

ESTIMATION OF SURFACE EXCESS OF SURFACTANT UNDER COEXISTING SALTS IN FOAM SEPARATION

KEIICHI KATŌ, KAZUYUKI ŌMORI AND TAKAAKI SHIMIDZU

Department of Resources Chemistry, Ehime University, Matsuyama 790

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Foam separation experiments were carried out by use of sodium dodecylbenzene sulphonate. In the presence of various coexisting salts, the dynamic surface excess of dodecylbenzene sulphonate ion (DBS^-), Γ_{DBS^-} , at the dynamic gas-liquid interface of bubble was experimentally and theoretically examined. The Davies adsorption isotherm could be well applied to Γ_{DBS^-} in the range of surfactant concentrations of $C_{\text{DBS}^-}/C_m \leq 0.15$: C_{DBS^-} and C_m mean bulk concentration of DBS^- and critical micelle concentration respectively. It was also found that the values of the ratio of adsorption constant to desorption constant in the Davies adsorption isotherm, B_1/B_2 , have values in the two regions of electrical potential, ϕ_0 : in the region of $-\phi_0 < 4.0 \times 10^{-4}$ esu, B_1/B_2 value is 6.85×10^{-7} cm and in that of $-\phi_0 > 4.0 \times 10^{-4}$ esu, the value is 6.07×10^{-6} cm. Moreover, the effect of various coexisting salts on the surface excess of DBS^- in static equilibrium determined by surface tension measurements could be thermodynamically interpreted by a two-dimensional state equation by use of reduced concentration of DBS^- based on CMC. Saturated surface excess of DBS^- in static equilibrium could also be correlated to the ionic strength of coexisting metal ions. Using the equation derived from both the Davies adsorption isotherm and the Gouy-Chapman theory of the diffuse double layer (G.C. model), Γ_{DBS^-} under various coexisting salts could be estimated within an error of about $\pm 10\%$. Estimations of Γ_{DBS^-} in various solution systems were also carried out.

Introduction

Many investigations^{9,10,11,12,14)} of foam separation technique have been carried out. In the technique, it is important to estimate the dynamic surface excess of surfactant at the dynamic gas-liquid interface of the bubble. By use of the Gibbs adsorption equation, many investigations on the estimation of the surface excess in static equilibrium at the static gas-liquid interface have been carried out by measurement of surface tension. It has been reported that the values of the surface excess in static equilibrium differ from those of dynamic surface excess in foam separation.^{4,9,14)} It is known that the gas-liquid interface of rising foam in bulk liquid vibrates cyclically at high speed.⁵⁾ The vibration may be a factor in the difference between the values at static equilibrium and those at the dynamic gas-liquid interface. However, the precise reason of the difference has not been clarified. It is necessary in studying the dynamic surface excess to take account of many kinetic conditions of dynamic foam.⁶⁾ In foam separation only a few investigations for the estimation of the dynamic surface excess have been carried out. By means of foam separation experiments, we previously proposed an estimation method⁹⁾ for the dynamic surface excess of DBS^- (dodecylbenzene sulphonate ion), Γ_{DBS^-} , in the

presence of coexisting salts. However, the estimation equation could be applied only to the case of the coexisting salts of NaCl and MgCl_2 . No general estimation method allowing for various kinds of coexisting salts nor limitation of concentration range for the estimation has been examined. Moreover, evaluation of saturated surface excess of DBS^- has not been clarified.

In this work, Γ_{DBS^-} at the dynamic gas-liquid interface and Γ_{s,DBS^-} which denotes surface excess of DBS^- in equilibrium, examined by using various coexisting salts. An estimation method was then proposed from the examination.

1. Experimental Apparatus and Procedures

The experimental apparatus and procedures in this work are almost the same as those described in the previous paper.⁹⁾ A foam column of cylindrical Pyrex tube, of 36 mm I.D. and 323 mm in height, was constructed. The column was surrounded by a constant-temperature bath at 30°C. Volumetric feed rates of gas and liquid were about 250–260 cm³/min and about 14–15 cm³/min respectively. The values of Γ_{DBS^-} were measured by varying the height of the foam column under constant concentration conditions of the bulk solution. From the experiments, it was found that the Γ_{DBS^-} values were constant in the range of the column heights. Therefore, it was regarded that adsorption equilibrium of DBS^- can be established

* Received March 9, 1990. Correspondence concerning this article should be addressed to K. Katō.

in a column of 323 mm height. The material balance between the solution out to the column and the feed solution into the column was within about $\pm 3\%$. The bulk solution in the foam column was also regarded as completely mixed. The metal concentrations were determined spectrophotometrically with 4-(2-pyridylazo) resorcinol or purpuric acid. In the cases of mixed metal ions, the metal concentrations were determined by a atomic absorption spectrophotometer (Hitachi-208). Surface tension measurements were carried out by means of the Wilhelmy method¹⁵⁾ by using FACE CBVP-P (Kyowa Kaimenkagaku Co., Ltd.). The gas-liquid interfacial area, S , and Γ_{DBS^-} were determined from Eqs. (1) and (2).

$$S = 6(\Sigma n_b d^2 / \Sigma n_b d^3) \quad (1)$$

$$\Gamma_{DBS^-} = \{V_o / (V_a S)\} \{(C_{DBS^-})_0 - C_{DBS^-}\} \quad (2)$$

where Eq. (2) can be introduced from the material balance at steady state. The surfactant used was sodium dodecylbenzene sulphonate (SDBS) and coexisting salts used were perchlorates.

2. Results and discussion

2.1 Surface excess of DBS^- in foam separation experiments

The effect of various kinds of coexisting salts or pH values on Γ_{DBS^-} was examined by means of foam separation experiments. The concentration conditions of measured solutions are listed in Table 1. Typical results of Γ_{DBS^-} 's with various coexisting salts (added-salt system) are shown in Figs. 1 to 4. The experimental results are compared with the calculated ones in 2.5. The experimental results for trivalent metal ions are almost omitted here. Details of the results will be discussed in the next paper.

Figure 1 shows Γ_{DBS^-} in the case of Co^{2+} as coexisting metal ion. The higher C_{DBS^-} becomes, the lower is the value of $C_{Co^{2+}}$ at which Γ_{DBS^-} reaches a constant value. The experimental results of coexisting Ni^{2+} and Cu^{2+} were similar to those in Fig. 1. The results of Ni^{2+} and Cu^{2+} are omitted here. From the results, it was found that Γ_{DBS^-} values increase with increase of bulk concentrations of Co^{2+} , Ni^{2+} , Cu^{2+} and C_{DBS^-} . **Figure 2** shows the case of three species of coexisting Co^{2+} , Ni^{2+} and Cu^{2+} . In **Fig. 3**, the effect of coexisting In^{3+} on Γ_{DBS^-} is shown with parameters of C_{DBS^-} 's. **Figure 4** shows the effects of pH values on Γ_{DBS^-} in the case of Co^{2+} , Ni^{2+} and Cu^{2+} . From these results, it was found that Γ_{DBS^-} values vary with both pH and concentrations of coexisting salts.

2.2 Adsorption isotherms of DBS^- in foam separation experiments

1) The Langmuir adsorption isotherm The Langmuir adsorption isotherm is shown as follows:

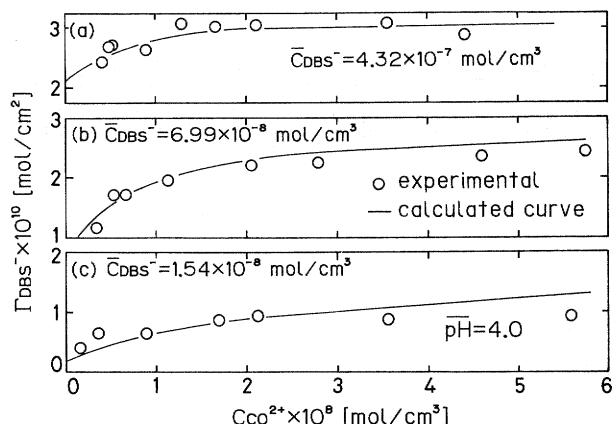


Fig. 1. Γ_{DBS^-} variations with bulk concentration of coexisting Co^{2+}

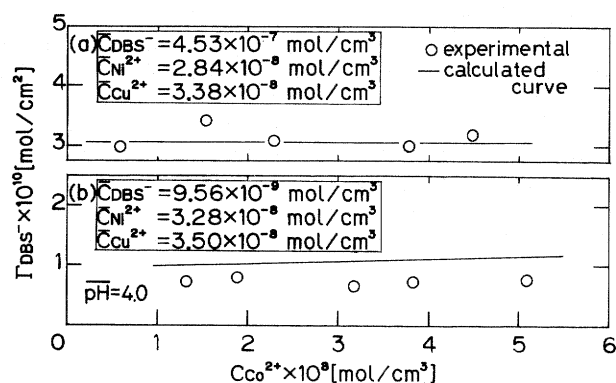


Fig. 2. Γ_{DBS^-} variations with $C_{Co^{2+}}$ for three species of coexisting Co^{2+} , Ni^{2+} and Cu^{2+}

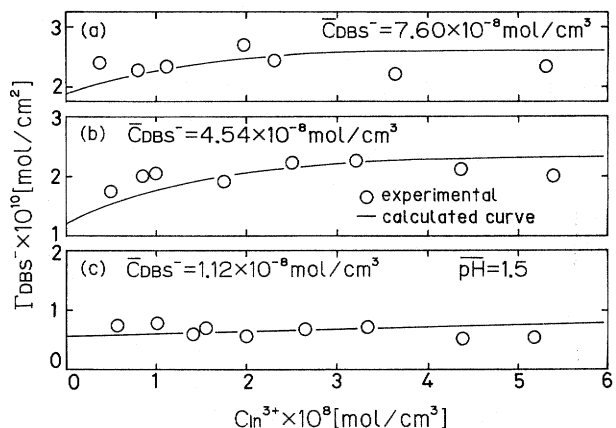


Fig. 3. Γ_{DBS^-} variations with bulk concentration of coexisting In^{3+}

$$1/\Gamma_{DBS^-} = K/C_{DBS^-} + 1/\Gamma_{DBS^-}^* \quad (3)$$

Figure 5 shows the Langmuir plots with pH in SDBS solutions to which no salts were added (non-salt system). **Figure 6** also shows the Langmuir plots in the cases of coexisting Co^{2+} and Ni^{2+} . The plots in the cases of pH 4.0 and 6.0 in the non-salt system (Fig. 5) deviate slightly from linearity. The reason could not be clarified. However, the plots of added-salt

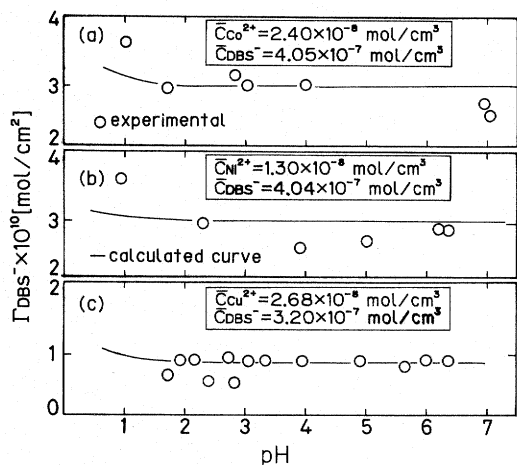


Fig. 4. Γ_{DBS^-} variations with pH for coexisting metal ions of Co^{2+} , Ni^{2+} and Cu^{2+} , respectively

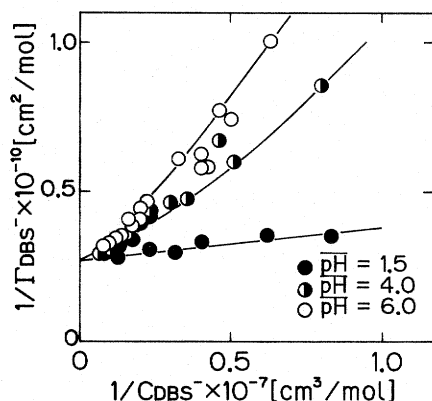


Fig. 5. Langmuir plots as parameters of pH values in non-salt systems

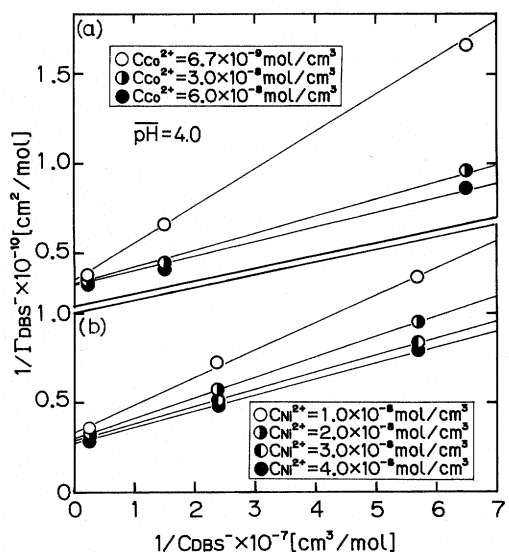


Fig. 6. Langmuir plots in added-salt systems

systems (Fig. 6) show approximate linearity. It was found that the Langmuir adsorption isotherm can be applied to the adsorption of DBS^- under constant bulk concentrations of coexisting salts.

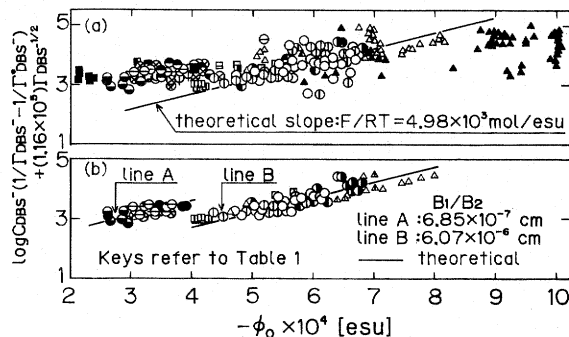


Fig. 7. Davies plots based on Eq. (6)

2) The Davies adsorption isotherm The Γ_{DBS^-} values vary with both species and concentrations of coexisting salts and also vary with pH. The Γ_{DBS^-} variations cannot be fully interpreted by the Langmuir adsorption isotherm. The Davies adsorption isotherm and the desorption energy are shown as follows²⁾:

$$\frac{1}{\Gamma_{DBS^-}} = \frac{1}{C_{DBS^-}} \left(\frac{B_2}{B_1} \right) \exp \left(\frac{zF\phi_0}{RT} - \frac{W}{kT} \right) + \frac{1}{\Gamma_{DBS^-}^*} \quad (4)$$

$$W/(kT) = 600 \text{ m}/(RT) - 1/(kT) \int_{500}^A A d\Pi_S \quad (5)$$

The surface pressure equation,³⁾ $\Pi_S = -400 \text{ m}/A^{2/3}$, is substituted in the Π_S of Eq. (5). Solving the two simultaneous equations Eqs. (4) and (5), the following equation is derived.⁹⁾

$$\log \left\{ C_{DBS^-} \left(\frac{1}{\Gamma_{DBS^-}} - \frac{1}{\Gamma_{DBS^-}^*} \right) \right\} + (1.16 \times 10^5) (\Gamma_{DBS^-})^{0.5} = (4.98 \times 10^3) (-\phi_0) - \{4.53 + \log(B_1/B_2)\} \quad (6)$$

Figure 7(a) shows the Davies plots of the term of the left-hand side in Eq. (6) against $-\phi_0$; ϕ_0 values were calculated from Eqs. (7) and (9) as mentioned later. The plots are based on the experimental results in Table 1. The concentration conditions and the keys in Fig. 7 are shown in Table 1. The plots scatter and deviate from the Davies theoretical slope of $4.98 \times 10^3 \text{ mol/esu}$. This is perhaps because the plots contain data above CMC and the ionic strength of the measured solutions has high values in the range of small $-\phi_0$ values. Therefore, we again tried the Davies plot by choosing data which are far below CMC by referring to C_{DBS^-}/C_m values in Table 1. As shown in Fig. 7(b) we could obtain plots having little scatter by means of setting the condition of $C_{DBS^-}/C_m \leq 0.15$. In the plots the data of non-salt system were omitted because of the deviation. The reason for the deviation in the system, like the non-linearity in Fig. 5, could not be clarified. We suspect that the plots in Fig. 7(b) can be essentially represented as a curve. To simplify the estimation method of Γ_{DBS^-} in dynamic equilibrium as mentioned later, we tried to approximate the plots in Fig. 7(b)

Table 1. Concentration conditions of measured solutions in foam separation experiments

key	added salts	coexisting metal con. $\times 10^8$ [mol/cm ³]	$C_{DBS^-} \times 10^8$ [mol/cm ³]	pH [—]	C_{DBS^-}/C_m [—]
○	Co(ClO ₄) ₂	0.1–5.7	1.3–50	4.0*	0.001–0.48
⊖	Co(ClO ₄) ₂	0.5–6.0	41*	1.7–7.2	0.22–0.45
⊕	Ni(ClO ₄) ₂	0.32–5.4	1.6–50	4.0*	0.006–0.37
⊕	Ni(ClO ₄) ₂	1.3*	4.0*	1.0–6.5	0.23*
●	Ni(ClO ₄) ₂ NaClO ₄	0.32–4.4 10–420	1.3–50	4.0*	0.06–0.34
□	Co(ClO ₄) ₂ Ni(ClO ₄) ₂	0.5–5.9 0.7–2.3	3.5–42	4.0*	0.024–0.45
▢	Cu(ClO ₄) ₂ Co(ClO ₄) ₂ Ni(ClO ₄) ₂	2.3–5.2 0.6–5.2 2.2–3.8	0.9–46	4.0*	0.001–0.66
●	Cu(ClO ₄) ₂	0.2–9.1	0.6–44	0.7–7.0	0.004–0.4
●	Fe(ClO ₄) ₃	0.9*	3.5*	0.8–2.2	0.35*
●	In(ClO ₄) ₃	0.4–5.4	0.6–8.8	1.5*	0.05–0.73
○	In(ClO ₄) ₃	1.3*	2.1*	0.8–2.1	0.17*
●	InCl ₃	1.8*	1.9*	0.7–2.0	0.15*
⊗	Ga(ClO ₄) ₃	0.28–5.9	1.3–9.6	1.5*	0.07–0.56
⊖	Ga(ClO ₄) ₃	0.8*	2.6*	0.8–2.0	0.14*
▢	In(ClO ₄) ₃ Co(ClO ₄) ₂	0.08–7.2 12*	5.9*	1.5*	0.49*
▢	Ga(ClO ₄) ₃ Cu(ClO ₄) ₂	0.7–7.3 5.1*	4.4*	1.5*	0.26*
▢	Fe(ClO ₄) ₃ In(ClO ₄) ₃	0.4–6.1 3.1*	5.4*	1.5*	0.54*
▢	Fe(ClO ₄) ₃ In(ClO ₄) ₃ Ni(ClO ₄) ₂	0.7–4.9 3.5* 18*	3.6*	1.5*	0.38*
▢	Fe(ClO ₄) ₃ In(ClO ₄) ₃ Cu(ClO ₄) ₂	0.9–6.2 5.0* 49*	1.7*	1.5*	0.17*
⊕	FeCl ₃	0.9*	3.0*	0.8–2.0	0.30*
△	NaCl ⁷⁾	200–10000	1.0–130	5.3–5.9	0.03–3.5
△	MgCl ₂ ⁷⁾	0.2–10	9–80	5.3–5.9	0.03–1.7
▲	No salts	—	20–150	1.5–5.9	0.005–4.5

note: 1) The keys in this table correspond to those in Fig. 7
2) * = average value (nearly constant in the solution system)

by two straight lines. As a result, the plots can be approximated by line A at about $-\phi_0 < 4 \times 10^{-4}$ esu and by line B at $-\phi_0 > 4 \times 10^{-4}$ esu. The B_1/B_2 values are 6.85×10^{-7} cm at $-\phi_0 < 4 \times 10^{-4}$ esu and 6.07×10^{-6} cm at $-\phi_0 > 4 \times 10^{-4}$ esu.

The B_1/B_2 difference may be due to the following reason. In the region of small values of $-\phi_0$, the ionic strength of the solution becomes high. Therefore, the assumption that the ion is a point charge in the Gouy-Chapman theory of the diffuse double layer (G. C. model) cannot be established in that region.

Moreover, the activity coefficients of the ions may deviate from unity.

2.3 Estimation method of Γ_{DBS^-}

Dynamic surface excess of DBS[−] is estimated as follows. The electrical potential is represented as Eq. (7).

$$\phi_0 = (-RT/F) \ln v_0 \quad (7)$$

Substituting Eq. (7) in Eq. (6), Eq. (8) can be obtained.⁹⁾

$$\begin{aligned}\log(C_{DBS^-}/v_0) = & -\{4.53 + \log(B_1/B_2)\} \\ & - (1.16 \times 10^5)(\Gamma_{DBS^-})^{0.5} \\ & - \log(1/\Gamma_{DBS^-} - 1/\Gamma_{DBS^-}^*)\end{aligned}\quad (8)$$

From the G.C. model, Eq. (9) is derived.⁷⁾

$$\Gamma_{DBS^-} = \{RT\varepsilon/(2\pi F^2)\}^{1/2} \{\sum C_i(v_0^z - 1)\}^{1/2} \quad (9)$$

where $\sum C_i$ denotes the summation of all the ion species in bulk liquid. The estimation of Γ_{DBS^-} values under various coexisting salts was calculated by solving the two simultaneous equations Eqs. (8) and (9) (see **Appendix 1**). In this work, the calculation was carried out by means of the Regular-Falsi method by use of a computer (FACOM M-360AP). The calculation results are shown in 2.5. In the calculation, the two values of B_1/B_2 determined previously were used, corresponding to the $-\phi_0$ regions described in 2.2.2). For estimation of the dynamic surface excess, the values of dynamic saturated surface-excess of DBS^- , $\Gamma_{DBS^-}^*$, are necessary in Eq. (8). The $\Gamma_{DBS^-}^*$ values were determined as follows.

2.4 Evaluation of saturated surface excess of DBS^-
1) static equilibrium As shown in Fig. 6, each value of $\Gamma_{DBS^-}^*$ in foam separation determined from the Langmuir plots varies slightly with the concentration of coexisting salts. To examine this phenomena precisely, Γ_{S,DBS^-}^* which denotes saturated surface-excess of DBS^- in static equilibrium was investigated by measuring surface tension as follows:

Prior to the examination of Γ_{S,DBS^-}^* , it was first tried to interpret thermodynamically the effect of coexisting salts on Γ_{S,DBS^-} in static equilibrium. Belton-Evans¹⁾ proposed the following equation, assuming an ideal mixture two-component system.

$$\begin{aligned}\exp\{-\gamma A/(kT)\} = & (1-x)\exp\{-\gamma_1 A/(kT)\} \\ & + x \cdot \exp\{-\gamma_2 A/(kT)\}\end{aligned}\quad (10)$$

Regarding water as a solvent and micelle as a solute,¹³⁾ the variables in Eq. (10) can be reduced as Eqs. (11) to (14):

$$\gamma_1 = \gamma_0, \gamma_2 = \gamma_m \quad (11)$$

$$x = C_{DBS^-}/C_m \equiv X \quad (12)$$

$$\Pi_m A/kT = b \quad (13)$$

$$(\gamma_1 - \gamma)/(\gamma_1 - \gamma_2) = (\gamma_0 - \gamma)/(\gamma_0 - \gamma_m) = \Pi/\Pi_m \equiv \Phi \quad (14)$$

Substituting Eqs. (11)–(14) to Eq. (10), Eq. (15) is derived.

$$\Phi = (1/b) \ln[1 + \{\exp(b) - 1\}X] \quad (15)$$

Figure 8 shows the plots of Φ against X according to Eq. (15). The plots could be represented by a curve, independently of both the species and the concentra-

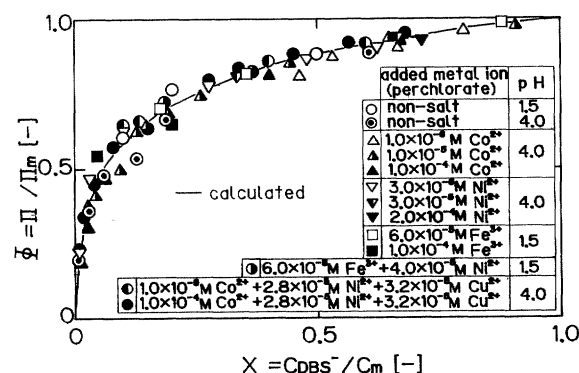


Fig. 8. Experimental verification of Eq. (15)

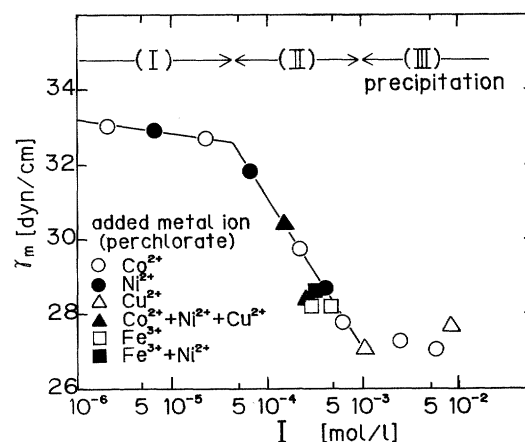


Fig. 9. Correlation of surface tensions at CMC with ionic strength of coexisting metal ions

tions of various coexisting salts. By means of the non-linear least squares method of Marquardt, the value of b was estimated from the curve. The value determined was 5.5. Equation (13) is transformed to the following equation.

$$\Pi_m A = b k T$$

where this equation has dimensions of kinetic energy. The equation is the two-dimensional state equation at CMC. It was found that the b value means the number of molecules of micelle.

By use of the b value thus determined, Γ_{S,DBS^-}^* in static equilibrium was estimated as follows: we assumed that the surface-tension value at CMC, γ_m , is nearly equal to the value at saturated adsorption. **Figure 9** shows the plots of γ_m against ionic strength of added metal ions, I . The plots are represented by straight lines. The slopes of the lines have different values with respect to the region of ionic strength: region (I) ($I = 1 \times 10^{-6} \sim 4 \times 10^{-5}$ M) and region (II) ($I = 4 \times 10^{-5} \sim 1 \times 10^{-3}$ M). In region (III), precipitation was observed. From the results of Fig. 9, the experimental equation shown below for Γ_{S,DBS^-}^* in static equilibrium was derived. The Gibbs equation for coexisting-salt solution is expressed as Eq. (16).

$$\Gamma_{S\cdot DBS^-} = \{-1/(RT)\} \{d\gamma/d\ln C_{DBS^-}\} \quad (16)$$

We derived Eq. (17) by combining Eqs. (12), (14) and (15) with Eq. (16) (see **Appendix 2**).

$$\Gamma_{S\cdot DBS^-} = \left(\frac{\gamma_0 - \gamma_m}{bRT} \right) \left\{ 1 - \exp \left(-b \frac{\gamma_0 - \gamma}{\gamma_0 - \gamma_m} \right) \right\} \quad (17)$$

Assuming $\Gamma_{S\cdot DBS^-} = \Gamma_{S\cdot DBS^-}^*$ at $\gamma = \gamma_m$, Eq. (18) is derived from Eq. (17).

$$\Gamma_{S\cdot DBS^-}^* = \eta(\gamma_0 - \gamma_m) \quad (18)$$

where $\eta = (1 - e^{-b})/(bRT)$.

The lines in Fig. 9 can be expressed as Eq. (19).

$$\gamma_m = -p \log I + q \quad (19)$$

Constant values of p and q were determined from the lines. The values of p and q were 0.437 dyn/cm, 30.6 dyn/cm in region (I) and 4.00 dyn/cm, 14.9 dyn/cm in region (II). Substituting Eq. (19) in Eq. (18), Eq. (20) is derived.

$$\Gamma_{S\cdot DBS^-}^* = \alpha \log I + \beta \quad (20)$$

where $\alpha = \eta p$ [mol/cm²], $\beta = \eta(\gamma_0 - q)$ [mol/cm²]

The values of α and β were calculated by using the values of p , q and b determined previously.

$$\begin{aligned} \text{Region (I): } \alpha &= 3.14 \times 10^{-12} \text{ mol/cm}^2, \\ \beta &= 2.92 \times 10^{-10} \text{ mol/cm}^2 \end{aligned}$$

$$\begin{aligned} \text{Region (II): } \alpha &= 2.88 \times 10^{-11} \text{ mol/cm}^2, \\ \beta &= 4.05 \times 10^{-10} \text{ mol/cm}^2 \end{aligned}$$

As shown below, $\Gamma_{S\cdot DBS^-}^*$ values calculated from Eq. (20) are approximately constant in the each region:

Region (I):

$$\Gamma_{S\cdot DBS^-}^* = 2.73 \times 10^{-10} \sim 2.78 \times 10^{-10} \text{ mol/cm}^2 \quad (21)$$

Region (II):

$$\Gamma_{S\cdot DBS^-}^* = 2.98 \times 10^{-10} \sim 3.19 \times 10^{-10} \text{ mol/cm}^2 \quad (22)$$

2) dynamic surface excess On the other hand, $\Gamma_{S\cdot DBS^-}^*$ values of dynamic saturated surface-excess in foam separation experiments were determined from the intercepts of the Langmuir plots of Fig. 6. It was also found that the $\Gamma_{S\cdot DBS^-}^*$ values thus determined from the plots are approximately constant, corresponding to the region of ionic strength in Fig. 9. In the Γ_{DBS^-} estimation, we use the following $\Gamma_{S\cdot DBS^-}^*$ values in Eq. (8).

$$\begin{aligned} \Gamma_{DBS^-}^* &= 2.78 \times 10^{-10} \text{ mol/cm}^2 \\ &\text{at } I = 1 \times 10^{-6} \sim 4 \times 10^{-5} \text{ M} \end{aligned} \quad (23)$$

$$\begin{aligned} \Gamma_{DBS^-}^* &= 3.08 \times 10^{-10} \text{ mol/cm}^2 \\ &\text{at } I = 4 \times 10^{-5} \sim 1 \times 10^{-3} \text{ M} \end{aligned} \quad (24)$$

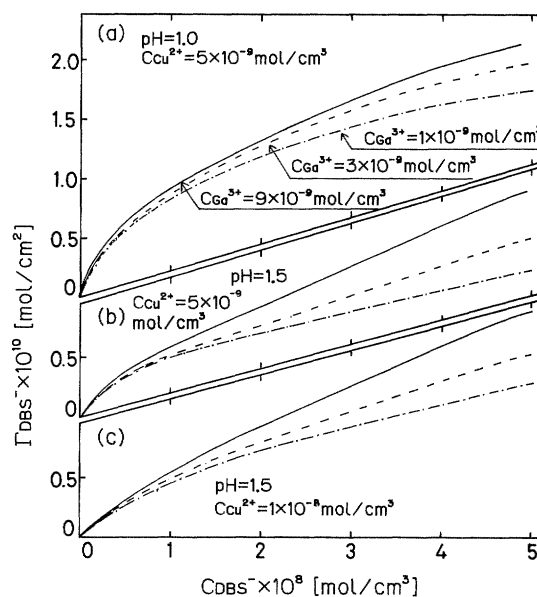


Fig. 10. Simulation of Γ_{DBS^-} adsorption-isotherms with $C_{Ga^{3+}}$, $C_{Cu^{2+}}$ and pH values in bulk solution

In comparison of Eqs. (21) and (22) with Eqs. (23) and (24), it is observed that $\Gamma_{DBS^-}^*$ values are fairly close to $\Gamma_{S\cdot DBS^-}^*$ values. It has also been reported that, only at saturated adsorption, the dynamic $\Gamma_{DBS^-}^*$ value is fairly close to $\Gamma_{S\cdot DBS^-}^*$ in static equilibrium.⁶⁾ However, many other investigators have reported a difference between the two values^{4,9,14)} even at saturated adsorption. From the strict viewpoint of both the saturated surface-excess values in this work, we suspect that $\Gamma_{DBS^-}^*$ values of Eqs. (23) and (24) differ from $\Gamma_{S\cdot DBS^-}^*$ of Eqs. (21) and (22).

2.5 Estimation of Γ_{DBS^-}

By means of the method described in 2.3, Γ_{DBS^-} values with various coexisting salts were estimated in foam separation. The curves in Figs. 1 to 4 were calculated by use of average values of bulk concentrations of the experimental data.

The calculated values were in agreement with the experimental ones in all the figures within an error of about $\pm 10\%$. In Fig. 2(b), the experimental values were slightly lower than the calculated ones, due to the difficulty of experimental determination of C_{DBS^-} at very low concentrations of DBS⁻. From the above results, it turned out that the estimation method of Γ_{DBS^-} can be applied to surfactant solutions in the presence of various coexisting salts.

2.6 Simulation of Γ_{DBS^-} in foam separation

In 2.5, it is found that Γ_{DBS^-} of the dynamic surface excess under various solution systems can be successfully estimated by means of our proposed method. We therefore tried to estimate Γ_{DBS^-} under more complicated solution systems and tried to examine the effect of the solution parameters on Γ_{DBS^-} . As a typical example, Fig. 10 shows the calculation

results for the variation of Γ_{DBS^-} - adsorption isotherms with $C_{Ga^{3+}}$, $C_{Cu^{2+}}$ and pH in bulk solutions, in the case of two species of coexisting metal ions, Ga^{3+} and Cu^{2+} . We can well understand the effect of the solution parameters on Γ_{DBS^-} . That is to say, in comparison of Fig. 10(a) with Fig. 10(b), it can be seen that the variation of the pH value from 1.0 to 1.5 has more effect on Γ_{DBS^-} than the values of $C_{Ga^{3+}}$ in the concentration range given here. In comparison of Fig. 10(b) with Fig. 10(c), it can be seen that the bulk concentration of Ga^{3+} of trivalent charge has more effect on Γ_{DBS^-} than that of Cu^{2+} of bivalent charge in the concentration range given here.

Conclusion

From surface tension measurements in static equilibrium, following conclusions were obtained.

- 1) Saturated surface excess of DBS^- , Γ_{S,DBS^-}^* , is expressed by Eq. (20) as a function correlated with the ionic strength of coexisting metal ions.
- 2) The effect of various coexisting salts on Γ_{S,DBS^-} can be thermodynamically interpreted by a two-dimensional state equation of $\Pi_m A = b k T$.
- From foam separation experiments, the following conclusions were obtained.
- 3) With various coexisting salts, Γ_{DBS^-} values can be generally estimated from Eqs. (8), (9), (23) and (24) within an error of about $\pm 10\%$ in the region of $C_{DBS^-}/C_m \leq 0.15$
- 4) The B_1/B_2 values in the Davies equation of Eq. (6) are 6.85×10^{-7} cm at $-\phi_0 < 4 \times 10^{-4}$ esu and 6.07×10^{-6} cm at $-\phi_0 > 4 \times 10^{-4}$ esu respectively.
- 5) The effect of solution parameters on Γ_{DBS^-} can be estimated by means of the proposed simulation method.

Appendix 1

For example, the calculation curve for the adsorption isotherm of Γ_{DBS^-} can be determined as follows: Equation (9) is represented as the variables Γ_{DBS^-} , C_{DBS^-} and v_0 at constant values of pH and coexisting-salt concentration, because all the C_i values except for C_{DBS^-} are constant in Eq. (9): the approximation of $C_{Na^+} \approx C_{DBS^-}$ can be applied. Equation (8) is also represented by those variables. Therefore, the relationships between Γ_{DBS^-} and C_{DBS^-} can be calculated by solving the two simultaneous equations (8) and (9), regarding v_0 as mediation parameters.

Appendix 2

From Eqs. (12), (14) and (15)

$$d \ln X = d \ln C_{DBS^-} = -\frac{b}{\Pi_m} \frac{d\gamma}{1 - \exp(-b\phi)} \quad (A-1)$$

is derived. Combining Eq. (A-1) and Eq. (10) leads to Eq. (17) as follows.

$$\begin{aligned} \Gamma_{S,DBS^-} &= \left(\frac{\gamma_0 - \gamma_m}{bRT} \right) \{ 1 - \exp(-b\phi) \} \\ &= \left(\frac{\gamma_0 - \gamma_m}{bRT} \right) \left\{ 1 - \exp \left(-b \frac{\gamma_0 - \gamma}{\gamma_0 - \gamma_m} \right) \right\} \end{aligned} \quad (17)$$

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Nomenclature

A	= area per molecule	[$\text{\AA}^2/\text{molecule}$]
B_1	= adsorption constant	[cm/s]
B_2	= desorption constant	[1/s]
b	= constant	[—]
C	= bulk concentration	[mol/cm ³]
$(C_{DBS^-})_0$	= concentration of DBS^- of feed solution to foam column	[mol/cm ³]
d	= bubble diameter	[cm]
F	= Faraday constant	[esu/mol]
I	= ionic strength of coexisting metal ion	[mol/l]
K	= constant defined by Eq. (3)	[1/cm]
k	= Boltzmann constant	[erg/K]
m	= number of $-\text{CH}_2-$	[—]
n_b	= number of bubbles having diameter d	[—]
p	= defined by Eq. (19)	[dyn/cm]
q	= defined by Eq. (19)	[dyn/cm]
R	= gas constant	[erg/mol/K]
S	= gas-liquid interfacial area per unit volume of gas	[cm ² /cm ³]
T	= absolute temperature	[K]
V_a, V_0	= volumetric flow rate of gas and feed liquid respectively	[cm ³ /min]
v_0	= reduced surface electrical potential	[—]
W	= disorption energy	[erg/molecule]
X	= reduced concentration of DBS^-	[—]
x	= mole fraction	[—]
z	= valency	[—]
α	= defined by Eq. (20)	[mol/cm ²]
β	= defined by Eq. (20)	[mol/cm ²]
Γ	= dynamic surface excess in foam separation	[mol/cm ²]
Γ_s	= surface excess in static equilibrium	[mol/cm ²]
γ	= surface tension of solution	[dyn/cm]
γ_1, γ_2	= surface tensions of solute and solvent respectively	[dyn/cm]
γ_0	= surface tension of distilled water	[dyn/cm]
ϵ	= dielectrical constant	[esu]
η	= constant defined by Eq. (18)	[mol/(dyn cm)]
Π	= surface pressure	[dyn/cm]
Π_s	= cohesive pressure within monolayer	[dyn/cm]
Φ	= reduced surface pressure	[—]
ϕ_0	= electrical potential at surface	[esu]

<Subscripts>

DBS^-	= dodecylbenzene sulphonate ion
i	= i species
m	= at CMC

<Superscripts>

$-$	= average
$*$	= saturation

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