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THE ANOMALOUS BEHAVIOR OF SURFACE TENSION OF AQUEOUS SOLUTIONS OF DIMETHYLOLEYLAMINE OXIDE, AND ITS MULTIMOLECULAR ADSORPTION ON AQUEOUS SURFACES

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ABSTRACT

Surface tension of aqueous solutions of dimethyloleylamine oxide in the absence of HCl and in the presence of 10^{-4}, 10^{-3} and 10^{-2} *M* HCl has been measured by the drop weight method over the surfactant concentration range 0—10^{-3} *M*. The surface tension drops suddenly above 10^{-5} *M* and becomes constant above 10^{-4} *M*, in most cases. It does not show any sign of electrolyte adsorption on aqueous surfaces, but it has a similar dependence on surfactant concentration, irrespective of the addition of HCl.

The application of the Gibbs adsorption isotherm, together with the assumption of solution ideality, leads to the surface excess density of total surfactant, suggesting the formation of multimolecular layers. On water and 10^{-4} *M* HCl, the adsorbed surfactants form quadrimolecular layers but, on 10^{-3} and 10^{-2} *M* HCl, bimolecular layers are formed. In the presence of HCl, especially to 10^{-4} *M*, the surface excess density of the surfactant has a maximum at a certain surfactant concentration. The occurrence of a maximum in the adsorption may be explained qualitatively by assuming that only the concentration of monomeric surfactant is directly related to the adsorption and that partially ionized micelles are formed.

INTRODUCTION

Amine oxide is a weak base with a p*K* value around 5, so that it is nonionic at neutral and alkaline pH, and cationic at acid pH. Owing to its strongly hydrophilic nature, a long-chain alkylamine oxide is soluble in water even in a nonionic form [1—9].

We have examined the surface tension of aqueous solutions of dimethyldodecylamine oxide at different degrees of neutralization and determined surface excess densities of solute species by means of an analysis of the Gibbs adsorption isotherm [7]. These results demonstrated that all the adsorption isotherms follow the Langmuir type, giving saturated adsorption at high concentrations and conforming with the formation of a monomolecular layer of dimethyldodecylamine oxide, either nonionic or cationic, on aqueous surfaces.

In the present work, we measure the surface tension of aqueous solutions of dimethyloleylamine oxide in the presence of different concentrations of HCl and determine the surface excess densities of solute species by means of the Gibbs adsorption isotherm. In general, we choose the condition of constant concentration of total added HCl rather than constant degree of neutralization, because we have to work at surfactant concentrations of $<10^{-4}$ M, owing to the low CMC (critical micelle concentration). A constant degree of neutralization alters the degree of protonation of amine oxide considerably with a change of its concentration.

EXPERIMENTAL

The sample of dimethyloleylamine oxide was kindly provided by Dr Fumio Hoshino as an aqueous solution of 9.00 g per 100 g of solution. The solution was jellylike and viscoelastic. The concentration of the solution was determined and confirmed by dehydrating an aliquot over P_2O_5 in a vacuum desiccator at room temperature until it gave a constant dry weight. The solution was reduced in weight to 9.00% after 1 month.

The surface tension of aqueous solutions was determined by the drop weight method at 25 ± 0.01°C. If a drop of a solution is suspended at the top of a capillary tip having outer radius r, and the fallen drop has a weight w, then the surface tension of the solution is given by

$$\gamma = \frac{wg}{r} F \qquad (1)$$

where F is the Harkins—Brown correction factor (determined by the drop volume and the effective radius of capillary tip, r) and g is the acceleration due to gravity. The effective radius of the tip was determined by distilled water, assuming its surface tension to be 71.96 dyn cm^{-1} at 25°C. Each drop of solution was suspended for 5 min after being formed, when equilibrium was attained, and 10 drops were collected in a weighing bottle placed under the tip. The error of the drop weight was <1%.

The pH of the solution was determined with an Hitachi—Horiba pH-meter Model F-7_{SS} at room temperature (25 ± 2°C).

RESULTS

Dilute solutions of the surfactant in water had pH values ~ 6 and, in the presence of 10^{-4} M HCl, its aqueous solutions had pH values of ~4.25, when the surfactant concentration is $<10^{-4}$ M. In 10^{-3} M HCl the surfactant is almost fully protonated in the concentration region studied and, in 10^{-2} M HCl, most of the added HCl is in excess over the amount necessary for protonating the surfactant at concentrations of $<10^{-3}$ M. For solutions having HCl and surfactant in equimolar concentration, the pH shifted to lower values with increasing surfactant concentration.

Figure 1 shows the results of surface tension measurements. The surface tension of solutions at constant HCl concentration is plotted against the logarithm of surfactant concentration. Without added HCl, the surface tension of the solution at very low concentrations is almost equal to that of water, and then it suddenly decreases with increasing concentration beyond $\sim 10^{-5}$ *M* and reaches a breakpoint at 4.03×10^{-5} *M*. The breakpoint may tentatively be assigned as the CMC. Above the CMC, the surface tension of the solution remains constant and has a value as low as 27.3 dyn cm^{-1}.

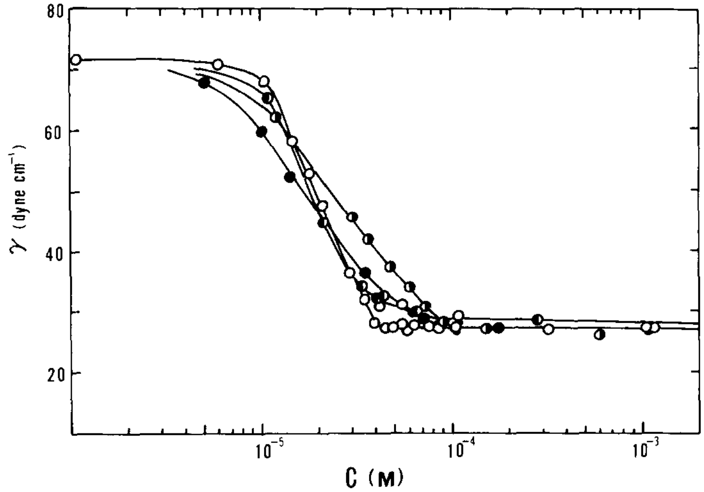

Fig. 1. Surface tension of aqueous solutions of dimethyloleylamine oxide in the absence and in the presence of HCl. (○), water; (◐), 10^{-4} *M* HCl; (◑), 10^{-3} *M* HCl; (●), 10^{-2} *M* HCl.

In the presence of 10^{-4} *M* HCl, the surface tension of solutions has values almost equal to that in water, with a surfactant concentration of $\leqslant 10^{-5}$ *M*. Above 3×10^{-5} *M*, the rate of decrease of surface tension with increasing concentration is more gradual compared with that in water, and even above 10^{-4} *M* the surface tension tends to approach the constant value, 27.3 dyn cm^{-1}, which is identical to the value in water above the CMC. This behavior is quite different from that of common surfactants, and the specification of the CMC by surface tension measurements is not possible, since there is no clear breakpoint.

Even in the presence of 10^{-3} and 10^{-2} *M* HCl, the surface tension of aqueous solutions does not show any electrostatic effect and remains only slightly lowered below 10^{-5} *M*. Above 2×10^{-5} *M*, its rate of decrease is less sharp compared with that in water, and the surface tension reaches a constant value, 27.3 dyn cm^{-1}, above certain breakpoints, which may be assigned to the CMC.

The values of the CMC, $C_{0,\gamma}$, derived from the breakpoints of the surface tension curves, are listed in Table 1. It is also remarkable that the CMC is located around 10^{-4} M or lower, and is of the same order of magnitude as that of common nonionic surfactants, even in the presence of added HCl. Previously, we have measured the surface tension of aqueous solutions of dimethyldodecylamine oxide and determined its CMC values [7]. According to these results, the surface tension increases and the CMC rises by adding HCl or by lowering pH, indicating explicitly the electrostatic effect of protonation of the surfactant. Accordingly, the surface tension and the CMC of dimethyloleylamine oxide behave differently from those of dimethyldodecylamine oxide.

TABLE 1

Adsorption properties of dimethyloleylamine oxide on aqueous surfaces

C_A (M)	$C_{0,\gamma}$ (10^{-5} M)	$C_{0,\Gamma_{max}}$ (10^{-5} M)	γ_C (dyn cm^{-1})	$(\Gamma_{DH^+} + \Gamma_D)_{max}$ (10^{-10} mol cm^{-2})	A_0 (Å^2 molecule^{-1})	pH at $C_{0,\gamma}$
0	4.03	1.20	27.3	12.2	13.7	6.1
10^{-4}	—	2.00	—	12.1	13.7	4.3
10^{-3}	8.91	1.20	27.3	6.82	24.4	3.1
10^{-2}	6.75	1.20	27.3	7.42	22.4	2.1

ANALYSIS

The Gibbs adsorption isotherm

If the surface excess density and chemical potential of species, i, are expressed by Γ_i and μ_i, the Gibbs adsorption isotherm for aqueous HCl solutions of dimethyloleylamine oxide is given by

$$-d\gamma = \Gamma_{H_2O}d\mu_{H_2O} + \Gamma_D d\mu_D + \Gamma_{H^+}d\mu_{H^+} + \Gamma_{DH^+}d\mu_{DH^+} + \Gamma_{OH^-}d\mu_{OH^-} + \Gamma_{Cl^-}d\mu_{Cl^-} \quad (2)$$

where D indicates the amine oxide and DH$^+$ its protonated form, i.e., the N-hydroxyammonium ion.

By means of the conditions of ionization equilibria

$$\mu_{H_2O} = \mu_{H^+} + \mu_{OH^-} \quad (3)$$

$$\mu_{DH^+} = \mu_D + \mu_{H^+} \quad (4)$$

we have

$$-d\gamma = (\Gamma_{H_2O} + \Gamma_{OH^-})d\mu_{H_2O} + (\Gamma_D + \Gamma_{DH^+})d\mu_D + (\Gamma_{H^+} + \Gamma_{DH^+} - \Gamma_{OH^-})d\mu_{H^+} + \Gamma_{Cl^-}d\mu_{Cl^-} \quad (5)$$

Since HCl is a strong electrolyte, its chemical potential can be expressed by

$$\mu_{\mathrm{HCl}} = \mu_{\mathrm{H}^+} + \mu_{\mathrm{Cl}^-} \tag{6}$$

Furthermore, introducing the condition of electroneutrality of the surface,

$$\Gamma_{\mathrm{H}^+} + \Gamma_{\mathrm{DH}^+} = \Gamma_{\mathrm{OH}^-} + \Gamma_{\mathrm{Cl}^-} \tag{7}$$

We have the Gibbs adsorption isotherm in terms of components

$$-\mathrm{d}\gamma = (\Gamma_{\mathrm{H_2O}} + \Gamma_{\mathrm{OH}^-})\mathrm{d}\mu_{\mathrm{H_2O}} + (\Gamma_{\mathrm{D}} + \Gamma_{\mathrm{DH}^+})\mathrm{d}\mu_{\mathrm{D}} + \Gamma_{\mathrm{Cl}^-}\mathrm{d}\mu_{\mathrm{HCl}} \tag{8}$$

At this stage we can specify the location of the dividing plane by the Gibbs convention

$$\Gamma_{\mathrm{H_2O}} + \Gamma_{\mathrm{OH}^-} = 0 \tag{9}$$

Then we arrive at the Gibbs adsorption isotherm in terms of solute components having definite surface excess densities as

$$-\mathrm{d}\gamma = (\Gamma_{\mathrm{D}} + \Gamma_{\mathrm{DH}^+})\mathrm{d}\mu_{\mathrm{D}} + \Gamma_{\mathrm{Cl}^-}\mathrm{d}\mu_{\mathrm{HCl}} \tag{10}$$

where we use the same symbols for the surface excess densities of species having definite values [7,10].

The chemical potentials of solute components are expressed by their molar concentrations, C and C_{A}, for the surfactant and HCl. Assuming solution ideality at temperature T, we have

$$\mu_{\mathrm{D}} = \mu_{\mathrm{D}}^0 + RT \ln C_{\mathrm{D}} \tag{11}$$

$$\mu_{\mathrm{HCl}} = \mu_{\mathrm{HCl}}^0 + RT \ln C_{\mathrm{H}^+}C_{\mathrm{Cl}^-} \tag{12}$$

where C_i is the molar concentration of species i, and the superscript 0 indicates the standard state with $C_i = 1\ M$, and R is the gas constant. If the degree of protonation and the ionization constant of the protonated surfactant, DH^+, are α and K, respectively, then

$$C_{\mathrm{D}} = (1 - \alpha)C \tag{13}$$

$$K = [(1 - \alpha)/\alpha]C_{\mathrm{H}^+} \tag{14}$$

and

$$C_{\mathrm{Cl}^-} = C_{\mathrm{A}} \tag{15}$$

Introducing the ionic product of water

$$C_{\mathrm{H}^+} \cdot C_{\mathrm{OH}^-} = K_{\mathrm{w}} \tag{16}$$

and the condition of electroneutrality in the bulk solution

$$C_{\mathrm{H}^+} + C_{\mathrm{DH}^+} = C_{\mathrm{OH}^-} + C_{\mathrm{Cl}^-} \tag{17}$$

we have an equation for C_{H^+} or α. Instead of solving this equation directly, we leave some variables and proceed further.

Finally, we arrive at the Gibbs adsorption isotherm in the form

$$-\mathrm{d}\gamma = RT(\Gamma\ \mathrm{d}\ln C + \Gamma_A\ \mathrm{d}\ln C_A) \tag{18}$$

where

$$\Gamma = \frac{C_A + 2\,C_{OH^-}}{C_A - \alpha^2 C + 2\,C_{OH^-}}(\Gamma_D + \Gamma_{DH^+}) - \frac{\alpha C}{C_A - \alpha^2 C + 2\,C_{OH^-}}\Gamma_{Cl^-} \tag{19a}$$

and

$$\Gamma_A = -\frac{\alpha C_A}{C_A - \alpha^2 C + 2\,C_{OH^-}}(\Gamma_D + \Gamma_{DH^+}) + \left(1 + \frac{C_A}{C_A - \alpha^2 C + 2\,C_{OH^-}}\right)\Gamma_{Cl^-} \tag{19b}$$

By solving Eqns (19) we can obtain the surface excess densities or adsorption densities of the total surfactant and Cl^-, i.e., $\Gamma_D + \Gamma_{DH^+}$ and Γ_{Cl^-}, as functions of Γ and Γ_A. Here, Γ and Γ_A can be derived from the variations of surface tension with respect to the surfactant concentration and HCl concentration as

$$\Gamma = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial \ln C}\right)_{C_A} \tag{20a}$$

$$\Gamma_A = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial \ln C_A}\right)_{C} \tag{20b}$$

Water

In the absence of added HCl, i.e., Eqn (19a) with $C_A = 0$ and $\Gamma_{Cl^-} = 0$, we have

$$\Gamma_D + \Gamma_{DH^+} = \left(1 - \frac{\alpha^2 C}{2\,C_{OH^-}}\right)\Gamma \tag{21}$$

It is very difficult to estimate the degree of protonation of the surfactant and the molar concentration of OH^- in the concentration region below the CMC. The pK value of dimethyldodecylamine oxide in water was determined as 4.78 [7,9], and we have evidence from the pH titration of micellar solutions that the pK value of dimethyloleylamine oxide is even lower. By means of Eqn (14) we can obtain a value of α of <0.05 for the present surfactant in water. This value, however, leads to a negative value for the coefficient of Eqn (21), which is unreasonable, and we would not proceed further.

It would be more reasonable to put $\alpha = 0$ in Eqn (21). This derives consistent results for the adsorption isotherm of the total surfactant, as will be seen later.

Presence of added HCl

In this case we have

$$\Gamma_D + \Gamma_{DH^+} = \left(1 - \frac{\alpha^2 C}{2(C_A + C_{OH^-})}\right)\Gamma + \frac{\alpha C}{2(C_A + C_{OH^-})}\Gamma_A \tag{22a}$$

$$\Gamma_{Cl^-} = \frac{\alpha C_A}{2(C_A + C_{OH^-})}\Gamma + \tfrac{1}{2}\left(1 + \frac{C_{OH^-}}{C_A + C_{OH^-}}\right)\Gamma_A \tag{22b}$$

Putting $pK = 4.78$ in Eqn (14), we can estimate the value of α from the observed pH. We have estimated the value of α in this way in the presence of 10^{-4} M HCl. In the presence of 10^{-3} and 10^{-2} M HCl, we may make the approximation $\alpha = 1$. In this way we can derive the adsorption densities of the surfactant and Cl^- by means of Eqns (22) with $C_{OH^-} = 0$.

Protonation of the adsorbed surfactant

In order to separate the adsorption density of the surfactant into those of nonionic and protonated forms, we have to make a nonthermodynamic assumption

$$\Gamma_{H^+} = \Gamma_{OH^-} \tag{23}$$

which corresponds to the fact that the surface layer of water is always neutral. Then, in water

$$\Gamma_D = \Gamma \tag{24a}$$

and

$$\Gamma_{DH^+} = 0 \tag{24b}$$

In the presence of HCl

$$\Gamma_D = \left(1 - \frac{\alpha(\alpha C + C_A)}{2C_A}\right)\Gamma + \frac{\alpha C - C_A}{2C_A}\Gamma_A \tag{25a}$$

$$\Gamma_{DH^+} = \Gamma_{Cl^-} = \frac{\alpha}{2}\Gamma + \tfrac{1}{2}\Gamma_A \tag{25b}$$

Adsorption densities of the surfactant

The values of Γ and Γ_A given by Eqns (20) can be derived from the slope of surface tension curves shown in Fig. 1 and from that redrawn in Fig. 2,

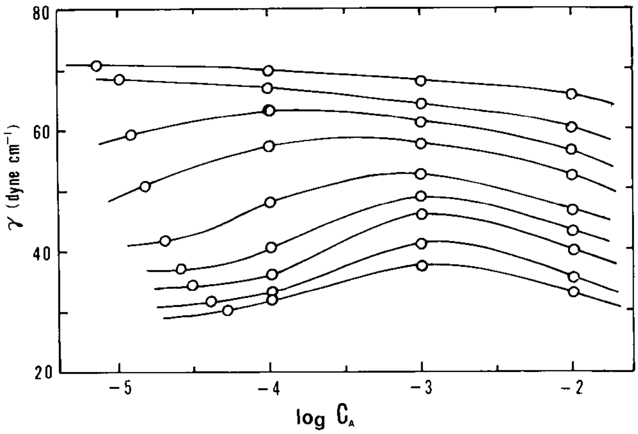

Fig. 2. Surface tension of aqueous solutions of HCl in the presence of dimethyloleylamine oxide. C (10^{-5} M): from top to bottom: 0.70, 1.00, 1.20, 1.50, 2.00, 2.50, 3.00, 3.50, 4.00.

respectively. The anomalous behavior of the surface tension of the solutions presented in Fig. 1 is again manifest in Fig. 2, exhibiting both negative and positive slopes depending on the concentration. By means of Eqns (21) and (22) we can obtain the adsorption density of the total surfactant, $\Gamma_D + \Gamma_{DH^+}$, as a function of concentration, C, at a given HCl concentration, C_A. Figure 3 shows these adsorption isotherms of the surfactant. They behave quite differently from those of the usual surfactants presented so far [11—14].

In the absence of HCl, the surfactant adsorbs somewhat cooperatively and

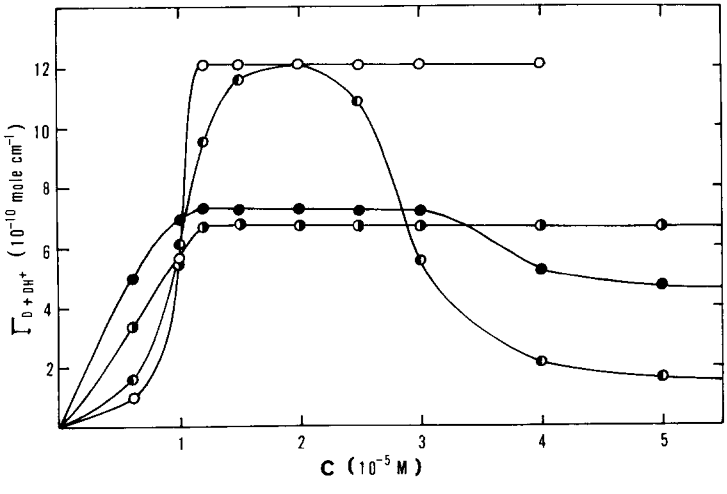

Fig. 3. Adsorption density of the total surfactant plotted against surfactant concentration. C_A : (○), water; (◐), 10^{-4} M HCl; (◑), 10^{-3} M HCl; (●), 10^{-2} M HCl.

its adsorption density reaches a maximum and constant value, 12.2×10^{-10} mol cm^{-2}, around 1.2×10^{-5} *M*. This concentration is less than one-third of the CMC identified by the breakpoint of the surface tension curve, and the saturated value of adsorption density is ~4 times larger than those found for the other surfactants [7,11—14]. This maximum adsorption of the surfactant corresponds to the molecular area of 13.7 Å^2 molecule^{-1}. Even if the adsorbed surfactant is nonionic, this area is too small, e.g., compared with the limiting area of a liquid-expanded film of oleic acid on 0.01 *M* HCl of 55 Å^2 molecule^{-1} [15,16].

These observations indicate that dimethyloleylamine oxide is adsorbed on aqueous surfaces and forms a layer having a thickness of four molecules. Such a multimolecular layer adsorption of a surfactant on aqueous surfaces has been found for a surface-active nonionic dye, *p*-t-octylphenol yellow amine polyethylene oxide [17]. Its adsorbed layer is 3—15 molecules thick, depending on the surfactant species and solvent composition. Even with dodecyldimethylammonium chloride, bimolecular layer adsorption on aqueous surfaces of 4.00 *M* NaCl solutions may be suggested [13]. A simple calculation of the adsorption densities from published data on the surface tension of aqueous solutions also gives very high adsorption densities for cetylpyridinium salicylate [18] and partially ionized dodecenesuccinic acid [19], which indicate formation of multimolecular layer adsorption.

In the presence of 10^{-4} *M* HCl the cooperativity of adsorption is weakened, but the maximum adsorption density of the surfactant is reached at 2.0×10^{-5} *M*, which is about the same as that found on water. However, a further increase in concentration beyond 2×10^{-5} *M* leads to a steep decrease in adsorption. This particular phenomenon of adsorption behavior may be attributed to micelle formation of the surfactant accompanying the change in degree of protonation, as will be explained below. At higher concentrations the adsorption density of the surfactant is as low as 1.5×10^{-10} mol cm^{-2}, or even lower at 5×10^{-5} *M*, and it corresponds to a molecular area of 111 Å^2 molecule^{-1}, which can be assigned to the limiting area of a monolayer of the protonated surfactant. Consequently, a multimolecular layer is formed at lower concentrations but it is disrupted by the increased protonation of the adsorbed surfactant at higher concentrations.

In contrast to the CMC assigned from the breakpoint of the surface tension, the maximum density of the nonionic—cationic surfactant might be more adequately assigned to the CMC, as will be shown qualitatively below. The values of the concentration where the maximum adsorption is attained are given as $C_{0,\Gamma_{\mathrm{max}}}$ in Table 1. In such an assignment, it is assumed that the adsorption of the surfactant is directly correlated with monomer concentration in solution, but not with the micelle concentration [20,21].

In the presence of 10^{-3} *M* HCl, the surfactant is almost completely protonated in solution, and its adsorption density increases almost linearly with increasing concentration. Above 1.2×10^{-5} *M*, which is only about one-seventh of the CMC value, $C_{0,\gamma}$, the adsorption density of the surfactant is 6.82×10^{-10} mol cm^{-2} and remains constant. This value still corresponds to bimolecular layer adsorption.

It is noted that the surfactant, if almost completely protonated in solution, can form bimolecular layers on aqueous surfaces, while the surfactant when partially protonated in solution can form quadrimolecular layers to monolayers, depending on the surfactant concentration. This can partly be explained by the degree of protonation of the adsorbed surfactant which differs from that of the surfactant in solution, and will be demonstrated below on the basis of Eqns (25). It is also likely that the nonionic and protonated forms of the surfactant can form a 1:1 complex through a hydrogen bond on aqueous surfaces. Such a complex may be formed in micelles in solution, as exhibited by an increase in turbidity or light scattering around pH 4.9, or in the half-protonated states of the present surfactant [22] as well as of dimethyldodecylamine oxide [4,8].

In the presence of 10^{-2} *M* HCl, the surfactant is completely protonated in solution, so that most of the added HCl is free and acts as a simple salt. This is seen from the CMC value, $C_{0,\gamma}$, in 10^{-2} *M* HCl, which is lower than in 10^{-3} *M* HCl, as seen in Table 1. The maximum adsorption density is attained at 1.2×10^{-5} *M* and remains constant up to 3×10^{-5} *M*. It is equal to 7.42×10^{-10} mol cm^{-2}, which suggests formation of bimolecular adsorption layers. However, at high concentrations, the electrostatic effect of free HCl in stabilizing the bimolecular layer becomes insufficient and the bimolecular layer reduces to a monolayer.

Ionization of the adsorbed surfactant

Based on the assumption, Eqn (23), we can calculate the adsorption densities of cationic and nonionic forms of the surfactant by means of Eqns (25).

Figure 4 shows the adsorption density of the nonionic form of the ad-

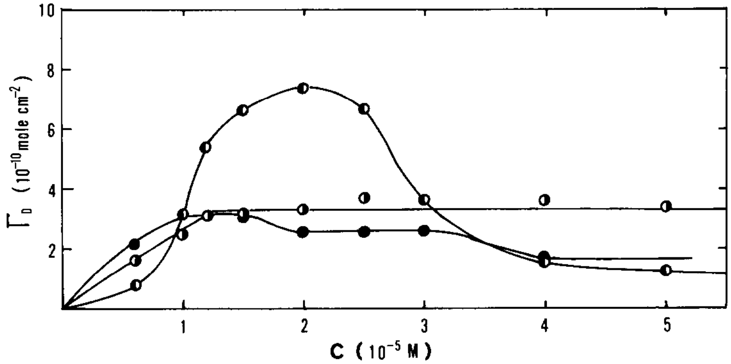

Fig. 4. Adsorption density of the nonionic form of dimethyloleylamine oxide plotted against surfactant concentration. C_A: (◐), 10^{-4} *M* HCl; (◑), 10^{-3} *M* HCl; (●), 10^{-2} *M* HCl.

sorbed surfactant. Comparing this with Fig. 3, we can estimate the degree of protonation of the adsorbed surfactant, $\Gamma_{DH^+}/(\Gamma_D + \Gamma_{DH^+})$. In water we have a constant adsorption density above 1.2×10^{-5} *M*, which would support the suggestion that the degrees of protonation of the surfactant in both the surface and the bulk are zero.

In the presence of 10^{-4} *M* HCl, the degree of surface protonation of the surfactant is $\lesssim 0.4$, but even in the presence of 10^{-3} *M* HCl it still remains at ~0.5, while the surfactant is almost fully protonated in the bulk. In 10^{-3} *M* HCl it is likely that the nonionic and protonated molecules of the surfactant form a 1:1 complex on aqueous surfaces. Such complex formation may occur in the micelles in solution, exhibiting increased turbidity at pH 4.9, or in the half-protonated state of micellar solutions. This has been observed for micellar solutions of dimethyldodecylamine oxide [4,8] and of dimethyloleylamine oxide [22]. Liquid—liquid phase separation of micellar solutions of dimethyldodecylamine oxide [4] and dimethyloleylamine oxide [23] occurs at pH 4.9 with the lowest concentration of added salt or at the lowest temperature. These phenomena may be the counterpart of the precipitation of acid soaps in fatty acid solutions [24—26].

DISCUSSION

Since we have established the multimolecular layer adsorption of dimethyloleylamine oxide on aqueous surfaces, we now proceed to examine the relationship between the adsorbed state and micelle formation of dimethyloleylamine oxide. Usually, it is assumed that the surfactant micelles are so strongly hydrated that they are not adsorbed on aqueous surfaces [27]. Thus, the multimolecular layer cannot be identified with the adsorption of micelles. We may then presume that the surfactant is sometimes adsorbed multimolecularly on aqueous surfaces, if it is sufficiently hydrophobic.

If the activity of a surfactant or its monomer concentration is responsible for the adsorption on aqueous surfaces or the lowering of surface tension, we may still use Eqn (18) by replacing the total concentration, C, by the monomer concentration, C_1. In this approximation and from the molecular standpoint, we should examine the behavior of the monomer concentration with respect to the total concentration. With the nonionic form of the surfactant, the monomer concentration remains constant above the CMC and has a value equal to the CMC. This is the reason why the surface tension is constant above the CMC.

For the nonionic—cationic surfactant in the presence of added HCl, the surfactant has differently ionized states, i.e. different degrees of protonation in the monomer and in the micelles. The micelle formation accompanies the change in ionization state of surfactant as expressed by

$$m\mathrm{D} + p\mathrm{H}^+ \rightleftarrows [\mathrm{D}_m\mathrm{H}_p]^{p+} \qquad (26)$$

for which the law of mass action is

$$\frac{C_{m,p}}{[(1-\alpha)C_1]^m C_{H^+}{}^p} = K_{m,p} \tag{27}$$

where $C_{m,p}$ is the molar concentration of the protonated micelle having aggregation number m and charge p, and $K_{m,p}$ is the equilibrium constant. The total concentration of surfactant is then equal to

$$C_1 + mC_{m,p} = C \tag{28}$$

In acid pH, where the concentration of OH^- is negligible, the condition of electroneutrality or the total concentration of HCl, C_A, is given by

$$C_{H^+} + C_{DH^+} + pC_{m,p} = C_A \tag{29}$$

If the molar concentration of H^+, C_{H^+}, is negligibly small compared with the other species in Eqn (29), so that $C_{DH^+} = C_1$, but, if it remains significantly high in Eqn (27), so that $C_A = C$, then the present problem is identical with that discussed previously for the formation of ionic micelles having definite numbers of bound counterions [20,21].

It was shown that the reduced problem gives a significant maximum value at C_1 at the CMC, instead of reaching a constant value. When the value of m is not very large, the upward curvature of C_1 at the maximum is more gradual. Thus, the micelle size would be small if the adsorption density of the surfactant changes like the molar concentration of its monomer.

For the more general problem at present, Eqns (27)—(29) cannot readily be solved explicitly. Nevertheless, we may anticipate that the maximum of C_1 should occur, as in the case above. Thus, the change in protonation of surfactant and the shift of monomer—micelle equilibrium of the surfactant would induce a complex variation of monomer concentration and, accordingly, of the adsorption density of the surfactant.

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