METHOD OF ESTIMATING SURFACE EXCESS OF METAL ION IN FOAM SEPARATION

KEIICHI KATŌ, TAKUO ISHIKAWA,** YŌICHI KASAHARA†
AND SHINJI MIYAKI††

Department of Applied Chemistry, Ehime University Matsuyama 790

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Foam separation experiments were carried out in various SDBS (sodium dodecylbenzene sulphonate) solutions containing several kinds of metal perchlorates. General estimation of the dynamic surface excess of various kinds of metal ions were tried by use of a model (G.C. model) derived on the basis of the Gouy-Chapman theory of the diffuse double layer. In the model the effect of hydration of the metal ions was taken into account. The surface excess of metal ion (Γ_{metal}) from bulk concentration composition was directly estimated by use of the surface excess of DBS⁻ (dodecylbenzene sulphonate) (Γ_{DBS^-}), which was estimated using both the Davies adsorption theory and the G.C. model. The calculated values of Γ_{metal} were in good agreement with the experimental ones far below the critical micelle concentration. Therefore, the enrichment and removal percentage in the foam separation technique can be predicted.

Introduction

The foam separation technique has been used for enrichment and removal of metal ions and of surfactant ions.^{7,8)} Recently, it appears that the technique can be applied to the separation of a protein. It is necessary to clarify the adsorption mechanism at the gas-liquid interface of a bubble in the foam separation technique for estimating the surface excess of adsorption ions at the interface. However, only a few investigations of this estimation have been carried out. This is probably because that the surface excess in foam separation differs from that in a static equilibrium^{2,6,10)} and the estimation is very difficult.

In the previous paper⁴⁾, estimation of the dynamic surface excess of metal ion in foam separation was tried. However, that estimation was limited to the case of Mg^{2+} . Neither general estimation for various kinds of metal ions nor various solution systems has been examined. The purpose of the present work was to establish a general method of estimating the surface excess of various kinds of metal ions for various solution systems, using the method of estimating the surface excess of surfactant ion which was proposed in the previous paper⁵⁾.

1. Experimental apparatus and procedures

The experimental apparatus and procedures in this work were the same as those described in the previous paper⁵⁾. Foam separation experiments were carried

out using a single-stage continuous foam column. A foam column consisting of a 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. The metal concentrations were determined spectrophotometrically with 4-(2-pyridylazo) resorcinol¹²⁾ or purpuric acid. In the case of mixed metal ions, the metal concentrations were determined by an atomic adsorption spectrophotometer (Hitachi-208). The concentration of DBS⁻ was determined by means of an ultraviolet spectrophotometer at a wave length of 220 μm . Perchlorate ion concentration was spectrophotometrically determined by the solvent-extraction method³⁾ at a wave length of 655 μm using dichloroethane as solvent. Surface tension was measured by means of the Wilhelmy method¹¹⁾, using the FACE CBVP-P (Kyowa Kaimenkagaku Co., Ltd.). The gas-liquid interface area per unit gas volume, S , and the surface excess of DBS⁻, Γ_{DBS^-} , were determined from Eqs. (1) and (2).

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

$$\Gamma = (V_o / V_a S)(C_o - C) \quad (2)$$

Equation 2 can be introduced from the material balance at steady state of the foam column⁶⁾. Experimental values of Γ_{metal} and Γ_{DBS^-} were determined by use of metal concentration and DBS⁻ concentration in Eq. (2), respectively. Sodium dodecylbenzene sulphonate (SDBS) was used as surfactant and the coexisting salts used were perchlorates so as to prevent metal-complexes formation.

* Received March, 3, 1992. Correspondence concerning this article should be addressed to K. Katō. ** T. Ishikawa is now with Sakai Chem. Indust. Co., Ltd., Kobe 654. † Y. Kasahara is now with Daisoh Co., Ltd., Amagasaki 660. †† S. Miyaki is now with Tokyo Electron Co., Ltd., Yokohama 227.

Table 1. Experimental conditions and objects

Fig. No.	Added ions ^{*)}	Experimental objects	$C_m \times 10^6$ ^{**) [mol/ml]}	Parameters ^{***)}
Fig. 1 Fig. 2 Fig. 3	Ni^{2+} Co^{2+} Cu^{2+}	Adsorption isotherm of metal ions in solution system in which single metal ion is contained	1.0–2.7 0.7–2.0 0.9–1.1	C_{DBS^-} ,
Fig. 4 Fig. 5	Ni^{2+} Cu^{2+}	Effect of coexisting metal ions on Γ_{DBS^-}	1.0–2.7 0.9–1.1	C_{DBS^-}
Fig. 9 Fig. 10	Ni^{2+} , Na^+ Ni^{2+} , Na^+	Effect of C_{Na^+} on $\Gamma_{\text{Ni}^{2+}}$ Effect of C_{Na^+} on Γ_{DBS^-}	0.2–1.5	C_{DBS^-}
(a) Fig. 11 (b) (c)	Co^{2+} Ni^{2+} Cu^{2+}	Effect of pH on Γ_{metal}	0.9–1.9	C_{DBS^-} , $C_{\text{Co}^{2+}} = \text{const.}$
			0.9–2.1	C_{DBS^-} , $C_{\text{Ni}^{2+}} = \text{const.}$
			0.7–1.1	C_{DBS^-} , $C_{\text{Cu}^{2+}} = \text{const.}$
Fig. 12 Fig. 13	Ni^{2+} , Co^{2+} Fe^{3+} , Ni^{2+}	Estimation of Γ_{metal} in the solution system in which two different metal ions are contained	0.8–1.5 0.1	C_{DBS^-} , $C_{\text{Ni}^{2+}} = \text{const.}$
Fig. 14	Co^{2+} , Ni^{2+} , Cu^{2+}	Estimation of Γ_{metal} in the solution system in which three different metal ions are contained	0.2–0.8 (Fig. 14-1) 0.8–1.0 (Fig. 14-2)	C_{DBS^-} , $C_{\text{Ni}^{2+}}$, $C_{\text{Cu}^{2+}} = \text{const.}$

^{*)} All the added ions were perchlorates.
<sup>**) Critical micelle concentration, C_m , is determined⁵⁾ by means of the Whilhelmy method.
^{***)} The concentration values are shown in each figure.</sup>

The experimental conditions and objects are summarized in Table 1.

2. Results and Discussion

2.1 Experimental results of the adsorption of Ni^{2+} , Co^{2+} and Cu^{2+}

The experimental equilibrium isotherms for adsorption of Ni^{2+} , Co^{2+} and Cu^{2+} are shown in Figs. 1 to 3 for different average bulk-concentrations of DBS^- , $\bar{C}_{\text{DBS}^-}$. It was previously confirmed from the surface tension measurements that the values of $\bar{C}_{\text{DBS}^-}$ were below the CMC: the calculated points (shown as closed circles) and the calculated curves will be discussed in 2.5. The experimental surface excesses of Ni^{2+} , Co^{2+} and Cu^{2+} increase with increasing $\bar{C}_{\text{DBS}^-}$. At a constant value of $\bar{C}_{\text{DBS}^-}$, the experimental surface excesses of the metal ions, Γ_{metal} ($=\Gamma_{\text{Ni}^{2+}}$, $\Gamma_{\text{Co}^{2+}}$ and $\Gamma_{\text{Cu}^{2+}}$) increase with increase in bulk concentrations of the metal ions, C_{metal} ($=C_{\text{Ni}^{2+}}$, $C_{\text{Co}^{2+}}$ and $C_{\text{Cu}^{2+}}$), and the values of Γ_{metal} become constant in the high region of C_{metal} .

Γ_{DBS^-} was measured together with Γ_{metal} in each foam-separation experiment. As a typical example, the experimental and calculated values of Γ_{DBS^-} with coexisting metal ions of Ni^{2+} or Cu^{2+} are shown in Figs. 4 and 5, respectively. Figures 4 and 5 correspond to Figs. 1 and 3, respectively. The calculated values in Figs. 4 and 5 will be discussed in 2.5.2. Γ_{DBS^-} increases with increase in $\bar{C}_{\text{DBS}^-}$, $C_{\text{Ni}^{2+}}$ and $C_{\text{Cu}^{2+}}$. The

Fig. 1. Adsorption isotherm of Ni^{2+} : (●) calculated by use of experimental Γ_{DBS^-} in the Γ_{metal} ($=\Gamma_{\text{Ni}^{2+}}$) calculation; (—) calculated by use of the Γ_{DBS^-} calculated from Eqs. (12) and (13) in the calculation

values of Γ_{DBS^-} become constant in the high region of $C_{\text{Ni}^{2+}}$ and $C_{\text{Co}^{2+}}$. These phenomena were discussed in the previous work⁵⁾.

2.2 The Langmuir adsorption isotherm

The Langmuir adsorption equation for metal ions

Fig. 2. Adsorption isotherm of Co^{2+} : the descriptions of (●) and (—) are the same as those in Fig. 1

Fig. 3. Adsorption isotherm of Cu^{2+} : the descriptions of (●) and (—) are the same as those in Fig. 1

is expressed as

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

On the basis of Eq. (3), the plots of $1/\Gamma_{\text{Ni}^{2+}}$ vs. $1/C_{\text{Ni}^{2+}}$ are shown in Fig. 6, where $\bar{C}_{\text{DBS}^-}$ is used as a parameter. In the solution system of the lowest bulk-concentration of DBS^- ($\bar{C}_{\text{DBS}^-} = 1.75 \times 10^{-8}$ mol/ml), the trends of the plots show approximate linearity. But at the other concentrations ($\bar{C}_{\text{DBS}^-} = 4.22 \times 10^{-8}$ mol/ml, 4.10×10^{-7} mol/ml), the trends of the plots deviate from linearity. This means that the Langmuir adsorption equation cannot be applied in the high region of C_{DBS^-} . The same trends were also observed for the adsorption of Co^{2+} and Cu^{2+} (data not shown). These results indicate that the theory of the monolayer adsorption mechanism cannot be

Fig. 4. Comparison of calculated Γ_{DBS^-} with experimental values in added Ni^{2+} system: in the calculation, experimental bulk ion-concentrations (●) and estimated ones from $\bar{C}_{\text{DBS}^-}$ and $\bar{\text{pH}}$ (—) were used respectively

Fig. 5. Comparison of calculated Γ_{DBS^-} with experimental values in added Cu^{2+} system: in the Γ_{metal} ($=\Gamma_{\text{Cu}^{2+}}$) calculation, the descriptions of (●) and (—) are the same as those in Fig. 4

applied in the high region of C_{DBS^-} because a few micelle-molecules begin to form as C_{DBS^-} is brought close to CMC. It is also found that $\Gamma_{\text{Ni}^{2+}}^*$ calculated from the intercepts of Fig. 6 varies with $\bar{C}_{\text{DBS}^-}$.

2.3 Estimation of the surface excess of metal and surfactant ions

1) Metal ion On the basis of the Gouy-Chapman theory of the diffuse double layer⁴⁾ (G.C. model), ion distribution model near the gas-liquid interface of a bubble is represented as the Boltzman distribution as shown in Fig. 7. Let's suppose that three different metal ions of species i , $i-1$ and $i-2$ exist in a bulk solution. The surface excess of the ion species i , Γ_i , can be derived as below.

Fig. 6. Langmuir plots for adsorption of Ni^{2+}

Fig. 7. Distribution model of metal concentrations near the gas-liquid interface of bubble

According to the Poisson equation, the potential distribution near the gas-liquid interface is given as Eq. (4) (see **Appendix 1**)

$$\frac{d\phi}{dx} = - \left(\frac{8\pi RT}{\epsilon} \right)^{1/2} \{ \sum C_i (v_i^z - 1) \}^{1/2} \quad (4)$$

where

$$v = \exp(-F\phi/RT) \quad (5)$$

Assuming that ions are points of charge, Eq. (6) (see **Appendix 2**) is derived from Eqs. (4) and (5) (refer to Fig. 7).

$$\begin{aligned} \Gamma_i &= \int_{x_0}^{\infty} C_i(v^{z_i} - 1) dx \\ &= - \left(\frac{RT\varepsilon}{8\pi F^2} \right)^{1/2} \int_{v_0}^1 \frac{C_i(v^{z_i} - 1) dv}{v \{ \sum C_i(v^{z_i} - 1) \}^{1/2}} \quad (6) \end{aligned}$$

where

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

However, ions are not points of charge actually. Equation 6 should, therefore, be corrected as Eq. (8) by the additional surface excess, $\Delta\Gamma_i$, obtained by integration in the $(B+C)$ region in Fig. 7

$$\Gamma_i = \left(\frac{RT\varepsilon}{8\pi F^2} \right)^{1/2} \int_1^{v_0} \frac{C_i(v^{z_i} - 1)dv}{v \{ \sum C_i(v^{z_i} - 1) \}^{1/2}} - \left(\frac{RT\varepsilon}{8\pi F^2} \right)^{1/2} \int_{v_i^*}^{v_0} \frac{C_i(v^{z_i} - 1)dv}{v \{ \sum C_i(v^{z_i} - 1) \}^{1/2}} \quad (8)$$

The second term of the right-hand side in Eq. (8) represents $-\Delta F_i$. The values of v_0 and v_0'' in Eq. (8) are calculated below.

By using the Gauss theorem and Eqs. (4), (9) is derived:

$$\begin{aligned}\sigma_1 &= - \int_{x_0}^{\infty} \rho dx = (\varepsilon/4\pi) \int_{x_0}^{\infty} (d^2\phi/dx^2) dx \\ &= -(\varepsilon/4\pi) (d\phi/dx)_{x=x_0} \\ &= -(RT\varepsilon/2\pi)^{1/2} \left\{ \sum C_i (v_{D_i}^{z_i} - 1) \right\}^{1/2}\end{aligned}\quad (9)$$

while Eq. (10) is given.

$$\sigma_z = z_s F \Gamma_s = (-1) F \Gamma_{\text{DBS-}} \quad (10)$$

Equalizing Eqs. (9) to (10), v_0 values can be obtained. Equation (11) is derived from Eqs. (4) and (5) by use of the boundary condition of $v=v_0$ at $x=x_0$ (see Appendix 2).

$$X = - \left(\frac{RT\varepsilon}{8\pi F^2} \right)^{1/2} \int_{v_0}^v \frac{dv}{v \{ \sum C_i (v^{z_i} - 1) \}^{1/2}} + x_0 \quad (11)$$

By use of the values of v_0 , the values of v'_0 and v''_0 can be calculated from Eq. (11) using the boundary conditions of $v=v'_0$ at $x=x'_0$ and $v=v''_0$ at $x=x'_0$, respectively. The calculation was carried out by the Regular-Falsi method by use of a computer (FACOM-360AP). The calculated value of Γ_i was obtained by integrating Eq. (8) by means of the Simpson method with the computer, using the calculated values of v_0 and v''_0 . In the same manner, Γ_{i-1} was also calculated using the estimated values of v_0 and v'_0 .

2) DBS⁻ The value of Γ_{DBS^-} is required in Eq. (10). As proposed in the previous paper⁵⁾, the Γ_{DBS^-} -value can be estimated by solving the two simultaneous equations of Eqs. (12) and (13).

$$\begin{aligned} \log(C_{\text{DBS}}/v_0) = & -\{4.53 + \log(B_1/B_2)\} \\ & - (1.16 \times 10^5)(\Gamma_{\text{DBS}})^{1/2} \\ & - \log(1/\Gamma_{\text{DBS}} - 1/\Gamma_{\text{DBS}}^*) \quad (12) \end{aligned}$$

$$\Gamma_{\text{DBS-}} = (RT\varepsilon/2\pi F^2)^{1/2} \{\sum_i C_i(v_0^{z_i} - 1)\}^{1/2} \quad (13)$$

Equation (12) is obtained by combining the Davis adsorption equation¹⁾ with the G.C. model, while Eq.

(13) is obtained by equalizing Eqs. (9) to (10).

2.4 Calculation of the potential curve

For the SDBS solution to which $\text{Ni}(\text{ClO}_4)_2$ and $\text{Fe}(\text{ClO}_4)_3$ were added (added $\text{Ni}^{2+} - \text{Fe}^{3+}$ system), typical calculated curves of v vs. x from Eq. (11) are shown in Fig. 8. The values of x_0 (1.21 Å), x'_0 (1.38 Å) and x''_0 (1.76 Å) show the radii of the hydrated ions of Na^+ , Ni^{2+} and Fe^{3+} , respectively⁹. The actual unit of ion movement in a solution is not the crystal size of the ion but its hydrated size. Therefore, the distance of the closest approach to the gas-liquid interface of a bubble (as shown in Fig. 7) corresponds not to the radius of the ion but to that of the hydrated ion. In the calculations of v vs. x , the Γ_{DBS^-} values obtained experimentally were used in Eq. (13) for the determination of the v_0 value.

From the calculated curves in Fig. 8, it is found that the potential curves become flat at approximately $x < 6$ Å. This value is at most about two or three times larger than the diameter of the hydrated metal ion. This implies that the hydration of a metal ion affects strongly the amount of the adsorptive metal ion.

2.5 Estimation of Γ_{metal}

The calculated Γ_{metal} values from the G.C. model are also compared with the experimental values in Figs. 1 to 3.

1) The fitness of the G.C. model The values of v_0 and v'_0 were determined by use of the experimental Γ_{DBS^-} values (as shown in Figs. 4 and 5) by the method described in 2.3.1. By use of the values of v_0 and v'_0 , Γ_{metal} values were calculated from Eq. (8) and are shown in Figs. 1 to 3 as a calculated point (closed circle). The figures (as shown in Fig. 1(b) and (c), Fig. 2(b) and (c) and Fig. 3(a) and (b)) indicate that the calculated points are in good agreement with the experimental values in the low region of $\bar{C}_{\text{DBS}^-}$. Therefore, it can be concluded that the G.C. model is well suited to adsorption of metal ion at the gas-liquid interface when C_{DBS^-} is sufficiently lower than CMC.

2) Direct estimation of Γ_{metal} On the other hand, it is necessary to estimate the Γ_{DBS^-} value in Eq. (10) for the direct estimation of Γ_{metal} from the concentration composition of the bulk solution. The Γ_{DBS^-} values were calculated by solving Eqs. (12) and (13) as mentioned in 2.3.2. As shown in Figs. 4 and 5, the calculated Γ_{DBS^-} values are in good agreement with the experimental values (see Appendix 3).

The calculated curves of Γ_{metal} in Figs. 1 to 3 were directly estimated from Eq. (8) by use of the calculated Γ_{DBS^-} values from Eqs. (12) and (13) as described above, where the metal ions are Ni^{2+} , Co^{2+} and Cu^{2+} . In the calculation, $\bar{C}_{\text{DBS}^-}$ was used as the bulk concentration of DBS^- . Figures 1 to 3 show that the calculated curves are in good agreement with the experimental values when $\bar{C}_{\text{DBS}^-}$ is sufficiently lower

Fig. 8. Typical curves of v vs. x calculated from Eq. (11)

Fig. 9. Variation of $\Gamma_{\text{Ni}^{2+}}$ with C_{Na^+} ; the descriptions of (●) and (—) are the same as those in Fig. 1

than CMC. It is, therefore, concluded that the Γ_{metal} value can be directly estimated from the concentration composition of the bulk solution by use of Eqs. (8), (12) and (13).

In Figs. 1(a) and 2(a), both the calculated points of the Γ_{metal} ($\Gamma_{\text{Ni}^{2+}}$, $\Gamma_{\text{Co}^{2+}}$; by use of the experimental Γ_{DBS^-} values in Eq. (13)) and the calculated curves of the Γ_{metal} (by use of the calculated Γ_{DBS^-} values from Eqs. (12) and (13)) tend to deviate from the experimental values of Γ_{metal} with decrease in the C_{metal} in the high region of $\bar{C}_{\text{DBS}^-}$. To explain the deviation between the calculated Γ_{metal} values and the experimental ones, the following experiments were carried out.

2.6 Competitive adsorption between Ni^{2+} and Na^+

The experimental $\Gamma_{\text{Ni}^{2+}}$ were measured by changing the concentration of NaClO_4 in the bulk solution in which SDBS, $\text{Ni}(\text{ClO}_4)_2$ and NaClO_4 were dissolved. The experimental and the calculated relations between C_{Na^+} (see Appendix 4) and $\Gamma_{\text{Ni}^{2+}}$ under two different concentration conditions are shown in Fig. 9. The relations between C_{Na^+} and Γ_{DBS^-} in the same solution systems as those in Fig. 9 are also shown in Fig. 10. In Fig. 10 the calculated curves of Γ_{DBS^-} from Eqs. (12) and (13) are shown in comparison with the experimental values of Γ_{DBS^-} . The calculated Γ_{DBS^-} values are in good agreement with the experimental ones. However, the calculated $\Gamma_{\text{Ni}^{2+}}$ values tend to

Fig. 10. Variation of Γ_{DBS^-} with C_{Na^+} in added Ni^{2+} system: the descriptions of (●) and (—) are the same as those in Fig. 1

deviate from the experimental ones in the low region of C_{Na^+} , as shown in Fig. 9(a) (in the case of high C_{DBS^-}) and are in good agreement with the experimental ones in all the region of C_{Na^+} as shown in Fig. 9(b) (in the case of low C_{DBS^-} ; far below CMC). The reason is explained as follows.

The surfactant ions of DBS^- begin to form the micelle as the bulk solution is brought close to CMC (Fig. 9(a)). Ni^{2+} is adsorbed to the surface of the DBS^- micelle, which is charged negatively, competing with Na^+ . Therefore, in the low region of $C_{\text{Ni}^{2+}}$ in comparison with C_{Na^+} , the actual $C_{\text{Ni}^{2+}}$ is lower than the estimated $C_{\text{Ni}^{2+}}$ used in the calculation of $\Gamma_{\text{Ni}^{2+}}$. Due to the difference in the values of $C_{\text{Ni}^{2+}}$, the experimental $\Gamma_{\text{Ni}^{2+}}$ values are lower than the calculated ones in the low region of $C_{\text{Ni}^{2+}}$ as shown in Fig. 9(a). On the other hand, in the high region of C_{Na^+} the difference between the actual free $C_{\text{Ni}^{2+}}$ values and the estimated values can be neglected. This is because Ni^{2+} is adsorbed little to the micelle due to the competitive adsorption between Ni^{2+} and Na^+ . Therefore, the experimental $\Gamma_{\text{Ni}^{2+}}$ values are in agreement with the calculated ones in the high region of $C_{\text{Ni}^{2+}}$ as shown in Fig. 9(a).

This is probably because the difference between the experimental results and the calculated ones for $\Gamma_{\text{Ni}^{2+}}$ and $\Gamma_{\text{Co}^{2+}}$ in the low region of $C_{\text{Ni}^{2+}}$ and $C_{\text{Co}^{2+}}$ as shown in Figs. 1(a) and 2(a) is due to the competitive adsorptions between Ni^{2+} and Na^+ or between Co^{2+} and Na^+ for the same reason above: the Na^+ is from SDBS.

2.7 Effect of pH in bulk solution on the surface excess

Figure 11 shows the plots of Γ_{metal} vs. pH. The experimental results for $\Gamma_{\text{Co}^{2+}}$, $\Gamma_{\text{Ni}^{2+}}$ and $\Gamma_{\text{Cu}^{2+}}$ are also in good agreement with the calculated ones. In the low region of pH, the experimental Γ_{metal} values increase with increase in pH values. The values of Γ_{metal} attain constant values in the region of about $\text{pH} > 4$. The reason can be explained as follows. The metal ions and H^+ are adsorbed competitively to the

Fig. 11. Variation of $\Gamma_{\text{Co}^{2+}}$, $\Gamma_{\text{Ni}^{2+}}$ and $\Gamma_{\text{Cu}^{2+}}$ with pH of bulk solution: the descriptions of (●) and (—) are the same as those in Fig. 1

gas-liquid interface which is negatively charged by the adsorption of DBS^- . Then, Γ_{metal} values increase with decrease in $[\text{H}^+]$. In the low region of $[\text{H}^+]$, the amount of Γ_{H^+} is negligible in comparison with that of Γ_{metal} . It is, therefore, considered that the Γ_{metal} values are constant.

2.8 Γ_{metal} estimation in SDBS solution containing two metal salts

It was also tried to estimate the surface excess for the SDBS solutions to which more than one metal salt was added. Figure 12 shows a comparison of the experimental results of $\Gamma_{\text{Ni}^{2+}}$ vs. $C_{\text{Co}^{2+}}$ and $\Gamma_{\text{Co}^{2+}}$ vs. $C_{\text{Co}^{2+}}$ with the calculated results. As shown in Fig. 12, $\Gamma_{\text{Ni}^{2+}}$ values decrease and $\Gamma_{\text{Co}^{2+}}$ values increase with increase in $C_{\text{Co}^{2+}}$. This is because Ni^{2+} is adsorbed in competition with Co^{2+} . Figure 13 shows a similar comparison of the plots of $\Gamma_{\text{Fe}^{3+}}$ vs. $C_{\text{Fe}^{3+}}$ and $\Gamma_{\text{Ni}^{2+}}$ vs. $C_{\text{Fe}^{3+}}$, where the fitness of the estimation method for the solution system containing three-valent metal ion, Fe^{3+} , was also examined. The plots in Fig. 13 indicate a similar tendency to those in Fig. 12. In Figs. 12 and 13, the results calculated from the method described in 2.3 are in good agreement with the experimental ones. Therefore, it is possible to estimate the surface excess of metal ions for the solution to which two metal salts are added.

2.9 Γ_{metal} estimation in the SDBS solution system containing three metal salts

Figure 14(1) and 14(2) show a comparison of the experimental results with the calculated ones for the

Fig. 12. Variation of $\Gamma_{\text{Ni}^{2+}}$ and $\Gamma_{\text{Co}^{2+}}$ with bulk concentration of Co^{2+} in the added $\text{Co}^{2+} - \text{Ni}^{2+}$ solution system: (●), (▲) calculated by use of experimental Γ_{DBS^-} ; (—), (---) calculated by use of Γ_{DBS^-} calculated from Eqs. (12) and (13)

Fig. 13. Variation of $\Gamma_{\text{Fe}^{3+}}$ and $\Gamma_{\text{Ni}^{2+}}$ with bulk concentration of Fe^{3+} in the added $\text{Fe}^{3+} - \text{Ni}^{2+}$ solution system: the descriptions of (●) and (—) are the same as those in Fig. 1

plots of $\Gamma_{\text{Co}^{2+}}$, $\Gamma_{\text{Ni}^{2+}}$ and $\Gamma_{\text{Cu}^{2+}}$ against $C_{\text{Co}^{2+}}$. The experimental values of $\Gamma_{\text{Ni}^{2+}}$ and $\Gamma_{\text{Cu}^{2+}}$ decrease with increase in the experimental value of $\Gamma_{\text{Co}^{2+}}$. This is because Ni^{2+} , Co^{2+} and Cu^{32+} are competitively adsorbed to each other under the condition that $\bar{C}_{\text{Ni}^{2+}}$ and $\bar{C}_{\text{Co}^{2+}}$ are constant.

The calculated Γ_{metal} values are more in agreement with the experimental ones in Fig. 14-2 (in the case of low $\bar{C}_{\text{DBS}^-}$) than in Fig. 14-1 (in the case of high $\bar{C}_{\text{DBS}^-}$). It is concluded from the results that Γ_{metal} in the solution system containing several metal salts for below the CMC can be estimated by means of the approach described in 2.3. As a result, we can predict the enrichment and removal percentage of metal ions in the foam separation technique by use of the proposed estimation method.

Fig. 14-1. Variation of $\Gamma_{\text{Co}^{2+}}$, $\Gamma_{\text{Ni}^{2+}}$ and $\Gamma_{\text{Cu}^{2+}}$ with $C_{\text{Co}^{2+}}$ in the added $\text{Co}^{2+} - \text{Ni}^{2+} - \text{Cu}^{2+}$ solution system (in the case of low $\bar{C}_{\text{DBS}^-}$): the descriptions of (●) and (—) are the same as those in Fig. 1

Fig. 14-2. Variation of $\Gamma_{\text{Co}^{2+}}$, $\Gamma_{\text{Ni}^{2+}}$ and $\Gamma_{\text{Cu}^{2+}}$ with $C_{\text{Co}^{2+}}$ in the added $\text{Co}^{2+} - \text{Ni}^{2+} - \text{Cu}^{2+}$ solution system (in the case of high $\bar{C}_{\text{DBS}^-}$): the descriptions of (●) and (—) are the same as those in Fig. 1

Conclusion

The adsorption of metal ion in the foam separation technique was experimentally and theoretically studied, and the main conclusions are as follows.

1) The Langmuir adsorption equation can be applied to the adsorption of metal ion far below the CMC.

2) The distribution distance of adsorptive metal ion near the gas-liquid interface is within about 6 Å. The magnitude of the hydrated metal ion strongly affects the amount of the adsorptive metal ion.

3) By means of the proposed method of estimating Γ_{DBS^-} by solving Eqs. (12) and (13), the surface excess of metal ion can be well estimated from the G.C. model far below the CMC.

4) The estimation method of surface excess of metal ions can be also applied to a solution containing more than one kind of metal ion.

Appendix 1

The Poisson equation and the Boltzman equation are given as Eqs. (A-1) and (A-2), respectively.

$$d^2\phi/dx^2 = -(4\pi/\epsilon)\rho \quad (\text{A-1})$$

$$\rho = \sum_i z_i F C_i v^{z_i} \quad (\text{A-2})$$

Let us define $d\phi/dx$ as Eq. (A-3).

$$d\phi/dx = p \quad (\text{A-3})$$

Equation (A-4) can be derived from Eqs. (A-1) and (A-3)

$$\frac{d}{dx} \left(\frac{d\phi}{dx} \right) = \frac{dp}{dx} = \frac{dp}{d\phi} \frac{d\phi}{dx} = p \frac{dp}{d\phi} = -\frac{4\pi}{\epsilon} \rho \quad (\text{A-4})$$

Substituting Eqs. (A-2) and (5) in Eq. (A-4), Eq. (A-5) can be obtained.

$$p dp = \left(-\frac{4\pi F}{\epsilon} \right) \sum_i \left\{ z_i C_i \exp \left(-\frac{z_i F \phi}{RT} \right) \right\} d\phi \quad (\text{A-5})$$

At a point which is far from the gas-liquid interface of a bubble, the values of the surface potential and the potential slope become zero. Therefore, the boundary condition is as follows.

$$\text{at } x, \quad p (= d\phi/dx) = 0, \quad \phi = 0, \quad v = 1$$

Integrating Eq. (A-5) by use of the above boundary conditions in the range of p : $p \rightarrow 0$ and ϕ : $\phi \rightarrow 0$, Eq. (4) can be obtained.

Appendix 2

From Eq. (5), Eq. (A-6) can be derived.

$$d\phi/dx = -(RT/Fv)(dv/dx) \quad (\text{A-6})$$

Substituting Eq. (A-6) in Eq. (4), Eq. (A-7) is derived.

$$dx = - \left(\frac{RT\epsilon}{8\pi F^2} \right)^{1/2} \frac{dv}{v \left\{ \sum_i C_i (v^{z_i} - 1) \right\}^{1/2}} \quad (\text{A-7})$$

On the other hand, surface excess of i species, Γ_i , can be expressed as Eq. (A-8) (refer to Fig. 7).

$$\Gamma_i = \int_{x_0}^{\infty} \{ C_i \exp(-F\phi/RT) - C_i \} dx = \int_{x_0}^{\infty} C_i (v^{z_i} - 1) dx \quad (\text{A-8})$$

Substituting Eq. (A-7) in Eq. (A-8), Eq. (6) can be obtained. Integrating Eq. (A-7) in the range of x : $x \rightarrow x_0$ (v : $v \rightarrow v_0$), Eq. (11) can be obtained.

Appendix 3

The calculated points (closed circles) were estimated by use of known values of C_{DBS^-} and other bulk ion-concentrations for the purpose of examining the validity of the estimation method⁵⁾ of Γ_{DBS^-} from Eqs. (12) and (13).

On the other hand, the calculated curves were theoretically estimated by use of about constant values of the bulk ion-concentrations determined from the constant values of C_{DBS^-} and the pH: the values of C_{H^+} , C_{Na^+} ($= C_{\text{DBS}^-}$), $C_{\text{ClO}_4^-}$ ($= C_{\text{H}^+}$) can be regarded as nearly constant; C_{OH^-} can be neglected compared with the other bulk ion-concentrations at pH = 4.

Appendix 4

In this work, the cations are H^+ , Na^+ and metal ion, M^{n+} , and the anions are DBS^- , ClO_4^- and OH^- . In applying the G.C. model, the bulk concentration of all the ion species must be determined. The concentrations were determined as follows. It is possible to disregard the complex formation of metal ions because the solution is kept acidic by perchlorate. Therefore, Eq. (A-9) is obtained from the electrically neutral condition of the bulk solution.

$$C_{\text{H}^+} + C_{\text{Na}^+} + n C_{\text{M}^{n+}} = C_{\text{ClO}_4^-} + C_{\text{DBS}^-} + C_{\text{OH}^-} \quad (\text{A-9})$$

Since C_{H^+} , $C_{\text{M}^{n+}}$, $C_{\text{ClO}_4^-}$, C_{DBS^-} and C_{OH^-} were measured, C_{Na^+} is determined from Eq. (A-9).

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Nomenclature

B_1	= constant	[cm/sec]
B_2	= constant	[1/sec]
C	= bulk concentration	[mol/cm ³]
$\bar{C}$	= average bulk concentration	[mol/cm ³]
C_0	= concentration of feed liquid	[mol/cm ³]
F	= Faraday constant	[esu/mol]
K	= constant defined by Eq. (1)	[1/cm]
n_b	= number of bubbles having the diameter, d	[—]
R	= gas constant	[erg/mol/K]
r	= radius of hydrated ion	[Å]
S	= gas-liquid interfacial area per unit gas volume	[cm ² /cm ³]
T	= absolute temperature	[K]
V	= volumetric flow rate	[cm ³ /min]
V_a	= volumetric flow rate of gas	[cm ³ /min]
V_0	= volumetric flow rate of liquid	[cm ³ /min]
v	= defined by Eq. (5)	[—]
v_0, v'_0, v''_0, v'''_0	= values of v at $x = x_0, x = x'_0, x = x''_0$ and $x = x'''_0$	[—]
x	= distance from interface	[cm]
x_0, x'_0, x''_0, x'''_0	= distances of closest approach to interface	[cm]
z	= valency of ion	[—]
Γ	= surface excess	[mol/cm ²]
ϵ	= dielectric constant	[esu]
ρ	= charge density at x from interface	[esu/cm ³]
ϕ	= electrical potential at x	[esu]
ϕ_0	= electrical potential at interface	[esu]

<Superscripts>

—	= average
*	= saturated

<Subscripts>

1	= at $x = x_0$
2	= at $x = 0$
Co^{2+}	= cobalt ion
Cu^{2+}	= copper ion
DBS^-	= dodecylbenzene sulphonate ion
Fe^{3+}	= iron ion
H^+	= hydrogen ion
$i, i-1, i-2$	= ion species $i, i-1$ and $i-2$, respectively
metal	= metal ion
Ni^{2+}	= nickel ion
Na^+	= sodium ion
s	= surfactant

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