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Effect of molecular packing on adsorption and micelle formation of a homologous cationic surfactant mixture of hexadecyltrimethylammonium bromide and dodecyltrimethylammonium bromide

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Abstract The surface tension of an aqueous solution of a hexadecyltrimethylammonium bromide (HTAB) and dodecyltrimethylammonium bromide (DTAB) mixture was measured as a function of the total molality and the composition of DTAB at 298.15 K under atmospheric pressure. The phase diagrams of adsorption and micelle formation were constructed and the excess Gibbs energy was evaluated by analyzing the phase diagrams thermodynamically. Both the excess Gibbs energy in the adsorbed film and the excess surface area are negative; therefore the mutual interaction between HTAB and DTAB is said to be stronger than that between the same species and is enhanced with increasing adsorption. By

combining the results with those obtained in previous studies, we claimed that DTAB molecules can use effectively the space among the hydrocarbon chains of HTAB molecules and their polar head groups take a staggered arrangement at the surface so as to reduce the electrostatic repulsion. Consequently the dispersion force between hydrophobic chains becomes stronger. Furthermore, the comparison of the excess Gibbs energy in the adsorbed film with that in the micelle shows that the staggered arrangement of molecules is not necessary in the spherical micelle.

Keywords Surface tension · Phase diagrams · Excess Gibbs energy · Adsorbed film · Micelle

Introduction

Miscibility of surfactants in molecular organized systems such as adsorbed films and micelles has been studied by many researchers, because of the interest from the theoretical and practical viewpoints, by means of thermodynamics and spectroscopy. The relationship between the miscibility and molecular interaction and nonideal mixing in the adsorbed film and micelles for surfactant mixtures is mainly investigated by thermodynamics [1, 2, 3]. In the course of our systematic and quantitative studies on the miscibility of molecules in adsorbed films and micelles by constructing the phase diagram and evaluating the excess Gibbs energy, we have shown that

the dispersion force between hydrophobic chains and the electrostatic interaction between polar head groups are important for governing the miscibility [4, 5, 6, 7, 8, 9, 10, 11, 12]. Furthermore, we have shown that the molecular packing can be one of the influential factors to determine the mixing of molecules in the adsorbed film and micelles [6, 7, 9]. For example, from the results of the excess Gibbs energy obtained in the mixed system of dodecyltrimethylammonium bromide (DTAB) and octyl methyl sulfoxide (OMS), it was proposed that OMS molecules can use effectively the space among the hydrocarbon chains of DTAB molecules and eventually the mutual interaction between DTAB and OMS is strengthened with increasing adsorption [6]. These

studies demonstrate that the thermodynamic method can offer information on even the structure of adsorbed films.

On the other hand, a lot of knowledge on the structure of an adsorbed film at the air/water interface has been accumulated in this decade by several surface-sensitive spectroscopic measurements such as ellipsometry [13], sum-frequency spectroscopy (SFS) [14, 15], X-ray absorption fine structure under total reflection condition [16, 17], X-ray reflection [18, 19], and neutron reflection (NR) [20, 21]. Casson and Bain [15] have shown that 1-dodecanol ($C_{12}OH$) and alkyltrimethylammonium bromide (C_nTAB) form a very densely packed structure like the crystalline phase in the adsorbed film below the phase-transition temperature by probing the strength of the symmetric stretch of the methyl and methylene groups by SFS. Lee et al. [20] have clarified that by measuring the NR from the adsorbed film decyltrimethylammonium bromide molecules at the air/water interface prefer the staggered to the plane arrangement at higher surface density, which is favorable to reduce the electrostatic repulsive force between the head groups with positive charge.

In the present paper, we demonstrate that the thermodynamic method provides information suggesting the staggered structures of the mixed adsorbed films [4]. A hexadecyltrimethylammonium bromide (HTAB) and DTAB mixture was employed for the following reasons:

1. The staggered structure of the adsorbed film of single C_nTAB systems has already confirmed by NR [20]. The staggered structure is responsible for the size of the polar head group being larger than the cross-sectional area of the hydrocarbon chain and therefore the space between hydrocarbon chains is available for other molecules.
2. The excess surface area, which is calculated from the dependence of the excess Gibbs energy of adsorption on surface tension, is closely connected with molecular packing in the mixed adsorbed films.

In addition to these points, since both HTAB and DTAB form micelles in their aqueous solutions, we can also examine the effect of the difference in the geometry between the air/water and micelle surfaces on the molecular packing and eventually on the miscibility in them.

The surface tension of the aqueous solution of the HTAB and DTAB mixture was measured as a function of the total molality of the mixture and the composition of DTAB. Applying our thermodynamic method to the experimental results obtained [5, 8], we constructed the phase diagrams of adsorption and micelle formation. Furthermore, the excess Gibbs energy and the excess area are evaluated to discuss the miscibility of HTAB and DTAB in the adsorbed film and in micelles quantitatively.

Experimental

Materials

HTAB and DTAB purchased from Nakarai Chemical and Tokyo Chemical Industry, respectively, were carefully purified by recrystallizing them three times from a mixture of ethanol and acetone. Their purities were confirmed by observing no minimum on the surface tension versus concentration curves in the vicinity of the critical micelle concentration (cmc) and no time dependence of the surface tension. The water used in the measurement was triply distilled, the second and third stages being done from alkaline permanganate solution.

Surface tension measurement

The surface tension γ of the aqueous solution of HTAB and DTAB was measured as a function of the total molality of the surfactants \hat{m} and the composition of DTAB \hat{X}_2 at 298.15 K under atmospheric pressure by the drop volume technique described previously [22, 23]. Here, taking account of the dissociation of surfactants, we defined \hat{m} and \hat{X}_2 by

$$\hat{m} = 2m_1 + 2m_2 \quad (1)$$

and

$$\hat{X}_2 = 2m_2/\hat{m}, \quad (2)$$

where m_1 and m_2 are the molalities of HTAB and DTAB, respectively [5]. The temperature was controlled by the use of a water thermostat. The experimental error of the γ values was within $\pm 0.05 \text{ mN m}^{-1}$.

Results and discussion

The results of the surface tension measurement are shown as a function of total molality \hat{m} at constant composition \hat{X}_2 , in Fig. 1. The γ value decreases with increasing \hat{m} below the cmc at which the γ versus \hat{m} curve shows a distinct breakpoint. It is noted that the shape of the curve changes regularly with \hat{X}_2 from the line of pure HTAB to that of the DTAB system.

First, let us examine the miscibility of HTAB and DTAB molecules in the adsorbed film. For the present system, the total differential of γ at constant temperature and atmospheric pressure is written as [5, 12]

$$d\gamma = -(RT\hat{\Gamma}^H/\hat{m})d\hat{m} - (\hat{X}_2^H - \hat{X}_2)(RT\hat{\Gamma}^H/2\hat{X}_1\hat{X})d\hat{X}_2, \quad (3)$$

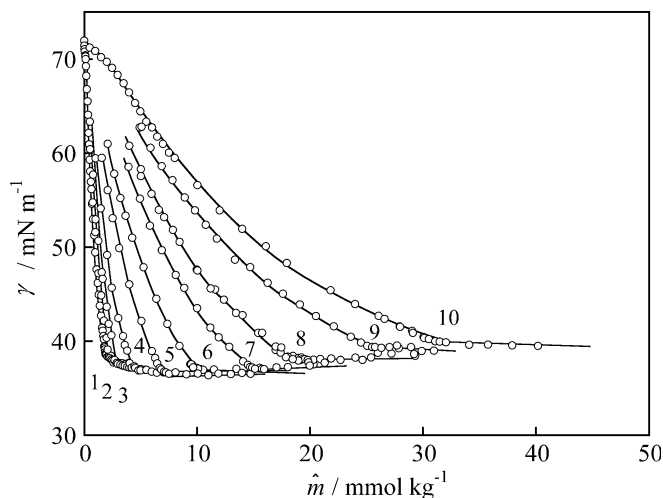


Fig. 1 Surface tension versus total molality curves at constant composition: $\hat{X}_2 = 0$ (1), 0.254 (2), 0.512 (3), 0.750 (4), 0.900 (5), 0.951 (6), 0.980 (7), 0.990 (8), 0.998 (9), 1 (10)

where $\hat{\Gamma}^H$ and \hat{X}_2^H are respectively the total surface density and the composition of DTAB in the adsorbed film given by

$$\hat{\Gamma}^H = 2\Gamma_1^H + 2\Gamma_2^H \quad (4)$$

and

$$\hat{X}_2^H = 2\Gamma_2^H / \hat{\Gamma}^H. \quad (5)$$

Here Γ_i^H is the surface density of component i with respect to the two dividing planes making the excess numbers of moles of air and water zero simultaneously. The \hat{X}_2^H values were calculated by applying the equation

$$\hat{X}_2^H = \hat{X}_2 - (2\hat{X}_1\hat{X}_2/\hat{m})(\partial\hat{m}/\partial\hat{X}_2)_{T,p,\gamma} \quad (6)$$

to the \hat{m} versus \hat{X}_2 curves (solid lines) and are shown as the \hat{m} versus \hat{X}_2^H curves (dashed lines) in Fig. 2. This diagram constructed by the \hat{m} versus \hat{X}_2^H and \hat{m} versus \hat{X}_2 curves is called a phase diagram of adsorption (PDA) and gives the relationship between the compositions between the adsorbed film and bulk solution in equilibrium. It is realized that the HTAB and DTAB molecules are miscible with each other in the adsorbed film, which is enriched in HTAB compared with the bulk solution.

It should be noted that the shape of the PDA is distorted at low \hat{X}_2^H at all γ and the \hat{m} versus \hat{X}_2^H curve deviates negatively from the dotted line representing the ideal mixing of molecules in the adsorbed film given by [8]

$$(\hat{m})^2 = (\hat{m}_1^0)^2 + [(\hat{m}_2^0)^2 - (\hat{m}_1^0)^2]\hat{X}_2^H, \quad (7)$$

where \hat{m}_i^0 is the molality of pure surfactant i at the given γ . The negative deviation becomes prominent with decreasing γ . This is quantitatively manifested by eval-

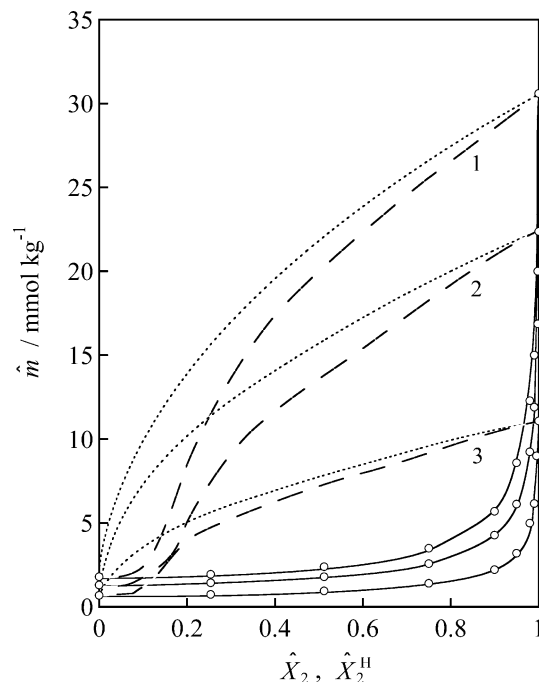


Fig. 2 Total molality versus composition curves at constant surface tension: $\gamma = 40 \text{ mN m}^{-1}$ (1), 45 mN m^{-1} (2), 55 mN m^{-1} (3); \hat{m} versus \hat{X}_2 (solid lines), \hat{m} versus \hat{X}_2^H (dashed lines), \hat{m} versus \hat{X}_2^H for ideal mixing (dotted line)

uating the excess Gibbs energy of adsorption $\hat{g}^{H,E}$ from the equation [8]

$$\hat{g}^{H,E} = RT \left(\hat{X}_1^H \ln \hat{f}_{1\pm}^H + \hat{X}_2^H \ln \hat{f}_{2\pm}^H \right), \quad (8)$$

where $\hat{f}_{i\pm}^H$ is the mean activity coefficient of component i in the adsorbed film evaluated by

$$\hat{f}_{i\pm}^H = (\hat{m}/\hat{m}_i^0) (\hat{X}_i/\hat{X}_i^H)^{1/2} \quad i = 1 \text{ and } 2. \quad (9)$$

The $\hat{g}^{H,E}$ versus \hat{X}_2^H curve at constant γ is shown in Fig. 3. The important point is that the $\hat{g}^{H,E}$ value is negative over the entire \hat{X}_2^H range and decreases with decreasing γ . A negative $\hat{g}^{H,E}$ reveals the stronger mutual interaction between HTAB and DTAB molecules than that between the same species. However, according to our results for the systems having the same counteranion and a difference in chain length by only 2, for example, tetradecyltrimethylammonium bromide (TTAB)–DTAB (K. Kashimoto, T. Nakano, H. Matsubara, M. Aratono, unpublished data) and dodecylammonium chloride–decylammonium chloride [8] systems, the $\hat{g}^{H,E}$ values are slightly positive and thus indicate the weaker mutual interaction between different species than that between the same ones. Thus, disclosing why there is such an appreciable difference in the $\hat{g}^{H,E}$ values between the HTAB–DTAB and TTAB–DTAB systems is expected to produce information on the molecular

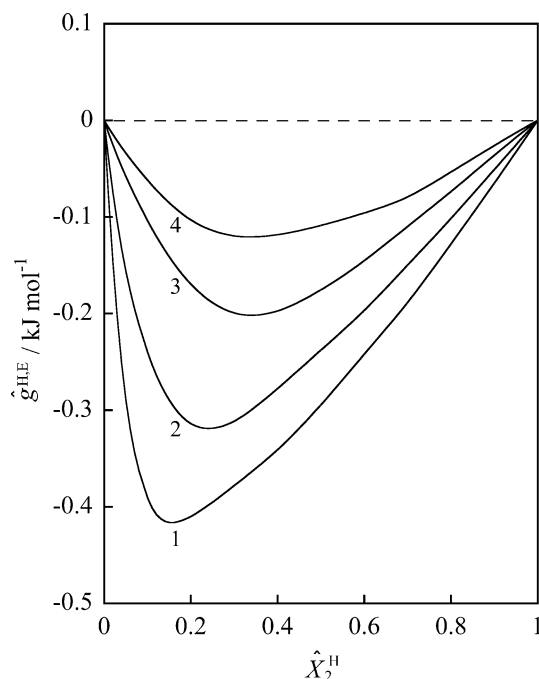


Fig. 3 Excess Gibbs energy in adsorbed film versus composition curves at constant surface tension: $\gamma = 40 \text{ mN m}^{-1}$ (1), 45 mN m^{-1} (2), 50 mN m^{-1} (3), 55 mN m^{-1} (4)

arrangement of the mixed adsorbed film. One of the appropriate thermodynamic ways for this purpose is to estimate the excess surface area per molecule from the dependence of $\hat{g}^{\text{H,E}}$ on γ by using the equation [7, 9]

$$\hat{A}^{\text{H,E}} = -[\partial(\hat{g}^{\text{H,E}}/N_A)/\partial\gamma]_{T,p,\hat{X}_2^{\text{H}}} \quad (10)$$

The $\hat{g}^{\text{H,E}}$ values given in Fig. 3 decrease clearly with decreasing γ and therefore the $\hat{A}^{\text{H,E}}$ value is negative for the whole composition range (Fig. 4). This shows that the decrease in the average molecular area compared with that of the ideal-mixing case is responsible for the negative values of $\hat{g}^{\text{H,E}}$.

Villeneuve et al. [6] have studied the miscibility of cationic DTAB and nonionic OMS in adsorbed films and micelles by analyzing the surface tension data thermodynamically. It was found that the $\hat{g}^{\text{H,E}}$ value is negative and decreases with decreasing γ . Considering that the cross-sectional area of the trimethylammonium group is larger than that of hydrocarbon chain and that the molecular geometries of the hydrophilic groups are different, it was suggested that the space among the hydrocarbon chains in the adsorbed film is used effectively for packing of OMS molecules and consequently the van der Waals interaction between tail groups and the ion-dipole interaction between the head groups are enhanced.

Casson and Bain [15] studied the mixed adsorption of C_{12}OH and C_nTAB at the air/water interface by using

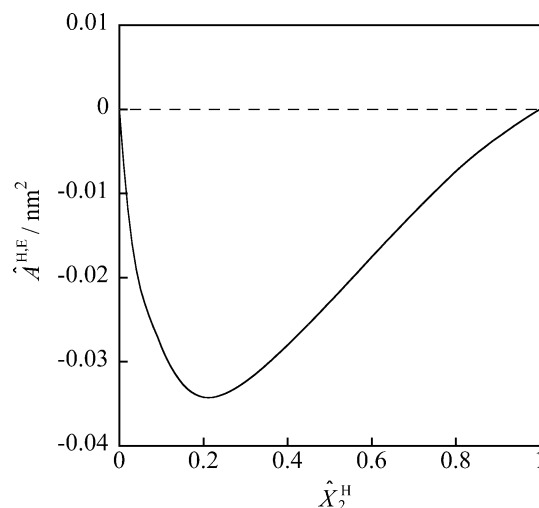


Fig. 4 Excess surface area versus composition curve at $\gamma = 50 \text{ mN m}^{-1}$

SFS and found that C_{12}OH and C_nTAB molecules form a crystalline phase in a low-temperature region. They proposed an arrangement whereby C_{12}OH molecules fill the space among the hydrocarbon chains of the alkyltrimethylammonium ions. Furthermore, Lee et al. [20] investigated the structure of an adsorbed film of decyltrimethylammonium bromide at the air/water interface by means of NR and claimed that decyltrimethylammonium ions take a staggered arrangement to minimize the electrostatic repulsion between the head groups (see Fig. 4 in Ref. [20]).

Considering the negative values of $\hat{g}^{\text{H,E}}$ and $\hat{A}^{\text{H,E}}$ together with the previous studies mentioned previously, we propose a model for a molecular arrangement in the mixed adsorbed film of HTAB and DTAB as follows. DTAB molecules may use effectively the space between HTAB molecules and their polar head groups take a staggered arrangement in order to minimize the electrostatic repulsion. Eventually, the interaction between the hydrocarbon chains of HTAB and DTAB molecules will be enhanced with increasing adsorption. Considering that the diameter of a hydrated trimethylammonium group is around 0.6 nm, which is close to the length of four methylene groups [24], the hydrocarbon chains of DTAB are assumed to be just buried within those of HTAB or to protrude slightly below or above the monolayer surface.

Now let us examine the miscibility in the micelle. To do this, the composition of DTAB in the micelle \hat{X}_2^{M} defined by

$$\hat{X}_2^{\text{M}} = 2N_2^{\text{M}} / (2N_1^{\text{M}} + 2N_2^{\text{M}}) = 2N_2^{\text{M}} / \hat{N}^{\text{M}} \quad (11)$$

was evaluated numerically by applying the relation [5]

$$\hat{X}_2^{\text{M}} = \hat{X}_2 - (2\hat{X}_1\hat{X}_2/\hat{C})(\partial\hat{C}/\partial\hat{X}_2)_{T,p} \quad (12)$$

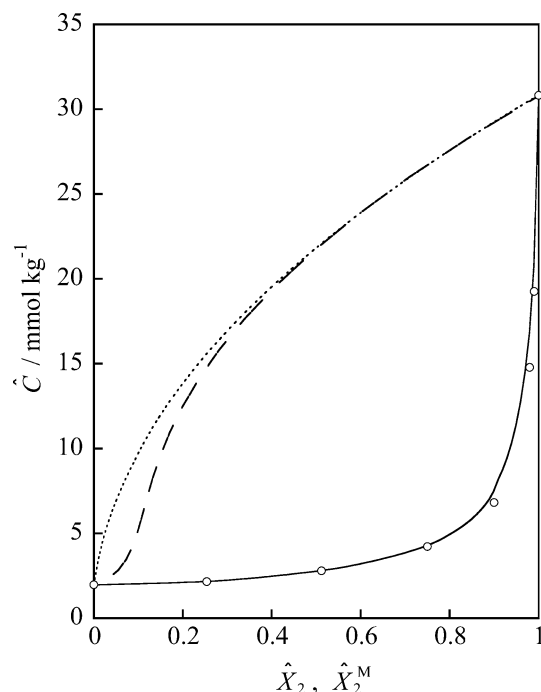


Fig. 5 Critical micelle concentration versus composition curves: \hat{C} versus \hat{X}_2 (solid line), \hat{C} versus \hat{X}_2^M (dashed line), \hat{C} versus \hat{X}_2^M for ideal mixing (dotted line)

to the total molality at the cmc \hat{C} versus \hat{X}_2 curve shown by the solid line in Fig. 5. Here, N_i^M is the excess number of molecules of component i per micelle particle with reference to a spherical dividing plane which makes the excess number of water zero. The phase diagram of micelle formation was constructed and is shown in Fig. 5. The HTAB molecule is richer in the micelle as well as in the adsorbed film than in the bulk solution.

Although the \hat{C} versus \hat{X}_2^M curve deviates negatively from the dotted line for ideal mixing in the micelle given by [8]

$$(\hat{C})^2 = (\hat{C}_1^0)^2 + [(\hat{C}_2^0)^2 - (\hat{C}_1^0)^2] \hat{X}_2^M, \quad (13)$$

where \hat{C}_i^0 is the cmc of the pure surfactant i , the deviation is not so large as that observed for the PDA in Fig. 2. Evaluating the excess Gibbs energy of the micelle formation $\hat{g}^{M,E}$ by the following equation [8]

$$\hat{g}^{M,E} = RT(\hat{X}_1^M \ln \hat{f}_{1\pm}^M + \hat{X}_2^M \ln \hat{f}_{2\pm}^M), \quad (14)$$

we shed light on the miscibility in the micelle more quantitatively. Here $\hat{f}_{i\pm}^M$ is the mean activity coefficient of surfactant i in the micelle calculated by [8]

$$\hat{f}_{i\pm}^M = (\hat{C}/\hat{C}_i^0)(\hat{X}_i/\hat{X}_i^M)^{1/2}. \quad (15)$$

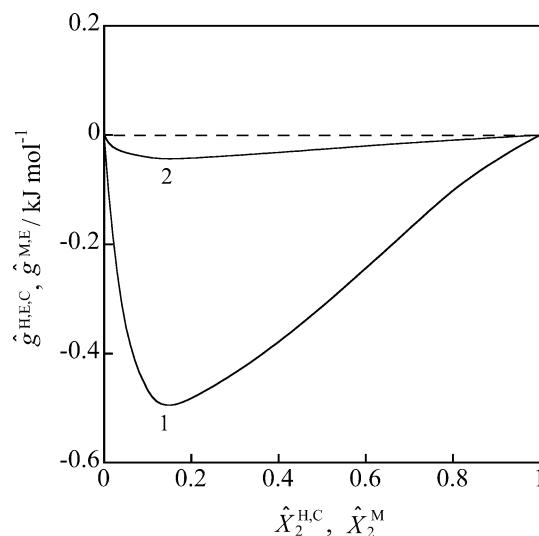


Fig. 6 Excess Gibbs energy versus composition curves at the critical micelle concentration: $\hat{g}^{H,E,C}$ versus $\hat{X}_2^{H,C}$ (1), $\hat{g}^{M,E}$ versus \hat{X}_2^M (2)

The result is shown as the $\hat{g}^{M,E}$ versus \hat{X}_2^M curve together with the excess Gibbs energy of adsorption at the cmc $\hat{g}^{H,E,C}$ versus $\hat{X}_2^{H,C}$ curve in Fig. 6 to visualize their difference clearly. The $\hat{g}^{M,E}$ value is negative at all compositions and its absolute value is much smaller than that of $\hat{g}^{H,E,C}$; the interaction between HTAB and DTAB molecules is weaker in the micelle than in the adsorbed film. This reflects that the geometrical structure of the interface as well as the molecular geometry affects appreciably the miscibility of molecules in the molecular organized system, i.e., the staggered arrangement of molecules is not necessary for reducing electrostatic repulsion between cationic groups in the spherical micelle because a smaller packing parameter is favorable to the micelle compared with the planar adsorbed film.

The present system was composed of the homologous surfactant cations and a bromide anion. In a system with another anion, the size of the hydrated anion and the binding of the counterion may affect the staggered arrangement in the adsorbed film and the aggregation number of the micelle. From this standpoint, an experiment on hexadecyltrimethylammonium chloride–dodecyltrimethylammonium chloride should be undertaken. Furthermore the effect of the preferential adsorption of the counterion to the adsorbed film and the micelle should be considered in the case of surfactant mixtures having different counteranions.

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