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On the Polarographic Limiting Current of Solubilized Dye in Nonionic Surfactant Solutions

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The nature of the limiting current of the reduction of solubilized dye with nonionic surfactants on a mercury-drop electrode was examined. The solution of anthraquinone derivatives solubilized in an aqueous solution of a nonionic surfactant showed a proportionality of the limiting current to the dye concentration. The linear dependence of the current on the square-root of the mercury-column height, the solpe of the log-plot, and the *i*-*t* curves indicated the limiting current to be diffusion-controlled. From the *i*-*t* curve measurements, the acceleration of the instantaneous current at the end of the mercury-drop growth was observed with the polyoxyethylene nonylphenylether and Triton X-100. This can be interpreted in relation to the reorientation of the surfactant molecules.

A previous paper treated[1] the polarographic reduction of the disperse-dyes solubilized in nonionic surfactant solutions in which the electrode process is diffusion-controlled. In that case, a linear relation of the limiting current to the dye concentration was assumed, but it could not be established.

In this paper, the nature of the limiting current of the solubilized dye will be examined in further detail in a system which shows a proportionality of the limiting current to the dye concentration.

Experimental

The 1-amino-2-methoxy-4-hydroxy anthraquinone was obtained by the recrystallization of a sample dye received through the courtesy of the Sumitomo Chemical Industry Co. from an ethanol-water mixture. Polyoxyethylene nonylphenyl ether (NP-$\overline{10}$, NP-$\overline{19}$), polyoxyethylene lauryl ether (L-$\overline{9}$), and Triton-X-100 (TX-100) were used as nonionic surfactants.

The solubilization and the polarographic procedure were the same as in the previous paper except that the solution was not irradiated with supersonic waves in this study.

The current-time curves were measured with a potentiostat (Hokuto Denko Co., Ltd.) and a XY-5121-type synchroscope (Iwasaki Tushinki Co., Ltd.) or a XY-recorder (Yokogawa Denki Co., Ltd.).

Results and Discussion

Relation of the Limiting Current to Dye Concentration. The solubilized dye in all four surfactant solutions showed a well-defined wave. $E_{1/2}$ is -0.625 V (*vs.* SCE), a value which accords with the peak potential of the ac polarogram. The dependence of the limiting current on the dye concentration is shown in Fig. 1. The linear relationship was obtained with a surfactant concentration of between 10^{-3} and 10^{-1} M. This proves that the diffusion coefficient of the surfactant micelle with the dye molecule is not affected by the surfactant concentration or the dye concentration. The value of the diffusion coefficient increases with an increase in the molecular weight of the surfactant, (NP-$\overline{10}$>L-$\overline{9}$>TX-100). The values are in accord with the volumes of these surfactant micelles, all of which have almost the same aggregation number, about 100.[2]

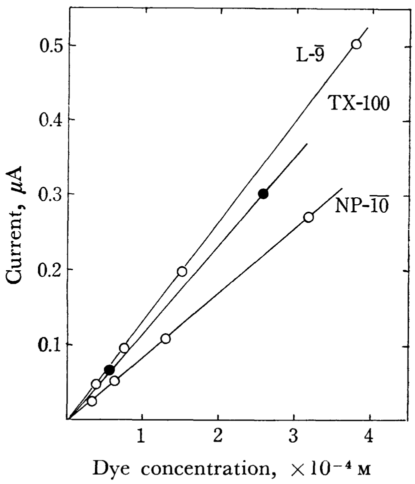

Fig. 1. Relation of limiting current to dye concentration.

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[1] S. Hayano and N. Shinozuka, This Bulletin, **42**, 1469 (1969).

[2] P. Becher, "Nonionic Surfactants," Marcel Dekker, New York (1967), p. 495.

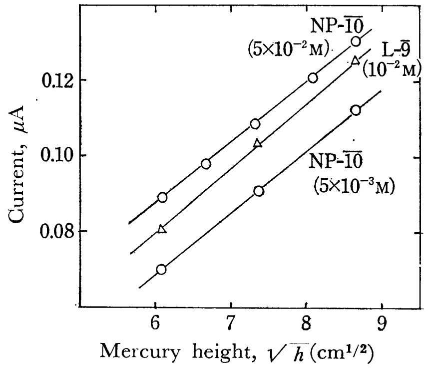

Fig. 2. Dependence of current on mercury height.

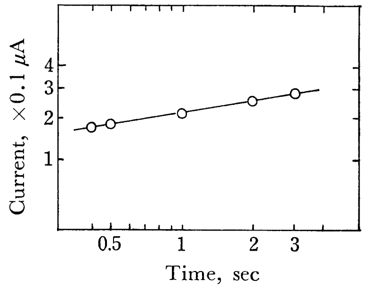

Fig. 3. log-Plots of i-t curve.
(L-$\overline{9}$: 6×10^{-2} M, Dye: 2.2×10^{-4} M, at −0.7 V)

The Nature of the Limiting Current. The linear dependence of the current on the square-root of the mercury-column height indicates that the limiting current is diffusion-controlled (Fig. 2). Furthermore, the i-t curves of the dye at the potential of the current-plateau show the relation of $i \propto t^{1/6}$ (Fig. 3).

The log-plot of the current against the potential gives a straight line with a slope of about 30 mV/log unit, showing that the reversibility of the reduction of solubilized dye is not affected by the solubilization with surfactants.

Current-time Curves. During the measurement of the i-t curves, a marked current increase, an increase which gave rise to a hump on the limiting current, was observed when the mercury head was lowered or/and the surfactant concentration was decreased at potentials between −0.8 and −1.3 V (Fig. 4). The log-plots of the curve showed that the current was diffusion-controlled until there was a marked current increase. This phenomenon was not found with the L-$\overline{9}$ surfactant in various concentrations or at various mercury-column heights. The following analysis of the curve indicates that the time of the sudden current increase corresponds to the constant surface area of a mercury drop.

The surface area of a mercury drop at time t is given as follows:[3]

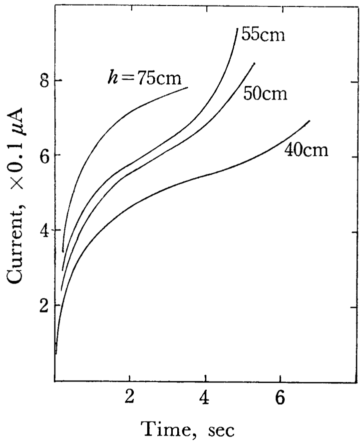

Fig. 4. Dependence of i-t curves on mercury height.
(NP-10: 5×10^{-2} M, Dye: 2.6×10^{-4} M at −0.8 V)

TABLE 1. DEPENDENCE OF THE TIME OF SUDDEN CURRENT INCREASE ON MERCURY COLUMN HEIGHT

Mercur height (cm)	t (sec)	$(Pt)^{2/3}$
75.5	2.2	30.2
65.5	2.5	29.9
55.5	2.9	29.5
45.5	3.5	29.3
40.5	4.1	30.1

$$a = 0.85m^{2/3}t^{2/3}$$

As the mercury flow rate, m, is proportional to the height of the mercury head, "P", and as P is easy to measure, "a" is written as,

$$a = kP^{2/3}t^{2/3} \qquad k\text{: constant}$$

From the i-t curves, the $(Pt)^{2/3}$ values, where t is the time at which the current increases, were calculated; they are listed in Table 1. The constant $(Pt)^{2/3}$ means that the current increases when the mercury surface attains a constant area.

It is known that surface-active cations accelerate the reduction of anions and that anionic surfactants accelerate the reduction of cations.[4] Such acceleration as in the case of a charged-type depolarizer with an ionic surfactant can be interpreted in terms of a change in the ψ-potential due to adsorption. On the other hand, for a neutral depolarizer with a nonionic surfactant system, no acceleration has yet been reported.

Recently, Jehring has discussed the reorientation of the surfactant on mercury by means of ac polarography and has concluded that, with NP-$\overline{10}$, a unimolecularly-dispersed surfactant is reoriented to a micelle or its hydrophilic portion extends toward

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[3] J. Heyrovsky, "Principles of Polarography," Acadimic Press, New York (1966), p. 40.

[4] I. M. Kolthoff and Y. Okinaka, *J. Amer. Chem. Soc.*, **81**, 2296 (1959); N. Gundersen and E. Jacobsen, *J. Electroanal. Chem.*, **20**, 13 (1969).

mercury in the potential range of -0.85—-1.1 V *vs.* SCE.[5] The potential range of its appearance, the dependence on the concentration of the surfactant, and the presence of a phenyl group in the surfactant molecule were the same as in this study.

From ac polarograms it is evident that surfactant molecules are adsorbed on the electrode; therefore, the above results can be interpreted as showing that the adsorbed surfactant molecules are reoriented when the mercury-drop surface reaches a certain size. The value of the area corresponding to the reorientation varies with the applied potential, the kind of surfactant, and the surfactant concentration. For a 5×10^{-2} M solution of NP-10 at -0.8 V, the value is 2.34×10^{-2} cm^2; this is reasonable compared with the value, 2.23×10^{-2} cm^2, that corresponds to the approximate monolayer coverage of Triton -X-100.[6] The accelerated current may be related to the reorientation of the surfactant molecules.

It is interesting to note that, although the electrode reaction of the solubilized dye occurs at a potential where the surfactant is strongly adsorbed, the current is diffusion-controlled and the reversibility of the reduction is not affected.

Work is now in progress to investigate the effect of micelles on the electrode reaction of the solubilizate and the adsorption of surfactant molecules on the electrode.

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[5] H. Jehring and A. Weiss, *Tenside*, **6**, 251 (1969).

[6] R. G. Barradas and F. M. Kimmerle, *J. Electroanal. Chem.*, **11**, 163 (1966).