


実験報告書様式(一般利用課題・成果公開利用)

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 	承認日 Date of Approval 2017/9/16 承認者 Approver Jun-ichi Suzuki 提出日 Date of Report 2017/6/23
課題番号 Project No. 2017A0006 実験課題名 Title of experiment SANS Study on Promotion of the Secondary Structure of Lysozyme in HFIP-D <sub>2</sub> O Mixed Solvents 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 Jun. 5 10:00–Jun. 7 9:00

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.

<p>1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.</p> <p>SANS measurements at 25 °C were made on the following four systems; System A: imidazolium-based ionic liquid-ethanol mixtures, System B: imidazolium-based ionic liquid-tetrahydrofuran (THF), System C: hen egg white lysozyme (Lys) in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP)-water solutions, System D: D<sub>2</sub>O-3-methylpyridine-NaBPh<sub>4</sub> + PPh<sub>4</sub>Cl and D<sub>2</sub>O-2,6-lutidine-NaBPh<sub>4</sub> solutions.</p> <p>System A:</p> <ol style="list-style-type: none"> <li>1. C<sub>4</sub>mimTFSA-Ethanol-<i>d</i><sub>6</sub> <math>x_{\text{EtOH}} = 0.85, 0.90, 0.925, 0.95, 0.97</math></li> <li>2. C<sub>8</sub>mimTFSA-Ethanol-<i>d</i><sub>6</sub> <math>x_{\text{EtOH}} = 0.90, 0.95, 0.97, 0.99</math></li> <li>3. C<sub>10</sub>mimTFSA-Ethanol-<i>d</i><sub>6</sub> <math>x_{\text{EtOH}} = 0.90, 0.95, 0.97, 0.99</math></li> </ol> <p>System B:</p> <ol style="list-style-type: none"> <li>1. C<sub>4</sub>mimTFSA-THF-<i>d</i><sub>8</sub> <math>x_{\text{THF}} = 0.80, 0.85, 0.90, 0.95, 0.97, 0.99</math></li> </ol> <p>System C:</p> <ol style="list-style-type: none"> <li>1. D<sub>2</sub>O-HFIP <math>x_{\text{HFIP}} = 0.01, 0.02, 0.03, 0.04, 0.05, 0.1</math></li> <li>2. Lys/D<sub>2</sub>O-HFIP <math>x_{\text{HFIP}} = 0.01, 0.02, 0.03, 0.04, 0.05, 0.1</math></li> </ol> <p>System D:</p> <ol style="list-style-type: none"> <li>1. D<sub>2</sub>O-3-methylpyridine-NaBPh<sub>4</sub> + PPh<sub>4</sub>Cl</li> <li>2. D<sub>2</sub>O-2,6-lutidine-NaBPh<sub>4</sub></li> </ol>
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## 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.

### System A:

The present and previous (2016A0008) SANS experiments with TAIKAN gave us the information on the mixing state of  $C_n$ mimTFSA-ethanol- $d_6$  solutions over the alkyl chain length range of  $n = 2-12$ . As shown in Fig. 1, the Ornstein-Zernike correlation lengths  $\xi$  for the solutions estimated from the SANS profiles suggested that the inhomogeneous mixing of the ionic liquid  $C_n$ mimTFSA and ethanol- $d_6$  is enhanced with decreasing the alkyl chain length  $n$ . This is the opposite to the mixing state of the ionic liquids with methanol- $d_4$ . Additionally, the maximum of the  $\xi$  values at each chain length  $n$  in the ethanol systems shifts toward the high ethanol mole fraction, while that for the methanol systems appeared at the fixed mole fraction  $x_{\text{MeOH}} \approx 0.97$ . The interesting differences between the ethanol and methanol systems may be attributed to the stronger nonpolar interaction between the ethyl group of ethanol and the alkyl group of the imidazolium cation. The consideration will be proved by the NMR and IR results.

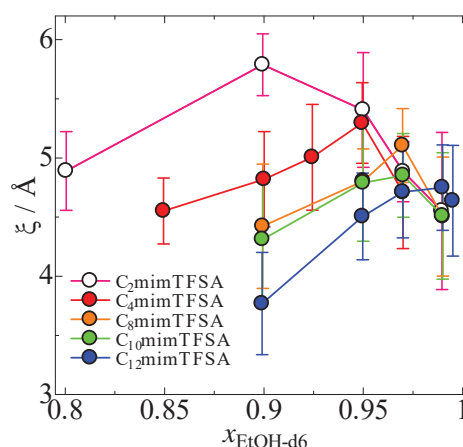


Fig. 1 Correlation lengths  $\xi$  for  $C_n$ mimTFSA-ethanol- $d_6$  solutions as a function of  $x_{\text{EtOH}}$ .

### System B:

Our results of infrared (IR) spectroscopy on ionic liquid  $C_4$ mimTFSA solutions with THF over the entire THF mole fraction range have shown that THF molecules are hydrogen-bonded with the imidazolium ring hydrogen atoms. On the other hand, THF molecules aggregate to form clusters through the dipole-dipole interaction among them even in the strong hydrogen bond donor of water. It is interesting thus whether THF molecules can form clusters in the ionic liquid or not. The present experiments surely detected SANS intensities of the  $C_4$ mimTFSA-THF- $d_6$  with the maximum at  $x_{\text{THF}} = 0.99$ . At the mole fraction, the imidazolium ring hydrogen atoms are saturated by the hydrogen bonding with THF. Thus, THF molecules interact with themselves through the dipole-dipole interaction to form THF clusters in the solutions. The present SANS experiments succeeded in observing the THF clusters.

### System C:

The present SANS experiments for lysozyme/ $D_2O$ -HFIP solutions are series from the previous ones (2016A0008). In the previous experiments, we measured only the lysozyme/ $D_2O$ -HFIP solutions and analyzed the SANS profiles of the solutions using a spherical micelle model. However, the SANS profiles were not well fitted by the model. In the present experiments, thus, the SANS profiles of  $D_2O$ -HFIP solvents were also measured to subtract the SANS intensities of the solvent from that of the lysozyme solution. As shown in Figs. 2 and 3, the subtraction of the SANS intensities of the solvent was well conducted on that for the solution. We are analyzing the corrected SANS profiles using a spherical micelle model.

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

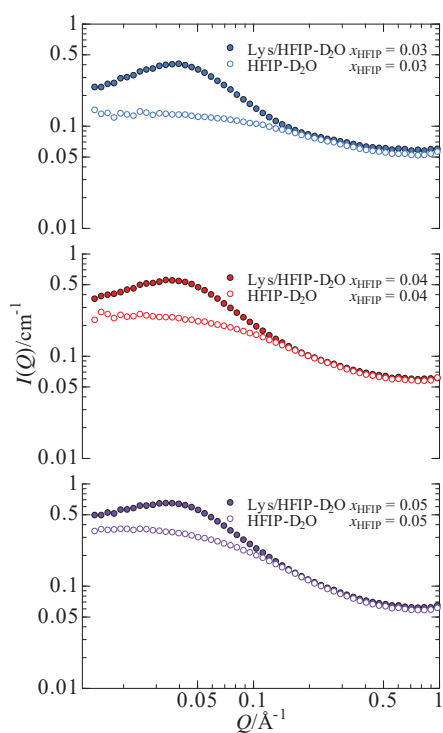


Fig. 2 SANS profiles of lysozyme/ $D_2O$ -HFIP and  $D_2O$ -HFIP solutions at  $x_{HFIP} = 0.03$ , 0.04, and 0.05.

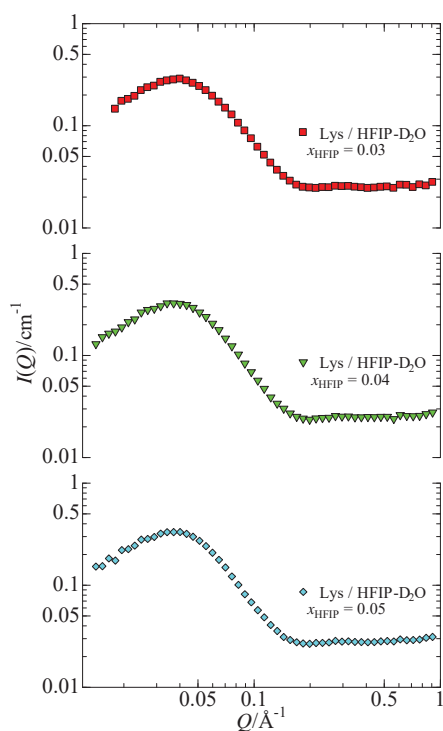


Fig. 3 SANS profiles of lysozyme/ $D_2O$ -HFIP solutions subtracted for those of  $D_2O$ -HFIP solutions at  $x_{HFIP} = 0.03$ , 0.04, and 0.05.

### System D:

We obtained various patterns of SANS profiles for  $D_2O$ -3-methylpyridine- $NaBPh_4$  +  $PPh_4Cl$  and  $D_2O$ -2,6-lutidine- $NaBPh_4$  solutions. To elucidate the structure of aggregates formed in the solutions, the SANS spectra will be analyzed using suitable model.