イオン液体 / 帯電固体界面溶媒和構造の AFM 分析: イオン液体成分の影響について

Effect of ionic liquid components on solvation structures at ionic liquid / charged solid interfaces detected by atomic force microscopy

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Understanding the interfacial solvation structures of ionic liquids (IL) on charged solid surfaces is crucial. We previously visualized the solvation structures of 1-methyl-1-propylpyrrolidinium bis (trifluromethanesulfonyl) imide (Py13-TFSI) and 1-ethyl-3-methylimidazolium (EMI-) TFSI on highly charged RbI(111) surfaces and discussed the response of an IL to high surface charge at the liquid / solid interface [1]. However, there are still several open questions regarding the IL / charged solid interfaces, including how an IL respond to a nearly neutral but slightly charged surface [2]. We extend our study on surface charge-dependent solvation structures at IL / solid interfaces by probing solvation structures of ILs on a nearly neutral but slightly charged RbI{100} surface using frequency-modulation atomic force microscopy (FM-AFM). Surface-charge dependent solvation structures of two ILs which have different cationic components, EMI-TFSI containing the EMI^+ cation with a delocalized charge distribution, and Py13-TFSI with a localized charge distribution in its cation, are discussed systematically.

The RbI{100} surface was obtained by evaporate crystallization of RbI crystals from a RbI-saturated aqueous solution and cleavage using a knife in a dry chamber. Figures 1(a) and (c) display 2D Δf maps imaging the cross-sectional interfacial structures of Py13-TFSI and EMI-TFSI normal to the RbI{100} surface. For Py13-TFSI, a distinct stripe-like pattern was observed along the RbI{100} surface, whereas EMI-TFSI exhibited a relatively unclear feature. The line profiles along the lines in (a) and (b) show oscillations with periods corresponding to the size of ion pairs at the grey-marked separation, while an oscillation with a smaller period was exclusively observed in Py13-TFSI, as indicated by red in Fig. 1(b). This discrepancy suggests the formation of distinct solvation structures in two RTILs, even on the same surface, emphasizing the crucial role of IL components in understanding the surface charge-dependent solvation structures at IL / solid interfaces.

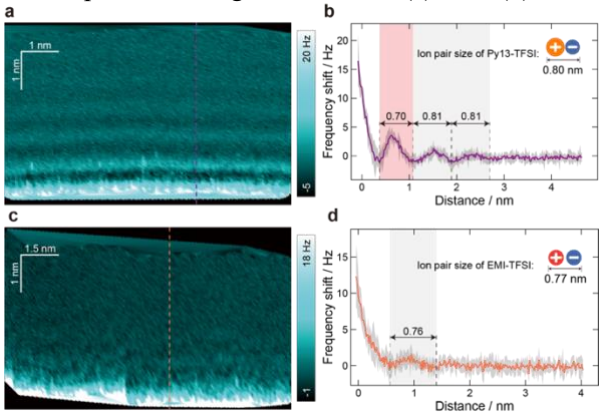

Fig. 1: (a, c) 2D Δf maps showing interfacial structures at (a) Py13-TFSI / RbI {100} and (c) EMI-TFSI / RbI {100} interfaces. (b, d) Line profiles obtained along lines in (a) and (c), respectively.

[1] Y. Bao *et al.,* The 70th JSAP Spring Meeting, 16a-D405-4 (2023).　[2] M. Belotti *et al., J. Am. Chem. Soc.* **143**, 17431-17440