Adsorption and Micelle Formation of Mixed Surfactant Systems in Water. III. A Comparison between Cationic Gemini/Cationic and Cationic Gemini/Nonionic Combinations

Tatsuo OIDA¹, Noriko NAKASHIMA², Shigemi NAGADOME², Jeong-Soo Ko³,
Se-Woung Oh³ and Gohsuke SUGIHARA^{2*}

¹ *Fac. Eng. & Design, Kyoto Institute of Technology
(Kyoto 606-0962, JAPAN)*

² *Dept. Chem, Fac. Sci., Fukuoka University
(Fukuoka 814-0180, JAPAN)*

³ *Dept. Chem., Mokpo National University
(Muan, Chonnam 534-729, KOREA)*

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Abstract: A surface tension study (drop volume method) was performed at 30°C on micellization and adsorbed film formation of a mixed system of a cationic Gemini-type surfactant with a cationic surfactant in comparison with another mixed system of the same Gemini-type surfactant with a nonionic surfactant. The systems studied were Bis-ammonium Gemini derived from tartaric acid dibromide salt [BAGTB, 1,4-Bis(trimethylammonio)-2,3-dodecyloxy butane dibromide] with hexadecyltrimethylammonium bromide (HTAB): BAGTB/HTAB mixed system and with n-decanoyl-N-methylglucamide (MEGA-10): BAGTB/MEGA-10 mixed system. The data of surface tension (γ) vs logarithmic molality plots as a function of mole fraction of surfactant 2 (2 corresponds to HTAB or MEGA-10), X_2 , enabled us to determine the critical micellization concentration (CMC), the surface tension at CMC (γ_{CMC}), surface excess concentration (Γ_1), the mean molecular surface area (A_m), the partial molecular area (PMA), and the measures of efficiency of adsorption ($\text{pC}_{20} = -\log C_{20}$) and CMC/C_{20} which is available for evaluating the facilitating balance between adsorption and micellization. In addition, a newly defined measure of synergism in surface activity, i. e., the minimum surface Gibbs energy ($G_{\text{min}}^{(S)}$) was employed. Based on these data, the examination of synergism in micelle formation and in surface tension reduction elucidated that the Gemini-type surfactant does not exhibit any positive synergism for either BAGTB/HTAB or BAGTB/MEGA-10 mixed systems. Most of these parameters are found to depend conspicuously on the mixing ratio for both mixtures; indicating that the state of adsorbed film is divided into three ranges of X_2 ; the lower, the middle and the higher. The compositions of micelles formed at CMC (Y_2) and of adsorbed film (Z_2) equilibrated with bulk solution at a fixed surface tension were estimated.

Key words: mixed surfactant systems, adsorption, Gemini, MEGA-10, hexadecyltrimethylammonium bromide, partial molecular area, surface excess concentration, Gibbs adsorption isotherm, Regular solution theory, minimum surface free energy

*Correspondence to: Gohsuke SUGIHARA, Dept. Chem, Fac. Sci., Fukuoka University, Nanakuma, Jonan-ku, Fukuoka 814-0180, JAPAN
E-mail: sugihara@cis.fukuoka-u.ac.jp

1 Introduction

In parallel with the growing development or application of Gemini-type surfactants, studies on mixed systems of conventional or simple surfactants with Gemini type ones have also been increasing in the last decade. Most concern in the studies on mixed surfactant systems is paid to synergism or blending effects in surfactant mixtures (1-9). As the mixing of different species of surfactants, needless to say, has a possibility to result in more useful performance caused by synergism, early representative studies on mixed surfactants have been introduced by a few useful monographs (10-12) and by books composed of systematically collected papers (13,14). Especially with regards to synergism, the monograph by Rosen has given a detailed explanation of the measures to evaluate it for various actual cases (10), and the one by Tsujii has presented important information on the physical chemistry of synergism (12). A strict thermodynamic consideration of the mixed micelles of surfactants (15) and a treatment of the excess thermodynamic quantities of adsorption (16) are also worthy of note.

Following the previous study on the adsorption and micelle formation of mixed systems in water for a combination of top-heavy type surfactants (17), we have reported as a series work on combination of a Gemini surfactant with a nonionic one (18). In the latter a bibliography regarding preparation and properties of Gemini-type surfactants was presented in addition to the physicochemical study of a Gemini/nonionic surfactants mixture; the Gemini was Bis-ammonium Gemini derived from tartaric acid di-bromide salts (BAGTB) and n-decanoyl-N-methylglucamide (MEGA-10) (See **Scheme 1**). In that paper, from the surface tension measurement (drop volume method), critical micellization concentration (CMC), minimum surface tension at CMC (γ_{CMC}), surface excess concentration (Γ_t), mean molecular area (A_m), partial molecular area (PMA) and minimum surface free energy ($G_{\text{min}}^{(S)}$) as a function of net mole fraction of MEGA-10 ($X_{\text{MEGA-10}}$) were determined. Further, on the basis of the regular solution theory (RST), not only the micellar composition ($Y_{\text{MEGA-10}}$) but also the adsorbed film composition ($Z_{\text{MEGA-10}}$) were estimated, and additionally, the interaction parameters, ω_R in the micelle and ω_A in the adsorbed films were evaluated. From these data we constructed a phase diagram composed of CMC- $X_{\text{MEGA-10}}$ and CMC- $Y_{\text{MEGA-10}}$ curves

and another one composed of m_t (total bulk concentration of the surfactants in molality)- $X_{\text{MEGA-10}}$ and m_t - $Z_{\text{MEGA-10}}$ curves. In the combination of BAGTB with MEGA-10, it was found that (i) properties of micelles as well as adsorbed film do depend markedly on the mixing ratio; the different properties are discontinuously varied with changing mole fraction, and (ii) synergism acts little although the interaction parameter values are slightly negative (18), as was found to show no or little synergism for some binary mixtures (2,3,6).

In this paper, the counterpart of BAGTB is a cationic surfactant, hexadecyl trimethylammonium bromide (HTAB). The properties were examined in the same terms as those of BAGTB/MEGA-10 (18) and results will be discussed by making a comparison between MEGA-10 and HTAB mixtures with BAGTB.

2 Experimental

2.1 Materials

As an optically active Gemini type surfactant having two hydrophilic ammonium groups and lipophilic alkyl chains (2+2 type), the present surfactant having two $\text{C}_{12}\text{H}_{25}$ chains was prepared from tetramethyltetramide [I], $(\text{CHOHCON}(\text{CH}_3)_2)_2$. After treatment of [I] with alkyl bromide (in the present case, $\text{C}_{12}\text{H}_{25}\text{Br}$) to produce O-alkylated tartaramide [II], the reduction of the product [II] was carried out to give the tertiary amines [III] with methyl bromide in acetonitrile, which produced the objective bis-ammonium Gemini surfactant [IV]: $[\text{CHO}(\text{C}_{12}\text{H}_{25})\text{CH}_2\text{N}^+(\text{CH}_3)_3]_2 \cdot 2\text{Br}^-$, i.e., 1,4-Bis(trimethylammonio)-2,3-dodecyloxy butane dibromide.

The details of the preparation of the present Gemini type surfactants, including Na salts of Bis-sulfate Gemini with alkyl chain whose carbon atoms number ranges 8 to 16 and Br salts of Bis-ammonium Gemini with

Scheme 1

C_8H_7 and $C_{16}H_{33}$, have been described elsewhere (19). In this paper, the compound [IV] is hereafter abbreviated as BAGTB. Hexadecyltrimethylammonium Bromide (HTAB) of guaranteed grade was purchased from NACALAI TESQUE, INC. Kyoto, Japan. As the plot of surface tension (γ) vs logarithmic molality gave no minimum coming from impurities, the HTAB was used as received (Lot No. MIN9186). Sodium Bromide, NaBr, was of guaranteed grade from NACALAI TESQUE (Lot No. M2R2659) and used with no further purification.

2.2 Preparation of Solutions

Using triple-distilled water, the respective solutions of differing molalities (mol kg^{-1}) were batchwisely prepared from a concentrated stock solution at every 0.1 mole fraction of HTAB (X_{HTAB}) in the BAGTB/HTAB mixture. For the solutions with added NaBr, aqueous solutions of NaBr at given concentrations were used as solvent when they were prepared. [The surfactant solutions with added NaBr were used for determination of the respective degrees of counterion binding by applying the Corrin-Harkins plot (20)]

2.3 Surface Tension Measurements

The surface tension (γ) measurements were performed on the basis of the same drop volume method as reported previously; using an automated surface tensio-

meter (Yamashita Giken YDS94) the temperature of which was kept at 30.0°C with an accuracy of $\pm 0.03^\circ\text{C}$ by the use of a temperature control system (Yamashita Giken YCS9211) (17,18,20).

3 Results and Discussion

3.1 Basic Data Obtained Directly from γ vs $\ln m_t$ Plots

The plots of surface tension (γ) against logarithmic molality ($\ln m_t$) are shown in **Fig. 1** for the respective single systems and a few selected mixed systems. **Fig. 1** indicates that (i) even for mixed systems no minimum appeared around CMC, (ii) the curves of mixed systems are located between those of the two single systems in the order of increased mole fraction of HTAB (X_{HTAB}), and (iii) regarding the minimum of surface tension at CMC (γ_{CMC}) no remarkable difference is observed among all the systems. Very clear breaks of the curves enable us to easily determine CMCs; these values are tabulated in **Table 1**.

From **Fig. 1** we can evaluate pC_{20} and CMC/C_{20} similarly to the previous work (18) based on Ref.10. The results are listed in **Table 1**. The pC_{20} value ranges between 3.75 (for BAGTB) and 3.52 (for HTAB) in the range above $X_{\text{HTAB}}=0.3$, but in the lower X_{HTAB} region it exceeds 3.75 slightly. On the other hand, CMC/C_{20} values in the same lower region below $X_{\text{HTAB}}=0.4$ are also

Fig. 1 The Curves of Surface Tension (γ) vs Logarithmic Molality ($\ln m$) for the Respective Single Systems (a) and for Three Selected Mixed Systems (b) (the Curves for the Mixed Systems at Different Mole Fractions are between Those of the Single Systems).

Table 1 Basic Data of BAGTB/HTAB Mixed System in Water at 30°C.

X_{HTAB}	$\frac{\text{CMC}}{\text{mmol kg}^{-1}}$	$\frac{\Gamma_t}{10^{-6} \text{ mol m}^{-2}}$	$\frac{A_m}{\text{\AA}^2 \text{ molecule}^{-1}}$	pC_{20}	$\frac{\text{CMC}}{C_{20}}$	$\frac{G_{\min}^{(S)}}{\text{kJ mol}^{-1}}$
0.0	0.728	1.88	88.5	3.75	4.09	18.8
0.1	0.748	1.80	92.1	3.78	4.51	19.8
0.2	0.754	1.83	90.6	3.79	4.61	19.3
0.3	0.797	2.00	83.0	3.76	4.60	17.7
0.4	0.817	2.09	79.6	3.71	4.14	17.0
0.5	0.835	2.27	73.2	3.67	3.86	15.6
0.6	0.846	2.44	68.1	3.64	3.69	14.6
0.7	0.894	2.52	65.9	3.62	3.72	14.1
0.8	0.959	2.67	62.1	3.58	3.68	13.4
0.9	1.023	2.69	61.6	3.59	3.98	13.3
1.0	1.080	3.14	52.9	3.52	3.54	11.3

higher than that of pure BAGTB and start to decrease with increasing X_{HTAB} , at $X_{\text{HTAB}}=0.2$, except for a sudden maximum reached at $X_{\text{HTAB}}=0.9$. The pC_{20} is a measure of the efficiency of adsorption (p.84 in Ref.10), while CMC/C_{20} is a tool to evaluate the facilitating balance between adsorption and micellization. The higher CMC/C_{20} values in the lower range of X_{HTAB} up to 0.3 compared with that of pure BAGTB suggests that micellization is a little inhibited more than adsorption, or adsorption is facilitated more than micellization; this situation may result from the introduction of some factor (p.143 in Ref.10). As for γ_{CMC} and CMC/C_{20} values for the respective single systems will be discussed later.

In order to examine the details of adsorption behavior of mixed systems, evaluation of the surface excess concentration, Γ_t , and analysis of the composition of adsorbed film phase are necessary. First of all the Gibbs adsorption isotherm must be considered for the present mixed system consisting of a divalent cationic and two mono-valent anionic surfactants.

Let us consider the Gibbs equation for ionic surfactants of $A^{2+}B_2^-$ (like BAGTB) and C^+B^- (like HTAB). The differentiation of surface tension $d\gamma$ is generally connected with the chemical potential of species i , μ_i in water as:

$$-d\gamma = \sum_i \Gamma_i d\mu_i \quad [1]$$

where Γ_i is the surface excess relative to H_2O (21). For

surfactant AB_2 , $d\gamma$, Γ_i and $d\mu_i$ are related as:

$$-d\gamma = \Gamma_{A^{2+}} d\mu_{A^{2+}} + 2\Gamma_{B^-} d\mu_{B^-} \quad [2]$$

or

$$-\frac{d\gamma}{RT} = \Gamma_{A^{2+}} d\ln a_{A^{2+}} + 2\Gamma_{B^-} d\ln a_{B^-} \quad [3]$$

Since the mean activity of AB_2 , a_{AB_2} , is given by

$$a_{AB_2}^3 = a_{A^{2+}} \cdot a_{B^-}^2 \quad [4]$$

and the activity coefficients are regarded as one (unity) in such a dilute solution as the present one, $a_{AB_2}^3$ is approximated as m_t^3 . Therefore, the following is derived.

$$-\frac{d\gamma}{RT} = 3\Gamma_{AB_2} d\ln m_t \quad [5]$$

On the other hand, as for the adsorption of CB, since the mean activity a_{CB} is given by $a_{CB}^2 = a_{C^+} \cdot a_{B^-} \approx m_t^2$, the next equation is obtained.

$$-\frac{d\gamma}{RT} = 2\Gamma_{CB} d\ln m_t \quad [6]$$

With regards to the mixed adsorbed film, the total surface excess, Γ_t , is the sum of both surface excesses and is presented as follows, when the composition of CB in

the adsorbed film is denoted as Z_{CB} .

$$\left. \begin{aligned} \Gamma_t &= (1 - Z_{CB})\Gamma_t + Z_{CB}\Gamma_t \\ \Gamma_{AB_2} &= (1 - Z_{CB})\Gamma_t \text{ and } \Gamma_{CB} = Z_{CB}\Gamma_t \end{aligned} \right\} \quad [7]$$

For the adsorbed film composed of binary mixture, eqs.5, 6 and 7 lead to the following relations.

$$\begin{aligned} -\frac{d\gamma}{RT} &= 3\Gamma_{AB_2}d\ln m_t + 2\Gamma_{CB}d\ln m_t \\ &= (3(1 - Z_{CB}) + 2Z_{CB})\Gamma_t d\ln m_t \end{aligned} \quad [8]$$

Therefore we have

$$\Gamma_t = -\frac{1}{(3 - Z_{CB})} \cdot \frac{1}{RT} \frac{d\gamma}{d\ln m_t} \quad [9]$$

where Z_{CB} corresponds to Z_{HTAB} in the present case.

It is noted that in the case of BAGTB/MEGA-10 of the previous paper (18), since MEGA-10 is a nonionic surfactant, the Gibbs adsorption isotherm was presented as:

$$\Gamma_t = -\frac{1}{(3 - 2Z_2)RTd\ln m_t} \frac{d\gamma}{d\ln m_t} \quad [10]$$

The Γ_t values obtained for BAGTB/HTAB mixtures at discrete mole fractions are tabulated in **Table 1**. The surface excess concentration determined at surface saturation using the Gibbs isotherm (eq.9 or eq.10) is a useful measure of the effectiveness of the surfactant adsorption, since it is the maximum value which adsorption can attain. The effectiveness of adsorption is an important factor in determining such properties of the surfactant as foaming, wetting, and emulsification, since tightly packed, coherent interfacial films have very different interfacial properties to loosely packed, noncoherent films (p.69 in Ref.10). The Γ_t is easily translated into mean surface area occupied by a molecule, A_m , by the next equation,

$$A_m = \frac{1}{\Gamma_t \cdot L} \quad [11]$$

where L is Avogadro's number. Calculated A_m values in $\text{\AA}^2$ unit are also included in **Table 1**. Note that when A_m in $\text{\AA}^2$ is calculated, eq.11 should be multiplied by 10^{20} .

The A_m value as a function of mixing ratio or mole fractions of X_{HTAB} or Z_{HTAB} can offer us important information concerning the interaction between molecules in the adsorbed film, as will be discussed later.

3·2 Composition Relations among Bulk Phase (X_2), Micellar Phase (Y_2), and Adsorbed Film Phase (Z_2)

3·2·1 Phase diagram of singly dispersed (bulk) phase and micellar phase

In **Fig. 2(a)** CMC values (indicated by closed circles) in mili molality are plotted against mole fraction of HTAB (Surfactant 2) X_{HTAB} , and a solid line is drawn connecting the data points. In the figure the broken line indicates the expected relation when the two surfactants were projected to form micelles of thermodynamically ideal mixing; this curve was obtained by the equations given in the previous paper (17, 23-26). Even if an error margin of around $\pm 5\%$ is taken into account, the measured values in the range of $X_{HTAB}=0.3-0.4$ do not coincide with those of ideal mixing, but deviate positively from it.

For any mixed system of either ideal or non-ideal mixing of ionic surfactants 1 and 2, we have applied the following equations including an interaction parameter, ω_o , and degrees of counterion binding, β_1 and β_2 (17, 22-26).

$$\ln \frac{Y_1}{X_1} + \kappa_1 \ln C_1^0 + (1 - Y_1)^2 \omega_o = \kappa_1 \ln C_m \quad [12]$$

$$\ln \frac{Y_1^U}{1 - Y_1} + \left[U(1 - Y_1)^2 - Y_1^2 \right] \omega_o - \ln \frac{X_1^U}{1 - X_1} = U\kappa_1 \ln \frac{C_2^0}{C_1^0} \quad [13]$$

where $U = \frac{\kappa_2}{\kappa_1} = \frac{(1 + \beta_2)}{(1 + \beta_1)}$, and C_1^0 and C_2^0 denote the CMC values of the respective single systems 1 and 2, and C_m , CMC of each mixed system. Here, the interaction parameter is related to the activity coefficients f_1 and f_2 and the micellar composition Y_1 , as follows.

$$\left. \begin{aligned} f_1 &= \exp\left\{ \omega_o(1 - Y_1)^2 \right\} \\ f_2 &= \exp\left(\omega_o Y_1^2 \right) \end{aligned} \right\} \quad [14]$$

Applying eqs. [12] and [13] in addition to eq. [14], the

Fig. 2 Phase Diagram of CMC vs. Composition for BAGTB/HTAB Mixed System at 30°C. The solid line along closed circles indicating CMC values as a function of mole fraction of HTAB corresponds to the monomeric phase curve and that along open circles corresponds to the micellar phase curve calculated on the basis of (a) our theoretical equations and (b) Rubingh's equations.

Table 2 Values of CMC, Y_i , ω_R , and f_i for BAGTB/HTAB Mixed Systems.

X_{HTAB}	Ideal CMC value $\text{mmol} \cdot \text{kg}^{-1}$	Real-Ideal $= \Delta \text{CMC}$ $\text{mmol} \cdot \text{kg}^{-1}$	Y_{HTAB}	ω_R	ω_O	f_{BAGTB}	f_{HTAB}
0.0	0.728	0					
0.1	0.753	-0.005	0.074	-0.14	0.0	1.00	0.87
0.2	0.779	-0.025	0.165	-0.28	-0.4	1.00	0.89
0.3	0.807	-0.010	0.231	-0.07	0.0	0.99	0.91
0.4	0.837	-0.020	0.319	-0.11	-0.1	0.98	0.93
0.5	0.870	-0.035	0.410	-0.17	-0.2	0.97	0.94
0.6	0.905	-0.059	0.502	-0.27	-0.3	0.96	0.96
0.7	0.943	-0.049	0.600	-0.23	-0.2	0.94	0.97
0.8	0.985	-0.026	0.718	-0.13	-0.1	0.92	0.99
0.9	1.03	-0.007	0.854	-0.05	0.0	0.89	1.00
1.0	1.08	0					

ω_R ave. = -0.16 ω_O ave. = -0.1

values of Y_{HTAB} , ω_O and activity coefficients f_1 and f_2 were determined, as listed in **Table 2**. It is necessary to obtain the data of β_1 and β_2 , so the CMC was measured as a function of bromide ion concentration in solution with added NaBr. Applying the Corrin-Harkins plot (11,27), that is, the plot of $\ln \text{CMC}$ against $\ln (\text{CMC} + \text{added NaBr})$, the degree of counterion binding was

determined as 0.75 for BAGTB and 0.81 for HTAB (the plot is not shown here). Using these values together with the respective CMC values, the theoretical curve for ideal mixing was calculated ($\omega_O = 0$). The broken curve in **Fig. 2(a)** corresponds to the CMC- Y_2 curve of ideal mixing. The real CMC- Y_{HTAB} curve also exhibits a clear deviation in the range from $Y_{\text{HTAB}} = 0.2$ to 0.4.

On the other hand, Rubingh has given theoretical equations for relating the composition of micelles formed at CMC with that of bulk solution; his useful equations have been widely applied to analyze the relations of CMC-compositions (of singly dispersed phase) with micellar phase (28). His equations were derived without taking into account the effect of counterions on mixed micelle formation in the case of ionic surfactant mixtures. It may be said that in his equations a mixed CMC value itself involves the effect of counterion binding on micelle formation. In other words his equations are conveniently applicable to any combination of ionic/ionic, nonionic/nonionic or ionic/nonionic surfactant mixtures. Rosen has extensively used the equations for evaluating the extent of synergism. For the same purpose, we apply his equation even to the present study. As shown in **Fig. 2(b)**, CMC- X_{HTAB} and CMC- Y_{HTAB} curves calculated from Rubingh's equations were used to construct a phase diagram. Calculated micellar composition and the interaction parameter, ω_R , are included in **Table 2**. The ω_R values are necessary when synergism in mixed micelle formation is examined as described later. In comparison of **Fig. 2(b)** and the corresponding figure for BAGTB/MEGA-10 in the previous paper, the latter resulted in comparatively regular changes with X_2 (18), while the curves giving the relations of CMC vs X_2 and CMC- Y_2 for the present BAGTB/HTAB mixture have clear inflection points as shown in **Fig. 2(b)**.

It should be noted that the CMC- Y curves obtained for ideal (dotted line) and real mixed systems from Rubingh's equations (**Fig. 2(b)**) are considerably different from those of our own equations provided (**Fig. 2(a)**); the former leads to the larger interaction parameter ($\omega_R = -0.16$) as well as the apparently larger negative deviation than the latter ($\omega_0 = -0.1$). The apparently larger deviation is regarded as a result without taking into account the counterion binding effect.

3.2.2 Phase diagram of singly dispersed (bulk) phase and adsorbed film phase

Adsorbed monolayer (Gibbs monolayer) of a given mixed system of surfactants 1 and 2 is equilibrated with singly dispersed species 1 and 2 in bulk phase. Depending on the activity difference between 1 and 2, the compositions in the adsorbed film (Z_1 and Z_2 , $Z_1 + Z_2 = 1$) may differ from that in bulk phase. Similar to the relation between X_2 and Y_2 , it is important to examine how Z_2 is

related to X_2 or whether Y_2 is equal to Z_2 or not. To answer this question we have employed the following equations to estimate Z_2 as a function of X_2 , which were derived on the basis of the regular solution theory (17,18). The activity coefficients of 1 and 2 in the adsorbed film, f_1 and f_2 can be related to Z_2 and the interaction parameter ω_A , where m_1^0 , m_2^0 and m_t are referred to as the bulk concentrations of the respective single systems and the total concentration of the mixture, respectively, at a constant surfactant surface tension, i.e., $\gamma_{\text{CMC}} = 35.6 \text{ mNm}^{-1}$ and m_2^0 is the CMC of HTAB.

$$\left. \begin{aligned} f_1 &= \exp \left[\omega_A Z_2^2 \right] \\ f_2 &= \exp \left[\omega_A (1 - Z_2)^2 \right] \end{aligned} \right\} \quad [15]$$

From analogy with the derivation of Rubingh's equations (28), we obtained the following equations.

$$\frac{(1 - Z_2)^2 \ln \left[(1 - X_2) m_t / (1 - Z_2) m_1^0 \right]}{Z_2^2 \ln (X_2 m_t / Z_2 m_2^0)} = 1 \quad [16]$$

$$\omega_A = \frac{\left[\ln (X_2 m_t / Z_2 m_2^0) \right]}{(1 - Z_2)^2} \quad [17]$$

Eqs. 16 and 17 simultaneously tell us that if the m_1^0 , m_2^0 and m_t at the given γ are determined against net mole fraction X_2 , then the adsorbed film composition Z_i is given by eq. 16, and ω_A can be evaluated from eq. 17 by using the Z_2 values (17,18, p.394 in Ref.10). The m_t for each mixed system was determined by reading the curves of the γ vs m_t plot (**Fig. 1**) and the read m_t values are listed in **Table 3** together with calculated Z_2 , ω_A , f_1 and f_2 . Compared to ω_R in the micelle, ω_A is slightly larger in absolute value.

Paying attention to the values of activity coefficients listed in **Tables 2** and **3**, (i) the values for BAGTB in the micelle as well as in the adsorbed film are greater (nearly equal to 1.0) than those for HTAB in the range from $X_{\text{HTAB}} = 0.1$ to 0.5 where BAGTB is the major component, (ii) at $X_{\text{HTAB}} = 0.6$ BAGTB and HTAB have the same activity coefficient and (iii) in the range between $X_{\text{HTAB}} = 0.7$ and 0.9 in the micelle or between $X_{\text{HTAB}} = 0.7$ and 0.8 (except for 0.9) in the adsorbed film, the activity coefficients of BAGTB are smaller than those of HTAB which is the major component.

Table 3 Values of m_t , Z_i , ω_A , and f_i for BAGTB/HTAB Mixed Systems.

X_{HTAB}	m_t	Z_{HTAB}	ω_A	f_{BAGTB}	f_{HTAB}
0.0	0.716	0.000			
0.1	0.747	0.078	-0.14	1.00	0.89
0.2	0.754	0.167	-0.26	0.99	0.84
0.3	0.787	0.239	-0.15	0.99	0.91
0.4	0.82	0.321	-0.13	0.99	0.94
0.5	0.83	0.412	-0.21	0.97	0.93
0.6	0.85	0.503	-0.26	0.94	0.94
0.7	0.89	0.601	-0.23	0.92	0.96
0.8	0.96	0.718	-0.14	0.93	0.99
0.9	1.04	0.865	+0.08	1.06	1.00
1.0	1.08	1.000			

 ω_A ave. = -0.2 **Fig. 3** The Phase Diagrams of Monomers in Bulk Solution and Adsorbed Film at Air/Water Interface for BAGTB/HTAB Mixed System (a) and for BAGTB/MEGA-10 Mixed System (b) Simulated from the Regular Solution Theory at 30°C.

In **Fig. 3(a)** and **(b)** are shown the results of BAGTB/HTAB and, for comparison, of BAGTB/MEGA-10, respectively. While the BAGTB/MEGA-10 mixed system gives comparatively regular curves both for X_2 - m_t and Z_2 - m_t relations, the BAGTB/HTAB shows, similar to the X_2 -CMC curve shown in **Fig. 2**, more clearly recognizable inflections in both curves. The shapes of the

X_2 - m_t and Z_2 - m_t curves for BAGTB/HTAB mixture resemble those shown in **Fig. 2(b)**, but Z_2 is not the same as Y_2 . Analyzed values for Z_2 , ω_A , f_1 and f_2 are tabulated in **Table 3**. The reason why the curves (seen in **Fig. 2(b)** and **Fig. 3(a)**) resemble the respectively corresponding ones is considered to result from the fact that each m_t value is very close to CMC because of little dif-

ference in γ_{CMC} and from use of similar equations based on the RST.

3.3 The Properties of the Gibbs Adsorption Monolayer

The surface excess concentration as a function in the surfactant mixture was evaluated from eq.9 for BAGTB/HTAB and from eq.10 for BAGTB/MEGA-10 as are shown in Fig. 4(a) and (b), respectively. As was previously reported and is shown in frame (b) the total surface excess Γ_t for BAGTB/MEGA-10 has two breaks at $X_{\text{MEGA}10} = \text{ca. } 0.45$ and $\text{ca. } 0.75$. Similar to this, Γ_t for

BAGTB/HTAB seems to have two breaks at the same mole fractions. Even if the error margin of the data points is taken into account, the existence of the breaks cannot be neglected as a correspondence was observed as inflection points in $\text{CMC}-X_{\text{HTAB}}$ and m_t-X_{HTAB} curves (Fig. 2 and Fig. 3).

Examining the mean molecular (occupation) area, A_m , more clearly the breaks are confirmed. In Fig. 5(a), the A_m is plotted as functions of X_{HTAB} (closed circles) and Z_{HTAB} (open circles) for BAGTB/HTAB and for BAGTB/MEGA-10 mixed system in (b). Because it is desirable for the behavior of the adsorbed film of a

Fig. 4 The Total Surface Excess Concentration, Γ_t As a Function of X_{HTAB} (a) Or $X_{\text{MEGA-10}}$ (b).

Fig. 5 The Mean Surface Area A_m Plotted against X_{HTAB} and Z_{HTAB} (a), and against $X_{\text{MEGA-10}}$ and $Z_{\text{MEGA-10}}$ (b).

given mixed system to be examined in terms of composition of the film, the A_m was plotted against Z_{HTAB} or $Z_{\text{MEGA-10}}$. Looking at A_m - Z_2 relations or comparing both mixed systems, two breaks are commonly found. And if the mixing is ideal, the A_m - Z_2 relation should be linear as indicated by the dotted line, however, as is seen in **Fig. 5(a)**, the left and right sides as well show a positive deviation except for the central region. In the central region the deviation of BAGTB/HTAB is in contrast with that of BAGTB/MEGA-10; the former is slightly negative while the latter's positive deviation is comparatively prominent. In the range of $X_2 = 0.5$ – 0.7 ($Z_2 = 0.4$ – 0.6 for the former and $Z_2 = 0.2$ – 0.4 for the latter), interestingly, the mode of the interaction between hydrophilic groups in BAGTB/HTAB is quite different from that in BAGTB/MEGA-10. That is, HTAB seems to be favorable to BAGTB, but MEGA-10 is unfavorable to BAGTB. This great contrast between the two combinations comes not only from the difference in electrostatic interaction, i.e., between the cationic Gemini and conventional cationic surfactants and between the Gemini and nonionic surfactants but also from the steric effect of head groups on packing each other in the adsorbed layer. The negative values of the interaction parameter ω_A in the range of $X_{\text{HTAB}} = 0.5$ – 0.7 are greater than those in the other range except for that at $X_{\text{HTAB}} = 0.2$ (a very similar trend is found even in ω_R . See **Tables 2 and 3**).

From the curve of A_m vs Z_2 , partial molecular area

(PMA) can be determined. As has been discussed previously (17,18), the resultant information on PMA enables us to know about the intermolecular interaction as a function of composition. For this study PMA was evaluated in a similar manner as described previously (17,18). The results are shown in **Fig. 6(a)** and (b) for BAGTB/HTAB and for BAGTB/MEGA-10. The latter was reproduced from the previous paper for comparison. Both frames clearly demonstrate that there exist two breaks, although the mole fraction giving the breaks differs between the two mixed systems; in (a) $Z_2 = \text{ca. } 0.35$ and $\text{ca. } 0.65$, while in (b) $Z_2 = \text{ca. } 0.18$ and $\text{ca. } 0.45$. As Z_2 approaches absolute zero, HTAB as well as MEGA-10 show an extraordinarily great value of PMA, but this very rapidly decreases in the range below $Z_2 = \text{ca. } 0.2$ while BAGTB dose little change. In both frames the dotted lines indicate the respective PMA values when the mixing is ideal and accordingly the additivity rule can hold. Both frames show that in the range above $Z_2 = 0.5$ HTAB as well as MEGA-10 does not show any marked change in PMA, while BAGTB at limiting mole fraction ($Z_1 = 0$) has an expanded PMA and decreases rapidly (in (a)) or slowly (in (b)) with increased mole fraction of BAGTB (See the right hand side of each frame). This means that the marked expansion of A_m in the higher Z_2 range comes only from the expanded PMA of BAGTB, especially in the case of the BAGTB/MEGA-10 mixed systems. In regard to Z_2 dependence the details cannot be further interpreted,

Fig. 6 Partial Molecular Areas (PMA) Determined from the Tangential Slope of Linear Relation at Points on the A_m vs Z_2 Curve (**Fig. 5**) as Functions of X_2 and Z_2 ; Two Breaks (Discontinuities) Creating Three Regions are Clearly Demonstrated for Both Mixed Systems.

however, it may be concluded that the relation of PMA also can be divided into three regions, viz. (i) the BAGTB-major region, (ii) the HTAB- or MEGA-10-major region and (iii) the middle region, as has been demonstrated in different aspects. In connection with the composition dependence of a mixed system of a Gemini type surfactant with an ionic one there have been interesting studies reported.

Tsubone and Tajima have studied the aqueous properties of mixed systems of an anionic Gemini surfactant $((\text{CH}_2)_2[\text{NCO}(\text{C}_{11}\text{H}_{23})\text{C}_2\text{H}_4\text{CO}_2\text{Na}]$, abbreviated as 212) and a conventional anionic surfactant $(\text{C}_{11}\text{H}_{23}\text{CO}_2\text{Na}$, soap) in terms of mixed CMC, foam volume and degree of micelle ionization (29), and solubilization of Orange OT by the same surfactant mixture (30). In these studies they found various interesting behaviors as a function of mole fraction of soap in the mixture, eg. (i) positive and negative deviations from ideal mixing in regard to micelle formation were found below and above $X_{\text{soap}} = 0.6$, (ii) minimum surface tension (γ_{CMC}) and maximum foam volume are attained at $X_{\text{soap}} = 0.6$ and (iii) in solubilization capacity a break at $X_{\text{soap}} = 0.6$ (possible another break at $X_{\text{soap}} = 0.1$) and a minimum at $X_{\text{soap}} = 0.9$ were found (30). They reached the conclusion that the mixture of the anionic surfactants, 212 and soap, forms 2:1 complexes over a broad region of composition during micellization. Similar behavior might be true for the present BAGTB/HTAB and BAGTB/MEGA-10 mixed systems in regard to micellization. In the very near

future a solubilization study should be performed even for the present mixtures (18).

We have proposed a thermodynamic quantity for evaluation of synergism in mixing, that is, the free energy of a given surface at equilibrium, $G_{\text{min}}^{(S)}$ (See **Table 1** and **Fig. 7**) which is defined as follows.

$$G_{\text{min}}^{(S)} = A_m \cdot \gamma_{\text{CMC}} \cdot L \quad [18]$$

It may be possible to regard $G_{\text{min}}^{(S)}$ as the work needed to make a surface area per mole or the free energy change accompanied by the transition from the bulk phase to the surface phase of solution components. The lower the value of the free energy, the more thermodynamically stable a surface is formed, or the more the surface activity is attained. The extent of lowering the free energy may be a measure for evaluation of synergism in mixed surfactant systems. In **Fig. 7** the $G_{\text{min}}^{(S)}$ value of the BAGTB pure system is connected with that of the HTAB (a) or MEGA-10 (b) pure system by a dotted straight line referring to the additivity rule for ideal mixing. The $G_{\text{min}}^{(S)}$ values are given by open circles.

The extent of deviation from the linear relation and the pattern of mole fraction and dependence (divided into three) are evidently recognizable for both mixed systems. Interestingly, in the range of $X_2 = 0.5$ to 0.7 the deviation of BAGTB/HTAB is small (0 or slightly positive), in contrast to this, the positive deviation of BAGTB/MEGA-10 is conspicuous. This contrast sug-

Fig. 7 The Minimum Surface Gibbs Energy, $G_{\text{min}}^{(S)}$ as well as CMC/ C_{20} Parameters Plotted against X_{HTAB} for BAGTB/HTAB (a) and against $X_{\text{MEGA-10}}$ for BAGTB/MEGA-10 (b) Mixed Systems.

gests that the interaction between head groups between HTAB and BAGTB is favorable for cooperatively reducing the surface tension but the interaction between MEGA-10 and BAGTB head groups is not so favorable. Anyway, the extent of the deviation in $G_{\min}^{(S)}$ from the additivity rule may be regarded as one of the measures for evaluating the synergism with respect to surface activity.

In order to evaluate a synergistic effect on surface activity resulting from the mixing of surfactants 1 and 2, if an excess amount of the minimum surface energy $\Delta G_{\min(\text{ex})}^{(S)}$ is considered for the mixed system, it may be defined as the following equation, meaning that $\Delta G_{\min(\text{ex})}^{(S)}$ at mole fraction X_2 is the difference of the real value $G_{\min(\text{at } X_2)}^{(S)}$ less the ideal one, satisfying the additivity rule of ideal mixing.

$$\Delta G_{\min(\text{ex})}^{(S)} = G_{\min}^{(S)} - \left\{ G_{\min(1)}^{(S)} + \left[G_{\min(2)}^{(S)} - G_{\min(1)}^{(S)} \right] X_2 \right\} \quad [19]$$

where, $G_{\min(1)}^{(S)}$ and $G_{\min(2)}^{(S)}$ are the minimum surface (Gibbs) free energies of the respective single systems. If an obtained value is negative, it corresponds to a positive synergism as to surface activity. The plot of $\Delta G_{\min(\text{ex})}^{(S)}$ vs X_2 will directly reflect a synergistic effect (not shown here).

Further, in **Fig. 7(a)** and **(b)**, the data points of CMC/C_{20} are also plotted by closed circles. As has been reported previously (18) and showing again in the frame **(b)**, the CMC/C_{20} - X_2 relation has two breaks corresponding to the other properties already seen in **Figs. 3–6**. In the BAGTB/HTAB mixed system too, the situation is similar to BAGTB/MEGA-10 in regard to the discontinuity and parallelism of $G_{\min}^{(S)}$ with CMC/C_{20} . According to the defined conditions of synergism in surface activity (10), firstly, concerning the effectiveness of surface tension reduction, the difference, $\omega_A - \omega_R$, must be negative, and secondly, as to its efficiency, $|\omega_A| = \left| \ln \left(m_{i_2}^0 / m_{i_1}^0 \right) \right|$ must be satisfied. As was pointed out previously (18), neither BAGTB/HTAB nor BAGTB sufficiently satisfies both conditions, meaning that the present two combinations of a cationic Gemini type surfactant, BAGTB with a cationic (HTAB) and a nonionic (MEGA-10) can exhibit little synergism in surface activity.

Finally, again paying attention to the γ_{CMC} values shown in **Fig. 1** as well as Γ_t (or A_m) and CMC/C_{20} values listed in **Table 1** for the respective single systems,

Γ_t and CMC/C_{20} are markedly different between the two surfactants, while γ_{CMC} is nearly equal. The surface pressure Π_{CMC} or the γ_{CMC} values of surfactants reflect their CMC/C_{20} ratio and Γ_t as the following equation (Ref.10 p.217, 29,30).

$$\Pi_{\text{CMC}} = \gamma_0 - \gamma_{\text{CMC}} = 20 + nRT\Gamma_t \ln(\text{CMC}/C_{20}) \quad [20]$$

where, γ_0 denotes the surface tension of pure solvent. As described above, the CMC/C_{20} ratio is a measure of the tendency to form micelles relative to the tendency to adsorb at the air/water interface. Eq.20 shows us that the γ_{CMC} value involves both the CMC/C_{20} ratio and A_m (or Γ_t) values. For applying this equation to the present single systems, the n value must be 3 for BAGTB and 2 for HTAB (see eqs.5 and 6). From the data in **Table 1**, almost the same Π_{CMC} value ($\Pi_{\text{CMC}}/\text{mNm}^{-1} = 20 + 7.94RT$) was obtained for both surfactants, just as seen in **Fig. 1**. This result suggests that in regard to Π_{CMC} (or γ_{CMC}) the number of ions n (whose surface concentration changes with change in the liquid-phase concentration of the surfactant) also acts effectively in reducing the surface tension of a solvent. Such a binary mixed surfactant system as the present mixture having almost the same γ_{CMC} values may lead to a poor synergism.

In conclusion, the $\text{CMC}-X_2$ relation of the BAGTB/HTAB mixed system is neither regular (monotonous) nor markedly deviated from ideal mixing. In this regard, that of the BAGTB/MEGA-10 mixed system gave an apparently regular but to some extent more negatively deviated curve. As for the adsorbed film formation, similar to the BAGTB/MEGA-10 mixture, the combination of BAGTB and HTAB resulted in a marked dependence on the mixing ratio of the binary surfactant system, viz., Γ_t , A_m , PMA , $G_{\min}^{(S)}$ and CMC/C_{20} as a function of X_{HTAB} or Z_{HTAB} have two breaks (discontinuities). When the mixing ratio of BAGTB: HTAB or MEGA-10 is 1~2:9~8 or 9~8:1~2, in other words when one is a notably major component and the other is a minority, the two dimensional packing of binary components is evidently different from intermediate mixtures. It is noted that in the intermediate mixtures remarkably negative synergism was observed for the BAGTB/MEGA-10 mixed system.

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