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(Citation)
ECS Transactions,16(49):69-77

(Issue Date)
2009

(Resource Type)
journal article

(Version)
Version of Record

ECS Transactions, 16 (49) 69-77 (2009)
10.1149/1.3159309 ©The Electrochemical Society

Liquid Ordering Structure in Binary Room Temperature Ionic Liquids Based on Aliphatic Quaternary Ammonium Ions

Minoru Mizuhata, Takeshi Minowa, Masanori Maekawa and Shigehito Deki

Department of Chemical Science and Engineering,
Faculty of Engineering, Kobe University,
1-1 Rokkodai-cho, Nada, Kobe, 657-8501 Japan
E-mail: mizuhata@kobe-u.ac.jp

The effects of hetero-species on the local ordering structure composed of AQA cation are discussed with alkali metal- and alkali earth metal cations (Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) as hetero-species, taking into account the difference of ionic potential of metal cations. The effects of secondary cationic species on the ordering structure in ILs are discussed. Binary ILs refer to mixture of N111,8[TFSI] and $M[TFSI]_z$ (M = Li+, Na+, K+, Rb+, Cs+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) in an appropriate molar ratio (x = 0.1, 0.2, 0.3, 0.5, z = 1, 2), denoted as $M_x N111,8_{1-x}[TFSI]_{\{1+(z-1)x\}}$. From the results of SAXS and WAXS measurement of $M_x N111,8_{1-x}[TFSI]_{\{1+(z-1)x\}}$, the intensity assigned to ordering structure increases with addition of $M[TFSI]_z$ and, is higher in mixed with alkali earth metal cation than alkali metal cation. Cationic structural ordering is enhanced by the effects of added metal cation.

1. Introduction

Room temperature ionic liquids (RTILs) have attracted much attention due to their unusual properties such as a negligible vapor pressure, non-flammability and good ability to dissolve organic and inorganic compounds, and polymeric materials. With these unusual properties, ionic liquids are expected to be superior media or solvent in various kinds of utilizations, for example, environmentally friendly solvents for chemical synthesis, biocatalysis, separation technologies and nanomaterial preparations. In addition, RTILs which have good ionic conductivity are also suitable as solvent-free electrolytes in electrochemical devices and processes, such as rechargeable lithium batteries, fuel cells, electrochemical capacitors and electrodeposition [1-3].

RTILs are salts with low melting point, typically below 100°C. In RTILs, the ionic species containing bulky cation have complex structure and symmetry. Such a chemical architecture may lead to specific property such as a very low melting point, wide temperature window and negligible vapor pressure that makes the liquid state stable [4]. Especially, aliphatic quaternary ammonium (AQA) and asymmetric imidazolium ionic species having long alkyl chain are expected to show intensive “intermolecular interaction” and to form assembling structure in liquid media[4-7]. 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[8-10]. 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, 6]. In our previous work, we have employed similar techniques to investigate RTILs. These techniques are useful tools to obtain experimental evidence of the information of nanoscale assembling structure. We have obtained the experimental evidence of the ordering structure formed by alkane moiety of cation in ILs containing aliphatic quaternary ammonium cation; $[R\mathrm{NMe_3}]^+$ where $R = n\text{-}\mathrm{C_nH_{2n+1}}$ (n = 3-12) which is denoted as “N111n”, bis(trifluorometane sulfonyl)imide anion; $[\mathrm{TFSI}]^-$ [5].

On the other hand, for the practical applications of RTILs in biocatalysis, separation technologies, and lithium batteries, mixed ionic systems are often more effective than pure ionic liquids. It is considered that the structure property of mixed solution is changed by the effects of different species. In this paper, we provide the information on the effects of hetero-species on the local ordering structure composed of AQA cation. We employed alkali metal- and alkali earth metal cations (Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) as hetero-species, taking into account the difference of ionic potential of metal cations.

2. Experimental

2.1. Synthesis of RTILs

All the ionic liquids were synthesized under ambient atmospheric conditions. In the case of aliphatic quaternary ammonium bis(trifluoromethanesulfoyl)imide (AQA[TFSI]), asymmetry AQA halides were obtained based upon the reaction of *n*-propyliodide, *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:

$$n\text{-}\mathrm{C_nH_{2n+1}X + (CH_3)_3N} \longrightarrow n\text{-}\mathrm{C_nH_{2n+1}(CH_3)_3NX} \quad (\mathrm{n} = 1\text{-}12,\ \mathrm{X} = \mathrm{I\ or\ Br}) \tag{1}$$

17 cm^3 of AQA halides and excess of trimethylamine were mixed and stirred in 100 cm^3 of propanone for 2 hr at 50°C. The resulting crystalline salts collected after evaporation of solvent and unreacted trimethylamine were recrystallized and washed with propanone and hexane until pure white salts were obtained, and vacuum dried for 2 hr at 120°C. Symmetry and cyclic AQA halides (tetra-*n*-pentylammoniumbromide, tetra-*n*-hexylammoniumbromide, N-methyl-*n*-propylpyrrolidiniumbromide, and N-methyl-n-propylpiperidiumbromide) and N,N-dimethyl,N-methyl,N-n-propylammoniumbromide were used on purchased (Tokyo Kasei Kogyo Co., Ltd). Synthesized or purchased AQA halide and Li[TFSI] (Morita Chemical Industries CO., LTD.) were submitted to anion-exchange reaction as follows :

$$\begin{aligned} & n\text{-}\mathrm{C_nH_{2n+1}(CH_3)_3NX + LiN(SO_2CF_3)_2} \\ & \qquad \longrightarrow n\text{-}\mathrm{C_nH_{2n+1}(CH_3)_3N^+\,N^-(SO_2CF_3)_2 + LiX} \quad (\mathrm{n} = 1\text{-}12,\ \mathrm{X} = \mathrm{I\ or\ Br}) \end{aligned} \tag{2}$$

5 g of Li[TFSI] 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 hr 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-dichloroehane (Nacalai Tesque, Inc., 99%), and repeatedly evaporated and refined with distilled water until no residual byproduct was detected. 0.1 M $AgNO_3$ (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 [5]. The structural characteristics of the used RTILs are shown in Fig 1.

2.2 Synthesis of organic metal salts

The organic metal salts, M(TFSI)*z* (M = Li, Na, K, Rb, Cs, Mg, Ca, Sr and Ba ; $z = 1, 2$) were purchased or synthesized [11-15] under ambient atmospheric conditions based upon acid-base reaction of inorganic salts (Na_2CO_3, Cs_2CO_3, $MgCO_3$, $Ca(OH)_2$, $BaCO_3$ (Nacalai Tesque, Inc.) $SrCO_3$ and Rb_2CO_3 (Wako Pure Chemical Industries, Ltd.)) with bis(trifluoromethanesulfonyl) imide (HTFSI ; Morita Chemical Industries CO.,LTD.) as follows :

$$M_{A2}CO_3 + 2H[TFSI] \longrightarrow 2M_A[TFSI] + CO_2 + H_2O \quad (M_A = Na, Rb, Cs) \qquad (3)$$

$$M_{Ae2}CO_3 + 2H[TFSI] \longrightarrow M_{Ae}[TFSI]_2 + CO_2 + H_2O \quad (M_{Ae} = Mg, Ca, Sr, Ba) \qquad (4)$$

5 g of H[TFSI] and a little excess of inorganic salt were separately dissolved in 20 cm^3 distilled water in order to prepare the respective aqueous solutions. These solutions were then mixed and stirred for 5 hr at 70°C using magnetic stirring unit. After removing unreacted inorganic salt by filtration, the solution was allowed to evaporation 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 hr at 120°C and kept in glove box under dry nitrogen atmosphere. (Na[TFSI] Yield 99.8% IR(KBr, cm^{-1}) : 1336, 1325, 1316, 1228, 1201, 1061, 801, 774, 744, 654, 603, 595, 573, Rb[TFSI] Yield 96.4% IR(KBr, cm^{-1}) : 1348, 1334, 1316, 1227, 1194, 1145, 1061, 796, 770, 740, 652, 608, 596, 577, Cs[TFSI] Yield 97.2% IR(KBr, cm^{-1}) : 1331, 1312, 1234, 1195, 1142, 1051, 841, 795, 770, 741, 660, 610, 598, 576, 535, 520, $Mg[TFSI]_2$ Yield 95.6% IR(KBr, cm^{-1}) : 1341, 1233, 1196, 1143, 1051, 801, 770, 745, 576, $Ca[TFSI]_2$ Yield 95.2% IR(KBr, cm^{-1}) : 1330, 1313, 1245, 1215, 1141, 1073, 805, 772, 750, 656, 618, 597, 576, $Sr[TFSI]_2$ Yield 97.1% IR(KBr, cm^{-1}) : 1318, 1237, 1206, 1152, 1130, 1073, 806, 775, 748, 655, 611, 597, 580, $Ba[TFSI]_2$ Yield 99.8% IR(KBr, cm^{-1}) : 1350, 1216, 1297, 1234, 1202, 1143, 1058, 802, 770, 748, 656, 604, 598, 573, 556) [13-17].

2.3 Preparation of binary ionic liquids

$M_xN111,8_{1-x}[TFSI]_{\{1+(z-1)x\}}$ (M = Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Molar ratio : x = 0.1, 0.2, 0.3 and 0.5, $z = 1, 2$) were prepared. ca. 1 cm^3 of RTILs was mixed with organic or organic metal salt at predefined molar ratio and stirred for 3 hr at 120°C in the glove box under dry nitrogen atmosphere.

2.4 Small angle X-ray scattering (SAXS)

The ordering structure was investigated using small angel X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) instrument (Anton Paar GmbH, “SAXSess”) equipped with optical arrangement, Kratky Camera as shown in Fig. 2. PW3830 laboratory X-ray generator (40 kV, 50 mA) with long fine-focus sealed-glass X-ray tube (CuKα, wavelength of λ=0.1542 nm) was used. Each sample was loaded into quartz capillaries by a syringe. Temperature range was from 10 to 70ºC. 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;

$$q = (4\pi/\lambda)\sin(\theta/2) \tag{5}$$

where θ is scattering angle. We focused scattering region $q \geq 0.2$ nm^{-1}.

2.5 Raman spectroscopy

Raman spectra were recorded at room temperature by a triple spectrometer (Jobin Yvon/HORIBA, T-64000) with a charge coupled device (CCD) detector cooled with liquid nitrogen. The 532 nm line of a Nd^{3+}: YVO_4 laser (JUNO 532-100S, Showa Optoronics Co.Ltd.) was used for excitation.

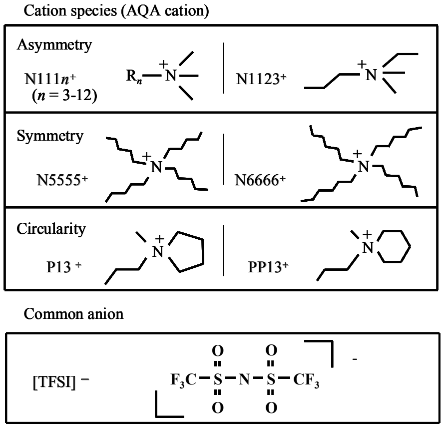

Fig. 1. Structure characteristics of used ionic liquids.

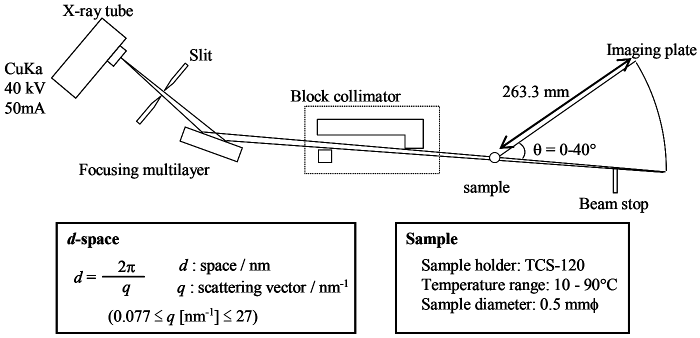

Fig. 2. Characteristics of SAXS and WAXS instrument.

3. Results and Discussion

3.1 Single ionic liquids

3.1.1 The local ordering structure in N111,n[TFSI]. The local ordering structure of RTILs based on AQA cation and TFSI anion was discussed in previous paper [5]. The results of SAXS and WAXS spectra of N111,*n*[TFSI] at 70°C are shown in Fig. 3. 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 N111,*n* cation. The bragg's d-space values were calculated according to equation (6) and plotted against alkyl carbon number n of N111,*n* cation in Fig. 4.

$$d = 2\pi/q \tag{6}$$

There is linear relationship between space *d* and alkyl carbon number *n*. For the first peak, it could be assigned to the local ordering structure formed by van der Waals force between alkyl chains of N111,*n* cation. Further details refer to our previous paper [5].

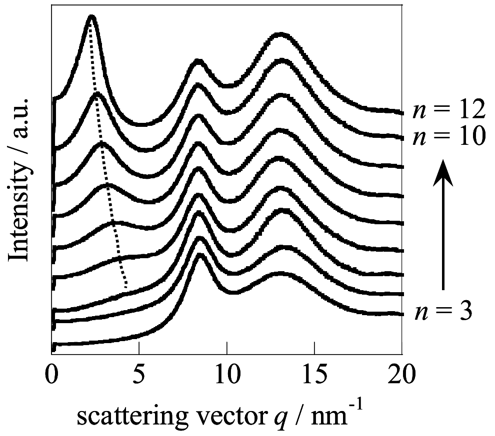

Fig. 3. SAXS and WAXS patterns of N111,*n*[TFSI] (*n* = 3-10,12) at 70°C.

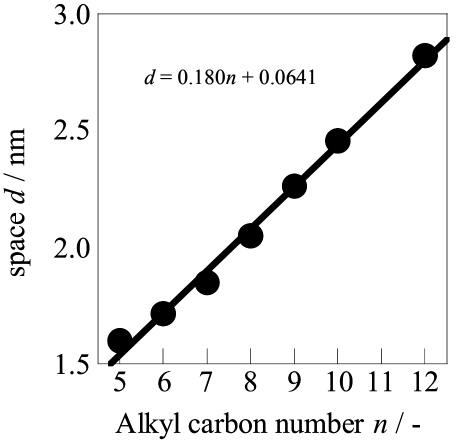

Fig. 4. Relationship between space d and alkyl carbon number n of AQA cation. Linear function approximated by least-squares method show equation as follow: $d = 0.180n + 0.0641$.

3.1.2 Cation-Anion interaction in RTILs. Raman spectra of various kinds of RTILs are shown in Fig. 5. Peaks of ca 1245 and 740 cm^{-1} are assigned to $\nu(\mathrm{CF_3})_s$ and $\delta(\mathrm{CF_3})_s$, respectively, arising from TFSI anion. The cation-anion interaction depends on the structure of constituent ions. Due to the difference of cationic structure, $\delta(\mathrm{CF_3})_s$ and $\nu(\mathrm{CF_3})_s$ of RTILs shifted toward lower wave numbers compared to these of N1113[TFSI]. On the other hand, for N111,*n*[TFSI] (*n* = 3-10), no shift is observed. It is suggested that TFSI anion interacts with AQA cation from the opposite side of N111,*n*[TFSI] long alkyl chain.

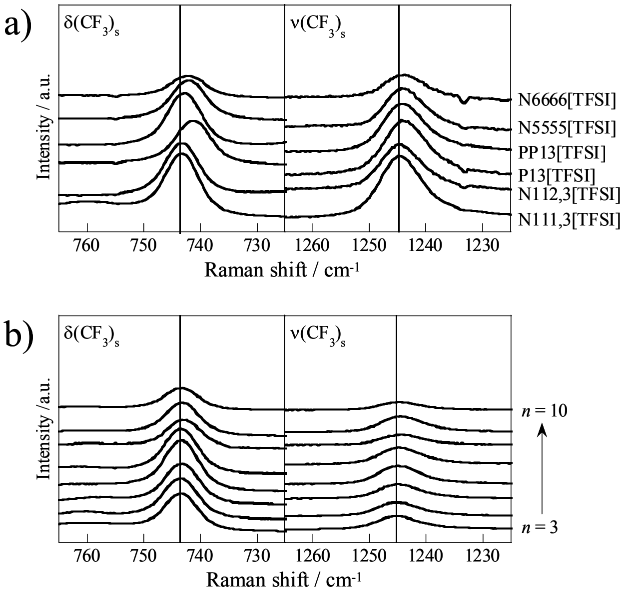

Fig. 5. Raman spectra of various kinds of ionic liquids. a) ionic liquids containing different cationic structure b) N111,*n*[TFSI] (n = 3-10)

3.2 Binary ionic liquids

3.2.1 The effect of added metal cation on the local ordering structure. To examine the effects of various metal cation on the local ordering structure, SAXS and WAXS of $M_xN111,8_{1-x}[TFSI]_{\{1+(1-z)x\}}$ (M = Li, Na, K, Rb, Cs, Mg, Ca, Sr and Ba, x = 0.1-0.5, z = 1, 2) were measured at 70°C The patterns are shown in Fig. 6. With addition of $M[TFSI]_z$, the intensity of second peak assigned to AQA cation decreased. Since AQA cation is substituted by metal cation, the relative number of AQA cation as scattering substance decreased. The intensity of the first peak against the intensity of third peak is enhanced in any system. The increase of intensity means increase of scattering substance in X-ray scattering method: the number of local ordering structure in the system increase. Normalized intensity is calculated according to equation (7) and shown in Fig. 7.

$$I_{Normalized\ intensity} = I_{first} / I_{third} \cdot \{1 + (z - 1)x\} \tag{7}$$

Normalized intensity increased with increasing ionic radius in each group. This trend is more effective in mixed alkali earth metal cation than alkali metal cation.

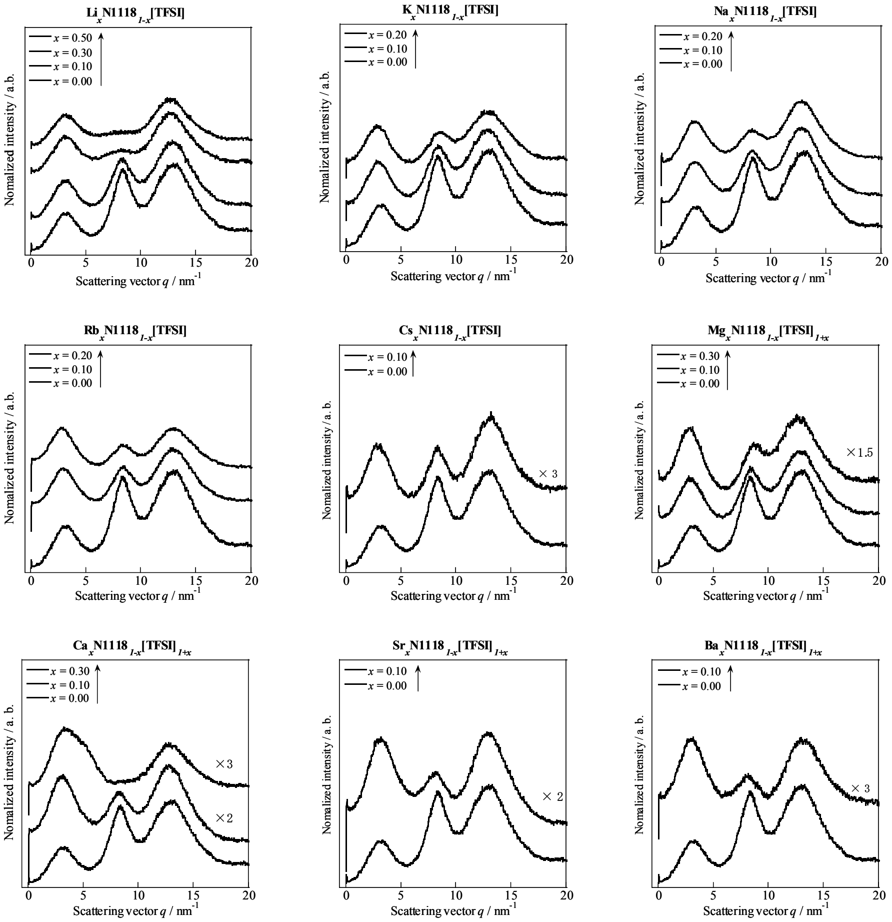

Fig. 6. SAXS patterns of $M_xN111,8_{1-x}[TFSI]_{\{1+(1-z)x\}}$ (M = Li, Na, K, Rb, Cs, Mg, Ca, Sr and Ba, x = 0.1-0.5, z = 1, 2) at 70°C.

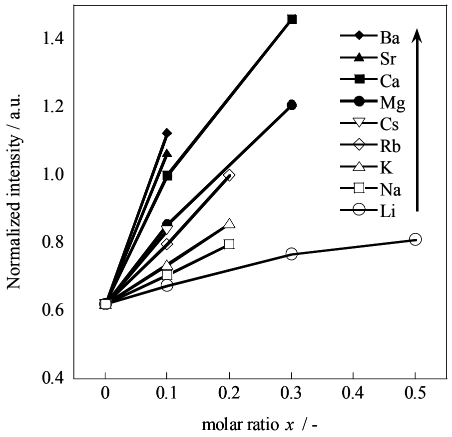

Fig. 7. Normalized intensity of $M_xN111,8_{1-x}[TFSI]_{\{1+(1-z)x\}}$ (M = Li, Na, K, Rb, Cs, Mg, Ca, Sr and Ba, $x = 0.1\text{-}0.5$, $z = 1, 2$) at 70°C.

3.2.2 Interaction between metal caiton and TFSI anion. Raman spectra of binary ionic liquids are shown in Fig. 8. Peak of ca 740 cm^{-1} is assigned to $\delta(CF_3)_s$ arising from TFSI anion. In the system mixed with alkali earth metal caiton, a new peak appears at 750-745 cm^{-1} and the intensity increases with additional metal ion. On the other hand, in the system mixed with alkali metal cation, except for that with lithium cation, a new peak is not observed. The band at 750-745 cm^{-1} means the formation of ion-pair or complex by TFSI anion strongly interacting with metal ion [18, 19]. Therefore, TFSI anion has stronger interaction with alkali earth metal cation than alkali metal cation.

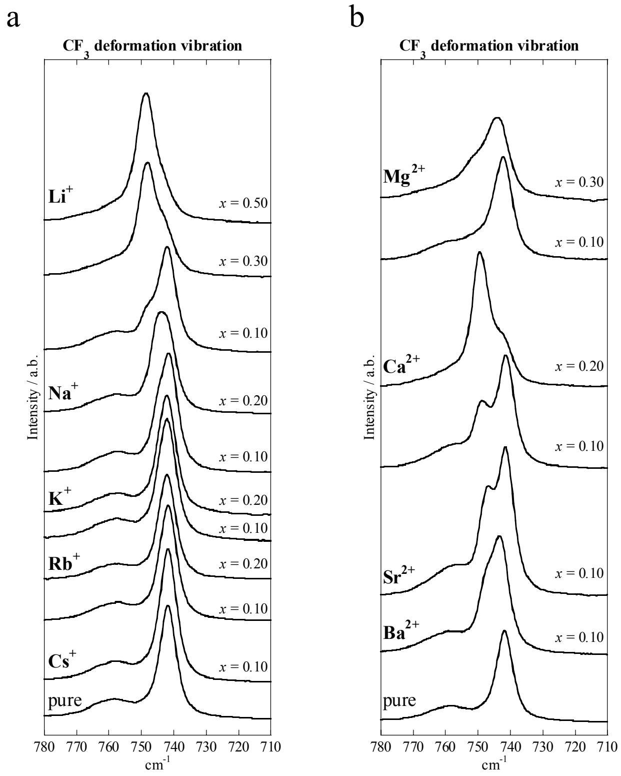

Fig.8. Raman spectra of binary ionic liquids a) the system with alkali metal ion b) the system with alkali earth metal ion.

3.2.3 Different behavior of ionic radius and ionic potential. We consider the formation mechanism of local ordering structure due to the additional metal cation. In pure RTILs, it is considered that there are random state and oriented state of AQA cations. Due to coulombic repulsive force and hydrophobic interaction in RTILs system, there is immiscibility between mixed metal cation and AQA cation. Therefore, metal cation is surrounded by TFSI anions. Because of the strong interaction between TFSI anions and metal cation, interaction between TFSI anion and AQA cation is weakened compared to the pure state. Those free AQA cations are stabilized by the formation of ordered structure as thermodynamic stable state [5].

The stronger the coulombic attraction force of metal cation, the higher the degree of freedom of AQA cation becomes and, the local ordering structure is easily formed. Basically, ordered structure is enhanced for alkali earth metal cation compared to alkali metal cation.

On the other hand, with increase of ionic radius, normalized intensity increased in each group. Because charge density decreases with increasing ionic radius, you may think above discussion to be conflicting. As metal cation directly interacts with only TFSI anion through the coulombic force, the formation of cationic ordering structure can not be handled by only coulombic force. It is suggested that the phenomenon of increasing normalized intensity with increasing ionic radius is related to a consistency between the size of metal cation and that of ionic species composed of ionic liquid.

However, in comparing the two systems which contain element with approximately the same ionic radius; (Li, Mg), (Na, Ca), (K, Ba) — ionic radius for added metal cation is shown in table 1[20]. — normalized intensity is higher with alkali earth metal cation than alkali metal cation. Therefore, there must be induced effect for the formation of local ordering structure by the strong interaction between metal cation and TFSI anion.

Table 1. Ionic radius.

	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Ba^{2+}
Radius / pm	90	116	152	86	114	149

4 Conclusions

The number of the local ordering structure composed of aliphatic quaternary ammonium (AQA) cation increased by the effect of alkali metal cation and alkali earth metal cation. Due to the strong interaction between TFSI anions and metal cation, AQA cations are released from TFSI anion and, free AQA cations are stabilized by the formation of stable local ordering structure. The stronger the coulombic attraction force of metal cation, the higher the degree of freedom of AQA cation becomes and, the local ordering structure is easily formed. Basically, ordered structure is enhanced for alkali earth metal cation compared to alkali metal cation.

5 Acknowledgments

Original salts including PP13, P13 and N5555, N6666 salts were gifted from Dr. H. Matsumoto of AIST Kansai, Japan. A part of this work was supported by Grant-in-Aid for Scientific Research (No. 17073017) “Science of Ionic Liquids” from MEXT of Japan.

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