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ORIGINAL CONTRIBUTION

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The effect of counterions on the surface adsorption and micelle formation in mixed surfactant systems of dodecyl sulfates

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Abstract The surface tension of the aqueous solutions of sodium dodecyl sulfate (SDS) and tetramethylammonium dodecyl sulfate (TMADS) was measured as a function of total molality of the surfactants at fixed composition of TMADS at 298.15 K under atmospheric pressure. The phase diagrams of adsorption and of micelle formation, the activity coefficients, and the excess Gibbs energy were calculated to estimate the deviation from the ideal mixing quantitatively. The preferential adsorption and the micelle formation for TMA^+ to Na^+ is attributable to some extent to the hydrophobicity of the methyl groups of TMA^+. The composition of TMA^+ in the micelle is larger than that in the adsorbed film at equilibrium. That is, a larger hydrated counterion is more likely to exist in the micelle than in the adsorbed film owing to geometrical benefit. The negative values of the excess Gibbs energy of the adsorbed film and of the micelle arise from the positive ones of the excess entropy greater than that of excess enthalpy. The counterions of very similar size are mixed ideally in the micelle and the size effect appears sensitively in the adsorbed film.

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

Introduction

Surfactant mixtures have been widely investigated from the viewpoint of theoretical and practical importance and have been well reviewed [1–4]. We have shown that our thermodynamic treatment together with a surface tension measurement is quite informative to clarify the behavior of adsorption and micelle formation of surfactants [5–7]. In our treatment we have estimated the compositions in adsorbed films and micelles and examined the miscibility of surfactants by phase diagrams of adsorption and micelle formation. Recently, we developed and summarized the thermodynamic relations in terms of an activity coefficient and excess Gibbs energy for several types of binary surfactant mixtures containing ionic surfactants [8–12].

We studied the successive N-methylation of dodecylammonium chloride (DAC) systematically to examine a contribution of a polar head group to the thermodynamic quantities [13]. It was concluded that a change in the molecular geometry and in the hydrophilicity of the polar head group of DAC affects the adsorbed film at a plane interface more significantly than micelles with a spherical structure.

It is known that a counterion of an ionic surfactant also influences the surface adsorption and the micelle formation of the surfactant by its characteristic configuration in the vicinity of the head group of the surfactant and in the diffuse layer of the assemblies. The important factor affecting the resulting configuration is not only the chemical structure of the counterion but also the interfacial geometry of the assemblies. Lu et al. [14] investigated how the variation of univalent counterions affects the adsorption and structure of dodecyl sulfate monolayers at the air/water interface by neutron reflection and by surface tension.

Previously we reported the adsorption and micelle formation of a series of dodecyl sulfates and discussed the effect of their counterions [Li^+, Na^+, NH_4^+, $N(CH_3)_4^+$] [15]. We concluded that there are some relationships between the values of critical micelle concentration (cmc), the surface tension at the cmc, the molecular surface area, etc., and the sizes of the counterions (Stokes radii) for lithium dodecyl sulfate (LiDS), sodium dodecyl sulfate (SDS), and ammonium dodecyl sulfate (ADS) but not for tetramethylammonium dodecyl sulfate (TMADS). It was briefly outlined for the miscibility of SDS and TMADS that the mixing behavior of TMA^+ in the adsorbed film and the micelle is greatly influenced by the difference in the geometry of the molecular assembly.

The purpose of the present study was to investigate further the counterion effect on the miscibility of SDS and TMADS from the viewpoints of an activity coefficient and the excess Gibbs energy. The surface tension of aqueous solutions of SDS and TMADS was measured as a function of the total molality of surfactants at fixed composition of TMADS at 298.15 K under atmospheric pressure. The phase diagrams of adsorption and of micelle formation, the activity coefficients, and the excess Gibbs energy were calculated to estimate the deviation from the ideal mixing quantitatively.

Materials and methods

Materials

SDS was synthesized from dodecanol by sulfonation with chlorosulfonic acid. After removal of unreacted dodecanol by heating in vacuo at 363.15 K for 7 hr., SDS was recrystallized twice from water and then three times from ethanol. TMADS was also synthesized and purified by recrystallization from ethanol solution [16, 17]. The purity of the surfactants was checked by confirming that there was no minimum on the surface tension versus concentration curve in the vicinity of the cmc. Water was distilled three times from alkaline permanganate solution.

Surface tension measurements

The surface tension, γ, of aqueous solutions of the mixture of SDS and TMADS was measured by the drop-volume technique at 298.15 K under atmospheric pressure [18]. The drop volume only for an aqueous solution of pure SDS was measured with a glass capillary coated with dimethylpolysiloxane [18]. Temperature was controlled by a thermostated bath within ± 0.01 K. The experimental error of the surface tension measurements was within ± 0.05 mNm^{-1}.

Results and discussion

We may choose four intensive variables as the experimental variables to describe this four-component two-phase system by considering Gibbs' phase rule and postulating that air is one component. We employed the total molality of the surfactants, m, and the composition of TMADS, X_2, together with temperature and pressure. We measured the γ as a function of m at fixed composition of TMADS, X_2, at 298.15 K under atmospheric pressure. Here m and X_2 are defined by

$$m = m_1 + m_2 \tag{1}$$

and

$$X_2 = m_2/m_1 \ , \tag{2}$$

where m_1 and m_2 are the molalities of SDS and TMADS, respectively. The results of the surface tension measurement of the SDS–TMADS system are shown in Fig. 1. All the curves have a distinct break point, indicating the formation of a micelle. The cmc is given by the total molality, C, of the break point on the γ versus m curve. The value of the surface tension at the cmc increases with increasing X_2, while that of the cmc decreases. As a result the surface tension above the cmc increases with increasing X_2, while the surface tension below the cmc decreases. The shape of the curve, however, changes smoothly with X_2 from SDS to TMADS without special irregularity.

From our thermodynamics of adsorption for mixtures of uni-univalent ionic surfactant with a common ion [7], the total surface density, Γ^H, is defined by

$$\Gamma^H = \Gamma_1^H + \Gamma_2^H \ , \tag{3}$$

where the surface densities of SDS and TMADS, Γ_1^H and Γ_2^H, are defined with respect to the two dividing planes chosen so as to make the excess numbers of moles of

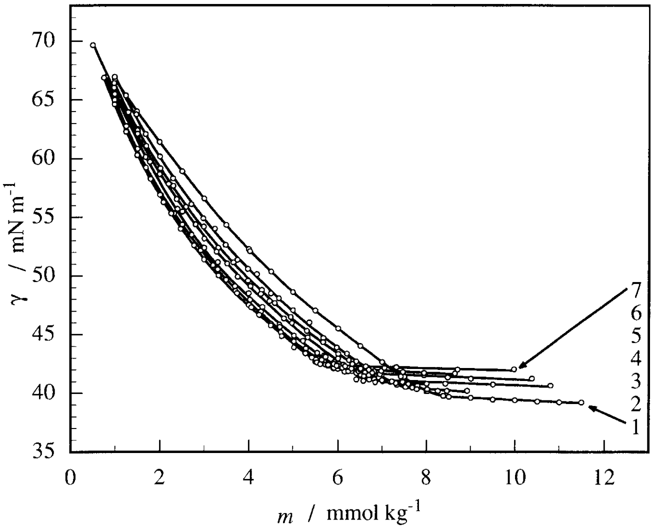

Fig. 1 Surface tension versus total molality curves at constant composition for $X_2 = 0$ (1) (SDS), 0.1510 (2), 0.2747 (3), 0.3695 (4), 0.6000 (5), 0.7997 (6), 1 (7) (TMADS)

water and air zero. The surface densities of SDS and TMADS are related to those of the constituent ions by

$$\Gamma^{\mathrm{H}}_{\mathrm{Na^+}} = \Gamma^{\mathrm{H}}_{1} \tag{4}$$

and

$$\Gamma^{\mathrm{H}}_{\mathrm{TMA^+}} = \Gamma^{\mathrm{H}}_{2} \ . \tag{5}$$

Then, the electroneutrality condition of surface density is written as

$$\Gamma^{\mathrm{H}}_{\mathrm{DS^-}} = \Gamma^{\mathrm{H}}_{1} + \Gamma^{\mathrm{H}}_{2} \ . \tag{6}$$

We calculated Γ^{H} by applying the equation

$$\Gamma^{\mathrm{H}} = -(m/2RT)(\partial\gamma/\partial m)_{T,P,X_2} \tag{7}$$

to the surface tension versus total molality curves given in Fig. 1. The evaluated Γ^{H} values at constant X_2 are plotted against m in Fig. 2. The Γ^{H} values at the cmc $\Gamma^{\mathrm{H,C}}$ are shown by solid circles. We can see that the total surface density decreases with increasing X_2 at higher concentration, while it increases at lower concentration. To view such behavior more clearly, the surface pressure, π, was plotted against the mean area per adsorbed molecule, A, of SDS and TMADS at several X_2 in Fig. 3. Here π and A are respectively defined by

$$\pi = \gamma^0 - \gamma \tag{8}$$

and

$$A = 1/N_{\mathrm{A}}\Gamma^{\mathrm{H}} \ , \tag{9}$$

where γ^0 is the surface tension of the pure air/water surface and N_{A} is Avogadro's constant. One glance at Fig. 3 informs us that the adsorbed film of the SDS–TMADS system exhibits the expanded state in this experimental region. It is clear from Fig. 3 that the value of A for pure TMADS is larger than that of pure SDS and that the mean A at the same surface pressure is proportional to X_2.

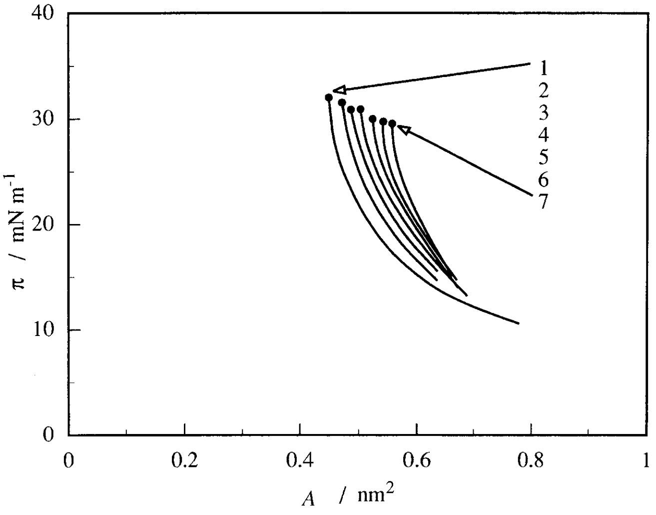

Fig. 3 Surface pressure versus area per molecule curves at constant composition for $X_2 = 0$ (1) (SDS), 0.1510 (2), 0.2747 (3), 0.3695 (4), 0.6000 (5), 0.7997 (6), 1 (7) (TMADS)

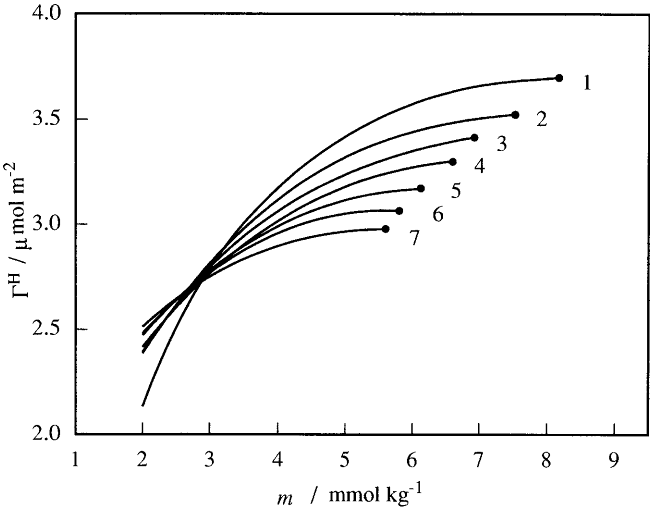

Fig. 2 Total surface density versus total molality curves at constant composition for $X_2 = 0$ (1) (SDS), 0.1510 (2), 0.2747 (3), 0.3695 (4), 0.6000 (5), 0.7997 (6), 1 (7) (TMADS)

Next, we illustrate phase diagrams for this system to consider the miscibility in the adsorbed film and the micellar state. First we draw the m versus X_2 curves at constant surface tension as shown in Fig. 4 by taking the m values at a given γ value from Fig. 1. The cmc values, C, are also shown by solid circles in Fig. 4. All the values of m and C decrease with increasing X_2. Here, the composition in the adsorbed film, X_2^{H}, is an essential thermodynamic quantity to describe the adsorbed film state and is defined by

$$X_2^{\mathrm{H}} = \Gamma^{\mathrm{H}}_2/\Gamma^{\mathrm{H}} \ . \tag{10}$$

We calculated X_2^{H} by applying the equation

$$X_2^{\mathrm{H}} = X_2 - (2X_1X_2/m)(\partial m/\partial X_2)_{T,P,\gamma} \tag{11}$$

to the m versus X_2 curves in Fig. 4 and is plotted in the form of m versus X_2^{H} curves in Fig. 5. We illustrated the m versus X_2 curves together with the m versus X_2^{H} in this figure to express a phase diagram at the surface, namely, a phase diagram of adsorption. The diagram indicates clearly that SDS and TMADS molecules are miscible in the adsorbed film at all compositions.

We reported thermodynamic relations describing nonideality of the ionic surfactant mixture with and without common ions in the adsorbed film and micelle [12]. Now we can examine a deviation of the adsorbed film behavior from ideal mixing for this common ion system. We obtained the equation for ideal mixing

$$m^2 = (m_1^0)^2 - [(m_1^0)^2 - (m_2^0)^2]X_2^{\mathrm{H}} \tag{12}$$

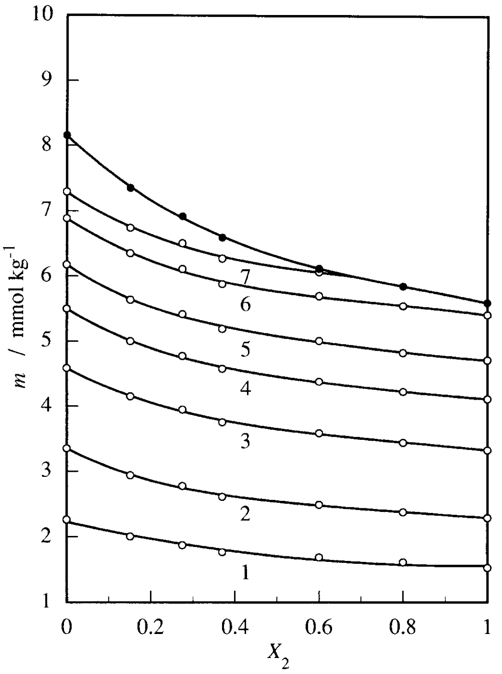

Fig. 4 Total molality versus composition curves at constant surface tension for $\gamma = 60$ (1), 55 (2), 50 (3), 47 (4), 45 (5), 43 (6), 42 mN m^{-1} (7); critical micelle concentration (cmc) (●)

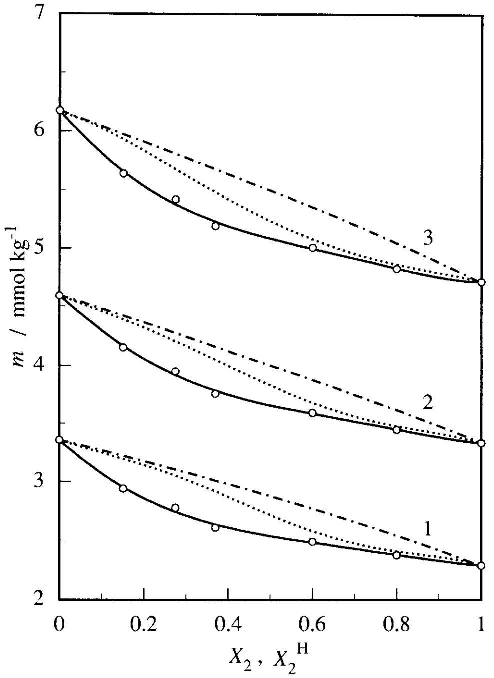

Fig. 5 Phase diagrams of adsorption at constant surface tension for $\gamma = 55$ (1), 50 (2), 45 mNm^{-1} (3); m versus X_2 (—); m versus X_2^{H} (···); m versus X_2^{H} (– · –) (ideal mixing)

from the equilibrium relation between the chemical potentials for the aqueous solution containing common surfactant ion and different counterions by assuming that the mean activity coefficients in the bulk solution are effectively unity or do not change appreciably on mixing, where m_1^0 and m_2^0 are the molality of pure surfactants 1 and 2, respectively, at the surface tension concerned. We added the curve for ideal mixing in Fig. 5. The significance of this phase diagram of adsorption is that the composition of TMA$^+$ in the adsorbed film is larger than that in the bulk solution. Another important point is that the total molality at a given X_2^{H} in the adsorbed film is smaller than that of ideal mixing over the entire range of composition and that the composition of TMA$^+$ in the adsorbed film is smaller than that of ideal mixing. Also the deviation from ideality increases at high concentration of TMA$^+$.

Next we discuss the miscibility of the surfactants in the mixed micelle. We define the composition of TMA$^+$ in the mixed micelle, X_2^{M}, by

$$X_2^{\mathrm{M}} = N_2^{\mathrm{M}}/(N_1^{\mathrm{M}} + N_2^{\mathrm{M}}) \tag{13}$$

and calculated it by applying the equation

$$X_2^{\mathrm{M}} = X_2 - (2X_1X_2/C)(\partial C/\partial X_2)_{T,P} \tag{14}$$

to the value of the cmc, C versus X_2 curve shown in Fig. 4. Furthermore we can obtain the equation

$$C^2 = \left(C_1^0\right)^2 - \left[\left(C_1^0\right)^2 - \left(C_2^0\right)^2\right]X_2^{\mathrm{M}} \tag{15}$$

for ideal mixing in the same way as for the adsorbed film, where C_1^0 and C_2^0 are the cmc of pure surfactants 1 and 2, respectively. We plotted the C versus X_2^{M} curves in Fig. 6 together with the C versus X_2 curves and for the ideal mixing in the micelle. It is clear from this figure that the value of the cmc at a given X_2^{M} in the micelle is smaller than that of ideal mixing over the entire range of composition and that the composition of TMA$^+$ in the micelle is larger than that in the bulk solution and is smaller than that of ideal mixing. This result is the same as the case of the adsorbed film. Namely the value of X_2^{H} and X_2^{M} is greater than that of X_2 but smaller than that of X_2^{H} and X_2^{M} in the ideal mixing states, respectively. It appears that the preferential adsorption and the micelle formation for TMA$^+$ to Na$^+$ is attributable to some extent to the hydrophobicity of the methyl groups of TMA$^+$.

Next we consider the equilibrium between the adsorbed film and the micelle at the cmc. The composition in the adsorbed film at the cmc, $X_2^{\mathrm{H,C}}$, is obtained by applying the equation

$$X_2^{\mathrm{H,C}} = X_2^{\mathrm{M}} - (X_1X_2/RT\Gamma^{\mathrm{H,C}})(\partial\gamma^{\mathrm{C}}/\partial X_2)_{T,P} \tag{16}$$

to the γ^{C} versus X_2 curve shown in Fig. 7. Thus, we can compare the value of X_2^{M} with that of $X_2^{\mathrm{H,C}}$ as shown in this phase diagram. The important point is that the

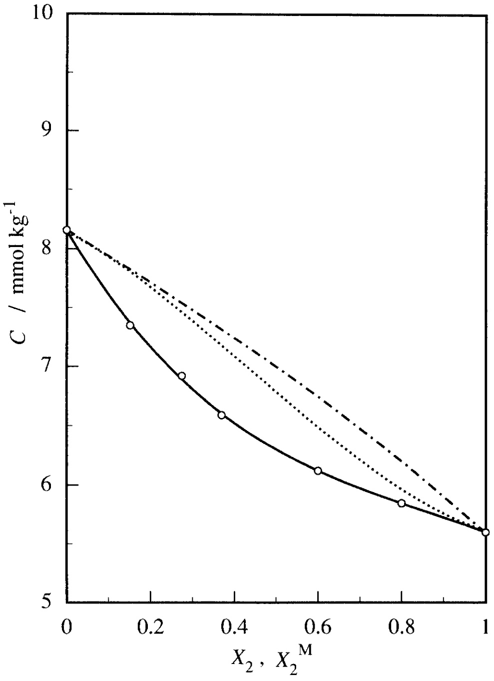

Fig. 6 Phase diagram of micelle formation: C versus X_2 (—); C versus X_2^M (···); C versus X_2^M (– · –) (ideal mixing)

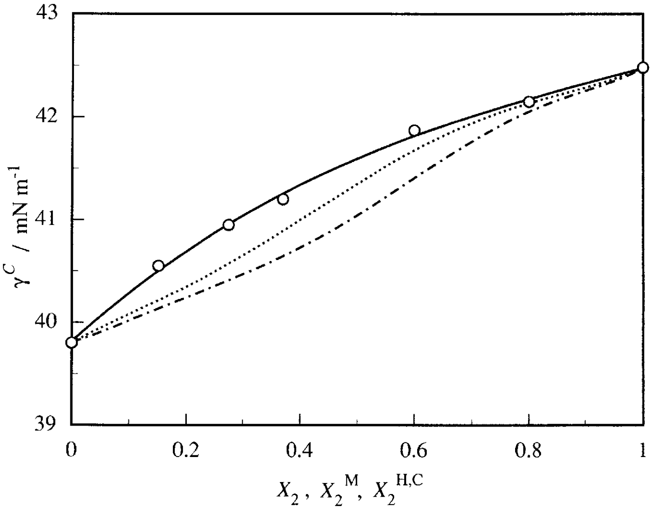

Fig. 7 Surface tension at the cmc versus composition curves: γ^C versus X_2 (——); γ^C versus $X_2^{H,C}$ (···); γ^C versus X_2^M (— · —)

composition of TMA$^+$ in the micelle is larger than that in the adsorbed film at equilibrium. It is apparent that this fact indicates a relation between the size of the hydrated counterion and the geometry of the surfaces. It is well known that the hydrated ionic radius of TMA$^+$ (0.204 nm) is greater than that of Na$^+$ (0.180 nm) [19]. That is, a larger hydrated counterion is more likely to exist in the micelle than in the adsorbed film owing to geometrical benefit.

Now, we consider the deviation from ideal mixing quantitatively by introducing the excess Gibbs energy of the adsorbed film and of the micelle [12]. We evaluated the activity coefficient of each state and estimated the excess molar Gibbs energy of the adsorbed film, $g^{H,E}$, and of the micelle, $g^{M,E}$, by equations

$$g^{H,E} = RT\left(X_1^H \ln f_{1\pm}^H + X_2^H \ln f_{2\pm}^H\right) \tag{17}$$

and

$$g^{M,E} = RT\left(X_1^M \ln f_{1\pm}^M + X_2^M \ln f_{2\pm}^M\right) \quad . \tag{18}$$

The excess molar Gibbs energy of the adsorbed film which coexists with the micelle, $g^{H,E,C}$, can be obtained by extrapolation of the $g^{H,E}$ versus m curve to the cmc. We compare the value of $g^{H,E,C}$ with that of $g^{M,E}$ in Fig. 8a. Both $g^{H,E,C}$ and $g^{M,E}$ exhibit a negative value. This result agrees with the negative deviation from ideality in the former phase diagrams. Now, we consider the meaning of the negative values of $g^{H,E}$ and $g^{M,E}$ by dividing the excess Gibbs energy into the terms of enthalpy and entropy. Since it is hard to think that the counterions Na$^+$ and TMA$^+$ interact attractively with each other, the excess entropy term is expected to exceed the positive excess enthalpy term and dominate the sign of the excess Gibbs energy; therefore, negative values of the excess Gibbs energy of the adsorbed film and of the micelle are expected to arise from positive ones of the excess entropy greater than that of the excess enthalpy. Such behavior of excess thermodynamic quantities has been observed in the case when molecules of different sizes are mixed [20].

Furthermore, it is obvious from Fig. 8a that the excess Gibbs energy of the adsorbed film is more negative than that of the micelle. Taking into account the explanation mentioned previously that the negative excess Gibbs energy is probably responsible for the positive excess entropy in this system, it seems that the positive value of the excess entropy in the adsorbed film is larger than that in the micelle. Namely, counterions have smaller available space in the adsorbed film than in the micelle, and so the effect of the difference of counterion size appears considerably in the adsorbed film. To confirm this elucidation, we present another mixed system of surfactants: decyl ammonium chloride (DeAC) and decyl ammonium bromide (DeAB) [21]. The DeAC–DeAB system has the same surfactant ion and different counterions as in the case of SDS–TMADS; however, the counterions in the DeAC–DeAB system are very similar in size, i.e., the hydrated ion radius of Cl$^-$ is 0.06 nm and that of Br$^-$ is 0.07 nm [19]. The comparison of $g^{H,E,C}$ with $g^{M,E}$ for the DeAC–DeAB system is shown in Fig. 8b. It is clear that the value of $g^{M,E}$ is almost zero over the entire range of

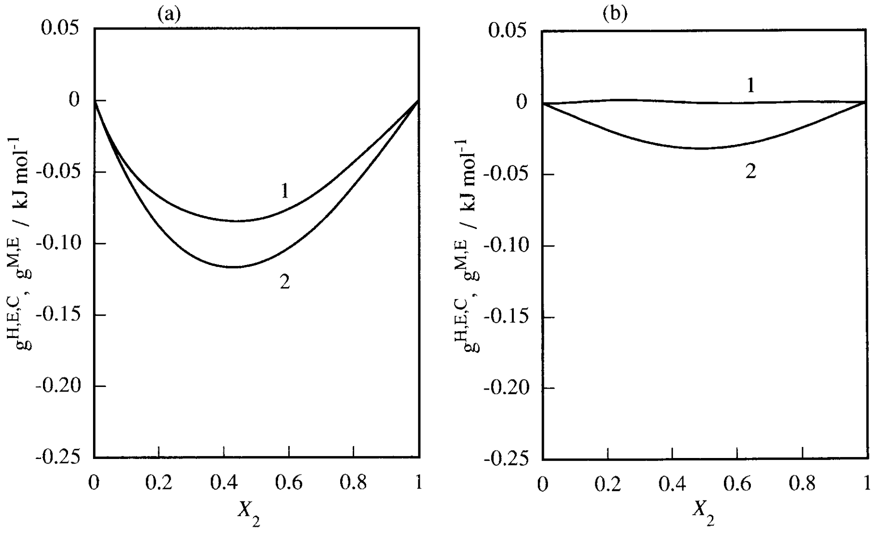

Fig. 8 Excess Gibbs energy of micelle formation and adsorption versus composition curves at the cmc: **a** SDS–TMADS system, **b** DeAC–DeAB system; $g^{M,E}$ versus X_2 (1), $g^{H,E,C}$ versus X_2 (2)

composition, while $g^{H,E,C}$ is slightly negative. This result demonstrates that counterions of very similar size are mixed ideally in the micelle and that the size effect appears sensitively in the adsorbed film. Thus, we can conclude that the mixing behavior of the counterions for surfactants is greatly influenced by the difference both in the geometry of the molecular assembly and in the size of the counterion.

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