Hydrogen-Bonded Structure of Alcohols Adsorbed on Silica Surface in Cyclohexane

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Liquid molecules at the solid-liquid interface often exhibit quite different properties from those in the bulk, which is attributed to the surface-induced structuring of liquids. We recently found a hydrogen-bonded ordered structure, which we call a "molecular macrocluster", of alcohols when we investigated the adsorption of them on silica (glass and oxidized silicon) surfaces from cyclohexane.

Alcohols studied were monohydric alcohol such as methanol and ethanol [1], and dihydric alcohol (ethylene glycol)[2]. A combination of colloidal probe atomic force microscopy, FTIR-ATR spectroscopy, and adsorption excess isotherm measurement was employed. The force measurement revealed the long ranged attraction (e.g. ca. 35 nm for ethanol) between silica (glass) surfaces, which was ascribed to the attraction due to the contact of the opposed adsorption layers bearing the high interfacial energy. FTIR-ATR spectroscopy demonstrated that alcohol molecules adsorbed on the silica (silicon oxide) surfaces formed hydrogen-bonded clusters (polymers), which extended 15~20 nm (for monohydric alcohol) from the surface silanol groups. Practically no cluster was formed on the hydrogen-terminated silicon surfaces. Interesting differences were observed in the mode of adsorption depending on the chemical structures. Dynamic properties of adsorbed alcohols were studied by NMR spectroscopy.

[1] Mizukami M., Moteki M., Kurihara K., *J. Am. Chem. Soc*., 2002, **124**, 12889. [2] Kurihara K., Nakagawa Y., Mizukami M., *Chem. Lett*., 2003, 84.

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