FM-AFM Observation of Competitive Adsorption on Graphite

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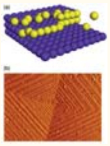
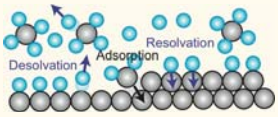
Motivation

Competitive Adsorption at Solid-Liquid Interface

Solute adsorption from a solution is a key process in many phenomena such as crystal growth. When a solution faces to a solid surface, solute and solvent molecules competitively adsorbed on the surface.





Interfacial liquids play a key role in adsorption process.

Direct observation of interfacial liquid structure can be an effective approach for understanding adsorption process.

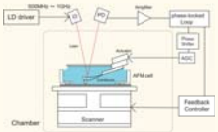
In this study…

Using an advanced FM-AFM, interfacial structures of long-chain organic compounds were visualized with sub-nanometer resolution over the graphite surface.

We focused on the interface where two components competitively adsorbed.

Frequency Modulation Atomic Force Microscopy in Liquids

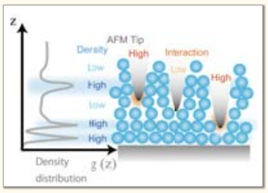
Instrument

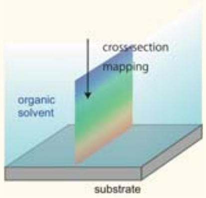


Our AFM is Shimadzu WET-SPM 9600 modified with a low noise optical deflection sensing system* allowing highly-sensitive force detection also in solutions.

*T. Fukuma *et al.*, Appl. Phys. Lett. 86 (2005) 193108.

Cross-sectional Δf distribution





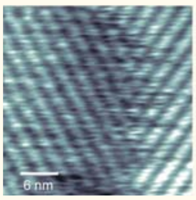
With precise measurement of the interaction force toward the tip as a function of the tip coordination, small force modulation appears which may be related with the site-specific density of liquid molecules.

K. Kimura *et al.*: J. Chem. Phys. 132 (2010) 194705. T. Hiasa *et al.*: J. Phys. Chem. C 114 (2010) 21423.

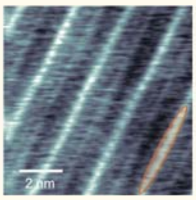
Pure Decanol Solvent

Topography of Decanol Adlayer on Graphite

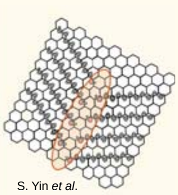
Wide-area



Narrow-area



Model



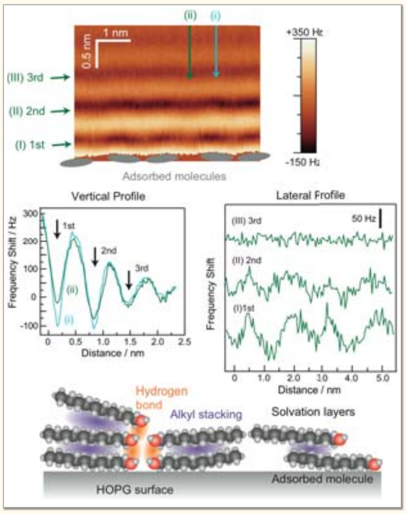
S. Yin *et al.* *Chem. Phys. Lett.* 348 (2001) 321.

Molecular layer of decanol was developed on graphite surface.

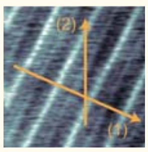
Dimerized OH groups appeared as bright spots at the center of the lamellae.

Interfacial Structure of Decanol Liquids

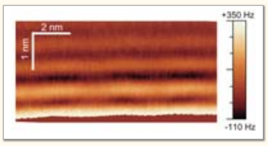
(1) Perpendicular to the lamellae axis



Direction of cross-sectional distribution



(2) Nearly parallel to the lamellae axis



Liquid structure was epitaxial to the adsorbed layer.

Density was enhanced on top of the adsorbed molecules.

Energy gain of van der Waals and hydrogen bond interactions were maximized on top of them.

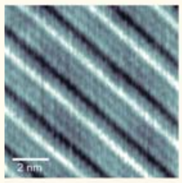
T. Hiasa *et al.*: J. Phys. Chem. C 116 (2012) 26475.

Competitive Adsorption of Solute and Solvent

Dilute Decanol Solution of Carboxylic Acids

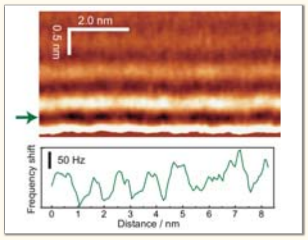
Stearic Acid ($C_{17}H_{35}COOH$: 10 mM)

Topography

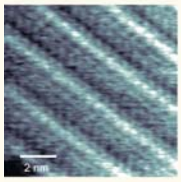


Decanol adlayer

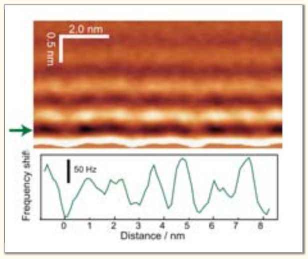
Δf distribution perpendicular to the lamellae axis



Lignoceric Acid ($C_{23}H_{47}COOH$: 0.5 mM)



Decanol adlayer



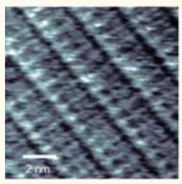
Adlayers composed exclusively of the solvent decanol were found for the diluted solutions.
Interfacial liquid structures were totally same as of pure decanol.
(There was no sign of contribution by the solute stearic acid, or lignoceric acid.)

Saturated ⇩ Condition

Saturated Decanol Solution of Carboxylic Acids

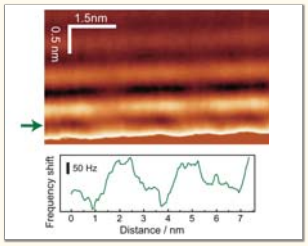
Saturated Stearic Acid (200 mM)

Topography



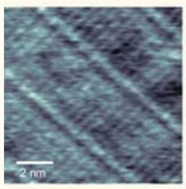
Stearic acid adlayer

Δf distribution perpendicular to the lamellae axis

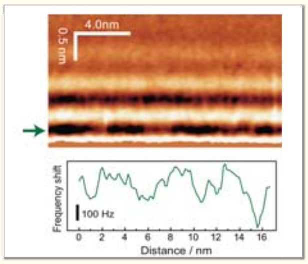


Saturated Lignoceric Acid (9 mM)

Topography



Lignoceric acid adlayer



Adlayers of the solute carboxylic acids were formed in the saturated solution.
Liquid structure at the interface was controlled by the solute concentration via the composition of adsorbed materials.

Saturated condition is a key in selective adsorption of the solute carboxylic acid and solvent decanol, not dependent to absolute concentration.
Interfacial liquids are structured epitaxial to the adlayer.

T. Hiasa and H. Onishi submitted.