BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1469—1472 (1969)

Polarographic Studies of the Solubilization of Disperse-dyes

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(Received June 20, 1968)

The apparent mean particle size of the solubilized dye in nonionic surfactant solutions is determined from the polarographic diffusion coefficient. The diffusion coefficient and the particle size obtained are in good agreement with those of the nonionic surfactant micelle reported in the literature. For the system of polyoxyethylene nonylphenyl ether (NP-$\overline{19}$) and 1,4-diaminoanthraquinone, the particle size increases with the dye concentration; however, the particle size is almost constant for the system of NP-$\overline{19}$ and 1,4,5,8-tetraaminoanthraquinone (TAA). When a certain quantity of TAA is solubilized into the 10^{-3}—10^{-2} M NP-$\overline{19}$ solution, the particle size is also constant. In the case of the polyoxyethylene lauryl ether (LA-$\overline{14}$) and TAA system, the particle size markedly decreases with the increase in the dye concentration. This tendency suggests that the numbers of micelles increase with the concentration of the solubilizate. The fact that the half-wave potential of the dye reduction is independent of the concentration of the surfactants is explained in terms of the similarity between the electrode process of the solubilized dye and that of the dissolved dye.

The solubilization of disperse-dyes has been the subject of many investigations.[1-3] Among the various methods used in the studies of solubilization, the spectroscopic method is most popular.[3-7] Few polarographic measurements have been made of the solubilization because such measurements need a large concentration of supporting electrolyte, and such a concentration has been thought to disturb the system.

To determine the CMC's, the polarographic technique was applied to anionic and nonionic surfactants,[8-10] but the polarographic CMC's sometimes did not agree with those obtained by other methods. The CMC's are found to be greatly affected by added electrolytes[11-13]: this is the reason for the above discrepancy. On the contrary, the size of the micelle is found not to change with the addition of electrolytes.[14]

Craven and Datyner[15] investigated the interaction between some acid wool dyes and nonylphenol-ethyleneoxide derivatives by means of diffusion measurements in which they calculated the apparent mean particle size of the dye-surfactant complex.

In this paper, the apparent mean particle size of the solubilized dye is determined by means of the polarographic diffusion coefficient, and the effects of the addition of nonionic surfactants are investigated. The electrode process of the solubilized-dye particle is also discussed.

Experimental

Materials. 1,4-Diaminoanthraquinone and 1,4,5,8-tetraaminoanthraquinone were used as the disperse-dyes. 1,4-Diaminoanthraquinone was recrystallized from ethyl alcohol, and 1,4,5,8-tetraaminoanthraquinone, from acetone; the melting points were 264°C and 324°C respectively.

Polyoxyethylene nonylphenyl ether (NP-$\overline{10}$,-$\overline{19}$) and polyoxyethylene lauryl ether (LA-$\overline{14}$) were received

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1) K. Shinoda, T. Nakagawa, B. Tamamushi and T. Isemura, "Colloidal Surfactants," Academic Press, New York (1963), p. 139.

2) M. J. Schick Ed., "Nonionic Surfactants," Marcel Dekker, New York (1967), p. 558.

3) B. R. Craven and A. Datyner, *J. Soc. Dyners & Colourists,* **83**, 41 (1967).

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5) K. Nemoto, *ibid.,* **62**, 1286 (1959).

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11) M. J. Schick, S. M. Atlas and F. R. Eirich, *J. Phys. Chem.,* **66**, 1326 (1962).

12) M. J. Schick, *J. Colloid. Sci.,* **17**, 801 (1962).

13) P. Becher, *ibid.,* **17**, 325 (1962).

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through the courtesy of Lion Oil and Fats Co. and the Meisei Chemical Co., and were used without further purification.

Procedure. A solution containing a nonionic surfactant, a 0.1 N acetic acid-sodium acetate buffer solution (pH=4.7), and a dye was irradiated with a 21.6 kHz supersonic wave for 5 min, and then agitated in a water bath at 25±0.1°C for 24 hr. The solution was then stored for a week at the same temperature. The equilibrium of the solution was thus confirmed. The excess dye was removed by filtration through a G4 glass filter. The solid dye remaining on the filter was dissolved with acetone, and its quantity was determined by means of the absorption at 620 mμ.

The polarographic measurements were carried out at 25°C for a filtrate, the dye concentration of which had been corrected. Yokogawa POL-11 and POL-21 polarographs were used, and a saturated calomel electrode was used as a reference electrode. The DME had the following characteristics; $m=1.70$ mg/sec (in pure water at zero applied potential *vs.* SCE) and $t=3.9$ sec (in 10^{-2} M NP-$\overline{19}$ buffer solution at −0.64 V *vs.* SCE). The height of the mercury head was 77.5 cm.

The viscosity of the basic solution was measured with an Ostwald viscometer.

Results and Discussion

Polalographic Measurements. Dye-solubilized aqueous nonionic surfactant solutions all showed a well-defined wave corresponding to the dye reduction (Fig. 1). If the current is diffusion-controlled, the diffusion coefficient of the reductive particle can be obtained from the Ilkovic[16] equation. The relation between the current and the square root of the mercury head is shown in Fig. 2. A linear relationship was obtained in all the cases of nonionic surfactant solutions and a 50% alcoholic solution. The half-wave potentials of the dye-solubilized solutions did not change with either the concentration or the kind of surfactants.

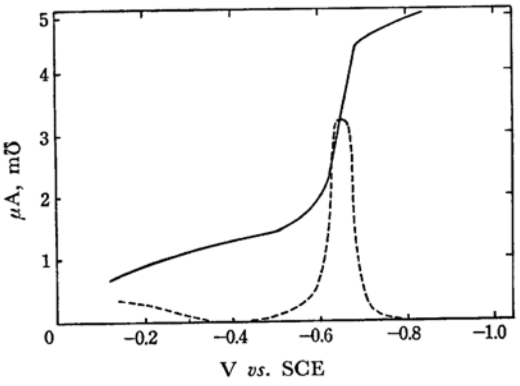

Fig. 1. DC and AC polarograms of the solubilized 1,4,5,8-TAA in NP-$\overline{19}$ solution.

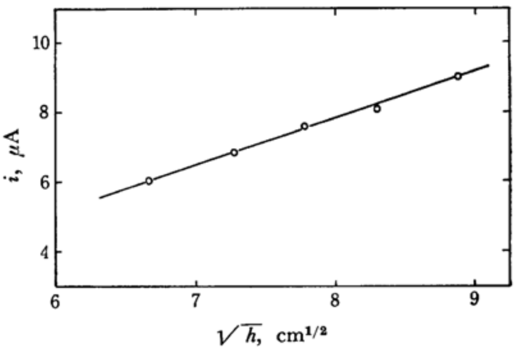

Fig. 2. Dependence of current on mercury height.

From these results, the limiting current is found to be a diffusion current, so the Ilkovic equation is applicable.

The water of hydration in the micelle has not been taken into account.

The diffusion coefficient calculated from the polalographic data is affected by the composition of the solution,[17] the ionic strength, and the species of the solvent. However, the polarographic measurement is a very convenient and simple method when the following assumptions are made: 1) the diffusion current has a linear relationship with the dye concentration; 2) the diffusing particles contain dye molecules only, and 3) the number of electrons transferred is known.

The number of electrons involved in the reduction of the dye is estimated to be 2 on the basis of the following results: 1) the AC polarograms and the cyclic voltammograms indicate a reversible dye reduction process (this makes possible the calculation of "n" from the log-plot of the currents; $n=2$ is obtained), and 2) the anthraquinone derivatives are reduced in a 2-electron step.

Concerning the diffusion coefficients from the polarographic data, an uncertainty of about ±10% usually appears, but the polarographic diffusion coefficients which are calculated in this study are in good agreement with the known values for nonionic surfactant micelles.[18]

Apparent Radii of Dye Particles in the Presence of Different Concentrations of Surfactants. By means of Stockes-Einstein's law for diffusion coefficients that the particles are spherical,[19] the apparent mean radii of dye particles at different concentrations of surfactant solutions are obtained; they are shown in Table 1. When a 0.446×10^{-4} M dye is solubilized into a 10^{-4} M surfactant solution, the particle size observed is 16 Å. This value is very small compared with

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[16] D. Ilkovic, *Collection Czechoslov. Chem. Commun.*, **6**, 498 (1934).

[17] L. Meites, "Polarographic Techniques," 2nd Ed., John Wiley & Sons, New York (1965), p. 144.

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[19] H. Schott, *J. Colloid & Interface Sci.*, **24**, 193 (1967).

TABLE 1. APPARENT MEAN PARTICLE RADII OF 1,4,5,8-TETRAAMINOANTHRAQUINONE IN NP-$\overline{19}$ SOLUTIONS

Surfactant concn. (M)	Dye concn. (10^{-4} M)	Diffusion coefficient (10^{-7} cm^2/sec)	Particle radius (Å)
1×10^{-1}	1.000	2.26	38
5×10^{-2}	1.000	2.41	63
1×10^{-2}	0.922	2.45	85
5×10^{-3}	0.865	2.57	84
1×10^{-3}	0.732	3.04	73
5×10^{-4}	0.619	2.83	79
3×10^{-4}	0.451	4.41	51
1×10^{-4}	0.446	13.6	16
50% Alcoholic solution	0.718	36.5	2.5

that in a 5×10^{-4} M surfactant solution. Since the CMC of NP-$\overline{19}$ is near 10^{-4} M, small, incomplete micelles may be formed at this low surfactant concentration.[20]

As the surfactant/dye ratio increases, the apparent mean radii become constant at about 80 Å in the range of surfactant concentration of 5×10^{-4} M —10^{-2} M. The corresponding diffusion coefficient, about 3×10^{-7} cm^2/sec, is in good agreement with that of the nonionic surfactant micelle.[18]

At a surfactant concentration of 10^{-1} M, the apparent radius decreases to about 40 Å. In this case, the reproducibility of the polarographic data is improved, because of the increase in the homogeniety of the solution. The more homogeneous state than micelle formation can be regarded as the reason.[21]

The radius in a 50% alcoholic solution is 2.5 Å; the value does not change when a 10^{-2} M surfactant was added. This may be compared with the results of Becher,[22] who found that in polyoxyethylene lauryl ether solutions micelle formation does not occur when the concentration of ethanol reaches approximately 30%.

TABLE 2. APPARENT MEAN PARTICLE RADII OF 1,4,5,8-TAA in 10^{-2} M NP-$\overline{19}$ SOLUTION

Dye concn. (mM)	Diffusion coefficient (10^{-7} cm^2/sec)	Particle radius (Å)
0.47	3.56	60
0.92	2.45	85
1.59	3.14	67
1.91	3.22	65
3.22	3.10	69

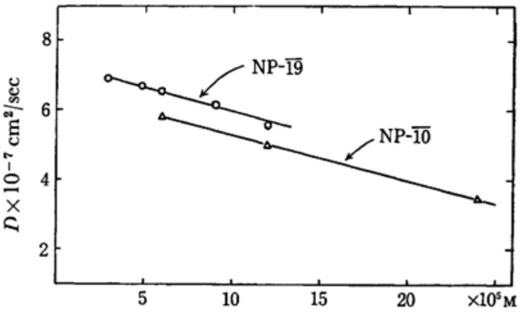

Fig. 3. Dependence of diffusion coefficient on dye concentration (1,4-DAA).

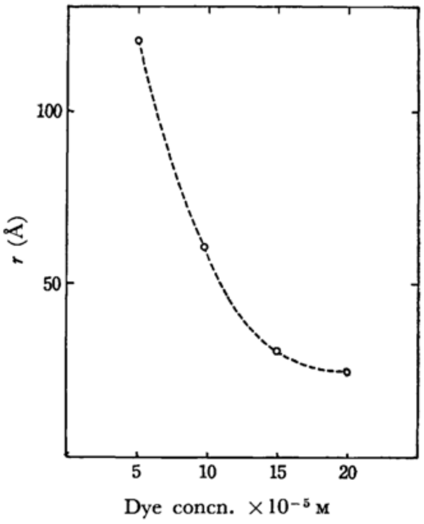

Fig. 4. Dependence of apparent mean particle radii on dye concentration (1,4,5,8-TAA in LA-$\overline{14}$ solution).

Effect of Dye Concentration on the Apparent Radii. The apparent mean radii of the particle at various dye concentrations are given in Table 2, Fig. 3, and Fig. 4. With the system of 1,4-diaminoanthraquinone and 10^{-1} M NP-$\overline{19}$, the radius of the particle increases with the dye concentration (Fig. 3). On the other hand, in the case of 1,4,5,8-tetraaminoanthraquinone solubilized in a 10^{-2} M NP-$\overline{19}$ solution, the dye particle size seems to be independent of the dye concentration. In the above NP-$\overline{19}$ systems, the diffusion coefficients are also of the same degree as those of nonionic surfactant micelles. From the polarographic diffusion coefficient, the aggregation number of NP-$\overline{19}$ can be estimated to be about 50. The above result is acceptable in comparison with the reported value of 62 for NP-$\overline{20}$.[12]

The radius of the dye particle solubilized into a polyoxyethylene lauryl ether surfactant solution markedly decreases with the dye concentration

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[21] S. Kuroiwa, *Yukagaku (J. Japan Oil Chem. Soc.)*, **17**, 125 (1968).

[22] P. Becher, *J. Colloid. Sci.*, **20**, 728 (1965).

(Fig. 4). The aggregation number of LA-$\overline{14}$ may be about 125; a large micelle ($r = ca.$ 40 Å) may be expected from this value. In this case, the radius of the particle falls from 60 Å to 25 Å when the 2.0×10^{-4} M dye is solubilized. This effect of the solubilizate concentration on the particle size appears to be due to the influence of the linear alkyl chain of the surfactant. The above tendency is similar to that found by Craven and Datyer,[7] but it is not ascribed to complex formation because of the constancy of the half-wave potentials. The mechanism of this phenomenone has not yet been explained.

Electrode Process of the Solubilized Dye. The fact that the half-wave potential of the dye reduction does not change when the dye is solubilized in a micellar solution indicates the similarity between the electrode process of the solubilized dye and that of the dissolved dye. It is clear that the diffusing particle is the micelle with the dye; this causes the diffusion current. The complex formation between dye and surfactant is inconceivable in this case; if it occurred, the half-wave potential might change with the concentration of the surfactant.

The rates of electron transfer are estimated by the method of Kambara-Ishii.[23] The rate constant of the solubilized dye is about 2×10^{-3} cm/sec; on the other hand, the dye dissolved into a 50% ethanolic aqueous solution has value of about 2×10^{-2} cm/sec. This difference may be attributed to the influence of the walls of the micelles near the electrode.

The authors wish to express their gratitude to Mr. O. Murakami for measuring the polarograms and to Professor S. Kuroiwa for his helpful discussions.

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