August, 1983] © 1983 *The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *56*, *2341—2347 (1983)*

Ionic Composition of Micelles and the Dissolved State of the Mixed Surfactant Solutions of Calcium and Sodium Decyl Sulfates

Masakatsu Koshinuma
Laboratory of Chemistry, Faculty of Education, Chiba University, Chiba 280

(Received February 20, 1982)

Single activities of the decyl sulfate (DeS$^-$), the calcium (Ca^{2+}), and the sodium (Na$^+$) ions in mixed surfactant solutions of varying mole ratios (R_m=Ca(DeS)$_2$/NaDeS) were obtained at 30±1 °C by means of three kinds of EMF cells with ion-exchange membranes or Na$^+$-selective electrode. The results showed that with increasing concentrations above the cmc, the activity of the DeS$^-$ decreases gradually, while that of the Na$^+$ increased linearly; the activity of the Ca^{2+} remained nearly constant in the solution of $R_m=2$, but it showed a minimum in the solutions of $R_m=1$, 0.5 and 0.2. From these activities, the counterion attachments of the Ca^{2+}(r_{Ca}) and the Na$^+$(r_{Na}) and the degree of micellar charge ($1-2r_{Ca}-r_{Na}$) were obtained. With increasing concentration, r_{Ca} diminished gradually and approached a constant value, while r_{Na} and $1-2r_{Ca}-r_{Na}$ changed reversely except in the solution of $R_m=2$ where they were nearly constant. The Ca^{2+} was bound preferentially to the micelle surface. The Na$^+$, which almost diffused away for the solution of $R_m=2$, bound increasingly to lessen the electrical potential of the micelle as R_m decreased. The specific adsorption potentials and the electrical free energies of transfer of Ca^{2+} and Na$^+$ from solution to micelle were calculated as 1.7 and −18.4 kJ mol^{-1}, and 1.1 and −14.3 kJ mol^{-1} respectively at their cmcs. It was showed clearly that little dehydration from the counterion occured and the coulombic interaction played an important role in the counterion binding.

It is well known that valences of counterions of ionic surfactants and of added electrolytes influence markedly both the micellization and the micellar properties of surfactant solutions. A number of authors have shown that the electrical potential at the micelle surface played an important role in the formation of micelles.[1)] For solutions of mixed surfactants, it has been shown that the cmc value, the ionic composition and the dissociation of micelles changed greatly depending on the valence and the concentrations of each counterion.[2,3)] In explanation of the changes in the cmc, Shinoda formulated some theoretical equations,[1,4)] further, Lange[5)] and Moroi *et al.*[6)] have independently proposed the theoretical relations.

On the other hand, the dissolved state of micellar solution containing counterions with different valences can not be clarified unless the behavior of each ion in the mixed solution is investigated separately. Recently the behavior and activities of single ions have been studied by means of the electromotive force measurements using ion-selective electrodes[7—9)] or ion-exchange membranes[10—12)] in the single surfactant solutions and in the solutions of the added electrolyte.[13)] In the present paper, the degrees of dissociation of micelles and the ionic composition of the counterion in the micelles are studied in solutions of mixed surfactants of different valences on the basis of the single ionic activities. Furthermore, the standard free energies and the coulombic interaction energies of counterions transferring from solution to micelle surface will be calculated and discussed.

Experimental

Materials. The surfactants, calcium (Ca(DeS)$_2$) and sodium (NaDeS) decyl sulfates, were synthesized and purified in the normal way.

Electromotive Force Measurements. In order to investigate the single ionic behavior of the decyl sulfate ion (DeS$^-$), the calcium ion (Ca^{2+}), and the sodium ion (Na$^+$) in the mixed surfactant solution, three kinds of cell systems were used for the measurement of the electromotive force. For the DeS$^-$, a concentration cell was constructed as follows.

Saturated Ag–AgCl electrode	2 mol dm^{-3}-NH$_4$NO$_3$, 2%-Agar bridge	Sample solution Ca(DeS)$_2$+NaDeS	Anion-exchange membrane AV-4T
Standard solution NaDeS	2 mol dm^{-3}-NH$_4$NO$_3$, 2%-Agar bridge	Saturated Ag–AgCl electrode.	

The solutions of 10.0 and 2.0 mmol dm^{-3} of NaDeS were used as standards for the sample solutions having the concentrations above and below 2.0 mmol dm^{-3} of the DeS$^-$. The electrical potential developing across the membrane is termed E_{DeS}. For the Ca^{2+}, the multi-ionic potential was measured and the following cell was used:

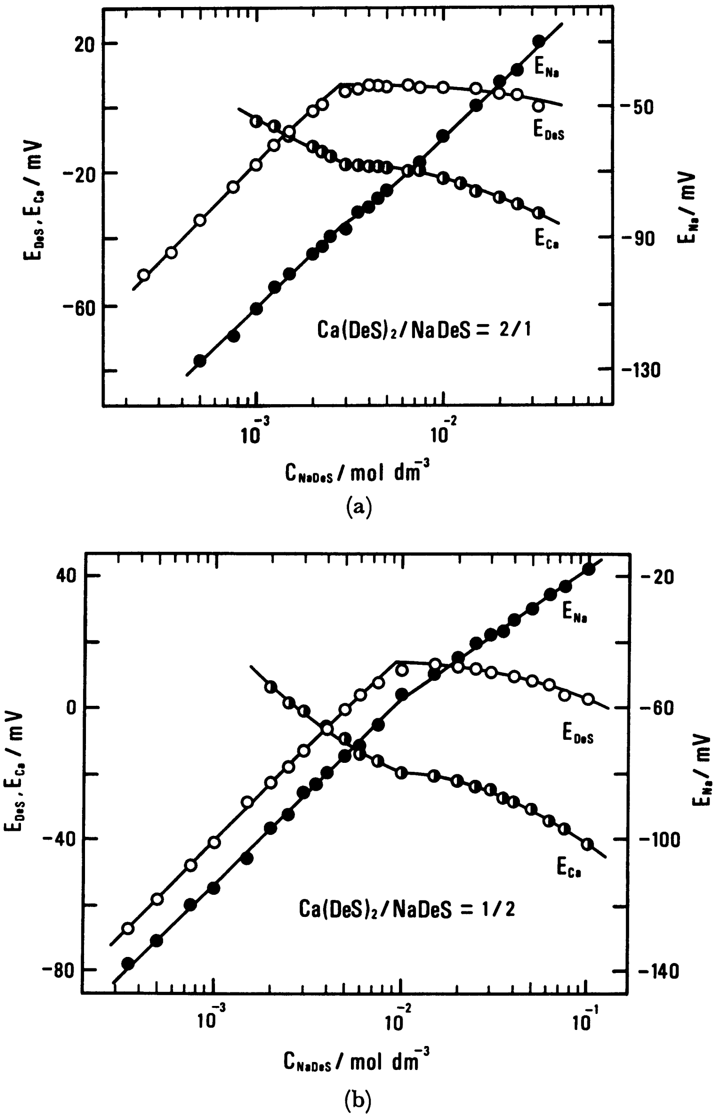
Saturated Ag–AgCl electrode	2 mol dm^{-3}-NH$_4$NO$_3$, 2%-Agar bridge	Sample solution Ca(DeS)$_2$+NaDeS	Cation-exchange membrane Cl-25T
Standard solution NaDeS	2 mol dm^{-3}-NH$_4$NO$_3$, 2%-Agar bridge	Saturated Ag–AgCl electrode,	

where the solution of 10.0 mmol dm^{-3} of NaDeS was also used as the standard solution. The potential generated on the membrane is denoted as E_{Ca}. The potentials of E_{DeS} and E_{Ca} were measured at 30±1 °C by means of an electrometer (Keithly, model 610C), and were recorded as functions of time. Other experimental conditions and procedures were the same as in a previous paper.[14)]

For the Na$^+$, the following cell was also set up:

Saturated Ag–AgCl electrode	2 mol dm^{-3}-NH$_4$NO$_3$, 2%-Agar bridge	Sample solution Ca(DeS)$_2$+NaDeS	Na$^+$-selective electrode

The potential, E_{Na}, of sodium-ion selective electrode (Horiba mfg. Co., model pNa-A) was measured with a pH meter (Hitachi-Horiba, model F-5) and recorded as a function of time.



(a)

(b)

Fig. 1. The electromotive force against the concentration of NaDeS in the mixed surfactant solutions of varying mole rations (R_m=Ca(DeS)$_2$/NaDeS).

Results and Discussion

Calculation of Single Ionic Activities. The observed values of E_{DeS}, E_{Ca}, and E_{Na} in the mixed surfactant solutions of $R_m=2$ and 0.5 (R_m: mole ratio of Ca(DeS)$_2$ to NaDeS) are plotted against the logarithmic concentration of NaDeS in Figs. 1a and b. From these EMF, the single ionic activities, though they are conventionally defined, can be calculated in terms of the following equations. According to the Nernst equation,

$$E_{DeS} = (2.303\,RT/F)\log(a_{DeS}/a_{ODeS}), \quad (1)$$

where R, T, and F denote the gas constant, the absolute temperature, and the Faraday constant. The activities of the DeS$^-$ in the sample and in the standard solutions are represented as a_{DeS} and a_{ODeS}, respectively. Since a_{ODeS} is obtained by the same procedure as in a previous paper,[14] the values of a_{DeS} can be calculated.

The multi-ionic potential is given by[15]

$$E_{Ca} = (2.303\,RT/F)[(a_{Na}+Ua_{Ca}-a_{ONa})/(a_{Na}+2U\,a_{Ca}-a_{ONa})]\log[a_{ONa}/(a_{Na}+2Ua_{Ca})], \quad (2)$$

where U is the ratio of the mobility of Ca^{2+} to that of Na$^+$ in the membrane, a_{ONa}, a_{Na}, and a_{Ca} denote the activities of the Na$^+$ in the standard solution, of the Na$^+$ and of the Ca^{2+} in the sample solution, respectively. Since a_{ONa} has been obtained as 9.16 mmol dm^{-3} in the solution of 10.0 mmol dm^{-3} of single NaDeS in the previous study,[14] the value of a_{Ca} can be calculated if those of U and a_{Na} are known exactly.

For Na$^+$, E_{Na} is also expressed;

$$E_{Na} = (2.303\,RT/F)\log(a_{Na}+K_{NaCa}a_{Ca}^{1/2}), \quad (3)$$

where K_{NaCa} is a selective factor of the Na$^+$ to the Ca^{2+}. The values of U and K_{NaCa} are functions of a_{Ca} and a_{Na} and must be known in the mixed surfactant solution prior to calculation. Unfortunately we can find neither U, K_{NaCa} nor a_{Ca} and a_{Na} in the literature. Therefore we measured the values of U and K_{NaCa} by use of mixed solutions of CaCl$_2$–NaCl at various mole ratios. From these, the single ionic activities of the Ca^{2+} and the Na$^+$ can be calculated with the assumption of pH convention.[16] Namely, the activity coefficient of

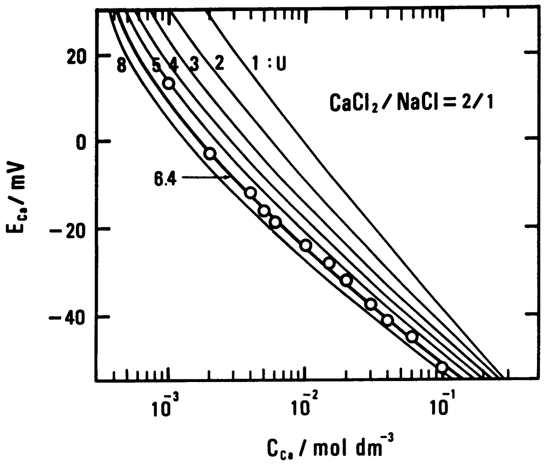


Fig. 2. Comparison of the observed E_{Ca} with the calculated E_{Ca} by use of the pH convention.
——: The calculated value. ○: the observed value.

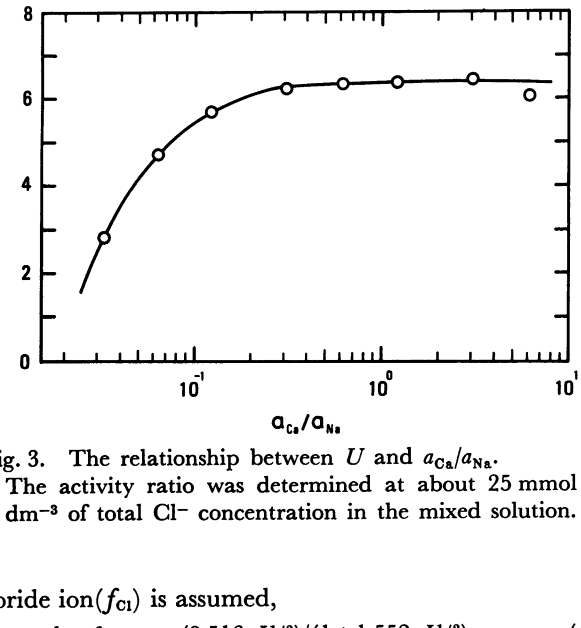


Fig. 3. The relationship between U and a_{Ca}/a_{Na}.
The activity ratio was determined at about 25 mmol dm^{-3} of total Cl$^-$ concentration in the mixed solution.

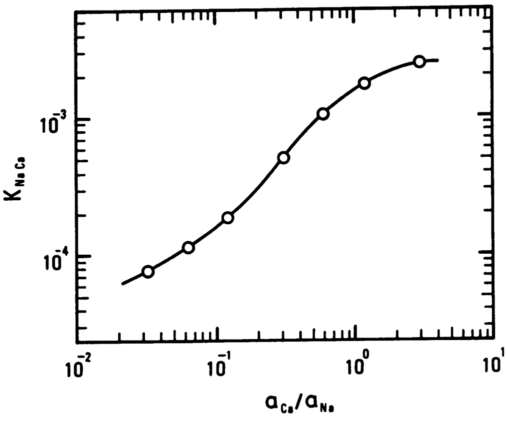


Fig. 4. The relationship between K_{NaCa} and a_{Ca}/a_{Na}.

chloride ion(f_{Cl}) is assumed,

$$\log f_{Cl} = -(0.516\cdot I^{1/2})/(1+1.552\cdot I^{1/2}), \tag{4}$$

where I is the total ionic strength in the solution. According to the Debye-Hückel theory, the mean activity coefficients of CaCl$_2$(f_{CaCl_2}) and of NaCl(f_{NaCl}) are given as follows;

$$\log f_{CaCl_2} = -(1.032\cdot I^{1/2})/(1+1.552\cdot I^{1/2}), \tag{5}$$

and $$\log f_{NaCl} = -(0.516\cdot I^{1/2})/(1+1.320\cdot I^{1/2}), \tag{6}$$

where the mean radii of hydrated ions in CaCl$_2$ and NaCl are assumed as 4.7 and 4.0 Å, respectively. From the definition of the mean activity coefficient, we also have

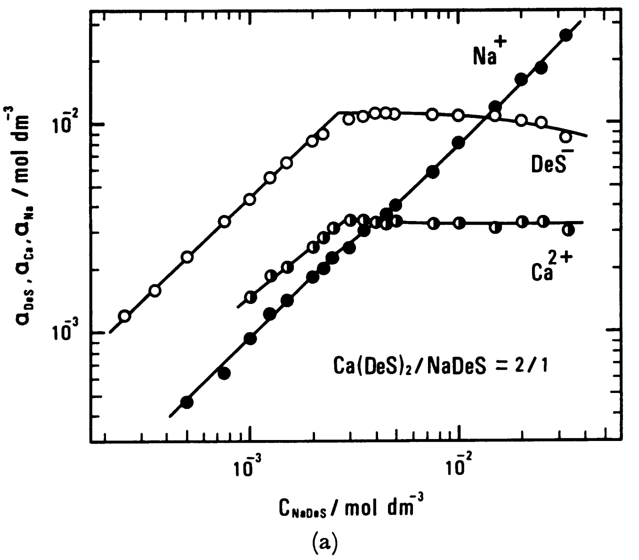
$$3\log f_{CaCl_2} = 2\log f_{Cl} + \log f_{Ca}, \tag{7}$$

and $$2\log f_{NaCl} = \log f_{Cl} + \log f_{Na}, \tag{8}$$

where f_{Ca} and f_{Na} denote the activity coefficients of the Ca^{2+} and the Na$^+$, respectively. In the mixed solution, a_{Ca} can be calculated from Eqs. 4, 5, and 7, and a_{Na} also from Eqs. 4, 6, and 8. By use of a_{Ca} and a_{Na} values obtained, U and K_{NaCa} can be determined from Eqs. 2 and 3. For example, Fig. 2 shows the curves of E_{Ca} calculated as a function of C_{Ca} with varying U and the observed values of E_{Ca}. In this calculation, the most suitable value of U was chosen as that for which the calculated E_{Ca} coincided with the experimental values. When 6.4 was adopted as U, they agreed fairly with each other except at low concentration. Figure 3 shows the U values determined in the various mixed solutions. The K_{NaCa} values, which were also determined from a_{Ca}, a_{Na}, and E_{Na} in the various mixed solutions by Srinivasan's method,[17] are shown in Fig. 4.

When the values of U and K_{NaCa} are used, a_{Ca} and a_{Na} in the mixed surfactant solutions can be computed from E_{Ca} and E_{Na} through the following successive calculations. First, a_{Na} was calculated from E_{Na} by Eq. 3, where K_{NaCa} was assumed to be zero because of its small value, and then a_{Ca} could be also obtained from the value of a_{Na} calculated above and E_{Ca} by Eq. 2, where the U value was determined with the assumption that a_{Ca}/a_{Na} was equal to C_{Ca}/C_{Na} in Fig. 3. Secondly, the K_{NaCa} value was also determined from a_{Ca}/a_{Na} in Fig. 4 by use of the values of a_{Ca} and a_{Na} obtained, and then a_{Na} was recalculated by Eq. 3. Moreover, a_{Ca} could be calculated again by Eq. 2 when the values of a_{Na} obtained above and of U determined from a_{Ca}/a_{Na} in Fig. 3 were used. This successive calculation having been performed, the activities were finally obtained as the converged values.

Figures 5a and b show a_{Ca} and a_{Na} together with a_{DeS} in the mixed surfactant solutions of $R_m=2$ and 0.5. The activities of all the ions increase linearly with the surfactant concentration up to the cmc. With an increase in the concentration above the cmc, a_{DeS} decreases. This shows that the smaller the R_m value becomes, a_{DeS} decreases slightly more steeply. Contrarily, a_{Na} increases linearly giving a break point in the curve of a_{Na} against the concentration of NaDeS; the slope of the curve above the CMC reduces as the R_m value decreases. Moreover, a_{Ca} in the solution of $R_m=2$ remains almost constant, but those of $R_m=1$, 0.5 and 0.2 show minima; the sum of the activities of the three kinds of ions in the mixed solution increases gradually with the the concentration in the same manner as in the solution of each single surfactant. From the fact that a_{Na} increases linearly with the concentration without a change in the slope of the curve of a_{Na} against concentration at the



(a)

(b)

Fig. 5. The single ionic activities against the concentration of NaDeS in the mixed surfactant solutions of varying mole ratios.

TABLE 1. THE VALUES OF cmc IN THE TOTAL CONCENTRATION OF THE DeS$^-$ AND OF K AND L IN EQ.10 IN THE MIXED SURFACTANT SOLUTIONS OF VARYING mole RATIO

R_m = Ca(DeS)$_2$/NaDeS	1/0	2/1	1/1	1/2	1/5	0/1
cmc / mmol dm^{-3}	12.8	13.5	14.4	18.4	22.4	32.8
K		0.052	0.049	0.046	0.039	
L		0.186	0.181	0.147	0.153	

cmc, it is suggested that most of the Na$^+$ in the solution of $R_m=2$ remains in the intermicellar solution. Further, from the decrease in the slope above the cmc with the decrease in R_m, the Na$^+$ may be considered to bind gradually on the micelle surface. These results can be explained by a change in the ionic composition which depends on the coulombic interaction of counterion with negatively charged micelles. Thus, the ionic composition of micelle will be determined and discussed later.

The cmcs in the mixed solutions are shown in Table 1 where these values were determined as the averages of the breaking points in the curves of activity *vs.* surfactant concentration.

Dissociation and Ionic Composition of Micelle. The valence effects of counterions on the dissociation of the micelle and on the mechanism of micelle formation have been studied in a previous paper.[14] In the mixed micellar solution of ionic surfactants, having counterions of uni and bivalence, it has been suggested that the binding of bivalent counterion occurred on the micelle surface in preference to the univalent one.[2,3] Thus the ionic composition of the micelles and the degree of micellar charge need to be investigated.

If a micelle is composed of p DeS$^-$, q Na$^+$, and s Ca^{2+} ions in equilibrium, the micelle formation is expressed by

$$p\,\mathrm{DeS}^- + q\,\mathrm{Na}^+ + s\,\mathrm{Ca}^{2+} \rightleftharpoons \mathrm{M}'$$

$$\mathrm{M}: [\mathrm{DeS}_p\mathrm{Na}_q\mathrm{Ca}_s]^{-(p-q-2s)}$$

and $$a_{\mathrm{M}}/(a_{\mathrm{DeS}}{}^p \cdot a_{\mathrm{Na}}{}^q \cdot a_{\mathrm{Ca}}{}^s) = K'_{\mathrm{M}},$$

where a_{M} is the activity of micelle and K'_{M}, a constant. This equation is rewritten;

$$\log a_{\mathrm{DeS}} + r_{\mathrm{Na}}\log a_{\mathrm{Na}} + r_{\mathrm{Ca}}\log a_{\mathrm{Ca}} = (1/p)\log(a_{\mathrm{M}}/K'_{\mathrm{M}}) = K_{\mathrm{M}}, \quad (9)$$

here, $r_{\mathrm{Na}}(=q/p)$ and $r_{\mathrm{Ca}}(=s/p)$ denote the counterion attachments of the Na$^+$ and of the Ca^{2+}, respectively. If p, q, s, a_{M}, and K_{M} are constant and independent of the surfactant concentration the phase separation theory,[18] which has described satisfactorily the formation of micelles in solutions of single NaDeS and Ca(DeS)$_2$,[14] is applicable. The solution of $R_m=2$ is this special cases so r_{Ca} and r_{Na} can be obtained by Eq. 9 because of the constants of a_{Ca} and K_{M}. But if p, q, and s change with the concentration, r_{Ca} and r_{Na}, in general, can not be calculated unless the value of K_{M} is given: K'_{M} and K_{M} also change.

On the other hand, we can compute r_{Ca} and r_{Na} from the intermicellar concentrations of the DeS$^-$(C_{DeS}), the Ca^{2+}(C_{Ca}) and the Na$^+$(C_{Na}) in the solution having the concentrations of C_{CaDeS} of Ca(DeS)$_2$ and C_{NaDeS} of NaDeS: $r_{\mathrm{Ca}} = (C_{\mathrm{CaDeS}} - C_{\mathrm{Ca}})/(2C_{\mathrm{CaDeS}} + C_{\mathrm{NaDeS}} - C_{\mathrm{DeS}})$ and $r_{\mathrm{Na}} = (C_{\mathrm{NaDeS}} - C_{\mathrm{Na}})/(2C_{\mathrm{CaDeS}} + C_{\mathrm{NaDeS}} - C_{\mathrm{DeS}})$. The values of C_{DeS}, C_{Ca}, and C_{Na} are given through the arrows illustrated schematically in Fig. 6; presence of micelle is assumed to give no effect on each activity coefficient of singly dispersed ions. Thus, C_{DeS} and C_{Ca} can be obtained provided the activity coefficient corresponding to the activity above the cmc is taken to be equal to that corresponding to the same activity below the cmc. C_{Na} is obtained with an aid of the dashed line. This is determined from the activity coefficient(f^s_{Na}) calculated with the assumption that the linear relation which holds between its activity coefficient and concentration below the cmc is also applicable to that of the Na$^+$ in the intermicellar solution above the cmc. Below the cmc, f^s_{Na} was successfully expressed by

$$\log f^s_{\mathrm{Na}} = -(K\log C_{\mathrm{NaDeS}} + L), \quad (10)$$

where K and L are the constant values which are sum-

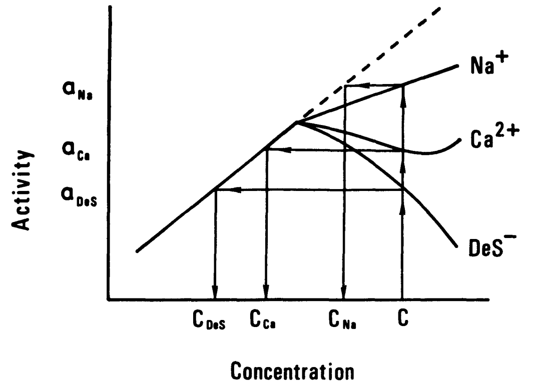
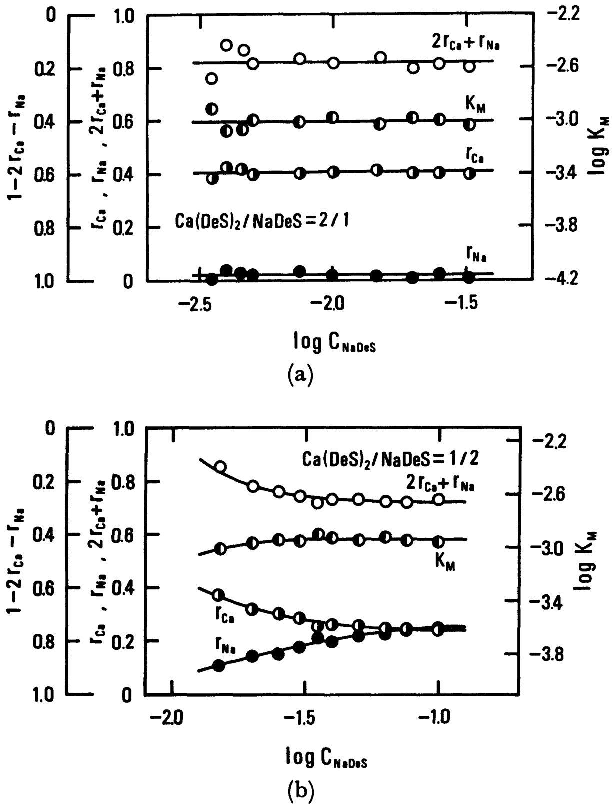


Fig. 6. Schematic description of determination of the intermicellar concentrations; C_{DeS}, C_{Ca}, and C_{Na} in the surfactant concentration of C are given through arrows. The dashed line is calculated with the assumption that the activity coefficient is given by the equation: $\log f_{Na}=-(K\log C_{NaDeS}+L)$.



(a)

(b)

Fig. 7. The degrees of counterion attachment of the Ca^{2+} (r_{Ca}), of the Na^+ (r_{Na}), of dissociation of micelle ($1-2r_{Ca}-r_{Na}$) and the value of log K_M against the concentration of NaDeS.

marized in Table 1 for the solution of varying R_m.

Figure 7a expresses r_{Ca} and r_{Na} together with the degree of micelle charge ($1-2r_{Ca}-r_{Na}$) in the solution of $R_m=2$ showing that they are nearly constant and independent of the concentration within an experimental error. As R_m becomes smaller, r_{Ca} decreases more steeply with the concentration, and it approaches asymptopically to a constant at high concentration as shown in Fig. 7b; r_{Na} and $1-2r_{Ca}-r_{Na}$ change reversely. The assumption of Eq. 10 may be applicable just above the cmc, but it should be tested at higher concentrations. If the assumption of Eq. 10 as well as the phase separation theory are set up, the value of K_M in Eq. 9 must be constant at the higher concentrations where r_{Ca} and r_{Na} are constant. The calculated values of K_M are shown in Figs. 7a and b, indicating that they do become constant at the high concentrations of various R_m and particularly K_M for the solution of $R_m=2$ is independent of the concentration. Therefore, the micelle formation in the mixed surfactant solution can be described by the phase separation theory at least in the solution of $R_m=2$ and in the high concentrations. The values obtained for r_{Ca}, r_{Na}, and $1-2r_{Ca}-r_{Na}$ suggest the following interpretation. Just above the cmc, the Ca^{2+} is bound on the micelle surface by the strong coulombic interaction in preference to the Na^+ from the intermicellar solution. The remaining $Na^+(C_{Na})$ increases with an increase in the surfactant concentration; the ratio of a_{Na}/a_{Ca} increases rapidly, therefore, r_{Na} increases and r_{Ca} reduces gradually. An increase in the total intermicellar concentration due to that in C_{Na} shields mainly the electrical potential at the micelle surface and consequently increases $1-2r_{Ca}-r_{Na}$.

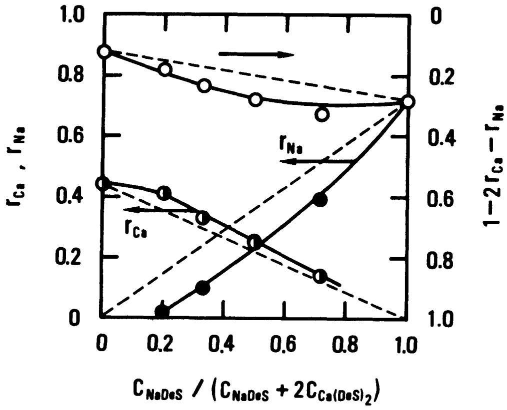


Fig. 8. The ionic composition of micelle and the degree of dissociation of micelle against the composition of the mixed surfactants.

The converged values of r_{Ca}, r_{Na}, and $1-2r_{Ca}-r_{Na}$ are plotted against the composition of mixed surfactant in Fig. 8, and these make the ionic composition of the micelle clearer. The dashed line indicates each calculated value from the assumption that r_{Ca} and r_{Na} vary proportionally to the fraction of each surfactant in the solution. The Ca^{2+} are bound preferentially on the micelle while the Na^+, which remains in the intermicellar solution of $R_m=2$, binds progressively to lessen the electical potential as R_m decreases; $1-2r_{Ca}-r_{Na}$ becomes larger mainly because of the shielding effect due to the increase in C_{Na} with the increasing content of NaDeS.

Specific Adsorption Potentials of the Ca^{2+} and the Na^+ Ions. With regard to the preferential binding of the Ca^{2+} on the micelle surface, free energies of transfer of counterions from solution to micelle surface, which have been referred to as specific adsorption potentials[19)] and calculated,[3,19,20)] are determined in the solution of two single surfactants for simplicity in calculation. In a solution of $Ca(DeS)_2$, we assume that a micelle consists of p DeS^- ions and $p\cdot r_{Ca}(=q)$ Ca^{2+} ions bound on the micelle surface and has $p(1-2r_{Ca})\varepsilon$ charges.

Equilibrium of the Ca^{2+} between the bulk phase and the micelle surface region is described by an equality of each electrochemical potential, $\bar{\mu}_{bCa}=\bar{\mu}_{mCa}$, in the two phases;

$$\bar{\mu}_{bCa} = \mu^{\circ}_{bCa} + kT\ln a_{Ca}, \tag{11}$$

$$\bar{\mu}_{mCa} = \mu^{\circ}_{mCa} + kT\ln C_{mCa} + \int_0^{2\varepsilon} \phi_{mCa}\mathrm{d}Q + W_{mCa}. \tag{12}$$

Here, $\bar{\mu}_{bCa}$, $\bar{\mu}^{\circ}_{bCa}$, $\bar{\mu}_{mCa}$, and $\bar{\mu}^{\circ}_{mCa}$ are the electrochemical and the standard chemical potentials in the bulk phase and in the micelle surface region, respectively; C_{mCa} the concentration of the Ca^{2+} bound in the micellar surface region of volume V_{Ca} and W_{mCa}, a free energy related to hydration of the ion. Further, it is assumed that the electrical free energy may be given by the electrical work done, $\int_0^{2\varepsilon} \phi_{mCa}\,\mathrm{d}Q$, when the Ca^{2+} having charge Q are brought about up to the micelle surface. The electrical potential, ϕ_{mCa}, at the micelle surface is given by[4)]

$$\phi_{mCa} = -(kT/2\varepsilon)[\ln(2000\,\pi\cdot\sigma^2/DNkT) - \ln C_{Ca}]. \tag{13}$$

Here, D and N denote the dielectric constant of water and the Avogadro number, respectively; C_{Ca}, the intermicellar concentration of the Ca^{2+} which has been calculated theoretically in a previous paper.[14)] The surface charge density of the micelle, σ, is expressed as follows;

$$\sigma = -(\varepsilon - r_{Ca}Q)/A_{CaD}, \tag{14}$$

where A_{CaD} is the molecular area occupied by the DeS^- at the surface of $Ca(DeS)_2$ micelle.

The concentration of the Ca^{2+} in the micelle surface region can be written as

$$C_{mCa} = 1000p\cdot r_{Ca}/NV_{Ca}. \tag{15}$$

If the thickness of the Stern layer can be assumed to be equal to the diameter, h_{Ca}, of the hydrated Ca^{2+}

$$V_{Ca} = pA_{CaD}h_{Ca} \tag{16}$$

is set up. From Eq. 11 to Eq. 16, we obtain the following relation,

$$\ln a_{Ca} = \Delta\mu^{\circ}_{tNa}/kT + \ln[DkTr_{Ca}A_{CaD}C_{Ca}/2\pi h_{Ca}\varepsilon^2(1-2r_{Ca})^2] + (1/r_{Ca})\ln(1-2r_{Ca}) + 2 + \Delta W_{tCa}, \tag{17}$$

where $\Delta\mu^{\circ}_{tCa}=\mu^{\circ}_{mCa}-\mu^{0}_{bCa}$ is a standard free energy of transfer of the Ca^{2+} from solution to micelle; similarly, ΔW_{tCa}, a hydration free energy of transfer due to changes in the state of hydration.

Similarly, in a solution of NaDeS,[3)]

$$\ln a_{Na} = \Delta\mu^{\circ}_{tNa}/kT + \ln[DkTr_{Na}A_{NaD}C_{Na}/2\pi h_{Na}\varepsilon^2(1-r_{Na})^2] + 2[(1/r_{Na})\ln(1-r_{Na})+1] + \Delta W_{tNa} \tag{18}$$

is given, where $\Delta\mu^{\circ}_{tNs}=\mu^{\circ}_{mNa}-\mu^{\circ}_{bNa}$, A_{NaD}, h_{Na}, and ΔW_{tNa} correspond to those for the Ca^{2+}, respectively.

The specific adsorption potentials, $\Delta\mu^{\circ}_{s}+\Delta W_{t}$, can be calculated by Eqs. 17 and 18 if, A_{CaD}, h_{Ca}, A_{NaD}, and h_{Na} are given, because D, k, T, and ε are constant values, while a_{Ca}, a_{Na}, C_{Ca}, C_{Na}, $r_{Ca}(=0.44)$, and $r_{Na}(=0.72)$ have been obtained and reported in a previous paper.[14)] Values of 4.6[3)] and 6.2 Å, calculated by Stokes law based on the limiting mobility, are used for h_{Na} and h_{Ca} respectively. For A_{NaD} and A_{CaD}, values of 53.6 and 43.7 Å^2 molecule^{-1} have been calculated from the saturated amount of adsorption at the air/solution interfaces.[21,22)] These values are employed respectively instead of those at the micelle surface. At the cmc, $\Delta\mu^{\circ}_{tNa}+\Delta W_{tNa}$ is computed as 1.1 kJ mol^{-1}, which fairly agrees with 1.3 kJ mol^{-1} expected theoretically,[19)] when $a_{Ca}=25.1$ mmol dm^{-3} and $C_{Na}=32.8$ mmol dm^{-3}; $\Delta\mu^{\circ}_{tCa}+\Delta W_{tCa}$ is 1.7 kJ mol^{-1} when $a_{Ca}=3.71$ mmol dm^{-3} and $C_{Ca}=6.40$ mmol dm^{-3}, but no value to be compared has been reported for calcium alkyl sulfate. In cationic surfactant solutions, investigations have shown that for various counterions the specific adsorption potentials became progressively larger as the valence of the counterion increased.[20)] This tendency is also observed in this experiment. These calculated values must be correlated to changes in the hydration of the counterions bound on the micelles on the basis not only of free energy but also of enthalpy and entropy to transfer the counterions from solution to the micelle surface, although the latter two were not determined in this experiment. However the changes may be roughly estimated, if the specific adsorption potentials can be attributed only to dehydration in binding the counterions on the micelles.

The enthalpy and the entropy of hydration[23)] and the number of primary hydrated water molecule (a hydrated water molecule being adjacent to an ion)[24)] of the Ca^{2+} have been reported at 25 °C as −1669 kJ mol^{-1}, −254 J deg^{-1} mol^{-1}, and 10, respectively and those of the Na^+ also as −443.9 kJ mol^{-1}, −110 J deg^{-1} mol^{-1} and 5. The value of $\Delta\mu^{\circ}_{tNa}+\Delta W_{tCa}$ corresponds to dehydration of 1.1×10^{-2} water molecule per the Ca^{2+} from the primary hydrated water and that of $\Delta\mu^{\circ}_{tNa}+\Delta W_{tNa}$ also to dehydration of 1.3×10^{-2} water molecule. From these small values, therefore, it may be considered that dehydration by counterions scarcely occurs in the binding. And if dehydration takes place, water molecules hydrated in the secondary, tertiary and outer layers, which weakly bind to the counterion, are perphaps dehydrated rather than those in the primary layer. The relation between the specific adsorption potential and the hydration entropy has been hitherto reported,[20)] and importance of entropy change in the formation of ionic pair, such as the Ca^{2+} and the $SO_4{}^{2-}$, has been also studied.[25)] Accordingly it would seem to be worthwhile to pay attention to such entropy changes in this study. However from the present results, it can not be clearly said what change in the hydration of the counterion is intimately correlated to the specific adsorption potential. Experimental and detailed studies are desirable on the state of the counterion near the micelle surface.

The electrical free energies, $\int\phi_{m}\mathrm{d}Q$, of the Ca^{2+} and the Na^+ at the cmc were calculated as −18.4 and −14.3 kJ mol^{-1}, respectively. It is indicated that the electrical free energy dominates in the specific adsorption potential in the counterion binding. Further, the value of $\int_0^{2\varepsilon}\phi_{mCa}\,\mathrm{d}Q$ is larger than that of $\int_0^{\varepsilon}\phi_{mNa}\mathrm{d}Q$, then the Ca^{2+} comes to bind preferentially even in low concentrations of surfactant.

Finally, we must say that the problem of the influence of micelles on the activities of single ions remains unconfirmed, although it has been reported that the surface tensions calculated above the cmc by use of the activities agreed satisfactorily with those observed.[11]

References

1) K. Shinoda, T. Nakagawa, B. Tamamushi, and T. Isemura, "Colloidal Surfactants," Academic Press, New York (1966), Chap. 1.

2) J. M. Corkill and J. F. Goodman, *Trans. Faraday Soc.*, **58**, 206 (1962).

3) I. Satake, T. Tahara, and R. Matuura, *Bull. Chem. Soc. Jpn.*, **42**, 319 (1969).

4) K. Shinoda, *Bull. Chem. Soc. Jpn.*, **28**, 340 (1955).

5) H. Lange, *Kolloid Z. Z. Polym.*, **131**, 96 (1953); **132**, 45 (1953).

6) Y. Moroi, K. Motomura, and R. Matuura, *J. Colloid Interface Sci.*, **46**, 111 (1970).

7) C. Gavach and P. Seta, *Anal. Chim. Acta*, **50**, 407 (1970).

8) B. J. Birch and D. E. Clarke, *Anal. Chim. Acta*, **61**, 159 (1972).

9) S. G. Cutler, P. Mears and D. G. Hall, *J. Chem. Soc., Faraday Trans., 1*, **47**, 1758 (1978).

10) K. Kaibara, T. Nakahara, I. Satake, and R. Matuura, *Mem. Fac. Sci. Kyushu Univ., Ser. C*, **7**, 1 (1970).

11) T. Sasaki, M. Hattori, J. Sasaki, and K. Nukina, *Bull. Chem. Soc. Jpn.*, **48**, 1397 (1975).

12) M. Koshinuma and T. Sasaki, *Bull. Chem. Soc. Jpn.*, **48** 2755 (1975).

13) A. Yamauchi, T. Kunisaki, T. Minematsu, Y. Tomokiyo T. Yamaguchi, and H. Kimizuka, *Bull. Chem. Soc. Jpn.*, **51**, 2791 (1978).

14) M. Koshinuma, *Bull. Chem. Soc. Jpn.*, **54**, 3128 (1981).

15) C. E. Marshall and C. A. Krinbill, *J. Am. Chem. Soc.*, **64**, 1814 (1942).

16) R. G. Bate, *Pure Appl. Chem.*, **36**, 407 (1973).

17) K. Srinivasan and G. A. Rechnitz, *Anal. Chem.*, **41**, 1208 (1969).

18) K. Shinoda and E. Hutchinson, *J. Phys. Chem.*, **66**, 942 (1962).

19) D. Stigter, *J. Phys. Chem.*, **68**, 3603 (1964).

20) C. Gamboa, L. Sepulveda, and R. Soto, *J. Phys. Chem.*, **85**, 1429 (1981).

21) K. Tajima, M. Muramatsu, and T. Sasaki, *Bull. Chem. Soc. Jpn.*, **43**, 1991 (1970).

22) J. Sasaki, K. Tajima, and T. Sasaki, *Bull. Chem. Soc. Jpn.*, **45**, 348 (1972).

23) H. L. Friedman and C. V. Krishman, "Thermodynamics of Ionic Hydration" in "Water," ed by F. Franks, Plenum, New York-London (1973), Vol. 3, Chap. 1, p. 55.

24) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth, London (1973), p. 126.

25) R. Fujishiro, G. Wada, and R. Tamamushi, "Yoeki No Seishitsu II," Tokyo Kagaku Dojin, Tokyo (1968), p. 129.