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ORIGINAL CONTRIBUTION

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Interfacial and aggregation properties of some anionic/cationic surfactant binary systems II. Mixed micelle formation and surface tension reduction effectiveness

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Abstract Mixed micelle formation and surface tension reduction effectiveness (γ_{cmc}) were investigated for the following systems: triethanolammonium dodecylpoly(oxyethylene)sulfate (TADPS, containing about two ethylene oxide units)/dodecyltrimethylammonium bromide, TADPS/hexadecyltrimethylammonium bromide and TADPS/hexadecylpyridinium chloride. For all these anionic/cationic systems, the mixed critical micelle concentration (cmc) values reflect a strong synergism in mixed micelle formation, with β^{M} values ranging from −13.8 to −18.3. The mixed micelle composition is mixing-ratio dependent and, for equimolar mixtures, the mixed micelle is richer in the surfactant with the lower cmc. Precipitation is inhibited to a certain extent, thanks to the presence of ethylene oxide groups in the anionic species. The conditions for synergism in γ_{cmc}, differently expressed in the literature, can be derived from the surface tension equations established in our previous article. They can be conveniently described by a few characteristic constants: Γ_i^{∞} (saturated Gibbs excess), K_i (constant in the Szyszkowski equation), the cmc of the individual surfactants and the interaction parameters, β^{S} and β^{M}, of their mixtures. Excellent agreement between theoretically predicted and experimental results is obtained. With the increase in surfactant chain length, the β^{M} values decrease faster than the β^{S} ones and this can result in the loss of synergism in γ_{cmc}.

Key words Anionic/cationic surfactants · Surface tension reduction effectiveness · Critical micelle concentration · Mixed micelle composition · β^{M} interaction parameter

Introduction

Although anionic/cationic surfactant systems show very strong synergisms in surface tension reduction efficiency and mixed micelle formation [1–13], the practical applications of such systems, limited by the precipitation of a complex or by liquid–liquid phase separation [10–17], are not so popular as those of ionic/nonionic ones. Recent research advances [12, 18, 19], however, have shown a way to make anionic/cationic systems practically applicable: introducing nonionic hydrophilic groups, namely ethylene oxide units, into the ionic surfactant molecule and choosing a bulky hydrophilic counterion result in enhanced excluded-volume constraints and increase the solubility of the anionic/cationic complex.

In most surfactant applications, the lowest possible surface tension is expected. The surface tension value at the critical micelle concentration (cmc) (γ_{cmc}) is generally taken as the minimum value obtainable for a given surfactant system under fixed conditions and is called surface tension reduction effectiveness [4, 9, 20–22]. Although very low γ_{cmc} values can be reached for some appropriately chosen anionic/cationic binary systems, all those systems do not show a synergism in surface tension reduction effectiveness [9]. The conditions for such a synergism are therefore greatly significant. Rosen and coworkers [4, 9, 20–22] have derived the conditions for a synergetic effect in surface tension reduction effectiveness using different methods and these conditions were differently expressed [9, 20, 21]. The relations between these expressions, however, did not seem to be fully interpreted. In a previous article [23], the surface tension equations for nonideal binary surfactant mixtures were established. In the present work we try to use these equations to discuss further the conditions for synergism in surface tension reduction effectiveness and to show the relations between the various expressions derived by Rosen and coworkers. Three anionic/cationic binary systems were studied: triethanolammonium dodecylpoly(oxyethylene)sulfate (TADPS, containing about two ethylene oxide units) mixed with dodecyltrimethylammonium bromide (DTABr), hexadecyltrimethylammonium bromide (CTABr) or hexadecylpyridinium chloride (CPCl).

Theory

Necessary and sufficient conditions for synergism in surface tension reduction effectiveness

The surface tension of a nonideal binary surfactant solution below the mixed cmc can be calculated using the following equations [23]:

$$\gamma_0 - \gamma_{12} = n_1 RT\Gamma_1^\infty \ln\left(1 + \frac{K_1 \alpha c_{12}}{f_1^{\mathrm{s}} x_1^{\mathrm{s}}}\right) , \tag{1}$$

$$\gamma_0 - \gamma_{12} = n_2 RT\Gamma_2^\infty \ln\left(1 + \frac{K_2(1-\alpha)c_{12}}{f_2^{\mathrm{s}}\left(1 - x_1^{\mathrm{s}}\right)}\right) , \tag{2}$$

where α is the mole fraction of surfactant 1 with respect to the total amount of surfactant, γ_{o} the surface tension of the solvent, γ_{12} that of a solution of surfactants 1 and 2 with bulk composition α at a total concentration c_{12}, Γ_i^∞ the saturated excess surface concentration of pure surfactant i (for ionic surfactants, only surface-active ions are considered), x_1^{S}, f_1^{S} and f_2^{S} the surfactant mole fraction and activity coefficients in the mixed monolayer, K_i the constants in the Szyszkowski equation [24], n_i the number of particles per molecule of surfactant, whose concentration changes with surfactant concentration, R the gas constant and T the absolute temperature.

For pure surfactant solutions, Eqs. (1) and (2) reduce to the Szyszkowski equation [24]:

$$\gamma_{\mathrm{o}} - \gamma_i = n_i RT\Gamma_i^\infty \ln\left(1 + K_i c_i^0\right), \tag{3}$$

where γ_{i} is the surface tension of a solution of pure surfactant i at the concentration c_i^0 (the superscript 0 represents pure surfactant). For pure and binary solutions at their cmcs, c_i^{M} and c_{12}^{M}, respectively, the corresponding surface tensions, $\gamma_{\mathrm{cmc}i}^0$ and γ_{cmc12}, can therefore be calculated as follows:

$$\gamma_{\mathrm{cmc1}}^0 = \gamma_{\mathrm{o}} - n_1 RT\Gamma_1^\infty \ln\left(1 + K_1 c_1^{\mathrm{M}}\right), \tag{4}$$

$$\gamma_{\mathrm{cmc2}}^0 = \gamma_{\mathrm{o}} - n_2 RT\Gamma_2^\infty \ln\left(1 + K_2 c_2^{\mathrm{M}}\right), \tag{5}$$

$$\gamma_{\mathrm{cmc12}} = \gamma_0 - n_1 RT\Gamma_1^\infty \ln\left(1 + \frac{K_1 \alpha c_{12}^{\mathrm{M}}}{f_{1,c}^{\mathrm{s}} x_{1,c}^{\mathrm{s}}}\right), \tag{6}$$

$$\gamma_{\mathrm{cmc12}} = \gamma_0 - n_2 RT\ \Gamma_2^\infty \ln\left(1 + \frac{K_2(1-\alpha)c_{12}^{\mathrm{M}}}{\mathrm{f}_{2,c}^{\mathrm{s}}\left(1 - x_{1,c}^{\mathrm{s}}\right)}\right), \tag{7}$$

where the subscript c refers to the cmc.

Now, if surfactant 1 micellizes at a lower concentration, the condition for synergism in γ_{cmc} is that the surface tension at the cmc of the mixture is lower than γ_{cmc1}^0 ($\gamma_{\mathrm{cmc12}} < \gamma_{\mathrm{cmc1}}^0$). From Eqs. (4) and (6) and Rubingh's treatment [1] of nonideal mixed micelles based on the regular solution theory, the following expression is obtained:

$$f_{1,c}^{\mathrm{s}} x_{1,c}^{\mathrm{s}} < f_1^{\mathrm{M}} x_1^{\mathrm{M}} \quad \left(\gamma_{\mathrm{cmc1}}^0 < \gamma_{\mathrm{cmc2}}^0\right), \tag{8}$$

where $x_1{}^{\mathrm{M}}$ is the mole fraction of surfactant 1 in the mixed micelle at the cmc of the mixture and f_1^{M} is the corresponding activity coefficient. Equation (8) was first derived by Hua and Rosen [20] by means of the Butler equation [25] and is taken as the condition for the synergism in surface tension reduction effectiveness.

At or near cmcs ($K_i c_i^{\mathrm{M}} >> 1, K_1 \alpha c_{12}^{\mathrm{M}} / f_{1,c}^{\mathrm{s}} x_{1,c}^{\mathrm{s}}$, $c^{\mathrm{S}} >> 1$ and $K_2(1-\alpha)c_{12}^{M} / f_{2,c}^{\mathrm{s}}(1 - x_{1,c}^{\mathrm{s}}) >> 1$), Eqs. (4), (5), (6), (7) and (8) can be simplified as

$$\gamma_{\mathrm{cmc1}}^0 \sim \gamma_{\mathrm{o}} - n_1 RT\Gamma_1^\infty \ln\left(K_1 c_1^{\mathrm{M}}\right), \tag{9}$$

$$\gamma_{\mathrm{cmc2}}^0 \sim \gamma_{\mathrm{o}} - n_2 RT\Gamma_2^\infty \ln\left(K_2 c_2^{\mathrm{M}}\right), \tag{10}$$

$$\gamma_{\mathrm{cmc12}} \sim \gamma_0 - n_1 RT\ \Gamma_1^\infty \ln\left(\frac{K_1 \alpha c_{12}^{\mathrm{M}}}{f_{1,c}^{\mathrm{s}} x_{1,c}^{\mathrm{s}}}\right), \tag{11}$$

$$\gamma_{\mathrm{cmc12}} \sim \gamma_0 - n_2 RT\ \Gamma_2^\infty \ln\left(\frac{K_2(1-\alpha)c_{12}^{\mathrm{M}}}{f_{2,c}^{\mathrm{s}}\left(1 - x_{1,c}^{\mathrm{s}}\right)}\right). \tag{12}$$

By omitting the subscript c and noticing that [20]

$$f_1^{\mathrm{s}} = \exp \beta^{\mathrm{s}}\left(1 - x_1^{\mathrm{s}}\right)^2 \tag{13}$$

Eq. (11) can be rewritten as

$$\gamma_{\mathrm{cmc12}} \sim n_1 RT\Gamma_1^{\infty}\left[\ln x_1^{\mathrm{s}} + \beta^{\mathrm{s}}\left(1 - x_1^{\mathrm{s}}\right)^2 - \ln\alpha - \ln c_{12}^{\mathrm{M}}\right] + \left(\gamma_0 - n_1 RT\Gamma_1^{\infty}\ln K_1\right). \tag{14}$$

In the case of synergism, there will be a minimum in the γ_{cmc12} versus α curve, i.e.

$$\frac{\mathrm{d}(\gamma_{\mathrm{cmc12}})}{\mathrm{d}\alpha} = n_1 RT\Gamma_1^{\infty}\left(\frac{1}{x_1^{\mathrm{s}}}\frac{\mathrm{d}x_1^{\mathrm{s}}}{\mathrm{d}\alpha} - 2\beta^{\mathrm{s}}\left(1 - x_1^{\mathrm{s}}\right)\frac{\mathrm{d}x_1^{\mathrm{s}}}{\mathrm{d}\alpha} - \frac{1}{\alpha} - \frac{\mathrm{d}\ln c_{12}^{\mathrm{M}}}{\mathrm{d}\alpha}\right) = 0 \tag{15}$$

or

$$\frac{\mathrm{d}\ln c_{12}^{\mathrm{M}}}{\mathrm{d}\alpha} = \left(\frac{1}{x_1^{\mathrm{s}}} - 2\beta^{\mathrm{s}}\left(1 - x_1^{\mathrm{s}}\right)\right)\frac{\mathrm{d}x_1^{\mathrm{s}}}{\mathrm{d}\alpha} - \frac{1}{\alpha} \tag{16}$$

and similarly from Eq. (12):

$$\frac{\mathrm{d}\ln c_{12}^{\mathrm{M}}}{\mathrm{d}\alpha} = \left(\frac{1}{1 - x_1^{\mathrm{s}}} - 2\beta^{\mathrm{s}}x_1^{\mathrm{s}}\right)\frac{\mathrm{d}x_1^{\mathrm{s}}}{\mathrm{d}\alpha} - \frac{1}{1 - \alpha}. \tag{17}$$

Zhu and Rosen [9] have also obtained Eqs. (16) and (17) from hypothetical surface tension equations and, according to their derivation, these two equations yield

$$x_1^{*\mathrm{S}} = x_1^{*\mathrm{M}}, \tag{18}$$

where the superscript * refers to the minimum of the γ_{cmc12} versus α curve. This means that, at this minimum, both mixed monolayer and mixed micelle have the same composition. Subtracting Eq. (11) from Eq. (9), Eq. (12) from Eq. (10), introducing Rubingh's treatment [1] and taking Eq. (18) into account lead to the general equation

$$\gamma_{\mathrm{cmc}i}^0 - \gamma_{\mathrm{cmc12}}^* = n_i RT\ \Gamma_i^{\infty}\ln\left(\frac{f_i^{*\mathrm{M}}}{f_i^{*\mathrm{S}}}\right). \tag{19}$$

Introducing the interaction parameters β^{S} [9, 20] and β^{M} [1] into Eq. (19) yields

$$\gamma_{\mathrm{cmc1}}^0 - \gamma_{\mathrm{cmc12}}^* = n_1 RT\ \Gamma_1^{\infty}\ln\left(\beta^{\mathrm{M}} - \beta^{\mathrm{S}}\right)\left(1 - x_1^{*\mathrm{M}}\right)^2, \tag{20}$$

$$\gamma_{\mathrm{cmc2}}^0 - \gamma_{\mathrm{cmc12}}^* = n_2 RT\ \Gamma_2^{\infty}\left(\beta^{\mathrm{M}} - \beta^{\mathrm{S}}\right)\left(x_1^{*\mathrm{M}}\right)^2. \tag{21}$$

For synergism in surface tension reduction effectiveness to occur, the differences in the right sides of Eqs. (20) and (21) should be positive. Now, since $n_i\mathrm{RT}\Gamma_i^{\infty}$ and the square terms are positive, the necessary condition for synergism is

$$\beta^{\mathrm{M}} - \beta^{\mathrm{S}} > 0. \tag{22}$$

If γ_{cmc1}^0 is lower than γ_{cmc2}^0, the sufficient condition for synergism is $\gamma_{\mathrm{cmc12}}^*$ lower than γ_{cmc1}^0. Rewriting Eq. (21)

$$\gamma_{\mathrm{cmc12}}^* = \gamma_{\mathrm{cmc2}}^0 - n_2 RT\ \Gamma_2^{\infty}\left(\beta^{\mathrm{M}} - \beta^{\mathrm{S}}\right)\left(x_1^{*\mathrm{M}}\right)^2 \tag{23}$$

and combining Eqs. (20) and (23) yield the sufficient condition for synergism,

$$\gamma_{\mathrm{cmc1}}^0 - \gamma_{\mathrm{cmc2}}^0 + n_2 RT\ \Gamma_2^{\infty}\left(\beta^{\mathrm{M}} - \beta^{\mathrm{S}}\right)\left(x_1^{*\mathrm{M}}\right)^2 > 0, \tag{24}$$

which, since $(x_1^{*\mathrm{M}})^2$ is smaller than 1, reduces to

$$\beta^{\mathrm{S}} - \beta^{\mathrm{M}} < \frac{\gamma_{\mathrm{cmc1}}^0 - \gamma_{\mathrm{cmc2}}^0}{n_2 RT\ \Gamma_2^{\infty}}. \tag{25}$$

Similarly, if γ_{cmc2}^0 is lower than γ_{cmc1}^0, the condition is

$$\beta^{\mathrm{S}} - \beta^{\mathrm{M}} < \frac{\gamma_{\mathrm{cmc2}}^0 - \gamma_{\mathrm{cmc1}}^0}{n_1 RT\ \Gamma_1^{\infty}}. \tag{26}$$

Therefore, the necessary and sufficient conditions for synergism in γ_{cmc} can be summarized as

$$\beta^{\mathrm{S}} - \beta^{\mathrm{M}} < 0,$$

$$\left|\beta^{\mathrm{S}} - \beta^{\mathrm{M}}\right| < \frac{\left|\gamma_{\mathrm{cmc2}}^0 - \gamma_{\mathrm{cmc1}}^0\right|}{n_i RT\ \Gamma_i^{\infty}}, \tag{27}$$

where the subscript i refers to the surfactant with the higher γ_{cmc}^0. Noticing that $n_{\mathrm{i}}RT\Gamma_i^{\infty}$ is approximately the slope of the γ–log$c$ curve for pure surfactant i at or near its cmc, the above conditions are the same as those derived by Zhu and Rosen [9]. Assuming that the individual surfactant concentration required to produce a surface tension $\gamma_{\mathrm{cmc12}}^*$ is $c_i^{0,\mathrm{cmc}}$, it comes from Eq. (9) or (10)

$$\gamma_{\mathrm{cmc}i}^0 - \gamma_{\mathrm{cmc12}}^0 = n_i RT\ \Gamma_i^{\infty}\ln\left(\frac{c_i^{0,\mathrm{cmc}}}{c_i^{\mathrm{M}}}\right). \tag{28}$$

Combining Eq. (28) with Eqs. (20) or (21) leads to

$$\ln\left(\frac{c_i^{0,\mathrm{cmc}}}{c_i^{\mathrm{M}}}\right) = \left(\beta^{\mathrm{M}} - \beta^{\mathrm{S}}\right)\left(x_j^{*\mathrm{M}}\right)^2 \qquad i,j = 1,2 \tag{29}$$

and to

$$\ln\left(\frac{c_1^{0,\mathrm{cmc}}c_2^{\mathrm{M}}}{c_1^{\mathrm{M}}c_2^{0,\mathrm{cmc}}}\right) = \left(\beta^{\mathrm{S}} - \beta^{\mathrm{M}}\right)\left(2x_1^{*\mathrm{M}} - 1\right). \tag{30}$$

This is the equation derived by Hua and Rosen [21]. Accordingly, the sufficient condition for synergism is

$$\left|\beta^{\mathrm{S}} - \beta^{\mathrm{M}}\right| > \left|\ln\left(\frac{c_1^{0,\mathrm{cmc}}c_2^{\mathrm{M}}}{c_2^{0,\mathrm{cmc}}c_1^{\mathrm{M}}}\right)\right|. \tag{31}$$

Thus, by using the surface tension equations for binary surfactant systems [23], the necessary and sufficient conditions for synergism in surface tension reduction effectiveness are obtained and shown to be strictly equivalent to those of Rosen and coworkers, although derived independently. A conclusion about synergism in γ_{cmc} for anionic/cationic binary mixtures can be drawn from the knowledge of the cmc, $c_{\mathrm{i}}^{\mathrm{M}}$, excess surface concentrations at saturation, Γ_i^{∞}, constants in the

Szyszkowski equation, K_i, of pure surfactants, as well of that of their interaction parameters, β^{S} and β^{M}.

Compositions of bulk solution, mixed monolayer and mixed micelle at the lowest surface tension value, γ_{cmc12}

The combination of Eqs. (20) and (21) to eliminate $\gamma^*_{\mathrm{cmc12}}$ gives

$$\frac{\gamma^0_{\mathrm{cmc1}} - n_1RT\,\Gamma_1^\infty\left(\beta^{\mathrm{M}} - \beta^{\mathrm{S}}\right)\left(1 - x_1^{*\mathrm{M}}\right)^2}{\gamma^0_{\mathrm{cmc2}} - n_2RT\,\Gamma_2^\infty\left(\beta^{\mathrm{M}} - \beta^{\mathrm{S}}\right)\left(x_1^{*\mathrm{M}}\right)^2} = 1. \tag{32}$$

From Eq. (32), $x_1^{*\mathrm{M}}$ (the mole fraction of surfactant 1 both in mixed monolayer and mixed micelle necessary to produce $\gamma^*_{\mathrm{cmc12}}$) can be obtained: $\gamma^*_{\mathrm{cmc12}}$ can then be calculated from Eq. (20) or Eq. (21). According to the nonideal micellization theory [1], α and x_1^{M} are related by

$$\alpha = \frac{\frac{\left(x_1^{\mathrm{M}}c_1^{\mathrm{M}}\right)}{\left[\left(1-x_1^{\mathrm{M}}\right)c_2^{\mathrm{M}}\right]}\exp\left[\beta^{\mathrm{M}}\left(1-2x_1^{\mathrm{M}}\right)\right]}{1 + \frac{\left(x_1^{\mathrm{M}}c_1^{\mathrm{M}}\right)}{\left[\left(1-x_1^{\mathrm{M}}\right)c_2^{\mathrm{M}}\right]}\exp\left[\beta^{\mathrm{M}}\left(1-2x_1^{\mathrm{M}}\right)\right]} \tag{33}$$

and, accordingly,

$$\alpha^* = \frac{\frac{\left(x_1^{*\mathrm{M}}c_1^{\mathrm{M}}\right)}{\left[\left(1-x_1^{*\mathrm{M}}\right)c_2^{\mathrm{M}}\right]}\exp\left[\beta^{\mathrm{M}}\left(1-2x_1^{*\mathrm{M}}\right)\right]}{1 + \frac{\left(x_1^{*\mathrm{M}}c_1^{\mathrm{M}}\right)}{\left[\left(1-x_1^{*\mathrm{M}}\right)c_2^{\mathrm{M}}\right]}\exp\left[\beta^{\mathrm{M}}\left(1-2x_1^{*\mathrm{M}}\right)\right]}. \tag{34}$$

For common-type anionic and cationic surfactants having similar Γ_i^∞ and $\gamma^0_{\mathrm{cmc}i}$ values (e.g. species with the same hydrocarbon chain length), $x_1^{*\mathrm{M}}$ approaches 0.5. Even if Γ_i^∞ and $\gamma^0_{\mathrm{cmc}i}$ are not strictly equal, $x_1^{*\mathrm{M}}$ will not greatly deviate from 0.5. This means that, for anionic/cationic systems at their lowest surface tension, both mixed monolayer and mixed micelle show symmetrical compositions, which has often been observed [9]. In this case, Eq. (34) reduces to

$$\alpha^* = \frac{c_1^{\mathrm{M}}}{c_1^{\mathrm{M}} + c_2^{\mathrm{M}}}. \tag{35}$$

When the surfactants have similar cmc values, α^* also approaches 0.5. On the other hand, however, when the surfactants have quite different cmc, α^* will approach extreme values, 0 or 1, for $c_1^{\mathrm{M}} << c_2^{\mathrm{M}}$ or $c_2^{\mathrm{M}} << c_1^{\mathrm{M}}$, respectively. This helps in selecting α to get the lowest γ_{cmc}. For example, if an anionic surfactant is mixed with a cationic one having a much higher cmc, the lowest γ_{cmc} will be obtained by adding a little anionic surfactant to a larger amount of the cationic one.

Experimental

TADPS, containing about two ethylene oxide units, was a liquid sample kindly provided by SEPPIC (commercial name Montelane LT4088, about 30% active matter) [23]. TADPS, DTABr and CTABr, from Aldrich, and CPCl, from Lancaster, were used as received since only a shallow minimum (~1 mN/m) was observed in the surface tension curve of TADPS (Fig. 1). Active matter percentages, from two-phase titration experiments against Hyamine 1622 or dodium dodecyl sulfate with the mixed indicator [26], are shown in Table 1.

The cmc values were determined by surface tension measurements (Du Noüy ring technique, LAUDA TD1 tensiometer, 25° ± 0.2 °C). Doubly distilled water was used throughout (γ = 72.3 mN/m at 25° ± 0.2 °C).

The precipitation region or turbid phase boundary was determined by visual inspection and optical density measurements at a wavelength of 300 nm (Hitachi U-2000 UV spectrophotometer) after the solutions were prepared and kept at 25 °C ± 0.2 °C for at least 4 days. In those conditions, light absorption by pure surfactant solutions is almost zero, whereas the apparent absorbance (actually due to light reflection and scattering) of visually turbid surfactant mixtures is large enough.

Results and discussion

Mixed cmc and mixed micelle composition

The surface tension versus log(concentration) curves for the TADPS/DTABr, TADPS/CTABr and TADPS/CPCl systems at 25 °C are shown in Figs. 1, 2 and 3.

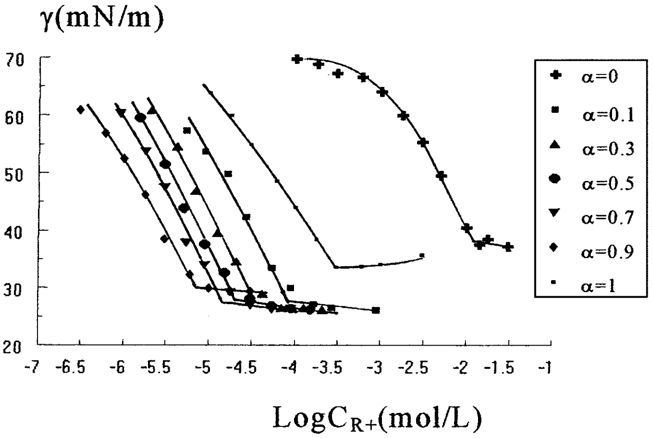

Fig. 1 Surface tensions of the triethanolammonium dodecylpoly(oxyethylene)sulfate (*TADPS*)/dodecyltrimethylammonium bromide (*DTABr*) system at 25 °C (for $\alpha = 1$, $c = c_{\mathrm{R-}}$)

Table 1 Active matter percentages of the surfactants triethanolammonium dodecylpoly(oxyethylene)sulfate (*TADPS*), dodecyltrimethylammonium bromide (*DTABr*), hexadecyltrimethylammonium bromide (*CTABr*) and hexadecylpyridinium chloride (CPCl)

Surfactant	TADPS	DTABr	CTABr	CPCl
Active matter (%)	31.6[a]	99.4	99.8	99.8

[a] Calculated on the basis of three ethylene oxide units per molecule and a measured concentration of 5.77 × 10^{-4} mol/g

The measured cmc of pure surfactants at 25 °C are 3.2×10^{-4} (TADPS), 1.4×10^{-2} (DTABr), 9.0×10^{-4} (CTABr) and 9.2×10^{-4} mol/l(CPCl). These values are in good agreement with published data [27, 28]. The experimental values of the mixed cmc are illustrated in Fig. 4, together with the curves predicted by Rubingh's nonideal theory [1] with average β^M values. The mixed micelle compositions at the cmc, calculated from β^M, are shown in Fig. 5.

As for other anionic/cationic pairs [4, 9], the systems studied show strong departure from ideality in mixed micelle formation. The β^M values found at various α for the systems studied are reported in Tables 2, 3 and 4. Figure 4 shows that the mixed cmc can be well predicted by Rubingh's theory with an average β^M value in the whole composition range: −13.8 ± 0.3, −15.7 ± 1.5 and −18.3 ± 1.4 for the TADPS (surfactant 1)/DTABr, TADPS/CTABr and TADPS/CPCl systems, respectively. They are of the same order of magnitude as the β^S values for the same systems [23] but show a larger effect of the alkyl group chain length. Furthermore, β^M (but not β^S) values reflect a stronger interaction of TADPS with CPCl than with CTABr (Tables 2, 3, 4). For TADPS/DTABr (C_{12-}/C_{12+}) systems, the mixed cmc can be accounted for by a single β^M value for the whole

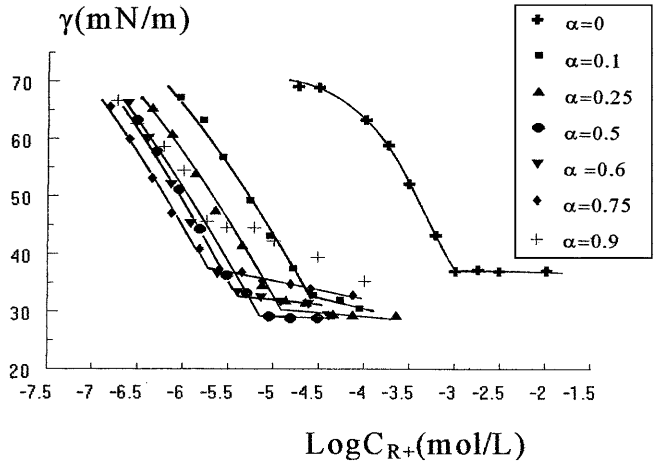

Fig. 2 Surface tensions of the TADPS/hexadecyltrimethylammonium bromide (*CTABr*) system at 25 °C

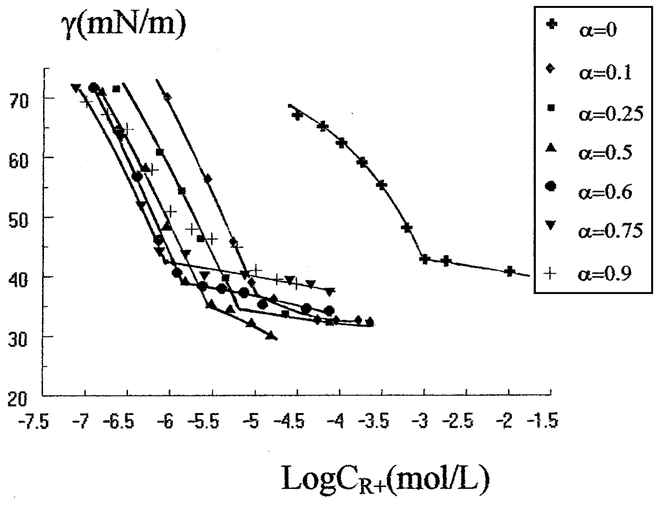

Fig. 3 Surface tensions of the TADPS/hexadecylpyridinium chloride(CPCl) system at 25 °C

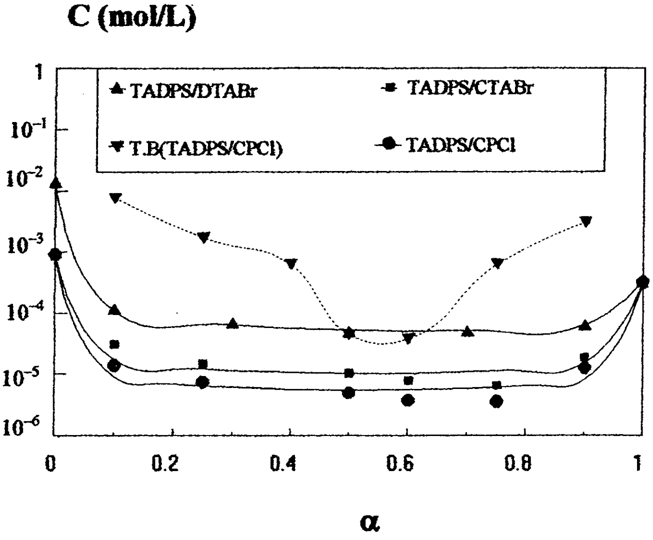

Fig. 4 Mixed critical micelle concentration (cmc) of the systems studied. *Symbols*: experimental results; *solid lines*: mixed cmc calculated from average β^M values (TADPS/DTABr: −13.8; TADPS/CTABr: −15.7; TADPS/CPCl: −18.2); *dashed line*: turbid boundary (TADPS/CPCl system)

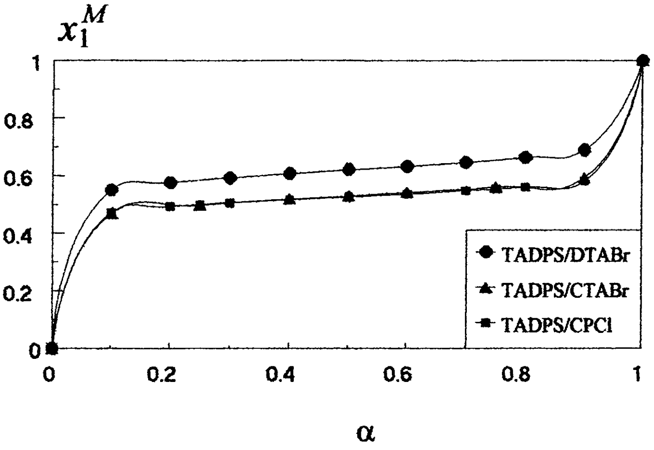

Fig. 5 Calculated composition of mixed micelles at mixed cmc based on average β^M values (see Fig. 4); 25 °C

Table 2 Synergism in surface tension reduction effectiveness for the TADPS/DTABr system (γ in mN/m, $c_i^{0,\mathrm{cmc}}$ in mmol/l)

α	0.1	0.3	0.5	0.7	0.9
$f^S_{1,c}x^S_{1,c}$	0.02382	0.03867	0.05105	0.07143	0.1531
$f^M_1 x^M_1$	0.03532	0.06417	0.07799	0.1092	0.1755
β^S	−15.9	−16.3	−16.5	−16.4	−15.1
β^M	−13.5	−13.5	−14.1	−14.0	−13.8
$\gamma_{\mathrm{cmc}12}$	27.1	26.5	27.0	27.7	29.5
$c_1^{0,\mathrm{cmc}}$	0.516	0.546	0.521	0.489	0.413
$c_2^{0,\mathrm{cmc}}$	23.2	24.1	23.2	22.3	20.0
$\ln\left(\frac{c_1^{0,\mathrm{cmc}}c_2^M}{c_2^{0,\mathrm{cmc}}c_1^M}\right)$	−0.0273	−0.00886	−0.0177	−0.0415	−0.1015
Synergism	Eq. (8): yes; Eqs. (22) and (27): yes; Eqs. (22) and (31): yes; experimental results: yes				

Table 3 Synergism in surface tension reduction effectiveness for the TADPS/CTABr system (γ in mN/m, $c_i^{0,\mathrm{cmc}}$ in mmol/l)

α	0.1	0.25	0.5	0.6	0.75	0.9
$f^S_{1,c}\ x^S_{1,c}$	0.008473	0.009706	0.01398	0.01765	0.02564	0.2230
$f^M_1\ x^M_1$	0.009554	0.01166	0.01625	0.01459	0.01547	0.05237
β^S	−14.8	−16.4	−17.1	−16.9	−16.6	−10.1
β^M	−13.4	−14.9	−15.9	−16.9	−17.9	−14.9
$\gamma_{\mathrm{cmc}12}$	32.8	32.0	29.1	33.6	37.4	44.5
$c_1{}^{0,\mathrm{cmc}}$	0.303	0.327	0.429	0.281	0.195	0.0982
$c_2{}^{0,\mathrm{cmc}}$	1.22	1.28	1.53	1.16	0.911	0.567
$\ln\left(\frac{c_1^{0,\mathrm{cmc}}c_2^M}{c_2^{0,\mathrm{cmc}}c_1^M}\right)$	−0.35	−0.33	−0.24	−0.38	−0.51	−0.72
Synergism	$\alpha \leq 0.5$, Eq. (8): yes; Eqs. (22) and (27): yes; Eqs. (22) and (31): yes; experimental results: yes $\alpha > 0.5$, Eq. (8): no; Eqs. (22) and (27): no; Eqs. (22) and (31): no; experimental results: no					

Table 4 Synergism in surface tension reduction effectiveness for the TADPS/CPCl system (γ in mN/m, $c_i^{0,\mathrm{cmc}}$ in mmol/l)

α	0.1	0.25	0.5	0.6	0.75	0.9
$f^S_{1,c}\ x^S_{1,c}$	0.00818	0.01020	0.01631	0.01771	0.2683	0.2194
$f^M_1\ x^M_1$	0.004349	0.005725	0.007826	0.007092	0.009027	0.03519
β^S	−16.6	−17.8	−17.9	−18.3	−17.8	−10.8
β^M	−16.6	−17.8	−18.7	−19.9	−20.0	−16.5
$\gamma_{\mathrm{cmc}12}$	34.0	34.5	35.5	38.4	40.1	47.9
$c_1{}^{0,\mathrm{cmc}}$	0.271	0.258	0.235	0.178	0.151	0.0697
$c_2{}^{0,\mathrm{cmc}}$	1.62	1.56	1.46	1.19	1.06	0.588
$\ln\left(\frac{c_1^{0,\mathrm{cmc}}c_2^M}{c_2^{0,\mathrm{cmc}}c_1^M}\right)$	−0.73	−0.74	−0.77	−0.84	−0.89	−1.08
Synergism	Eq. (8): no; Eqs. (22) and (27): no; Eqs. (22) and (31): no; experimental results: no					

composition range, whereas for TADPS/CTABr and TADPS/CPCl (C_{12-}/C_{16+}) mixtures, $|\beta^M|$ increases with the anionic species mole fraction in the bulk phase. A similar but much weaker tendency is observed for $|\beta^S|$ (Tables 2, 3, 4).

Figure 5 shows that the TADPS/CTABr and TADPS/CPCl systems form nearly equimolar micelles in the interval $0.1 < \alpha < 0.9$. In fact, as mentioned earlier, CTABr and CPCl have very close cmc values, not far from that of TADPS. On the other hand, the TADPS/DTABr system behaves differently, with an asymmetrical mixed micelle composition, to be compared with its asymmetrical monolayer [23].

Precipitation

The problem hampering the application of mixed anionic/cationic systems is the precipitation or coacervation (liquid–liquid phase separation) which appears even at quite low concentrations, either beyond the cmc [10–14] or even below [15, 16], especially around an equimolar ratio, depending on the nature and the alkyl chain length of the surfactants [29]. For the systems investigated in this work, this problem is also unavoidable, but, as shown in Fig. 4 and Table 5 there is a concentration gap between the precipitation or turbid boundary and the mixed cmc. For the TADPS/CPCl system, Fig. 4 indicates that the clear/turbid boundary and the cmc curve become relatively close to each other at a nearly equimolar ratio ($\alpha \sim 0.5$) but strongly diverge towards both ends. For the other two systems, in the anionic-rich range ($\alpha > 0.5$), transparent solutions containing visible solid particles are observed, whereas in the cationic-rich range ($\alpha < 0.5$), the mixtures become cloudy then clear again with a further total concentration increase. Surprisingly, for α smaller than about 0.3, the TADPS/CTABr system shows no such turbid region up to a total concentration higher than 1×10^{-2} mol/l.

The inhibition of precipitation or coacervation in the systems investigated can be attributed to the presence of ethylene oxide units in the anionic surfactant molecule. In fact, ethylene oxide groups weaken the interaction between oppositely charged head groups because of their hydrophilicity and their steric hindrance effect [12, 18, 19]. In contrast to the SDS/DTABr and SDS/DPCl systems, whose total alkyl chain carbon number is 24 and for which the precipitation concentration is smaller than the mixed cmc [15, 16], the TADPS/CTABr and TADPS/CPCl systems show a precipitation concentration larger than their mixed cmc, although the total alkyl chain carbon number reaches 28: the effect of the ethylene oxide groups in the TADPS molecule is therefore obvious.

The disappearance of the turbid or coacervation region with an increase in the total surfactant concentration is usually explained by the solubilization of the coacervate complex in the mixed micelle [15, 29]; however, Zhao and Xiao [30] have shown that, along the total concentration scale, at a given anionic/cationic ratio, there is a micelle shape transition (from rodlike to spherical) which could result in a clarification phenomenon. In fact, in anionic/cationic systems, the precipitation or coacervation is considered to be the result of a great increase in the micelle aggregation number [31, 32], which depends on micelle composition. As predicted by Rubingh's nonideal theory, while the total concentration increases, the mixed micelle composition changes gradually from nearly equimolar to the bulk solution composition. It thus results in a decrease in the micelle aggregation number [31] and in a shape transition [32], so the reason for the clarification could be the decrease in the micelle aggregation number.

Let us note that the break point in the γ–log$c$ curves for some anionic/cationic systems, such as SDS/DTABr and SDS/DPCl [15, 16], has often been attributed to complex precipitation instead of micelle formation because of the appearance of a precipitate just beyond the break point [16, 17, 32]. Zhu and Zhao [33], however, have shown that this event corresponds to a true cmc.

Surface tension reduction effectiveness

The data regarding the synergism in surface tension reduction effectiveness for the systems studied are presented in Tables 2, 3 and 4. The surface activities $(f^{S}_{1,c} x^{S}_{1,c})$ are calculated from the measured surface tensions near the cmc for each mixing ratio. For the TADPS/CTABr and TADPS/CPCl systems, the surface tension often decreases after the break point of the γ–log$c$ curve. In those cases, the first surface tension value deviating distinctly from the steepest part of the γ–log$c$ line was taken as γ_{cmc}. For each system, $\gamma^{0}_{\mathrm{cmc1}}$ is 33.6 mN/m with $\gamma^{0}_{\mathrm{cmc1}}$ smaller than $\gamma^{0}_{\mathrm{cmc2}}$.

Tables 2, 3 and 4 show the excellent agreement between predicted and experimental results. Over the whole composition range, the TADPS/DTABr system shows synergism but the TADPS/CPCl one does not. As for the TADPS/CTABr system, synergism only exists in a certain mixing-ratio range ($\alpha \leq 0.5$). The various expressions characterizing the conditions of synergism in surface tension reduction effectiveness, although derivable by different methods [9, 20, 21], are indeed equivalent and can all be derived from the surface tension equations for binary surfactant systems. Among those expressions, the set of Eqs. (22) and (27) is perhaps the most convenient for only the properties, Γ^{∞}_{i}, K_i and c^{M}_{i}, of the individual surfactants (Table 6) and the interaction parameters, β^{S} and β^{M}, of the mixture are required.

The lowest γ_{cmc12}, $\gamma^{*}_{\mathrm{cmc12}}$, predicted theoretically, and the corresponding bulk and micelle or monolayer compositions, $\alpha^{*}, x^{*\mathrm{S}}_{1}$ or $x^{*\mathrm{M}}_{1}$, together with the lowest γ_{cmc12} measured for a bulk composition close to α^{*}, are reported in Table 7. For the TADPS/DTABr system, average β^{S} and β^{M} values, -16.0 and -13.8, respectively, are used in the calculations. For the TADPS/CTABr system, -16.5 and -14.9 (measured at $\alpha = 0.25$) are used. The lowest γ_{cmc12} values, although not measured at the exact α^{*}, show excellent agreement with the predicted ones. As analyzed in the theoretical part, even for a system of surfactants with rather distant cmc (TADPS/DTABr), $x^{*\mathrm{S}}_{1}$ or $x^{*\mathrm{M}}_{1}$ is close to 0.5. On the other hand, α^{*} can greatly deviate from 0.5, approaching 0 or 1. Thus,

Table 5 Ratios of precipitation concentration (c_{p}) to mixed critical micelle concentration (*cmc*) for equimolar mixtures of TADPS with different cationic surfactants

Cationic species	DTABr	CTABr	CPCl
c_{p}/cmc	4.8	5.7	8.9

Table 6 Characteristic constants of individual surfactants

Property	TADPS	DTABr	CTABr	CPCl
$10^{10}\Gamma^{\infty}_{i}$ (mol/cm^2)	2.2	3.52	3.69	3.26
$10^{3}K_{\mathrm{i}}$	120	0.532	6.30	6.00
cmc (mmol/l)	0.32	14	0.9	0.92

Table 7 Lowest γ_{cmc} (mN/m) and corresponding bulk and micelle (monolayer) compositions

System	γ^0_{cmc1}	γ^0_{cmc2}	$x_1^{*S} = x_1^{*M}$	α^*	$\gamma^*_{\mathrm{cmc12}}$ from Eqs. (20) or (21)	$\gamma^*_{\mathrm{cmc12}}$ measured
TADPS/DTABr	33.6	37.5	0.503	0.0245	27.5	27.1[a]
TADPS/CTABr	33.6	37.0	0.520	0.4173	29.4	29.1[b]

[a] $\alpha = 0.1$
[b] $\alpha = 0.5$

for such a binary system, when the synergism in γ_{cmc} exists, the lowest γ_{cmc12} is reached by adding a small amount of surfactant with the lower cmc to the other. For a system of surfactants with similar cmc, however, the lowest γ_{cmc12} is obtained at a nearly equimolar bulk composition. As shown in Figs. 2 and 3 and Tables 2, 3 and 4, γ_{cmc12} greatly increases with α in the anionic-rich region, so, for large α values (e.g. $\alpha = 0.9$), β^{M} and especially β^{S}, greatly deviate from their average values and the γ–log$c$ curves appear abnormal.

Tables 2, 3 and 4 also show that, with the increase in the total alkyl chain length, β^{M} decreases faster than β^{S} and this will result in the loss of synergism in surface tension reduction effectiveness; therefore, to ensure this kind of synergism, surfactant alkyl chains should not be too long. This agrees with Zhu and Rosen's results [9].

Conclusions

1. Very strong synergism in mixed micelle formation exists in the anionic/cationic systems investigated. Mixed cmc values can be well predicted by a nonideal micellization theory. The mixed micelle composition is mixing-ratio dependent and, for equimolar mixtures of surfactants with quite different cmc, the micelle is richer in the surfactant with the lower cmc.
2. The presence of a few ethylene oxide units in the anionic surfactant molecule suffices to inhibit the precipitation of the anionic/cationic complex to a certain extent. So, a rather large concentration gap is observed between the mixed cmc and the precipitation boundary, especially in the cationic-rich region.
3. The necessary and sufficient conditions for synergism in surface tension reduction effectiveness can be described by various expressions and are finally equivalent. In particular, they can all be derived from the surface tension equations for binary surfactant mixtures. obtained by combining the Szyszkowski equation with nonideal micellization theory.
4. Synergism in surface tension reduction effectiveness can be characterized from the knowledge of some properties of the individual surfactants: Γ_i^{∞}, K_i and cmc, and from the interaction parameters, β^{S} and β^{M}, of their mixtures. Good agreement is observed between predicted and measured synergism in surface tension reduction effectiveness.
5. With the increase in the surfactant alkyl chain length, β^{M} decreases faster than β^{S}; thus, synergism in surface tension reduction effectiveness can be lost.

References

1. Rubingh DN (1979) In: Mittal KL (ed) Solution chemistry of surfactants, vol 1. Plenum, New York, pp 331–354
2. Holland PM, Rubingh DN (1983) J Phys Chem 87:1984–1990
3. Scamehorn JF, Schechter RS, Wade WH (1982) J Dispersion Sci Technol 3:261–278
4. Rosen MJ (1986) In: Scamehorn JF (ed) Phenomena in mixed surfactant systems. ACS Symposium Series 311. American Chemical Society, Washington, DC, pp 144–162
5. Graciaa A, Ben Ghoulam M, Marion G, Lachaise J (1989) J Phys Chem 93:4167–4173
6. Ishikawa M, Matsumura K, Esumi K, Meguro K (1991) J Colloid Interface Sci 141:10–20
7. Ding HJ, Hon XL, Zhao GX (1993) Gaodeng Xuexiao Huaxue Xuebao 12:222–226
8. Yu ZJ, Zhao GX (1993) J Colloid Interface Sci 156:325–328
9. Zhu BY, Rosen MJ (1984) J Colloid Interface Sci 99:435–442
10. Yang WS, Zhao GX (1985) Huaxue Xuebao 43:705–711
11. Ding HJ, Zhao GX (1986) Beijing Daxue Xuebao Ziran Kexueban 2:1–11
12. (a) Zhao GX, Zhu BY (1992) Proceedings of the '92 International Seminar on Surfactants and Detergents, 21–24 April, 1992, Shanghai, China. Research Institute of Daily Chemical Industry, Ministry of Light Industry, pp 406–412; (b) Zhao GX, Zhu BY (1995) J Dispersion Sci Technol 16:305–332
13. Anton RE, Gomez D, Graciaa A, Lachaise J, Salager JL (1993) J Dispersion Sci Technol 14:401–416
14. Filipovic-Vincekovic N, Skrtic D (1989) Prog Colloid Polym Sci 79:308–12
15. Lucassen-Reynders EH, Lucassen J, Giles D (1981) J Colloid Interface Sci 81:150–157
16. Stellner KL, Amante JC, Scamehorn JF, Harwell JH (1988) J Colloid Interface Sci 123:186–200
17. Amante JC, Scamehorn JF, Harwell JH (1991) J Colloid Interface Sci 144:243–253
18. Mehreteab A, Loprest FJ (1988) J Colloid Interface Sci 125:602–609
19. Li XG, Zhao GX (1992) Colloids Surf 64:185–190

20. Hua XY, Rosen MJ (1982) J Colloid Interface Sci 90:212–219
21. Hua XY, Rosen MJ (1988) J Colloid Interface Sci 125:730–732
22. Rosen MJ (1994) Prog Colloid Polym Sci 95:39–47
23. Cui ZG, Canselier JP (2000) Colloid Polym Sci 278:22–29
24. Adamson AW (1990) Physical chemistry of surfaces, 5th edn. Wiley, New York
25. Butler JAV (1932) Proc R Soc Lond Ser A 135:348
26. Longman GF (1975) The Analysis of detergents and detergent products. Wiley, New York, p 237
27. Rosen MJ (1978) Surfactants and interfacial phenomena. Wiley, New York
28. Lindman B, Wennerström H (1980) Top Curr Chem 87:1–83
29. Tomlinson E, Davis SS, Mukhayer GI (1979) In: Mittal KL (ed) Solution chemistry of surfactants, vol 1. Plenum, New York, pp 3–43
30. Zhao GX, Xiao JX (1994) Wuli Huaxue Xuebao 10:577–580
31. Malliaris A, Binana-Limbele, Zana R (1986) J Colloid Interface Sci 110:114–120
32. (a) Kato T, Takeuchi H, Seimiya T (1990) J Colloid Interface Sci 140:253–257; (b) Kato T, Takeuchi H, Seimiya T (1992) J Phys Chem 96:6839–6843
33. Zhu BY, Zhao GX (1991) Wuli Huaxue Xuebao 7:385–388