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Studies of the Dissolved State of Sodium Tetradecyl Sulfate in Ethanol-Water Mixtures by Measurements of the Activity

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The details of electromotive-force measurement by means of a concentration cell consisting of sodium tetradecyl sulfate (NaTS) in ethanol–water mixtures and of anionic and cationic ion-exchange membranes as septams were described. The membranes used proved to be permeable exclusively to the surfactant (TS^-) and Na^+ ions respectively. The activities of the TS^- and Na^+ ions were measured separately, and then the mean activity was computed as a function of the ethanol content in the solvent. Below the CMC, the activities for TS^- and Na^+ ions and the mean activity increased with an increase in the NaTS concentration, but decreased with an increase in the ethanol concentration. Above the CMC, the activity of the TS^- ion decreased, whereas that of the Na^+ ion increased; the mean activity also slightly increased with an increase in the NaTS concentration. The values of CMC obtained were 1.5×10^{-3}, 1.7×10^{-3}, and 2.2×10^{-3} mol/dm^3 for 5, 10, and 15 vol % ethanol concentrations respectively. The mechanism of mixed micelle formation was also expressed by a charged phase-separation model in an ethanol–water mixture much as in the case of a simple aqueous solution. The degrees of counterion attachment were found to be 0.73, 0.68, and 0.62 for 5, 10, and 15 vol % ethanol respectively. The intermicellar concentrations of TS^-, (C_{TS}), and Na^+ ions, (C_{Na}), were calculated. With an increase in the NaTS concentration, C_{Na} monotonously increased, but C_{Na} decreased. At a given NaTS concentration, C_{Na} increased with an increase in the ethanol concentration, while C_{Na} was approximately constant.

It is well known that the addition of a nonelectrolyte to a surfactant solution greatly affects the nature of the solution. Many studies regarding the influence of nonelectrolytes on the CMC values have been performed with anionic[1–4] and cationic[1,5,6] surfactants. On the addition of alcohols, the decrease in the CMC was explained by the diluted surface-charge density and the enhanced hydrophobic interaction on a micelle.[7,8] The increase in the CMC was correlated by the hydrophobic nature of the additives and their micellar breaking-up power.[1] Though there have been investigations of the effects of the addition of nonelectrolytes, there have been relatively few studies of the adsorption from the solution,[9] the state of the solution[10] and the micellar state;[11] this has been due in part to the difficulty of activity measurement. In a previous report, the various properties of an aqueous sodium tetradecyl sulfate (NaTS) solution were investigated by measuring its activity.[12] In the present paper, the dissolved state of NaTS in an ethanol–water mixture was studied by measuring the electromotive force (EMF) of the concentration cell. Ethanol was used as a nonelectrolyte additive since it mixes with water in all proportions; also, it is a good solvent for the surfactant. From the activity measurements, the mechanism of micelle formation, the degree of counterion attachment to the micelle, and the intermicellar concentration will be discussed.

Experimental

Materials. The sodium tetradecyl sulfate used was synthesized and purified as in the previous paper.[12] Special-grade ethanol was dehydrated by calcium oxide and distilled before use. Deionized water was used for the EMF measurement.

Procedure. The construction of the concentration cell and the method of measurement were the same as in the previous paper.[12] For the EMF measurements, a solution of 4.0×10^{-3} mol/dm^3 NaTS was used as a reference for each composition of the ethanol–water mixture. The surface tension was measured by the Wilhelmy plate method.[13]

Results and Discussion

Calculation of Activities. The values of the EMF of the TS^- ion, E_{TS}, and of the Na^+ ion, E_{Na}, were obtained from the concentration cells. According to Nernst's equation, E_{TS} and E_{Na} in an ethanol–water mixture are given by

$$E_{TS} = (\lambda_{TS}-\lambda_{Na})(2.303RT/F)\log(a_{TS}/a_{OTS}) \tag{1}$$

$$E_{Na} = (\lambda'_{TS}-\lambda'_{Na})(2.303RT/F)\log(a_{Na}/a_{ONa}) \tag{2}$$

where λ_{TS}, and λ_{Na} are the transport numbers of the TS^- and Na^+ ions for an anionic exchange membrane, and λ'_{TS}, and λ'_{Na}, those for a cationic membrane; F, the Faraday constant; R, the gas constant, and T, the absolute temperature. The values of a_{TS} and a_{Na} are the activities of the TS^- and Na^+ ions in a given solution, and a_{OTS} and a_{ONa}, the corresponding values in a reference solution. If the following Eqs. 3 and 4, may be assumed:

$$\lambda_{TS} = 1, \qquad \lambda_{Na} = 0, \tag{3}$$

$$\lambda'_{TS} = 0, \qquad \lambda'_{Na} = 1. \tag{4}$$

Eqs. 5 and 6 are obtained:

$$E_{TS} = (2.303RT/F)\log(a_{TS}/a_{OTS}) \tag{5}$$

$$E_{Na} = -(2.303RT/F)\log(a_{Na}/a_{ONa}). \tag{6}$$

If the values of a_{OTS} and a_{ONa} are known, the activities of the given solutions can be computed from Eqs. 5 and 6 by the substitution of the E_{TS} and E_{Na} measured. Plotting the following extrapolation function,[14] a_{OTS} and a_{ONa} can be obtained:

$$\begin{aligned} E'_{TS} &= (2.303RT/F)\log C - E_{TS} \\ &= (2.303RT/F)(-\log f_{TS} + \log a_{OTS}) \end{aligned} \tag{7}$$

$$\begin{aligned} E'_{Na} &= (2.303RT/F)\log C + E_{Na} \\ &= (2.303RT/F)(-\log f_{Na} + \log a_{ONa}). \end{aligned} \tag{8}$$

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Here, C denotes the concentration of NaTS, and f_{TS} and f_{Na}, the activity coefficients of the TS$^-$ and Na$^+$ ions at the C concentration respectively. If E'_{TS} and E'_{Na} are plotted against $C^{1/2}$ and the curves are extrapolated C to 0, a_{OTS} and a_{ONa} can be calculated by Eq. 9 from the extrapolated values of E'_{OTS} and E'_{ONa};

$$\left.\begin{aligned} \log a_{OTS} &= (F/2.303RT)E'_{OTS} \\ \log a_{ONa} &= (F/2.303RT)E'_{ONa} \end{aligned}\right\} \qquad (9)$$

because f_{TS} and f_{Na} are unity at $C=0$ in Eqs. 7 and 8. The mean activity and also each activity are calculated by introducing Eq. 9 into Eqs. 5 and 6.

The assumption of Eqs. 3 and 4 of NaTS in an ethanol–water mixture must be confirmed by experiments; however, verification is difficult. The influences were examined, as the addition of ethanol might affect the nature of the ion-exchangers by swelling, dissociation of ion-exchange fixed groups, and transport of the solvent through them; (osmosis effect), depending on the ethanol concentration. It has been reported that swelling, which is closely related to the effective mean pore size of a membrane, its decrease interfering with the ion transport because of the steric disturbance, is little affected by the addition of a low concentration of a lower alcohol, and even in a 20% concentration is nearly equal to that in water.[15] Therefore, the other influences were investigated from the point of view of whether or not Eqs. 10 and 11 for the anionic and cationic exchange membranes hold, using NaCl, the activities of which have been established.

$$\lambda_{Cl} = 1, \qquad \lambda_{Na} = 0 \qquad (10)$$

$$\lambda'_{Cl} = 0, \qquad \lambda'_{Na} = 1 \qquad (11)$$

The EMF values of the Cl$^-$ ion, E_{Cl}, and of the Na$^+$ ion, E_{Na}, resulting from the concentration cell with the reference solution containing the 4.0×10^{-3} mol/kg mixed solvent, were measured for NaCl in an ethanol–water mixture containing 20 wt % ethanol at 25 °C in a manner similar to that used for NaTS. The results obtained are shown in Fig. 1. The value of E_{Cl} increased, and that of E_{Na} decreased, linearly with an increase in the logarithmic concentration of NaCl in a way analogous to that in water. The activities were calculated from these results. The equations corresponding to those from 1 to 9 were also set up in the case of NaCl. The extrapolated E'_{OCl} and E'_{ONa} values were obtained as −144.3 and −144.5 mV respectively; then, a_{OCl} and a_{ONa} were calculated to be 3.64×10^{-3} and 3.61×10^{-3} mol/kg mixed solvent respectively. The activities of the Cl$^-$ and Na$^+$ ions and the mean activity were calculated separately. The mean activities of NaCl in the ethanol–water mixture are shown by the circles in Fig. 2. A rule for the activity coefficients of NaCl in ethanol–water mixtures has been states as[16,17]

$$(f_{\pm NaCl})_{org} = (f_{\pm NaCl})_{water}[(f_{\pm HCl})_{org}/(f_{\pm HCl})_{water}]. \qquad (12)$$

Here, $(f_{\pm NaCl})_{water}$ and $(f_{\pm HCl})_{water}$ are the activity coefficients of NaCl and HCl respectively, in water and $(f_{\pm NaCl})_{org}$ and $(f_{\pm HCl})_{org}$ are the activity coefficients of NaCl and HCl respectively in ethanol–water mixtures. In Eq. 12, $(f_{\pm NaCl})_{water}$ and $(f_{\pm HCl})_{water}$ were calculated using the Debye-Hückel equation, with the mean ionic radii of 4.0 Å for NaCl and of 4.3 Å for HCl. On the other hand, $(f_{\pm HCl})_{org}$ has been given by this empirical equation:[18]

$$\log (f_{\pm HCl})_{org} = -[0.6428C^{1/2}/(1+1.529C^{1/2})] + 0.1293 - \log(1+0.04104m) \qquad (13)$$

where C and m denote the concentrations of NaCl in a mol/dm^3-mixture and in a mol/kg-mixture respectively. The computed mean activities of NaCl in an ethanol–water mixture containing 20 wt % ethanol are shown as a solid line in Fig. 2. The experimental mean activities were in good agreement with the values calculated by means of Eqs. 12 and 13; therefore, Eqs. 10 and 11 were verified. Even in an ethanol–water mixture containing below 20 wt % ethanol, no significant changes occur in the characteristics of anionic and cationic exchange membranes; that is they swell well, their ion-exchange fixed groups fully dissociate, and no solvent transport takes place, as in water. Eqs. 3 and 4 for NaTS can also be established as in water.[12]

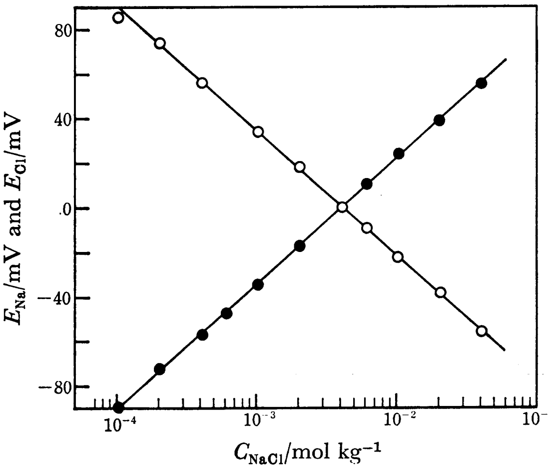

Fig. 1. Electromotive force of Na$^+$ and Cl$^-$ ions against NaCl concentration.
○; Na$^+$ ion, ●; Cl$^-$ ion.

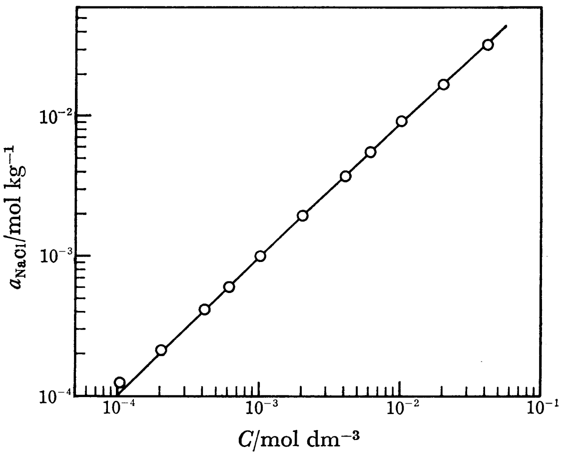

Fig. 2. Mean activity of NaCl in the 20 wt % ethanol–water mixture against NaCl concentration.
○; Experimental value, ——; calculated value by the Eqs. 12 and 13.

The values of E_{TS} and E_{Na} measured for NaTS in ethanol–water mixtures containing 5, 10, and 15 vol %

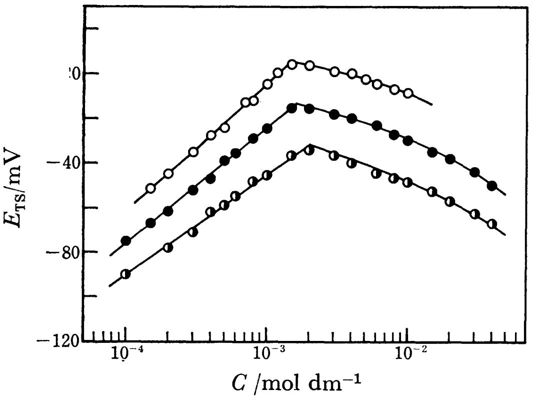

Fig. 3. Electromotive force of TS^- ion against NaTS concentration. Ethanol concentrations for 5 vol %; ○, 10 vol %; ●, and 15 vol %; ◑.
The curves for 10 and 15 vol % ethanol were transferred downward by 20 and 40 mV respectively.

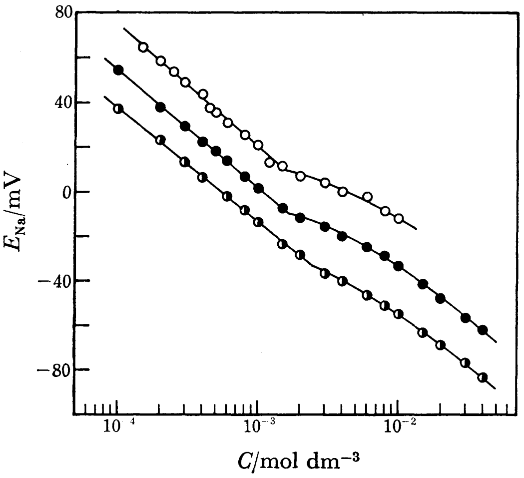

Fig. 4. Electromotive force of Na^+ ion against NaTS concentration. Ethanol concentrations for 5 vol %; ○, 10 vol %; ●, and 15 vol %; ◑.
The curves for 10 and 15 vol % ethanol were transferred downward by 20 and 40 mV respectively.

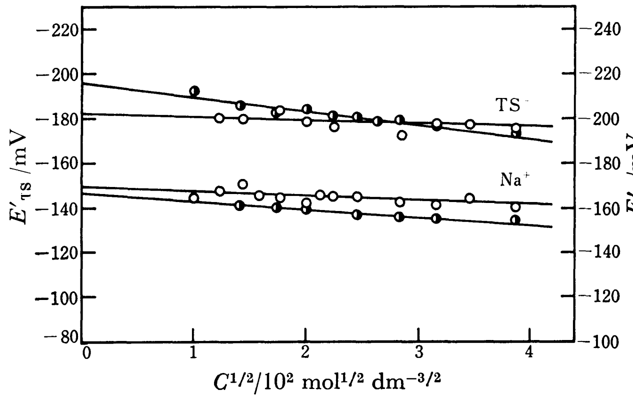

Fig. 5. Extrapolation of E'_{TS} and E'_{Na} against NaTS concentration.
○; 5 vol % etflanol concentration,
◑; 15 vol % etflanol concentration.

ethanol are shown in Figs. 3 and 4. With an increase in the logarithmic concentration of NaTS, E_{TS} increased linearly to the CMC and then decreased, while E_{Na} decreased linearly to the CMC and through a plateau region decreased in all ethanol concentrations. In order to calculate the activities of the TS^- and Na^+ ions, the plots by the extrapolation functions, 7 and 8, are shown in Fig. 5 for 5 and 15 vol % ethanol concentrations. The extrapolated values of E'_{OTS} and E'_{ONa}, and also the activities of a_{OTS} and a_{ONa} as computed by Eq. 9, are shown in Table 1. The activities of the TS^- and Na^+ ions, as calculated from Eqs. 5 and 6, are shown in Figs. 6 and 7. With an increase in the NaTS concentration, the activities of the TS^- and Na^+ ions increased, but above a breaking point concentration that of the TS^- ion decreased. The increase in the ethanol concentration caused a decrease in the activities of the TS^- and Na^+ ions. The breaking points agreed with the CMC's determined from the surface-tension measurements, which are shown in Fig. 8 for different ethanol concentrations. The CMC values were 1.5×10^{-3} for 5 vol%, 1.7×10^{-3} for 10 vol%, and 2.2×10^{-3} mol/dm^3 or 15 vol% ethanol. The mean activities, as calculated from the definition, are shown in Fig. 9. Above the

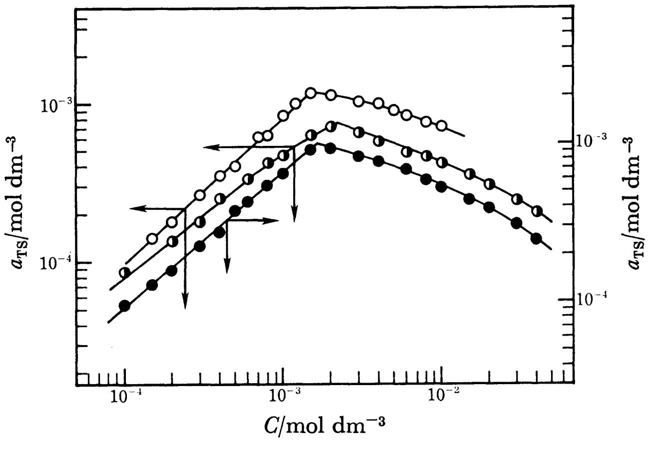

Fig. 6. Activity of TS^- ion against NaTS concentration. Ethanol concentrations for 5 vol %; ○, 10 vol %; ●, and 15 vol %; ◑.

TABLE 1. CALCULATED VALUES OF E_0' AND a_0 AT VARIOUS ETHANOL CONCENTRATIONS

C_E/vol %	E'_{OTS}/mV	E'_{ONa}/mV	a_{OTS}/mol dm^{-3}	a_{ONa}/mol dm^{-3}
0[a]	−183.0	−155.0	9.59×10^{-4}	2.78×10^{-3}
5	−182.1	−169.0	9.93×10^{-4}	1.63×10^{-3}
10	−189.0	−169.3	7.64×10^{-4}	1.61×10^{-3}
15	−196.3	−166.3	5.79×10^{-4}	1.81×10^{-3}

a) The data for 0 vol % ethanol are quoted from a previous report,[12] where the 10.0×10^{-3} mol/dm^3 NaTS solution was chosen as the reference solution.

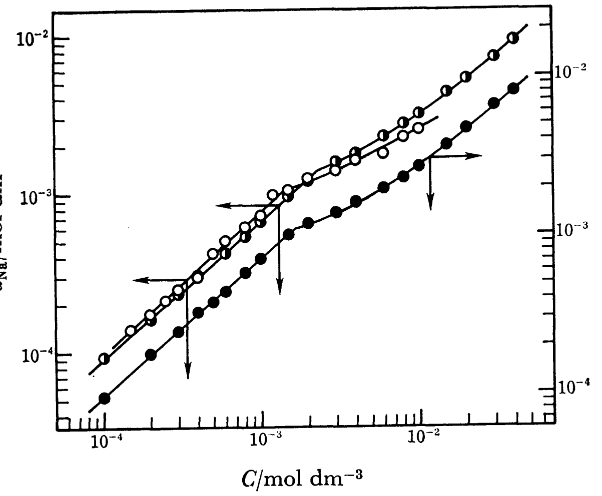

Fig. 7. Activity of Na^+ ion against NaTS concentration. Ethanol concentrations for 5 vol %; ○, 10 vol %; ●, and 15 vol %; ◑.

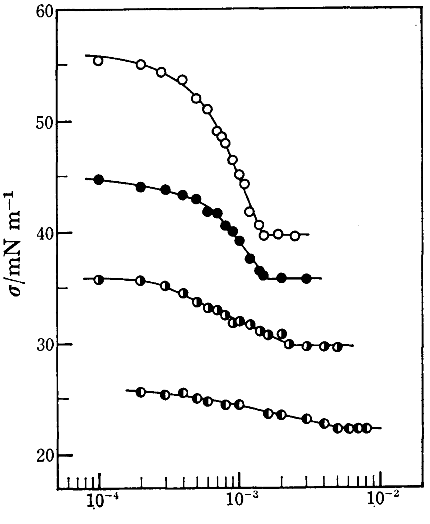

Fig. 8. Surface tension of NaTS in ethanol-water mixtures against NaTS concentration.
Ethanol concentrations for 5 vol %; ○, 10 vol %; ●, 15 vol %; ◑, and 20 vol %; ◐.
The curves for 10, 15, and 20 vol % ethanol were transferred downward by 5, 10, and 15 mN/m respectively.

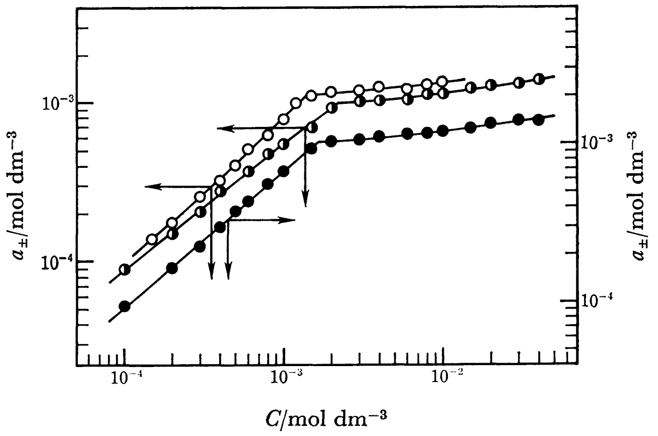

Fig. 9. Mean activity of NaTS against NaTS concentration. Ethanol concentrations for 5 vol %; ○, 10 vol %; ●, and 15 vol %; ◑.

CMC, the mean activities were not constant, but increased slightly with an increase in the NaTS concentrations, as in the aqueous solution without ethanol; also, the tangents increased with an increase in the ethanol concentration. The mean activity coefficients of NaTS are given for different ethanol concentrations, both below the CMC down to 1.0×10^{-4} mol/dm^3 and above it up to 40.0×10^{-3} mol/dm^3, by

$$\log f_{\pm} = -(\alpha \log C + \beta), \qquad (14)$$

where α and β are constants, the values of which are shown in Table 2.

TABLE 2. CONSTANT VALUES OF α AND β BELOW AND ABOVE THE CMC AT VARIOUS ETHANOL CONCENTRATIONS

C_{E}/vol %	$C\leq$CMC		$C>$CMC	
	α	β	α	β
0	0.070	0.283	0.996	2.702
5	0.102	0.421	0.924	2.932
10	0.157	0.648	0.904	2.725
15	0.212	0.890	0.868	2.673

Micelle Formation and Counterion Attachment. It has been reported that the micelle formation of NaTS in water can be explained by the charged phase-separation model[12] according to

$$p\mathrm{TS}^- + q\mathrm{Na}^+ \rightleftarrows \mathrm{TS}_p\mathrm{Na}_q{}^{-(p-q)}$$

where a micelle consists of $p\mathrm{TS}^-$ ions and $q\mathrm{Na}^+$ ions; therefore,

$$p \log a_{\mathrm{TS}} + q \log a_{\mathrm{Na}} = \text{constant}. \qquad (15)$$

Since, in the ethanol-water mixture, the mixed micelles are considered to be formed by the penetration of ethanol, penetration is taken account of in the discussion of the micelle-formation mechanism. If the charged phase-separation model holds in the mixed micelles, the formation of a mixed micelle, which consists of $p\mathrm{TS}^-$ ions, $q\mathrm{Na}^+$ ions, and n ethanol molecules, can be expressed as follows:

$$p\mathrm{TS}^- + q\mathrm{Na}^+ + n\mathrm{EtOH} \rightleftarrows \mathrm{TS}_p\mathrm{Na}_q\mathrm{EtOH}_n{}^{-(p-q)}$$

and also: $(a_{\mathrm{TS}})^p(a_{\mathrm{Na}})^q(a_{\mathrm{E}})=$constant where EtOH denotes ethanol. Then, the following equation is given:

$$p \log a_{\mathrm{TS}} + q \log a_{\mathrm{Na}} + n \log a_{\mathrm{E}} = \text{constant}. \qquad (16)$$

In the present study, the activity of ethanol is considered to be constant in Eq. 16 because the experiments were performed with the concentration of ethanol kept constant when that of NaTS was varied. Moreover, the decrease in the ethanol activity due to the formation of the mixed micelle can be neglected because the concentration of ethanol was much larger than that of NaTS. The value of n can be regarded as constant, since the concentrations of NaTS were varied within a narrow range of NaTS concentrations above the CMC. Therefore, Eq. 16 can be simplified to

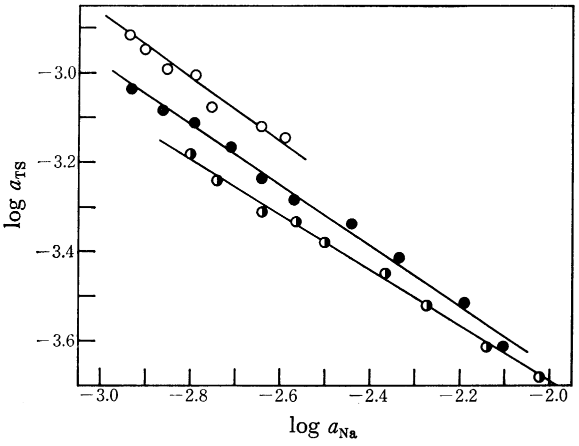

Fig. 10. Relation between log a_{TS} and log a_{Na} above the CMC. Ethanol concentrations for 5 vol %; ○, 10 vol %; ●, and 15 vol %; ◑.

$$p \log a_{TS} + q \log a_{Na} = \text{constant}, \qquad (17)$$

which can then be reduced to the same form as Eq. 15. According to Eq. 17, the degree of counterion attachment can be estimated from the slope of the curves if a linear relation is obtained when log a_{TS} is plotted against log a_{Na}. We attempted to examine whether or not Eq. 17 holds. The relations between log a_{TS} and log a_{Na} are shown in Fig. 10, where the plots give good linear relationships for each ethanol concentration. Thus, the mixed-micelle formation in the ethanol–water mixtures can also be explained by the charged phase-separation model. Moreover, the value of n proves to be constant in each concentration range. The degree of counterion attachment, $r = -q/p$, was obtained as 0.73 for 5 vol %, 0.68 for 10 vol %, and 0.62 for 15 vol % ethanol. Figure 11 shows the degrees of counterion attachment and the CMC values obtained. The CMC values decrease, pass through a minimum near the 5 vol % ethanol concentration, and then increase, while the degree of counterion attachment gradually decreases with an increase in the ethanol concentration.

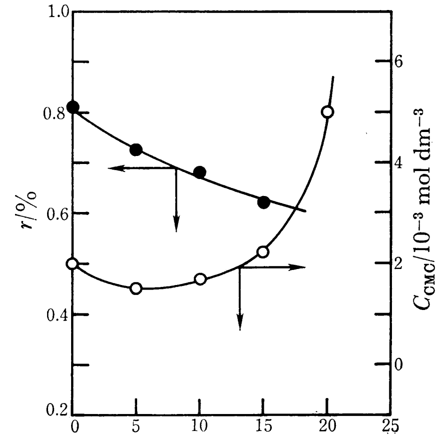

Fig. 11. Degree of counterion attachment and CMC value against ethanol concentration.
●; Degree of counterion attachment,
○; CMC value.

The decrease in the CMC value in the low ethanol-concentration range can be explained by the penetration of ethanol into the NaTS micelle forming the mixed micelle; this causes the decrease in the electrostatic energy on the micelle surface by the dilution of the charge density and the increase in the entropy of mixing.[7,8] The increase in the CMC value in the high ethanol-concentration range results from the increasing affinity of the hydrocarbon chain for ethanol; consequently, the ethanol-rich mixture is a good solvent for NaTS. The degree of counterion attachment gradually decreases; therefore, the charge density on the micelle surface decreases, the result mainly of the penetration of ethanol into the micelle and the decrease in the micelle size.[19]

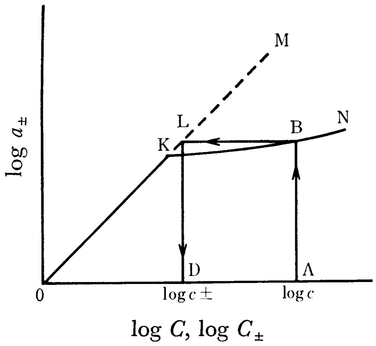

Fig. 12. Schematic representation of calculation of intermicellar concentration.
The broken line determined by the Eq. 14.

Calculation of Intermicellar Concentration. The principles of the calculation of the intermicellar concentration are shown schematically in Fig. 12, where the OKBN line represents the mean activity curve observed and where the K point is the CMC. If a relation between the mean activities and the concentrations of NaTS below the CMC is held similarly above the CMC, the broken line, KLM, which is obtained by the extension of the OK line to above the CMC indicates the relation between the mean activity and the intermicellar concentration. It can be considered that the micelles have no effects upon the relation between the mean activity above the CMC and the intermicellar concentration; that is the activity cofficient for the mean intermicellar concentration behaves the same as just below the CMC when the micelle concentration is very dilute. The mean concentration is defined by the same relation as that of below the CMC;

$$a_{\pm} = f_{\pm} \cdot C_{\pm} \qquad (18)$$

where $f_{\pm}$ and $C_{\pm}$ denote the intermicellar activity coefficient and the intermicellar concentration respectively. The value of $f_{\pm}$ is assumed to be expressed by Eq. 14. On the other hand, the mean intermicellar concentration is given by

$$C_{\pm} = (C_{Na} \cdot C_{TS})^{1/2}. \qquad (19)$$

Here, C_{TS} and C_{Na} express the intermicellar concentrations of the TS$^-$ and Na$^+$ ions, since they are not necessarily equal to each other. Then, the intermicellar mean concentration corresponding to the total concen-

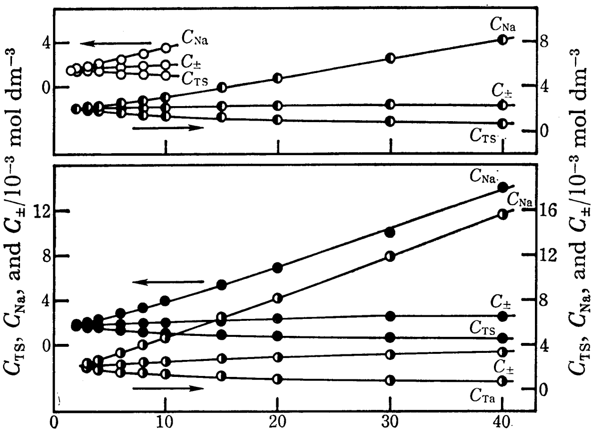

Fig. 13. Intermicellar concentrations of Na^+ and TS^- ions and intermicellar mean concentration.
C_{Na}, C_{TS}, and $C_\pm$ represent intermicellar concentrations of Na^+, TS^- ions and intermicellar mean concentration respectively. Ethanol concentrations for 0 vol %; ◐, 5 vol %; ○, 10 vol %; ●, and 15 vol %; ◑.

tration, C, of NaTS is obtained by the process of ABLD on the diagram shown in Fig. 12, while the intermicellar concentration of the TS^- and Na^+ ions for the solution with a total concentration of C are related to each other[20] thus:

$$C_{Na} = (C-C_{TS})(1-r) + C_{TS} \tag{20}$$

where r denotes the degree of counterion attachment. From Eqs. 18, 19, and 20, the intermicellar concentrations are given thus:

$$\begin{aligned} C_{TS} &= -(1-r)(C/2r) + (1/2r)[(1-r)^2C^2+4rC_\pm^2]^{1/2}, \\ C_{Na} &= -(1-r)(C/2) - (1/2)[(1-r)^2C^2+4rC_\pm^2]^{1/2}. \end{aligned} \tag{21}$$

The results calculated are shown in Fig. 13 for the four ethanol-water mixtures; in the calculation for the 0 vol% ethanol medium, the experimental data are quoted from the previous paper.[12] The intermicellar concentration of C_{Na} increased monotonously, while that of C_{TS} decreased and then asymptotically approached a constant value, with an increase in the NaTS concentration. It was noticed further that C_{TS} was approximately constant, independent of the ethanol concentration, while C_{Na} increased with an increase in the ethanol concentration. The intermicellar mean concentration also increased with increases in both the NaTS and ethanol concentrations. This increase indicates the effect of a good solvent for NaTS, as has been mentioned previously. Also, the difference in inclinations between the C_{TS} and C_{Na} curves in Fig. 13 is roughly proportional to $(1-r)$, which is the degree of dissociation of the Na^+ ion from the micelles.

It should be noted that such relations[21] as

$$C_{Na} = (C-C_{CMC})(1-r) + C_{CMC}$$

and $$a_{Na} = f_{Na}(C-C_{CMC})(1-r) + C_{CMC}$$

are not correct because C_{CMC} varies with an increase in C, as is shown in Fig. 13. The problem, however, remains of to what extent the presence of micelles influences the activity of intermicellar ions.

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