Observation of the dynamic behaviors of ions and liquid structures in ionic liquids

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Ionic liquids have characteristic properties, such as non-volatility, high ionic density and designable hydrophilicity. Owing to these properties, they have been applied in a variety of industrial fields, for example, as electrolytes and extraction/reaction solvents. However, the microscopic origins of the ionic liquid properties are not clear because there are few analytical methods with high spatial resolution of a single nanometer scale. Thus, developing new high-resolution methods and analyzing microscopic structures inside the ionic liquid and their dynamic behaviors have been desired. We have recently developed a new method using scanning transmission electron microscopy (STEM) for imaging individual heavy atoms in ionic liquids, and investigated the distribution and dynamics of solute ions in several ionic liquids [1,2].

In this study, we have observed 1-Methyl-3-octylimidazolium bromide (C_8mimBr), which is composed of heavy-element ion (Br^-) and forms several-nanometer-size domain structures inside, and we have aimed to elucidate the distribution of Br^- ion, the shape of the domain structures and their dynamics. In addition, we have performed the visualization of the preferential solvation states of solute ions in the domain structures. In the observation, we have used annular dark-field STEM (ADF-STEM), whose image intensity is approximately proportional to the square of the atomic number (Z). Thus, in ionic liquid C_8mimBr, Br^- ions (heavy element: Z=35) are imaged much brighter than the other atoms/molecules. We fabricated liquid film samples for the STEM observation by dropping the ionic liquid onto holey carbon films; the ionic liquid forms free-standing ultrathin films in the holes owing to surface tension [3]. We used aberration-corrected STEM (JEM-ARM200CF) at an acceleration voltage of 200kV.

Figure 1 is an ADF-STEM image of ionic liquid C_8mimBr (thickness: ~10 nm). This image shows numerous bright spots. These spots are speculated to be Br from the image intensity. Their mean size is ~0.08 nm (right bottom corner in Figure 1), corresponding to the electron beam size; this means that the bright spots are single Br^- ions. Moreover, network-like bright regions and hole-like dark ones are observed in the background of Figure 1. They would correspond to the nanometer-size domain structures in the ionic liquid. We will report both static and dynamic observation results of the ion distribution and domain structures in the ionic liquid sample.

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The STEM measurements were conducted under the support of "Nanotechnology Platform" (no. 12024046) of MEXT, Japan. This study was supported by the Mitsubishi Science Foundation (27143), Grants-in-Aid for Scientific Research from MEXT (nos. 25106003, 26630302, 26249092, and JP17H06094), a Grant-in-Aid from the Japan Society for the Promotion of Science Fellows (no. 15J11146) and JST - PRESTO.

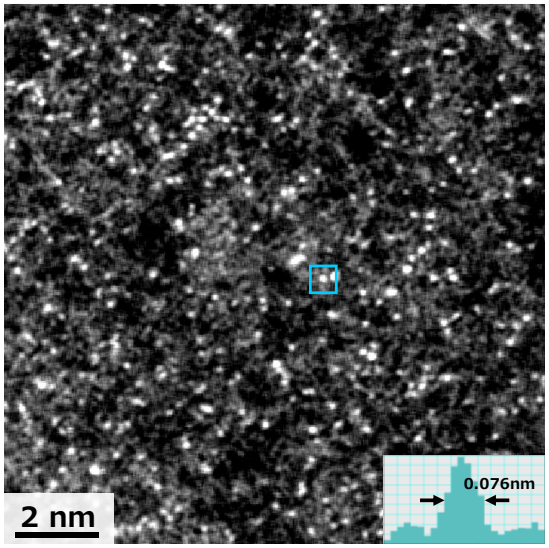

Figure 1 ADF-STEM image of C_8mimBr.