Neutron reflectometry at electrochemical liquid/liquid interfaces and Single-step deuteration of ionic liquids

K. Ishii, and N. Nishi

Kyoto University, Nishikyo-ku Kyoto-shi, Kyoto 615-8510, Japan

Hydrophobic liquids, such as hydrophobic ionic liquids (ILs) and fluorous solvents (Fs), are immiscible with water (W) and form a two-phase system. The protein nanolayers (PNL) formed on the F|W and IL|W interface have recently been applied as cell culture media.[1,2] The structures of PNL are changed by the molecular structures of F and IL, which vary the cell differentiations. [1,2] These changes are likely due to the hydrophobic and coulombic interactions between F and IL, and proteins.

Using x-ray reflectometry[3] and molecular dynamics simulation,[4] we revealed that the compositions of the first layer in the IL side at the IL|W interface can be switched by controlling the interfacial potential difference. When IL is added to F, the composition of IL at the F side of the F|W interface where the PNL is formed can be tuned by controlling the interfacial potential difference, $E_{\mathrm{F}}^{\mathrm{W}}(=\varphi^{\mathrm{W}}-\varphi^{\mathrm{F}}+\text{const.})$. The manipulation of ionic composition on the F side of the interface is expected to change the IL-protein interaction, inducing the structural change of PNL.

By using neutron reflectometry (NR), the structures of IL at the F|W interface without proteins were successfully analyzed under the controlled condition of $E_{\mathrm{F}}^{\mathrm{W}}$. NR was performed using a horizontal-type neutron reflectometer, SOFIA, at BL16 of MLF in J-PARC. The reflectivity profiles at the F|W interface indicated that the segregation of IL ions at the F side of the interface was triggered by externally controlled $E_{\mathrm{F}}^{\mathrm{W}}$. The presence of an IL-rich layer on the F side of the interface was observed even at the potential of zero charge, which cannot be explained with the classical Gouy-Chapman model. This reflects that the fluorophiliicity and lipophobicity of the F molecule strongly affected the structures at the F side of the F|W interface.[5]

When protein was added to W at pH 7.4, the structure of PNL was successfully measured at each $E_{\mathrm{F}}^{\mathrm{W}}$. At $E_{\mathrm{F}}^{\mathrm{W}}$ where the F side of the interface was positively charged, the thickness of PNL was increased compared with that at other $E_{\mathrm{F}}^{\mathrm{W}}$. This is because the negatively charged protein at pH 7.4 was more accumulated at the interface due to the coulombic interaction between proteins and IL cations. The thickness change of PNL suggests that the structures of PNL were varied by controlling $E_{\mathrm{F}}^{\mathrm{W}}$.[6]

For a further detailed analysis of the interfacial structure using contrast variation NR, we developed a single-step method to deuterate ILs. [7] We will also report the deuteration method in the presentation.

[1] X. Jia et al, Small, 15, 1 (2019). [2] T. Ueki et al., Adv. Mater., 2310105, 1 (2024). [3] S. Katakura et al., J. Phys. Chem. B, 124, 6412 (2020).[4] K. Ishii et al., Phys. Chem. Chem. Phys., 23, 22367 (2021). [5] K. Ishii et al., to be submitted. [6] K. Ishii et al., to be submitted. [7] K. Ishii et al., to be submitted.