Interfacial solvation structure analysis of ionic liquid/water mixtures by qPlus AFM

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Many of the cations that compose ionic liquids (ILs) contain hydrophobic groups such as alkyl chains, and some ILs are known to be phase-separated into nanoscale hydrophobic and hydrophilic domains when they are mixed with water. Furthermore, the metal ions of metal salts added into the IL/water mixture are reported to localize in the hydrophilic domains. As a result, the metal ion diffusion in this mixture is limited, and it is expected to be a novel electrolyte in electrodeposition processes [1]. Thus, IL–water mixtures are attracting attention as next-generation functional electrolytes. However, their structural analysis has been limited to small-angle X-ray scattering (SAXS) and computer simulations, and sufficient knowledge on their interfacial structure is still lacking. In this study, we analyzed the interfacial structure between an IL–water mixture and a solid substrate using frequency modulation atomic force microscopy (FM-AFM) with a qPlus sensor [2].

A mixture of 1-hexyl-3-methylimidazolium chloride (HMI-Cl) and water with a molar ratio of 2:15 was prepared, and the interface with a mica substrate was investigated. Figures 1(a) and 1(c) show the two-dimensional frequency shift (Δf) map and the simultaneously acquired energy dissipation map (E_d), respectively. The Δf map shows a layered structure with a thickness of 0.88–1.07 nm. ILs are well known to form interfacial layered structures corresponding to their ion pair size, which is approximately 0.7 nm for HMI-Cl. The size of water molecules is about 0.2–0.3 nm. The observed layer thickness is slightly larger than the ion pair size, which might originate from the presence of water. However, the observed layer thickness was significantly smaller than the domain size measured by SAXS (~2 nm) [1]. This suggests that the interfacial structure is different from the bulk structure in this system. Furthermore, we observed a similar layered structure even in the E_d image (Fig. 1(c)). This result is much different from the previous AFM studies performed in pure ILs [2].

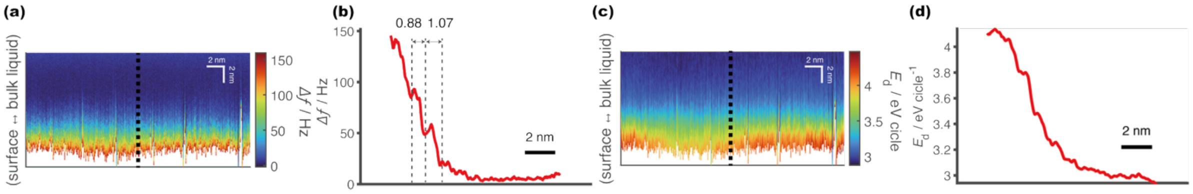

Figure 1. 2D maps of Resonance frequency shift (Δf) (a) and energy dissipation (E_d) (c) and obtained at the interface between HMI-Cl/H_2O mixture (molar ratio 2:15) and a mica substrate. Δf-z curve (b) and Ed-z curve (d) were obtained along broken black lines in (a) and (c), respectively. $f_0 = 15304$ Hz, $Q = 95$, $A_{p\text{-}p} = 270$ pm

Reference

[1] Y. Murakami *et al.* Adv. Funct. Mater. 2418621 (2025)

[2] Y. Bao *et al*. ACS Nano, 18, 25302 (2024)