CHEMISTRY LETTERS, pp. 921-922, 1986.

IN SITU ELECTROCHEMICAL MEASUREMENTS OF THE REDOX-ACTIVE MONOLAYER BY THE HORIZONTAL TOUCHING METHOD UNDER A CONTROLLED SURFACE PRESSURE

Masamichi FUJIHIRA* and Toshinari ARAKI
Department of Chemical Engineering, Tokyo Institute of Technology,
Ohokayama, Megro-ku, Tokyo 152

An *in situ* cyclic voltammetric measurement of anthraquinone (AQ) moieties in the monolayer assembly spread on water was carried out by horizontal touching with a glassy carbon disk electrode (GC) under various surface pressures. Some unexpected findings on the reactivity of the AQ film in a low surface pressure, which cannot be transferred to the electrode surface as it is on water by other methods than the horizontal touching method, are described.

In the course of development of the modified electrodes,[1)] such properties as high surface density, well-defined molecular organization, and thinness of the layer are of crucial importance. The application of the Langmuir-Blodgett (LB) technique ensures the molecular level fabrication of the layer. Although there have been a few reports on the LB film modified electrodes,[2-5)] the conventional LB film usually suffers from destruction of the film structure to some extent during the film transfer onto the electrode: movement of the substrate across the film formed at the air-water interface entails the surface flow of the monolayer. Thus especially at a low surface pressure, where the amphipathic molecules can move easily, the film transferred onto the electrode surface does not retain its original structure on the aqueous subphase. The horizontal touching method employed here overcomes this disadvantage by keeping the electrode surface parallel to the air-water interface during bringing of the surface into contact with the monolayer followed by cyclic voltammetry *in situ* with the electrode kept in that position.[6)]

A mixed monolayer of the electroactive cationic surfactant AQS, di(n-dodecyl)-2-anthraquinonylmethylmethylammonium bromide, and arachidic acid of the molar mixing ratio 1:3 was prepared by spreading a dilute chloroform solution of these compounds on a surface of an aqueous subphase containing 0.1 M KCl and 0.1 M HCl in a Langmuir trough (Kyowa Kaimenkagaku Co.), which was equipped with a platinum wire, a saturated calomel electrode, and a GC as a counter, a reference, and a working electrode, respectively. The surface pressure of the film was automatically controlled by a Teflon barrier. The horizontal touching method is schematically shown in Fig. 1. A solid line in Fig. 2 shows a surface pressure-area isotherm of the mixed monolayer. The number on the abscissa denotes the surface concentration of AQS, d_{sp}, instead of the area. Some of the cyclic voltammograms under different d_{sp} are shown in Fig. 3. The surface density of the reacted AQ moiety on the electrode surface, d_{elec}, can be evaluated from graphical integration of the cyclic

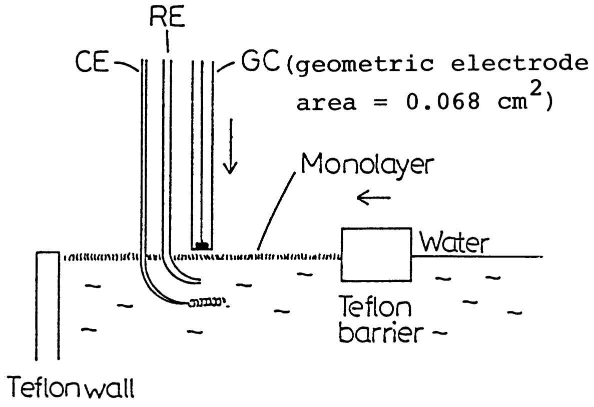

Fig. 1. Horizontal touching method. RE: saturated calomel electode. CE: platinum wire counter electrode.

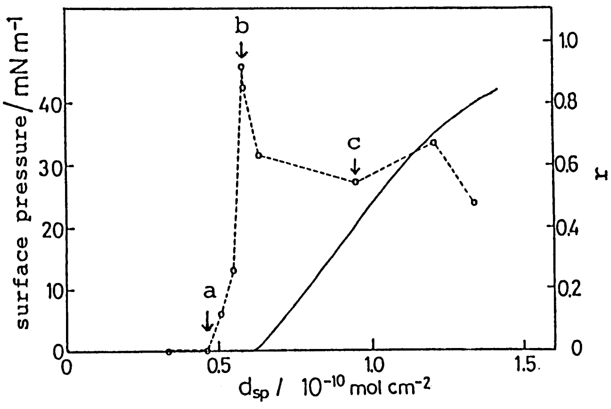

Fig. 2. Surface pressure-area isotherm of AQS-arachidic acid mixed monolayer at 25 °C. The dashed line denotes r value.

voltammograms. The ratio of d_{elec} to d_{sp}, r, is also plotted in Fig. 2. The result shows two interesting points: first, there is a drastic increase in the current due to the redox reaction of AQ moiety before the surface pressure rises (Fig. 3a and b). Secondly, r reaches the maximum near the onset value of d_{sp} of the isotherm and drops at higher surface pressures. Details of these interesting phenomena are now under study.

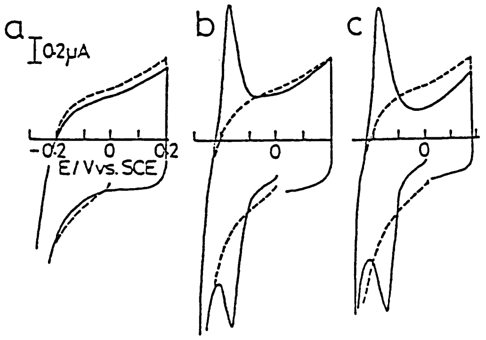

Fig. 3. Cyclic voltammograms of the monolayer taken at a, b, and c in Fig. 2. Scan rate: 100 mV s^{-1}. Dashed line: the background current on the naked GC.

The present method will be applicable to the study of a change in electrochemical nature of monolayers under wide range of surface pressures.

References

1) R.W.Murray, "Electroanalytical Chemistry," ed by A.J.Bard, Marcel Dekker, New York (1984), Vol. 13, p.191; M.Fujihira, "Topics in Organic Electrochemistry,"ed by A.J.Fry and W.E.Briton, Plenum Publishing Corp., New York, Chap. 6, in press.
2) M.Fujihira and S.Poosittisak, Chem. Lett., 1986, 251; J. Electroanal. Chem., in press.
3) M.Fujihira and T.Araki, Bull. Chem. Soc. Jpn.; J.Electroanal. Chem., submitted.
4) M.Fujihira, K.Nishiyama, and H.Yamada, Thin Solid Films, in press.
5) S.G.Park, K.Aoki, K.Tokuda, and H.Matsuda, J. Electroanal. Chem., 195, 157 (1985).
6) Care was taken to avoid air bubble on the electrode surface so that the fairly reproducible results were obtained in the electrochemical measurements.

(Received March 13, 1986)