

Stabilization of Stearic Acid LB Monolayer Film by Addition of n-Alkylthiol

Takahiro SAWAGUCHI, Matsuhiro NISHIZAWA, Tomokazu MATSUE,
and Isamu UCHIDA*

Department of Molecular Chemistry and Engineering, Faculty of Engineering,
Tohoku University, Aramaki-Aoba, Aoba-ku, Sendai 980

Stability of stearic acid LB monolayer in an aqueous solution is remarkably improved by the addition of n-alkylthiol. n-Alkylthiol adsorbs strongly on gold surface and acts as anchor of the stearic acid monolayer so as not to diffuse away from the substrate.

Organic ultra-thin films by using Langmuir-Blodgett (LB) technique have been attracting great attention, since it is easy to control the thickness, the orientation and the packing density of the films at molecular level.^{1,2)} The electrochemical characterization of LB films and their application to electrochemical devices have recently been reported by many authors.³⁻⁹⁾ However, the LB films have the instability of LB matrix molecules that they tend to detach from the substrate in aqueous solution. This is a major problem in construction of molecular electronic and electrochemical devices. Recent efforts have shown that polymerization¹⁰⁻¹³⁾ and bonding to the substrate¹⁴⁻¹⁷⁾ improve the stability of LB films.

In this paper, we report the improvement of stability of a stearic acid LB monolayer by the addition of n-alkylthiol, which adsorbs strongly on metal surfaces. We have investigated the electrochemical properties of the LB monolayer and the blocking effect on electrode reactions.

Stearic acid and 1-hexadecanethiol (C₁₆SH) were recrystallized twice from benzene and heptane, respectively, before use. A benzene solution of two amphiphiles mixture (total amphiphile concentration, 1.0 mM; C₁₆SH fraction, 0.1, 1, or 10 mol%) was used as a spreading solution onto pure water. The mixture gave a typical surface pressure vs. area isotherm with a solid condensed region as was observed for pure stearic acid, indicating that the C₁₆SH molecule was mixed uniformly in stearic acid monolayer. The isotherm curves of the mixtures containing 0.1 mol% and 1 mol% C₁₆SH were similar to that of pure stearic acid. The limiting areas per molecule were calculated from the curves and found to be 20.6 Å². For the 10 mol% mixture we found a slightly larger value of 22.1 Å². The condensed LB monolayer films containing C₁₆SH can be transferred and deposited on a substrate at surface pressure of 40 N/m. However, a 50 mol% mixture and pure C₁₆SH did not show remarkable solid state region.

We used a 1000 Å thick gold-sputtered glass as a substrate. The monolayer modified Au electrode was exposed to the electrolyte solution by clamping with an O-ring (electrode area 0.13 cm^2) after drying in the desiccator for four hours. Cyclic voltammetry was carried out by using a PAR polarographic analyzer (model 364). AC-impedance measurements were conducted using an NF 5020 Frequency Response Analyzer coupled with a Solartron 1186 potentiostat. Frequencies were varied from 1 Hz to 10 kHz and the signal amplitude was 5 mV rms. Data were transferred to microcomputer (NEC PC-9801) for faradaic impedance analysis.

Figure 1 shows time dependence of cyclic voltammograms (CVs) for 1.0 mM $\text{K}_4\text{Fe}(\text{CN})_6$ in a 0.1 M Na_2SO_4 solution at the Au electrodes modified with different LB monolayers; i.e., (A) pure stearic acid, (B) 1.0 mol% C_{16}SH mixture and (C) 10 mol% C_{16}SH mixture. In the first potential sweep, no voltammetric response was observed at all the LB modified electrodes. This indicates that hydrophobic alkyl chains of amphiphiles block the electrode reaction⁷⁾ and the blocking effects were almost similar. Continuous exposure of the electrode (A) to the electrolyte solution resulted in gradual appearance of voltammetric response and after 10 hours the shape of CV agreed closely with that obtained at a bare Au electrode. On the other hand, the electrode (C) showed almost no change in the voltammetric response even after 30 hours. These results indicate that C_{16}SH molecules adsorb strongly on the gold surface and prevent the surrounding stearic acid molecules diffusing away from the substrate by hydrophobic interaction between the long alkyl chains. Such anchoring effect of C_{16}SH molecules in the monolayer matrix improves the stability of LB monolayer in aqueous solution and a ratio of one C_{16}SH molecule to 9 stearic acid molecules is effective for long periodical stability.

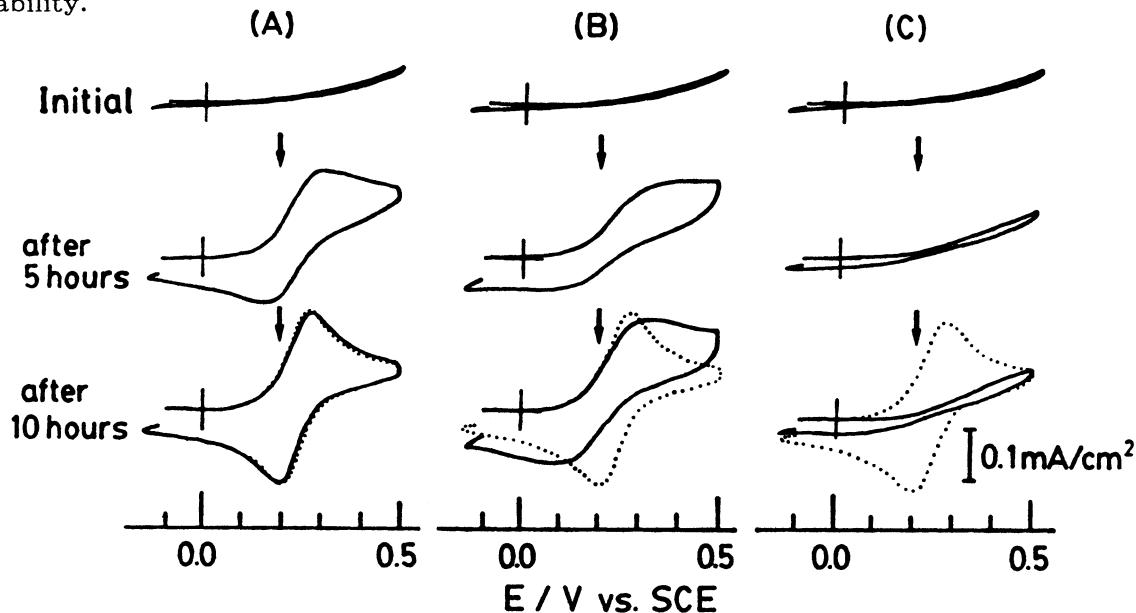


Fig. 1. Cyclic voltammograms of 1.0 mM $\text{K}_4\text{Fe}(\text{CN})_6$ at various Au electrodes in 0.1 M Na_2SO_4 . (A) pure stearic acid, (B) 1 mol% C_{16}SH mixture and (C) 10 mol% C_{16}SH mixture. ··· : bare Au. Scan rate : 100 mV/s.

To investigate the stabilizing effect in more detail, we employed AC impedance analysis in which small amplitude voltage is applied to the electrode. Figure 2 shows time dependence of cole-cole plots of 1.0 mM $K_4Fe(CN)_6$ and 1.0 mM $K_3Fe(CN)_6$ at the open circuit potential (0.2 V vs. SCE). The size of circular arc of the cole-cole plot decreases gradually, but the change for the electrode (C) was much smaller than that for the electrode (A), indicating the same tendency of the stability as was observed in CV measurements. We estimated the electrochemical reaction parameters of the redox couple by parameter fitting, assuming a Randles' type equivalent circuit as shown in Fig. 3. We especially noticed the time dependence of C_d and R_{ct} because these values are sensitive to the detachment of monolayer molecules. In the initial exposure, both electrode (A) and (C) gave similar values of C_d , ca. $2 \mu F/cm^2$. Since C_d of bare Au electrode is more than $20 \mu F/cm^2$, the presence of the monolayer film results in a pronounced decrease in the double layer capacity.⁷⁾ The C_d value gradually increases with immersion time in the solution according to detachment of the monolayer.

We also obtained the R_{ct} value for $Fe(CN)_6^{4-/-3-}$ redox couple at monolayer modified Au electrodes and the results were shown in Fig. 4. On the bare Au electrode the heterogeneous rate constant (k_0) of $Fe(CN)_6^{4-/-3-}$ redox couple has been reported to be $2 \times 10^{-2} \text{ cm/s}$,¹⁸⁾ which corresponds to R_{ct} of $13.3 \Omega \text{ cm}^2$ according to the following equation;¹⁹⁾

$$R_{ct} = \frac{RT}{n^2 F^2 C^* k_0} \quad (1)$$

where C^* is the bulk concentration of

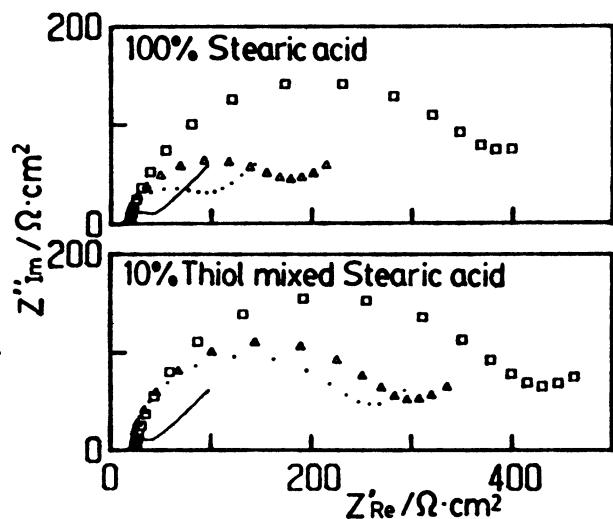


Fig. 2. Time dependence of Cole-Cole plot of 1.0 mM $Fe(CN)_6^{4-/-3-}$ in 0.1 M Na_2SO_4 . \square : $t=0$, \triangle : 4 h, \dots : 8 h, — : bare Au. Electrode potential : 0.2 V vs. SCE.

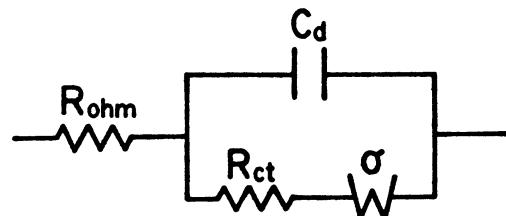


Fig. 3. Randles' equivalent circuit. R_{ohm} : ohmic resistance of electrolyte solution. C_d : differential capacitance of solution-electrode interface. R_{ct} : charge transfer resistance. σ : warburg impedance.

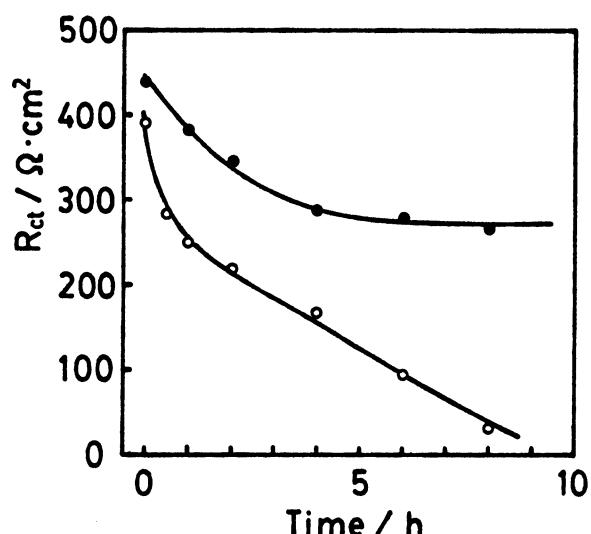


Fig. 4. Time dependence of charge transfer resistance (R_{ct}) for $Fe(CN)_6^{4-/-3-}$ at monolayer modified Au electrodes. \bigcirc : pure stearic acid, \bullet : 10 mol% $C_{16}SH$ mixture.

redox species. Both the electrodes (A) and (C) had R_{ct} more than $400 \Omega \text{ cm}^2$ in the initial exposure and the electrode (C) kept high R_{ct} values of about $300 \Omega \text{ cm}^2$ even after 8 hours. While the R_{ct} value for the pure stearic acid monolayer (electrode (A)) decreased gradually and reached the level for bare Au electrode after 8 hours.

The results described above obviously demonstrate that $C_{16}SH$ molecules provide the anchoring effect to prevent the detachment of stearic acid molecules from the gold electrode surface and improve the stability of the stearic acid LB monolayer film. This method would be applicable for improving the stability and reproducibility of monolayer electrochemical devices in aqueous solution.

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