Ordering Structure of Binary Aliphatic Quaternary Ammonium Ionic Liquids: AQA-TFSA Systems

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The effects of secondary cationic species on the ordering structure in room temperature ionic liquids (RTILs) are discussed. Binary RTILs refer to mixture of trimethyl-n-octylammonium bis(trifluoromethanesulfonylimide) \( \text{N}_{110} \text{[TFSA]} \) and alkali or alkali-earth metal bis(trifluoromethanesulfonylimide) \( \text{M}[\text{TFSA}] \); \( \text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba} \) in an appropriate molar ratio \( (x = 0.1, 0.2, 0.3, 0.5) \), denoted as \( \text{M}_{x} \text{N}_{110-x} \text{[TFSA]} \). From SAXS and WAXS measurements of \( \text{M}_{x} \text{N}_{110-x} \text{[TFSA]} \), the intensity of first peak derived from the ordering structure increases with addition of \( \text{M}[\text{TFSA}] \). It is suggested that the metal cation has an intensive interaction with TFSA anion and cationic structural ordering are enhanced. We discussed the relationship between ionic size and the formation mechanism of the local ordering structure in binary ionic liquids containing alkali metal and alkali earth metal based on aliphatic quaternary ammonium (AQA) cations is clarified.

**Key Words**: Binary Ionic Liquids, Lithium Containing Ionic Liquids, Battery Electrolyte, Ionic Strength, Local Ordering Structure, Small Angle X-ray Scattering, Raman Spectroscopy

1 Introduction

Recently, there is a considerable interest in the structural features of RTILs, for example, (i) as oriented solvents which can impart selectivity in reactions by ordering reactants, (ii) as templates for the synthesis of mesoporous and zeolitic materials and in the formation of ordered thin films.\(^{1-3}\) In some kinds of ionic liquids, ordering structures have been examined by small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) techniques.\(^{4-5}\) In our previous work, we have employed similar techniques to investigate RTILs based on AQA cation and TFSA anion.\(^{6}\) These techniques are useful tools to obtain experimental evidence of the information of nanoscale assembling structure formed by AQA cations in RTILs. In this paper, we provide the information on effects of heterogeneous species on local ordering structure consisting of AQA cation. We employed alkali metal and alkali earth metal ion (Li, Na, K, Rb, Cs, Mg, Ca, Sr, and Ba) as heterogeneous species, taking into account the difference of ionic radius and ionic potential of metal cation.

2 Experimental

All the ionic liquids were synthesized under ambient atmospheric conditions. In the case of aliphatic quaternary ammonium bis(trifluoromethanesulfonylimide) (AQA-TFSA), asymmetry AQA halides were obtained based upon the reaction of \( n \)-propylchloride, \( n \)-butylbromide, \( n \)-pentylbromide, \( n \)-hexylbromide, \( n \)-heptylbromide, \( n \)-octylbromide, \( n \)-nonylbromide, \( n \)-decylbromide, \( n \)-dodecylbromide, respectively (above 95%, Tokyo Kasei Kogyo Co., Ltd.) with stoichiometric amount of trimethylamine (30 wt%, Nacalaitesque Inc.) as follows:

\[
\begin{align*}
n-C_{n} \text{H}_{2n+1} \text{X} + (\text{CH}_{3})_{2} \text{N} & \rightarrow n-C_{n} \text{H}_{2n+1}(\text{CH}_{3})_{2} \text{NX} \quad (n = 1-12, \text{X} = \text{I or Br}) \\
n-C_{n} \text{H}_{2n+1}(\text{CH}_{3})_{2} \text{NX} + \text{LiN(SO}_{2} \text{CF}_{2})_{2} & \rightarrow n-C_{n} \text{H}_{2n+1}(\text{CH}_{3})_{2} \text{N}^{+} \text{N}^{-} \text{(SO}_{2} \text{CF}_{2})_{2} + \text{LiX} \\
(n = 1-12, \text{X} = \text{I or Br})
\end{align*}
\]

Here, samples of \( n-C_{n} \text{H}_{2n+1}(\text{CH}_{3})_{2} \text{N}^{+} \text{N}^{-} \text{(SO}_{2} \text{CF}_{2})_{2} \) are denoted \( \text{N}_{110} \text{[TFSA]} \). LiTFSA and equimolar amount of AQA halides were separately dissolved in 20 cm\(^{3}\) of distilled water in order to prepare the respective aqueous solutions. These solutions were mixed and agitated for 3 h at 70°C using magnetic stirring unit. The mixed solution consisted of organic phase and aqueous phase containing LiX. Organic phase obtained by separation funnel was extracted with 1, 2-dichloroethane (Nacalai Tesque,
Inc., 99%), and repeatedly evaporated and refined with distilled water until no residual byproduct was detected. 0.1 M AgNO₃ (Nacalai Tesque, Inc.) was used to check the byproduct. The recovered organic phase was dried under vacuum for 3 hr at 120°C and stored in glove box under dry nitrogen atmosphere.

As the secondary components, the organic metal salts, M[TFSAl₄]: (M = Li, Na, K, Rb, Cs, Mg, Ca, Sr and Ba) were purchased or synthesized under ambient atmospheric conditions based upon acid-base reaction of inorganic salts (Na₂CO₃, Cs₂CO₃, MgCO₃, Ca(OH)₂, BaCO₃ (Nacalai Tesque, Inc.) SrCO₃ and Rb₂CO₃ (Wako Pure Chemical Industries, Ltd.)) with 1,1,1-trifluoro-N-(trifluoromethyl) sulfonamide (HTFSA ; Morita Chemical Industries CO., LTD.) as follows:

\[
\begin{align*}
\text{M₂CO₃ + 2HTFSA} & \rightarrow 2\text{M₃[TFSAl₄]} + \text{CO}_2 + \text{H}_2\text{O} \\
\text{M₃CO₃ + 2HTFSA} & \rightarrow \text{M₄[TFSAl₄]} + \text{CO}_2 + \text{H}_2\text{O}
\end{align*}
\]

\( M = \text{Na, Rb, Cs} \) (3)

\( M = \text{Mg, Ca, Sr, Ba} \) (4)

5 g of HTFSA and a little excess of inorganic salt were separately dissolved in 20 cm³ distilled water in order to prepare the respective aqueous solutions. These solutions were then mixed and stirred for 5 h at 70°C using magnetic stirring unit. After removing residual inorganic salt by filtration, the solution was allowed to evaporate until yielding a white solid. In the case of the synthesis using water-soluble inorganic salt, the resulting solid was dissolved in ethanol to remove inorganic salt of low solubility. The recovered salts was dried under vacuum for 1 h at 120°C and kept in glove box under dry nitrogen atmosphere.

Small angle X-ray scattering (SAXS) and wide angle X-ray scattering instrument, Anton Parr SAXS system SAXSess was adopted to discuss the local ordering structure of RTILs. The small angle and wide angle X-ray scattering instrument from Anton Parr GmbHI was used in slit collimation configuration with PW3830 laboratory X-ray generator (40 kV, 50 mA) with long fine-focus sealed-glass X-ray tube (CuKα, wavelength of \( \lambda = 0.1542 \) nm). Each sample was loaded into quartz capillaries by a syringe. Temperature range of SAXS and WAXS measurements was from 10 to 70 °C. X-ray accumulation of each measurement was executed for 10 minutes. The detection was performed with the 2D imaging-plate reader Cyclone® by Perkin Elmer. From obtained scattering pattern, the scattering vector; \( q \), was calculated from the following equation:

\[
q = (4\pi/\lambda) \sin(\theta/2)
\]

where \( \theta \) is scattering angle. We focused scattering region \( \geq 0.2 \) nm⁻¹.

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**Fig. 1** SAXS/WAXS profiles of \( \text{N}_{1114} \text{[TFSAl₄]} \) at 70°C.

**Fig. 2** Variation of \( d \) values with carbon number in alkyl group of cation for \( \text{N}_{1114} \text{[TFSAl₄]} \).

### 3 Results and Discussion

#### 3.1 The local ordering structure in \( \text{N}_{1114} \text{[TFSAl₄]} \)

The results of SAXS and WAXS spectra of \( \text{N}_{1114} \text{[TFSAl₄]} \) at 70°C are shown in Fig. 1. There are two or three scattering peaks observed; the first peak confirmed above \( n = 5 \) ca. \( q = 2-4 \) nm⁻¹ at SAXS region and the second peak ca. \( q = 8 \) and the third peak ca. \( q = 13 \) at WAXS region. The intensity and position of the first peak increased and shifted toward low \( q \)-values with the increasing of alkyl chain length of \( \text{N}_{1114} \) cation. The bragg’s \( d \) values were calculated according to Eq. 6.

\[ d = 2\pi/q \] (6)

The variation of \( d \) values with alkyl carbon number \( n \) of \( \text{N}_{1114} \) cation is shown in Fig. 2. There is linear relationship between space \( d \) and alkyl carbon number \( n \). The first peak could be assigned to the local ordering structure formed by van der Waals force between alkyl chains of \( \text{N}_{1114} \) cation.

#### 3.2 Effect of secondary elements on the ordering structure of binary ionic liquids

In order to examine the influence of various heteroge-
Fig. 3  SAXS/WAXS spectra of $M_2[N_{1116}]_4[\text{TFSA}]_{1-x+y}$, $M=$ (a) Li, (b) Na, (c) K, (d) Rb, (e) Cs, (f) Mg, (g) Ca, (h) Sr, and (i) Ba.

neous metal cation on the local ordering structure, SAXS and WAXS of $M_2[N_{1116}]_4[\text{TFSA}]_{1-x+y}$, $M=$ Li, Na, K, Rb, Cs, Mg, Ca, Sr, and Ba. Molar ratio : $x = 0.1, 0.2, 0.3$ and $0.5, y = 1, 2$) were measured at 70°C. The SAXS spectra are shown in Fig. 3. With addition of $M[\text{TFSA}]_4$, the intensity of second peak assigned to AQA cation decreased. Since AQA cation was substituted by metal cation, the relative number of AQA cation as scattering substance decreased. The intensity ratio of first peak around $q = 4\sim5$, to third peak around $q = 12$ increased for each system. Second peak assigned to the cationic species decreased. Third peak is constant due to the same anionic species TFSA. The increase of intensity ratio means scattering substance increasing in X-ray scattering method: the number of local ordering structure in the system increase. Normalized intensity which
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Fig. 4 Variations of Normalized intensity: $I_{\text{first}}/I_{\text{morse}}$ with molar ratio of metal cations for SAXS/WAXS spectra of \( \text{Li}^+ \text{[N}_{11}\text{[\text{TFSA}]_{-e}} \).

is the intensity of first peak divided by the intensity of third peak ($I_{\text{normalized}} = I_{\text{first}}/I_{\text{morse}}$). It is shown in Fig. 4. Normalized intensity increased with increasing ionic radius. This trend is more effective in mixed alkali earth metal than alkali metal. There must be coherent relationship between the enhancement of local ordering structure and heterogeneous metal cation.

The local ordering structure is enhanced in mixing metal ion which has larger ionic radius and valence of ion. We discussed this behavior from the viewpoints of ionic radius and ionic potential (surface charge) calculated according to Eq. 7:

Ionic potential (pm$^{-1}$) = valence/ionic radius (pm) (7)

Comparing the group of similar ionic radius with various ionic potential; (Li$^+$, Mg$^{2+}$), (Na$^+$, Ca$^{2+}$), (K$^+$, Ba$^{2+}$) and of similar ionic potential with various ionic radius; (K$^+$, Rb$^+$, Cs$^+$), we consider the formation mechanism of local ordering structure by mixing metal cation. It is considered that ionic interaction between metal cation and TFSA- anion can be estimated by the Raman spectra of CF$_3$ group of TFSA ion. Raman spectra of CF$_3$ symmetric deformation bands are shown in Fig. 5. In a (K$^+$, Rb$^+$, Cs$^+$) group which has similar ionic potential with various ionic radius, the lower intensity was observed for small ionic radii. On the other hands, no shift of CF$_3$ deformation band was observed for the systems containing K$^+$, Rb$^+$, and Cs$^+$, due to similar ionic potential. It is suggested that the main disturbing factors are the steric hindrance and coulombic repulsive force between TFSA- anions attracted to metal cation and, disorientation of cationic ordering structure. Thus, disturbance through steric hindrance and coulombic repulsive force between TFSA- anions is stronger in the system with smaller ionic radius. Such a disturbance interrupts the formation of ordering structure in AQA cations, leading to a decrease of the normalized intensity compared to the system with larger ionic radius. In the opposite, mixing with larger metal ion considerably reduces the stress caused by steric hindrance and coulombic repulsive force. As a result, ordering structure is formed.

In (Na$^+$, Ca$^{2+}$) and (K$^+$, Ba$^{2+}$) groups which contain elements with approximately the same ionic radius shows different ionic potentials: Ca$^{2+}$ and Ba$^{2+}$ have higher ionic potential than Na$^+$ and K$^+$ in each group. According to Raman spectra of CF$_3$ symmetric deformation bands, a new peak appears at 750-745 cm$^{-1}$ and the intensity increases with additional metal ion. The bands at 750-745 cm$^{-1}$ mean the formation of ion-pair or complex by TFSA anion strongly interacting with metal ion. Based on the above-mentioned hypothesis, the formation of local ordering structure makes flexible AQA cations stabilized. The stronger the coulombic attraction force of metal ion, the higher the degree of freedom becomes, and the local ordering structure is easily formed. An ordered structure is enhanced for cations with high ionic potential in each group as it is confirmed for Ca$^{2+}$ and Ba$^{2+}$ in (Na$^+$, Ca$^{2+}$) and (K$^+$, Ba$^{2+}$) groups. Similar trend observed for elements with higher ionic radii could be seen for (Li$^+$, Mg$^{2+}$) group which has small ionic radii; Mg$^{2+}$ emerges with higher ionic potential than Li$^+$. From $x = 0.1$ to 0.5, the band at 750-745 cm$^{-1}$ derived from complex enhanced as a molar ratio increased. On the other hand, normalized intensity showed signs of leveling off. It is suggested that complex or aggregate of lithium ion with TFSA anion is easily formed, and the local ordering structure is disturbed. Normalized intensity is higher for larger ionic potential with either group and, with the larger ionic radius for each element.
Consequently, it is suggested that ionic radius is predominant factor to form local ordering structure.

4 Conclusions

The effect of alkali metal cation and alkali earth metal cation caused enhancement of the local ordering structure containing aliphatic quaternary ammonium (AQA) cation. Due to the strong interaction between TFSA anions and metal cation, AQA cations become flexible and, much flexibility facilitates the formation of stable local ordering structure. Regarding the behavior of ionic radius and ionic potential, there are two factors: (i) the ionic potential depends on the strength of the coulombic attractive force between the metal cation and TFSA anion, (ii) the ionic radius is disturbed by steric hindrance and coulombic repulsive force among attracted TFSA anions. The ionic radius is the predominant factor to form local ordering structure. However the formation of local ordering structure becomes difficult in the system containing large ions, no matter stronger is the coulombic force. The foregoing clarifies the formation mechanism of the local ordering structure in binary ionic liquids containing alkali metal and alkali earth metal based on AQA cation and TFSA anion.

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References