Studies of Aqueous Sodium Dodecyl Sulfate Solutions by Activity Measurements

Tsunetaka Sasaki, Michihiro Hattori,*1 Jun Sasaki,*2 and Kenji Nukina*3
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya, Tokyo 158

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The activities of surfactant ions (a_D) and counterions (a_{Na}) were directly obtained by the EMF measurement of a concentration cell with an ion-exchange membrane and by pNa measurements respectively for aqueous solutions of sodium dodecyl sulfate (NaDS) below and above the CMC. The mean activity and activity coefficient were also calculated. From these data, together with the surface tension (γ) measured by the Wilhelmy method and the amount of adsorption (Γ) measured by the radiotracer method, the following results were obtained: (1) Mean activity was not constant, but increased with the concentration above the CMC. (2) The Gibbs adsorption isotherm was directly verified from the a_D and a_{Na} *vs.* concentration relations. (3) The decrease in γ observed above the CMC was in agreement with that calculated from the activity data. (4) The log a_D *vs.* log a_{Na} plots above the CMC showed a linear relation, indicating the validity of the charged phase separation model as the mechanism of micelle formation. The degree of the counterion attachment of the micelles was found to be 0.73 up to about 80 mmol/l. (5) The intermicellar concentrations of Na^+ and DS^- ions were calculated; the former increases, while the latter decreases with the concentration. (6) The product of the concentration with an osmotic coefficient was linear with the concentration above the CMC, tangent of the slope being about 0.7.

A number of problems remain unconfirmed as regards the properies of aqueous solutions of surface active substances, in spite of their theoretical and practical importance. For instance: 1) Surface tension of an aqueous surfactant solution usually shows aging, and empirical equations to give a correct surface tension by extrapolating it to the sufficiently long time have been proposed.[1–4] On the other hand, some are of the opinion that such aging is due to the presence of impurities and that purification largely eliminates the time effect.[5–7] 2) The formation of dimers or premicelles below the CMC and the second- and higher-order CMC's have been suggested,[8–11] but the absence of such aggregates has also been insisted on.[12,13] 3) The constancies of the activity,[14] the intermicellar concentration,[15–17] and the surface tension above the CMC have often been stated or assumed,[14] whereas a gradual decrease in the surface tension,[5,6] in the intermicellar surfactant concentration,[18,19] and an increase in the activity[6,20] have also been reported. 4) As to the micelle formation, theories based upon the mass action law[6,21,22] and the phase separation mechanism[14,23–25] have been proposed and discussed. Also, a theory covering both mechanisms has been stated.[14] The degrees of the counterion attachment of the ionic micelle thus far reported widely differ from each other according to the method of measurement.[26–28] 6) The equation for the calculation of the activity coefficient of large organic ions has been proposed,[29] but a large deviation from the calculated value has also been experimentally confirmed.[11] 7) A number of studies of the experimental confirmation of the Gibbs adsorption isotherm for an aqueous solution of the surfactant have been reported,[30–34] but no confirmation based upon the direct measurements of all the quantities involved in the isotherm, *i.e.*, the surface tension of the solution, the amount of adsorption and the activity of the surfactant, has yet been attempted as far as the present authors are aware.

The measurement of the activity of a surfactant, together with measurements of the amounts of the adsorption and surface tension of the surfactant solution, enables us not only to make a direct confirmation of the Gibbs adsorption isotherm, but also to solve most of the other problems listed above without any assumptions. The present paper will deal with these studies of an aqueous solution of sodium dodecyl sulfate.

Experimental

Materials. The surfactant used was sodium dodecyl sulfate (NaDS), which has been prepared by the sulfation of dodecanol free from its homologues with chlorosulfonic acid,[35] followed by purification by solvent extraction using ethyl ether and recrystallization from ethanol. The purity was confirmed by the absence of a minimum in the surface tension *vs.* concentration curve. The ammonium nitrate used for the agar bridges was recrystallized from a pure commercial product.

Activity Measurement. The activity of sodium ions, a_{Na} was measured by using a Hitachi-Horiba N-5 pNa meter as a sodium responsive electrode. The cell used was

$$\text{pNa electrode}\left|\begin{matrix}\text{NaDS}\\(a_{Na})\end{matrix}\right|\begin{matrix}NH_4NO_3\\(1M)\end{matrix}\left|\begin{matrix}\text{KCl}\\(\text{saturate})\end{matrix}\right|\begin{matrix}\text{calomel electrode}\\(\text{saturate})\end{matrix}$$

Sodium chloride of a known activity was used to confirm that the electrode was acting correctly according to the Nernst equation. The activity of sodium ions, a_{Na}, was then calculated according to the following equation:

$$\log a_{Na} = \frac{0.4343F}{RT}(E_{Na} - E_{Na,0}) \tag{1}$$

where E_{Na} is the EMF of the cell; F, the Faraday constant; T, the absolute temperature; R, the gas constant, and $E_{Na,0}$, a constant depending on the calomel and the glass electrodes. The $E_{Na,0}$ value was determined by extrapolating an extrapolation function;[36]

[*1] Present address: Household Good Research Laboratory Kao Soap Co. Ltd., Sumida, Tokyo.

[*2] Present address: Fuji Photo-Film Co. Ltd., Nakanuma 210, Minami-Ashigara.

[*3] Present adress: Kawamura Institute of Chemical Research, Kamikizaki 2-7-8, Urawa.

$$\varDelta_{\text{Na}} = \frac{0.4343F}{RT}E_{\text{Na}} - \log C$$

to $C=0$; namely,

$$E_{\text{Na},0} = \frac{RT}{0.4343F}\lim_{C\to 0}\varDelta_{\text{Na}} \qquad (2)$$

where C is the concentration of sodium dodecyl sulfate.

As for the measurement of the activity of dodecyl sulfate ions, a_D, methods using the Hg/HgDS electrode[37] and a concentration cell using an ion-exchange membrane[28,38] or an oil-phase as a semipermeable septum[39] have been reported. However, the Hg electrode liberates Hg ions, which may influence the dissolved state of DS$^-$ ions in an unpredictable way, and the oil-phase cell is unfavorable because of the possibility of the solubilization of the oil by the surfactant micelles. Thus, the concentration cell using an ion-exchange membrane is preferable. A cell of the following type was used in the present experiment:

$$\begin{array}{c|c|c|c||c|c|c|c} \text{calomel} & \text{KCl} & \text{NH}_4\text{NO}_3 & \text{NaDS} & \text{NaDS} & \text{KCl} & \text{NH}_4\text{NO}_3 & \text{calomel} \\ \text{electd.} & & & & & & & \text{electd.} \\ (\text{sat}) & (\text{sat}) & (1\text{M}) & (a_\text{D}) & (a_{\text{D},10}) & (\text{sat}) & (1\text{M}) & (\text{sat}) \end{array}$$

Here, || indicates the anion-exchange membrane, NEOSEPTA AV-4T, the product of the Tokuyama Soda Co., Ltd.; NaDS ($a_{\text{D},10}$), the reference solution of 10 mmol/l NaDS, and (sat), a saturated solution. A 1 M NH_4NO_3 solution was used for the agar bridges.

The ion-exchange membrane used was 0.16 cm thick. It was cut in 1.5 cm square piece and was made permeable only to dodecyl sulfate ions by soaking it in a 10 mmol/l NaDS solution for two days. Immediately before use, it was rinsed with as little water as possible and firmly supported by pressing it between two franged tubes, 5 mm in inner diameter, containing the sample and referenee solutions. The reference solution of 10 mmol/l NaDS was chosen since the electrode potential was confirmed to be almost constant near this concentration. A steady EMF value, E_D', was exhibited after 30 to 60 min, and the equilibrium value, E_D, was obtained by subtracting from E_D', the asymmetry potential measured, after each measurement of E_D', for the cell prepared by filling both sides of the membrane with the 10 mmol/l NaDS solution. To obtain reproducible results, the membrane was renewed after three successive measurements. The calculation of the activity, a_D, will be described later.

Surface Tension Measurement. The surface tension was measured by the Wilhelmy method using a Shimadzu Surface Tensiometer, ST-1. The vassel containing the solution was doubly covered with glass plates, each having a small hole at its center for the passage of a rod attached to a vertical hanging plate. Contamination from the surrounding atmosphere and the evaporation of water during the measurement were practically avoided by this device. The surface tension was automatically recorded with the time, In cases in which the surface tension decreased with the time, the steady values finally obtained or extrapolated were used for the calculation.*

The EMF and surface tension measurements were carried out at 25 °C.

Results and Discussion

Surface Tension. The surface tension *vs.* concentration relation is shown in Fig. 1. As may be seen, the surface tension decreases with an increase in the concentration and a sharp break point appears at about 7.6 mmol/l, contrary to the curve without a sharp break near the CMC reported by Mysels.[6] Above the CMC, the surface tension stays nearly constant up to about 20 mmol/l, beyond which it decreases slowly with the concentration. Since, above CMC, the surface tension does not change with the time, a gradual though slight decrease is certain, as Mysels indicated.[6] It should be noted that the constancy of the surface tension of the surfactant solution above the CMC often cited[14,17] is not always valid.

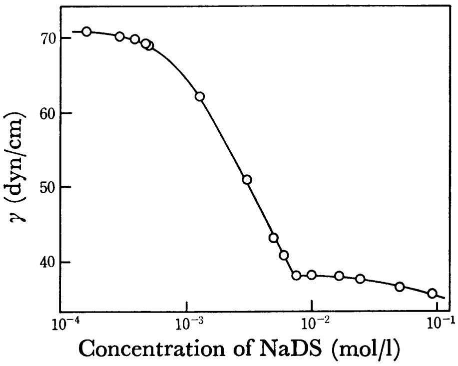

Fig. 1. Surface tension of aqueous NaDS solution.
γ: Surface tension of NaDS soln.

Activity and Activity Coefficient. The activity of Na$^+$ ions was calculated according to

$$\log a_{\text{Na}} = \frac{0.4343F}{RT}E_{\text{Na}} + 0.01 \quad (a_{\text{Na}} \text{ in mol/l}) \qquad (3)$$

which was obtained by putting the observed value of Eq. (2) into Eq. (1). The calculation of a_D is similar to that of a_{Na}, but it is somewhat complicated.

The EMF of the DS$^-$ ion-concentration cell is expressed as

$$E_\text{D} = \frac{\lambda RT}{0.4343F}\log\frac{a_\text{D}}{a_{\text{D},10}} \qquad (4)$$

where $\lambda = u_- - u_+$, and u_- and u_+ are the transport numbers of DS$^-$ and Na$^+$ ions respectively in the membrane. Then the extrapolation function takes the following form:

$$\varDelta_\text{D} = \frac{0.4343F}{\lambda RT}E_\text{D} - \log C \qquad (5)$$

By putting $\lambda=1$ in Eq. (5), we obtain, similarly to Eq. (2),

$$\log a_{\text{D},10} = -\lim_{C\to 0}\varDelta_\text{D}$$

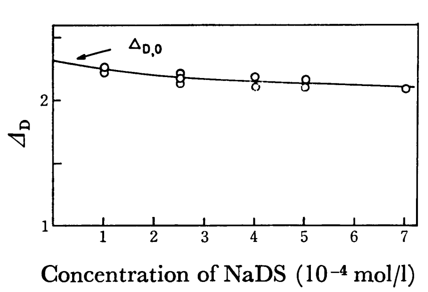

Fig. 2. Extrapolation of $\varDelta_\text{D}$ function.
$\varDelta_\text{D}$: Extrapolation function (see text)
$\varDelta_{\text{D},0}$: $\varDelta_\text{D}$ extrapolated to $C=0$

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* As to the aging of an aqueous surfactant solution, we should like to discuss it in detail elsewhere.

The plot of Δ_D *vs.* C is shown in Fig. 2; extrapolation gave $\log a_{D,10} = -2.30$. Then, a_D was calculated, according to Eq. (4), by

$$\log a_D = \frac{0.4343F}{RT} E_D - 2.30 \quad (a_D \text{ in mol/l}) \tag{6}$$

Here the assumption of $\lambda = 1$ might be valid, considering that the value of $dE_D/d \log C$ observed is equal to the value of $RT/0.4343F$ and that Δ_D *vs.* C is linear as a whole down to a low concentration of NaDS, where the plots are expected to deviate markedly from linearity if λ is slightly less than unity.* A rough estimation shows that λ is larger than 0.99. Also, the agreement between the calculated and observed values of the amount of adsorption below the CMC, to be discussed later, indicates λ as unity.

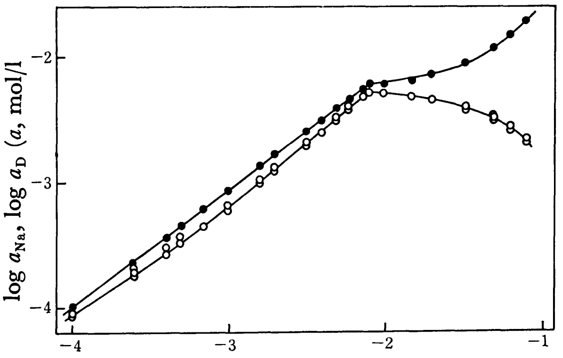

Fig. 3. Activities of Na$^+$ and DS$^-$ *vs.* NaDS concentration.
a_{Na}, a_D: Activies of Na$^+$ and DS$^-$ ions, respectively

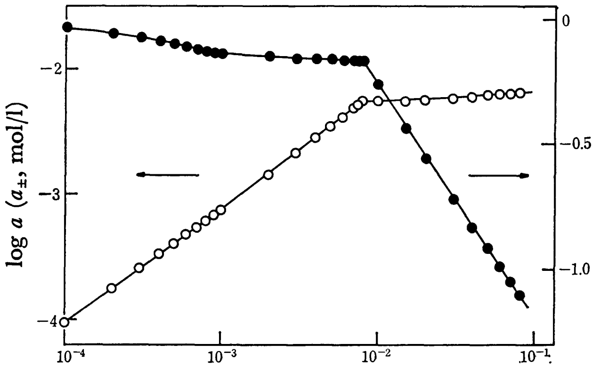

Fig. 4. Mean activity and activity coefficient of NaDS.
$a_\pm$, $f_\pm$: Mean activity and activity coefficient, respectively

The values of a_{Na} and a_D calculated according to Eqs. (3) and (6) are plotted against log C in Fig. 3. The mean activity, $a_\pm$, and the mean activity coefficient, $f_\pm$, are shown in Fig. 4. It is found that

$$\log f_\pm = -(0.033 \log C + 0.240) \quad (C \text{ in mol/l}) \tag{7}$$

holds for the concentration region from 1×10^{-3} mol/l up to the CMC and that

$$\log f_\pm = -(0.930 \log C + 2.125) \quad (C \text{ in mol/l}) \tag{8}$$

holds above the CMC up to about 80×10^{-3} mol/l. The coefficient of 0.033 of Eq. (7) is in accord with the estimation of Mysels.$^{6)}$ However, rather unexpectedly, $f_\pm = 0.68$ was obtained at the CMC. This is considerably smaller than the value of about 0.9 calculated by the modified Debye-Hückel equation, taking account of the molecular size.$^{29)}$ In this connection, it is noticable that a similar value of $f_\pm = 0.7$ was recently reported for cetyltrimethylammonium bromide near the CMC.$^{11)}$ Whether or not this low $f_\pm$ value is due to the dimerization or premicelle formation of surfactant molecules, as has been suggested in the report, requires further study. However, it is necessary at least to check experimentally the validity of the conventional formula used for the calculation of the activity coefficients of the large organic ions mentioned above.$^{29)}$

Adsorption Isotherm below the CMC. The Gibbs adsorption isotherm is written in its general form as:

$$-d\gamma = RT\sum_i \Gamma_i \ln a_i \tag{8}$$

where γ is the surface tension of a solution, and Γ_i and a_i, the amounts of adsorption and the activity of the i'th component of the solutes in the solution respectively. For the 1—1 electrolyte, Eq. (8) takes the form:

$$\Gamma = -\frac{d\gamma}{2RTd \ln a_\pm} = -\frac{d\gamma}{2RTd \ln f_\pm C} \tag{9}$$

A number of studies of the verification of the Gibbs adsorption isotherm have been reported, in which the activity coefficient has been properly calculated by, for instance, using a modified Debye-Hückel equation,$^{29,40)}$ or has been assumed to be unity.$^{41)}$ However, in the present experiment, it is possible to confirm Eq. (8) by a direct measurement of the activity change with the concentration of NaDS without reference to the activity coefficient.

For this purpose, Eq. (8) is rewritten for an aqueous solution of NaDS as

$$\Gamma = \frac{0.4343 d\gamma/d \log C}{RT(d \log a_{Na}/d \log C + d \log a_D/d \log C)} \tag{10}$$

According to Eq. (10), the amount of adsorption can be calculated from $d\gamma/d$ log C, d log a_{Na}/d log C and d log a_D/d log C, which are obtained from the tangents to the curves of Figs. 1 and 3. The calculated values of

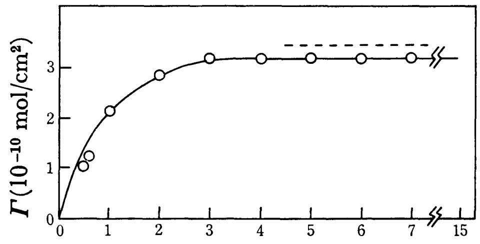

Fig. 5. Direct confirmation of Gibbs adsorption isotherm for NaDS soln.
Γ: Amount of adsorption
○: Γ calculated from steady γ value
----: Γ calculated from γ extrapolated to time zero
——: Γ observed

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* A detailed discussion of λ will be made in a following paper.

Γ are plotted against C in Fig. 5 as a solid line, together with the observed amount of adsorption (open circles) obtained by the radiotracer method using tritiated NaDS.[42] The agreement is seen to be satisfactory, except for a slight deviation for dilute solutions. This is the most direct confirmation of the Gibbs adsorption isotherm in that the calculation is solely based on the observed data, without any assumptions.

It may also be pointed out that, as was mentioned above, the surface tension used for the calculation is the steady value attained after a sufficient time. The value of Γ calculated by using the surface tension extrapolated to time zero is also shown as a broken line, but it does not agree with the observed value . This is an indication that the steady value of the surface tension is better taken as an equilibrium, and the attribution of the surface aging to impurities is not valid, at least in the present case.

The agreement of the calculated and observed Γ's also indicates that λ is unity, since the introduction of a λ value of less than unity reduces the calculated Γ to $\lambda\Gamma$, resulting in a disagreement of the observed and calculated Γ's. The argument is the same for Eq. (11).

Surface Tension above the CMC. As is shown in Fig. 1, the surface tension remains nearly constant above the CMC up to about 20 mmol/l, and then it decreases with the concentration of NaDS. Since it is often stated that the surface tension above the CMC is constant and that the constancy is an indication of the micelle formation being the phase separation,[14] it is worthwhile to confirm the observed decrease in the surface tension by an independent calculation. In this connection, Mysels has made an elaborate computer calculation of the surface tension of an aqueous NaDS solution above the CMC, assuming that the micelle formation obeys the mass action law and that the activity coefficient is independent of the concentration.[6] In the present study, however, the observed $a_{\pm}$ *vs.* C relation shown in Fig. 4 makes possible a simple and direct calculation of the surface tension above the CMC without such assumptions.

Since Γ is confirmed to be constant, 3.19×10^{-10} mol/cm^2,[42] the integration of Eq. (9) above the CMC gives

$$\gamma = \gamma_8 - \frac{2RT}{0.4343}\Gamma_8[\log a_{\pm} - a_{\pm,8}] \qquad (11)$$

where γ_8, Γ_8 and $a_{\pm,8}$ denote the γ, Γ and $a_{\pm}$ values of NaDS respectively, at the concentration of 8×10^{-3}mol/l. From the observed relations of $a_{\pm}$ *vs.* C, the surface tension above the CMC was calculated according to Eq. (11). The values of γ calculated are plotted against C in Fig. 6 as open circles, together with the observed surface tension, shown by a solid line. An agreement between the observed and calculated values is seen. Here, the constancy of Γ has been confirmed experimentally up to about 15 mmol/l,[42] but the agreement seen in Fig. 5 may suggest a further constancy of Γ up to about 80 mmol/l NaDS.

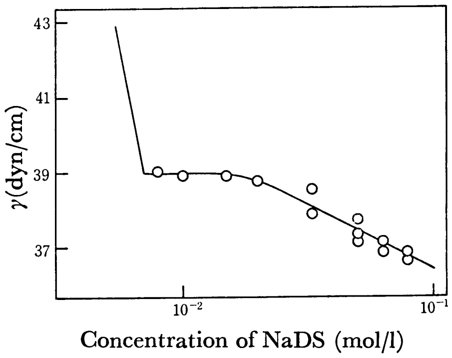

Fig. 6. Observed and calculated surface tension above CMC.
γ: Surface tension of NaDS soln
——: Observed γ
○: Calculated γ

TABLE 1. COUNTERION ATTACHMENT OF NaDS MICELLES

Degree of counterion attachment (r)	Method of measurement	Reference[a]
0.86	EMF (a_{Na})	26
0.85	Light scattering	43
0.84	EMF (a_{Na})	15, 37
0.82	Mass action law	22
0.82	Equil. dialysis	44
0.80	Osmotic coef.	45
0.78	EMF (a_{Na})	46
0.75	Mass action law	6, 47
0.74	Osmotic coef.	45
0.73	EMF (a_{Na}, a_{D})	Present exp.
0.72	Electrophoresis	48
0.63	EMF (E_{Na}, E_{D})	28
0.50	Zeta-potential	27
0.46	Mass action law	49

a) For further references see, E. W. Anacker, "Cationic Surfactants," edited by E. Jungermann, Marcel Dekker, Inc., New York (1970), p. 272.

Micelle Formation and Counterion Attachment. As has been mentioned, various mechanisms of micelle formation have been proposed,[14,23–25] but no satisfactory understanding has yet been obtained, at least experimentally. A similar situation prevails as to the degree of counterion attachment, r, of an ionic micelle. Various methods have been employed to estimate r; values ranging from 0.46 to 0.86 have been reported for NaDS, as shown in Table 1. The wide scattering of the data comes from the differences in the methods of measurement and in the assumptions necessary for the calculation. Also, in this case, the activity measurement enables us to give convincing answers to the questions of both the mechanism of micelle formation and the degree of counterion attachment.

According to the mass action law, the micelle formation of NaDS is expressed as a homogeneous equilibrium by[21,22]

$$p\mathrm{DS}^- + q\mathrm{Na}^+ \rightleftharpoons \mathrm{Na}_q\mathrm{DS}_p{}^{-(p-q)}$$

and the condition of equilibrium by

$$a_{\mathrm{M}}/(a_{\mathrm{D}}{}^q \cdot a_{\mathrm{Na}}{}^p) = \text{constant} \qquad (12)$$

where a_{M} is the activity of micelles, and p and q, the numbers of DS$^-$ and Na$^+$ ions respectively forming a micelle.

On the other hand, according to the phase separation theory,[23–25] micelles are considered as a separate microphase or pseudophase, and the micelle formation is expressed:

1) in the case of an unchanged phase separation, by

$$p\mathrm{DS}^- + p\mathrm{Na}^+ \rightleftarrows \mathrm{Na}_p\mathrm{DS}_p \quad \text{(separate phase)}$$

and the equlibrium condition by

$$a_{\mathrm{Na}}\cdot a_{\mathrm{D}} = \text{constant} \tag{13}$$

2) in the case of a charged phase separation, by

$$p\mathrm{DS}^- + q\mathrm{Na}^+ \rightleftarrows \mathrm{Na}_q\mathrm{DS}_p{}^{-(p-q)} \quad \text{(separate phase)}$$

and the equlibrium condition by

$$a_{\mathrm{Na}}{}^q\cdot a_{\mathrm{D}}{}^p = \text{constant}, \quad p \doteqdot q \tag{14}$$

Eqs. (12), (13), and (14) may be summarized as

$$\left.\begin{array}{ll} \log a_{\mathrm{D}} + r\log a_{\mathrm{Na}} \doteqdot \text{constant} & \text{mass action law} \\ \log a_{\mathrm{D}} + r\log a_{\mathrm{Na}} = \text{constant} & \\ \quad r = 1, \text{uncharged phase separation model} & \\ \quad r \doteqdot 1, \text{charged phase separation model} & \end{array}\right\} \tag{15}$$

where $r=q/p$.

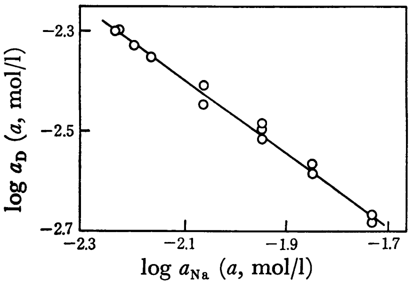

Fig. 7. Log a_{D} *vs.* log a_{Na} above CMC.
a_{D},a_{Na}: Activities of Na$^+$ and DS$^-$ ions, respectively observed above CMC

As is shown in Fig. 7, the plot of log a_{D} *vs.* log a_{Na} gives a straight line expressed by

$$\log a_{\mathrm{D}} + r\log a_{\mathrm{Na}} = \text{constant} \tag{16}$$

with $r=0.73$ and the constant $=-3.94$. According to Eq. (15), Eq. (16) clearly indicates that the charged phase separation is the most probable mechanism of micelle formation; the charged micelles with the degree of counterion attachment of 0.73 are considered to form up to a concentration of about 80 mmol/l. The value of $r=0.73$ is also listed in Table 1. It may be noted that, among the widely scattered values of r, that obtained in the present study is sufficiently reliable, since it is almost free from any assumptions or approximations. It should be noticed in connection with Eq. (16) that it is the product of $a_{\mathrm{D}}{}^p\cdot a_{\mathrm{Na}}{}^q$ that becomes constant above the CMC. Since $p\doteqdot q$ has been confirmed, $a_\pm=(a_{\mathrm{D}}\cdot a_{\mathrm{Na}})^{1/2}$ is not constant, but slowly increases with the concentration, as is shown in Fig. 4. This is not in agreement with the constancy of $a_\pm$ often stated in connection with the phase separation theory.[14,25] However, it is also contrary to the opinion that the phase separation requires a constancy of $a_\pm$ above the CMC,[20] since the charged phase separation model explains the change of $a_\pm$ above the CMC as has been described above.

The only question remaining is whether or not the aggregates bearing the net electrical charge can be separated as a phase. It may be possible only when the aggregates are separated as such a microphase as the form of micelles. For this reason, it is better called microphase separation or pseudophase separation, as has been proposed by Shinoda.[14,25] The increase in $a_\pm$ above the CMC also corresponds to the decrease in the surface tension in this region, as is shown in Fig. 1.

Equation (16) bears another implication. It is known[21,22,49] that the CMC of an ionic surfactant, C_{M}, decreases with the concentration of added salt, C_{S}, as

$$\log C_{\mathrm{M}} = -k\log(C_{\mathrm{M}}+C_{\mathrm{S}}) - m \tag{17}$$

where $C_{\mathrm{M}}+C_{\mathrm{S}}$ expresses the total counterion concentration, and k and m are constant. Here, if we replace C_{M} by a_{D} and $C_{\mathrm{M}}+C_{\mathrm{S}}$ by a_{Na}, we obtain an equation similar to Eq. (16), with k corresponding to r. This means that the application of Eq. (17) is not restricted to the solution at the CMC, but is extended above the CMC to the relation between the intermicellar activities (concentration) of single surfactant ions and counterions.

The numerical values of k and m of Eq. (17) have been reported to be 0.88 and 3.89[21] or 0.679 and 3.508[50] respectively. The constant of Eq. (16) is in close agreement with the former m value with an opposite sign, while the r value of Eq. (16) lies between the above two k's. The disagreement comes from the differences in the activity and concentration involved respectively in Eqs. (16) and (17). It is interesting to notice that the slope of Eq. (17) can be interpreted as the degree of counterion attachment from the viewpoint of mass action theory also, provided the aggregation number of the micelle (p in Eq. (12)) is large.[21,22]

The second- and higher-order CMC's could not be confirmed up to 80 mmol/l for an aqueous NaDS solution as far as the counterion attachment and activity measurements are concerned.

Intermicellar Ion Concentration. Although suggestions have been made referring the decrease in the intermicellar concentration of surfactant ions,[18,19] the constancy of the intermiceller concentration is practically assumed to be equal to C_{M} in most studies,[15–17] and its actual measurement has not been attempted.

Considering the electrical neutrality of the ions in the solution of NaDS as a whole, and the excess number of DS$^-$ ions compared with that of the Na$^+$ ions in Na DS micelles, the intermicellar concentration of the DS$^-$ ions is expected to be smaller than that of the Na$^+$ ions. In addition, the increase and decrease in the activities of the Na$^+$ and DS$^-$ ions respectively with concentrations above the CMC may suggest an increase and a decrease in the concentration of the respective ions. The intermicellar concentration of the DS$^-$ and Na$^+$ ions can be estimated from the a_{D} and a_{Na} measurenents as follows.

The activities of Na$^+$ and DS$^-$ ions above the CMC are expressed by

$$a_{\mathrm{Na}} = f_{\mathrm{Na}}C_{\mathrm{Na}} \quad \text{and} \quad a_{\mathrm{D}} = f_{\mathrm{D}}C_{\mathrm{D}} \tag{18}$$

where f_{Na} and f_{D} are the true activity coefficients, and C_{Na} and C_{D}, the intermicellar concentrations of the Na$^+$ and DS$^-$ ions respectively. Then we obtain from Eq.

(18)

$$a_\pm = f_\pm C_\pm \tag{19}$$

where

$$C_\pm = C_{\mathrm{Na}} C_{\mathrm{D}} \tag{20}$$

Further, we obtain from the condition of the electrical neutrality,

$$C_{\mathrm{Na}} = (C - C_{\mathrm{D}})(1-r) + C_{\mathrm{D}} \tag{21}$$

Now, if we neglect the effect of micelles on the activity coefficient above the CMC, Eq. (7) can be considered to hold above the CMC,⁶⁾ with C being replaced by $C_\pm$, and the following relation is obtained:

$$\log f_\pm = -(0.033 \log C_\pm + 0.240) \tag{22}$$

From Eqs. (19) to (22) with $r=0.73$, we obtain

$$C_{\mathrm{D}} = -0.185 + 0.685[0.0729C^2 + 2.92 \times 10^{0.496+2.068 \log a_\pm}]^{1/2} \tag{23}$$

According to Eq. (23), the intermicellar concentration, C_{D}, can be calculated from the $a_\pm$ *vs.* C relation above the CMC as is shown in Fig. 4. The values of C_{Na} can be calculated by putting the value of C_{D} thus obtained into Eq. (21). The C_{D} and C_{Na} values thus calculated are plotted against C in Fig. 8, together with $C_\pm$.

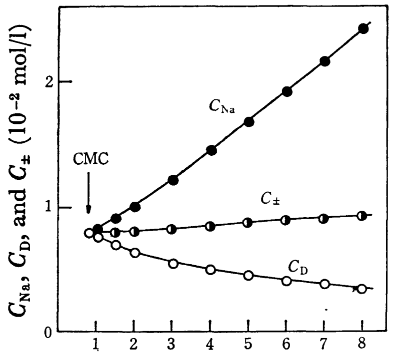

Fig. 8. Intermicellar concentrations of Na⁺ and DS⁻ ions and $C_\pm$.
C_{Na}, C_{D}: Intermicellar concentrations of Na⁺ and DS⁻ ions, respectively
$C_\pm$: $(C_{\mathrm{Na}} \cdot C_{\mathrm{D}})^{1/2}$

It may be seen that C_{Na} increases, while C_{D} decreases, with the increase in the NaDS concentration. The mean intermicellar concentration, $C_\pm$, is seen to be nearly constant or to increase only slightly with the concentration. Here, it should be noted that the actual micellar concentration, $C - C_{\mathrm{D}}$, is larger than the usually assumed concentration, $C - C_{\mathrm{M}}$.¹⁵˒¹⁶˒²¹˒²²⁾ However, the problem of the influence of micelles on the activity coefficient of NaDS remains unsolved; it may affect the calculation of the intermicellar concentration of the surfactant.

Osmotic Coefficient above the CMC. Brady reported that, for some surfactants, the product of the concentration, C, and the osmotic coefficient, g, plotted against C consists of two straight lines, with a break point at the CMC, and that the slope of the straight line:

$$\mathrm{d}(gC)/\mathrm{d}C = \beta \tag{24}$$

is proper to each substance.⁵¹⁾

Applying the Gibbs-Duhem relation to Eq. (24), we obtain

$$\frac{\mathrm{d}(gC)}{\mathrm{d}C} = \frac{\mathrm{d}\ln a_\pm}{\mathrm{d}\ln C} = 1 + \frac{\mathrm{d}\log f_\pm}{\mathrm{d}\log C} = \beta \tag{25}$$

Eqs. (8) and (25) give $\beta=0.07$ above the CMC, which is comparable with the value of 0.06 for dodecylsulfonic acid.⁵²⁾

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