

BY TOYOKO IMAE, CHISAKO MORI AND SHOICHI IKEDA\*

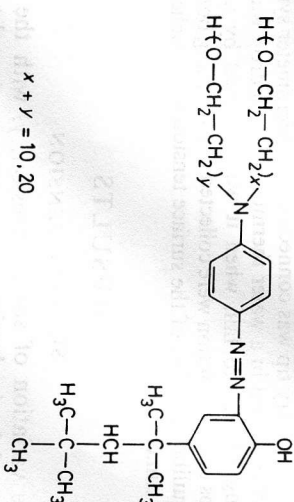
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa,  
Nagoya 464, Japan

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The surface tension of aqueous methanol solutions of a surface-active dye, *p*-1-octylphenol yellow amine poly(ethylene oxide), has been measured by means of the drop weight method. At a given methanol content,  $< 20\%$ , the surface tension of methanol + water solutions of the dye exhibits two break points when plotted against the logarithm of the dye concentration, which indicates a two-step micellisation of the dye molecules. The adsorption of the dye on aqueous surfaces is cooperative and multimolecular. An analysis of the surface tension data leads to the following results: the primary micelles are formed when the concentration is higher than  $ca. 10^{-5}$  mol dm $^{-3}$ , and their aggregation number, at most, 15, suggesting that the micellar structure there consists of a stack of molecules; the secondary micelles are formed when the concentration exceeds  $ca. 10^{-4}$  mol dm $^{-3}$ , and their formation is induced by the hydrophobic mechanism, as for the common surfactant. In methanol + 0.1 mol dm $^{-3}$  HCl solutions the dye is protonated and is adsorbed monomolecularly on aqueous surfaces; the micellisation occurs as for the common surfactant.

Most dyes associate into reversible aggregates in aqueous solutions,<sup>1-6</sup> with a structure composed of a stack of planar dye molecules. On the other hand, surfactants in aqueous solutions associate into micelles above a certain critical micelle concentration (c.m.c.).<sup>7</sup> We anticipate that a combination of an amphiphilic structure with a conjugated  $\pi$ -electron system in a single molecule will develop a new feature of micellisation.

*p*-t-Octylphenol yellow amine poly(ethylene oxide), whose chemical formula is given by



is a non-ionic surface-active dye, consisting of a hydrophilic part and a hydrophobic part linked by an azobenzene group. The surface activity and micelle formation of this dye can be observed in the behaviour of the surface tension of its aqueous solutions.

In this paper we describe the results of surface tension measurements and discuss the adsorption of the surface-active dye on aqueous surfaces and its micellisation in solutions. Since the dye is sparingly soluble in water, aqueous methanol solutions of

low methanol content are used as solvent. To examine the effect of protonation of the dye on the adsorption and micellisation, we also measure the surface tension of acid solutions of the dye, for which the solvents are mixtures of methanol and 0.1 mol dm<sup>-3</sup> HCl.

## EXPERIMENTAL

### MATERIALS

Two samples of *p*-t-octylphenol yellow amine poly(ethylene oxide) with different degrees of polymerisation of the polyethylene oxide parts were kindly donated by Dr F. Tokiwa of the Kao Soap Co. Ltd. The hydrophobic part of the dye, which is called *p*-t-octylphenol yellow amine, was prepared by reacting an aqueous solution of *p*-nitrophenyldiazonium chloride with an alkaline ethanol solution of *p*-t-octylphenol followed by reaction of the product with an alkaline ethanol solution of Na<sub>2</sub>S.

Both dyes were dark red oils and were used without further purification. The average degree of polymerisation of the polyoxyethylene parts,  $x + y$ , of the given dye samples was 10 and 20, respectively.

Methanol was a spectrograde reagent from Nakarai Chemical Co. Ltd and water was redistilled from alkaline KMnO<sub>4</sub> in a glass still.

### METHODS

A stock solution of the surface-active dye was prepared by dissolving the dye in methanol and then adding water to the solution until the desired methanol content was obtained. The composition of the solvent is expressed as the volume fraction or molar concentration of methanol. The methanol + water solution of the dye was prepared by diluting the stock solution with the solvent mixture. The methanol + 0.1 mol dm<sup>-3</sup> HCl solution of the dye was prepared in the same way using 0.1 mol dm<sup>-3</sup> HCl in place of water.

The surface tension,  $\gamma$  (mN m<sup>-1</sup>), of a solution was measured by the drop weight method and was calculated from the weight,  $w$ , of a drop falling from a capillary tip having an outer radius,  $r$ , by the Harkins-Brown equation

$$\gamma = (w g / r) F \quad (1)$$

where  $g$  is the gravitational acceleration and  $F$  is the correction factor having an argument  $V/r^3$ , in which  $V$  is the volume of a drop. Two capillary tips were used and their effective radii,  $r$ , were determined to be 0.3504 and 0.3384 cm, respectively, referring to the surface tension of water. The temperature was kept at  $25 \pm 0.01^\circ\text{C}$ .

The upper end of the capillary tip was connected to a micrometer syringe and its lower end was kept in a glass bottle dipped in a water thermostat. Each drop was suspended on the tip for 5 min before being allowed to fall, when it was detached by a final screwing of the micrometer. Five drops of each solution were collected in a weighing bottle for weighing. It was confirmed that the equilibrium value of the surface tension was reached within 3 min even in the range around the c.m.c.

## RESULTS

### SURFACE TENSION

Fig. 1 shows the variation of surface tension,  $\gamma$ , with the logarithm of molar concentration,  $\log C$ , of the dye having  $x + y = 10$  in methanol + water solution. With increasing concentration of the dye, the surface tension changes in roughly four steps. At low concentrations it is almost constant and remains essentially equal to the value for the methanol + water mixture. Above  $ca. 9 \times 10^{-6}$  mol dm<sup>-3</sup> it decreases sharply and almost linearly until it reaches a break point. Beyond this break it decreases less sharply but almost linearly and reaches a second break, above which the surface tension remains constant and is almost independent of methanol content.

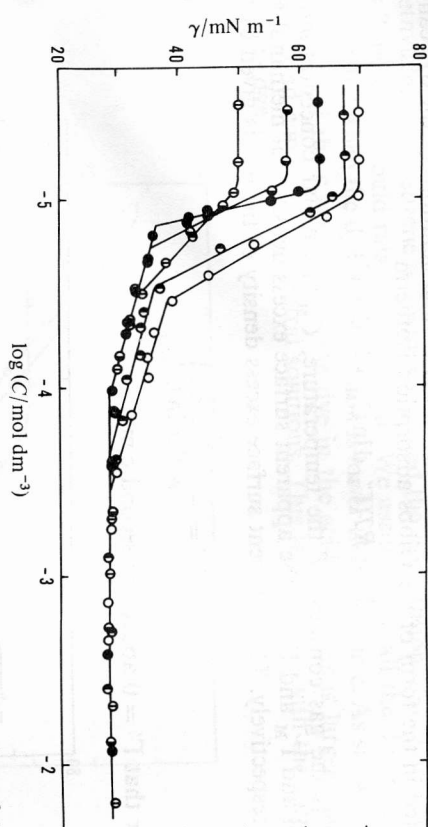


Fig. 1.—Plot of surface tension against the logarithm of the molar concentration of the dye for methanol + water solutions of the dye having  $x + y = 10$ . Methanol content (volume %):  $\circ$ , 1;  $\bullet$ , 2;  $\bullet$ , 5;  $\circ$ , 10;  $\circ$ , 20.

TABLE 1.—SURFACE ADSORPTION AND MICELLISATION OF THE DYE HAVING  $x + y = 10$  IN METHANOL + WATER SOLUTIONS

methanol content (vol. %)	$C_0^I$ / $10^{-5}$ mol dm <sup>-3</sup>	$C_0^{II}$ / $10^{-5}$ mol dm <sup>-3</sup>	$\Gamma_D^I$ / $10^{-10}$ mol cm <sup>-2</sup>	$\Gamma_D^{II}$ / $10^{-10}$ mol cm <sup>-2</sup>	$m$	$A_0/\text{\AA}^2$ molecule <sup>-1</sup>	$\gamma_c$ / mN m <sup>-1</sup>
1	3.50	36.3	9.8	1.71	5.8	17.0	28.0
2	2.91	23.4	11.4	1.54	7.4	14.6	27.8
5	1.38	10.0	25.2	1.67	15.1	6.59	28.2
10	1.83	9.8	11.3	1.54	7.3	14.9	28.2
20	3.20	10.3	5.3	1.55	3.4	31.3	28.5

$$a \text{ } 1 \text{ \AA} \equiv 10^{-10} \text{ m} = 10^{-1} \text{ nm.}$$

In the region where the surface tension decreases with increasing concentration, the dye is adsorbed on aqueous surfaces, and at the two break points the first and second micellisations occur. The primary micelles are formed beyond the first break and the secondary micelles are formed above the second break, beyond which a constant surface tension is exhibited. The values of the first and second c.m.c.,  $C_0^I$  and  $C_0^{II}$ , are listed in table 1, together with the value of the constant surface tension,  $\gamma_c$ . Note that the rate of lowering of surface tension is largest for a methanol content of 5%. Addition of methanol to aqueous solutions of the dye generally reduces the surface tension, but in the presence of  $(1-2) \times 10^{-5}$  mol dm<sup>-3</sup> of the dye the surface tension is lowest at a methanol content of 5%.

The surface tension curves of methanol + water solutions of the dye having  $x + y = 20$  are similar to those of the dye having  $x + y = 10$  above, as shown in fig. 2. The values of the two c.m.c.,  $C_0^I$  and  $C_0^{II}$ , are listed in table 2. The rate of lowering of the surface tension with an increase in dye concentration is lowest at a methanol content of 2%.

The change in surface tension of the methanol + water solutions of the dye can be represented in the form of the Gibbs adsorption isotherm

$$-d\gamma = RT(\Gamma'_M \ln C_M + \Gamma' \ln C) \quad (2)$$

where  $R$  is the gas constant,  $T$  the temperature,  $C_M$  the molar concentration of methanol and  $\Gamma'_M$  and  $\Gamma'$  are the apparent surface excess densities of methanol and the dye, respectively. The apparent surface excess density of the dye is given by

$$\Gamma' = -\frac{1}{RT} \left( \frac{\partial \gamma}{\partial \ln C} \right)_{C_M} \quad (3)$$

It is clear that  $\Gamma' = 0$  above the second c.m.c.

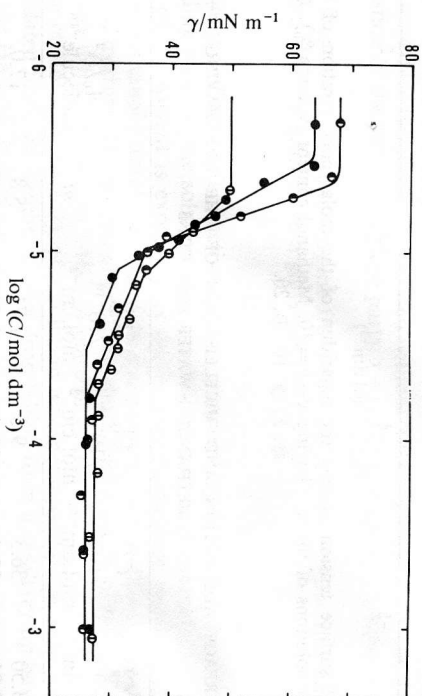


Fig. 2.—Plot of surface tension against the logarithm of the molar concentration of the dye for the methanol + water solutions of the dye having  $x+y=20$ . Methanol content (volume %): ○, 2; ●, 5; ○, 20.

TABLE 2.—SURFACE ADSORPTION AND MICELLISATION OF THE DYE HAVING  $x+y=20$  IN METHANOL + WATER SOLUTIONS

methanol content (vol. %)	$C_0^I$ / $10^{-5}$ mol dm $^{-3}$	$C_0^{II}$ / $10^{-5}$ mol dm $^{-3}$	$\Gamma_D^I$ / $10^{-10}$ mol cm $^{-2}$	$\Gamma_D^{II}$ / $10^{-10}$ mol cm $^{-2}$	$m$	$A_0/\text{\AA}^2$ molecule $^{-1}$	$\gamma_c$ /mN m $^{-1}$
2	0.95	6.18	14.3	2.44	5.9	11.7	25.9
5	1.23	3.27	9.6	2.21	4.3	17.3	26.4
20	1.33	6.17	5.4	2.12	2.5	31.0	27.6

Fig. 3 shows the surface tension of methanol + 0.1 mol dm $^{-3}$  HCl solutions of the dye as a function of molar concentration of the dye having  $x+y=20$ . In this case the surface tension curve has a single break point corresponding to the c.m.c. The rate of lowering of surface tension is larger in 2 and 5% methanol solutions than in the 20% methanol solution. This behaviour is also similar to that observed without HCl.

In the methanol + 0.1 mol dm $^{-3}$  HCl solutions the surface-active dye should be

protonated at the azo or amino group, since the  $pK$  value of 4-dimethylaminoazobenzene is 3.5 in water<sup>8</sup> and the substitution of a hydroxyl group at its 2-position would raise the  $pK$  value. We assume that all the dye molecules are protonated when the dye concentration is lower than the c.m.c. As shown in table 3, the value of the c.m.c.,  $C_0^I$ , of the dye in the acid solutions is larger than that of the second c.m.c. in the neutral solutions. This is in accord with the formation of charged dye.

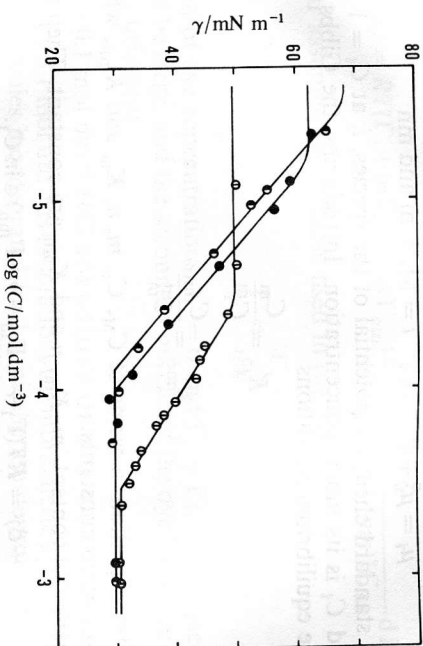


Fig. 3.—Plot of surface tension against the logarithm of the molar concentration of the dye for the methanol + 0.1 mol dm $^{-3}$  HCl solutions of the dye having  $x+y=20$ . Methanol content (volume %): ○, 2; ●, 5; ○, 20.

TABLE 3.—SURFACE ADSORPTION AND MICELLISATION OF THE DYE HAVING  $x+y=20$  IN METHANOL + 0.1 mol dm $^{-3}$  HCl SOLUTIONS

methanol content (vol. %)	$C_0^I$ / $10^{-5}$ mol dm $^{-3}$	$\Gamma_{DHCl}^I$ / $10^{-10}$ mol cm $^{-2}$	$A_0/\text{\AA}^2$ molecule $^{-1}$	$\gamma_c$ /mN m $^{-1}$
2	8.02	4.80	34.6	29.7
5	10.6	4.72	35.2	29.5
20	34.5	3.39	49.0	30.5

Since we are not concerned with the change in HCl concentration but fix it at 0.1 mol dm $^{-3}$  HCl in water, we can relate the change in surface tension in terms of eqn (2) and (3). Again it is clear that  $\Gamma' = 0$  above the c.m.c.

#### THE GIBBS ADSORPTION ISOTHERM

METHANOL + WATER SOLUTIONS OF THE DYE

The Gibbs adsorption isotherm for the methanol + water solutions of the dye is examined in a general way. The species present in the solutions are water (W), methanol (M), and monomer (1), primary micelle (m) and secondary micelle (mn) of the dye. Then the Gibbs equation is written

$$-d\gamma = \Gamma_W d\mu_W + \Gamma_M d\mu_M + \Gamma_1 d\mu_1 + \Gamma_m d\mu_m + \Gamma_{mn} d\mu_{mn} \quad (4)$$



where  $\Gamma_i$  and  $\mu_i$  are adsorption density and chemical potential of the species,  $i$ , respectively. Two-step micellisation equilibria



hold for the dye,  $D$ . We assume ideal solutions, so that chemical potentials of solute species are expressed by

$$\mu_i = \mu_i^0 + RT \ln C_i \quad i = M, 1, m \text{ and } mn \quad (7)$$

where  $\mu_i^0$  is the standard chemical potential of the species,  $i$ , at  $C_i = 1 \text{ mol dm}^{-3}$  in pure water, and  $C_i$  is its molar concentration. Introducing the Gibbs convention,  $\Gamma_w = 0$ , and the equilibrium conditions

$$K_m = \frac{C_m}{C_1^m} \quad (5')$$

$$K_{mn} = \frac{C_{mn}}{C_1^n} \quad (6')$$

we have the Gibbs equation in terms of  $C_w$ ,  $C_1$ ,  $m$ ,  $n$ ,  $K_m$  and  $K_{mn}$ , where  $K_m$  and  $K_{mn}$  are the association constants.

At a given methanol content,  $m$ ,  $K_m$ ,  $n$  and  $K_{mn}$  are constant. Then we have

$$-d\gamma = RT(\Gamma_1 + m\Gamma_m + mn\Gamma_{mn}) d \ln C_1. \quad (8)$$

Here the total dye concentration is given by

$$C = C_1 + mC_m + mnC_{mn}. \quad (9)$$

We apply eqn (8) separately for the three regions divided by the two c.m.c.

$$(i) \quad C \leq C_1^I: \quad C_1 = C \quad \text{and} \quad \Gamma_m = \Gamma_{mn} = 0.$$

$$\text{Eqn (8) reduces to} \quad -d\gamma = RT\Gamma_1 d \ln C. \quad (10)$$

Comparison of eqn (10) with eqn (2) gives

$$\Gamma' = \Gamma_1. \quad (11)$$

Then the saturated adsorption density of the dye,  $\Gamma_b^I$ , is given by the apparent surface excess density of the dye at the first c.m.c. and just below it. The values of  $\Gamma_b^I$  are given in tables 1 and 2. The forms of the surface tension curve, *i.e.* the constancy of surface tension and its steep decrease above  $9 \times 10^{-6} \text{ mol dm}^{-3}$ , indicate abrupt or cooperative adsorption of the dye on the aqueous surface above (approximately) this concentration.

$$(ii) \quad C_1^I < C \leq C_1^{II}: \quad C_1 + mC_m = C \quad \text{and} \quad \Gamma_{mn} = 0.$$

$$\text{Eqn (8) leads to} \quad -d\gamma = RT(\Gamma_1 + m\Gamma_m) \frac{C}{C_1 + m^2C_m} d \ln C. \quad (12)$$

When  $mC_m \gg C_1$  we have

$$\Gamma' = \frac{\Gamma_1 + m\Gamma_m}{m}. \quad (13)$$

If the primary micelle is not adsorbed on an aqueous surface, because of its more hydrophilic nature, we may set

$$\Gamma' = \frac{\Gamma_1}{m}. \quad (14)$$

The constant slope of the surface tension curves in this region gives the adsorption density,  $\Gamma_b^{II}$ , as given in tables 1 and 2. In eqn (14)  $\Gamma' = \Gamma_b^{II}$  and  $\Gamma_1$  is equal to  $\Gamma_b^I$ . Then we can obtain the aggregation number of the primary micelle by using eqn (14). These values are listed in tables 1 and 2. The aggregation number of the primary micelle of the dye is rather small, as compared with that of the surfactant micelle.

$$(iii) \quad C > C_1^{II}: \quad C_1 + mC_m + mnC_{mn} = C.$$

Eqn (8) gives

$$-d\gamma = RT(\Gamma_1 + m\Gamma_m + mn\Gamma_{mn}) \frac{C}{C_1 + m^2C_m + (mn)^2C_{mn}} d \ln C. \quad (15)$$

Using similar assumptions to those used in (ii), we have

$$\Gamma' = \frac{\Gamma_1}{mn}. \quad (16)$$

In this region of dye concentrations,  $\Gamma' = 0$  and  $\Gamma_1 = \Gamma_b^I$ . Consequently, the values of  $mn$  should be large, and the secondary micelle of the dye has a size as large as that of the usual surfactant.

#### METHANOL + 0.1 mol dm<sup>-3</sup> HCl SOLUTIONS OF THE DYE

In methanol + 0.1 mol dm<sup>-3</sup> HCl solutions the monomeric dye is completely ionized, but the dye molecules incorporated in the micelle are deprotonated and non-ionic, as the absorption spectra show.<sup>9</sup> Then the Gibbs equation is written in terms of neutral species as

$$-d\gamma = \Gamma_w d\mu_w + \Gamma_M d\mu_M + \Gamma_{HCl} d\mu_{HCl} + \Gamma_1 d\mu_1 + \Gamma_p d\mu_p \quad (17)$$

where the suffixes, 1 and  $p$ , represent the protonated monomer (DHCl) and the non-ionic micelle ( $D_p$ ) having aggregation number  $p$ . The micellisation equilibrium is expressed by

$$p \text{ DHCl} \rightleftharpoons D_p + p \text{ HCl}. \quad (18)$$

We assume that the solution is ideal so that eqn (7) holds for  $i = M$  and  $p$ , and the chemical potentials of HCl and 1 are given by

$$\mu_{HCl} = \mu_{HCl}^0 + RT \ln (C_A - C_1) C_A \quad (19a)$$

$$\mu_1 = \mu_1^0 + RT \ln C_1 C_A \quad (19b)$$

where  $\mu_{HCl}^0$  and  $\mu_1^0$  are the standard chemical potentials of pure HCl and pure protonated monomer at  $C_A = 1 \text{ mol dm}^{-3}$  and  $C_1 = 1 \text{ mol dm}^{-3}$ , respectively, and  $C_A$  is the molar concentration of added HCl. Then the equilibrium condition is given by

$$K_p = \frac{C_p(C_A - C_1)^p}{C_1^p} \quad (18')$$

where  $K_p$  is the equilibrium constant.

At a given methanol content and the fixed HCl concentration,  $p$  and  $K_p$  are constant. Then we have

$$-d\gamma = RT \left( -\Gamma_{HCl} \frac{C_1}{C_A - C_1} + \Gamma_1 + p\Gamma_p \frac{C_A}{C_A - C_1} \right) d \ln C_1. \quad (20)$$

Here the Gibbs convention,  $\Gamma_w = 0$ , has been introduced and also we have

$$C = C_1 + pC_p. \quad (21)$$

In the present work we may set  $C_A \gg C_1$ .

$$(i) \quad C \leq C_0 : C_1 = C \quad \text{and} \quad \Gamma_p = 0.$$

$$\text{Eqn (20) reduces to} \quad -d\gamma = RT\Gamma_1 d \ln C. \quad (22)$$

Comparison of eqn (22) with eqn (2) leads to

$$\Gamma' = \Gamma_1. \quad (23)$$

The saturated adsorption density of the protonated dye,  $\Gamma_{\text{DHC1}}^0$ , is given by the apparent surface excess density of the dye at the c.m.c. and just below it. The values of  $\Gamma_{\text{DHC1}}^0$  are given in table 3.

$$(ii) \quad C > C_0 : C_1 + pC_p = C.$$

$$\text{When } pC_p \gg C_1, \text{ we have} \quad \Gamma' = \frac{\Gamma_1 + p\Gamma_p}{p}. \quad (24)$$

If the micelle is not absorbed on an aqueous surface, we may set

$$\Gamma' = \frac{\Gamma_1}{p}. \quad (25)$$

As seen in fig. 3,  $\Gamma' = 0$  and  $\Gamma_1$  is equal to  $\Gamma_{\text{DHC1}}^0$ . Consequently, the aggregation number of the micelle,  $p$ , of the dye is very large, as in the case of the usual surfactant.

## DISCUSSION

### ADSORPTION DENSITY AND MOLECULAR AREA OF THE DYE

The behaviour of the surface tension of methanol + water solutions of the dye is unique, showing two-step micellisation. As can be seen in tables 1 and 2, however, the adsorption density,  $\Gamma_b^1$ , of the dye, ca.  $10^{-9}$  mol cm $^{-2}$ , is several times larger than that of the usual surfactant.<sup>10-12</sup> The molecular area,  $A_0 = 1/\Gamma_b^1$ , of the dye, where  $N$  is Avogadro's number, ca.  $15 \text{ \AA}^2$  or less, is also correspondingly small when compared with the values obtained for polyoxyethylene alkylphenyl ether on aqueous surfaces.<sup>10, 13</sup> The surface pressure-area curves of insoluble monolayers of several 1,3-diglycerides consisting of an azo group and a long-chain fatty acid group gave limiting molecular areas of ca.  $40 \text{ \AA}^2$ .<sup>14</sup>

Note also that the observed molecular area of the dye depends on the methanol content of the solvent. This observation together with the small molecular area imply that the dye is adsorbed multimolecularly on surfaces of methanol + water solutions.

In methanol + 0.1 mol dm $^{-3}$  HCl solutions the surface tension behaves as for aqueous solutions of the usual surfactant. The adsorption density,  $\Gamma_{\text{DHC1}}^0$ , is equal to ca.  $(4.0 \pm 0.8) \times 10^{-10}$  mol cm $^{-2}$ , and is close to the values for various ionic surfactants.<sup>12, 15</sup> The corresponding molecular area,  $A_0 = 1/\Gamma_{\text{DHC1}}^0$ , equal to  $40 \text{ \AA}^2$ , indicates that the protonated dye is adsorbed monomolecularly on aqueous surfaces.

### CRITICAL MICELLE CONCENTRATION

The first c.m.c. of the dye in methanol + water solutions occurs at ca.  $10^{-5}$  mol dm $^{-3}$  and is lower than the c.m.c. of the usual non-ionic surfactants by approximately an order of magnitude.<sup>10, 11, 13</sup> The primary micelle of the dye in methanol + water solutions consists of, at most, 15 dye molecules. The formation of such a small micelle would not be caused merely by the hydrophobic effect, and the structure of the primary

micelle would consist of a stack of dye molecules, as proposed for some other dye micelles.<sup>2, 5, 6</sup>

The second c.m.c. of the dye in methanol + water solutions has values comparable with the c.m.c. of polyoxyethylene derivatives having dodecyl,<sup>16-18</sup> octylphenyl or nonylphenyl<sup>10, 13, 19</sup> groups. The secondary micelle has an aggregation number sufficiently high to protect the hydrophobic part of the dye molecules from water.

Similarly, the micelles of the dye in methanol + 0.1 mol dm $^{-3}$  HCl solutions would have a structure similar to those of the usual surfactants.

Note that in methanol + water solutions the c.m.c. of the more hydrophilic dye having  $x + y = 20$  are lower than those of the homologue having  $x + y = 10$ . Such an apparently opposing phenomenon has been observed with some polyoxyethylene derivatives of *n*-octadecanol.<sup>13, 20</sup> Consequently, this seems to be characteristic of polyoxyethylene derivatives having a strongly hydrophobic group.

### THE EFFECT OF ADDED ALCOHOL

It is known<sup>21-23</sup> that the addition of a small amount of short-chain alcohol to aqueous surfactant solutions lowers the c.m.c., but further addition of alcohol increases the c.m.c. Consequently, the minimum c.m.c. is observed at a certain content of added alcohol. The present observation of the effect of added methanol on the second c.m.c. in methanol + water solutions is in agreement with values previously found. However, in methanol + 0.1 mol dm $^{-3}$  HCl solutions the effect of added methanol is to raise the c.m.c., and this would be caused by the effect of deprotonation of the dye upon micellisation.

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