BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (1), 214—218`(1975) [Vol. 48, No. 1

The Effect of the pH on the Adsorption of an Ampholytic Surfactant, *N*-Dodecyl-*β*-alanine, at the Aqueous Surface

Akio NAKAMURA, Kazuo TAJIMA, and Tsunetaka SASAKI

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Tokyo 158

(Received August 7, 1974)

The effect of the pH on the adsorption of an ampholytic surfactant, *N*-dodecyl-*β*-alanine (NDA), at the nitrogen/solution interface was studied by the radiotracer method, using a tritiated compound. The saturated amount of NDA adsorption was found to depend on the pH of the bulk solution; it shows a flat maximum in the isoelectric region from pH 4 to 10, and decreases distinctly on the both acid and alkaline sides. The Gibbs adsorption isotherm for an aqueous solution of the ampholytic surfactant was derived. Using this relation, the amount of adsorption in the pH range from 2 to 6 was calculated from the surface tension *vs.* concentration and the surface tension *vs.* pH relations observed for the NDA solution. The calculated values were in good agreement with those obtained by the radiotracer method. The degree of dissociation of the adsorbed monolayer was estimated from the pH dependence of NDA and the chloride ion adsorption.

The present authors and their collaborator have previously reported radiotracer studies on the adsorption of an ampholytic surfactant, *N*-dodecyl-*β*-alanine (NDA),[1] at type of surfactant upon which the adsorption had not been studied precisely;[2] they found that, in the isoelectric pH region, the Gibbs adsorption isotherm can be applied in the same form as for an aqueous nonionic surfactant[3] and that the NDA molecules in the solution were mainly in the state of the simple zwitterion.[4]

It is evident that, for such an ampholytic surfactant, a change in the pH markedly influences the state of the solute species of NDA; this further affects the adsorption and the surface tension of the solution. However, the studies of the pH effects have been mainly restricted to properties of bulk solution.[4,5]

In the present report, the pH dependence of the adsorption of NDA is studied in the pH region from 1 to 13. A Gibbs adsorption isotherm applicable to such a system is derived and experimentally confirmed. The ionic states of the adsorbed molecules are discussed, taking account of the pH dependence of NDA and the chloride ion adsorption.

Experimental

Materials and Procedures. All of the reagents used, including tritiated NDA(TNDA), and the methods of the radioactivity and surface tension measurements are the same as have been described in the previous paper.[1]

Theoretical

Gibbs Adsorption Isotherm. The Gibbs adsorption isotherm is written, in its general form, as:[6]

$$-\mathrm{d}\gamma/RT = \sum_i \Gamma_i \mathrm{d}\ln a_i \qquad (1)$$

where γ denotes the surface tension, and Γ_i and a_i, the surface excess and activity of the *i*'th solute in the solution respectively. Equation (1) is rewritten for the ampholytic surfactant solution containing hydrochloric acid as:

$$\begin{aligned}-\mathrm{d}\gamma/RT = {} & \Gamma_{\mathrm{A}^\pm}\mathrm{d}\ln C_{\mathrm{A}^\pm} + \Gamma_{\mathrm{A}^+}\mathrm{d}\ln C_{\mathrm{A}^+} \\ & + \Gamma_{\mathrm{A}^-}\mathrm{d}\ln C_{\mathrm{A}^-} + \Gamma_{\mathrm{H}^+}\mathrm{d}\ln C_{\mathrm{H}^+} \\ & + \Gamma_{\mathrm{OH}^-}\mathrm{d}\ln C_{\mathrm{OH}^-} + \Gamma_{\mathrm{Cl}}\mathrm{d}\ln C_{\mathrm{Cl}} \qquad (2)\end{aligned}$$

where the $\mathrm{A}^\pm$, A^+, A^-, H^+, OH^-, and Cl subscripts refer to the zwitterion, the cation, the anion of NDA, the hydrogen ion, the hydroxide ion, and the chloride ion respectively. In Eq. (2) the activities can be replaced by the concentrations, since the surfactant concentrations are dilute, and the activity coefficients can be taken as unity. The concentration of HCl is not dilute in some cases, but this does not cause much error, as may be seen from the results.

Further, we have the following relations:

$$K_1 = C_{\mathrm{A}^\pm}C_{\mathrm{H}^+}/C_{\mathrm{A}^+} \qquad (3)$$

$$K_2 = C_{\mathrm{A}^-}C_{\mathrm{H}^+}/C_{\mathrm{A}^\pm} \qquad (4)$$

$$K_{\mathrm{w}} = C_{\mathrm{H}^+}C_{\mathrm{OH}^-} \qquad (5)$$

$$\Gamma_{\mathrm{A}^+} + \Gamma_{\mathrm{H}^+} = \Gamma_{\mathrm{OH}^-} + \Gamma_{\mathrm{A}^-} + \Gamma_{\mathrm{Cl}} \qquad (6)$$

where K_1 and K_2 express the first and second dissociation constants of NDA, considered as a dibasic acid, and K_{w}, the dissociation constant of water. Equation (6) represents the electrical neutrality of the adsorbed ionic species.

By substituting the logarithmic forms of Eqs. (3) and (4) into Eq. (2), we obtain:

$$\begin{aligned}-\mathrm{d}\gamma/RT = {} & (\Gamma_{\mathrm{A}^\pm}+\Gamma_{\mathrm{A}^+}+\Gamma_{\mathrm{A}^-})\mathrm{d}\ln C_{\mathrm{A}^\pm} \\ & + (\Gamma_{\mathrm{A}^+}-\Gamma_{\mathrm{A}^-}+\Gamma_{\mathrm{H}^+})\mathrm{d}\ln C_{\mathrm{H}^+} \\ & + \Gamma_{\mathrm{OH}^-}\mathrm{d}\ln C_{\mathrm{OH}^-} + \Gamma_{\mathrm{Cl}}\mathrm{d}\ln C_{\mathrm{Cl}} \qquad (7)\end{aligned}$$

Using

$$\Gamma^{\mathrm{A}} = \Gamma_{\mathrm{A}^\pm} + \Gamma_{\mathrm{A}^+} + \Gamma_{\mathrm{A}^-} \qquad (8)$$

as the total adsorption amount of NDA, and

$$C^{\mathrm{A}} = C_{\mathrm{A}^\pm} + C_{\mathrm{A}^+} + C_{\mathrm{A}^-} \qquad (9)$$

as the bulk concentration of NDA, we obtain, from Eqs. (5), (6), (7), and (8):

$$-\mathrm{d}\gamma/RT = \Gamma^{\mathrm{A}}\mathrm{d}\ln C_{\mathrm{A}^\pm} + \Gamma_{\mathrm{Cl}}\mathrm{d}\ln C_{\mathrm{H}^+}C_{\mathrm{Cl}} \qquad (10)$$

Equation (10), together with Eqs. (3), (4), and (9), then gives:

$$\begin{aligned}-\mathrm{d}\gamma/RT = {} & \Gamma^{\mathrm{A}}\mathrm{d}\ln C^{\mathrm{A}} + K\Gamma^{\mathrm{A}}\mathrm{d}\ln C_{\mathrm{H}^+} \\ & + \Gamma_{\mathrm{Cl}}\mathrm{d}\ln C_{\mathrm{H}^+}C_{\mathrm{Cl}} \qquad (11)\end{aligned}$$

where:

$$K = (C_{\mathrm{A}^-}-C_{\mathrm{A}^+})/C^{\mathrm{A}}$$

or, using Eqs. (3), (4), and (9),

$$K = (K_1K_2-C_{\mathrm{H}^+}^2)/(C_{\mathrm{H}^+}^2+K_1C_{\mathrm{H}^+}+K_1K_2) \qquad (12)$$

By differentiating Eq. (11) with respect to ln C^{A}, keeping C_{Cl} constant, and with respect to ln C_{Cl}, keeping C^A constant, we obtain:

$$I_{Cl} = \Gamma^A + (K\Gamma^A + \Gamma_{Cl})\alpha \tag{13}$$

$$I_A = \Gamma_{Cl} + (K\Gamma^A + \Gamma_{Cl})\beta \tag{14}$$

where:

$$I_{Cl} = -(\mathrm{d}\gamma/RT\mathrm{d}\ln C^A)_{C_{Cl}} \tag{15}$$

$$I_A = -(\mathrm{d}\gamma/RT\mathrm{d}\ln C_{Cl})_{C^A} \tag{16}$$

$$\alpha = (\mathrm{d}\ln C_{H^+}/\mathrm{d}\ln C^A)_{C_{Cl}} \tag{17}$$

$$\beta = (\mathrm{d}\ln C_{H^+}/\mathrm{d}\ln C_{Cl})_{C^A} \tag{18}$$

Equations (13) and (14) finally give:

$$\Gamma^A = [(1+\beta)I_{Cl} - \alpha I_A]/[1+\beta+\alpha K] \tag{19}$$

$$\Gamma_{Cl} = -[\beta K I_{Cl} - (1+\alpha K)I_A]/[1+\beta+\alpha K] \tag{20}$$

From Eqs. (19) and (20), Γ^A and Γ_{Cl} can be calculated from the measurements of I_A, I_{Cl}, α, and β according to Eqs. (15) to (18).

The validity of Eq. (19) can be checked by comparing the Γ^A calculated from this equation with those measured directly by the radiotracer method. Equation (20) enables us to calculate Γ_{Cl}, the direct measurement of which is impossible due to the lack of a soft radioactive nuclide.

Adsorption equations for alkaline NDA solution containing sodium hydroxide can be derived by a similar calculation. The final expressions for Γ^A and Γ_{Na^+} are the same as in Eqs. (19) and (20) except for the sign of β being the opposite and the subscript Cl being replaced by Na^+.

Results and Discussion

Effect of the pH on the Saturated Amount of Adsorption. Figure 1 shows the adsorption isotherm obtained by the radiotracer method for TNDA solutions kept at a constant pH by the addition of HCl. The amount of adsorption increases with the NDA concentration for each pH and attains a saturation values at a bulk TNDA concentration above *ca.* 2.5×10^{-4} mol/l for the pH region from 3.5 to 6 and above *ca.* 6×10^{-4} mol/l for the more acid region. Also, it can be seen that the amount of NDA adsorption is independent of the pH in the range from 4 to 6 and that it decreases below this region, with a minimum at pH 2. The measurements of the saturated amount of adsorption were further extended over the alkaline region, and the values plotted against the pH. The results are shown by Curve A in Fig. 2. In these measurements, the concentration of NDA was maintained at 6.0×10^{-4} mol/l, which was high enough to secure the saturated adsorption. Curve A shows that the saturated amount of adsorption is nearly constant in the pH region from 4 up to 10, including the isoelectric point of pH 7, and decreases on the acid and alkaline sides, with a minimum located near pH 2.

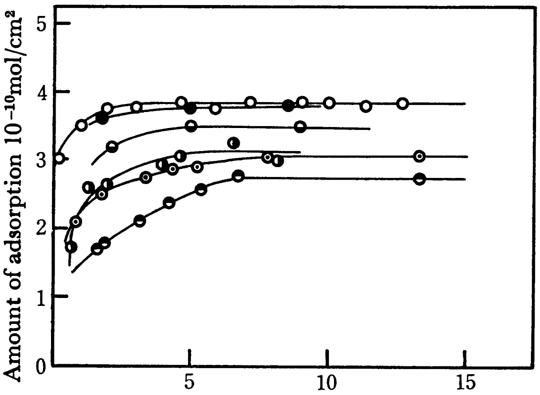

Fig. 1. Adsorption isotherm of NDA.
pH of solutions
○: 6.0 ●: 3.5 ◒: 3.0 ◑: 2.5 ◓: 2.0 ⊙: 1.0

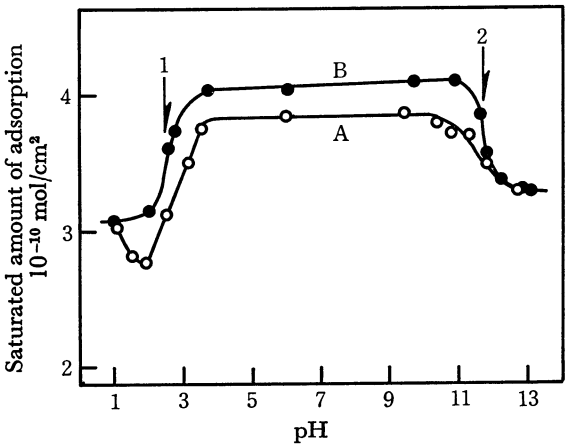

Fig. 2. Saturated amount of adsorption *vs.* pH.
○: in the absence of added NaCl
●: at constant ionic strength (μ=0.1) adjusted by NaCl

The slight increase observed below pH 2 is considered to be due to the salting out effect on the adsorption of HCl added in a relatively large amount. To confirm this effect, another measurement was made under a constant ionic strength adjusted by the addition of NaCl. The results are shown by Curve B in the same figure. The amount of NDA adsorption in this case is also seen to be nearly constant in the pH region from 4 up to 11, while it decreases rather sharply below and above this region, tending to constant values. The minimum values increases, and the minimum disappears.

In order to elucidate the pH dependence of ampholyte adsorption, it is necessary to know the dissociation equilibrium of ampholyte in the substrate solution with which the adsorbed monolayer is in equilibrium. For this purpose, the molar fractions of NDA cations, anions, and zwitterions are calculated using two dissociation constants, $K_1=3.2\times10^{-4}$, $K_2=1.3\times10^{-11}$ mol/l[4] of the NDA as a dibasic acid; they are plotted against the pH in Fig. 3. As is shown by the curves in the figure, the two dissociations occur step-by-step, and Curve (2) indicates that, in the pH region from 5.5 up to 9, most NDA molecules exist as zwitterions in a bulk solution. Thus, the agreement, as a whole, of the plateau region of adsorption at the surface (shown by Curve B in Fig. 2) with the zwitterionic region of the bulk solution (Curve (2) in Fig. 3) might be taken as the indication that the adsorbed NDA in this pH region consists mainly of zwitterions, considering the similarity of the ionic states between the surface and

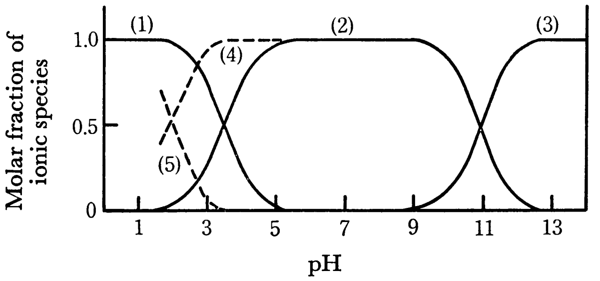

Fig. 3. Molar fractions of ionic species in the bulk solution and at the surface.
(1) —— cationic species
(2) —— zwitterionic species
(3) —— anionic species
in the bulk solution
(4) ---- zwitterionic species
(5) ---- cationic species
at the surface

the bulk. The agreement of the pH regions of relatively weak adsorptions on the acid and alkaline sides of Curve B in Fig. 2 with those of Curves (1) and (3) in Fig. 3 also indicates that cations (anions) are the main adsorbed species in the low (high) pH region.

According to these considerations, the adsorbed layer is cationic at pH 1, zwitterionic at pH values from 4 to 11, and anionic at pH 13 in Curve B of Fig. 2. Then, at the pH corresponding to the middle point between the adsorption amounts of cationic and zwitterionic molecules (Arrow 1), half of the molecules adsorbed at the surface are considered to exist as cations and half as zwitterions, while at a similar pH on the alkaline side (Arrow 2), half of the molecules adsorbed may exist as zwitterions and half as anions. These two pH values of the half-ionization of the adsorbed NDA are read as 2.5 and 11.7 respectively from Curve B. It is noticeable that the pH value of 2.5, *i.e.* the point of the half-ionization of carboxyl groups, is by 1.0 pH unit to the acid side of the point at which carboxyl groups half-ionize in the bulk solution, and that the pH value of 11.7, the point of the half-ionization of imino groups, is by 0.8 unit to the alkaline side of the point at which imino groups half-ionize in the bulk solution.

In the case of soluble and insoluble monolayers, such a shift of the half-ionization in the surface phase has been reported by many investigators on the basis of measurements of the surface potential,[7] the calcium ion adsorption,[8] *etc.*[9] These results have been explained in terms of the existence of a large potential difference, ψ, across the surface characteristic of the charged monolayer.[10] The electric charge attracts or repels hydrogen ions to or from the surface according to the Boltzmann equation:

$$[H^+]_s = [H^+]_b \exp(-\varepsilon\psi/kT)$$

or:

$$pH_s = pH_b + \varepsilon\psi/2.3kT \qquad (21)$$

where the s and b subscripts denote the surface and the bulk respectively, and ε, the protonic charge. It follows from Eq. (21) that:

$\psi > 0 \quad pH_s > pH_b$ for a cationic monolayer

$\psi < 0 \quad pH_s < pH_b$ for an anionic monolayer

This may explain the observed phenomena. In the case of the cationic monolayer formed in acid region, $pH_s > pH_b$ and the degree of ionization of carboxyl groups is larger at the surface than in the bulk solution. Accordingly, half-ionization at the surface occurs at a lower pH than the pH of half-ionization in the bulk solution. A similar consideration leads to the conclusion that the half-ionization of imino groups at the surface occurs at a higher pH than the pH of half-ionization in the bulk solution. Thus, we have a system of pH shifts occurring in two opposite directions each other as compared with the shift in one direction usually observed for insoluble monolayers which contain only one kind of dissociation group. The ψ values tentatively calculated according to Eq. (21) are 60 mV for the cationic monolayer and −50 mV for the anionic monolayer; these values are, however, roughly half of the values calculated according to the Gouy theory.[11] This discrepancy will be explained below.

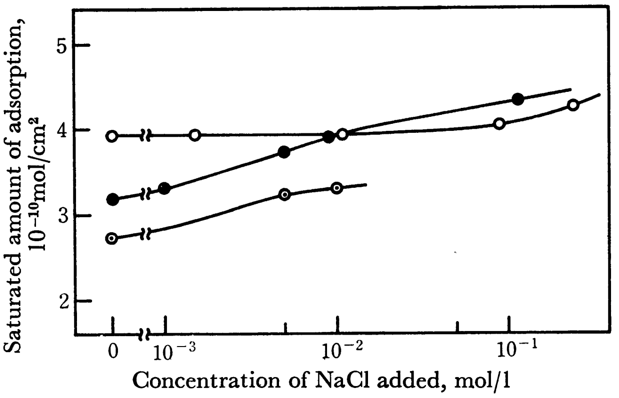

Fig. 4. Effect of polar head group and added NaCl on the saturated amount of adsorption.
Surfactants (Concentration)
○: NDA (5×10^{-4}mol/l) ●: SDS (4×10^{-3}mol/l)[12]
⊙: $D(EO)_6$ (4×10^{-5}mol/l)[13]

Effect of the Polar Head Structure and Added Salt on the Saturated Amount of Adsorption. The effect of salt on the saturated amount of adsorption of a few surfactants with equal hydrocarbon chain lengths hitherto measured directly by the radiotracer method using tritium labeled compounds are shown in Fig. 4, together with the present data. It is evident that the nature of the polar head and NaCl added affect the amount of adsorption. In the absence of added salt, the adsorption of NDA is relatively large compared with those of the sodium dodecylsulfate (SDS)[12] and hexaoxyethylenedodecylmonoether ($D(EO)_6$).[13] This may be due to the electrical repulsion between negatively charged groups in the case of SDS and due to bulky head groups in the case of $D(EO)_6$. The relatively large amount of adsorption for NDA is due to the zwitterionic and relatively compact head groups forming intra- and intermolecular salts, as has been reported for, for instance, the phospholipid monolayers.[8,14] It may be seen in Fig. 4 that the addition of a small amount of NaCl distinctly increases the adsorption of SDS and $D(EO)_6$, while it has no effect on NDA. In the case of SDS, the increase in adsorption is mainly caused by the decrease in electrical repulsion between adsorbed molecules due to the increase in the ionic strength. In the case of D(EO)$_6$, the dehydration of weakly hydrated nonionic molecules may result in an increase in the adsorption.[15] The absence of these effects in the case of NDA in the neutral region in Fig. 4 and perhaps in the whole plateau region may explain the absence of any effect of NaCl addition. Figure 4 further shows the increase in the adsorption of NDA in the concentrated solution of NaCl, much as in the cases of SDS and D(EO)$_6$. This may be interpreted as a salting out effect of NaCl. A similar effect is also seen near pH 1 in Fig. 2, where HCl is added in a large amount.

Calculation of the Amount of Adsorption. Figures 5 to 8 show the plots of γ *vs.* log C^A (C_{Cl}=constant), of γ *vs.* pCl (C^A=constant), of pH *vs.* pCl (C^A=constant), and of pH *vs.* log C^A (C_{Cl}=constant) respectively, from which I_{Cl}, I_A, α, and β values required in Eqs. (19) and (20) may be calculated from the slopes of these curves. Γ^A and Γ_{Cl} were calculated at the NDA concentrations of 2.25×10^{-4} mol/l and 5.0×10^{-4} mol/l. Similar results were thus obtained. Figure 9 shows the plot of Γ against pH for the latter case, together with the observed values obtained by the interpolation of the curves in Fig. 1. A good agreement is seen between the calculated and observed amounts of adsorption; this shows the validity of the Gibbs adsorption isotherm derived.

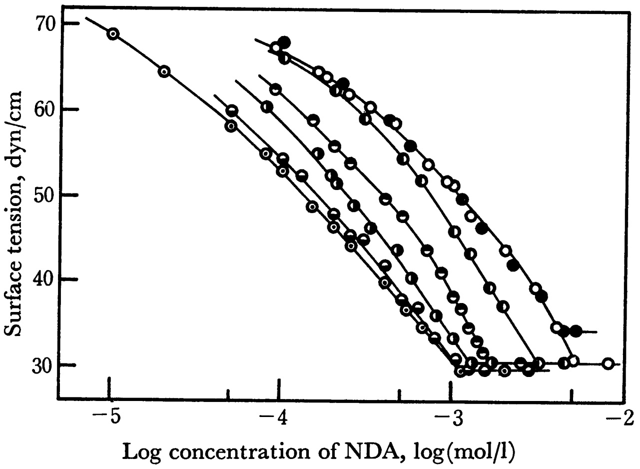

Fig. 5. Surface tension vs. concentration of NDA.
Initial concentration of HCl(pCl)
⊙: 6.0 ◒: 4.0 ◑: 3.5 ◓: 3.0 ◐: 2.5 ○: 2.0 ●: 1.5

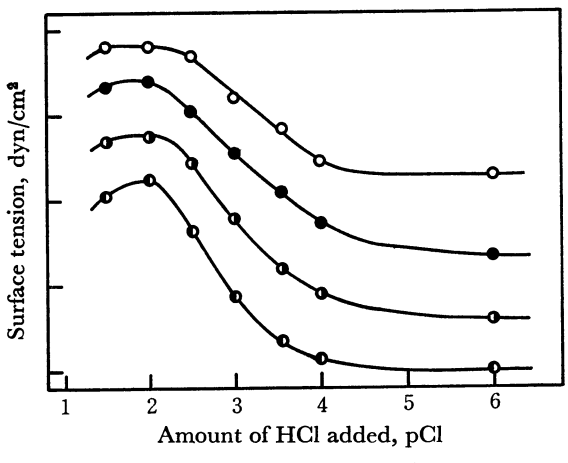

Fig. 6. Surface tension of NDA solution *vs.* amount of HCl added.
Concentration of NDA (10^{-4} mol/l)
○: 1.0 ●: 2.25 ◑: 5.0 ◐: 10.0

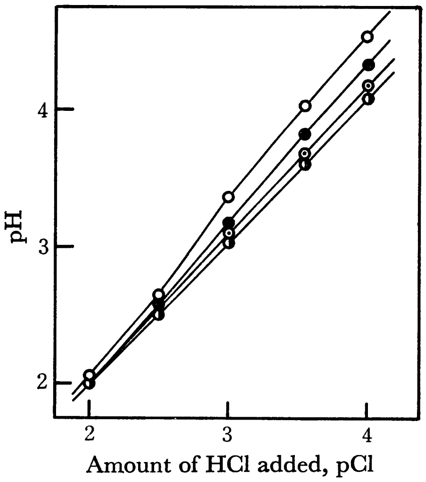

Fig. 7. pH of NDA solution *vs.* amount of HCl added.
Concentration of NDA (10^{-4} mol/l)
○: 10.0 ●: 5.0 ⊙: 2.25 ◑: 1.0

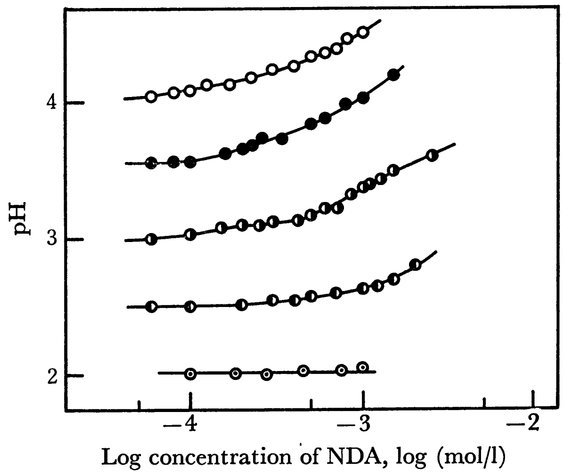

Fig. 8. pH of HCl solution *vs.* concentration of NDA.
Initial concentration of HCl(pCl)
○: 4.0 ●: 3.5 ◑: 3.0 ◐: 2.5 ⊙: 2.0

It is worth noting that, in the limiting cases of $\alpha=0$, which is actually the case near pH 2 and in the neutral pH region, Eq. (19) is reduced to a simple form:

$$\Gamma^A = I_{Cl} \qquad (22)$$

As was mentioned, in the neutral region NDA exclusively exists as one zwitterionic species, regardless of the pH, while near pH 2 NDA exist mainly as cations with excess of HCl. Therefore, Eq. (22) for NDA, in the neutral pH region and near pH 2, is valid much as in the cases of the adsorption of a nonionic surfactant (D(EO)$_6$)[3] and an anionic surfactant (SDS) with excess salt[16] respectively. In the intermediate

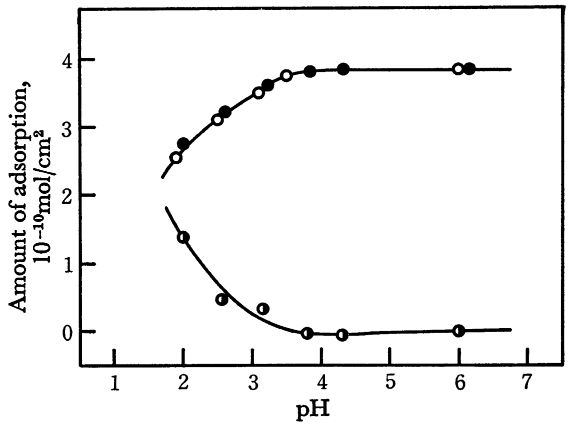

Fig. 9. Amount of adsorption of NDA and chloride ion *vs*. pH at NDA concentration of 5.0×10^{-4}mol/l.
○: observed values for NDA
●: calculated value for NDA
◑: calculated value for chloride ion

pH region from 2 to 5, the general form of Eq. (19) should be used.

As regards the adsorption of the chloride ion, calculated values are nearly zero in the pH region from 4 to 6, as may be seen in Fig. 9. This may imply the zwitterionic structure of NDA, which requires no counter ions. In a more acid region, the values increase with a decrease in the pH. Since the zwitterions change into cations at the surface in this region (Curves A and B in Fig. 2), the positive adsorption of chloride ion as counter ions can reasonably be expected. This enables another calculation of the degree of the ionization of zwitterions into cations at the surface, expressed as $\Gamma_{\mathrm{Cl}}/\Gamma^{\mathrm{A}}$ at each pH, independently of the former estimation made from the curve of Fig. 2. The degrees of ionization, $\Gamma_{\mathrm{Cl}}/\Gamma^{\mathrm{A}}$, namely, the molar fraction of A^+ and the molar fraction of $A^{\pm}$ given as $1-\Gamma_{\mathrm{Cl}}/\Gamma^{\mathrm{A}}$, are shown in Fig. 3 as two broken (4) and (5) respectively. The point of the half-ionization pH at the surface estimated from Curve (5) is read as 2, which is 1.5 pH unit to the acid side of the point at which carboxyl groups half-ionize in the bulk solution, and is lower than the value obtained by the former method from the Curve B shown in Fig. 2. The discrepancy is probably due to the adsorbed film at the lowest pH in Fig. 2 not being in a pure cationic form, but containing some zwitterions. The ψ value in Eq. (21), calculated assuming a half-ionization at pH 2, was found to be 90 mV, roughly which is two-thirds of the values obtained according to the Gouy theory. The discrepancy might come from taking only the net charge density into account and neglecting the ampholytic nature of the adsorbed NDA in the estimation of ψ. At any rate, it may be noted that not only the total amount of adsorption, but also the composition of each ionic species or the state of the ionization of the adsorbed surface phase, can be determined for the ampholyte NDA. It is also shown that the composition is different between the surface and the bulk of the aqueous NDA solution.

References

1) T. Okumura, A. Nakamura, K. Tajima, and T. Sasaki, This Bulletin, **47**, 2986 (1974).

2) K. Durham, "3rd Inst. Congr. Surface Active Substances," Vol. 2, (1960), p. 130.

3) K. Tajima, M. Iwahashi, and T. Sasaki, This Bulletin, **44**, 3251 (1971).

4) T. Okumura, K. Tajima, and T. Sasaki, *ibid.*, **47**, 1067 (1974).

5) M. Corkill, K. Gemmel, J. Goodman, and T. Walker, *Trans. Faraday Soc.*, **66**, 1817 (1970); F. Tokiwa, and K. Ohki, *J. Phys. Chem.*, **71**, 1824 (1967); S. H. Yalkowsky, and G. Zografi, *J. Colloid Sci.*, **34**, 525 (1970); K. Tori, and T. Nakagawa, *Kolloid-Z.*, **187**, 44 (1963).

6) E. A. Guggenheim, "Thermodynamics," North Holland Publishing Co., Amsterdam (1957), p. 50.

7) J. J. Betts, and B. A. Pethica, *Trans. Faraday Soc.*, **52**, 1581 (1956); J. A. Spink, *J. Colloid Sci.*, **18**, 512 (1963); H. C. Parreira, *ibid.*, **20**, 742 (1965); E. D. Goddard, and H. C. Kung, *ibid.*, **37**, 585 (1971).

8) T. Seimiya, and S. Ohki, *Biochim. Biophys. Acta*, **298**, 546 (1973).

9) D. Deutsch, *Z. Phys. Chem.*, **60**, 353 (1928); J. F. Danielli, *Proc. Roy. Soc., Ser. B*, **122**, 155 (1937); *Biochem. J.*, **35**, 470 (1941).

10) J. T. Davies, and E. K. Rideal, "Interfacial Phenomena," Academic Press, New York and London (1963), p. 94.

11) *ibid.*, p. 75.

12) K. Tajima, This Bulletin, **44**, 1767 (1971).

13) K. Tajima, and M. Iwahashi, *ibid.*, **46**, 3370 (1973).

14) B. A. Pethica, Surface Activity and Microbial Cell Soc. Chem., Int London, Monograph, **19**, 85 (1965).

15) K. Shinoda, and H. Takeda, *J. Colloid Sci.*, **32**, 642 (1970); H. Schott, *ibid.*, **43**, 150 (1973).

16) K. Tajima, This Bulletin, **43**, 3063 (1970).