BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1503—1506 (1971)

The Solubilization of Orange OT in Anionic Surfactant Solutions: A Polarographic Study

Shigeo HAYANO and Noriko SHINOZUKA
Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo

(Received December 1, 1970)

Orange OT (1-*o*-tolyl-azo-β-naphthol) solubilized in sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (SDBS) solutions showed a well-defined irreversible polarographic wave. The proportionality of the limiting current to the square root of the mercury height and to the dye concentration indicates the wave to be diffusion-controlled. It is noted that the anionic surfactants showed the waves due to the adsorption-desorption and reorientation of the surfactant molecules on the electrode. The apparent diffusion coefficients of the solubilized dye calculated from the polarographic data were in good agreement with those of the anionic surfactant micelle with electrolyte. We may conclude that the polarographic diffusion coefficient of the solubilized dye is equal to that of the micelle of the solubilizer surfactant. The marked surfactant concentration dependence of the diffusion coefficient was observed with both surfactants and was attributed to the interaction of the micelles. The transfer coefficient of the electrode reaction of Orange OT increased with an increase in the concentration of the surfactant. This tendency is different from the effect of the surface-active agents on the transfer coefficient in the reduction of inorganic ions. From the experimental observations, it seems that the electrode reaction of the solubilized dye is little effected by the charged micelles.

The preceding papers[1,2] described the polarographic behavior of the solubilized dye in nonionic surfactant solutions. The solubilized neutral dyes (anthraquinone derivatives) showed well-defined, diffusion-controlled polarographic waves, and the diffusion constants calculated from the polarographic data were in good accordance with those for the micelles of the nonionic surfactants. This means that the solubilized dye diffused from the bulk solution to the electrode with micelles of the surfactant and that the dye was reduced polarographically where the surfactant micelles seemed to have little effect on the reduction process of the dye.

In this paper, we shall report the polarographic results of the solubilized dye (Orange OT), which showed a well-defined, irreversible, diffusion-controlled wave in anionic surfactant solutions and shall conclude that the diffusion coefficient of the dye is equal to that of the micelle of the surfactant.

Experimental

Materials. Orange OT (1-*o*-tolyl-azo-β-naphthol) was recrystallized twice from ethanol. Sodium dodecylbenzene sulfonate (SDBS) was obtained through the courtesy of the Lion Oil and Fats Co. and was recrystallized from petroleum ether. Sodium dodecyl sulfate (SDS) made by the Kao-Atlas Co., Ltd., was extracted from ether and was recrystallized from ethanol.

Procedure. Orange OT was solubilized in an anionic surfactant solution containing a 0.1 M sodium acetate-acetic acid buffer solution (pH=4.62) as a supporting electrolyte. The solution was stored for a week at 25°C. The excess dye was removed by filtration through a G4 glass filter. The concentration of the filtrates were rechecked by their solid contents on the filter, which had been determined by the measurement of the spectroscopic absorbancy.

The polarographic measurements were carried out at 25°C with Yokogawa POL-11 and POL-21 polarographs. The DME had the following characteristics: $m=2.075$ mg/sec (in pure water without applied potential) and $t=3.58$ sec (in a 10^{-2} M SDBS buffer solution at -0.5 V *vs.* SCE). The height of the mercury head was 75.5 cm.

Results

Orange OT in the Ethanol-water Solution. The polarogram of Orange OT in an 40% ethanolic solution showed pH-dependent waves. In an alkaline solution a maximum of the first kind was observed, while in an acidic solution the wave was well-defined and the current was proportional to the square root of the mercury-column height. (Fig. 1) From the log-plots of the waves, a value of $n\alpha=1.22$ (α being the transfer coefficient) was obtained in a solution of pH=4.6. Supposing that the reduction of Orange OT proceeds with a two-electron transfer,[3] the diffusion coefficient of the dye in an ethanolic solution at pH=4.6 was calculated to be 3.8×10^{-6} cm^2/sec.

---

[1] S. Hayano and N. Shinozuka, This Bulletin, **42**, 1469 (1969).
[2] S. Hayano and N. Shinozuka, *ibid.*, **43**, 2083 (1970).
[3] I. F. Wladimirzew and I. J. Posstowski, *Ber. Akad. Wiss. USSR*, **83**, 855 (1952).

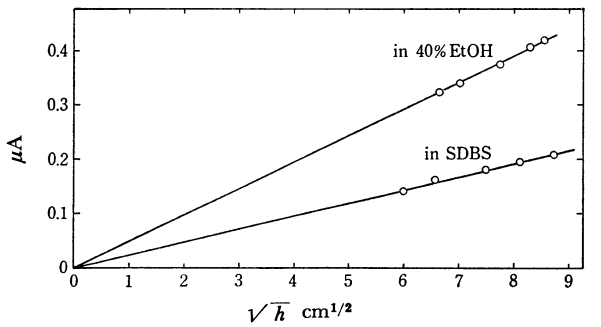

Fig. 1. Dependence of current of Orange OT on mercury height.

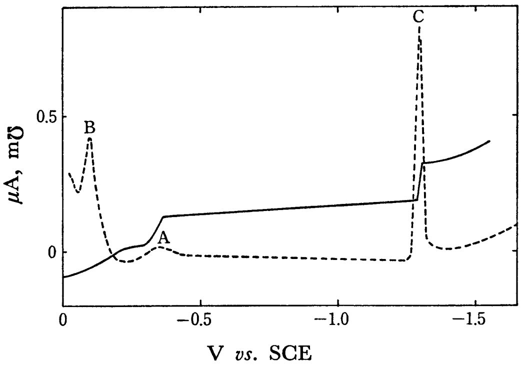

Fig. 2. DC and AC polarograms of the solubilized Orange OT in SDBS solution.

Orange OT Solubilized in SDBS Solution. Orange OT solubilized in a SDBS solution showed a well-defined, irreversible wave in DC polarograms; the AC polarographic peak was very small and round (Fig. 2). In the polarograms of the solubilized dye in anionic surfactant solutions, there appear waves due to the adsorption-desorption of the surfactant molecules on the electrode. In Fig. 2, the A wave is attributed to the reduction of Orange OT, while the B and C waves are adsorption and desorption waves respectively of SDBS molecules. These waves were of course observed with the base solution containing no Orange OT.

The relation of the limiting current to the mercury height shown in Fig. 1 indicates the diffusion-controlled character of the current. A linear line between the current and the dye concentration was also obtained. From these experimental results, the limiting current of Orange OT may be thought to be diffusion-controlled.

TABLE 1. DEPENDENCE OF POLAROGRAPHIC PARAMETERS ON SDBS CONCENTRATION

SDBS concn. (M)	$-E_{1/2}$ (V)	i_d (μA)	D ($\times 10^{-6}$ cm^2/sec)	$n\alpha$
10^{-2}	0.380	0.182	1.77	0.72
3×10^{-2}	0.375	0.166	1.35	0.71
5×10^{-2}	0.392	0.152	1.14	—
8×10^{-2}	0.410	0.120	0.71	0.80
10^{-1}	0.400	0.104	0.53	0.81

Dye concn. 5.78×10^{-5} M

Table 1 summarizes the effects of the SDBS concentration on $E_{1/2}$, i_d, D, and $n\alpha$ of the dye.

The half-wave potential of the dye reduction became more negative with the increase in the SDBS concentration, but the change in $E_{1/2}$ was small compared with the potential shift when the complex formation occurred. The 3rd column of Table 1 shows a marked effect of the concentration of SDBS upon the current; this indicates that the diffusion coefficient of the dye decreased with the increase in the SDBS concentration.

The change in $n\alpha$ values with the surfactant concentration is shown in the 5th column of Table 1. It is evident that the $n\alpha$ value increased with the SDBS concentration.

The effects of the solubilized dye concentration upon $E_{1/2}$, D, and $n\alpha$ were also investigated, but the changes in these factors were very small.

Orange OT Solubilized in the SDS Solution. The polarogram of Orange OT solubilized in a SDS solution is shown in Fig. 3, where the A wave is the diffusion current of Orange OT. The B, C, D, and E waves were observed without Orange OT and were due to the adsorption phenomena of SDS molecules on the electrode. The change in the peak potentials of these waves with the SDS concentration is shown in Fig. 4. The behavior of the C and D waves, which were attributed to the reorientation of the surfactant

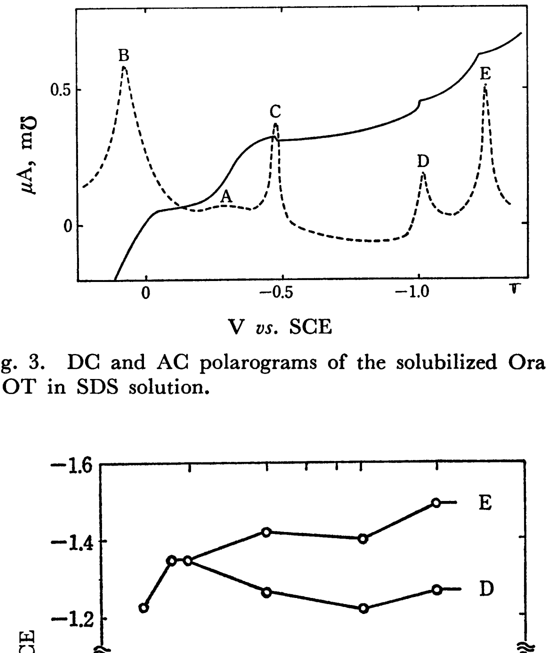

Fig. 3. DC and AC polarograms of the solubilized Orange OT in SDS solution.

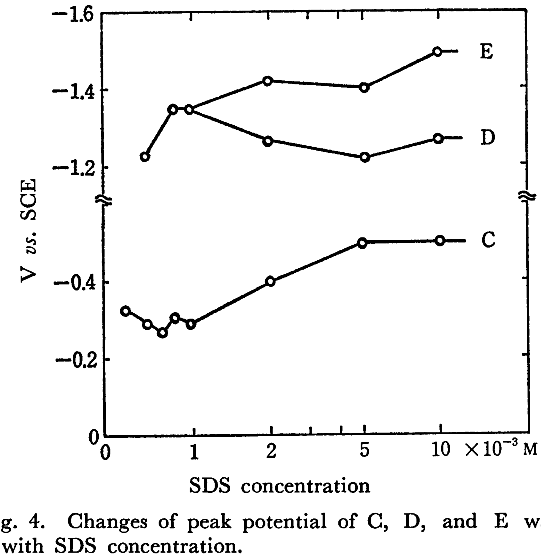

Fig. 4. Changes of peak potential of C, D, and E waves with SDS concentration.

molecules by Eda,4) was carefully observed in order to evaluate the limiting current of Orange OT; the overlap of these waves with the limiting current of Orange OT may cause considerable error. The B and E waves may be adsorption and desorption waves respectively. The details of these nonfaradaic currents will be published elsewhere.

The effects of the SDS concentration on $E_{1/2}$, i_d, D, and $n\alpha$ are given in Table 2. $E_{1/2}$ was almost constant throughout the SDS concentrations used in this study, and in this case the complex formation was also negligible. The apparent diffusion coefficient of the dye was markedly decreased with the increase in the SDS concentration in a way similar to that in SDBS solutions. The value of $n\alpha$, which was larger than that for SDBS solutions, increased with the SDS concentration.

TABLE 2. DEPENDENCE OF POLAROGRAPHIC PARAMETERS ON SDS CONCENTRATION

SDS concn. (M)	$-E_{1/2}$ (V)	i_d (μA)	D ($\times 10^{-6}$ cm^2/sec)	$n\alpha$
2×10^{-2}	0.295	0.170	2.18	1.13
3×10^{-2}	0.303	0.150	1.80	1.14
5×10^{-2}	0.301	0.115	1.06	1.23
7×10^{-2}	0.295	0.108	0.935	1.25
9×10^{-2}	0.303	0.085	0.580	1.25

Dye concn. 5.0×10^{-5} M

Discussion

Diffusion Coefficient of the Solubilized Dye. The apparent diffusion coefficients of the solubilized dye, as calculated from the polarographic data, were in good agreement with those of the anionic surfactant micelle with the electrolyte reported in the literature. Mankowich5) calculated the molecular weight to be about 20,000 for a SDBS micelle in a 1% SDBS solution with 0.1 N Na_2SO_4. This molecular weight corresponds to a D value of about 8.7×10^{-7} cm²/sec. Mysels' values6) of the self-diffusion coefficient for 1.7—10.1×10^{-2} M SDS with 0.1 N NaCl were between 0.92 and 0.82×10^{-6} cm²/sec. Although our results are somewhat larger than the above values, on the whole, there seems to be no great discrepancy. This fact indicates the diffusing particle to be the micelle solubilizing the dye in it.

The marked surfactant concentration dependence of D could be due to a large growth of the micelle, to the interaction with other micelles, or to the diffusion of the dye not solubilized in the micelle at the lower surfactant concentrations. Schott7) has reported, that in SDS solutions, only one dye molecule was solubilized per micelle above the critical micelle concentration and that the aggregation number of SDS in the presence of 0.1 M NaCl was 131. With the present dye/surfactant ratio (below 1/170), all the dye molecules were solubilized in micelles. As to the size of the micelle reported in the literature8), no drastic change appears throughout the experimental range; SDS concentration was 10^{-2}—10^{-1} M, and the dye concentration, 10^{-5}—1.5×10^{-4} M, in the presence of the 0.1 M acetate buffer. Therefore, it is the interaction with other micelles that must be responsible for the concentration dependence of D.

The empirical plots of $1/D$ *vs.* the square roots of the surfactant concentration suggested by Stigter *et al.*6) are shown for SDBS in Fig. 5. The extrapolated value to the cmc (approximately 10^{-3} M) is 2.8×10^{-6} cm²/sec, which is rather large compared with that in the literature.5) The bending point of the line may be attributed to the change in the interaction of the micelles, but it cannot be interpreted in detail.

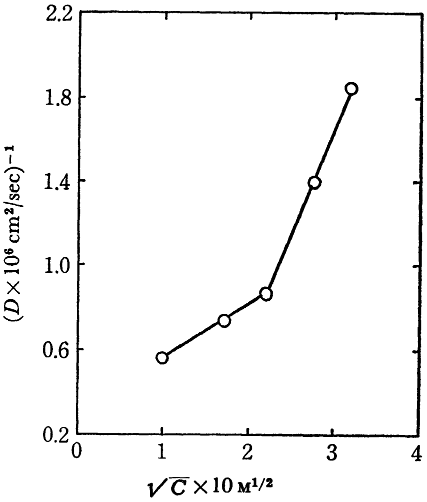

Fig. 5. Relation of the reciprocal of D to the square root of the SDBS concentration.

The value of D for SDS at 7×10^{-2} M, 0.935×10^{-6} cm²/sec, is somewhat different from the value of Stigter *et al.*6) at 7×10^{-2} M SDS, 0.858×10^{-6} cm²/sec (with 0.1 M NaCl), but these values may be thought to be equal considering the difference in methods.

The Change in the Transfer Coefficient. The change in $n\alpha$ values with the surfactant concentration indicates the effect of the surfactant molecules on the electrode process. Kuta and Smoler9) have been studied the transfer coefficient of TiO_2^+ and the vanadyl ion with surface-active substances such as polyvinyl alcohol and tribenzyl amine; they concluded that the α on the covered surface is usually less than that on the free surface. In this study, the transfer coefficient increases with an increase in the concentration of the surfactant, and the value for SDS is greater than that for SDBS. The latter fact can be interpreted by the fact that SDS is adsorbed in the micelle-like form at the potential of Orange OT reduction.4) In 5×10^{-2} M SDS, $n\alpha$ is 1.23; this is comparable with the value of $n\alpha=1.22$ in 40% ethanolic solution. The change in the transfer coefficient with the surfactant and its

---

4) K. Eda, *Nippon Kagaku Zasshi*, **80**, 349 (1959).

5) A. M. Mankowich, *Ind. Eng. Chem.*, **47**, 2175 (1955).

6) D. Stigter, R. J. Williams, and K. J. Mysels, *J. Phys. Chem.*, **59**, 330 (1955).

7) H. Schott, *J. Phys. Chem.*, **70**, 2966 (1966).

8) J. N. Phillips and K. J. Mysels, *J. Phys. Chem.*, **59**, 325 (1955).

9) J. Kuta and I. Smoler, *Z. Elektrochem.*, **64**, 285 (1960).

concentration is now under investigation in our laboratory.

The Effect of the Surfactant Adsorption on the Reduction of the Solubilized Dye. The adsorption-desorption waves of the SDBS and SDS molecules show that, at the potential of Orange OT reduction, the anionic surfactant molecules are adsorbed on the electrode. Therefore, an effect from the anionic-charged particles may be expected. The dye is reduced at the potential of the positively-charged DME range; however, the dye gives a diffusion-controlled wave and remains unaffected by the anionic surfactant. These results, and the large α value obtained with a large surfactant concentration, suggest that the electrode reaction proceeds as if there were no effect of charged micelles near the electrode.