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Electrochemistry of the Redox-Active Langmuir-Blodgett Films Coated on Glassy Carbon Electrodes

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In order to study the electrochemical behavior of a redox species in the Langmuir-Blodgett (LB) film on a glassy carbon (GC) electrode, three kinds of amphiphilic redox compounds, each carrying an anthraquinone, a viologen, and a ferrocene moiety, were confined on the electrode surfaces. Prior to the deposition of the film on the electrode, surface pressure-area isotherms for a number of mixed films of the redox-active amphiphiles and arachidic acid were recorded and the stability of the monolayers was discussed. Finally, the cyclic voltammetric behavior of the LB film-modified electrodes was discussed in terms of the changes in the structure and the nature of the LB film caused by the redox reactions.

In the course of the development of the modified electrodes,[1,2] a high density of the immobilized functional species,[1] a regularity in the molecular organization,[3,4] and an ultrathinness of the coated film on the electrode surface[2,5] are of crucial importance. The LB method, the technological possibilities of which have been widely appreciated in connection with molecular engineering,[6,7] was utilized to fulfill these requirements. This technique not only ensures the molecular electrochemical devices,[3,4] but also gives some insights into the structure of the electrical double-layer.[8]

In the present work, we confined redox-active amphiphiles, such as an anthraquinone (AQS), a viologen (VS), and a ferrocene surfactant derivative (FcS), on a GC electrode by the use of the LB method, thereby organizing the desired film structure in which electroactive and electroinactive layers were assembled in a deliberate way. Arachidic acid (AA) was used to form the stable electroactive mixed layers with each redox-active amphiphile and also to build the electroinactive layers. The cyclic voltammetry of these LB modified electrodes and some of the unexpected findings therefrom are discussed in terms of i) the charge on, or in the vicinity of, the redox moieties; ii) the environment and location of the redox moieties, and iii) the change in some of these characteristics by the redox reaction and its effect on the structure and nature of the LB multilayer film.

Experimental

Materials. The redox-active amphiphiles used in the present work are shown in Fig. 1. The AQS was prepared according to the following procedure: dodecylamine was transformed into *N*,*N*-didodecylmethylamine by the method of Ralston et al.[9]; 2-methylanthraquinone was treated with *N*-bromosuccinimide in the presence of benzoyl peroxide in carbon tetrachloride,[10] and the resulting 2-(bromomethyl)-anthraquinone was reacted with *N*,*N*-didodecylmethylamine in 1,4-dioxane to yield AQS. For the preparation of FcS, the method of Ohkawara[11] for amide formation from 1,1′-ferrocenedicarboxylic acid was used, as previously.[4] The VS was synthesized according to the method of Fendler et al.[12]

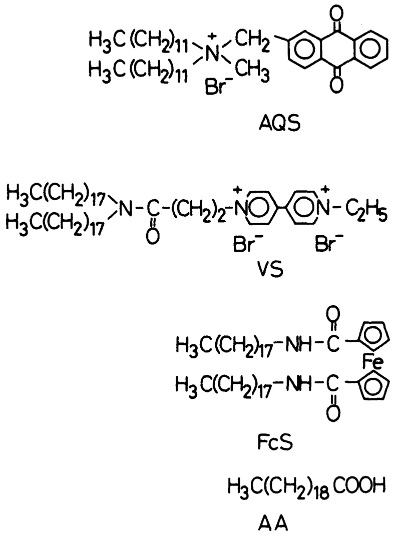

Fig. 1. The structures of the redox-active amphiphiles and a fatty acid used in this work.

Monolayer Preparation and Surface Pressure-Area Isotherms. The surface pressure-area isotherms were studied by using a commercially available Langmuir trough equipped with a film balance (Kyowa Kaimenkagaku Co.). Monolayers were obtained by spreading chloroform solutions of amphiphiles on the air-water interface of the trough and by then compressing the surface at 2 Å^2 molecule^{-1} min^{-1}. Doubly distilled water was used as the subphase; it contained no salt unless otherwise stated. The surface pressure-area isotherms were measured at 24 °C.

Film Deposition on the Electrode Surface. The monolayer formed at the air-water interface was deposited at 40 mN m^{-1} on the GC disk electrode (diameter: 0.3 cm) at a dipping rate of 3 mm min^{-1}, except in the case of the pure monolayer of AQS or VS, which was deposited at 35 mN m^{-1}. Since the surface of GC is hydrophilic, little material was deposited on the first insertion of the electrode surface into the subphase, but a good coverage was obtained on the withdrawal of the electrode surface through the film. With repetitive strokes, the multilayer structure of a typical Y film was formed on the GC electrode. For the sake of accuracy, the transfer ratio was determined independently with a GC plate possessing a larger area (6 cm^2). In every case, the apparent transfer ratios for both downward and upward strokes were between 0.8 and 1.1.

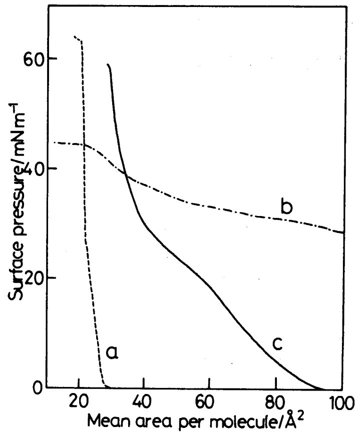

Fig. 2. Surface pressure-area isotherms of (a) AA, (b) AQS, and (c) a mixture of AQS and AA (1:3); on pure water at 24 °C.

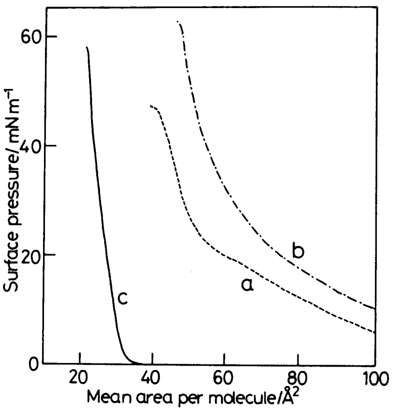

Fig. 3. Surface pressure-area isotherms of (a) VS on pure water, (b) on 0.3 mM Na_2CO_3, and (c) a mixture of VS and AA (1:3) on pure water, at 24 °C.

Cyclic Voltammetry. The electrochemical characteristics of the LB film-modified GC electrodes were examined by means of cyclic voltammetry. A three-electrode configuration was employed: an SCE was used as the reference, and a platinum wire as the counter electrode, in addition to the LB film-modified working electrode. Measurements were carried out at room temperature (24 °C). An aqueous solution of 0.5 M† KCl was used as the electrolyte. For the AQS-modified electrode, hydrochloric acid was added also to make the pH of the solution two, for in an acidic solution, although there are kinetic complications due to proton addition during the electron transfer, the anthraquinone derivative attached to the GC electrodes exhibits a clear two-electron and two-proton reduction peak to hydroanthraquinone.[8]

Results and Discussion

Stability of the Mixed Monolayers. The isotherms were compared between the mixed monolayer and the monolayer that contained only a redox surfactant, as is shown in Figs. 2—4. For a pure AQS monolayer, only a liquid-expanded film was formed (Fig. 2b). The mixed film of AQS and AA in the molar mixing ratio of 1:3, however, exhibited a condensed state at high surface pressures (Fig. 2c). A pure VS monolayer was unstable on the pure-water subphase (Fig. 3a). The stability was improved on an aqueous solution of 0.3 mM Na_2CO_3 (Fig. 3b). A remarkable stability was achieved by mixing with AA (Fig. 3c). A pure FcS monolayer collapsed at a low surface pressure (Fig. 4a). When mixed with AA, the film was stabilized (Fig. 4b). In all the cases mentioned above, the mixed monolayer, when compressed, formed an extremely stable monolayer, with no appreciable collapse being evident over a period of many hours. The molar mixing ratio of the

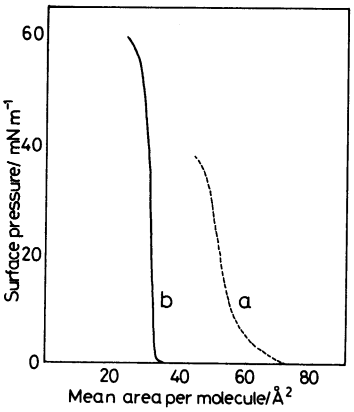

Fig. 4. Surface pressure-area isotherms of (a) FcS and (b) a mixture of FcS and AA (1:3), on pure water at 24 °C.

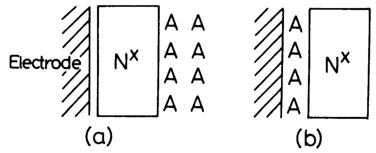

Fig. 5. Schematic structures of multilayer-deposited electrodes. (a): N^xA^2, (b): AN^x.

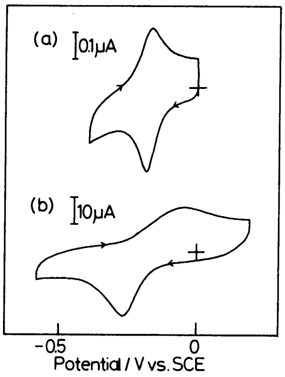

Fig. 6. Cyclic voltammograms for an N^3A^2 type of the AQS modified electrode in 0.1 M KCl solution containing 0.01 M HCl. Scan rate. (a): 0.01 V s^{-1}, (b): 1 V s^{-1}. A: a mixed monolayer of AQS and AA (1:3). N: a pure AA monolayer.

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† 1 M=1 mol dm^{-3}.

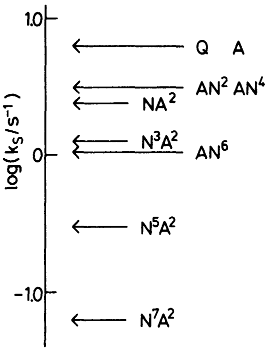

Fig. 7. Comparison of the apparent surface reaction rates of N^{x}A^2 and AN^x types of the AQS modified electrodes. Q: a pure AQS monolayer. A: a mixed monolayer of AQS and AA (1:3).

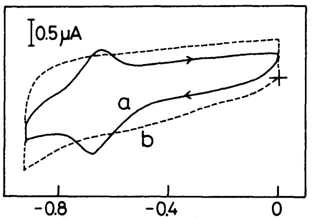

Fig. 8. Cyclic voltammograms for (a) an N^{3}A^2 type of the VS modified electrode and (b) the naked electrode, in 0.1 M KCl. Scan rate: 0.05 V s^{-1}. A: a mixed monolayer of VS and AA (1:3).

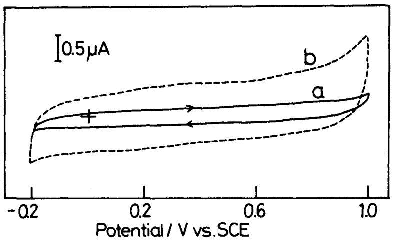

Fig. 9. Cyclic voltammograms for (a) an N^{3}A^2 type of the FcS modified electrode and (b) the naked electrode, in 0.1 M KCl. Scan rate: 0.05 V s^{-1}. A: a mixed monolayer of FcS and AA (1:3).

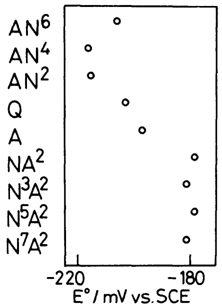

Fig. 10. The formal reversible peak potentials of the AQS modified electrodes. Q: a pure AQS monolayer. A: a mixed monolayer of AQS and AA (1:3).

redox surfactant and AA (1:3) was chosen in view of both the film stability and the accuracy required for the electrochemical measurements.

Electrochemistry of the LB Film-Modified GC Electrode. We have concentrated our attention on two types of multilayer-deposited electrodes: in one, some AA layers as an electroinactive matrix were sandwiched between the electrode surface and the AA-redox surfactant mixed bilayer, while in the other the relative locations of the AA layers and the AA-redox surfactant monolayer were reversed. The former system is termed an N^{x}A^2 type, and the latter AN^x, where A, N, and x signify the electroactive AA-redox surfactant mixed layer, the electroinactive AA layer, and the number of the AA layers respectively (Fig. 5).

Figure 6 shows cyclic voltamograms for an N^{3}A^2 type of AQS modified electrode.* The peak separation became significant as the sweep rate increased. This irreversibility of the electrode process observed on the cyclic voltammogram makes possible the calculation of an apparent surface-reaction rate, k_s.[8,13–15] Figure 7 shows a comparison of the k's for various kinds of N^{x}A^2 and AN^x electrodes. It should be noted that, in the series of N^{x}A^2 electrodes, k_s becomes smaller as x increases.

The VS modified electrodes behaved reversibly as long as the potential range was limited to between 0 and −0.9 V vs. SCE. The only peak observed in this region corresponds to $V^{2+}+e=V^+$ (Fig. 8). For the FcS modified electrodes, an unexpected result was obtained: no peak for ferrocene site oxidation was observed in any N^{x}A^2 and AN^x structure (Fig. 9). The decrease in the charging current compared with the background current for the naked GC electrode (a dashed line in Fig. 9), however, suggests a compact structure of the FcS–AA mixed film. A similar decrease in the charging current was also observed for the VS–AA mixed film (Fig. 8), but the decrease is not so enormous as that of the FcS–AA mixed film.

The formal reversible peak potential, $E°$, was estimated by the extrapolation of the E_{pa}, E_{pc} vs. v plots to v=0, where the E's are peak potentials for the anodic and cathodic sweeps and where v is the sweep rate. The definition of the formal reversible peak potential is available in the literature.[15] Figures 10 and 11 show the formal potentials of the AQS and the VS modified electrodes respectively. On the AQS modified electrodes, the $E°$ values are classified roughly according to the structure of the film: on the N^{x}A^2-type electrodes, whatever the number of the AA layer was, the $E°$'s were concentrated at values around −0.18 V, whereas on the AN^x-type electrodes the $E°$'s were distributed between −0.22 and −0.20 V. In Fig. 10, Q

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* The electroreactivity of the redox-surfactant in N^{x}A^2 may need mediators in the N^x matrix, since the direct electron transfer from the electrode to the A layers through the N^x matrix seems to be impossible. As candidates for the mediators, the redox-surfactant itself diffusing into the N^x matrix and redox-active impurities such as a trace of oxygen are considered.

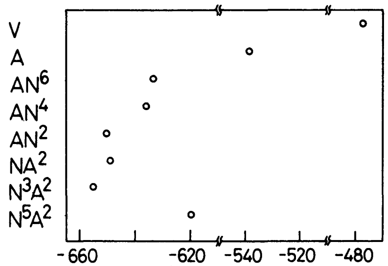

Fig. 11. The formal reversible peak potentials of the VS modified electrodes. V: a pure VS monolayer. A: a mixed monolayer of VS and AA (1:3).

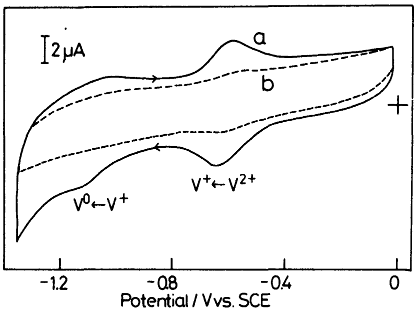

Fig. 12. Cyclic voltammograms for an AN^4 type of the VS modified electrode in 0.1 M KCl. (a): the first cycling, (b): after several cyclings. Scan rate: 0.5 V s^{-1}. A: a mixed monolayer of VS and AA (1:3).

denotes the pure AQS layer. The difference in the E°'s may be attributed to the electrical potential difference between the film and the solution phases. As the AA layers act as a cation-exchange membrane, the negative bias may be created between these two phases and may be effective for the shift of E° for AN^x.

On the VS electrodes, however, no such regular effect of the film structure on the E° in the multilayer system was observed (Fig. 11). Rather, we found a different kind of shift in E° that was not encountered in the AQS modified electrodes. On the pure VS monolayer modified electrode (denoted by V), $E^\circ=-0.48$ V, whereas on the mixed monolayer modified electrode (denoted by A), $E^\circ=-0.54$ V. The mixing of VS with AA thus resulted in a shift of E° to a more negative value. A further negative shift was observed in any type of multilayer modified electrode (−0.62 — −0.66 V). One possible interpretation for the large negative shift up to 180 mV may be an ion-pair formation of the viologen moiety with the carboxylate anion of AA rather than the membrane potential effect. The ion-pair interaction increases in a more hydrophobic environment,[16,17] such as $\mathrm{N}^x\mathrm{A}^2$ and AN^x, than in A. The ion-pair may also be formed between cationic AQS and AA, but in this case the neutral anthraquinone redox moiety does not interact directly with the carboxylate anion; therefore, the effect of the ion-pair formation on E° is not so obvious as that for the VS–AA mixed film. Alternatively, the negative shift may be attributed to the less preferable dimer formation between the viologen monocation radicals resulting from the dilution of VS by mixing with AA and from the decrease in polarity[18] in the multilayer films.

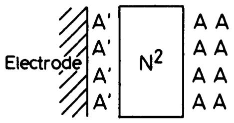

Fig. 13. A schematic structure of the multilayer-deposited electrode possessing both AQS and VS layers. A′: a mixed monolayer of AQS and AA (1:3). A: a mixed monolayer of VS and AA (1:3).

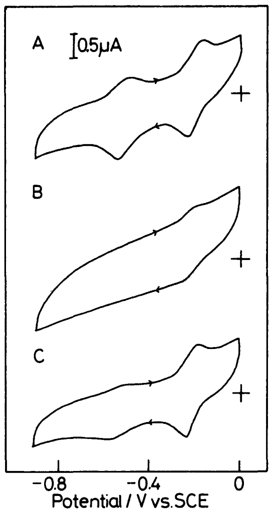

Fig. 14. Cyclic voltammograms for the electrode schematically shown in Fig. 13 in 0.1 M KCl. Scan rate: 0.05 V s^{-1}. A: the potential range is limited between 0 and −0.9 V. B: after holding the potential at −1.5 V for 1 min. C: after holding the potential at 0 V for 5 min. subsequently to B.

An Ion-Gate Function of the VS-Modified Electrode. Figure 12 shows by the solid line, a cyclic voltammogram for an AN^4 type of VS-modified electrode over the potential range from 0 to −1.3 V for the first cycling. At ca. −1.1 V, appeared the second redox peaks corresponding to $\mathrm{V}^+ + e = \mathrm{V}^0$. The two pairs of peaks for viologen gradually diminished as the sweep was repeated, until finally the shape represented by the dashed line was obtained. This diminution was not observed when the potential was limited to the region with di/monovalent viologens. The disappearance of the peaks was common to any $\mathrm{N}^x\mathrm{A}^2$- and AN^x-type electrode except for the monolayer-modified electrodes. This phenomenon indicates that VS, when reduced to an electrically neutral state, forms a compact structure with AA in the multilayer and also makes the film more hydrophobic, so that the reoxidation of V^0 is hindered by blocking the supporting electrolyte. If this is taken into account, the inactivity of the electrically neutral FcS film described above becomes very reasonable. Recently, Tokuda, Matsuda, and their co-workers[19] have found that the electrochemical reactivity of the LB film of a surface-active nitroxide radical deposited on an SnO_2 electrode was affected by the kinds and concentrations of ions in the solution and was diminished strongly under some conditions. Such an effect has been ascribed to the change in the structure of the LB film caused by the "salt-out" effect. Consequently, if the ion-blocking ability is controlled by changing the charge of the head group of the redox-active surfactants electrochemically, a novel function, i.e., an ion gate,[20] can be expected in the LB-modified electrode.

Taking these findings into consideration, a multilayer possessing both AQS and VS layers was fabricated on the electrode, as is shown schematically in Fig. 13. An AQS layer as the electrochemical probe was inserted between the electrode and an N^2A^2-type VS multilayer. Cyclic voltammograms of this electrode are shown in Fig. 14. In Fig. 14A, two cathodic peaks due to the AQS reduction and the first reduction of VS and the corresponding anodic peaks appeared. After the potential had been held at -1.5 V for one minute instead of the negative sweep, the first wave of viologen completely disappeared, and that of anthraquinone showed a remarkable decrease in the peak current as well (Fig. 14B). Here again, the V^0 formation in the multilayer made the viologen site itself and the anthraquinone site electrochemically inactive. The neutral compact structure and the hydrophobicity of the completely reduced N^2A^2-type VS multilayer film possibly obstructs the approach of various ions to the proximity of the anthraquinone site and therefore hinders the ions from establishing an electrochemical neutrality or an electrochemical double-layer in the LB film. If the latter effect is true, the anthraquinone site lies in a potential inadequate for the electron transfer. The further decrease in the capacitive current shown in Fig. 12 after the complete reduction of V^{2+} to V^0 and the comparison with the background current of the naked GC electrode in Fig. 8 may support this interpretation. When the electrode potential was kept at 0 V for five minutes afterwards, a total recovery of the AQS wave and a partial recovery of the VS wave were observed (Fig. 14C). One possible explanation of this observation is that a partial amount of neutral viologen is reoxidized to the initial cationic states and that the resulting partial breakdown of the compactness and hydrophobicity allows the electrochemical response of the anthraquinone site.

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References

1) R. W. Murray, "Electroanalytical Chemistry," ed by A. J. Bard, Marcel Dekker, New York (1984), Vol. 13, p. 191.

2) M. Fujihira, "Topics in Organic Electrochemistry," ed by A. J. Fry and W. E. Britton, Plenum Publishing Corp., New York (1985), Chap. 6, p. 255.

3) P. Fromherz and W. Arden, *J. Am. Chem. Soc.*, **102**, 6211 (1980).

4) M. Fujihira, K. Nishiyama, and H. Yamada, *Thin Solid Films*, **132**, 77 (1985).

5) M. Fujihira and S. Poosittisak, *Chem. Lett.*, **1986**, 251.

6) "Molecular Electronic Devices," ed by F. L. Carter, Marcel Dekker, New York (1982).

7) H. Kuhn, *Thin Solid Films*, **99**, 1 (1983).

8) M. Fujihira and T. Araki, *J. Electroanal. Chem. Interfacial Electrochem.*, in press.

9) A. W. Ralston, D. N. Eggenberger, and P. L. Du Brow, *J. Am. Chem. Soc.*, **70**, 977 (1948).

10) M. Fujihira, S. Tasaki, T. Osa, and T. Kuwana, *J. Electroanal. Chem. Interfacial Electrochem.*, **150**, 665 (1983).

11) M. Ohkawara, Y. Takemoto, H. Kitaoka, E. Haruki, and E. Imoto, *Kogyo Kagaku Zasshi*, **65**, 685 (1962).

12) P. Tundo, D. J. Kippenberger, M. J. Politi, P. Klahn, and J. H. Fendler, *J. Am. Chem. Soc.*, **104**, 5352 (1982).

13) E. Laviron, *J. Electroanal. Chem. Interfacial Electrochem.*, **101**, 19 (1979).

14) M. Sharp, M. Petersson, and K. Edstrom, *J. Electroanal. Chem. Interfacial Electrochem.*, **95**, 123 (1979).

15) M. Sharp and M. Petersson, *J. Electroanal. Chem. Interfacial Electrochem.*, **122**, 409 (1981).

16) S. Hayano and M. Fujihira, *Bull. Chem. Soc. Jpn.*, **44**, 2051 (1971).

17) M. E. Peover, "Electroanalytical Chemistry," ed by A. J. Bard, Marcel Dekker, New York (1967), Vol. 2, p. 1.

18) E. M. Kosower and J. L. Cotter, *J. Am. Chem. Soc.*, **86**, 5524 (1964).

19) S. G. Park, K. Aoki, K. Tokuda, and H. Matsuda, *J. Electroanal. Chem. Interfacial Elechrochem.*, **195**, 157 (1985).

20) P. Burgmayer and R. W. Murray, *J. Am. Chem. Soc.*, **104**, 6139 (1982); *J. Phys. Chem.*, **88**, 2515 (1984).