liquid crystallinity of the obtained AILs. Table 1 shows the summary of phase transition behavior of AILs (**a**, **b**, **c**, and **d**). 1,3-Dimethylimidazolium salt (**a**) showed enantiotropic smectic A phase (S_A). Imidazolium salts having methyl groups on the 1, 3, and 4-position (**c**) showed monotropic S_A phase. Furthermore, 1,3,4,5-tetramethylimidazolium salt (**d**) showed no liquid crystalline phase. These results strongly suggested that the increase in the number of methyl groups onto imidazolium ring gradually suppressed the liquid crystallinity. Seddon et al.[9] reported that the temperature range of mesophase for *N*-alkylpyridinium hexafluorophosphate was narrowed by further methyl substitution.[9] There is no further study on the effect of methyl substitution on the properties of AILs.

On the other hand, the importance of proton at the 2-position of imidazolium ring has already been reported through the experiments analyzed with X-ray diffraction study and ^1H NMR.[3] The salt **b** where proton at the 2-position was substituted into methyl group showed no liquid crystallinity. This result clearly shows that the proton at the 2-position is quite important for the liquid crystallinity of AILs.

Table 1. Phase transition temperature (°C) for **a**, **b**, **c**, and **d** (enthalpy/kJ mol^{-1} in parentheses) detected by DSC (signal peak) from the second heating and cooling between −60 and 250 °C at the rate of 10 °C min^{-1}

Comp.	Cycle	Phase transition behavior							ΔT
		Cr′		Cr		S$_A$		Iso	
a	Heat			•	90.3 (52.1)	•	177.2 (0.62)	•	45.5
	Cool			•	44.8 (49.6)	•	174.5 (0.55)	•	
b	Heat	•	98.2 (46.7)	•	202.0 (9.84)			•	11.8
	Cool	•	69.3 (49.6)	•	190.2 (10.4)			•	
c	Heat			•	95.3 (41.5)			•	54.3
	Cool			•	41.0 (41.3)	•	92.5 (0.18)	•	
d	Heat			•	108.9 (51.9)			•	33.3
	Cool			•	75.6 (49.4)			•	

Iso = Isotropic liquid, S$_A$ = Smectic A phase,
Cr and Cr′ = Crystal

Phase transition temperature of these AILs is also shown in Table 1. The salt **b** showed the highest melting point and low supercooling characteristics (ΔT; difference between melting point and freezing point). However, the salt **c** had the same number of methyl groups on the imidazolium ring as **b**, **c** kept good liquid crystallinity like **a**. These results strongly suggested the following two points. One is that the proton at 2-position is important for liquid crystallinity of amphiphilic ionic liquid. The other is that the introduction of methyl group to prepare asymmetric structure of imidazolium cation is effective to keep liquid crystalline phase without elevation of freezing point. Also, this salt **c** showed the largest ΔT. This is one of advantages of AILs to spread temperature range of liquid crystalline phase.

Figure 2 shows the temperature dependence of ionic conductivity for monotropic liquid crystalline compound **c**. On heating, a big conductivity jump was found reflecting crystal-isotropic phase transition temperature. The ionic conductivity started to deviate at around 80 °C as seen in Figure 2. This behavior agreed with the DSC results (data not shown). On cooling, ionic conductivity was lowered in isotropic phase, it jumped at the phase transition from isotropic to S$_A$ phase (around 100 °C). This jump was comprehensible as the formation of successive ion conductive pathway of ionic liquids in the phase separated domain. Then, the ionic conductivity dropped at the freezing point. The monotropic liquid crystalline compound **c** showed a large hysteresis in the temperature dependence of the ionic conductivity reflecting characteristic phase transition behavior. The salts **a** and **d** also showed some hysteresis in the Arrhenius plot of the ionic conductivity, but monotropic S$_A$ phase was found only in salt **c**.

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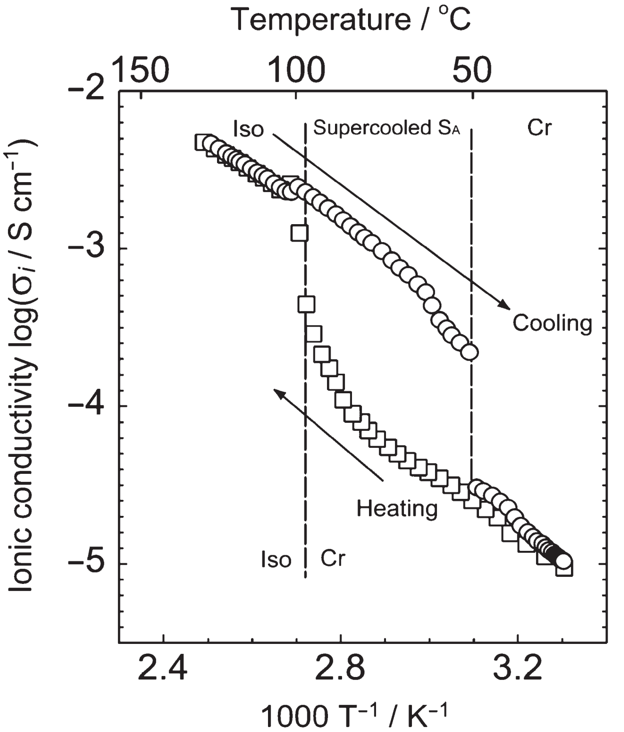

Figure 2. Temperature dependence of ionic conductivity for **c** on heating (□) and cooling (○).

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