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ORIGINAL CONTRIBUTION

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Mixed adsorption and surface tension prediction of nonideal ternary surfactant systems

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Abstract To deal with the mixed adsorption of nonideal ternary surfactant systems, the regular solution approximation for nonideal binary surfactant systems is extended and a pseudo-binary system treatment is also proposed. With both treatments, the compositions of the mixed monolayer and the solution concentrations required to produce given surface tensions can be predicted based only on the γ-LogC curves of individual surfactants and the pair interaction parameters. Conversely, the surface tensions of solutions with different bulk compositions can be predicted by the surface tension equations for mixed surfactant systems. Two ternary systems: SDS/Hyamine 1622/AEO$_7$, composed of homogeneous surfactants, and AES/DPCl/AEO$_9$, composed of commercial surfactants, in the presence of excess NaCl, are examined for the applicability of the two treatments. The results show that, in general, the pseudo-binary system treatment gives better prediction than the extended regular solution approximation, and the applicability of the latter to typical anionic/cationic/nonionic nonideal ternary surfactant systems seems to depend on the combined interaction parameter, $(\beta^s_{an}+\beta^s_{cn})/2-\beta^s_{ac}/4$: the more it deviates from zero, the larger the prediction difference. If $(\beta^s_{an}+\beta^s_{cn})/2-\beta^s_{ac}/4\to 0$, good agreements between predicted and experimental results can be obtained and both treatments, though differently derived, are interrelated and tend to be equivalent.

Keywords Anionic/cationic/nonionic surfactant system · Ternary surfactant system · Nonideal mixed adsorption · Surface tension · Interaction parameters

Introduction

Thanks to synergism in surface tension reduction and micelle formation, inducing various end-use properties [1, 2, 3, 4, 5, 6, 7, 8], surfactant mixtures are widely used in practical applications. The fundamentals of the synergism in binary systems have been well understood on the basis of nonideal theories [1, 3, 9, 10, 11, 12, 13], especially the Regular Solution Approximation (RSA) [1, 3, 6, 14, 15, 16, 17, 18, 19, 20], and the mixed CMCs and the concentrations required to produce a given surface tension reduction can be predicted by means of β parameters experimentally determined [1, 3, 4, 5, 6, 7, 8, 14, 15, 16, 17] or theoretically calculated [11, 18, 19, 20]. In practical applications such as detergency and enhanced oil recovery, ternary and other multicomponent surfactant mixtures are often encountered: it is therefore significant to understand the behavior of multicomponent systems. The RSA has been extended to deal with mixed micelle formation of nonideal multicomponent systems [14] and for some systems the mixed CMCs have been successfully predicted from experimental [14, 15, 16, 17] or theoretical [20] pair interaction parameters of binary systems. To our knowledge, however, rare studies on mixed adsorption and surface tension reduction of nonideal multicomponent systems can be found in the literature.

In studying mixed adsorption of anionic/cationic binary systems we have successfully established a surface tension equation for mixed surfactant solutions by combining nonideal adsorption theory with the Szyszkowski equation [21, 22]. Once the mole fraction and activity coefficient of either surfactant in the mixed monolayer are found out, for example, by RSA treatment, the surface tensions of mixed solutions can be predicted. For multicomponent systems, the surface tension equations are theoretically applicable, provided that the mole fraction and activity coefficient of one of the surfactants in the mixed monolayer can be obtained.

Since the RSA treatments for mixed micelle formation and mixed adsorption are quite similar, the RSA treatment for nonideal adsorption of binary systems can be analogously extended to nonideal multicomponent systems. In dealing with mixed micelle formation of ternary surfactant systems by an extended RSA (ERSA) treatment, however, for some typical anionic/cationic/nonionic ternary systems, where the anionic/cationic interaction is much stronger than anionic/nonionic and cationic/nonionic interactions, the predicted activity coefficient of the nonionic in the mixed micelle has been found to be larger than unity, or its mole fraction in the mixed micelle close to zero. This has been explained as micellar demixing [23]: due to its low hydrophilicity, the anionic/cationic complex forms micelles at very low total concentration and the micelles contain almost no nonionics. With the increase of total surfactant concentration, these micelles will combine with other micelles composed of mainly nonionics. Similar results would be expected in applying ERSA treatment to the mixed adsorption of multicomponent systems. On the other hand, however, ideal mixing between equimolar anionic/cationic mixture and nonionic surfactant has been confirmed [16, 24], and a monolayer composed of an anionic/cationic complex, but excluding nonionic surfactant, seems impossible, since even a hydrocarbon-based surfactant and a fluorocarbon-based one form a miscible adsorption film in spite of the coexistence of two kinds of micelles in certain conditions [25, 26], Therefore, the application of the ERSA treatment to mixed adsorption of nonideal multicomponent systems might be conditional.

Both surface tension equation and γ-LogC curve of surfactant mixtures show similarity to those of individual surfactants, and the mixing of a binary mixture with the third component looks like that of two individual components [27]: namely, the mixing of an equimolar anionic/cationic mixture with a nonionic is similar to that of two nonionic surfactants [24]. This implies that the mixture of two surfactants can be regarded as a pseudo-individual surfactant: a ternary system can then be simplified as a pseudo-binary system (PBS) and the RSA for binary systems can be applied. In this paper both ERSA and PBS treatments are considered and the predicted and measured surface tensions for two typical anionic/cationic/nonionic ternary systems: SDS/Hyamine1622/AEO$_7$, composed of homogeneous surfactants, and AES/DPCl/AEO$_9$, composed of commercial surfactants, in the presence of excess NaCl, are compared.

Theory

The general surface tension equation of multicomponent systems

The surface tension, γ_{12}, of a binary mixed surfactant solution at a total concentration C_{12} (lower than the mixed CMC), can be predicted by the following equation [21]:

$$\gamma_0 - \gamma_{12} = n_i RT\Gamma_i^\infty \ln\left(1 + \frac{K_i \alpha_i f_i C_{12}}{x_i^s f_i^s}\right)(i = 1,2) \quad (1)$$

where γ_0 is the surface tension of pure water or excess electrolyte solution, Γ_i^∞ and K_i the excess surface concentration at saturation and the Langmuir-Szyszkowski constant of surfactant *i*, respectively, α_i the mole fraction of surfactant *i* in total mixed solute in bulk solution, f_i the activity coefficient of surfactant *i* in bulk solution, x_i^s and f_i^s the mole fraction and activity coefficient of surfactant *i* in the mixed monolayer, respectively, *R* the gas constant, *T* the absolute temperature, and n_i the number of particles per molecule of surfactant *i* whose concentration varies with surfactant concentration. For a pure surfactant solution, $\alpha_i = 1$, $x_i^s = 1$, $f_i^s = 1$, and Eq. (1) reduces to the Szyszkowski equation:

$$\gamma_0 - \gamma_i^0 = n_i RT\Gamma_i^\infty \ln\left(1 + K_i f_i^0 C_i^0\right) \quad (2)$$

where C_i^0 and γ_i^0 are solution concentration and surface tension of surfactant *i*, respectively, and f_i^0 its activity coefficient in bulk solution. For a nonionic surfactant, f_i^0 can be regarded as unity, due to its very low concentration. For an ionic surfactant, f_i^0 can be calculated from the Debye-Hückel equation [28]. In the presence of excess electrolyte, f_i^0 will not change with surfactant concentration at a given temperature and can thus be combined with K_i to constitute a new constant, $K'_i = K_i f_i^0$, which, together with Γ_i^∞, can be obtained directly by fitting the Szyszkowski equation to the γ-LogC curve of the individual surfactant *i*. In the case where the same concentration of excess electrolyte is added to both pure and mixed surfactant solutions, $f_i = f_i^0$, the surface tension of a binary surfactant solution can be calculated from Eq. (1), once x_i^s and f_i^s

are obtained, for instance, from RSA treatment [21]. For ternary or other multicomponent systems, the general relationship [4, 5, 21]:

$$\alpha_i f_i C_{123\ldots} = f_i^s x_i^s f_i^0 C_i^0 \quad (i = 1, 2, 3\ldots) \tag{3}$$

still holds: thus, the general surface tension equation for a multicomponent system can be written as

$$\gamma_0 - \gamma_{123\ldots} = n_i R T \Gamma_i^\infty \ln\left(1 + \frac{K_i \alpha_i f_i C_{123\ldots}}{x_i^s f_i^s}\right) \quad (i = 1, 2, 3\ldots) \tag{4}$$

where $C_{123\ldots}$ and $\gamma_{123\ldots}$ are the total concentration and surface tension of the multicomponent solution, respectively. To apply Eq. (4), the key is to obtain x_i^s and f_i^s. For this purpose, ERSA and PBS treatments are considered.

The ERSA treatment

Holland and Rubingh [14] have extended the RSA for binary mixed micelle formation to nonideal multicomponent systems by considering only the pair interaction parameters. Similarly the RSA for binary mixed adsorption [4, 5, 6] can also be extended to multicomponent systems and the following expressions can be obtained:

$$\alpha_i f_i C_{ijk\ldots} = f_i^s x_i^s f_i^0 C_i^0 \tag{3.1}$$

$$\ln f_i^s = \sum_{\substack{j=1 \\ (j \neq i)}}^{n} \beta_{ij}^s \left(x_j^s\right)^2 + \sum_{\substack{j=1 \\ (j \neq k \neq i)}}^{n} \sum_{k=1}^{j-1} \left(\beta_{ij}^s + \beta_{ik}^s - \beta_{jk}^s\right) x_j^s x_k^s \tag{5}$$

where the subscripts i, j, and $k\ldots$ represent the components constituting the mixture ($i \neq$ j $\neq$ k). Thus, $C_{ijk\ldots}$, as $C_{123\ldots}$, denotes the total concentration of the mixed solution, and β_{ij}^s ($i \neq j$) is the pair interaction parameter between surfactants i and j in the mixed monolayer.

In the presence of excess electrolyte, the bulk activity coefficient of an ionic surfactant will deviate from unity, but tend towards a constant value, according to the Debye-Hückel equation [28]. When the same concentration of excess electrolyte is added to a pure or a mixed surfactant solution, the ionic strengths are equal, f_i and f_i^0 on both sides of Eq. (3) counteract each other and can be eliminated.

For a ternary system, the development of Eq. (5) and combined with Eq. (3) gives

$$\alpha_1 C_{123} = x_1^s C_1^0 \exp\left[\beta_{12}^s \left(x_2^s\right)^2 + \beta_{13}^s \left(x_3^s\right)^2 + \left(\beta_{12}^s + \beta_{13}^s - \beta_{23}^s\right) x_2^s x_3^s\right] \tag{6}$$

$$\alpha_2 C_{123} = x_2^s C_2^0 \exp\left[\beta_{12}^s \left(x_1^s\right)^2 + \beta_{23}^s \left(x_3^s\right)^2 + \left(\beta_{12}^s + \beta_{23}^s - \beta_{13}^s\right) x_1^s x_3^s\right] \tag{7}$$

$$\alpha_3 C_{123} = x_3^s C_3^0 \exp\left[\beta_{13}^s \left(x_1^s\right)^2 + \beta_{23}^s \left(x_2^s\right)^2 + \left(\beta_{13}^s + \beta_{23}^s - \beta_{12}^s\right) x_1^s x_2^s\right] \tag{8}$$

always with

$$\sum x_i^s = 1 \tag{9}$$

For known α_i (i = 1,2,3), β_{ij}^s (i = 1,2,3; j = 1,2,3; $i \neq j$) and C_i^0 (i = 1,2,3), the mixture concentration, C_{123}, required to produce a given surface tension reduction and the mixed monolayer composition, x_i^s (i = 1,2,3), can be numerically calculated from Eqs. (6), (7), (8) and (9), and the f_i^s (i = 1,2,3) can then be calculated from Eq. (5).

For a binary mixture, Eqs. (6), (7), (8) and (9) reduce to the following ones, derived by Rosen and Hua [4, 5, 6]:

$$\alpha_1^* C_{12} = f_1^{*s} x_1^{*s} C_1^0 \tag{10}$$

$$(1 - \alpha_1^*) C_{12} = f_2^{*s} (1 - x_1^{*s}) C_2^0 \tag{11}$$

where the asterisk denotes binary system, C_{12} is the total bulk concentration of a binary mixture composed of surfactants 1 and 2 required to produce the same surface tension reduction, and

$$f_1^{*s} = \exp[\beta_{12}^s (1 - x_1^{*s})^2] \tag{12}$$

$$f_2^{*s} = \exp[\beta_{12}^s (x_1^{*s})^2] \tag{13}$$

If two of the components, for example, surfactants 1 and 2, are homologues, ideal mixing is usually expected and their interaction parameters with the third one are supposed to be equal ($\beta_{12}^s = 0$ and $\beta_{13}^s \approx \beta_{23}^s = \beta_{(12)3}^s$), where the subscript (12) refers to the mixture of components 1 and 2. Adding Eq. (6) to Eq. (7) gives

$$(\alpha_1 + \alpha_2) C_{123} = \left(x_1^s C_1^0 + x_2^s C_2^0\right) \exp\left[\beta_{(12)3}^s (x_3^s)^2\right] \tag{14}$$

For an ideal binary mixture, $f_1^{*s} = f_2^{*s} = 1$ and $x_1^{*s} + x_2^{*s} = 1$. From Eqs. (10) and (11) it is easy to obtain

$$x_1^{*s} C_1^0 + x_2^{*s} C_2^0 = C_{12} \tag{15}$$

In a ternary system, $x_1^s + x_2^s \neq 1$, but $\left(\frac{x_1^s}{x_1^s + x_2^s} + \frac{x_2^s}{x_1^s + x_2^s}\right) = 1$. By making some transformation, the following equation can be obtained:

$$x_1^s C_1^0 + x_2^s C_2^0 = (x_1^s + x_2^s)\left(\frac{x_1^s C_1^0}{x_1^s + x_2^s} + \frac{x_2^s C_2^0}{x_1^s + x_2^s}\right) = (x_1^s + x_2^s) C_{12} \tag{16}$$

Thus, Eq. (14) can be written as

$$(\alpha_1 + \alpha_2) C_{123} = (x_1^s + x_2^s) C_{12} \exp\left[\beta_{(12)3}^s (x_3^s)^2\right] \tag{17}$$

or

$$(1 - \alpha_3) C_{123} = (1 - x_3^s) C_{12} \exp\left[\beta_{(12)3}^s (x_3^s)^2\right] \tag{18}$$

Equation (17) or (18) suggests that a ternary system can be simplified as a binary one when two of the components are homologues or show ideal mixing properties. Commercial surfactants are often mixtures of homologues and can be regarded as "pure" surfactants while dealing with their interactions with other surfactants. Thus, the RSA is applicable to commercial products.

The PBS treatment

In nonideal ternary surfactant systems the mixing between any two components is nonideal and the pair interaction parameters are usually different from each other. It is possible, however, to regard the binary mixture as a pseudo-individual component and to use an apparent activity coefficient to describe its behavior in the mixed monolayer. The ternary system is thus simplified as a pseudo-binary system and the RSA can be applied.

To form a ternary system, the following steps are considered: first, the components 2 and 3 are mixed to constitute a pseudo-component 23 which displays a γ-LogC curve noted (23) in Fig 1; then the pseudo component 23 is mixed with component 1 to form the ternary system which shows a γ-LogC curve noted (123) in Fig. 1. Applying RSA to this pseudo-binary system gives

$$\alpha_1 C_{123} = f_1^s x_1^s C_1^0 \tag{19}$$

$$(1-\alpha_1)C_{123} = f_{23}^s(1-x_1^s)C_{23} \tag{20}$$

$$\frac{(x_1^s)^2 \ln\left[\frac{\alpha_1 C_{123}}{x_1^s C_1^0}\right]}{(1-x_1^s)^2 \ln\left[\frac{(1-\alpha_1)C_{123}}{(1-x_1^s)C_{23}}\right]} = 1 \tag{21}$$

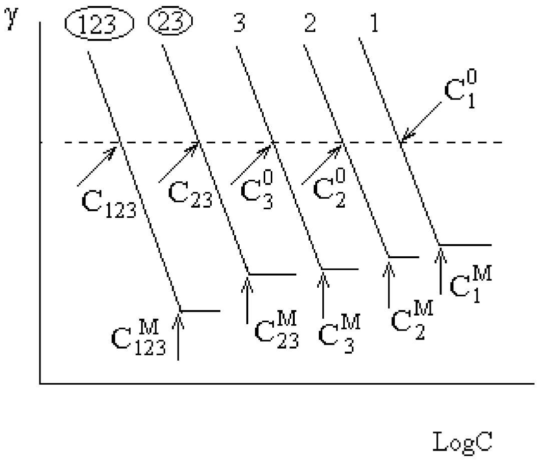

Fig. 1 Surface tension variations for pure and mixed surfactant solutions: pseudo-binary system treatment

where C_{23} is the bulk concentration of the pseudo-component 23 with a bulk composition ratio α_2/α_3 required to produce the same surface tension reduction as the ternary solution at a total concentration C_{123}, f_{23}^s is the apparent activity coefficient of the pseudo-component 23 in the mixed monolayer, describing the deviation from ideality of its mixing with component 1. Other symbols have the same meanings as above.

It is also reasonable to mix the components in any other order (1 with 2, then with 3, or 1 with 3 then with 2). The general equations can then be obtained:

$$\alpha_i C_{123} = f_i^s x_i^s C_i^0 \tag{22}$$

$$\frac{(x_i^s)^2 \ln\left[\frac{\alpha_i C_{123}}{x_i^s C_i^0}\right]}{(1-x_i^s)^2 \ln\left[\frac{(1-\alpha_i)C_{123}}{(1-x_i^s)C_{123-i}}\right]} = 1 \tag{23}$$

Since the order of mixing could be random, the total concentration, C_{123}, of the ternary surfactant system should satisfy Eqs. (22) and (23) for $i=1,2,3$ simultaneously, and Eq. (9) always holds.

From Eq. (23) for $i=1,2,3$ and Eq. (9), x_i^s ($i=1,2,3$) and C_{123} can be solved numerically without calculating f_i^s and f_{ij}^s, if C_{ij} is known.

The C_{ij} can be predicted based on the pair interaction parameters, β_{ij}^s, from Eq. (10):

$$C_{ij} = \frac{x_i^{*s} C_i^0 \exp[\beta_{ij}^s(1-x_i^{*s})^2]}{\alpha_i^*} \tag{24}$$

where x_i^{*s}, corresponding to the bulk composition α_i^*, can be calculated numerically by combining Eqs. (10) and (11):

$$x_i^{*s} = \frac{\alpha_i^*(1-x_i^{*s})C_2^0 \exp\left[\beta_{ij}^s(x_i^{*s})^2\right]}{(1-\alpha_i^*)C_1^0 \exp\left[\beta_{ij}^s(1-x_i^{*s})^2\right]} \tag{25}$$

If β_{ij}^s is a constant for a binary mixture (i.e. it does not change with monolayer composition and surface pressure), it can then be obtained by measuring the γ-LogC curves of individual surfactants and the surface tension of only one binary mixture [21].

To predict the surface tension of a ternary solution at C_{123} by Eq. (4), f_i^s should be known: it can be calculated from Eq. (22).

It is interesting to notice that, with the PBS treatment, the ternary solution concentration, C_{123}, required to produce a given surface tension reduction and the mixed monolayer composition, x_i^s, can be predicted without knowing f_{ij}^s, the apparent activity coefficients of pseudo components, nor even knowing f_i^s, the activity coefficients of individual surfactants, though they are introduced into the equations.

Extended to systems with m ($m>3$) components, the following general equations can be derived from Eqs. (22) and (23):

$$\alpha_i C_{123\ldots m} = f_i^s x_i^s C_i^0 \tag{26}$$

$$\frac{\left(x_i^s\right)^2 \ln\left[\frac{\alpha_i C_{123\ldots m}}{x_i^s C_i^0}\right]}{\left(1 - x_i^s\right)^2 \ln\left[\frac{(1-\alpha_i) C_{123\ldots m}}{(1-x_i^s) C_{123\ldots m-i}}\right]} = 1 \tag{27}$$

and Eq. (9) also holds. In Eqs. (26) and (27), $C_{123\ldots m}$ and $C_{123\ldots m-\mathrm{i}}$ are the concentrations of solutions, containing *m* and *m*–i components, respectively, required to produce a given surface tension reduction. Based on the pair interaction parameters and γ-logC relationships of individual surfactants, the concentrations of binary, ternary, ... and finally *m*-component solutions, required to produce a given surface tension reduction can be predicted successively, or, alternatively, the surface tensions of the corresponding solutions can be predicted by Eq. (4).

Two questions are immediately put forward:

- Are the predictions based on ERSA and PBS treatments equivalent?
- Are the predictions in agreement with experimental results?

To answer these questions, two ternary systems, SDS/Hyamine 1622/AEO_7, composed of homogeneous surfactants, and AES/DPCl/AEO_9, composed of commercial surfactants, both in the presence of excess NaCl, were examined.

Experimental

For the ternary system composed of homogeneous surfactants, the anionic surfactant, sodium dodecyl sulfate (SDS) with a purity of higher than 99% from Sigma Chemical Co., and the nonionic surfactant, heptaethyleneglycol monododecylether (AEO_7) from Nikko Chemical Co. (Tokyo Japan), were used as received as no minima in the surface tension curves were found near their CMCs. The cationic surfactant, Hyamine 1622 or benzethonium chloride $[C(CH_3)_3\text{-}CH_2\text{-}C(CH_3)_2\text{-}C_6H_4\text{-}(O\text{-}CH_2\text{-}CH_2)_2\text{-}N(CH_3)_2\text{-}CH_2\text{-}C_6H_5]^+Cl^-\cdot H_2O$ (simply called Hyamine in this paper) from Sigma Chemical Co., which showed a shallow minimum (less than 1 $mN\cdot m^{-1}$) in its surface tension curve, was eluted with petroleum ether for 48 h and dried at 105 °C before use. The minimum in its surface tension curve disappeared.

For the ternary system composed of commercial surfactants, the anionic surfactant was an alkyl ether sulfate (AES) from Rhodia Co. (Wuxi, China): it was a slurry product with about 70% active matter produced by sulfating a C_{12}~C_{15} fatty alcohol ethoxylate containing about three ethylene oxide units in average; its exact concentration was determined by two-phase titration with a mixed indicator [29]. The nonionic surfactant was a polyethoxylated dodecyl alcohol containing about nine ethylene oxide units in average (AEO_9), with a purity of higher than 99% from Lion Co. Both were used as received as no minima were found in their surface tension curves. The cationic surfactant, dodecylpyridinium chloride monohydrate (DPCl) from Aldrich, was recrystallized three times from an 80/20(v/v) mixture of petroleum ether and ethanol and the crystals were dried under reduced pressure slightly above room temperature. The active matter percentage of the purified DPCl was 99.8% measured by two-phase titration against SDS (mixed indicator method) [29]: only a very shallow minimum (0.3 $mN\cdot m^{-1}$) in its γ-LogC curve near the CMC was observed.

Sodium chloride (NaCl) of A.R. degree from Shanghai Chemicals Co. was used as received.

Surface tensions were measured by the Du Noüy ring technique with a Krüss K10 tensiometer at 25 ± 0.2 °C. A constant surface tension value was reached after 10–30 min for individual surfactant solutions and after 2.5~3 h for binary and ternary surfactant systems. High-purity water with an electrical conductivity of 0.78 $\mu S\cdot cm^{-1}$ at 25 ± 0.2 °C was used and the measured surface tensions of pure water and 0.1 mol/L NaCl solution at 25 ± 0.2 °C were 71.9 and 72.2 $mN\cdot m^{-1}$, respectively.

Results and discussion

Surface tensions of individual surfactants and pair interaction parameters

SDS, Hyamine and AEO_7 are homogenous surfactants. Hyamine is chosen as a cationic surfactant for its molecule containing EO groups and is expected not to form a precipitate at low concentration once mixed with SDS. The surface tensions of the three individual surfactants in pure water and in 0.1 mol/LNaCl solution are illus-

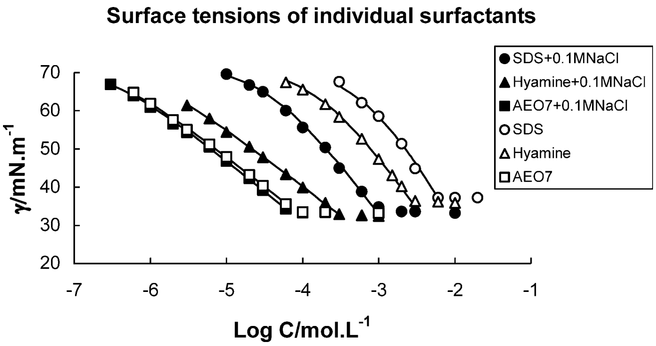

Fig. 2 Surface tensions of individual SDS, Hyamine, and AEO_7 solutions with or without NaCl at 25 °C. *Points*: measured values; *lines*: calculated by the Szyszkowski equation (parameters in Table 1)

Table 1 Excess surface concentrations, Langmuir-Szyszkowski constants and CMCs of individual surfactants at 25 °C

	Without NaCl			With 0.1 mol/L NaCl					
	SDS(1)	Hyamine(2)	AEO$_7$(3)	SDS(1)	Hyamine(2)	AEO$_7$(3)	AES(1)	DPCl(2)	AEO$_9$(3)
Γ_i^∞ (mol/cm^2)	3.1×10^{-10}	2.5×10^{-10}	2.74×10^{-10}	4.65×10^{-10}	2.66×10^{-10}	2.82×10^{-10}	4.55×10^{-10}	5.00×10^{-10}	4.31×10^{-10}
K_i	1.41×10^{3}	6.2×10^{3}	3.36×10^{6}						
$K'_i = K_i f_i$				2.90×10^{4}	1.30×10^{6}	3.74×10^{6}	8.35×10^{5}	8.30×10^{3}	2.36×10^{6}
CMC(mol/L)	6.00×10^{-3}	2.75×10^{-3}	8.30×10^{-5}	1.00×10^{-3}	3.00×10^{-4}	6.80×10^{-5}	2.35×10^{-5}	3.00×10^{-3}	2.00×10^{-5}

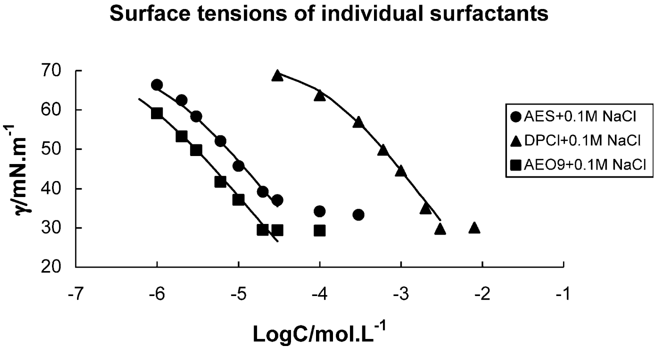

Fig. 3 Surface tensions of individual AES, DPCl, and AEO$_9$ solutions with 0.1 mol/L NaCl at 25 °C. *Points*: measured values; *lines*: calculated by the Szyszkowski equation (parameters in Table 1)

trated in Fig. 2. The curves can be well fitted by the Szyszkowski equation with two parameters: the excess surface concentration at saturation, Γ_i^∞, calculated from the Langmuir equation, and the Langmuir-Szyszkowski constant, (K_i or K_i'), listed in Table 1 together with the measured CMCs. With the addition of excess NaCl, the γ-Log C curves of SDS and Hyamine move to more dilute concentration ranges but that of AEO$_7$ shows almost no change, reflecting the quite different tolerance of ionic and nonionic surfactants to electrolyte. The saturated adsorption of Hyamine, however, has little increase with addition of NaCl, probably the branch hydrocarbon structure hindered the further decrease of the molecular area at the surface (Fig. 2 and Table 1)

AES and AEO$_9$ are commercial surfactants composed of homologues. Ideal mixing between these homologues can be expected and the interactions of these homologous molecules with another type of surfactant are likely to be similar. Therefore they can be regarded as "individual" surfactants while dealing with their mixing with other surfactants. In fact their γ-Log C behavior can be well described by the Szyszkowski equation with a single adsorption parameter and the Langmuir-Szyszkowski constant (Table 1), as shown in Fig. 3. It is therefore expected that the nonideal adsorption theory is applicable to them.

The presence of EO groups in the AES molecule makes the negative charge density of the hydrophilic group decrease and, accordingly, the interaction of AES with cationic and nonionic surfactants weaken. Thus, the anionic/cationic complex has relatively high water solubility and will not precipitate at low concentration.

The individual surfactant concentrations, C_i^0, required to produce given surface tension reductions, (γ_0−γ), in the presence of 0.1 mol/L NaCl are listed in Table 2. From these C_i^0 and C_{ij} (not listed for brevity), the pair interaction parameters, β_{ij}^s, are calculated from the relationship

$$\beta_{ij}^s = \frac{\ln\left(\frac{\alpha_i^* C_{ij}}{x_i^{*s} C_i^0}\right)}{(1 - x_i^{*s})^2} = \frac{\ln\left(\frac{(1-\alpha_i^*)C_{ij}}{(1-x_i^{*s})C_j^0}\right)}{(x_i^{*s})^2} \tag{28}$$

and shown in Table 3. For the SDS/Hyamine/AEO$_7$ system, although the β_{ij}^s calculated at different bulk compositions are similar, the main interaction parameter, β_{12}^s, is found to change significantly with surface tension reduction. It is noticed that in the presence of excess NaCl, the saturated adsorption of SDS greatly increases, whereas that of Hyamine slightly increases, compared with the systems without NaCl. This suggests that the molecular area of Hyamine in mixed monolayer will not greatly decrease as that of SDS does due to electrostatic interaction. At lower bulk concentration, SDS is less surface-active than Hyamine and has a smaller mole fraction in mixed monolayer (0.363 at $\gamma = 65$ mN·m^{-1} for $\alpha^* = 0.5$). With increasing bulk concentration, however, the surface activity of SDS increases faster than that of Hyamine, the mole fraction of SDS in mixed monolayer then increases (0.464 at $\gamma = 35$ mN·m^{-1} for $\alpha^* = 0.5$). The mixed monolayer composition then changes from asymmetric to nearly symmetric (1:1) with surface tension reduction and the interaction parameter increases correspondingly. Thus it is inappropriate to find an average β_{ij}^s for this system and all related calculations are based on the local β_{ij}^s listed in Table 3. On the other hand, in the AES/DPCl/AEO$_9$ ternary system in the presence of 0.1 mol/L NaCl, β_{12}^s, determined at a bulk composition $\alpha_i^* = 0.5$, does not change with surface tension reduction (the mixed monolayer is always symmetric with surface tension reduction). Although β_{23}^s is not a constant, the absolute values are much smaller compared with that of β_{12}^s; it is therefore reasonable to use single β_{ij}^s values: $\beta_{12}^s = -10.25$, $\beta_{13}^s = -1.64$, and $\beta_{23}^s = -4.36$, calculated

Table 2 Individual surfactant concentrations, C_i^0 (mol/L), required to produce a given surface tension reduction in the presence of 0.1 mol/L NaCl at 25 °C

γ(mN/m)	SDS(1)/Hyamine(2)/AEO$_7$(3) system			AES(1)/DPCl(2)/AEO$_9$(3) system		
	C_1^0	C_2^0	C_3^0	C_1^0	C_2^0	C_3^0
60.0	6.10×10^{-5}	4.20×10^{-6}	1.05×10^{-6}	2.57×10^{-6}	1.91×10^{-4}	1.07×10^{-6}
55.0	1.12×10^{-4}	9.30×10^{-6}	2.62×10^{-6}	4.47×10^{-6}	3.55×10^{-4}	1.74×10^{-6}
50.0	1.95×10^{-4}	2.05×10^{-5}	6.20×10^{-6}	7.24×10^{-6}	5.89×10^{-4}	2.82×10^{-6}
45.0	3.12×10^{-4}	4.50×10^{-5}	1.30×10^{-5}	1.15×10^{-5}	9.12×10^{-4}	4.47×10^{-6}
40.0	5.30×10^{-4}	1.00×10^{-4}	2.65×10^{-5}	1.82×10^{-5}	1.35×10^{-3}	7.24×10^{-6}
35.0	8.80×10^{-4}	2.40×10^{-4}	5.40×10^{-5}			

Table 3 Pair interaction parameters, β_{ij}^s ($i \neq j$), in binary systems in the presence of 0.1 mol/L NaCl at 25 °C

γ (mN/m)	SDS(1)/Hyamine(2)/AEO$_7$(3)									AES(1)/DPCl(2)/AEO$_9$ (3)		
	$\alpha_i^*=0.333$ ($i=1,1,2$)			$\alpha_i^*=0.500$ ($i=1,1,2$)			$\alpha_i^*=0.667$ ($i=1,1,2$)			$\alpha_i^*=0.500$($i=1,1,2$)		
	β_{12}^s	β_{13}^S	β_{23}^S	β_{12}^s	β_{13}^S	β_{23}^S	β_{12}^s	β_{13}^S	β_{23}^S	β_{12}^s	β_{13}^S	β_{23}^S
60.0	−8.78	−5.03	−0.40	−9.64	−4.04	−0.64	−9.08	−3.89	−0.22	−9.48	−2.30	−5.10
55.0	−10.24	−4.03	−0.36	−10.93	−3.65	−0.68	−10.45	−3.76	−0.34	−9.80	−1.49	−4.96
50.0	−11.57	−4.48	−1.00	−12.22	−3.90	−1.01	−11.74	−3.81	−0.42	−10.25	−1.64	−4.36
45.0	−12.73	−3.91	−1.09	−13.30	−3.48	−1.17	−12.78	−3.35	−0.59	−10.32	−1.45	−3.20
40.0	−13.96	−3.37	−0.99	−14.54	−3.02	−1.24	−14.02	−2.97	−0.81	−10.43	−1.61	−2.31
35.0	−15.30	−2.86	−1.06	−15.90	−2.63	−1.42	−15.32	−2.51	−1.36			
Average										−10.04 ± 0.36	−1.70 ± 0.31	−3.99 ± 1.07

from the data at $\gamma = 50$ mN·m^{-1}, throughout the calculations, for they are nearly equal to the average values, as listed in Table 3.

Mixed adsorption and surface tension of ternary systems

SDS(1)/Hyamine(2)/AEO$_7$(3) system

The predicted concentrations, C_{123}, required to produce given surface tension reductions, the mole fractions, x_i^s, and activity coefficients, f_i^s, of surfactants in a mixed monolayer, and the predicted surface tensions based on ERSA and PBS treatments are shown in Tables 4 and 5 and Figs. 4, 5 and 6, respectively. Table 4 shows that the predicted C_{123} values based on the ERSA treatment are generally higher than the measured ones by 22 to 29%, on average, whereas those based on the PBS treatment are close to the measured ones with a negative difference less that 5%. Correspondingly, as illustrated in Figs. 4, 5 and 6, the predicted surface tensions are 1.3–2.7 mN·m^{-1} higher than and 0.1–0.3 mN·m^{-1} lower than experimental results on average, with ERSA and PBS treatments, respectively.

Table 4 Experimental and calculated C_{123} values (mol/L) for the SDS(1)/Hyamine(2)/AEO$_7$(3) ternary system in the presence of 0.1 mol/L NaCl at 25 °C (ERSA and PBS treatments)

γ (mN/m)	$\alpha_1/\alpha_2/\alpha_3 = 0.4/0.4/0.2$			$\alpha_1/\alpha_2/\alpha_3 = 0.4/0.2/0.4$			$\alpha_1/\alpha_2/\alpha_3 = 0.2/0.4/0.4$		
	C_{123} $^{(m)}$	C_{123} $^{(c)}$		C_{123} $^{(m)}$	C_{123} $^{(c)}$		C_{123} $^{(m)}$	C_{123} $^{(c)}$	
		ERSA treatment	PBS treatment		ERSA treatment	PBS treatment		ERSA treatment	PBS treatment
60.0	9.80×10^{-7}	1.32×10^{-6}	1.05×10^{-6}	1.30×10^{-6}	1.40×10^{-6}	1.20×10^{-6}	1.10×10^{-6}	1.19×10^{-6}	1.08×10^{-6}
55.0	1.72×10^{-6}	2.16×10^{-6}	1.72×10^{-6}	2.22×10^{-6}	2.92×10^{-6}	2.20×10^{-6}	2.00×10^{-6}	2.57×10^{-6}	2.06×10^{-6}
50.0	2.77×10^{-6}	3.29×10^{-6}	2.62×10^{-6}	3.55×10^{-6}	4.63×10^{-6}	3.44×10^{-6}	3.30×10^{-6}	4.23×10^{-6}	3.24×10^{-6}
45.0	4.10×10^{-6}	4.92×10^{-6}	4.02×10^{-6}	5.50×10^{-6}	7.56×10^{-6}	5.47×10^{-6}	5.40×10^{-6}	6.91×10^{-6}	5.12×10^{-6}
40.0	6.10×10^{-6}	7.22×10^{-6}	5.97×10^{-6}	8.50×10^{-6}	1.16×10^{-5}	8.40×10^{-6}	8.50×10^{-6}	1.08×10^{-5}	7.96×10^{-6}
35.0	9.10×10^{-6}	1.05×10^{-5}	8.76×10^{-6}	1.33×10^{-5}	1.72×10^{-5}	1.28×10^{-5}	1.35×10^{-5}	1.21×10^{-5}	1.22×10^{-5}
δ (%)		+22.13	−4.89		+28.81	−2.86		+23.61	−4.64

(m): measured
(c): calculated

Table 5 Mixed monolayer compositions, x_i^s, and activity coefficients, f_i^s, for the SDS(1)/Hyamine(2)/AEO$_7$(3) ternary system in the presence of 0.1 mol/L NaCl at 25 °C (ERSA and PBS treatments)

	γ (mN/m)	ERSA treatment						PBS treatment					
		60.0	55.0	50.0	45.0	40.0	35.0	60.0	55.0	50.0	45.0	40.0	35.0
$\alpha_1/\alpha_2/\alpha_3$ = 0.4/0.4/0.2	x_1^s	0.3332	0.3770	0.4071	0.4294	0.4457	0.4614	0.3118	0.3424	0.3687	0.3858	0.3992	0.4093
	f_1^s	0.02590	0.02048	0.01654	0.01471	0.01221	0.01032	0.02208	0.01790	0.01458	0.01336	0.01129	0.00973
	x_2^s	0.5062	0.5467	0.5556	0.5522	0.5451	0.5336	0.4037	0.4269	0.4382	0.4452	0.4496	0.4512
	f_2^s	0.2477	0.1701	0.1157	0.07923	0.05288	0.03277	0.2477	0.1733	0.1167	0.08026	0.05311	0.03236
	x_3^s	0.1607	0.0764	0.0374	0.0183	0.0093	0.0051	0.2843	0.2303	0.1929	0.1686	0.1507	0.1394
	f_3^s	1.560	2.168	2.851	4.140	5.938	7.692	0.7035	0.5701	0.4381	0.3668	0.2990	0.2327
$\alpha_1/\alpha_2/\alpha_3$ = 0.4/0.2/0.4	x_1^s	0.2347	0.3131	0.3628	0.4139	0.4512	0.4743	0.2421	0.2868	0.3194	0.3442	0.3664	0.3847
	f_1^s	0.03910	0.03322	0.02617	0.02340	0.01934	0.01653	0.03250	0.02740	0.02209	0.02037	0.01730	0.01512
	x_2^s	0.2397	0.3690	0.4300	0.4797	0.5063	0.5075	0.2499	0.3116	0.3452	0.3659	0.3825	0.3919
	f_2^s	0.2780	0.1698	0.1050	0.06997	0.04566	0.02827	0.2287	0.1518	0.09722	0.06644	0.04392	0.02722
	x_3^s	0.5257	0.3180	0.2073	0.1065	0.0426	0.0183	0.5076	0.4014	0.3351	0.2894	0.2511	0.2231
	f_3^s	1.016	1.402	1.444	2.185	4.129	6.922	0.9006	0.8368	0.6623	0.5816	0.5050	0.4250
$\alpha_1/\alpha_2/\alpha_3$ = 0.2/0.4/0.4	x_1^s	0.2065	0.2612	0.3146	0.3653	0.4039	0.4318	0.2163	0.2540	0.2917	0.3169	0.3383	0.3575
	f_3^s	0.01993	0.01754	0.01375	0.01211	0.01011	0.008604	0.01637	0.01448	0.01139	0.01036	0.008879	0.007756
	x_2^s	0.3013	0.4214	0.4698	0.5194	0.5437	0.5446	0.2950	0.3598	0.3831	0.4019	0.4141	0.4205
	f_2^s	0.3765	0.2623	0.1753	0.1182	0.07956	0.05002	0.3487	0.2463	0.1650	0.1132	0.07689	0.04836
	x_3^s	0.4923	0.3175	0.2157	0.1154	0.0524	0.0237	0.4887	0.3860	0.3257	0.2810	0.2475	0.2216
	f_3^s	0.9235	1.238	1.264	1.845	3.112	5.140	0.8419	0.8148	0.6418	0.5606	0.4855	0.4078

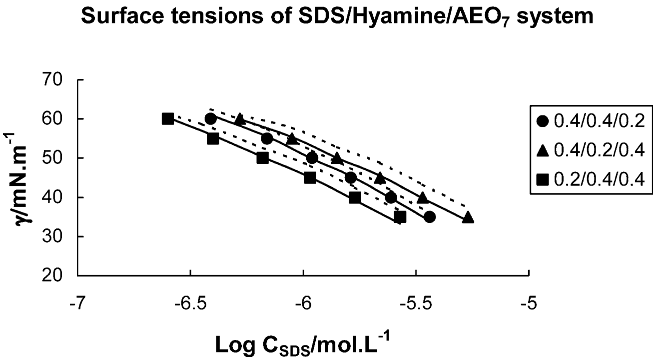

Fig. 4 Surface tensions of the SDS/Hyamine/AEO$_7$ ternary system with 0.1 mol/L NaCl at 25 °C vs SDS concentration. *Points*: measured values; *dashed lines*: calculated by Eq. (4) (ERSA treatment); *solid lines*: calculated by Eq. (4) (PBS treatment)

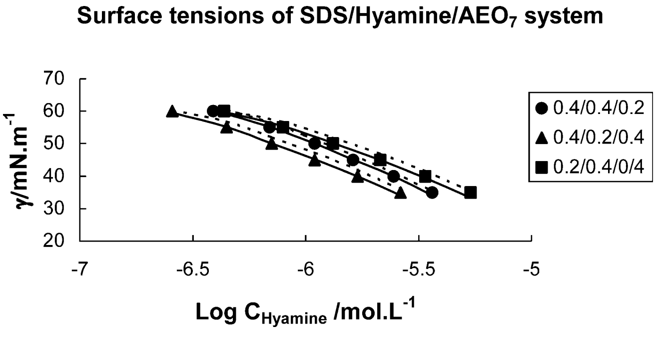

Fig. 5 Surface tensions of the SDS/Hyamine/AEO$_7$ ternary system with 0.1 mol/L NaCl at 25 °C vs Hyamine concentration. *Points*: measured values; *dashed lines*: calculated by Eq. (4) (ERSA treatment); *solid lines*: calculated by Eq. (4) (PBS treatment)

For a ternary mixture containing equal amounts of SDS and Hyamine (0.4/0.4/0.2 mixture), the mole fraction of Hyamine in the mixed monolayer is larger than that of SDS, as in their binary monolayer. This is because Hyamine has a relatively higher surface activity [30, 31]. The activity coefficients of SDS and Hyamine greatly deviate from unity, confirming the expected strong interaction between the two surfactants. However, with the increase of the total bulk concentration, according to ERSA treatment, the predicted mole fraction of AEO$_7$ tends to zero and the activity coefficient of AEO$_7$ is much larger than unity, so that the mixed monolayer tends to be nearly completely composed of SDS and Hyamine. This is of course the result of Eq. (5) for $i = 3$ ($f_3^s > 1$ because of β_{12}^s much more negative than β_{13}^s and β_{23}^s). A similar situation has been met while applying the ERSA treatment to ternary mixed micelle formation: the micelles formed initially were nearly completely composed of anionic and cationic surfactants (micellar demixing) [23]. On the other hand, since the mixing of an anionic/cationic mixture with a nonionic surfactant is nearly ideal [16, 24], this implies that the mole fraction of a nonionic surfactant in a mixed monolayer could not be zero. It is relatively difficult to determine the actual composition of a mixed monolayer, but, from surface tension measurements, it could be concluded that the ERSA treatment is inappropriate for this system, while the PBS treatment gives satisfactory predictions (Table 4). Apparently, the PBS treatment is more empirical, but, actually, it is related to the RSA and also well theoretically based. The reason why the two treatments give different results

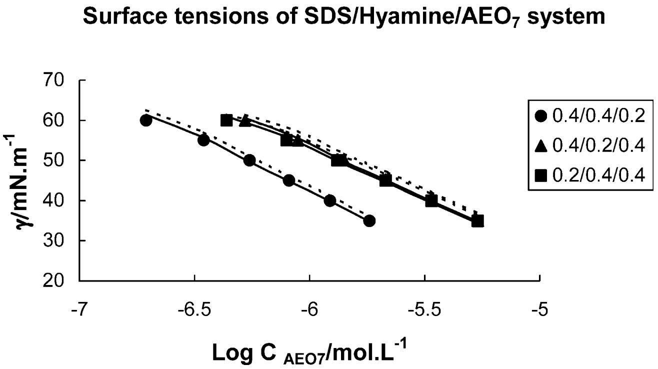

Fig. 6 Surface tensions of the SDS/Hyamine/AEO$_7$ ternary system with 0.1 mol/L NaCl at 25 °C vs AEO$_7$ concentration. *Points*: measured values; *dashed lines*: calculated by Eq. (4) (ERSA treatment); *solid lines*: calculated by Eq. (4) (PBS treatment)

and the interrelationship between them will be discussed later.

AES/DPCl/AEO$_9$ system

As shown in Table 6, the average differences in prediction of ternary solution concentrations based on the ERSA treatment for this system are also positive (12–14%) but much lower than those found for the SDS/Hyamine/AEO$_7$ system, and the consistence seems acceptable. Other differences include that the mixed monolayer is theoretically composed of three surfactants, the monolayer composition does not change with an increase of bulk concentration, and the calculated activity coefficient of the nonionic surfactant is not larger than unity (Table 7). With average negative differences of 4–6%, the prediction of ternary solution concentrations based on the PBS treatment again seems better.

It is noticeable that, for this system, the predicted mole fractions, activity coefficients, and their products based on both treatments approach each other, and a quite good agreement between predicted surface tensions and experimental results is obtained (Table 7, Figs. 7, 8 and 9). The good prediction precision with both treatments for this system is very significant. First, the ternary solution concentrations and the surface tensions were only predicted from the γ-logC curves of individual surfactants and the pair interaction parameters, which can be determined by measuring only one surface tension of a binary solution; second, the predictions based on the two different treatments approach each other, indicating that both treatments are interrelated.

On the other hand, however, the different prediction precisions obtained with the ERSA treatment for the two ternary systems studied suggest that the applicability of the ERSA treatment to nonideal ternary systems is limited or conditional. By comparison of the pair interaction parameters of these two systems, the only apparent difference is that the anionic/cationic interaction in the SDS/Hyamine/AEO$_7$ system is much stronger than that in the AES/DPCl/AEO$_9$ system. Therefore, it seems that the ERSA treatment is only applicable to ternary systems where the anionic/cationic interaction is not too strong. The following discussion should clarify this point.

Applicability of the ERSA treatment and interrelation between the two treatments

Let us designate the anionic, cationic and nonionic surfactants as component *a*, *c*, and *n* (corresponding to component 1, 2 and 3) respectively and assume that the mixing between an anionic/cationic surfactant mixture and a nonionic surfactant is nearly ideal. With the PBS treatment, this mixing can be described by

$$\alpha_n C_{acn} = f_n^s x_n^s C_n^0 \tag{29}$$

$$(1-\alpha_n) C_{acn} = f_{ac}^s \left(1 - x_n^s\right) C_{ac} \tag{30}$$

and the activity coefficients can be calculated from the following relationships, similar to Eqs. (12) and (13):

$$f_n^s = \exp\left[\beta_{(ac)n}^s \left(1 - x_n^s\right)^2\right] \tag{31}$$

Table 6 Predicted C_{123} (mol/L) for the AES(1)/DPCl(2)/AEO$_9$(3) ternary system in the presence of 0.1 mol/L NaCl at 25 °C (ERSA and PBS treatments)

γ (mN/m)	$\alpha_1/\alpha_2/\alpha_3=(1/3)/(1/3)/(1/3)$			$\alpha_1/\alpha_2/\alpha_3=0.5/0.25/0.25$		
	C_{123} (m)	C_{123} (c)		C_{123} (m)	C_{123} (c)	
		ERSA treatment	PBS treatment		ERSA treatment	PBS treatment
60.0	9.12×10^{-7}	1.07×10^{-6}	9.16×10^{-7}	8.51×10^{-7}	1.02×10^{-6}	8.70×10^{-7}
55.0	1.51×10^{-6}	1.83×10^{-6}	1.58×10^{-6}	1.51×10^{-6}	1.76×10^{-6}	1.51×10^{-6}
50.0	2.57×10^{-6}	2.98×10^{-6}	2.57×10^{-6}	2.51×10^{-6}	2.87×10^{-6}	2.46×10^{-6}
45.0	4.47×10^{-6}	4.70×10^{-6}	4.06×10^{-6}	4.07×10^{-6}	4.53×10^{-6}	3.87×10^{-6}
40.0	7.59×10^{-6}	7.41×10^{-6}	6.40×10^{-6}	6.76×10^{-6}	7.13×10^{-6}	6.08×10^{-6}
δ (%)		+12.2	−5.98		+13.5	−3.84

Table 7 Mixed monolayer compositions, x_1^s, and activity coefficient, f_1^s, for the AES(1)/DPCl(2)/AEO$_9$(3) ternary system in the presence of 0.1 mol/L NaCl at 25 °C (ERSA and PBS treatments)

	γ (mN/m)	ERSA treatment					PBS treatment				
		60.0	55.0	50.0	45.0	40.0	60.0	55.0	50.0	45.0	40.0
$\alpha_1/\alpha_2/\alpha_3=(1/3)/(1/3)/(1/3)$	x_1^s	0.4350	0.4248	0.4248	0.4249	0.4287	0.3995	0.3932	0.3931	0.3930	0.3958
	f_1^s			0.3219					0.3010		
	$x_1^s f_1^s$			0.1367					0.1183		
	x_2^s	0.1927	0.1836	0.1823	0.1837	0.1894	0.2031	0.1947	0.1932	0.1952	0.1996
	f_2^s			0.009202					0.007527		
	$x_2^s f_2^s$			0.001678					0.001454		
	x_3^s	0.3724	0.3917	0.3930	0.3917	0.3820	0.3973	0.4115	0.4128	0.4118	0.4045
	f_3^s			0.8943					0.7358		
	$x_3^s f_3^s$			0.3515					0.3037		
$\alpha_1/\alpha_2/\alpha_3=0.5/0.25/0.25$	x_1^s	0.5178	0.5092	0.5092	0.5090	0.5125	0.4648	0.4596	0.4598	0.4594	0.4615
	f_1^s			0.3886					0.3695		
	$x_1^s f_1^s$			0.1979					0.1699		
	x_2^s	0.1985	0.1903	0.1890	0.1903	0.1958	0.2066	0.1997	0.1982	0.1999	0.2040
	f_2^s			0.006416					0.005268		
	$x_2^s f_2^s$			0.001213					0.001044		
	x_3^s	0.2838	0.3006	0.3019	0.3008	0.2918	0.3286	0.3412	0.3415	0.3408	0.3347
	f_3^s			0.8420					0.6386		
	$x_3^s f_3^s$			0.2542					0.2181		

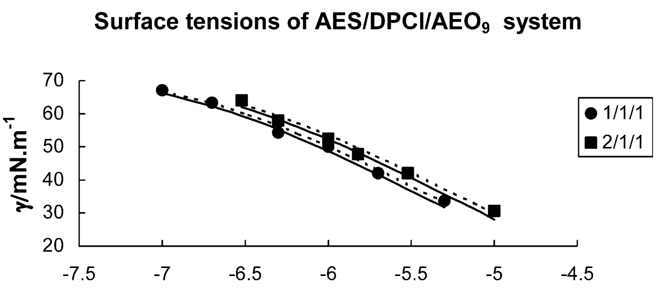

Fig. 7 Surface tensions of the AES/DPCl/AEO$_9$ ternary system with 0.1 mol/L NaCl at 25 °C vs AES concentration. *Points*: measured; *dashed lines*: calculated by Eq. (4) (ERSA treatment); *solid lines*: calculated by Eq. (4) (PBS treatment)

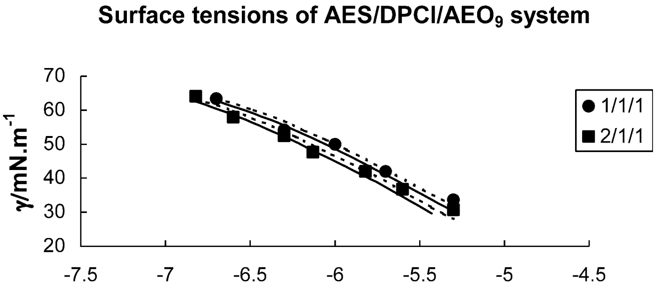

Fig. 8 Surface tensions of the AES/DPCl/AEO$_9$ ternary system with 0.1 mol/L NaCl at 25 °C vs DPCl concentration. *Points*: measured; *dashed lines*: calculated by Eq. (4) (ERSA treatment); *solid lines*: calculated by Eq. (4) (PBS treatment)

$$f_{ac}^s = \exp\left[\beta_{(ac)n}^s (x_n^s)^2\right] \tag{32}$$

where $\beta_{(ac)n}^s$ is the apparent interaction parameter of pseudo-component (ac) with component n and f_{ac}^s the apparent activity coefficient of pseudo-component (ac). From the measured C_n^0 and C_{ac} values and the bulk mole fraction balance ($\alpha_{ac}=\alpha_a+\alpha_c=1-\alpha_n$), x_n^s can be calculated from Eq. (23) and $\beta_{(ac)n}^s$ can be calculated by

$$\beta_{(ac)n}^s = \frac{\ln\left[\frac{\alpha_n C_{acn}}{x_n^s C_n^0}\right]}{(1-x_n^s)^2} = \frac{\ln\left[\frac{(1-\alpha_n)C_{acn}}{(1-x_n^s)C_{ac}}\right]}{(x_n^s)^2} \tag{33}$$

Thus f_{ac}^s can be calculated from Eq. (32). Now, ideal mixing means $f_{ac}^s \to 1$, or $\beta_{(ac)n}^s \to 0$.

From Eqs. (10) and (11) the following relationship can be obtained:

$$C_{ac} = x_a^{*s} C_a^0 f_a^{*s} + x_c^{*s} C_c^0 f_c^{*s} \tag{34}$$

It is reasonable to suppose that, because of the strong Coulombic interaction, the anionic/cationic mole fraction ratio in a ternary monolayer, x_a^s/x_c^s, at a bulk composition α_a/α_c is the same as that in a binary monolayer at the same bulk composition. Thus, the mole fractions of components a and c in the binary monolayer at bulk composition α_a/α_c can be expressed as

$$x_a^{*s} = \frac{x_a^s}{x_a^s + x_c^s} \tag{35}$$

$$x_c^{*s} = \frac{x_c^s}{x_a^s + x_c^s} \tag{36}$$

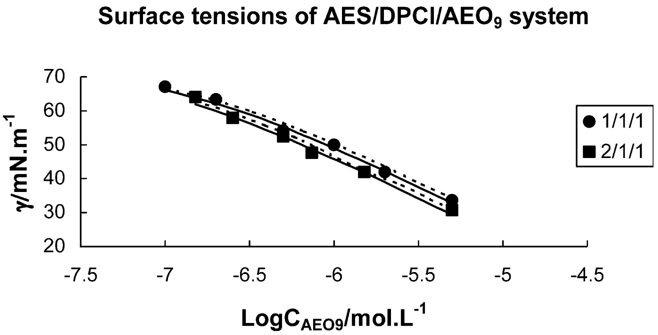

Fig. 9 Surface tensions of the AES/DPCl/AEO$_9$ ternary system with 0.1 mol/L NaCl at 25 °C vs AEO$_9$ concentration. *Points*: measured; *dashed lines*: calculated by Eq. (4) (ERSA treatment); *solid lines*: calculated by Eq. (4) (PBS treatment)

Combining Eqs. (30), (34), (35) and (36) gives

$$(1-\alpha_n)C_{acn} = f^s_{ac}\left(x^s_a C^0_a f^{*s}_a + x^s_c C^0_c f^{*s}_c\right) \tag{37}$$

On the other hand, from both treatments, the following equation can be obtained:

$$(1-\alpha_n)C_{acn} = x^s_a C^0_a f^s_a + x^s_c C^0_c f^s_c \tag{38}$$

Comparing Eqs. (37) and (38), the following relationship is derived:

$$f^s_{ac} = \frac{x^s_a C^0_a f^s_a + x^s_c C^0_c f^s_c}{x^s_a C^0_a f^{*s}_a + x^s_c C^0_c f^{*s}_c} \tag{39}$$

The relationship at Eq. (39) indicates that the apparent activity coefficient of the pseudo-component (ac), f^s_{ac}, is a kind of average activity coefficient, and, with this relationship, Eqs. (30) and (38) are convertible. Equation (30) is thus reasonable and the PBS treatment has a firm theoretical basis. Again due to strong Coulombic interaction, the activity coefficients of anionic and cationic surfactants in binary systems are expected to greatly deviate from unity but not to change significantly once a nonionic surfactant is added. Thus, from Eq. (39) it is expected that $f^s_{ac} \to 1$ (ideal mixing).

For the two systems studied, f^s_{ac}, calculated from Eq. (39) based on the ERSA treatment, listed in Table 8 as $f^{s(c)}_{ac}$, is equal or extremely close to unity, indicating that the ERSA treatment predicts ideal mixing between an anionic/cationic mixture and a nonionic successfully. The f^s_{ac} calculated from experimental data and Eqs (32) and (33) derived from the PBS treatment, expressed as $f^{s(m)}_{ac}$, are also listed in Table 8. On the whole, they are in agreement with $f^{s(c)}_{ac}$.

From Eq. (32), it is expected that, when $f^s_{ac} \to 1$, either $\beta^s_{(ac)n}$ or x^s_n must approach zero. Considering the strong interaction, it is also reasonable to suppose that anionic and cationic surfactant mole fractions in the mixed monolayer are almost equal ($x^s_a \approx x^s_c$); $\beta^s_{(ac)n}$ can then be estimated, based on the ERSA treatment, by combining Eqs. (5) and (31):

$$\beta^s_{(ac)n} \approx \frac{\beta^s_{an}\left(x^s_a\right)^2 + \beta^s_{cn}\left(x^s_a\right)^2 + \left(\beta^s_{an} + \beta^s_{cn} - \beta^s_{ac}\right)\left(x^s_a\right)^2}{\left(2x^s_a\right)^2} \approx \frac{\beta^s_{an} + \beta^s_{cn}}{2} - \frac{\beta^s_{ac}}{4} \tag{40}$$

It is clear that, only in the case where $(\beta^s_{an} + \beta^s_{cn})/2 - \beta^s_{ac}/4 \to 0$, $\beta^s_{(ac)n}$ will approach zero. If $(\beta^s_{an} + \beta^s_{cn})/2 - \beta^s_{ac}/4 > 0$, x^s_n must be close to zero in order for f^s_{ac} to get close to unity. The AES/DPCl/AEO$_9$ system meets the requirement and the predictions based on the ERSA treatment are in good agreement with experiments. For the SDS/Hyamine/AEO$_7$ system, $(\beta^s_{an} + \beta^s_{cn})/2 - \beta^s_{ac}/4$ is positive and its value increases with surface tension reduction: therefore, the calculated x^s_n decreases and finally tends towards zero, as predicted by Eq. (32), and correspondingly f^s_n is larger than unity and increases with surface tension reduction (Table 5). In fact, in the absence of excess NaCl, the anionic/cationic interaction is even much stronger and certainly results in $(\beta^s_{an} + \beta^s_{cn})/2 - \beta^s_{ac}/4 > 0$ for such a system, so that bigger differences between predictions and experiments will be expected when applying the ERSA treatment.

The $\beta^s_{(ac)n}$ calculated from Eq. (31) or (32) based on the PBS treatment is not exactly zero but slightly negative. This is because the composition of the anionic/cationic mixed monolayer is not absolutely symmetric, but enriched with the more surface-active component [21, 30, 31]. Therefore, the mixed monolayer is not

Table 8 Apparent activity coefficients, f^s_{ac}, and combined pair interaction parameters, $(\beta^s_{an} + \beta^s_{cn})/2 - \beta^s_{ac}/4$, for the systems studied

γ(mN/m)	SDS/Hyamine/AEO$_7$(0.4/0.4/0.2) + 0.1 mol/L NaCl			AES/DPCl/AEO$_9$((1/3)/(1/3)/(1/3)) + 0.1 mol/L NaCl		
	$f^{s\ (c)}_{ac}$	$f^{s\ (m)}_{ac}$	$(\beta^s_{an} + \beta^s_{cn})/2 - \beta^s_{ac}/4$	$f^{s\ (c)}_{ac}$	$f^{s\ (m)}_{ac}$	$(\beta^s_{an} + \beta^s_{cn})/2 - \beta^s_{ac}/4$
60.0	1.011	0.9134	0.36	0.9773	0.8585	0.016
55.0	1.003	0.9551	0.68			
50.0	1.000	0.9761	0.94			
45.0	1.001	0.9701	1.36			
40.0	0.9986	0.9735	1.74			
35.0	0.9995	0.9793	2.04			

completely electroneutral and will have a weak interaction with the added nonionic surfactant.

It is difficult to know the actual composition of the mixed monolayer, but, from surface tension measurements, it could be concluded that the applicability of the ERSA treatment to the ternary system seems to depend on the combined pair interaction parameter, $(\beta^s_{an} + \beta^s_{cn})/2 - \beta^s_{ac}/4$. The more it deviates from zero, the bigger the difference between predictions and experiments. When $(\beta^s_{an} + \beta^s_{cn})/2 - \beta^s_{ac}/4 \to 0$, the predictions based on the ERSA treatment are in good agreement with experimental results, and ERSA and PBS treatments tend to be equivalent. On the other hand, however, the PBS treatment is generally applicable to the nonideal ternary system.

Conclusions

1. The regular solution approximation for mixed adsorption of nonideal binary surfactant systems is extended to nonideal ternary surfactant systems. With the ERSA treatment, the mixed adsorption and surface tension of nonideal ternary surfactant systems can be predicted based only on the γ-LogC curves of individual surfactants and pair interaction parameters.
2. A pseudo-binary system treatment is proposed which considers the surfactant mixture as an "individual" component interacting with other surfactants. With the PBS treatment, similar predictions can also be realized.
3. In the case of two components showing ideal mixing, a nonideal ternary system is in fact reduced to a nonideal binary system and the ERSA and PBS treatments are equivalent. It means that the RSA is applicable to nonideal binary systems composed of commercial surfactants that are mixtures of homologues.
4. For two typical anionic/cationic/nonionic nonideal ternary surfactant systems in the presence of excess inorganic electrolyte, the PBS treatment gives better prediction than the ERSA treatment.
5. The PBS treatment is generally applicable to nonideal ternary systems. The applicability of the ERSA treatment, however, seems to depend on the combined interaction parameter, $(\beta^s_{an} + \beta^s_{cn})/2 - \beta^s_{ac}/4$: the more positive it is, the larger the difference between predictions and experimental results. In the case where $(\beta^s_{an} + \beta^s_{cn})/2 - \beta^s_{ac}/4 \to 0$, good agreements between predictions and experiments can be obtained with both treatments, which, though differently derived, are interrelated and tend to be equivalent.

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