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Surface Structure of Ionic Liquids Determined by X-ray reflectivity and Sum-Frequency Generation Spectroscopy DOSEOK KIM, YOONNAM JEON, JAEHO SUNG, Department of Physics and Program of Integrated Biotechnology, Sogang University, Seoul, Korea, WEI BU, DAVID VAKNIN, Ames laboratory and Department of Physics and Astronomy, Iowa State University, USA, YUKIO OUCHI, Department of Chemistry, Nagoya University, Japan — X-ray reflectivity and surface sum-frequency generation spectroscopy were used to study the surface of [BMIM][X] ionic liquids (BMIM = 1-butyl-3-methylimidazolium, X = BF_4, PF_6, and I). Sum-frequency signal strength from the terminal methyl groups of the cation at the surface indicates the topmost surface of these ionic liquids are occupied by polar-oriented hydrophobic butyl chains having $\sim$1/3 of the alkyl chain density of fully-packed hexadecanol Langmuir monolayer. X-ray reflectivity data could be fitted well by the assuming the first layer with low electron density followed by the electron-rich second layer on top of bulk ionic liquid. Detailed analysis of the reflectivity data in conjunction with the sum-frequency findings strongly suggests the molecules forming the top-most layer are on average oriented with their butyl chains (loosely packed) towards the gas/liquid interface while the core/anions (densely-packed) are in contact with the bulk liquid.

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