（ ※本報告書は英語で記述してください。ただし、産業利用課題として採択されている方は日本語で記述していただいても結構です。 ）

CROSS TOKAI **Experimental Report** J-PARC	承認日 Date of Approval 承認者 Approver 提出日 Date of Report
課題番号 Project No. 2017A0002 実験課題名 Title of experiment Does Aggregation of Ethanol Molecules in Imidazolium-based Ionic Liquids Affect the Complex Formation of Metal Ions? 実験責任者名 Name of principal investigator Toshiyuki Takamuku 所属 Affiliation Saga University	装置責任者 Name of Instrument scientist Jun-ichi Suzuki 装置名 Name of Instrument/(BL No.) TAIKAN/(BL15) 実施日 Date of Experiment 2017 Nov. 11 10:00–Nov. 14 10:00

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）

Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

In the present machine time for 72 h, SANS experiments were conducted on the following systems.

System A:

Imidazolium-based ionic liquids–ethanol (EtOH) solutions at 25 °C

1. C_6mimTFSA–Ethanol–d_6 $x_{EtOH\text{-}d6}$ = 0.85, 0.90, 0.925, 0.95, 0.97, 0.99

System B:

Imidazolium-based ionic liquids–dimethyl sulfoxide (DMSO) solutions at 25 °C

1. $C_n$mimTFSA–DMSO–d_6 with n = 2–12 at $x_{DMSO\text{-}d6}$ = 0.95, 0.97

System C:

Imidazolium-based ionic liquids–acetonitrile (AN) solutions at 25 °C

1. C_2mimTFSA–Acetonitrile–d_3 $x_{AN\text{-}d3}$ = 0.80, 0.90, 0.95, 0.99
2. C_8mimTFSA–Acetonitrile–d_3 $x_{AN\text{-}d3}$ = 0.80, 0.90, 0.95, 0.99

System D:

Temperature dependence of the inhomogeneity of Imidazolium-based ionic liquids–1,4-dioxane (DIO) solutions

1. C_8mimTFSA–1,4-Dioxane–d_8 $x_{DIO\text{-}d8}$ = 0.9825 in the temperature range of 50–31 °C

System E:

Lysozyme–alcohol–water solutions at 25 °C

1. Lys/2-PrOH–d_8–D_2O–HFIP $x_{2\text{-}PrOH\text{-}d8}$ = 0.3, 0.35
2. Lys/2-PrOH–d_8–D_2O/H_2O–HFIP $x_{2\text{-}PrOH\text{-}d8}$ = 0.3, 0.35
3. Lys/D_2O–HFIP x_{HFIP}= 0.2

System F:

1. D_2O–3-methylpyridine (fixed at 9 vol.%) + $NaBPh_4$ (0 to 85 mM) + PPh_4Cl (0 to 40 mM)

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）

Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

Systems A–C:

The SANS measurements for Systems A–C were made to clarify the relation between the inhomogeneity of the ionic liquids (ILs)–molecular liquids (MLs) solutions and the complex formation of Ni^{2+} in their binary solutions. The MLs includes EtOH, DMSO, and AN.

From the present SANS experiments, together with the previous ones (2015A0038, 2016A0008, 2017A0006), the mixing states of the $C_n$mimTFSA–ML solutions with n = 2–12 can be clarified at the mesoscopic level. The DMSO and AN solutions did not show significant SANS intensities. Thus, both MLs are homogeneously mixed with the imidazolium-based ILs. On the contrary, the SANS intensities of the EtOH solutions were recorded on the TAIKAN spectrometer. The Ornstein–Zernike correlation lengths ξ were estimated for all of the $C_n$mimTFSA–Ethanol–d_6 solutions and plotted as a function of ethanol mole fraction x_{EtOHd6} in Fig. 1. As seen, the maximum of the ξ appears at the higher x_{EtOHd6} with elongating the IL alkyl chain n. Moreover, the maximum ξ decreases with the alkyl chain length. The dispersion force between the EtOH ethyl group and the IL alkyl group may influence the mixing states of the IL–ML solutions. On the basis of the SANS results, we will discuss the effects of the mixing states of the IL–ML solutions on the complex formation of Ni^{2+} in their solutions.

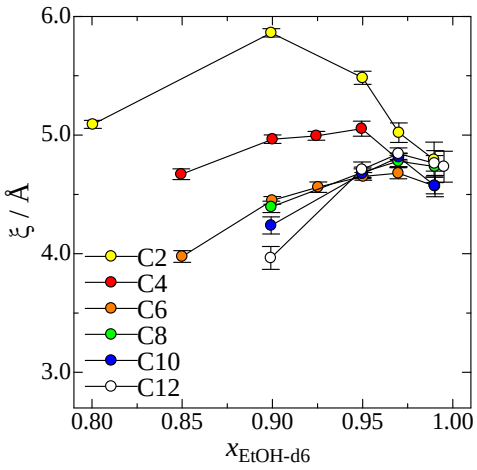

Fig. 1 Ornstein–Zernike correlation lengths ξ of $C_n$mimTFSA–Ethanol–d_6 solutions as a function of ethanol mole fraction.

System D:

We found that C_8mimTFSA–DIO solutions separate into the IL-rich and DIO-rich phases with lowering temperature. As shown in the phase diagram (Fig. 2), the solutions show the upper critical solution temperature (UCST) at 31.6 °C and x_{DIO} = 0.9825. In the present experiments, we observed SANS profiles of the C_8mimTFSA–DIO solution at x_{DIO} = 0.9825 with lowering temperature toward the UCST. Fig. 3 shows the Ornstein–Zernike correlation lengths ξ estimated for the solution as a function of temperature. The ξ remarkably increases with lowering temperature. This suggests that the inhomogeneity of the solution enhances as the temperature decreases towards the UCST. Moreover, the plots of the ξ values against the reciprocal temperature showed that phase separation of the C_8mimTFSA–DIO solution takes place in the 3D–Ising manner. This is the first result on the mechanism of phase separation of IL–ML solutions.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

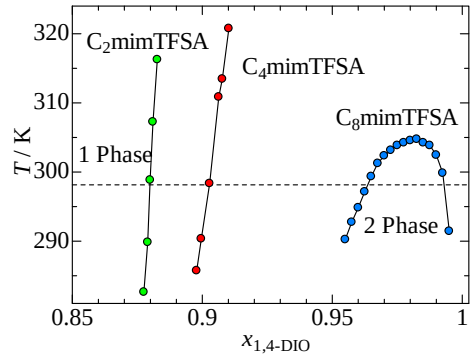

Fig. 2 Phase diagram of $C_n$mimTFSA–DIO solutions with n = 2, 4, and 8.

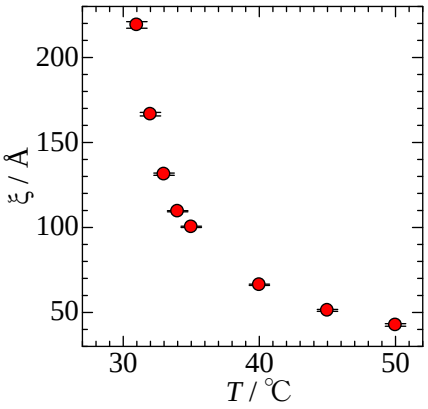

Fig. 3 Ornstein–Zernike correlation lengths ξ of C_8mimTFSA–DIO solution at x_{DIO} = 0.9825.

System E:

In the present and previous machine times (2015A0038, 2016A0008, 2017A0006), we made the SANS measurements at 25 °C on lysozyme–alcohol–water solutions using the TAIKAN spectrometer to elucidate the change in the 3D structure of lysozyme depending on the alcohols and their mole fraction. Here, the alcohols are 2–propanol (2–PrOH) and 1,1,1,3,3,3–hexafluoroisopropanol (HFIP). The SANS profiles of the 2–PrOH solutions did not significantly change with increasing $x_{2\text{–PrOH}}$ from 0 to 0.3. Thus, the 3D structure of lysozyme is not affected by 2–PrOH in the mole fraction range. In contrast, the SANS intensities of the HFIP solutions strengthened with increasing x_{HFIP} from 0 to 0.05. With further increasing x_{HFIP} to 0.2, the intensities decrease. Therefore, the 3D structure of lysozyme obviously changes with increasing HFIP content. This finding agrees with the results of 2D structure by circular dichroism (CD) spectroscopy. We are analyzing the SANS profiles using several structure models to determine the dimension of lysozyme in the solutions. The effects of HFIP on the 3D structure of lysozyme in aqueous solutions will be clarified on the basis of the SANS results, together with the results of the CD and IR spectroscopy.

System F:

In the present and previous machine times (2017A0006), the feature of the lamellar structure formed in System F was investigated by changing the concentration of $NaBPh_4$ and PPh_4Cl. One example of the SANS results is shown in Fig. 4. Here, the concentration of NaBPh4 was fixed at 85 mM. With increasing the amount of PPh_4Cl, the Bragg peak around Q = 0.03 Å^{-1} disappears, while the intensity at low–Q region increases. In this manner, it was shown that the addition of PPh_4Cl decreases the regularity of the membrane, however, induces the micrometer–sized ordered structures. This finding is an important clue to clarify how the charged substance affects the membrane composed of organic solvent and antagonistic salts.

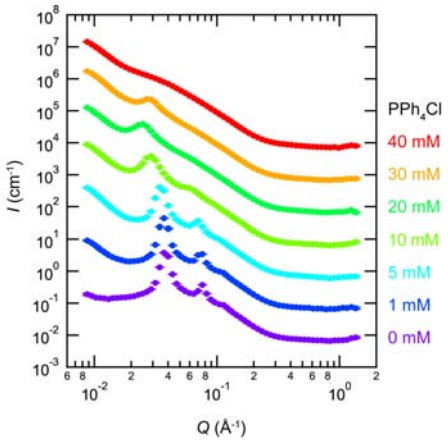

Fig. 4 SANS profile for the mixture of D_2O/3MP/$NaBPh_4$/PPh_4Cl.