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Dissociation of Micelles and Intermicellar Concentrations of Aqueous Solutions of Calcium and Sodium Decyl Sulfates

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Activities of the surfactant ions and the counterions were calculated from the electromotive forces of concentration cell with ion-exchange membranes for the aqueous solutions of calcium ($Ca(DeS)_2$) and sodium (NaDeS) decyl sulfates. Moreover, the mean activities and the activity coefficients were obtained. From these activities, the valence effects of the counterions on the dissolved state of micellar solutions were studied. The following results were obtained: (1) The mean activities were not constant, but increased with the increase in the concentration of the two surfactants above the CMC; the slope of curve of the mean activity for $Ca(DeS)_2$ against its concentration was smaller than that for NaDeS. (2) The CMCs were 6.4 for $Ca(DeS)_2$ and 32.8 mmol dm^{-3} for NaDeS, respectively. (3) For the mechanism of micelle formation, the phase separation model was set up in both cases. (4) From this model, the degrees of dissociation of the micelles were calculated as 0.12 for $Ca(DeS)_2$ and 0.28 for NaDeS, respectively. (5) The intermicellar concentrations of the Ca^{2+}, the Na^+, and the decyl sulfate (DeS^-) ions were calculated; those of the counterions increased but those of the DeS^- ions decreased with the increase in their surfactant concentrations. Moreover, those of the DeS^- for $Ca(DeS)_2$ changed slowly while those for NaDeS changed steeply.

The dissolved state properties of surfactant solutions, *e.g.* the dissociation of micelles, a critical micellar concentration (CMC), effects of addition of electrolytes on the CMC and dissociation, theories and mechanisms of micelle formation, have been studied by many investigators in terms of surfactant concentrations but in disregard of the activity coefficients.1) Taking surface energy of micelles into account, Hall and Pethica have proposed recently a detailed theory of micelle formation.2) But on the other hand, from an experimental point of view, the activities of the surfactant ion and the counterion, being in equilibrium with the micelle, are necessary to investigate the dissolved state of micellar solution. This is because the micellar properties and validity of these theories can not be discussed without any assumption until the activities are obtained. Recently, correct measurements of activity for ionic surfactants by use of solid3–6) or liquid7–11) ion-exchange membranes have been reported. From these results for sodium alkyl sulfates, the following new knowledge has been obtained.4–6) With an increase in the surfactant concentration, (1) the mean activity and the mean intermicellar concentration of the surfactant above the CMC increased; (2) the activity of the surfactant ion decreased, (3) while that of the counterion increased. (4) The activity of the surfactant ion above the CMC was approaching a constant when much more electrolyte was added into the surfactant solution.10) (5) Depression of the surface tension above the CMC could be explained by the change of the mean activity.4,5)

It has been well known that the bivalent-metal ions affected the dissolved state of a micellar solution. Some reports on the activities for monovalent-metal alkyl sulfates are available, but those for bivalent- and polyvalent-metal alkyl sulfates are few.11) In the present paper, effects of valence in the counterions on the dissolved state are studied on the basis of the activities which are calculated from the membrane potentials developed across the ion-exchange membranes. Among these effects, we discuss the dissociation of micelles, the mechanism of micelle formation, and the intermicellar concentrations in the aqueous solutions of calcium ($Ca(DeS)_2$) and sodium (NaDeS) decyl sulfates.

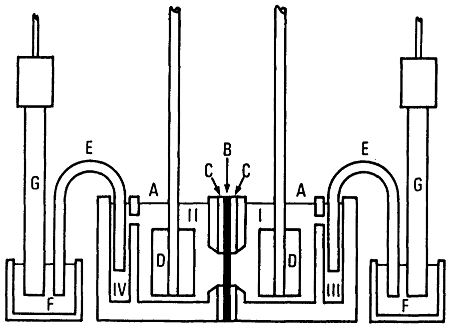

Fig. 1. Apparatus of surfactant concentration cell. A: Cell and solutions; (I) standard solution, (II), sample solution, and (III), (IV), compartments of bridge inserted. B: Anion or cation-exchange membrane. C: Silicon rubber washer. D: Stirrer. E: Agar bridge (2 M NH_4NO_3, 2% agar). F: Saturated KCl solution. G: Reference electrode.

Experimental

In order to obtain good stability and reproducibility in the measurement of electromotive force (EMF), the cell shown in Fig. 1 was used. The cell consisted of four compartments. A standard solution was poured into I and a sample solution into II. The compartments III and IV were connected to them through small holes to avoid any contamination of KCl by agar bridges into it, because EMF was greatly affected by such contamination. The solutions in I and II were gently stirred by means of stirrers, D, rotating at a constant velocity (130 rmp). The EMF developed across a solid ion-exchange membrane, B, was measured at 30±1 °C by means of an electrometer (Keithley, model 610C) through agar bridges (2 M NH_4NO_3, 2%-agar), E, and reference electrodes (Orion, model 90-01), G, and was recorded with time. The EMF was determined as an extraporated value at the time zero since it changed during the first 5 min and then decreased very slowly with time after it had passed a flat region. The solutions of 5.0 and 1.0 mmol dm^{-3} for $Ca(DeS)_2$, and 10.0 and 2.0 mmol

dm^{-3} for NaDeS were used as the standard solutions. Other experimental conditions and procedures were the same as in a previous paper.[5]

Results and Discussion

Single Ionic Activities and Mean Activities. The EMFs developing in the concentration cell of surfactant solution were measured for the two surfactants. The experimental values of the Ca^{2+} ion, E_{Ca}, and of the decyl sulfate (DeS^-) ion, E_{DeS}, are plotted against the concentration of $Ca(DeS)_2$ in Fig. 2 and those of the Na^+ ion, E_{Na}, and of the DeS^- ion, E_{DeS}, against the concentration of NaDeS in Fig. 3. According to Nernst's equation, the single ionic activities are given by

$$\left.\begin{aligned} E_{Ca} &= -(2.303RT/2F)\log(a_{Ca}/a_{OCa}) \\ E_{Na} &= -(2.303RT/F)\log(a_{Na}/a_{ONa}) \\ E_{DeS} &= (2.303RT/F)\log(a_{DeS}/a_{ODeS}), \end{aligned}\right\} \quad (1)$$

where R, T, and F are the gas constant, the absolute temperature, and the Faraday constant, respectively. The activities of the Ca^{2+}, the Na^+, and the DeS^- ions in the sample solutions are represented as a_{Ca}, a_{Na}, and a_{DeS}; those of the corresponding ions in the standard solutions as a_{OCa}, a_{ONa}, and a_{ODeS}. Their values, which were determined in the same way as in the previous paper,[5,6] are listed in Table 1. The activities of the individual ions for $Ca(DeS)_2$, having been calculated by Eq. 1, are shown in Fig. 4 and for NaDeS in Fig. 5. All the activities increased linearly with the increase in the surfactant concentration up to the CMC; after that concentration, those of the DeS^- ions in the two surfactant solutions decreased, while those of the Ca^{2+} and the Na^+ ions increased monotonously. It is also notable that the changes of activity of the Ca^{2+} and the DeS^- ions with the concentration of $Ca(DeS)_2$ are smaller than those of the Na^+ and the DeS^- ions of NaDeS. This finding comes mainly from the difference in the valence between the counterions and will be discussed later in connection with the dissociation of micelle and the intermicellar concentration. The mean activities calculated from the single ionic activities according to the usual definition are shown in Fig. 6; the values of the CMC, which were determined from the breaking points in their curves, are listed in Table 2 and agreed with those reported in the literature.[11,12] Below the CMC, the slope of the curve (mean activity coefficient) for $Ca(DeS)_2$ was smaller than that of NaDeS. This result can be explained by the difference

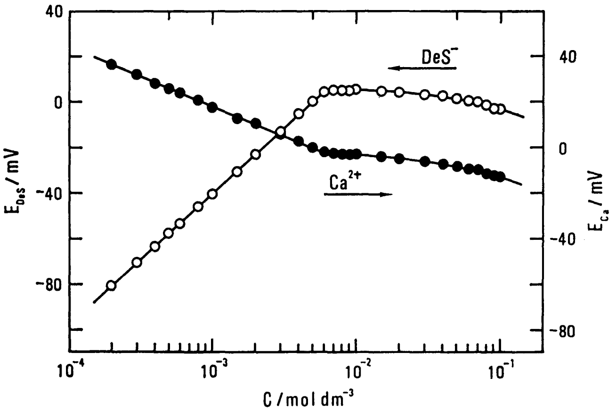

Fig. 2. Electromotive force of the Ca^{2+} and the DeS^- ions against concentration of Ca $(DeS)_2$.

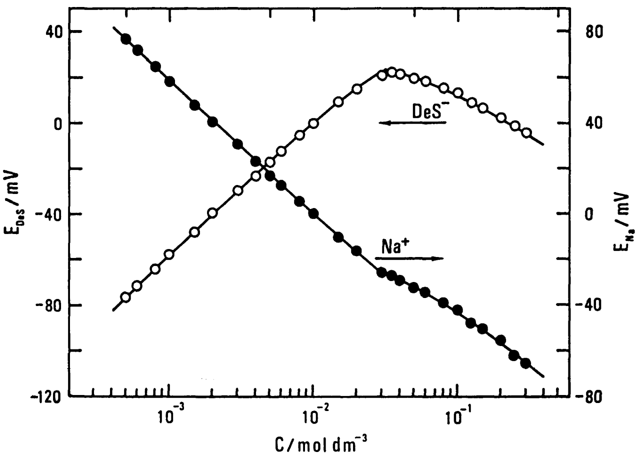

Fig. 3. Electromotive force of the Na^+ and the DeS^- ions against concentration of NaDeS.

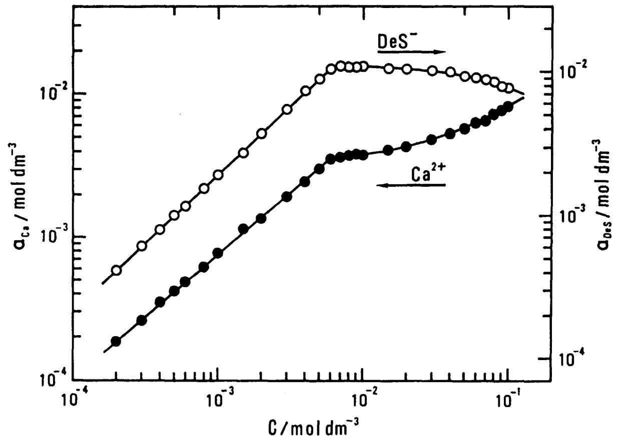

Fig. 4. Activities of the Ca^{2+} and the DeS^- ions against concentration of $Ca(DeS)_2$.

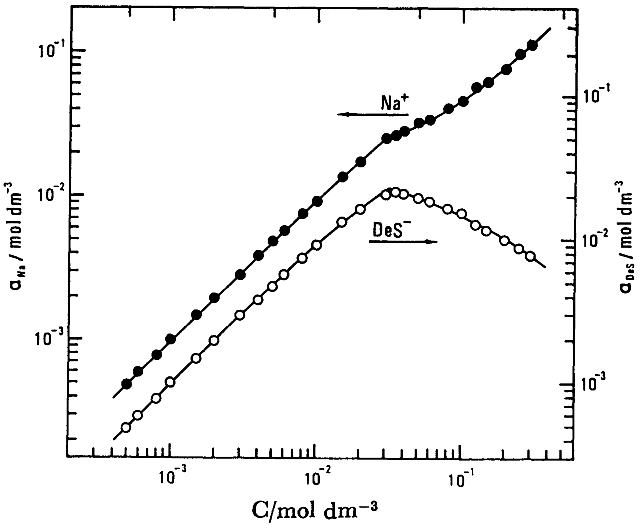

Fig. 5. Activities of the Na^+ and the DeS^- ions against concentration of NaDeS.

TABLE 1. ACTIVITIES OF THE STANDARD SOLUTIONS AND THE CONSTANTS OF K, L, AND M IN Eqs. 2 and 3

Surfactant	$\frac{a_{\mathrm{ODeS}}}{\mathrm{mmol\ dm^{-3}}}$	$\frac{a_{\mathrm{OCa}},\ a_{\mathrm{ONa}}}{\mathrm{mmol\ dm^{-3}}}$	$C\pm \leqq C_{\mathrm{CMC}}$			$C\pm > C_{\mathrm{CMC}}$	
			K	L	M	K	L
$\mathrm{Ca(DeS)_2}$	8.85	3.01	0.078	0.274	—	0.984	2.087
NaDeS	9.16	9.16	0.022	0.073	97.0	0.898	1.477

TABLE 2. THEDEGREES OF COUNTERION ATTACHMENT (r) AND DISSOCIATION OF MICELLES, CONSTANT ($\log K_{\mathrm{CaD}}$, $\log K_{\mathrm{NaD}}$), AND THE CMC

Surfactant	r	Dissociation		$\log K$	CMC/mmol dm^{-3}	
		This exp.	Literature		This exp.	Literature
$\mathrm{Ca(DeS)_2}$	0.44	0.12		−3.014	6.4	6.7(30 °C)[a]
NaDeS	0.72	0.28	0.38[12] 0.30[18] 0.23[10]	−2.788	32.8	31.6(25 °C)[12] 33.0(25 °C)[10]
$\mathrm{Co(DS)_2}$[b]			0.10[11]			1.15(30 °C)[11]

a) The value was obtained as an extrapolated one by means of the reference(Y. Moroi, K. Motomura, and R. Matuura, *J. Colloid Interface Sci.*, **46**, 111 (1974).), when $K_g=0.95$ and $\sigma=8.64\times10^4$ were used. b) Cobalt dodecyl sulfate.

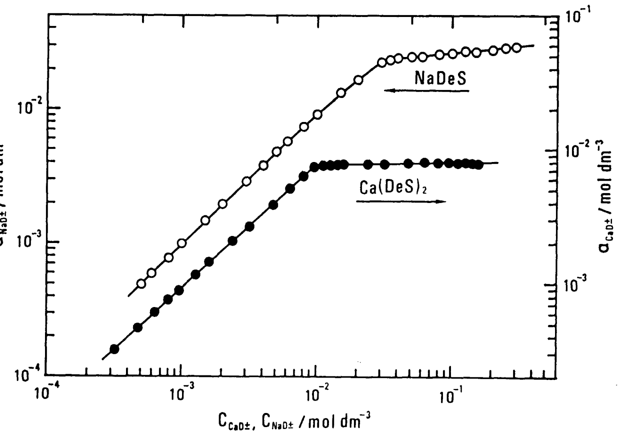

Fig. 6. Mean activities of $\mathrm{Ca(DeS)_2}$ and NaDeS against their mean concentrations.

in the valence of the counterions, like that considered in simple electrolytes. In spite of the decrease in the activities of the $\mathrm{DeS^-}$ ion above the CMC (shown in Figs. 4 and 5), the mean activities of $\mathrm{Ca(DeS)_2}$ and NaDeS did not remain constant, but increased gradually with the increase in their concentrations owing to a large increase in the activities of the corresponding counterions compensating completely for the decrease in the activities of the $\mathrm{DeS^-}$ ions. Figure 6 and K in Table 1, which will be defined by Eq. 2, show clearly that the mean activity of NaDeS above the CMC changes with the concentrations steeper than that of $\mathrm{Ca(DeS)_2}$, but the activity of the $\mathrm{DeS^-}$ ion decreases slowly in comparison with that of NaDeS (Fig. 4). This is because the increase in the activity of the $\mathrm{Na^+}$ ion was much larger than that in the activity of the $\mathrm{Ca^{2+}}$ ion. The mean activity coefficients of these surfactants within the concentration ranges illustrated are given by the following formula,[4-6] except for that of NaDeS below the CMC:

$$\log f_\pm = -(K\log C_\pm + L), \tag{2}$$

where $f_\pm$ and $C_\pm$ denote the mean activity coefficient and the mean concentration of the surfactant, respectively. The constants of K and L are tabulated in Table 1. The activity coefficient of NaDeS solution below its CMC is expressed empirically and satisfactorily by

$$\log f_\pm = -(K\log C_\pm + L) - MC_\pm^2, \tag{3}$$

where M is a constant and also shown in Table 1.

Formation and Dissociation of Micelles. Various mechanisms of micelle formation have been proposed, but little satisfactory experimental investigation has yet been reported. Recently the mechanism and the dissociation of micelles have been discussed by use of the activity only on 1-1 electrolytic surfactants, such as sodium dodecyl sulfate[4] or sodium tetradecyl sulfate.[5,6] But they should be also focussed on the micelles of 2-1 electrolytic surfactants such as $\mathrm{Ca(DeS)_2}$ in connection with the valence effect of counterions. If a micelle of $\mathrm{Ca(DeS)_2}$ is composed of $p\mathrm{DeS^-}$ ions and $q\mathrm{Ca^{2+}}$ ions which are always in equilibrium with the micelle, the micelle formation is expressed by

$$p\mathrm{DeS^-} + q\mathrm{Ca^{2+}} \rightleftarrows \mathrm{Ca}_q\mathrm{DeS}_p{}^{-(p-2q)}.$$

According to the mass action theory,[13-15]

$$a_{\mathrm{M}}/(a_{\mathrm{DeS}}{}^p\cdot a_{\mathrm{Ca}}{}^q) = \mathrm{const}$$

holds, where a_{M} denotes the activity of micelle. Then,

$$p\log a_{\mathrm{DeS}} + q\log a_{\mathrm{Ca}} \neq \mathrm{const} \tag{4}$$

is obtained. On the other hand, according to the phase separation theory,[15-17] in which a_{M} is assumed to be constant, the micelle formation is expressed by

$$a_{\mathrm{DeS}}{}^p\cdot a_{\mathrm{Ca}}{}^q = K_{\mathrm{CaD}},$$

therefore, $$p\log a_{\mathrm{DeS}} + q\log a_{\mathrm{Ca}} = K_{\mathrm{CaD}} \tag{5}$$

holds, where K_{CaD} is a constant. We can test which mechanism of the two is applicable, by plotting $\log a_{\mathrm{DeS}}$ against $\log a_{\mathrm{Ca}}$. Figure 7 shows two linear relationships for $\mathrm{Ca(DeS)_2}$ and NaDeS. Therefore, the phase separation theory is also a more probable mechanism for the micelle formation of $\mathrm{Ca(DeS)_2}$, as in the cases of 1-1 electrolytic surfactants.[4-6] The degrees of counterion attachment, $r=-q/p$, for $\mathrm{Ca(DeS)_2}(r_{\mathrm{Ca}})$ and NaDeS (r_{Na}) were obtained from each slope of the straight lines, and the constants were also calculated independl-

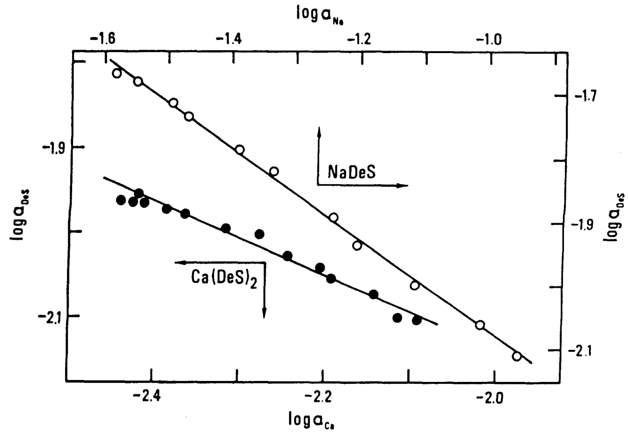

Fig. 7. Curves of log a_{Ca} and log a_{Na} against log a_{DeS} above their CMCs.

ently. The degrees of dissociation of micelles, therefore, are given as $1-2r_{Ca}$ and $1-r_{Na}$. Table 2 shows these values together with those reported.[10–12,18] It is found that the dissociation of Ca(DeS)$_2$ micelles was less than a half of that of NaDeS micelles. This finding can be explained by the idea that the Ca^{2+} ions remain rather near the surface of micelles because of the stronger coulombic interaction of the Ca^{2+} ion than that of the Na$^+$ ion; as the result of this, the micelle has a smaller dissociation. The observed degree of dissociation of Ca(DeS)$_2$ micelle can not be compared with ones reported in the literature, because there were few found. But the value, being slightly larger than that of bivalent-metal dodecyl sulfate as shown in Table 2, seems reasonable, because the shielding effect resulting from the high intermicellar concentration of Ca(DeS)$_2$ must lessen the counterion binding. The values for the NaDeS micelle in Table 2 scatter, but this discrepancy comes from the differences in the methods of measurement and in the assumptions made in the calculation. The value in the present study is reliable since it is almost free from assumption or approximations.

The smaller increase in the activity of the Ca^{2+} ion than in the Na$^+$ ion with the increasing concentrations of their surfactants above the CMCs observed already in Figs. 4 and 5 can be directly ascribed to the smaller degree of dissociation of the Ca(DeS)$_2$ micelle; in other words, the activity of Ca^{2+} ion varies with the increase in the intermicellar concentration of the Ca^{2+} ion which will be calculated later. Moreover, the mean activity of Ca(DeS)$_2$ is given by

$$a_{CaD\pm} = (a_{DeS}{}^2 \cdot a_{Ca})^{1/3} \tag{6}$$

according to the definition. If Eq. 5 is introduced into Eq. 6,

$$a_{CaD\pm} = (K_{CaD})^{2/3} \cdot a_{Ca}{}^{(1-2r_{Ca})/3} \tag{7}$$

is obtained. For NaDeS,

$$a_{NaD\pm} = (K_{NaD})^{1/2} \cdot a_{Na}{}^{(1-r_{Na})/2}, \tag{8}$$

where $a_{CaD\pm}$ and $a_{NaD\pm}$ denote the mean activities of Ca(DeS)$_2$ and NaDeS, respectively. The slope of the curves of mean activity are also given by

$$\left.\begin{aligned} \mathrm{d}\ln a_{CaD\pm}/\mathrm{d}\ln C_\pm &= [(1-2r_{Ca})/3] \cdot \mathrm{d}\ln a_{Ca}/\mathrm{d}\ln C_\pm, \\ \mathrm{d}\ln a_{NaD\pm}/\mathrm{d}\ln C_\pm &= [(1-r_{Na})/2] \cdot \mathrm{d}\ln a_{Na}/\mathrm{d}\ln C_\pm \end{aligned}\right\} \tag{9}$$

which are equal to the osmotic coefficients of their solutions.[4] As a_{Ca} and a_{Na} (shown in Figs. 4 and 5) increase, the gradual increases in their mean activities with the increasing concentration of their surfactants in Fig. 6 can be explained by Eqs. 7 and 8. Their increments are mainly restricted by the terms of $(1-2r_{Ca})/3$ and $(1-r_{Na})/2$ in Eq. 9. Therefore, the increment of $a_{CaD\pm}$ becomes smaller than that of $a_{NaD\pm}$. The osmotic coefficient of Ca(DeS)$_2$ was 0.03 and that of NaDeS was 0.10, which almost agreed with 0.07 of sodium dodecyl sulfate.[4]

Calculation of the Intermicellar Concentrations. From the definition, a_{Ca} and a_{DeS} above the CMC are expressed

$$a_{Ca} = f_{Ca} \cdot C_{Ca} \text{ and } a_{DeS} = f_{DeS} \cdot C_{DeS} \tag{10}$$

where f_{Ca}, f_{DeS}, C_{Ca}, and C_{DeS} are the activity coefficients and the intermicellar concentrations of Ca^{2+} and DeS$^-$ ions, respectively. According to Eq. 6,

$$a_{CaD\pm} = f_{CaD\pm} \cdot C_{CaD\pm} \tag{11}$$

holds, where

$$f_{CaD\pm} = (f_{Ca} \cdot f_{DeS}{}^2)^{1/3} \tag{12}$$

and

$$C_{CaD\pm} = (C_{Ca} \cdot C_{DeS}{}^2)^{1/3} \tag{13}$$

are the mean activity coefficient and the mean intermicellar concentration, respectively. If micelles have no effect upon the relation between the mean activity and the mean intermicellar concentration, namely if the

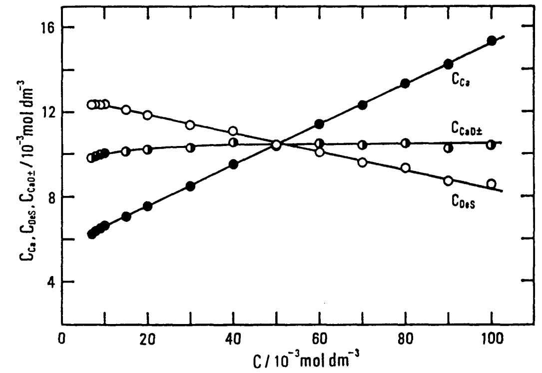

Fig. 8. Intermicellar concentrations of the Ca^{2+} and the DeS$^-$ ions and intermicellar mean concentration against concentration of Ca(DeS)$_2$.

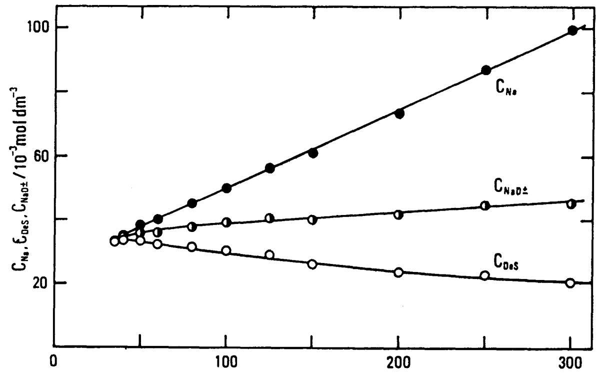

Fig. 9. Intermicellar concentrations of the Na$^+$ and the DeS$^-$ ions and intermicellar mean concentration against concentration of NaDeS.

The values were calculated by use of K=0.301 and L=0.591 in Eq. 2 which was set up satisfactorily within the range of concentration from 10.0 to 30.0 mmol dm^{-3} in stead of Eq. 3.

mean activity coefficient shows the same behavior as just below the CMC, then Eq. 2 holds above the CMC. Moreover, the conditions of electrical neutrality hold

$$C_{\mathrm{Ca}} = [(2C - C_{\mathrm{DeS}})(1-2r_{\mathrm{Ca}}) + C_{\mathrm{DeS}}]/2, \tag{14}$$

where C is the concentration of $\mathrm{Ca(DeS)_2}$. Substituting Eqs. 2, 6, 11, 12, and 13 into Eq. 14 yields

$$r_{\mathrm{Ca}}C_{\mathrm{DeS}}^3 + (1-2r_{\mathrm{Ca}})C\cdot C_{\mathrm{DeS}}^2 - 1000^{(L+\log a_{\mathrm{CaD}\pm})/(1-K)} = 0. \tag{15}$$

As a solution of Eq. 15, C_{DeS} is obtained, and then C_{Ca} is found by substituting C_{DeS} into Eq. 14. With respect to NaDeS, the intermicellar concentrations are given in a manner similar to that of $\mathrm{Ca(DeS)_2}$.[4,6]

$$\left.\begin{aligned} C_{\mathrm{DeS}} &= -(1-r_{\mathrm{Na}})(C/2r_{\mathrm{Na}}) + (1/2r_{\mathrm{Na}}) \\ &\quad \times[(1-r_{\mathrm{Na}})^2\cdot C^2 + 4r_{\mathrm{Na}}C_{\mathrm{NaD}\pm}^2]^{1/2} \\ C_{\mathrm{Na}} &= -(1-r_{\mathrm{Na}})(C/2) - (1/2) \\ &\quad \times[(1-r_{\mathrm{Na}})^2\cdot C^2 + 4r_{\mathrm{Na}}C_{\mathrm{NaD}\pm}^2]^{1/2} \\ C_{\mathrm{NaD}\pm} &= 100^{(L+\log a_{\mathrm{NaD}\pm})/(1-K)} \end{aligned}\right\} \tag{16}$$

Figures 8 and 9 show the calculated results, which are essentially similar in the two surfactants: namely, the intermicellar mean concentrations and the intermicellar concentrations of counterions increase, while those of the $\mathrm{DeS^-}$ ion decrease monotonously. But the increment and the decrement of $\mathrm{Ca(DeS)_2}$ with the increasing concentration are smaller than those of NaDeS.

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