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The Adsorption of Dodecyldimethylammonium Bromide on Aqueous Surfaces of Sodium Bromide Solutions

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The surface tension of aqueous NaBr solutions of dodecyldimethylammonium bromide has been measured by the drop weight method at different surfactant and NaBr concentrations. By applying the Gibbs adsorption isotherm, surface excess densities of surfactant cation, Na^+ and Br^- are derived as functions of surfactant concentration at different NaBr concentrations. The rational mean activity coefficients of surfactant and NaBr are both approximated by a common expression satisfying the Brønsted principle for mixed electrolytes and containing the ionic strength as a variable. Surface excess density of surfactant cation increases with increasing surfactant concentration and has a general tendency still increasing even at the critical micelle concentration. Some comparison of the behavior of surface excess densities of ions between the present bromide system and the previous chloride system is made. The Corrin-Harkins plot for the critical micelle concentration consists of two straight lines intersecting at 0.015 mol dm^{-3} NaBr.

We have recently established the thermodynamic method for estimating surface excess densities of ionic species or solute components on aqueous surfaces of electrolyte solutions from measurements of their surface tension as functions of solute concentrations.[1–3] This method is based on the Gibbs adsorption isotherm for plane surfaces of dilute solutions and has been applied for aqueous solutions of mixed electrolytes having a common counterion, such as aqueous NaCl solutions of dodecyldimethylammonium chloride (DDAC).[4,5]

In the present work we briefly review the thermodynamic method, measure the surface tension of aqueous NaBr solutions of dodecyldimethylammonium bromide (DDAB), and apply the method to the experimental data. We will be concerned with the Gibbs adsorption isotherm for aqueous NaBr solutions of DDAB, in which no micelles are yet formed. Then we can derive the surface excess densities of three ionic species. We will further examine the effects of counterion species on the adsorption isotherms of ionic species and the critical micelle concentration (cmc) and standard free energy of micellization of dodecyldimethylammonium ions, by comparing the present results with those previously obtained for aqueous NaCl solutions of DDAC.[5]

Theoretical

Let us denote a cationic surfactant and sodium halide by DX and NaX, respectively, which have a common halide anion X^-. As we have already derived the Gibbs adsorption isotherm for aqueous solutions of DDAC–NaCl system,[5] we will here present brief derivation of the Gibbs adsorption isotherm.

In terms of species present in solution, H_2O, D^+, Na^+, and X^-, we can represent the Gibbs adsorption isotherm in the form

$$-\mathrm{d}\gamma = \Gamma_{H_2O}\mathrm{d}\mu_{H_2O} + \Gamma_{D^+}\mathrm{d}\mu_{D^+} + \Gamma_{Na^+}\mathrm{d}\mu_{Na^+} + \Gamma_{X^-}\mathrm{d}\mu_{X^-}, \tag{1}$$

where γ is the surface tension of solution, Γ_i and μ_i are the surface excess density and chemical potential of species, i, respectively. Introducing the Gibbs convention, $\Gamma_{H_2O}=0$, the surface excess densities of ions have definite values. Then, by means of the condition of electroneutrality on aqueous surfaces

$$\Gamma_{D^+} + \Gamma_{Na^+} = \Gamma_{X^-}, \tag{2}$$

we have the Gibbs adsorption isotherm in terms of components

$$-\mathrm{d}\gamma = \Gamma_{D^+}\mathrm{d}\mu_{DX} + \Gamma_{Na^+}\mathrm{d}\mu_{NaX}. \tag{3}$$

The chemical potentials of solute components, DX and NaX, can be expressed by their molar concentrations, C and C_s, and from these expressions we obtain

$$\begin{aligned}-\mathrm{d}\gamma = RT\Bigg[&\left\{\left(1+\frac{C}{C+C_s}\right)\Gamma_{D^+}+\frac{C}{C+C_s}\Gamma_{Na^+}\right\}\mathrm{d}\ln C\\ &+\left\{\frac{C_s}{C+C_s}\Gamma_{D^+}+\left(1+\frac{C_s}{C+C_s}\right)\Gamma_{Na^+}\right\}\mathrm{d}\ln C_s\\ &+\Gamma_{D^+}\,\mathrm{d}\ln y_{\pm}^2+\Gamma_{Na^+}\,\mathrm{d}\ln y_{s\pm}^2\Bigg],\end{aligned} \tag{4}$$

where R is the gas constant, T the temperature, and $y_{\pm}$ and $y_{s\pm}$ are the molar mean activity coefficients of DX and NaX, respectively.

The molar mean activity coefficients of DX and NaX, $y_{\pm}$ and $y_{s\pm}$, can be related to their rational mean activity coefficients, $f_{\pm}$ and $f_{s\pm}$, by[6a)]

$$\frac{y_{\pm}}{f_{\pm}} = \frac{y_{s\pm}}{f_{s\pm}} = \frac{\rho_w}{\rho - \frac{M-2M_w}{1000}C - \frac{M_s-2M_w}{1000}C_s}, \tag{5}$$

where M_w, M, and M_s are the molecular weights of H_2O, DX, and NaX, respectively, and ρ_w and ρ are the densities of water and solution, respectively.

As was demonstrated previously,[5] the rational mean activity coefficients of DX and NaX can both be approximately represented as a function of ionic strength, $C+C_s$,

$$\log f_{\pm} = \log f_{s\pm} = -\frac{P\sqrt{C+C_s}}{1+Qa\sqrt{C+C_s}} + B_s(C+C_s), \tag{6}$$

where the constants, P and Q, of the Debye-Hückel electrostatic term are determined by the temperature and the dielectric constant, and the ionic radius, a, serves as an adjustable parameter.[6b] The salting-out constant, B_s, is characteristic of NaX.

Then we have following identities, which are abbreviated by η and η_s, respectively:

$$\eta = \left(\frac{\partial \ln y_{\pm}^2}{\partial C}\right)_{C_s} = \left(\frac{\partial \ln y_{s\pm}^2}{\partial C}\right)_{C_s}, \tag{7}$$

$$\eta_s = \left(\frac{\partial \ln y_{\pm}^2}{\partial C_s}\right)_{C} = \left(\frac{\partial \ln y_{s\pm}^2}{\partial C_s}\right)_{C}. \tag{8}$$

The change of surface tension of solution can be formally related to the changes in concentrations of DX and NaX by

$$-\mathrm{d}\gamma = RT(\Gamma' \,\mathrm{d}\ln C + \Gamma'_s \,\mathrm{d}\ln C_s), \tag{9}$$

where Γ' and Γ'_s are given by

$$\Gamma' = \left(1+\frac{C}{C+C_s}+\eta C\right)\Gamma_{D^+} + \left(\frac{C}{C+C_s}+\eta C\right)\Gamma_{Na^+}, \tag{10}$$

$$\Gamma'_s = \left(\frac{C_s}{C+C_s}+\eta_s C_s\right)\Gamma_{D^+} + \left(1+\frac{C_s}{C+C_s}+\eta_s C_s\right)\Gamma_{Na^+}. \tag{11}$$

Solving equations 10 and 11, we obtain the surface excess densities of two cations as

$$\Gamma_{D^+} = \frac{1}{2+\eta C+\eta_s C_s}\left\{\left(1+\frac{C_s}{C+C_s}+\eta_s C_s\right)\Gamma' - \left(\frac{C}{C+C_s}+\eta C\right)\Gamma'_s\right\}, \tag{12}$$

$$\Gamma_{Na^+} = \frac{1}{2+\eta C+\eta_s C_s}\left\{-\left(\frac{C_s}{C+C_s}+\eta_s C_s\right)\Gamma' + \left(1+\frac{C}{C+C_s}+\eta C\right)\Gamma'_s\right\}, \tag{13}$$

and that of an anion as

$$\Gamma_{X^-} = \frac{1}{2+\eta C+\eta_s C_s}(\Gamma'+\Gamma'_s), \tag{14}$$

From Eqs. 5 and 6, we obtain

$$\eta = \eta_0 - \frac{2\left\{\left(\frac{\partial \rho}{\partial C}\right)_{C_s} - \frac{M-2M_w}{1000}\right\}}{\rho - \frac{M-2M_w}{1000}C - \frac{M_s-2M_w}{1000}C_s}, \tag{15}$$

$$\eta_s = \eta_0 - \frac{2\left\{\left(\frac{\partial \rho}{\partial C_s}\right)_{C} - \frac{M_s-2M_w}{1000}\right\}}{\rho - \frac{M-2M_w}{1000}C - \frac{M_s-2M_w}{1000}C_s}, \tag{16}$$

where

$$\eta_0 = \frac{2.303P}{(1+Qa\sqrt{C+C_s})^2\sqrt{C+C_s}} - 4.606B_s. \tag{17}$$

The density of aqueous NaX solution of DX is given by

$$\rho = \rho_s + (1-\bar{v}\rho_s)c, \tag{18}$$

where c (g cm^{-3})$=MC/1000$ is the weight concentration of solution, ρ_s is the density of solvent or aqueous NaX solution, and $\bar{v}$ is the partial specific volume of surfactant, DX. At surfactant concentrations lower than the critical micelle concentration

$$\left(\frac{\partial \rho}{\partial C}\right)_{C_s} = \frac{(1-\bar{v}\rho_s)M}{1000}, \tag{19}$$

$$\left(\frac{\partial \rho}{\partial C_s}\right)_{C} = \left(1-\frac{\bar{v}MC}{1000}\right)\left(\frac{\partial \rho_s}{\partial C_s}\right)_{C}. \tag{20}$$

Experimental

Materials. Dodecyldimethylammonium bromide (DDAB) was prepared from pure *N*,*N*-dimethyldodecylamine by passing dry HBr gas through its ethanolic solution and recrystallizing the resulting crystals from 1:1 acetone–diethyl ether mixtures three times. Commercial *N*,*N*-dimethyldodecylamine was purchased from Tokyo Kasei Kogyo Co., Inc., and purified by fractional distillation.

NaBr was of reagent grade from Wako Pure Chemical Industries, Inc., and was ignited on an evaporating dish and stored in a desiccator.

Methods. The surface tension of aqueous solutions was determined at 25±0.01 °C by means of the drop weight method, using a capillary tip of outer radius, r. The capillary was kept perpendicular, and its upper end was connected through rubber tubing to a burette, half-filled with water, so that the drop formed on the capillary tip could be kept at a desired size or released to fall at a desired instant by manipulating the burette. The capillary tip was kept in a glass bottle dipped in a water thermostat. Each drop was suspended on the tip for over 3 min before being allowed to fall, and five to ten drops of each solution were collected in a weighing bottle for weighing.

Surface tension, γ (mN m^{-1}), of solution was calculated from the weight, m, of a drop by the Harkins-Brown equation[7a]

$$\gamma = (mg/r)F, \tag{21}$$

where g is the gravitational acceleration (980 cm s^{-2}) and F is the correction factor, defined by V/r^3, V being the drop volume. The effective outer radius, r, of the capillary tip was determined by measuring the drop weight of distilled water, by assuming its surface tension to be 71.96 mN m^{-1},[7b] and it was found to be 0.3484 cm.

Density measurements of aqueous solutions were performed on an Anton Paar Precision Density Meter, DMA 02D. The temperature was kept at 25±0.01 °C by circulating water of constant temperature around the cell housing. The density meter was calibrated by using distilled water and air as standards, by assuming their densities to be 0.99704 g cm^{-3} and 0.00119 g cm^{-3}, respectively.

Results

Figure 1 shows the relation of surface tension, γ, with the logarithm of molar concentration of DDAB, log C, at different NaBr concentrations, C_s. Surface tension decreases with increasing surfactant concentration at concentrations up to the cmc, C_0, and also with increasing NaBr concentration. Values of Γ' can be obtained from the slope of the surface tension curves by

$$\Gamma' = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \ln C}\right)_{C_s}. \tag{22}$$

At concentrations up to the cmc, we can apply the expression of the Gibbs adsorption isotherm developed above. At concentrations higher than the cmc, surface tension always remains constant, which is designated as γ_0, and it is clear that $\Gamma'=0$ for $C \geqq C_0$.

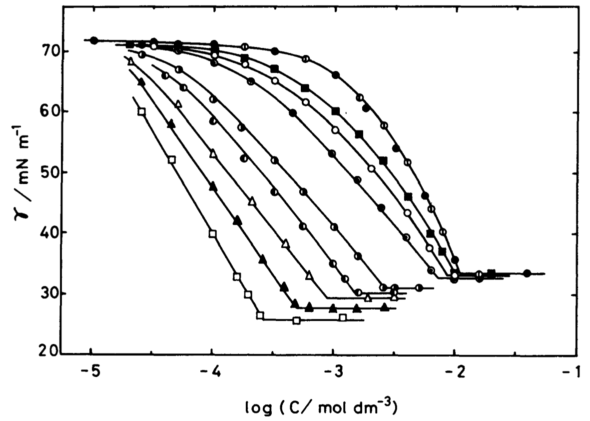

Fig. 1. Variation of surface tension with the logarithm of surfactant concentration at different NaBr concentrations.

C_s/mol dm^{-3}: ●; 0, ⦶; 1×10^{-4}, ■; 5×10^{-3}, ○; 0.01, ⊙; 0.02, ◑; 0.10, ◐; 0.20, △; 0.50, ▲; 1.00, □; 2.00.

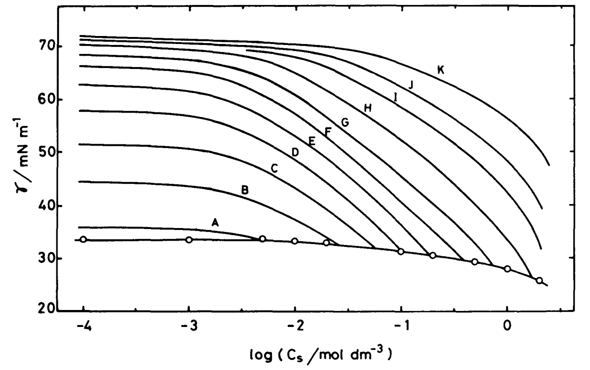

Fig. 2. Variation of surface tension with the logarithm of NaBr concentration at different surfactant concentrations. ○: Constant surface tension, γ_0, at a given NaBr concentration, obtained at surfactant concentrations higher than the critical micelle concentration.

$-\log C$/mol dm^{-3}: A; 2.0, B; 2.2, C; 2.4, D; 2.6, E; 2.8, F; 3.0, G; 3.2, H; 3.5, I; 3.8, J; 4.0, K; 4.3.

In Fig. 2 surface tension is replotted against the logarithm of molar concentration of NaBr at different surfactant concentrations. The lowest curve gives dependence of the constant surface tension on NaBr concentration, the constancy being observed at surfactant concentrations higher than the cmc. From the slope of surface tension curves we can obtain values of Γ'_s by

$$\Gamma'_s = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \ln C_s}\right)_C. \tag{23}$$

Table 1 summarizes relevant numerical data at the cmc derived from Figs. 1 and 2. With increasing NaBr concentration, values of Γ' at the cmc decreases in the range of NaBr concentrations up to 0.10 mol dm^{-3}, and then increases at higher NaBr concentrations. On the other hand, values of Γ'_s at the cmc increases monotonously with increasing NaBr concentrations.

Figure 3 shows the density of aqueous NaBr solutions of DDAB as a function of surfactant concentration. It is

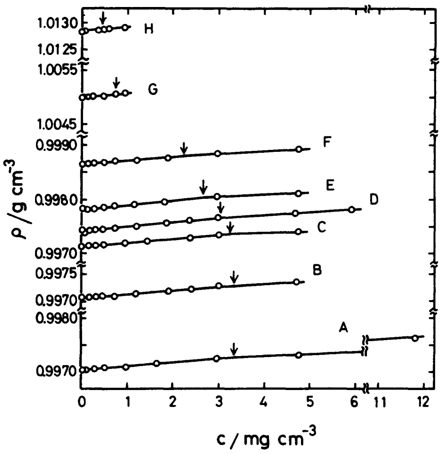

Fig. 3. Density of aqueous NaBr solutions of surfactant as a function of its concentration (g cm^{-3}). Arrows indicate the location of the critical micelle concentrations.

C_s/mol dm^{-3}: A; 0, B; 1×10^{-4}, C; 1×10^{-3}, D; 5×10^{-3}, E; 0.01, F; 0.02, G; 0.10, H; 0.20.

TABLE 1. CRITICAL MICELLE CONCENTRATION, APPARENT SURFACE EXCESS DENSITIES, AND CONSTANT SURFACE TENSION AT THE CRITICAL MICELLE CONCENTRATION FOR AQUEOUS NaBr SOLUTIONS OF DODECYLDIMETHYLAMMONIUM BROMIDE AT 25 °C

C_s / mol dm^{-3}	C_0 / mmol dm^{-3}	Γ' at C_0 / 10^{-10} mol cm^{-2}	Γ'_s at C_0 / 10^{-10} mol cm^{-2}	γ_0 / mN m^{-1}
0	11.1	8.96		33.6
1×10^{-4}	11.1	8.96	0.08	33.6
1×10^{-3}	10.9	8.41	0.23	33.6
5×10^{-3}	10.1	6.58	1.02	33.3
0.01	8.83	5.42	1.74	33.2
0.02	7.38	4.54	2.63	32.9
0.10	2.51	4.45	3.40	31.2
0.20	1.51	4.48	3.38	30.4
0.50	0.859	4.56	3.80	29.1
1.00	0.506	4.99	5.16	27.6
2.00	0.269	5.24	7.07	25.7

TABLE 2. PARTIAL SPECIFIC VOLUME AND PARTIAL MOLAR VOLUME OF DODECYLDIMETHYLAMMONIUM BROMIDE BELOW AND ABOVE THE CRITICAL MICELLE CONCENTRATION IN AQUEOUS NaBr SOLUTIONS

		$C \leqq C_0$		$C \geqq C_0$	
C_s / mol dm^{-3}	c_0 / mg cm^{-3}	$\bar{v}$ / cm^3 g^{-1}	$\bar{V}$ / cm^3 mol^{-1}	$\bar{v}$ / cm^3 g^{-1}	$\bar{V}$ / cm^3 mol^{-1}
0	3.27	0.935	275.2	0.958	282.0
1×10^{-4}	3.27	0.930	273.7		
1×10^{-3}	3.21	0.926	272.5		
5×10^{-3}	2.97	0.928	273.1	0.955	281.1
0.01	2.60	0.928	273.1		
0.02	2.17	0.933	274.6	0.950	279.6

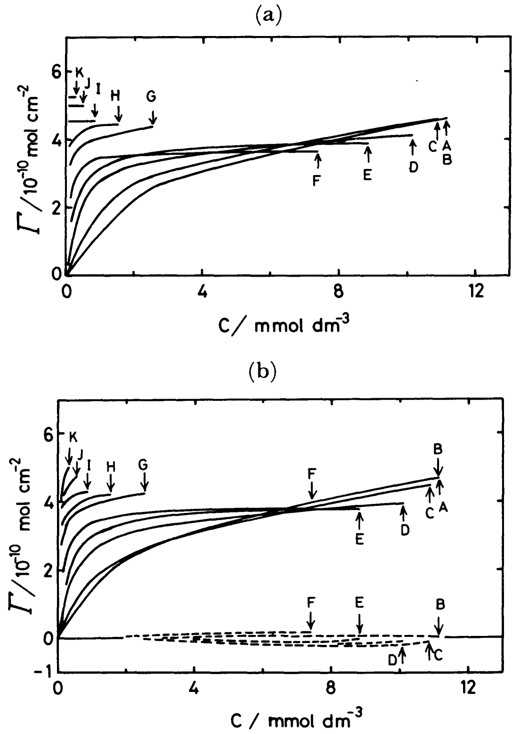

Fig. 4. Adsorption isotherms of ions on aqueous surfaces at different NaBr concentrations. (a) Γ_{D^+} *vs.* *C*, (b) Γ_{Na^+} (----) and Γ_{Br^+} (——) *vs.* *C*. Arrows indicate the location of the critical micelle concentrations.

C_s/mol dm^{-3}: A; 0, B; 1×10^{-4}, C; 1×10^{-3}, D; 5×10^{-3}, E; 0.01, F; 0.02, G; 0.10, H; 0.20, I; 0.50, J; 1.00, K; 2.00.

seen that Eq. 18 holds well for the relation between the density and surfactant concentration below the cmc, and, as shown in Table 2, the partial specific volume of DDAB is found to be 0.93 cm^3 g^{-1} at surfactant concentrations lower than the cmc, irrespective of NaBr concentration. Above the cmc, the slope of the density curves becomes less steep, indicating that the partial specific volume of DDAB abruptly increases beyond the cmc, as shown in Table 2.

In applying Eqs. 12, 13, and 14 we use the values

$$P = 0.5115, \quad Qa = 1.316, \quad B_s = 0.075, \tag{24}$$

where the value of B_s has been determined by adapting the tabulated activity data of NaBr up to 4.0 mol dm^{-3} [6c] to Eq. 6. Then we can derive the surface excess densities of surfactant cation, Na$^+$ and Br$^-$. Figure 4 shows the surface excess densities of ions plotted against the surfactant concentration. It is seen in Fig. 4(a) that the value of Γ_{D^+} increases more rapidly and approaches the saturated value at a low surfactant concentration, as the NaBr concentration is 5×10^{-3}, 0.01, or 0.02 mol dm^{-3} or it is higher than 0.20 mol dm^{-3}. When the NaBr concentration is 0.10 mol dm^{-3} or it is lower than 1×10^{-3} mol dm^{-3}, Γ_{D^+} appears to increase without reaching their saturation even at the cmc. It is seen in Fig. 4(b) that the value of Γ_{Br^-} increases without reaching its saturated value except that the NaBr concentration is 0.01 or 0.02 mol dm^{-3}. The value of Γ_{Na^+} is very low in its absolute value and is almost zero for all NaBr concntrations.

Recently, it was found that the surface tension-concentration curves of aqueous solutions of decylammonium chloride or dodecylammonium chloride show a break point at a low surfactant concentration.[8,9] Such a break point can be more clearly observed when the mixed adsorbed film is present.[9] The presence of the break point gives the discontinuity to the surface excess density of surfactant ion, indicating the establishment of equilibrium between two kinds of "surface phases." In the present data such a break point is not detectable at all NaBr concentrations and there is no discontinuity in the surface excess density curves.

Table 3 gives the values of Γ_{D^+}, Γ_{Na^+}, and Γ_{Br^-} at the cmc for different NaBr concentrations, and Fig. 5 shows these values as functions of the square root of NaBr concentration. With increasing NaBr concentration up to 0.01 mol dm^{-3}, the value of Γ_{D^+} at the cmc decreases. After passing the minimum, it increases gradually with increasing NaBr concentration.

Discussion

Surface Excess Densities of Ions. As shown in Fig. 4(a), the surface excess density of surfactant cation, Γ_{D^+}, at several NaBr concentrations still increases without reaching its saturation even at the cmc. Such behavior was not observed in the DDAC–NaCl system.[4,5] As shown in Fig. 4(b), the surface excess density of Br$^-$, Γ_{Br^-}, also increases even at the cmc at several NaBr concentrations. In the DDAC–NaCl system Γ_{Cl^-} behaves in the same way only at high NaCl concentrations.

Table 3. Surface excess densities of surfactant cation, Na^+ and Br^- at the critical micelle concentration

C_s $mol\ dm^{-3}$	Γ_{D^+} at C_o $10^{-10}\ mol\ cm^{-2}$	Γ_{Na^+} at C_o $10^{-10}\ mol\ cm^{-2}$	Γ_{Br^-} at C_o $10^{-10}\ mol\ cm^{-2}$
0	4.68		4.68
1×10^{-4}	4.68	0.04	4.73
1×10^{-3}	4.55	−0.11	4.44
5×10^{-3}	4.22	−0.18	4.04
0.01	3.83	−0.05	3.78
0.02	3.62	0.19	3.81
0.10	4.36	−0.11	4.25
0.20	4.45	−0.22	4.23
0.50	4.55	−0.26	4.30
1.00	4.99	−0.18	4.81
2.00	5.24	−0.23	5.02

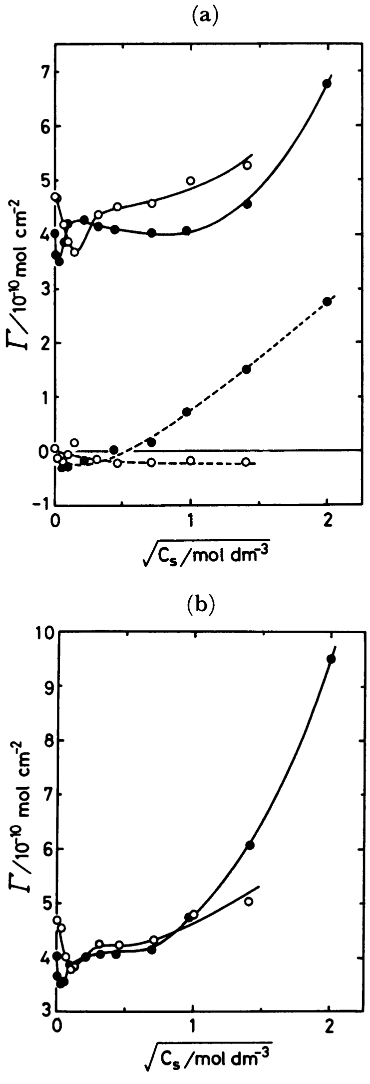

Fig. 5. The change of surface excess densities of ions at the critical micelle concentration.

(a) Γ_{D^+} (——) and Γ_{Na^+} (----) *vs.* $\sqrt{C_s}$, (b) Γ_{X^-} *vs.* $\sqrt{C_s}$. X^-: Br^- or Cl^-.

○: DDAB–NaBr, ●: DDAC–NaCl.

The values of Γ_{D^+} and Γ_{Br^-} at the cmc in the DDAB–NaBr system are essentially equal to their saturated values, respectively, at a given NaBr concentration. In Fig. 5 the values of Γ_{D^+}, Γ_{Na^+} and Γ_{Br^-} at the cmc are plotted against the square root of NaBr concentration, together with the saturated values of Γ_{D^+}, Γ_{Na^+}, and Γ_{Cl^-} in the DDAC–NaCl system.[4,5]

It is clear in Fig. 5(a) that the value of Γ_{D^+} at the cmc for the DDAB–NaBr system is higher than that for the DDAC–NaCl system at the same concentrations of sodium salts except at 0.01 and 0.02 mol dm^{-3}. This means that the effect of salting-out of Br^- is stronger than that of Cl^-, which is apparently exhibited in the values of B_s in Eq. 6, *i.e.*, 0.075 for NaBr and 0.055 for NaCl.[5,6b] It is also seen that the value of Γ_{Na^+} at the cmc for the DDAB–NaBr system is almost constant at NaBr concentrations higher than 0.20 mol dm^{-3}. For the DDAC–NaCl system the value of Γ_{Na^+} at the cmc increases rapidly and becomes positive at NaCl concentrations higher than 0.20 mol dm^{-3}. The reason for the large difference in Γ_{Na^+} at high salt concentrations is not clear, but it is certain that the difference between the two systems arises from the surface tension data themselves, since the treatment based on the ideal solution approximation also leads to such a difference in Γ_{Na^+}.

In Fig. 5(b) it is seen that the value of Γ_{Br^-} at the cmc for the DDAB–NaBr system is of the same order of magnitude as that of Γ_{Cl^-} at the cmc for the DDAC–NaCl system, as long as the concentrations of sodium salts are lower than 1.0 mol dm^{-3}. At concentrations higher than 1.0 mol dm^{-3}, the value of Γ_{Cl^-} at the cmc for the DDAC–NaCl system increases rapidly. This is because the value of Γ_{Na^+} for the DDAC–NaCl system, *i.e.*, the adsorption of NaCl, increases more rapidly.

The Corrin-Harkins Relation. Figure 6 shows the Corrin-Harkins plot for the cmc of the DDAB–NaBr system together with that of the DDAC–NaCl system. For the DDAB–NaBr system a linear relation holds at low and high counterion concentrations, respectively:

$$\log C_o = -0.452 \log (C_o+C_s) - 2.83,\quad C_s\leqq 0.015, \tag{25}$$

$$\log C_o = -0.758 \log (C_o+C_s) - 3.33,\quad C_s\geqq 0.015. \tag{26}$$

The threshold concentration of NaBr for the two linear plots at low and high counterion concentrations, 0.015 mol dm^{-3}, is lower than that obtained by light scattering measurement,[10] 0.095 mol dm^{-3}.

For the DDAC–NaCl system the Corrin-Harkins plot of the cmc is linear at NaCl concentrations up to 0.50 mol dm^{-3}:

$$\log C_o = -0.621 \log (C_o+C_s) - 2.98,\quad C_s\leqq 0.50, \tag{27}$$

and at higher NaCl concentrations than 0.50 mol dm^{-3}, a linear relation no longer holds between the logarithm of the cmc and the logarithm of the concentration of Cl^-.[5]

As the cmc is a good measure of stability of the micellar state relative to the monomeric state, the lower value of the cmc for the DDAB–NaBr system than that for the DDAC–NaCl system clearly indicates the stabili-

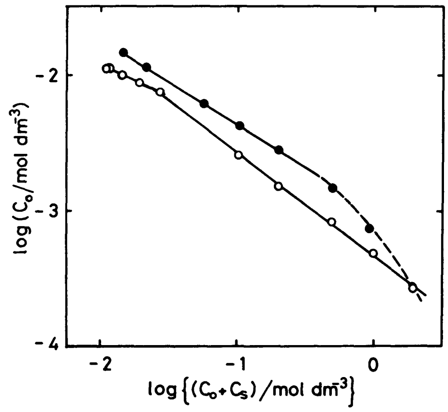

Fig. 6. Relation of the logarithm of the critical micelle concentration with the logarithm of ionic strength. ○: DDAB-NaBr, ●: DDAC-NaCl.

zation of dodecyldimethylammonium micelle by binding of Br^- stronger than binding of Cl^-. Similar relations of the lower value of the cmc of the bromide system than that of the chloride system were observed for surfactants having a dodecyl group[11,12] and surfactants having an octadecyl group.[13]

Standard Free Energy of Micellization. In terms of the pseudo-phase model for the micelle,[14] in which the solution of surfactant monomer is an ideal solution and the micelle is a separated phase, the standard free energy of micellization per mole of surfactant is given by

$$\Delta G_m^{\circ} = RT \ln X_o, \tag{28}$$

where X_o is the mole fraction of surfactant at the cmc. When expressed by the molar concentration of surfactant at the cmc, C_o, we have

$$\Delta G_m^{\circ} = RT \ln \frac{M_w C_o}{1000\rho_o - (M_s - M_w)C_s}, \tag{29}$$

where ρ_o denotes the density of solution at the cmc.

Table 4 gives the values of $-\Delta G_m^{\circ}$ for the DDAB–NaBr system, together with those for the DDAC–NaCl system. The micelles are both stabilized more as the ionic strength is increased. The stabilization of micelle is 0.7 kJ mol^{-1} more effective for the DDAB-NaBr system compared with that for the DDAC–NaCl system, as long as the ionic strength is lower than 0.05 mol dm^{-3}.

Surface Tension. We had originally attempted to measure the surface tension of solution by means of the Wilhelmy hanging plate method, but the downward shift of the plate was not reproducible at all. Thus we decided to employ the drop weight method for surface tension measurements.

For the surface tension measurements of aqueous solutions of a cationic surfactant, either in the presence or absence of added salt, we have found that the hanging plate method does not give any reproducible results, owing to the built-up of the cationic on the glass plate (and also possibly on the platinum plate) and the resulting change in contact angle. For the surface tension measurements of aqueous solutions by means of Wilhelmy hanging plate method, the contact angle of solution on the plate must be nearly zero. But in the case of cationic surfactants such as the derivatives of long-chain alkylammonium, this condition is never satisfied generally.

Table 4. Standard free energy of micellization of dodecyldimethylammonium bromide in aqueous NaBr solutions and dodecyldimethylammonium chloride in aqueous NaCl solutions at 25 °C

C_s mol dm^{-3}	DDAB–NaBr $-\Delta G_m^{\circ}$ kJ mol^{-1}	DDAC–NaCl $-\Delta G_m^{\circ}$ kJ mol^{-1}
0	21.1	20.4
1×10^{-4}	21.1	20.4
1×10^{-3}	21.2	20.5
5×10^{-3}	21.3	20.6
0.01	21.7	21.0
0.02	22.1	
0.05		22.5
0.10	24.8	23.5
0.20	26.0	24.5
0.50	27.4	26.1
1.00	28.7	27.9[a)]
2.00	30.3	30.3
4.00		34.1

a) C_s=0.94 mol dm^{-3}.

The drop weight method is universally applicable for the measurements of surface tension of aqueous solutions of any surfactant. It permits to measure even the time change of surface tension, as referred to above.

The tendency of the relations between surface tension and surfactant concentration and between surface tension and the concentration of sodium salt in the present DDAB–NaBr system is analogous to those of the previous DDAC–NaCl system.[5] As it is seen in Fig. 1, the surface tension of the DDAB–NaBr system decreases with increasing the surfactant concentration up to the cmc and also with increasing the NaBr concentration, as was observed for the DDAC–NaCl system. At surfactant concentrations higher than the cmc, the surface tension remains constant in both of these systems.

Comparing the surface tension of two systems at the same concentration of the sodium salt, the surface tension of the DDAB–NaBr system is lower than that of the DDAC–NaCl system at all surfactant concentrations and also at all concentrations of sodium salt.

Partial Molar Volume. Table 2 gives the values of the cmc identified as the break point of the density curves of solution. These values are in agreement with those derived from the surface tension measurements.

The partial molar volume, $\bar{V}=M\bar{v}$, of DDAB changes abruptly at the cmc, and their values above and below the cmc are given in Table 2. The change in partial molar volume of DDAB by the micellization is 5—8 cm^3 mol^{-1}, depending on the NaBr concentration. The observed values for DDAB are comparable with that for DDAC in water, 8.4 cm^3 mol^{-1}. They are also roughly of the same order of magnitude or smaller than those for surfactants having a dodecyl group.[15,16]

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