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ORIGINAL CONTRIBUTION

Takashi Matsuda
Yoko Asoh
Masumi Villeneuve
Hiroki Matsubara
Takanori Takiue
Makoto Aratono

Nonideal mixing of dodecyltrimethylammonium halides and nonionic surfactant in adsorbed films and micelles

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T. Matsuda (✉) · Y. Asoh
H. Matsubara · T. Takiue · M. Aratono
Department of Chemistry and
Physics of Condensed Matter,
Graduate School of Sciences,
Kyushu University,
Hakozaki 6-10-1, 812-8581,
Higashiku, Fukuoka, Japan
E-mail: matsudascc@mbox.nc.kyushu-u.ac.jp
Tel.: +81-92-6422580
Fax: +81-92-6422607

M. Villeneuve
Department of Chemistry,
Faculty of Science, Saitama University,
338-8570 Saitama, Japan

Abstract The ion–dipole interaction between dodecyltrimethylammonium cations and nonionic surfactant molecules in adsorbed films and micelles was investigated by concentrating on the difference in the degree of counterion binding by employing dodecyltrimethylammonium chloride (DTAC)–octyl methyl sulfoxide (OMS) and dodecyltrimethylammonium bromide (DTAB)–OMS mixtures. The phase diagrams of adsorption and micelle formation were constructed and then the nonideal mixing of different species of surfactants was demonstrated in terms of the excess Gibbs free energies of adsorption and micelle formation, and the surface excess areas. Furthermore the dependence of them on the counterion was clearly shown. All these results were found to support our previous view that the direct interaction between surfactant cation and the dipole of the hydrophilic part of a nonionic surfactant is essential in cationic-nonionic surfactant mixtures, i.e., the DTAC system with a lower counterion biding has more negative excess thermodynamic quantities than the DTAB system with a higher one.

Keywords Surface tension · Miscibility in adsorbed films and micelles · Counterion binding · Excess thermodynamic quantity

Introduction

Mixed-surfactant systems are employed commonly in industrial applications and therefore have been studied extensively toward the understanding of the underlying principles of observed phenomena [1, 2, 3]. Although some advanced techniques, such as NMR, neutron reflection, IR reflection absorption spectroscopy, sum-frequency spectroscopy, serve as powerful ones for clarifying the structures of surfactant solutions and adsorbed films [4, 5, 6, 7, 8, 9] thermodynamic studies in a systematic also way give important information on the macroscopic and often microscopic nature of them. We have applied the following procedure to several surfactant mixtures and shed light on the miscibility and the molecular interaction of surfactants; the surface tension is measured very precisely as a function of the total concentration and mole fraction of surfactant mixture and, then, the excess Gibbs energy is evaluated on the basis of the phase diagrams of adsorption (PDA) and micelle formation (PDM) [10, 11, 12].

In a series of studies on ionic–nonionic surfactant mixtures [13, 14, 15], we have pointed out the strong mutual interaction between the different kinds of species for both cationic and anionic surfactants, and suggested that it is due to

1. The direct ion–dipole interaction between the cationic surfactant ion and nonionic surfactant.
2. The indirect interaction through the countercation between the anionic surfactant ion and nonionic surfactant.

Now it is required to confirm these suggestions by using more detailed and systematic thermodynamic studies, and/or by means of some advanced techniques cited earlier.

We have already demonstrated by investigating the adsorption and micelle formation of the dodecylammonium chloride–octyl methyl sulfoxide (OMS) and dodecyltrimethylammonium bromide (DTAB)–OMS systems that the strong mutual interaction is enhanced more on decreasing the surface density in the former mixture, while on increasing it in the latter. This gives supporting evidence of the point 1 from the viewpoint of the molecular packing in the adsorbed film and micelle [16]. In further corroboration of point 1, another available way is to control the counterion binding to surfactant cations and consequently to alter the magnitude of the cation–nonionic surfactant interaction. The more counterions are bound to surfactant cations, the less the interaction becomes. Considering that DTAB has a lower critical micelle concentration (cmc) and higher surface density at a given concentration than dodecyltrimethylammonium chloride (DTAC) and that both the adsorbed film and micelles are enriched in Br^- compared to Cl^- in the bromide–chloride surfactants mixture [17], the comparison of the magnitude of the nonideal mixing between the DTAB–nonionic surfactant and DTAC–nonionic surfactant systems is expected to offer further supporting evidence of point 1. Since the strong interaction has been already reported for the DTAB–OMS mixture [16], the DTAC–OMS mixture is the best one for this purpose.

We measured the surface tension of the aqueous solution of DTAC and OMS mixture against air and analyzed the results by means of our thermodynamic theory [12] to construct the PDA and PDM and then to evaluate the excess thermodynamic quantities. The results were compared with those of the DTAB–OMS system and it was examined whether point 1 is substantiated from the viewpoint of the counterion binding in the adsorbed films and micelles.

Experimental

DTAC was synthesized from dodecyl chloride, which was distilled under reduced pressure, and an aqueous solution of trimethylamine. The product was recrystallized several times from an ethyl acetate/ethanol (10/1 volume ratio) mixture. OMS was synthesized by oxidizing octyl methyl sulfide, which was distilled under reduced pressure, by *t*-butyl hypochlorite in methanol. The crude materials were recrystallized from a petroleum ether/ethanol (99/1 volume ratio) mixture. The purity was checked by observing no minimum on the surface tension versus molality curve around the cmc. Water was distilled three times from alkaline permanganate solution.

The surface tension, γ, of the aqueous solution of the mixture was measured as a function of the total molality, $\hat{m}$ and composition of OMS, $\hat{X}_2$ defined by

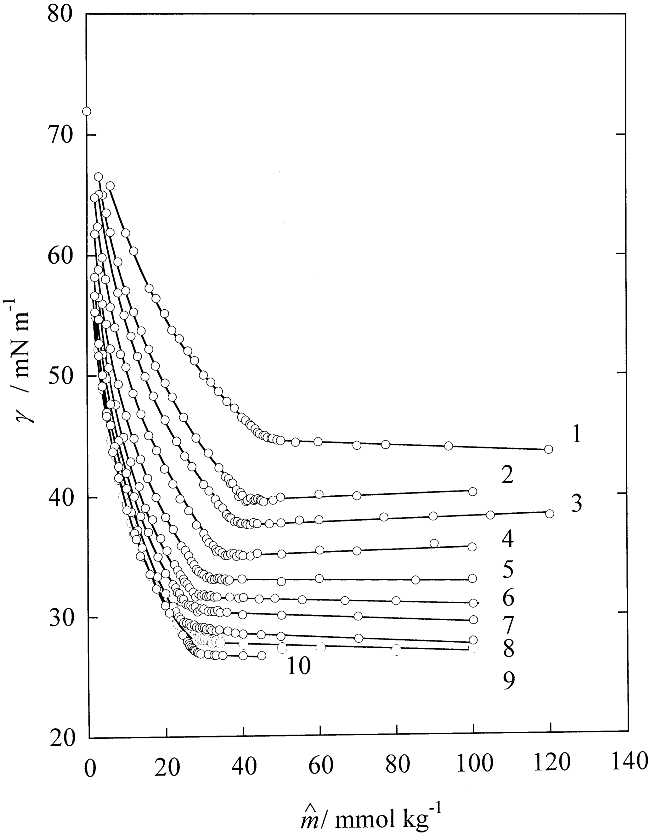

Fig. 1 Surface tension versus total molality curves of the dodecyltrimethylammonium chloride (DTAC)–octyl methyl sulfoxide (OMS) system at fixed compositions: $\hat{X}_2 = 0.010$ (1), 0.050 (2), 0.0998 (3), 0.200 (4), 0.350 (5), 0.500 (6), 0.640 (7), 0.840 (8), 0.921 (9), 1.000 (10)

$$\hat{m} = m_{1+} + m_{1-} + m_2 = 2m_1 + m_2 \tag{1}$$

and

$$\hat{X}_2 = m_2/\hat{m} \tag{2}$$

at 298.15 ± 0.01 K under atmospheric pressure by the drop-volume technique [18]. Here m_1 and m_2 are the molalities of DTAC and OMS, respectively. The experimental error of the surface tension was about ± 0.05 mN m^{-1}.

Results and discussion

Qualitatively the behavior of adsorption and micelle formation of the DTAC–OMS mixture is similar to that of the DTAB–OMS mixture on the whole. For the present purpose, however, the quantitative difference between the two systems is essential and therefore the results of the experiments and their analysis are demonstrated in a rather repetitious way by quoting the results of the previous DTAB–OMS system.

The surface tension of the aqueous solution of the mixture is plotted against $\hat{m}$ in Fig. 1. The γ value decreases rapidly with increasing $\hat{m}$ and takes an almost constant value at high molalities. The cmc was determined from the breakpoints on the γ versus $\hat{m}$ curves. The cmc, $\hat{C}$, and the surface tension γ^{C} at the cmc are plotted against $\hat{X}_2$ together with the corresponding curves of the DTAB system in Fig. 2. The $\hat{C}$ versus $\hat{X}_2$ curves have a minimum at $\hat{X}_2 \approx 0.7$–0.8, where the minimum of the DTAC system is steeper than that of the DTAB one. The γ^{C} value decreases with increasing $\hat{X}_2$, and the difference between the two curves is not so large but distinct. The difference between the two systems demonstrated in Fig. 2 asserts that the nature of the counterions affects undoubtedly the miscibility and, therefore, the mutual interaction between surfactant molecules in the adsorbed film and micelles.

First, let us examine the miscibility in the adsorbed film on the basis of the PDA shown in Fig. 3a. The solid and broken lines show the $\hat{m}$ versus $\hat{X}_2$ and $\hat{X}_2^{\mathrm{H}}$ curves at a given γ, respectively. Here the composition of OMS in the adsorbed film, $\hat{X}_2^{\mathrm{H}}$, is defined in terms of the surface densities of the species, Γ_i^{H} by

$$\hat{X}_2^{\mathrm{H}} = \Gamma_2^{\mathrm{H}}/(2\Gamma_1^{\mathrm{H}} + \Gamma_2^{\mathrm{H}}) \tag{3}$$

and is evaluated by applying the relation

$$\hat{X}_2^{\mathrm{H}} = \hat{X}_2 - (\hat{X}_1\hat{X}_2/\hat{m})(\partial\hat{m}/\partial\hat{X}_2)_{T,p,\gamma} \tag{4}$$

to the solid lines in Fig. 3a [10, 11, 12]. It should be noted that the PDA has a deformed cigar shape and that the $\hat{m}$ versus $\hat{X}_2^{\mathrm{H}}$ curve deviates negatively from the straight line connecting the $\hat{m}$ values of pure components, $\hat{m}_i^0$, given by

$$\hat{m} = (\hat{m}_2^0 - \hat{m}_1^0)\hat{X}_2^{\mathrm{H}} + \hat{m}_1^0. \tag{5}$$

Since Eq. (5) is the criterion for the ideal mixing of surfactants in the adsorbed film [10, 11, 12], the deviation from the straight line in Fig. 3a proves the nonideal mixing of DTAC and OMS molecules. The excess Gibbs energy of adsorption, $\hat{g}^{\mathrm{H,E}}$, calculated by using the equation [12]

$$\hat{g}^{\mathrm{H,E}} = RT\left[\hat{X}_1^{\mathrm{H}} \ln\left(\hat{m}\hat{X}_1/\hat{m}_1^0\hat{X}_1^{\mathrm{H}}\right) + \hat{X}_2^{\mathrm{H}} \ln\left(\hat{m}\hat{X}_2/\hat{m}_2^0\hat{X}_2^{\mathrm{H}}\right)\right] \tag{6}$$

demonstrates the nonideal mixing quantitatively and is plotted against $\hat{X}_2^{\mathrm{H}}$ at a given γ in Fig. 3b. The $\hat{g}^{\mathrm{H,E}}$ value is negative over the whole composition region and thus suggests stronger mutual interaction between ionic and nonionic surfactants than between the same kinds of surfactants. If this were due to the interaction between cationic surfactant ions and the hydrophilic part of OSM, its magnitude should depend on the degree of neutralization of the surfactant cation (counterion binding). The more negative values of the DTAC system compared to the DTAB system at a given surface tension support our view of this interaction scheme.

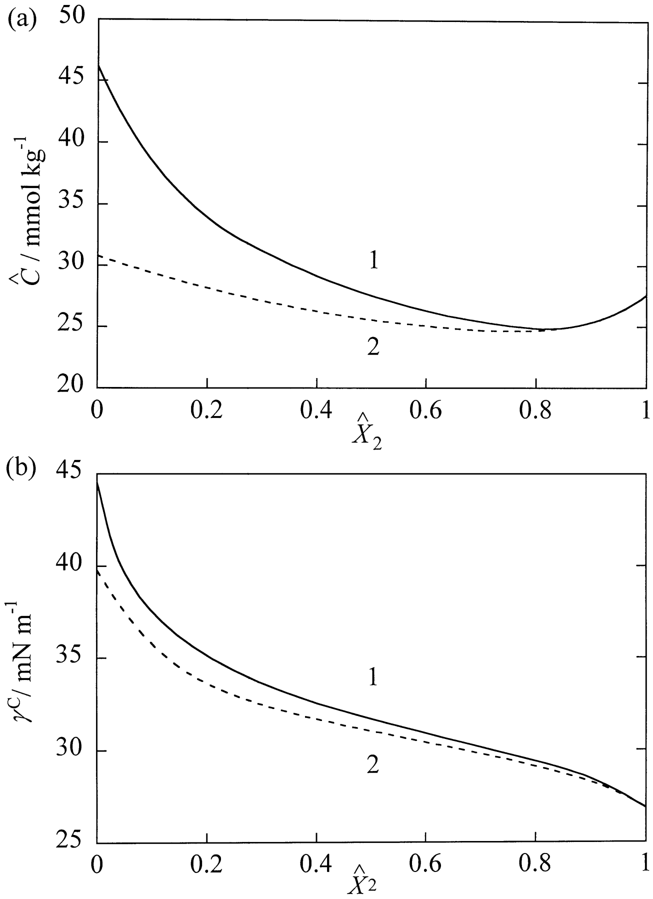

Fig. 2 a Critical micelle concentration (*cmc*), $\hat{C}$, versus $\hat{X}_2$: DTAC–OMS system (1); dodecyltrimethylammonium bromide (DTAB)–OMS system (2). **b** Surface tension, γ^{C}, versus $\hat{X}_2$ at the cmc: DTAC–OMS system (1); DTAB–OMS system (2)

Furthermore it should be noted that the $\hat{g}^{\mathrm{H,E}}$ value increases with rising γ and that the magnitude of the increase is larger for the DTAC system. Then the surface excess area, $\hat{A}^{\mathrm{H,E}}$, evaluated by the equation [19]

$$\hat{A}^{\mathrm{H,E}} = -(1/N_{\mathrm{A}})\left(\partial\hat{g}^{\mathrm{H,E}}/\partial\gamma\right)_{T,p,\hat{X}_2^{\mathrm{H}}} \tag{7}$$

is negative and more negative for the DTAC system as shown in Fig. 4. Taking into account that the mean area per adsorbed molecule of DTAC and that of OMS are respectively 0.60 and 0.33 nm^2 at the cmc, the mixing of DTAC and OMS molecules in the adsorbed film is accompanied by a decrease of several percent in the occupied area. Thus it is said that the effective filling of OMS molecules into the available space among the hydrocarbon chains of DTAC enhances the surfactant cation–dipole interaction between the polar head

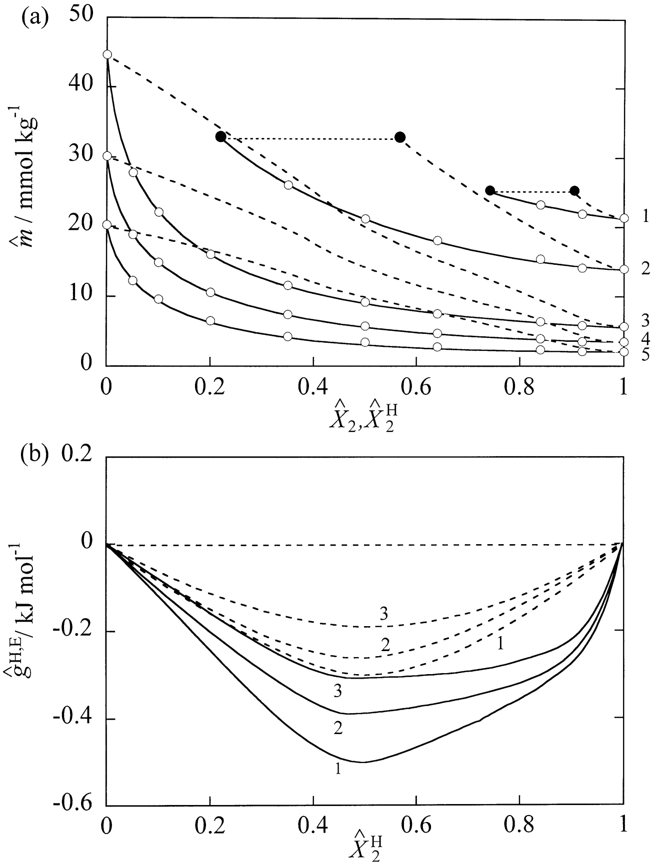

Fig. 3 **a** Total molality versus composition at fixed surface tension: γ/mN m^{-1} = 30 (1), 35 (2), 45 (3), 50 (4), 55 (5). $\hat{m}$ versus $\hat{X}_2$ (–); $\hat{m}$ versus $\hat{X}_2^{\rm H}$ (- – -). **b** Excess Gibbs energy in the adsorbed film versus composition at constant surface tension: γ/mN m^{-1} = 45 (1), 50 (2), 55 (3). DTAC–OMS system (–); DTAB–OMS system (– –)

groups. The smaller decrease in the DTAB system shows the less strong surfactant cation–nonionic surfactant interaction and again this justifies our view of the interaction scheme.

Next, let us inspect whether the miscibility of the surfactants in the micelle also supports our view of the interaction scheme. The composition in the micelle, $\hat{X}_2^{\rm M}$, calculated by applying the following equation [11]

$$\hat{X}_2^{\rm M} = \hat{X}_2 - \left(\hat{X}_1\hat{X}_2/\hat{C}\right)\left(\partial\hat{C}/\partial\hat{X}_2\right)_{T,p} \qquad (8)$$

to the $\hat{C}$ versus $\hat{X}_2$ curve in Fig. 2a is shown in the form of the PDM in Fig. 5. The PDM has an azeotropic point at $\hat{X}_2 \approx 0.8$ and then suggests that the mutual interaction between DTAC and OMS molecules is stronger than that between the same species. To demonstrate the difference in nonideal mixing in micelles between the DTAC and DTAB systems, the excess Gibbs energy of the micelle formation, $\hat{g}^{\rm M,E}$, was calculated by the following equation [12]

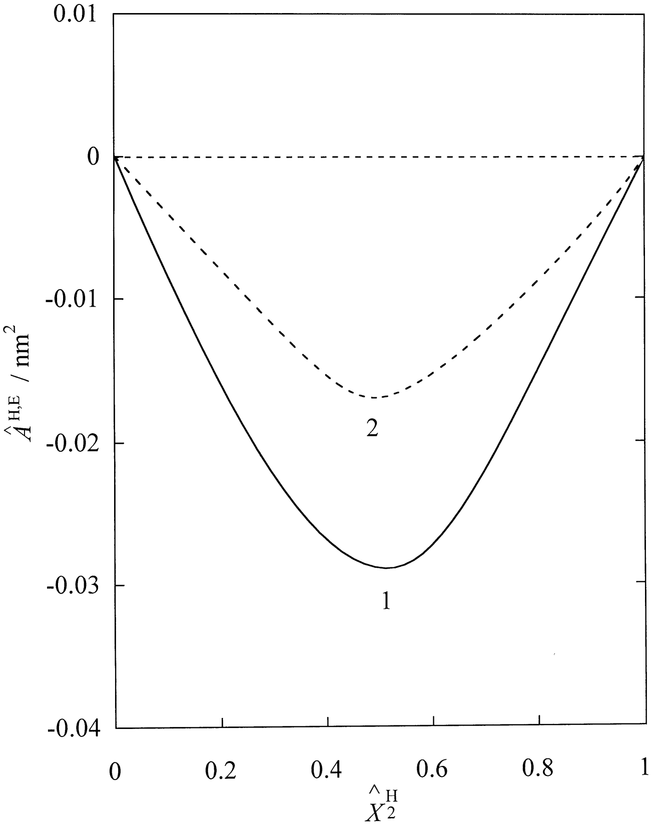

Fig. 4 Excess area versus composition at 50 mN m^{-1}: DTAC–OMS system (1); DTAB–OMS system (2)

$$\hat{g}^{\rm M,E} = RT\left[\hat{X}_1^{\rm M}\ln\left(\hat{C}\hat{X}_1/\hat{C}_1^0\hat{X}_1^{\rm M}\right) + \hat{X}_2^{\rm M}\ln\left(\hat{C}\hat{X}_2/\hat{C}_2^0\hat{X}_2^{\rm M}\right)\right], \qquad (9)$$

where $\hat{C}_i^0$ is the cmc value of pure component i. The calculated $\hat{g}^{\rm M,E}$ value is plotted against $\hat{X}_2^{\rm M}$ (curves 1) in Fig. 6. It should be noted that the effect of counterions on the molecular interaction in micelles is exhibited very distinctly and that the DTAC system has more negative $\hat{g}^{\rm M,E}$ values than the DTAB system. Taking note that the degree of counterion binding at the micelle surface is considered to be larger for the bromide ion than for the chloride ion and providing that our view of the interaction scheme is correct, the interaction between polar head groups of the DTA$^+$ ion and the OMS molecule should be enhanced and thus $\hat{g}^{\rm M,E}$ is expected to be more negative in the DTAC system compared to that in the DTAB one. The results in Fig. 6 again substantiate our idea that the strong mutual interaction is due to the direct interaction between the hydrophilic part of the nonionic surfactant and the cationic surfactant ion.

If surfactant cations and nonionic surfactants interact with each other according to the proposed scheme, the magnitude of the interaction is affected by the geometry

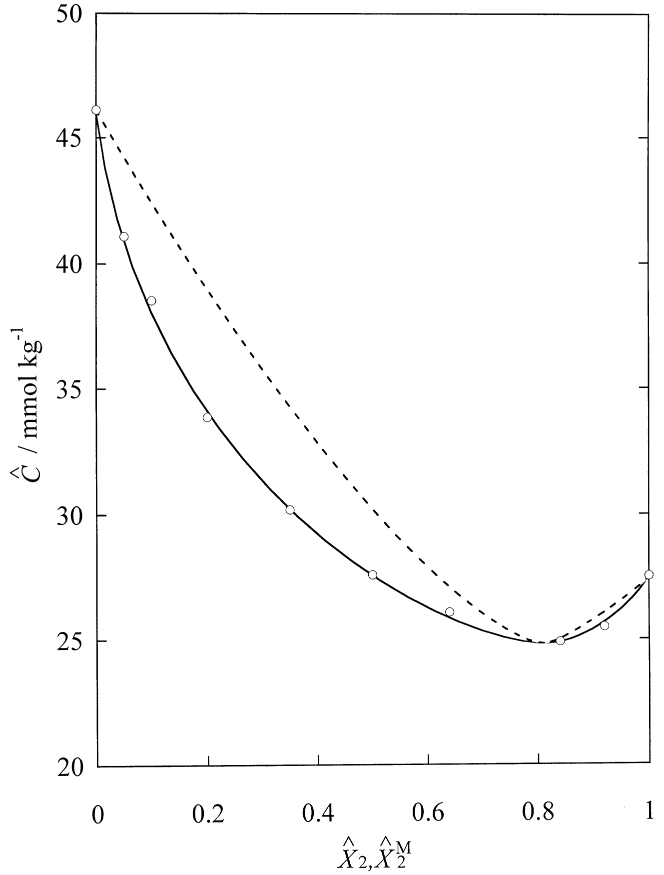

Fig. 5 cmc versus composition: $\hat{C}$ versus $\hat{X}_2$ (–); $\hat{C}$ versus $\hat{X}_2^M$ (– –)

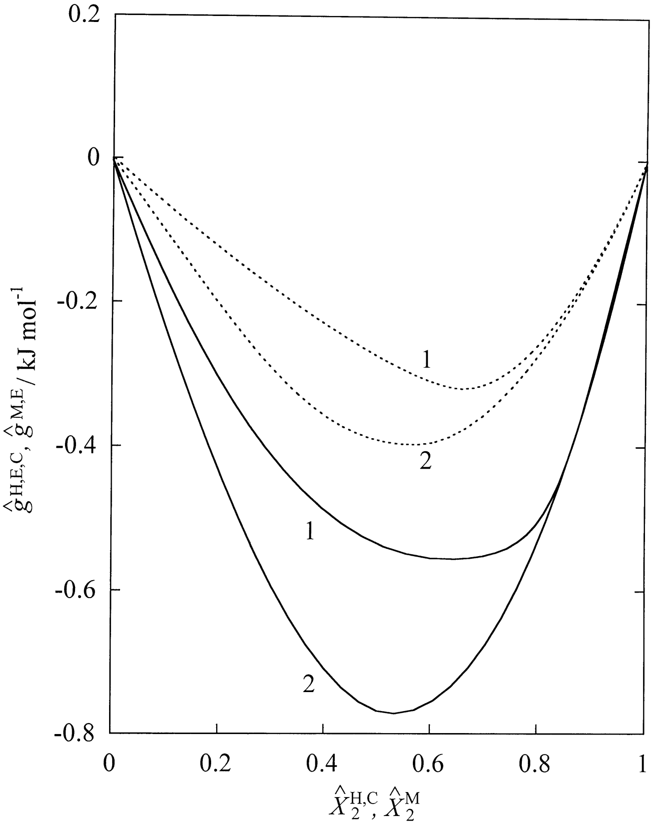

Fig. 6 Excess Gibbs energy versus composition: $\hat{g}^{M,E}$ versus $\hat{X}_2^M$; $\hat{g}^{H,E,C}$ versus $\hat{X}_2^{H,C}$. DTAC–OMS system (–); DTAB–OMS system (– –)

where the interaction takes place. Therefore it is useful to examine whether a difference in the excess Gibbs free energy exists between the micelle (curved interface) and the adsorbed film (flat interface) when they have the same composition of surfactants. In Fig. 6, the excess Gibbs energy of adsorption at the cmc, $\hat{g}^{H,E,C}$ versus $\hat{X}_2^{H,C}$ curves, are compared with the $\hat{g}^{M,E}$ versus $\hat{X}_2^M$ curves. It is clear that the $\hat{g}^{H,E,C}$ value is more negative than the $\hat{g}^{M,E}$ one at a given composition for both systems. Therefore it is said that the molecular interaction between the different species is more strengthened in the adsorbed film than in the micelle. Taking account of the negative value of $\hat{A}^{H,E}$ given in Fig. 4, the difference is due to the more effective packing of OMS and cationic surfactant molecules for the ion–dipole interaction in the adsorbed film than in the micelle; OMS molecules may use the space among the hydrocarbon chains of cationic surfactant ions more effectively in the planar adsorbed film than in the spherical micelle [16]. It is noted that there is a significant difference between $\hat{g}^{H,E,C}$ and $\hat{g}^{M,E}$ even when the adsorbed film and micelle are mostly constructed of DTA$^+$ ions, while there is no appreciable difference when they mostly consist of OMS molecules. This means that the geometrical advantage of the planer adsorbed film against the spherical micelle is realized even when a smaller amount of OMS can accommodate effectively in the space among the hydrocarbon chains of DTA$^+$ ions, while it is not realized when smaller numbers of DTA$^+$ ions are present in the fields of OMS molecules. This is consistent with our view of the interaction scheme.

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