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Studies on the Aqueous Solutions of Guanidinium Salts. XIV. Effect of Guanidinium Bromide on the Surface Tension of Aqueous Solutions of the Cationic Surfactants

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The surface tensions of decyl-, tetradecyl-, and hexadecyl-trimethylammonium bromides were measured in the aqueous solutions of potassium bromide (KBr) and guanidinium bromide (GuBr). The critical micelle concentrations (CMC's) of the above surfactants decreased with increase of the concentration of KBr, while the CMC's showed minimum values in the aqueous GuBr solution, as the concentration of GuBr increased. The Langmuir coefficient, K_C, increased with decrease of the CMC. The influence of the salts on the surface tension and the micellization were well described in terms of the activity of the surfactant calculated by combining the Debye-Hückel law and Setschenow's equation.

A large number of studies have been reported on the effect of various electrolytes on the surface tension, the adsorption on the air-water interface and the micellization of surfactants.[1-9] The association and the adsorption to the air-water interface of ionic surfactant in aqueous solution are governed by two opposing forces. The hydrophobic force which is mainly due to the ordered water molecules around the hydrophobic tail of surfactant repelles the surfactant molecules or ions from the aqueous bulk solution to the interface or the micelle core. The polar head group favour the aqueous bulk phase rather than such ordered phase, because the electrostatic repulsive force between the head groups makes the surfactant molecule difficult to associate. In this connection, inorganic salts decrease the CMC and increase the adsorption to the air-water interface. The effect of the inorganic electrolytes were roughly described in terms of the change of the activity of surfactant in the presence of the salts.[10,11] In this treatment, however, the activity of surfactant was estimated by the Debye-Hückel theory and the effect of the salts on the hydrophobic hydration was ignored.

The organic salts, such as guanidinium and biguanide salts have been known to influence significantly the hydrophobic hydration.[12-14] The reduction of the hydrophobic hydration must decrease the activity of surfactant and increase the CMC.

From these point of view, we measured the surface tension of some alkyltrimethylammonium bromides (C_nBr) in aqueous solutions of guanidinium bromide (GuBr) and KBr, and obtained anomalous results for the C_nBr–GuBr–H_2O system. To interpret these results by the phase separation model, we introduced a new expression for the activity coefficient of ionic surfactant in salt solutions by taking into consideration the effects of salts on the hydrophobic group besides the ionic head group. Based on the activity thus obtained, the variations of CMC and surface tension depending on the concentration and the kind of salts were well interpreted in terms of the change of the activity of the surfactants in salts solutions.

Experimental

Materials. Dodecyl-, tetradecyl-, and hexadecyltrimethylammonium bromides were synthesized from corresponding alkyl bromides and trimethylamine by the method described elsewhere.[15] The crude product was recrystallized from ethanol two or three times. To remove the raw materials, Soxhlet's extracter was employed using ether as the solvent. After extraction, recrystallization from ethanol-ether mixture gave a white crystalline product. In elementary analysis, the experimental values were in good agreement with those of the calculated values as shown in Table 1. Guanidinium bromide used was the same compound reported previously.[12] Reagent grade 1-butanol, 1-hexanol, 1-octanol, and 1-decanol (Nakarai Chemical Co., Ltd.) were used without further purification. The purities of these alcohols were more than 98%. All solutes were dissolved in deionized and redistilled water. Aqueous solutions of GuBr and KBr were purified through activated charcoal powder before use.

Surface Tension Measurements. The surface tension was measured by Du Nouy tensiometer. The platinum ring with diameter 23 mm was heated by oxidizing flame before use. All glass apparatus were preserved in chromate-sulfric acid mixture and linsed well with distilled water before use. Temperature of the thermostat was maintained at 25±0.2 °C. For the calculation of the surface tension of aqueous solutions, the value of 71.96 mN·m^{-1} was used as the surface tension of pure water at 25 °C. The experimental determination of the surface tension was precise to ±0.1 mN·m^{-1}.

TABLE 1. ELEMENTARY ANALYSIS OF CATIONIC SURFACTANTS (%)

		H	C	N
Dodecyltrimethylammonium bromide ($C_{12}Br$)	Calcd	11.11	58.42	4.54
	Exp.	11.32	58.32	4.45
Tetradecyltrimethylammoniumbromide ($C_{14}Br$)	Calcd	11.38	60.69	4.16
	Exp.	11.64	60.74	4.02
Hexadecyltrimethylammonium bromide ($C_{16}Br$)	Calcd	11.61	61.61	3.84
	Exp.	11.70	62.86	3.77

Solubility Measurements. The saturated aqueous solutions of alcohols were obtained by mixing the excess amount of alcohol and water in a thermostat bath with magnetic stirrer at 25±0.1 °C. It took 2—3 d to reach equilibrium. After equilibrium, UV spectra of the saturated solutions were measured for the detection of the emulsification of alcohols. The differences of the intensities at 265 nm between water and the saturated aqueous alcohol solutions were not observed except for aqueous 1-butanol solution. The solubilized amount of alcohol was determined from the peak height of the gas chromatogram (GC). GC conditions are as follows; Column: 10% PEG20M on Chromosorb W, 100—200 mesh packed in 3 mm×1 m glass tubing; Column temperature: 120 °C; Carrier gas: He; Flow rate: 40 cm^3·min^{-1}; Injection temperature: 170—190 °C; Detector: FID.

Results

Surface Tensions of C_nBr Solutions. The surface tension, γ, at constant salts concentrations are shown as a function of logarithm of the concentration of $C_{14}Br$ in Figs. 1 and 2. The concentrations of surfactant and the added salts are expressed by C/mol·dm^{-3} and C_s/mol·dm^{-3}, respectively. At constant C_s, the surface tension decreased with increase of C. The break point for each curve is regarded as the critical micelle concentration (CMC) which is given in Table 2 together with those of $C_{12}Br$ and $C_{16}Br$. As shown in Fig. 1, the surface tension at a constant C decreases with increase of the concentration of KBr. Therefore, the curve of surface tension *vs.* log C shifts to the lower concentration region of surfactant with increase of C_s. However, as shown in Fig. 2, the behavior of the surface tension *vs.* log C curves for the $C_{14}Br$–GuBr–H_2O system is different from that of the $C_{14}Br$–KBr–H_2O system. At constant C, the surface tension decreases with increase of C_s up to about 1 mol·dm^{-3} and above this concentration, the surface tension increases with the concentration of GuBr. This phenomenon was also observed in the $C_{12}Br$–GuBr–H_2O and $C_{16}Br$–GuBr–H_2O systems.

Table 2. The CMC values of alkyltrimethylammonium bromides in aqueous KBr and GuBr solutions

KBr; C_s/ mM	CMC/ mol·dm^{-3}	GuBr; C_s/ mM	CMC/ mol·dm^{-3}
	$C_{12}Br$		
0	1.10×10^{-2}	83.8	3.98×10^{-3}
0.96	1.07×10^{-2}	424	2.04×10^{-3}
9.58	2.88×10^{-3}	894	1.95×10^{-3}
95.8	8.71×10^{-4}	1392	2.69×10^{-3}
	$C_{14}Br$		
0	3.16×10^{-3}	0.79	2.95×10^{-3}
1.06	2.75×10^{-3}	7.87	1.48×10^{-3}
10.6	1.29×10^{-3}	78.7	3.89×10^{-4}
98.5	3.16×10^{-4}	394	2.14×10^{-4}
956	4.77×10^{-4}	1076	2.00×10^{-4}
		1685	3.24×10^{-4}
		2624	5.62×10^{-4}
	$C_{16}Br$		
0	9.42×10^{-4}	0.90	5.69×10^{-4}
0.96	6.08×10^{-4}	8.76	1.58×10^{-4}
10.0	1.32×10^{-4}	81.9	3.55×10^{-5}
95.4	2.60×10^{-5}	305	2.00×10^{-5}
820	5.96×10^{-6}	573	2.09×10^{-5}
		912	2.24×10^{-5}

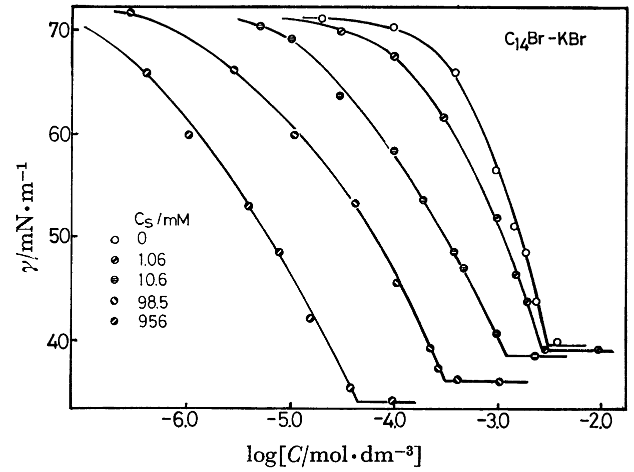

Fig. 1. The plot of the surface tension, γ, against the concentration of $C_{14}Br$, C, in aqueous KBr solution.

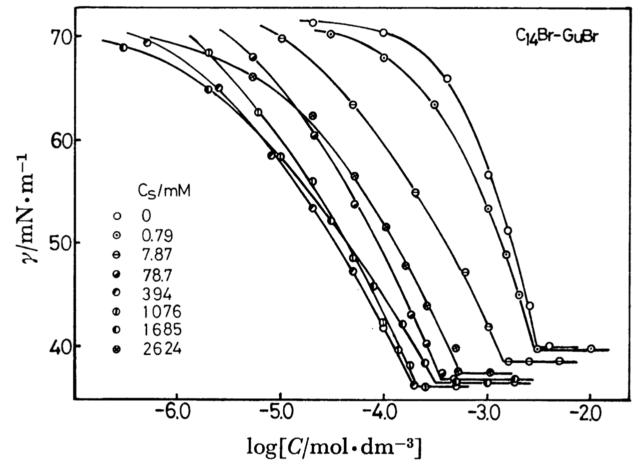

Fig. 2. The plot of the surface tension, γ, against the concentration of $C_{14}Br$, C, in aqueous GuBr solution.

Effect of the Counter Ion Concentration on CMC. Using the CMC values obtained from Figs. 1 and 2, the values of log CMC were plotted against logarithm

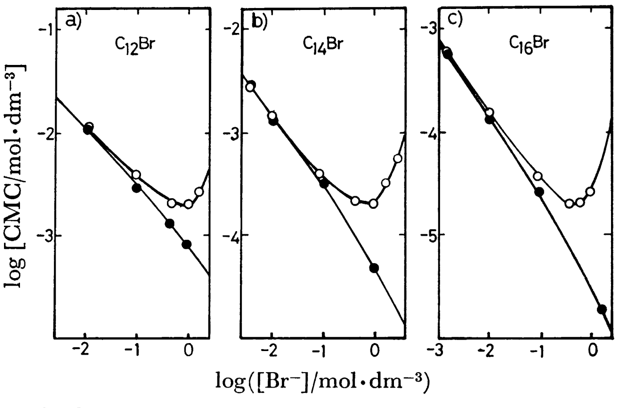

Fig. 3. The plot of log CMC against log [Br$^-$] in aqueous salt solution.
Salt; ○: GuBr, ●: KBr.

of counter ion concentration, log[Br$^-$].[1,3] They are shown in Figs. 3-a, 3-b, and 3-c. In the C_nBr–KBr–H_2O system, the values of log CMC decrease with increase of log[Br$^-$] values. The degree of CMC-lowering increases with the alkyl chain length. However, in the C_nBr–GuBr–H_2O system, the value of log CMC decreases with increase of log[Br$^-$], reaches a minimum and then increases with log[Br$^-$]. The concentrations of counter ion at the minimum points decrease with increase of alkyl chain length.

Adsorption at the Air-Water Interface. The adsorption amount of surfactant, Γ, is essentially defined by the Gibbs adsorption equation.[1,16]

$$\Gamma = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \ln a}\right)_{T,P}, \tag{1}$$

where a is the activity of surfactant. If the activity coefficient can be regarded as unity, Eq. 1 is rewritten as Eq. 2,

$$\Gamma = -\frac{1}{iRT}\left(\frac{\partial \gamma}{\partial \ln C}\right)_{T,P}, \tag{2}$$

where

$$i = \nu_-\left(\frac{\nu_- C}{\nu_- C + \nu_{s-} C_s}\right) + \nu_+. \tag{3}$$

In Eqs. 1, 2, and 3, R, T, and P are the usual meanings, and ν_+ and ν_- are the number of moles of cation and anion formed from 1 mol of ionic surfactant, respectively, and ν_{s-} is the number of moles of anion fully dissociated from 1 mol of the added salt. As shown in Figs. 4 and 5, the Γ values of $C_{14}Br$ calculated from Eq. 2 are plotted against C at various C_s's. The Langmuir equation was applied to these systems.

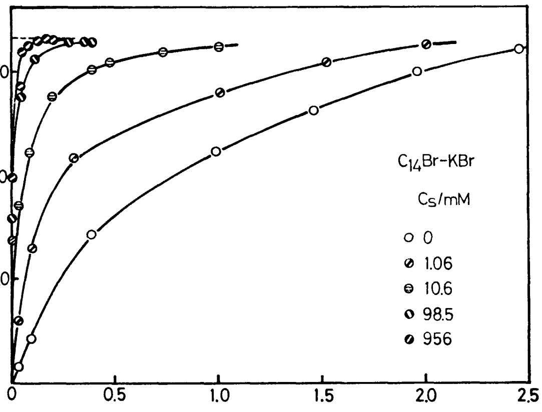

Fig. 4. Adsorption isotherms of $C_{14}Br$ in various concentrations of KBr solutions at 25°C.

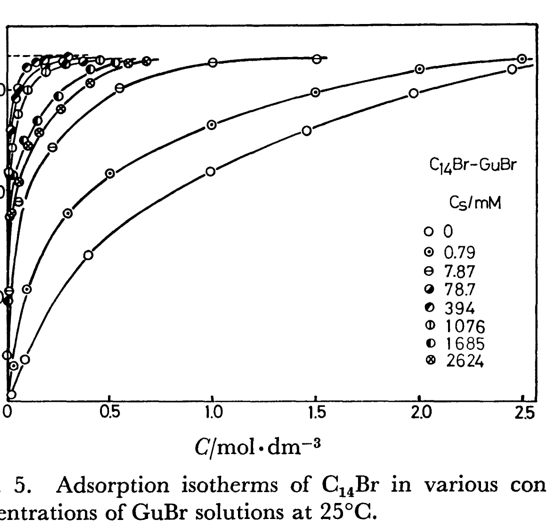

Fig. 5. Adsorption isotherms of $C_{14}Br$ in various concentrations of GuBr solutions at 25°C.

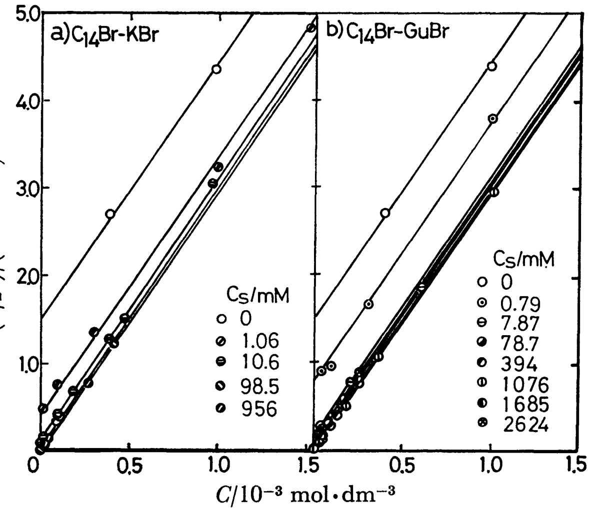

Fig. 6. Plots of C/Γ *vs.* C in various concentrations of salt solutions.

$$\Gamma = \frac{\Gamma_s K_c C}{1 + K_c C}, \tag{4}$$

where Γ_s is the saturated adsorption amount and K_c is the constant concerning the strength of adsorption. Equation 4 is rewritten as,

$$\frac{C}{\Gamma} = \frac{1}{\Gamma_s K_c} + \frac{1}{\Gamma_s} C. \tag{5}$$

The plot of C/Γ against C for the $C_{14}Br$–KBr–H_2O and $C_{14}Br$–GuBr–H_2O systems are shown in Figs. 6-a and 6-b, respectively. In accordance with Eq. 5, linear relationships exist between C/Γ and C. The values of Γ_s and K_c obtained from the slopes and the intercepts are shown in Table 3. In both the systems, Γ_s takes a constant value, 3.32×10^{-10} mol/cm^2, *i.e.* 50.1 Å^2/molecule. In the $C_{14}Br$–KBr–H_2O system, K_c values increase with the concentration of KBr, but in the $C_{14}Br$–GuBr–H_2O system, K_c values once increase and then decrease

TABLE 3. THE VALUES OF K_c AND Γ_s OF $C_{14}Br$ IN AQUEOUS KBr AND GuBr SOLUTIONS

KBr		GuBr	
C_s/mM	K_c/dm^3·mol^{-1}	C_s/mM	K_c/dm^3·mol^{-1}
0	2.17×10^3	0.79	4.01×10^3
1.06	6.49×10^3	7.87	2.00×10^4
10.6	1.95×10^4	78.7	1.95×10^5
98.5	1.20×10^5	394	2.03×10^5
956	5.50×10^5	1076	9.80×10^4
		1685	3.64×10^4
		2624	2.96×10^4
Γ_s		Γ_s	
3.32×10^{-10} mol·cm^{-2}		3.32×10^{-10} mol·cm^{-2}	

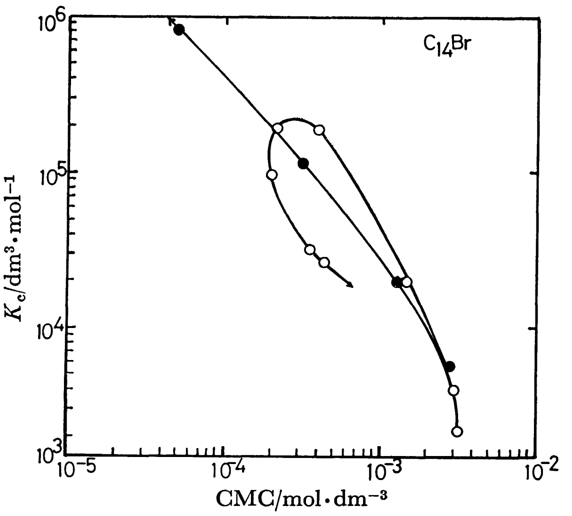

Fig. 7. The relationship between K_c and CMC. Salt; ○: GuBr, ●: KBr.

with increase of the concentration of GuBr.

Relationship between CMC and K_c. In order to elucidate the relation between micelle equilibrium and adsorption equilibrium in aqueous salt solution, the values of log K_c were plotted against the values of log CMC. (Fig. 7) The arrow sign represents the direction of the increase of salt concentrations. Though the shapes of two curves are different from each other, the relation between K_c and CMC is similar, that is, the value of log K_c increases with decrease of the value of log CMC. This fact indicates that the adsorption at air-water interface is closely related to the micellization.

Discussion

Micellization. In most studies concerning the effect of electrolyte on the micelle formation, the plot of log CMC against the logarithm of counter ion concentration has been considered linear. The slope was regarded as a parameter related to the state of the dissociation of counter ion or the formation of ionic atmosphere by counter ions around the micelle. However, our investigation revealed that these plots are not linear in aqueous ternary system, especially in the C_nBr–GuBr–H_2O system. Therefore, it is not adequate to take into account the effect of electrolyte on micellization on the basis of only electrostatic effect of counter ion. Shinoda and Huchinson,[16] and Herraman[17] analyzed the experimental results thermodynamically, by regarding the micellization phenomenon as a kind of phase separation and met with success. Recently, it was pointed out that the activity, instead of the concentration, of surfactant should be used for the analysis of the experimental data.[10] Therefore, we used the activity of surfactant for the analysis of data. According to the phase separation model, it may be considered that the micelle formation occured when the activity of surfactant has reached a certain value.

The activity of cationic surfactant at CMC, a_m, in the aqueous solution of electrolyte with common anion may be written as,

$$a_m = f_\pm^{\nu}(CMC)^{\nu_+}(\nu_-(CMC)+\nu_{s-}C_s)^{\nu_-}, \qquad (6)$$

where $f_\pm$ is the mean ionic activity coefficient of surfactant and $\nu=\nu_++\nu_-$. In this work, $\nu_+=\nu_-=\nu_{s-}=1$ and $\nu=2$. $f_\pm$ in Eq. 6 has been mostly determined from the Debye-Hückel equation for the activity coefficient.[18] However, only the electrostatic interaction is taken into consideration with the Debye-Hückel theory. In this respect, this law is originally suitable for inorganic electrolytes or their mixtures. Organic electrolytes such as surfactants have a large hydrophobic group besides an ionic head group. The hydrophobic group of surfactant is surrounded by the ice-like structure which decreases the entropy of the system and leads to the micelle formation. Inorganic electrolytes such as KBr and CsBr have a different effect from organic electrolytes such as guanidinium salts on the activity coefficient of hydrophobic compound. Alkali halides usually salt out the hydrophobic compound, while guanidinium halides salt in.[12] Therefore, when we discuss the activity coefficient of ionic surfactant in the presence of another salt, we must take into consideration the interaction between the hydrophobic moiety and ions, besides the interaction between the ionic head group and ions. In this connection, the salt effect on the activity of surfactant is considered to be the sum of these two contributions. The Debye-Hückel equation for $f_\pm$ represents the contribution from the interionic interaction. Güntelberg's approximation of the Debye-Hückel law[18] was used for the estimation of this interaction. In order to estimate the salt effect on the hydrophobic group, we introduced the Setschenow equation which represents the effect of salt on the solubility of nonelectrolyte.[19] This equation is written as,

$$\log(f_s/f_{s0}) = \log(S_0/S) = k_s'C_s, \qquad (7)$$

where $f_s(f_{s0})$ and $S(S_0)$ are the activity coefficient and the solubility of nonelectrolyte in the presence (absence) of salt, respectively, and k_s' is the salting-out coefficient of nonelectrolyte. Assuming that the value of f_{s0} is

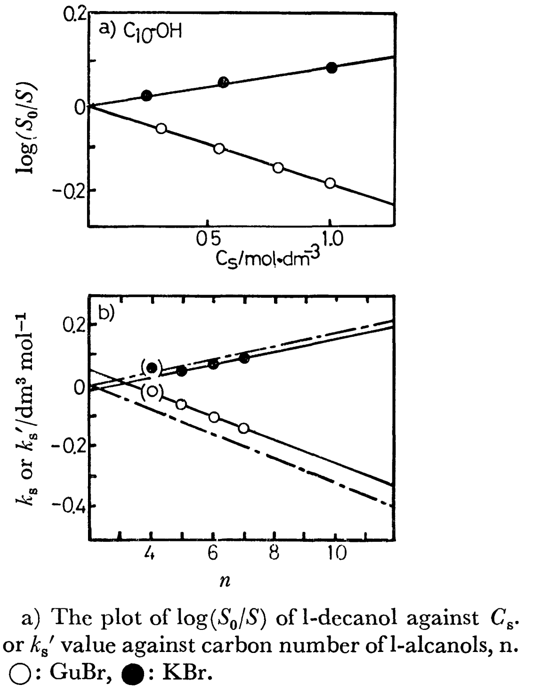

Fig. 8. a) The plot of log(S_0/S) of 1-decanol against C_s. b) k_s or k_s' value against carbon number of 1-alkanols, n. Salt; ○: GuBr, ●: KBr.

unity because of the low solubility of hydrophobic nonelectrolyte, Eq. 7 reduces to Eq. 8,

$$\log f_s = k_s' C_s. \tag{8}$$

Based on the above discussion, the activity coefficient of the ionic surfactant may be expressed by Eq. 9,

$$\log f_{\pm} = \frac{-A\sqrt{I}}{1+\sqrt{I}} + k_s C_s, \tag{9}$$

where I is the ionic strength and A is the constant, 0.5115 for 1 : 1 electrolyte at 25 °C, and k_s is the salting-out coefficient for the hydrophobic alkyl group. In order to obtain the k_s values for the hydrocarbon group of surfactant, the solubilities of *n*-alcohols with 6, 8, and 10 carbons were measured in the aqueous solutions of KBr and GuBr. As shown in Fig. 8, the value of $\log(S_0/S)$ for 1-decanol increases with the concentration of KBr and decreases with increase of the concentration of GuBr. From the slopes, the k_s' values were determined to be 0.092 and −0.147 for KBr and GuBr solutions, respectively. The values of k_s' of 1-hexanol and 1-octanol were obtained from the similar plots to 1-decanol. These values are shown in Table 4. To obtain the k_s values of dodecyl, tetradecyl, and hexadecyl groups, k_s' value was plotted against the carbon number of alcohols, *n*. As shown in Fig. 8-b, linear relationships exist between the k_s' values and *n* in each salt system. Therefore it is reasonable to determine the k_s' values of higher alcohols by extraporation. These k_s' values are not for the alkyl groups, but for alcohols, because they include the contribution of OH group. The salting-out coefficients of alkyl groups, k_s were obtained by subtracting the value of intercept from the k_s' values, on the assumption that the intercept represents the contribution of OH group. The k_s values of alkyl group thus obtained are also shown in Table 4. From the signs of k_s values, the effects of KBr and GuBr on the solubility of alcohols are consistent with those of these salts on the solubility of tetraalkylammonium salts.[20] Judging from the signs of k_s, the hydrophobic tails of surfactant molecules can associate more easily in the salt solution with a positive sign of k_s and less easily in the salt solution with a negative sign of k_s than in pure water. The difference of the sign of k_s indicates that the influence of KBr on the water structure in the vicinity of surfactant molecule is different from that of GuBr.[12,13]

Table 4. The values of salting-out coefficients of *n*-alkyl alcohols and *n*-alkyl groups in aqueous KBr and GuBr solutions

		k_s'/dm³·mol⁻¹ KBr	GuBr
Alcohol	1-Butanol	0.049	−0.023
	1-Hexanol	0.056	−0.066
	1-Octanol	0.069	−0.106
	1-Decanol	0.092	−0.147
Alkyl group	Dodecyl	0.12	−0.21
	Tetradecyl	0.14	−0.26
	Hexadecyl	0.16	−0.32

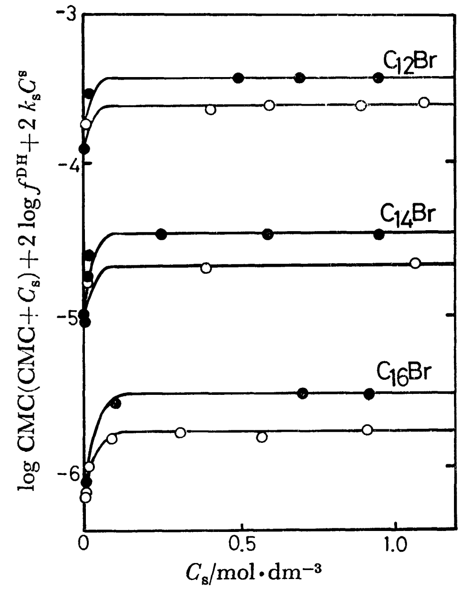

Fig. 9. The plot of log CMC (CMC+C_s)+2 logf^{DH}+2 k_sC_s against C_s in aqueous salts solutions.
Salt; ○: GuBr ●: KBr.

From Eqs. 6 and 9, we obtain,

$$\log a_m = \log \mathrm{CMC}(\mathrm{CMC}+C_s) + 2\log f^{DH} + 2k_sC_s, \tag{10}$$

where $\log f^{DH}$ is the first term of the right hand side of Eq. 9. If the micellization occurs at constant activity in the aqueous solution, Eq. 10 must be constant. As shown in Fig. 9, the value of a_m is constant irrespective of C_s, except the low concentration of salt. Since the value of (CMC+C_s) is equal to [Br$^-$], Eq. 10 is rewritten as,

$$\log \mathrm{CMC} + 2\log f^{DH} + 2k_sC_s = \log a_m - \log[\mathrm{Br}^-]. \tag{11}$$

When Eq. 11 is applied to the C_{14}Br–KBr(or GuBr)–H_2O system, the slope of (log CMC+2 log f^{DH}+2 k_sC_s) *vs.* log [Br$^-$] curve must be −1. As shown in Figs. 10-a and 10-b, the plots of log CMC or (log CMC+2 log f^{DH}) against log [Br$^-$] are not linear, but the plot (log CMC+

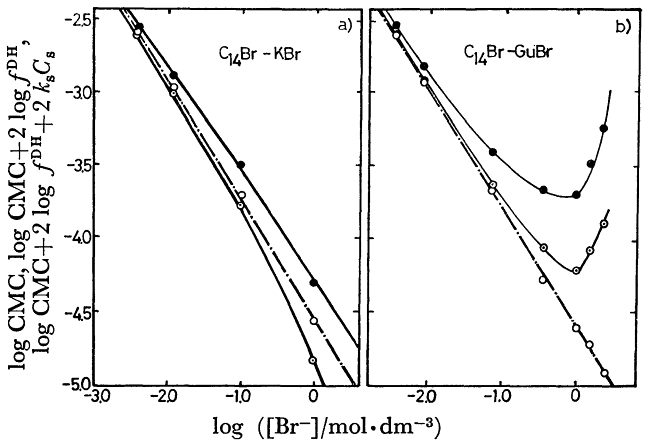

Fig. 10. The plot of log CMC, (log CMC+2 logf^{DH}), or (log CMC+2 logf^{DH}+2 k_sC_s) against log [Br$^-$] for the C_{14}Br–salt–H_2O system.
Salt; a) KBr, b) GuBr.
●: log CMC *vs.* log [Br$^-$],
⊙: log CMC+2 log f^{DH} *vs.* log [Br$^-$],
○: log CMC+2 log f^{DH}+2 k_sC_s *vs.* log [Br$^-$].

$2\log f^{DH}+2k_sC_s$) against $\log[\mathrm{Br}^-]$ is linear in each ternary system and the slopes of both systems are −0.9, *which is close to* −1.

Surface Tension and Adsorption at Air-Water Interface. In the previous section, the micellization phenomena of cationic surfactants in salt solution were interpreted in terms of the constant activity of surfactant. Similarly, the behaviour of surfactant below CMC in salt solution was considered on the basis of the activity, a, defined by Eq. 12,

$$a=f_{\pm}^{2}C(C+C_s) \qquad (12)$$

where $f_{\pm}$ is the activity coefficient defined by Eq. 9.

The modified Szyszkowski equation obtained from the integration of Eq. 1 with the Langmuir equation by using a instead of C was applied to these ternary systems.[10]

$$\gamma_0-\gamma=\Gamma_sRT\ln(1+K_a\cdot a), \qquad (13)$$

where γ_0 and γ are the surface tension of pure water and surfactant solution, respectively, and K_a is the Langmuir coefficient. As shown in Figs. 11 and 12, the quantity of $\exp[(\gamma_0-\gamma)/\Gamma_sRT]-1$ is proportional to a. The values of K_a obtained from the slopes and Γ_s (3.32×10^{-10} mol/cm^2) are 4.16×10^{6} dm$^6\cdot$mol^{-2} and 3.82×10^{6} dm$^6\cdot$mol^{-2} for the $C_{14}Br\cdot KBr-H_2O$ and $C_{14}Br-GuBr-H_2O$ systems, respectively. The value of K_a is a constant independent of C_s, while the K_c value varies with C_s.

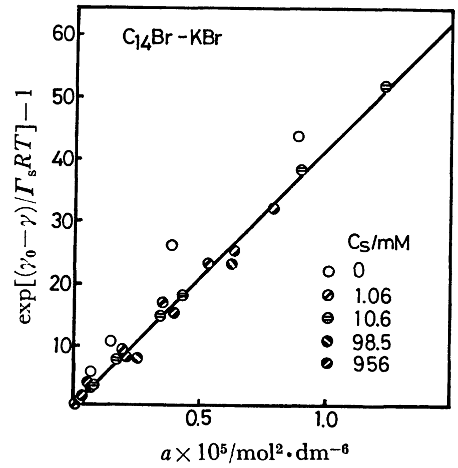

Fig. 11. The plot of $\exp[(\gamma_0-\gamma)/\Gamma_sRT]-1$ against a in aqueous KBr solution.

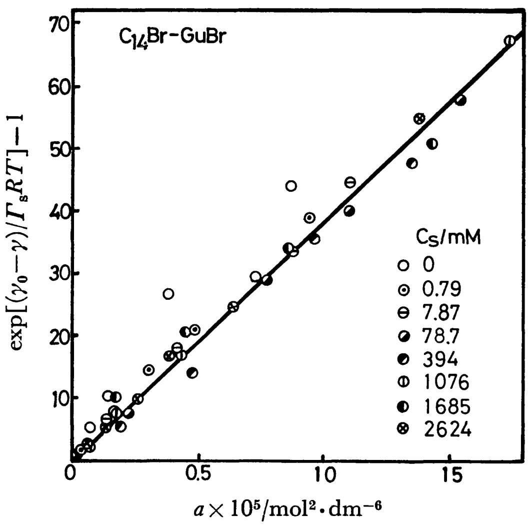

Fig. 12. The plot of $\exp[(\gamma_0-\gamma)/\Gamma_sRT]-1$ against a in aqueous GuBr solution.

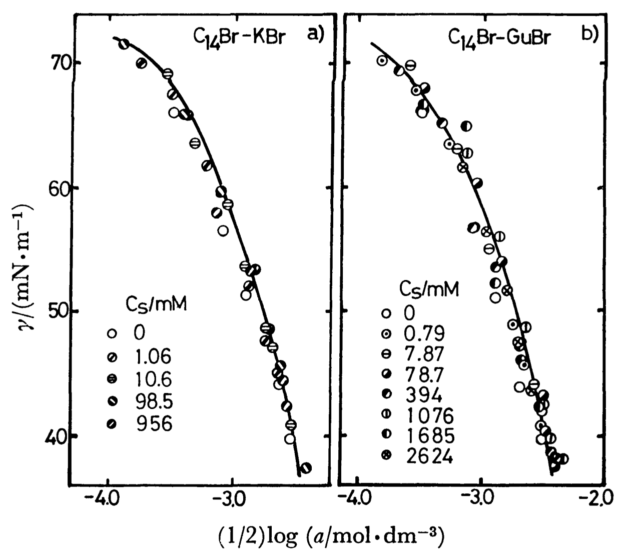

Fig. 13. The relationship between γ and $1/2\log a$ for the $C_{14}Br$– salt–H_2O system.

When the surface tension of $C_{14}Br$ is replotted against $(1/2)\log a$ as shown in Figs. 13-a and 13-b, every experimental value is located on the same curve obtained from Eq. 13 by using the values of K_a and Γ_s. The comparison of these figures with Figs. 1 and 2 indicates that the variation of curves in Figs. 1 and 2 is originally caused by the ignorance of the activity coefficient.

Conclusion

For the analysis of the salt effect on the CMC and the surface tension of cationic surfactant, we introduced a new expression for the activity coefficient in salt solution by taking into consideration the salt effect on the hydrophobic group of surfactant, besides the ionic head group. The electrostatic interaction between the ionic residue of surfactant and ions always decreases the activity of surfactant. However, the interaction between the hydrophobic group of surfactant and salt increases or decreases the activity of surfactant according to the sign of salting-out coefficient of salt. The salt with the negative sign of k_s decreases the activity coefficient of surfactant, resulting in the increase of CMC and the decrease of Γ, and *vice versa* for the salt with the positive sign. The opposite effect of GuBr to KBr on the CMC at relatively high concentration is mainly due to the difference of the sign of k_s.

Guanidinium salts denaturate proteins in aqueous solution. The main effect for the denaturation is believed to be the reduction of hydrophobic bonding in protein. Our experimental results are consistent with the above view of protein denaturation by guanidinium salts,

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