Study on Potential-Dependent Dynamics of Small Oil Droplet at Au Electrode/Water Interface

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Dynamics of organic molecules at an electrode surface can be driven by an applied potential. The investigation of the interfacial chemistry of the electrode in molecular view is directly connected to the understanding of the electrical double layer structures governing the functions of electric devices such as supercapacitors. Understanding of the behavior of organic molecules on the electrode surface provides us with new insight into physical chemistry of the interface. The dynamic processes of interest at electrified interfaces include an adsorption-desorption and an orientation change of molecules, a two-dimensional (2D) phase transition to form a condensed monolayer, and an ingress/egress of water molecules into/from the adlayer.

Electrified interfaces such as a potential-controlled electrode/water and oil/water interfaces are the typical regions where the interfacial energy change takes place as a function of an applied potential following electrocapillarity. When the interfacial energy of the electrified interface is changed, the value of contact angle (θ) of a liquid droplet on the electrode surface will change as described by Young’s equation (Fig. 1). Measurements of θ of the liquid droplet on the electrode interface enable us to monitor the dynamics of molecules at the interface.

In this study, I first focused on the dynamics of alkanes as insulating oils on a Au(1 1 1) electrode surface in aqueous solutions. The dynamics of alkanes at a mesoscopic level was described by both morphological changes controlled by changing the interfacial tension balance at the macroscopic three-phase contact line and the molecular-level direct interaction between alkane molecules and electrode surface atoms. Then, the potential-dependent dynamics of n-hexadecane (HD) and sodium dodecyl sulfate (SDS) on Au(1 1 1) electrode was investigated by the use of voltammetric, fluorescence microscopic, and surface-enhanced infrared reflection adsorption spectroscopic (SEIRAS) measurements. The study for coexistence of HD and DS molecules on a metal surface was planned to reveal the molecular-level conditions for interaction between oil and surfactant, whichever they tend to mix or to be phase-separated.
This thesis consists of nine chapters. Introduction to this doctoral dissertation research is given in Chapter 1. Chapter 2 is a review on the dynamics of materials driven by interfacial energy change. Chapter 3 contains experimental methods including electrochemical measurements, fluorescence microscopic measurement, and SEIRAS measurement.

In Chapter 4, I focused on the electrochemical measurements for Au(1 1 1) electrode with HD in electrolyte aqueous solution. HD prepared by the touching method did not block the redox reaction of Fe(CN)$_6^{3-}$-$^{4+}$. Fluorescence measurements using Perylene as a fluorescence probe revealed that the HD (prepared by touching method) formed into many tiny microdroplets with their diameter smaller than 50 μm. The change of fluorescence intensity as a function of the electrode potential revealed that the height of the microdroplets became greater beyond the double layer thickness region at more negative potentials.

Chapter 5 shows that specifically absorbed Br$^-$ at the Au(1 1 1) electrode/water interface induced the retraction of both HD microdroplets and 1.0 μL droplet. The electrowetting of HD was largely affected by specific adsorption of Br$^-$ on the Au surface. Measurements of θ as a macroscopic observable was sensitive to the atomic level change of the electrode surface such as surface reconstruction and Br$^-$ adsorption.

In Chapter 6, I described the effects of DS$^-$ adlayer on the shape change of HD microdroplets on Au(1 1 1) electrode surface. The DS$^-$ adlayer lowered the interfacial tensions of HD/water and electrode/water interfaces, and a HD droplet spread wider. In situ SEIRAS measurements revealed that the alkyl phase of the mixed adlayer was more liquid-like than the DS$^-$ adlayer alone and more solid-like than the HD droplet alone.

In Chapter 7, the electrowetting of a hydrofluoroester solvent of a low adhesion energy, Novec 7100™, was examined as a liquid droplet on a Au(1 1 1) electrode. No hysteresis was observed for Novec 7100 in a cosθ–E curve obtained by potential step measurement in contrast to conventional organic solvent. The adhesion energy of a liquid droplet was found to play an important role on the electrowetting behavior.

Chapter 8 focused on the analysis of the potential-dependent shape change and the 2D mapping of HD microdroplets using fluorescence microscopy. I used Di$_{18}$ASP-PS as a surfactant probe dye to analyze the microdroplet shape in detail. The fluorescence intensity profile of the bright spot reflected on the microdroplets spreading and its height gradually changing in potential sweeping to positive direction.

In Chapter 9, I described a summary of the potential-dependent self-assemblies and dynamics of the organic molecular at the electrode/water interface observed in this thesis.