Activity Measurement and Colloid Chemical Studies of Aqueous Sodium Tetradecyl Sulfate Solutions

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A concentration cell using an ion-exchange semipermeable membrane as a septum for the measurement of the activities of ionic surfactants has been constructed, the method of measurement is here in described. The membranes used proved each to be exclusively permeable to one ion. The activities of both the tetradecyl sulfate ion (TS^-) and the counterion (Na^+) were determined. In the concentration region from 4.0×10^{-4} mol/l to CMC, $\log f_{\pm} = -(0.070 \log C + 0.283)$ held for the mean activity coefficient, $f_{\pm}$. The $f_{\pm}$ value at the CMC was found to be 0.81, considerably smaller than the value, 0.978, calculated by the Debye-Hückel equation taking account of the ionic size, 5.5 Å. Above the CMC the activity of the TS^- ion decreased, that of the Na^+ ion increased, and the mean activity slightly increased with the NaTS concentration. The Gibbs adsorption isotherm was applied for the adsorption of NaTS, using exclusively the observed data of the amount of adsorption, the surface tension, and the activities. A satisfactory agreement was obtained between the amount of adsorption observed and that calculated. The observed decrease in the surface tension above the CMC was confirmed by calculations using the Gibbs adsorption iostherm, the observed data of activity, and the amount of adsorption. The charged-phase separation model was verified as the mechanism of the micelle formation, and the degree of counterion attachment was calculated to be 0.81.

In order to elucidate various properties of the surfactants, such as the adsorption, the micelle formation, the solubilization, the dispersibility, the emulsification, and the detergency, the study of the activity of the aqueous surfactant solutions is important as a basis. However, there have been few such reports$^{1-5)}$ because of the difficulty of measurement at the low concentrations where surfactants are generally used and of the inevitable error involved in the method of measurement. Amoung the various methods of measurements,$^{4-7)}$ that of the electromotive force of a concentration cell with an ion-exchange membrane semipermeable to a surfactant anion has proved effective, and one of the present authors has previously applied this method to the study of sodium dodecylsulfate.$^{8)}$ The activity measurement of the ionic surfactant requires those of both the surfactant ion and the counterion; in the case of the anionic surfactant, the counterion activity can be measured also by means of a pNa-responsive electrode.$^{8-10)}$ The measurements of the activities of both ions by the concentration cells using anion and cation-exchange membranes are also possible.$^{1,2)}$ In the present paper, the activities of both the surfactant anion and the counterion were measured for aqueous sodium tetradecyl sulfate solutions by the EMF measurement of the concentration cell with an ion-exchange membrane, which had been specially constructed to prolong the life of the membrane and to obtain reproducible results. The activity coefficients were calculated for sodium tetradecyl sulfate, which was selected as a surfactant for comparison with the sodium dodecyl sulfate (NaDS) already reported,$^{8)}$ in order to study the effect of the change in the hydrophobic chain length on various properties of the aqueous solution.

The surface tension and the amount of adsorption were also measured by the Wilhelmy plate method and the radiotracer method respectively. From these results, the applicability of the Gibbs adsorption isotherm was examined with the results obtained below the CMC.$^{11-13)}$ The mechanism of the micelle formation and the surface tension lowering above the CMC were also discussed. Moreover, the counterion attachment of the micelle was calculated and compared with that of NaDS.

Experimental

Materials. For the preparation of sodium tetradecyl sulfate (NaTS), 99% tetradecyl alcohol, obtained by fractional distillation and its purity checked by gas chromatography (apparatus : Yanagimoto GC G-3DH), was sulfated with chlorosulfonic acid and neutralized with an aqueous sodium hydroxide solution. The inorganic salts thus formed were removed, and the product was then recrystallized several times from ethanol. To remove the unreacted tetradecyl alcohol, extractions with ether were continued until the minimum in the surface tension *vs.* concentration curve disappeared. The tritium-labelled sodium tetradecyl sulfate used for the adsorption measurement was synthethesized much$^{14)}$ as has previously been reported.$^{13)}$ Deionized water was used for the EMF measurement, and thrice-distilled water, for the surface-tension and absorption measurements. The ion-exchange membranes used for the surfactant-ion and Na^+-ion activities were an anion exchanger, Neosepta AV-4T, and a cation exchanger, Neosepta CL-25T, both supplied by the Tokuyama Soda Co., Ltd.

Apparatus and Measurements. *Adsorption*: The amounts of adsorption were measured by means of a thin-window gas-flowing tube devised for soft β-ray radioactivity measurements.$^{15)}$

Surface Tension: The surface tension was measured by Wilhelmy's vertical plate method using a strain gauge as a transducer; the steady value recorded after 4 hr was regarded as an equilibrium value.$^{16)}$ The error in the surface-tension measurement was ±0.05 dyne/cm for a glass plate 4 cm in perimeter.

Electromotive Force Measurement: The anion- and cation-exchange membranes used for the activity measurment were stored in an aqueous 0.5 M-NaCl solution. They were then rinsed with water and soaked in an aqueous 10.0×10^{-3}

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Saturated Calomel Electrode	1M-NH_4NO_3 2%-Agar Bridge	STS (C)	Membrane AV-4T or CL-25T	STS (C_0) 10 mM	1M-NH_4NO_3 2%-Agar Bridge	Saturated Calomel Electrode

Fig. 1. Surfactant concentration cell.

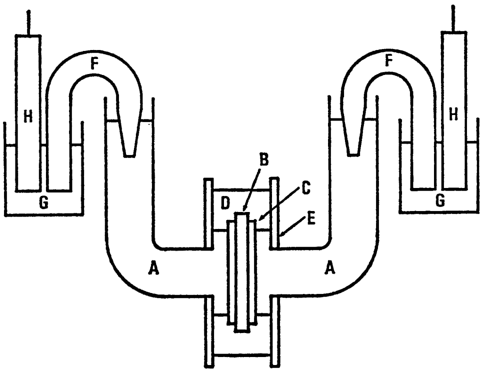

Fig. 2. Apparatus of surfactant concentration cell.
A: U-shaped glass cell with surfactant solution. B: Anion or cation exchange membrane. C: Silicone rubber washer. D: Low melting paraffin. E: Aluminum frame. F: 1 M-NH_4NO_3 agar bridge. G: Saturated KCl aqueous solution. H: Calomel electrode.

mol/l NaTS standard solution for two or three days in order to replace all of the exchangeable ions with TS^- or Na^+ ions. The membranes were then rinsed with deionized water and immediately fixed to the cells. The concentration cell shown in Fig. 1, which had been improved from a former one, was constructed as in illustratd in Fig. 2. In this figure, a U-shaped cell, A, with flanges held an ion-exchange membrane, B, with the aid of silicon rubber washers, C. They were tightly fixed between aluminum frames, E. Water evaporation from the open edge of the ion-exchange membranes, causing craks in the film and reducing the life of the membrane, was avoided by sealing the edge with low-melting-point paraffin, as is shown by D. A sample solution and the standard NaTS solution were introduced separately into the two chambers of A, one on either side of the membrane. The aqueous 10.0×10^{-3} mol/l NaTS solution was chosen as the standard solution because the change in the concentration of the standard solution in this region gave the relative insensitivity of the EMF. Each of the two calomel electrodes, H, was connected through 1 M-NH_4NO_3 agar bridges, F, to the solutions in A. Two-percent agar was used to prepare the bridges, and NH_4NO_3 was used to avoid the direct contact of NaTS with the KCl of the calomel, which would form insoluble potassium tetradecyl sulfate. Measurements of the EMF were made by using a high-impedance electrometer, Keithly model 610 C, with an input impedance of more than 10^{14} ohm, in an air-thermostated box at 32±1 °C; the EMF was recorded on a recorder of the Riken Electronic Co., Ltd., model SP-5. Both the chambers of A were filled with the same aqueous 10.0×10^{-3} mol/l NaTS solution, and they were renewed several times until the asymmetry potential (E_{as}) became constant. Each chamber was rinsed several times with each solution to be measured before the setting of the cell. Then, the solution in one chamber of A was replaced by the NaTS solution to be measured; the recording of the potential was started about 20 min after the setting. A steady EMF, E_l, was usually obtained 20 min after the setting and kept constant for about 20 min, after which it gradually decreased. The E_{as} value was confirmed to be nearly constant during each measurment. The potential, E, of the concentration cell is obtained as:

$$E = E_l - E_{as}$$

When not in use, both chambers of the cell, A, were filled with the standard solution and the cell was placed in a vessel saturated with the vapor of the standard solution in order to avoid any evaporation of the solution in the cell and any change in the membrane properties. The membrane thus protected could be used continuously for about two weeks before the renewal of the membrane.

Results and Discussion

Calculation of Activity. The EMF of the concentration cell using a membrane permeable to the TS^- ion is given according to Nernst's equation as follows:

$$E_{TS} = (\lambda_- - \lambda_+)(2.303\,RT/F)\log(a_{TS}/a_{O,TS}) \qquad (1)$$

where λ_+ and λ_- are the transport numbers of the TS^- and Na^+ ions in the membrane respectively: a_{TS} and $a_{O,TS}$, the activities of the TS^- ion in the sample and the standard solutions respectively: F, the Faraday constant: R, the gas constant, and T, the absolute temperature. To determine the activity from Eq. (1), the values of λ_- and λ_+ must be estimated. The evaluation of $\lambda_- - \lambda_+$, usually made by referring to ions of known activities, is impossible in the present experiment because no activity coefficient data are available, but we have several reasons to believe that $\lambda_- - \lambda_+$ is close to unity. First, the differenciation of Eq. (1) with respect to log C gives:

$$\mathrm{d}E_{TS}/\mathrm{d}\log C = (\lambda_- - \lambda_+)(2.303\,RT/F)(\mathrm{d}\log a_{TS}/\mathrm{d}\log C) \qquad (2)$$

where C is the concentration of NaTS. In Eq. (2), since $\mathrm{d}E_{TS}$/dlog C is found to be nearly equal to 2.303 RT/F in the concentration range from 4.0×10^{-4} to 2.0×10^{-3} mol/l, Eq. (2) gives:

$$(\lambda_- - \lambda_+)\,\mathrm{d}\log a_{TS}/\mathrm{d}\log C = 1$$

Since dlog a_{TS}/dlog C is considered to be not larger than unity for such dilute solutions as in the present experiment, $\lambda_- - \lambda_+$ is expected to be nearly equal or larger than unity. However, from the definition, $\lambda_- + \lambda_+ = 1$. In order to satisfy both of these requirements, $\lambda_- = 1$ and $\lambda_+ = 0$ must hold, so $\lambda_- - \lambda_+$ may reasonably be taken to be close to unity. Moreover, as will be discussed below the linearity of the extrapolation function down to low concentrations of the NaTS solution, as is shown in Fig. 3, and the agreement between the calculated and observed amounts of the NaTS adsorption (Fig. 6) also indicate that $\lambda_- - \lambda_+$ may safely be taken to be unity. Thus, Eq. (1) is reduced to:

$$E_{TS} = (2.303\,RT/F)\log(a_{TS}/a_{O,TS}) \qquad (3)$$

According to similar reasoning and similar observed data, the conditions of $\lambda_-=0$ and $\lambda_+=1$ also hold for the cation-exchange membrane in the concentration range from 3.0×10^{-4} to 2.0×10^{-3} mol/l, and the EMF of the Na$^+$-ion concentration cell is given by:

$$E_{Na} = -(2.303\,RT/F)\log(a_{Na}/a_{0,Na}) \tag{4}$$

where $a_{0,Na}$ is the activity of the Na$^+$ ion in the solution of the standard electrode.

Experimental results of the EMF *vs.* concentration curve are expressed by Eqs. (3) and (4). In order to calculate the values of $a_{0,TS}$ and $a_{0,Na}$, the following extrapolation function, E', is constructed:[17]

$$E'_{TS} = (2.303\,RT/F)\log C - E_{TS} \tag{5}$$

The substitution of Eq. (3) into Eq. (5) gives:

$$\begin{aligned} E'_{TS} &= (2.303\,RT/F)(\log C - \log a_{TS} + \log a_{0,TS}) \\ &= (2.303\,RT/F)(-\log f_{TS} + \log a_{0,TS}) \end{aligned}$$

Since $f_{TS}=1$ for $C=0$, the value of E'_{TS} extrapolated to $C=0$ gives:

$$E'_{TS,C=0} = (2.303\,RT/F)\log a_{0,TS}$$

from which $a_{0,TS}$ can be calculated. The activity, $a_{0,Na}$, is similarly calculated from the corresponding function, E'_{Na}. Figure 3 shows the E'_{TS} and E'_{Na} *vs.* $C^{1/2}$ plots and their extrapolation. The activities calculated, $a_{0,TS}$ and $a_{0,Na}$, are:

$$\log a_{0,TS} = -3.018 \text{ and } \log a_{0,Na} = -2.556$$

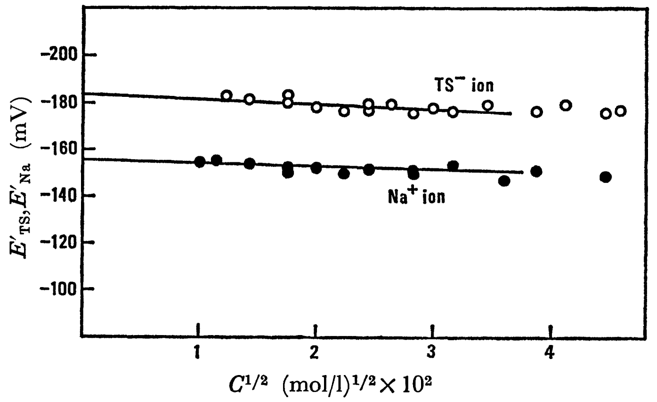

Fig. 3. Extrapolation of E'_{TS} and E'_{Na} function.
○: Extrapolation function (E'_{TS}) for TS⁻ ion.
●: Extrapolation function (E'_{Na}) for Na⁺ ion.

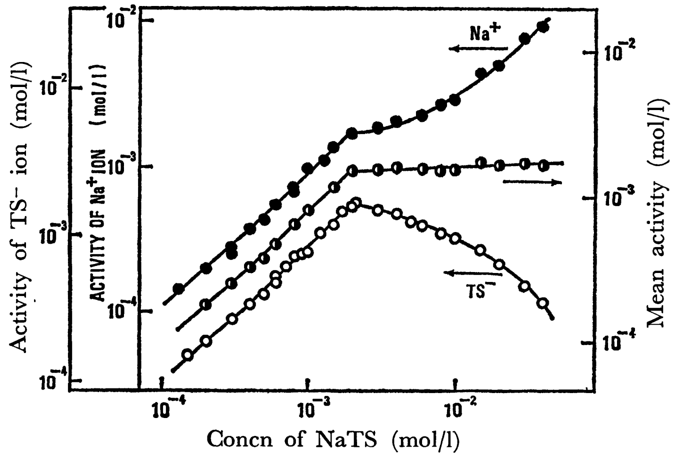

Fig. 4. Activities of TS⁻ ion, Na⁺ ion and the mean activity *vs.* NaTS concentration.
○: TS⁻ ion activity. ●: Na⁺ ion activity.
◑: Mean activity.

The a_{Na} and a_{TS} values calculated according to Eqs. (3) and (4) are shown in Fig. 4, together with the mean activity calculated by means of this definition:

$$a_\pm = (a_{TS}\cdot a_{Na})^{1/2} \tag{6}$$

The activity coefficient, $f_\pm$, calculated from the $a_\pm$ thus obtained was nearly unity at the concentration of 1.5×10^{-4} mol/l, and it gradually decreased with an increase in the concentration. In the concentration region from 4.0×10^{-4} to 2.0×10^{-3} mol/l (CMC),

$$\log f_\pm = -(0.070\log C + 0.283) \qquad C;\ \text{mol/l}$$

holds. It is noted that the mean activity coefficient at the CMC was found to be 0.81, considerably smaller than the value, 0.978, calculated according to the modified equation of Debye-Hückel using the mean ionic diameter of 5.5 Å.[18] Such a difference is similar to the cases of cetyltrimethylammonium bromide[19] and sodium dodecyl sulfate.[8] It may be explained by the effect of the long hydrophobic chain in the molecule, which is neglected in the Debye-Hückel equation, or by the so-called "premicelle" formation.[20]

Above the CMC the activity of the TS⁻ ion was found to decrease, while that of the Na⁺ ion increased with an increase in the concentration of the surfactant. As a result, the mean activity is not constant, as has been stated,[21] but slightly increases, as in the case of sodium dodecyl sulfate.[8] It should be noticed that the linearity of the extrapolation functions, E'_{TS} and E'_{Na}, observed down to a low concentration, C, proves $\lambda_- - \lambda_+$ and $\lambda'_+ - \lambda'_-$ to be unity for the anion- and cation-exchange membranes. This is because, for instance, Eqs. (1), (3) and (5) give:

$$E'_{TS} = (2.303\,RT/F)\{(1-\Delta)\log C - \Delta\log f_{TS} + \log a_{0,TS}\}$$

where $\Delta=\lambda_- - \lambda_+$. This equation means that, for $\Delta\neq1$, the $(1-\Delta)\log C$ term becomes infinity at $C=0$: a marked deviation from the linearity may be expected as tending to zero, but the linear plots of E'_{TS} down to low C values may exclude such a possibility. A similar argument can be made for the cation-exchange membrane.

Application of the Gibbs Adsorption Isotherm. The Gibbs adsorption isotherm was used to calculate the amount of adsorption, putting only the observed data of surface tension and activities into the isotherm; the values were then compared with the observed amounts of adsorption for NaTS at the surface of an aqueous solution. The amount of adsorption was calculated according to the Gibbs adsorption isotherm:

$$\Gamma = -(1/2.303RT)(d\sigma/d\log C)/\{(d\log a_{TS}/d\log C) + (d\log a_{Na}/d\log C)\} \tag{7}$$

by putting the dlog a_{TS}/dlog C, dlog a_{Na}/dlog C, and dσ/dlog C values, which were obtained from Fig. 4 and from the surface tension *vs.* log C plots in Fig. 5 respectively, into Eq. (7). Figure 6 shows the calculated value of Γ by a solid line and the observed value obtained by the radiotracer method, by circles. A

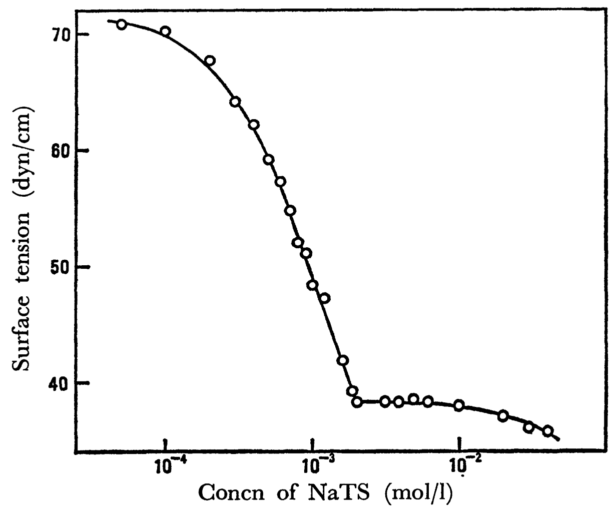

Fig. 5. Surface tension *vs.* NaTS concentration.

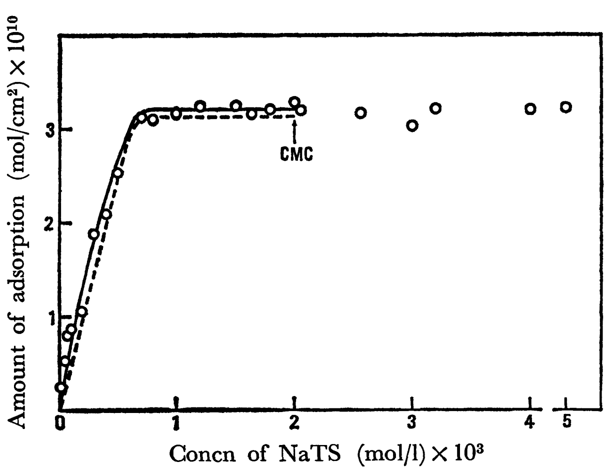

Fig. 6. Direct confirmation of the Gibbs adsorption isotherm.

○: Amount of adsorption observed. ——: Amount of adsorption calculated from activities data. ----: Amount of adsorption calculated assuming activity coefficient to be unity.

satisfactory agreement was obtained between them, and the saturate value of Γ was found to be 3.21×10^{-10} mol/cm². It should be noted that the agreement obtained here is another evidence that the $\lambda_- - \lambda_+$ value for the anion-exchange membrane is unity and that the $\lambda'_+ - \lambda'_-$ value for the cation-exchange membrane is also unity, since the introduction of $\lambda_- - \lambda_+$ and $\lambda'_+ - \lambda'_-$ values less than unity reduces the calculated Γ values according to:

$$\Gamma = -(1/2.303RT)(\mathrm{d}\sigma/\mathrm{d}\log C)/\{(\mathrm{d}\log a_{\mathrm{TS}}/(\lambda_- - \lambda_+)\mathrm{d}\log C + (\mathrm{d}\log a_{\mathrm{Na}}/(\lambda'_+ - \lambda'_-)\,\mathrm{d}\log C\}$$

from that calculated by Eq. (7), and this causes a disagreement between the calculated and the observed values. That the values of λ_- and λ'_+ are unity and the observed activity of NaTS are thus confirmed to be valid.

The value calculated assuming the activity coefficient to be unity is shown as a broken line in Fig. 6. The agreement between these values and the observed ones is not so good as in the case of Γ calculated in terms of the activity data, but the deviation is not very large. Thus, the assumption of $f_{\pm} = 1$ often made proves invalid in this case also.

Calculation of the Surface Tension above the CMC. As is shown in Fig. 5, the surface tension of the NaTS solution above the CMC is not constant, but gradually decreases with an increase in the concentration of the surfactant. It is worthwhile to confirm the validity of the observed a_{TS} and a_{Na} values by comparing the surface tension observed and that calculted from the Gibbs adsorption isotherm using these activity data and the observed Γ values above the CMC. For this purpose, the following equation is used:

$$\sigma = \sigma_{\mathrm{CMC}} - 2.303RT\Gamma_{\mathrm{CMC}}\{(\mathrm{d}\log a_{\mathrm{TS}} + \mathrm{d}\log a_{\mathrm{Na}})_C - (\mathrm{d}\log a_{\mathrm{TS}} + \mathrm{d}\log a_{\mathrm{Na}})_{\mathrm{CMC}}\} \qquad (8)$$

which is obtained by the integration of the Gibbs adsorption isotherm:

$$\mathrm{d}\sigma = -2.303\,RT\Gamma(\mathrm{dlog}\,a_{\mathrm{TS}} + \mathrm{dlog}\,a_{\mathrm{Na}})$$

from the CMC up to the C concentration, taking account of the fact that the amount of adsorption observed above the CMC, Γ_{CMC}, was constant (3.21×10^{-10} mol/cm²), as is shown in Fig. 6. The surface tension calculated according to Eq. (8) is shown by circles in Fig. 7, where the observed value is indicated by a solid line. The agreement as a whole is good, just as in the case of sodium dodecyl sulfate.[8] Thus, the observed decrease in the surface tension, together with the observed a_{Na}, a_{TS} and $a_{\pm}$ values above the CMC may be comfirmed as valid. It is emphasized that the calculation of σ needs no assumption such as is necessary in the case of the calculation by the mass-action law.[22]

Micelle Formation and Degree of Counterion Attachment. As has been mentioned,[8] the mechanism of micelle formation by the mass-action law[22-24] gives:

$$a_{\mathrm{M}}/(a_{\mathrm{TS}})^p(a_{\mathrm{Na}})^q = K$$

or

$$p\log a_{\mathrm{TS}} + q\log a_{\mathrm{Na}} = \log a_{\mathrm{M}}/K \neq \text{const.} \qquad (9)$$

where a_{M} denotes the activity of micelles composed of p TS⁻ ions and q Na⁺ ions.

On the other hand, the phase-separation model[25]

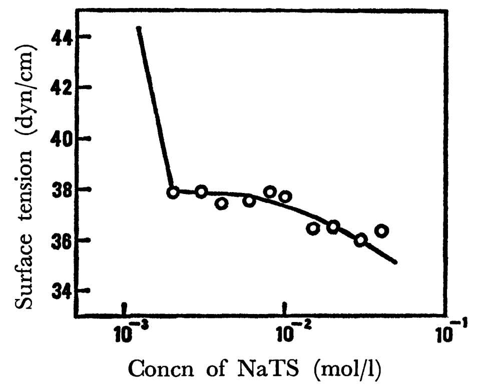

Fig. 7. Observed and calculated surface tension above CMC.

○: Surface tension calculated. ——: Surface tension observed.

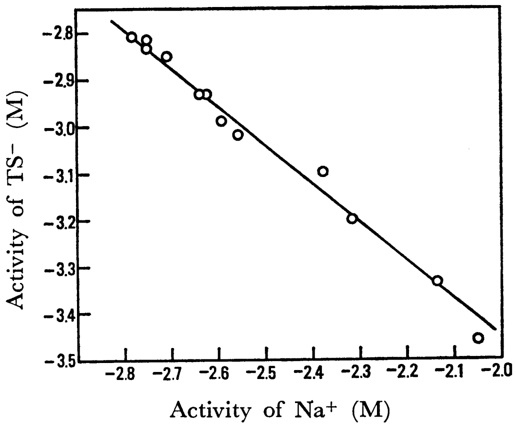

Fig. 8. $\log a_{TS}$ *vs.* $\log a_{Na}$ above CMC.

gives:

$$(a_{TS})^p(a_{Na})^q = a_M = \text{const.}$$

or

$$p \log a_{TS} + q \log a_{Na} = \text{const.} \tag{10}$$

where $p=q$ represents the uncharged-phase separation model, and $p \neq q$, the charged-phase separation model, respectively.

The plots of log a_{TS} against log a_{Na} are shown in Fig. 8. As is shown in the figure, a linear relation with $p \neq q$ is obtained; this proves that the charged-phase separation model is valid, just as in the case of sodium dodecyl sulfate.[8] The value of $p/q=0.81$ obtained as the degree of counterion attachment is somewhat larger than the latter. Though such a tendency is theoretically to be expected, it is significant that it is experimentally confirmed by reliable data. Similar results are also obtained in the system of NaTS in ethanol–water mixtures of various compositions, they will be reported in the following paper.

The gradual increase in $a_\pm$ with the surfactant concentration is expressed from Eqs. (6) and (10) with $p/q=0.81$ as:

$$a_\pm = K^{1/2}(a_{Na})^{0.095} \tag{11}$$

According to Eq. (11), $a_\pm$ slowly increases as a_{Na} increases, that is, with an increace in the concentration of the surfactant.

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