

Capillary Wave at Liquid-Liquid Interface under Electrochemical Instability

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It has been reported that the adsorption and partition of surface-active ions in liquid-liquid interface make the interface unstable within a certain potential region. The electrochemical instability shows some disordering features such as interfacial turbulence and chaotic oscillation in current, resulting from the transfer of emulsion particles formed in the vicinity of the interface.

Thermal fluctuation in liquid-liquid interface excites a surface tension wave called capillary wave whose behavior provides information such as interfacial tension and viscosity. In this research, optical heterodyne detection for scattered light was performed at the flat liquid-liquid interface and capillary wave spectra under electrochemical instability were obtained in a noncontact manner.

EXPERIMENTAL

Tetrabutylammonium tetraphenylborate (TBATPB) and LiCl were used as the supporting electrolytes in 1,2-dichloroethane (DCE) and aqueous phases, respectively. We used 1mM sodium decyl sulfonate as an anionic surfactant and 1mM decylamine as a cationic surfactant. For comparison, sorbitan monooleate, a nonionic surfactant, was added to stabilize the system. The electrochemical cell employed in this study can be expressed as $\text{Ag} | \text{AgCl} | \text{TBACl} | \text{MgCl}_2 (\text{W}_{\text{ref}}) | \text{TBATPB} (\text{DCE}) | \text{LiCl} (\text{W}) | \text{AgCl} | \text{Ag}$. The interface between the DCE solution containing TBATPB and the aqueous solution was investigated. Cyclic voltammetry, chronoamperometry, and capillary wave spectrum measurement were performed. Electrochemical measurements were made with a four-electrode potentiostat configuration. By fitting the capillary wave spectra to the theoretical curves based on hydrodynamics, interfacial tension and viscosity were obtained.

RESULTS AND DISCUSSION

The notable features of electrochemical instability were observed when the solution contained only ionic surfactant. Capillary wave spectra were obtained in the potential range in which irregular current appeared in the cyclic voltammogram. The shapes of the spectra were very similar to each other, irrespective of the addition of each surfactant. They fit well to the theoretical curves based on hydrodynamics. We cannot confirm any anomalous change caused by the electrochemical instability such as the broadening of the spectra which indicates the increase in viscosity. Even when anomalous increase of current was observed during chronoamperometry, capillary wave spectra were still observed (Fig. 1). We investigated the change of the capillary wave spectra with the anomalous increase of current under electrochemical instability.

The electrocapillary curve (ECC) obtained for solution containing no surfactant corresponds well with the values that have been reported. ECC exhibits discontinuities at the both end of the instability window in the presence of an ionic surfactant. In contrast, ECC for solution that contains both the ionic and nonionic surfactants shows the regular curvature for entire potential range and have a maximum (Fig. 2). The trend in ECC was in good agreement with the theoretical prediction

proposed by Kakiuchi et al.

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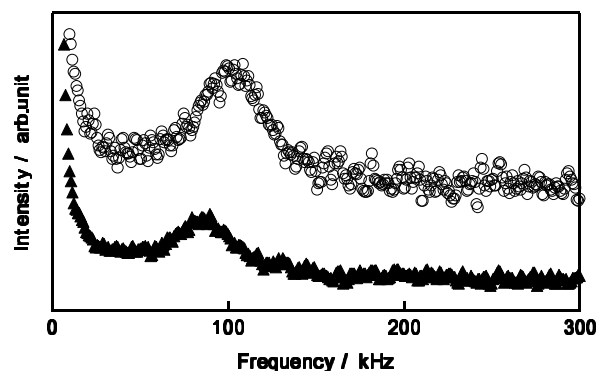


Fig. 1 Spectra of capillary waves observed in solutions containing no surfactant (\circ) and 1mM sodium decyl sulfate (\blacktriangle) at 100mV.

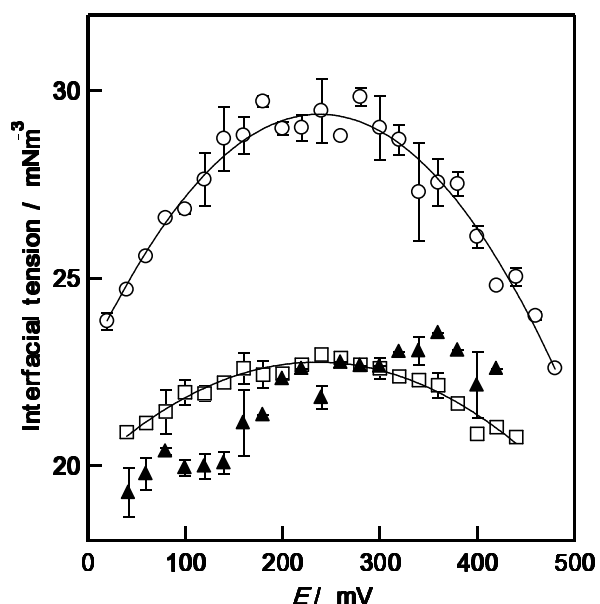


Fig. 2 Electrocapillary curves for solutions containing no surfactant (\circ), 1mM sodium decyl sulfate (\blacktriangle), and 1mM sodium decyl sulfate and 1mM sorbitan monooleate (\square).