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ORIGINAL CONTRIBUTION

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Interfacial and micellar properties of some anionic/cationic binary surfactant systems.
1. Surface properties and prediction of surface tension

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Abstract The surface tension equations of binary surfactant mixtures are established by combining the Szyszkowski equation for pure surfactant solutions and extended nonideal theory for mixed adsorption. They are then successfully applied to two relatively long-chain anionic/cationic binary surfactant systems: triethanolammonium dodecylpoly(oxyethylene)sulfate, as an anionic species (containing about 2 ethylene oxide units), mixed with dodecyltrimethylammonium bromide or hexadecyltrimethylammonium bromide. The composition of the mixed monolayer is mixing-ratio dependent and is slightly asymmetric: for overall equimolar mixtures, the larger mole fraction in the mixed monolayer is that of the more surface-active ion. The strong synergetic effects observed in the surface tension reduction efficiency are reflected by large negative β^s parameters, according to regular solution theory. They can be interpreted by the more negative adsorption free energy of each surfactant and the smaller area occupied by surfactant hydrocarbon chains in the mixed monolayer.

Key words Surface tension · Anionic/cationic surfactants · Mixed monolayer composition · β^s interaction parameter · Gas–liquid adsorption free energy

Introduction

It has been well known for a long time that among the various types of surfactant binary systems anionic/cationic ones show the strongest synergisms both in surface tension reduction and in mixed micelle formation (critical micelle concentration, cmc) [1–13]. Such synergetic effects are important for a wide range of surfactant-based phenomena such as foaming, emulsification, solubilization, detergency, etc. On the other hand, however, precipitation or phase separation often occurs in such mixed systems beyond their cmc, especially for equimolar mixtures [6, 7, 11, 12, 14]; for some mixed systems, the solubility product of the anionic/cationic 1:1 complex is so small that the precipitation concentration is lower than the cmc [6, 15–17]. Formerly, this drawback limited the in-depth study of such systems to relatively short-chain surfactants (total carbon number usually not larger than 20). Mehreteab and Loprest [18] and more recently Zhao and coworkers [11, 19] have shown that the introduction of a poly(oxyethylene) separator between the hydrophobe and the polar head of an anionic surfactant molecule can greatly improve the solubility of anionic/cationic complexes. A bulky hydrophilic counterion also contributes to better solubility. These features, resulting in more diffuse Coulombic attraction and enhanced excluded-volume constraints, made it possible to extend research work to relatively long-chain anionic/cationic mixed systems.

Rosen and Hua [3, 5, 20, 21] have successfully extended Rubingh's treatment for mixed micelle formation [1] to the adsorption of binary mixtures of surfactants, including anionic/cationic systems. Rosen et al. [3, 5, 21–24] derived the conditions for the synergetic effects in the surface tension reduction efficiency, the surface tension reduction effectiveness and mixed micelle formation. In this paper, we try to derive an equation allowing the prediction of the surface tension of binary surfactant systems and try to apply it to the anionic/cationic mixtures of triethanolammonium dodecylpoly(oxyethylene) sulfate (containing about 2 ethylene oxide units) (TADPS) with dodecyltrimethylammonium bromide (DTABr) and with hexadecyltrimethylammonium bromide (CTABr). Mixed adsorption phenomena and synergism in the surface tension reduction efficiency are also discussed.

Theory

The mole fraction of either surfactant in the surface phase for binary mixtures can be calculated by the Gibbs equation [6, 7, 20] based on γ versus log c data obtained experimentally, at a fixed concentration of the second surfactant and in the presence of excess counterions, or from the Butler equation and phase-equilibrium principles [25]. In the former treatment, however, the concentrations of both surfactants cannot be changed simultaneously and the addition of excess counterions usually decreases the interaction strength between surfactants [5, 8], while in the latter, the activity coefficients of the surfactants in a mixed monolayer, different from those in a pure monolayer [15], are difficult to know. Rosen and Hua's work [3, 5, 20, 21] dealing with the adsorption of binary mixtures of surfactants made it simple to calculate the composition of the mixed monolayer. The basic equations are as follows:

$$\alpha f_1 c_{12} = f_1^s x_1^s f_1^0 c_1^0 \tag{1}$$

$$(1-\alpha) f_2 c_{12} = f_2^s (1-x_1^s) f_2^0 c_2^0 \tag{2}$$

$$\frac{(x_1^s)^2 \ln\left[\frac{\alpha f_1 c_{12}}{f_1^s x_1^s f_1^0 c_1^0}\right]}{(1-x_1^s)^2 \ln\left[\frac{(1-\alpha) f_2 c_{12}}{f_2^s (1-x_1^s) f_2^0 c_2^0}\right]} = 1 \tag{3}$$

$$\beta^s = \frac{\ln\left(\frac{\alpha f_1 c_{12}}{f_1^s x_1^s f_1^0 c_1^0}\right)}{(1-x_1^s)^2} = \frac{\ln\left(\frac{(1-\alpha) f_2 c_{12}}{f_2^s (1-x_1^s) f_2^0 c_2^0}\right)}{(x_1^s)^2} \tag{4}$$

$$f_1^s = \exp \beta^s (1-x_1^s)^2 \tag{5}$$

$$f_2^s = \exp \beta^s (x_1^s)^2 \ , \tag{6}$$

where α is the mole fraction of surfactant 1 with respect to the total amount of surfactant in solution, x_1^s is the mole fraction (defined as above) of surfactant 1 in the mixed monolayer, c_1^0, c_2^0 and c_{12} are the bulk solution concentrations of pure surfactants 1 and 2 and the total concentration of their mixture, respectively, required to produce a given surface tension reduction, f_1^0, f_2^0, f_1 and f_2 are the corresponding activity coefficients in the bulk, f_1^s and f_2^s are the activity coefficients of surfactants 1 and 2, respectively, in the mixed monolayer and β^s is the empirical parameter (interaction parameter in the surface phase) measuring the deviation from ideality in the mixed monolayer. For mixed anionic/cationic systems, f_1 and f_2 can be taken as unity because of the very low total concentration, while f_1^0 and f_2^0, which deviate from unity when the concentration of pure surfactant is large enough, can be replaced by average activity coefficients of ions $f_{\pm,1}^0$ and $f_{\pm,2}^0$, easily obtained from the Debye–Hückel equation applied to uni-univalent electrolytes [26]:

$$\log f_{\pm,i}^0 = \frac{0.509\sqrt{I_i}}{1+1.58\sqrt{I_i}} \tag{7}$$

$$I_i = 1/2\, \Sigma\, c_j z_j^2 = c_i^0 \ , \tag{8}$$

where c_j is the concentration of the jth ion in the bulk solution and z_j is its valence.

To analyze the adsorption state of surfactants in a mixed monolayer and to derive the surface tension equation for binary mixtures, let us first consider binary mixtures of nonionic surfactants. The chemical potential, μ_1^s, of surfactant 1 in the surface phase of an aqueous mixture can be written [21, 24]

$$\mu_1^s = \mu_1^{s0} + RT \ln f_1^s x_1^s - \gamma_{12} A_1 \ , \tag{9}$$

where A_1 is the partial molar area of surfactant 1 in the surface phase (mixed monolayer), x_1^s and f_1^s are its mole fraction and activity coefficient, respectively, γ_{12} is the surface tension of the solution and μ_1^{s0} is the chemical potential of a hypothetical monolayer of zero surface tension composed of only pure surfactant 1. R is the gas constant and T is the absolute temperature. The chemical potential, μ_1^β, of surfactant 1 in the solution with the surface tension γ_{12} is

$$\mu_1^\beta = \mu_1^{\beta 0} + RT \ln \alpha f_1 c_{12} \ , \tag{10}$$

where $\mu_1^{\beta 0}$ is the standard chemical potential of surfactant 1 in the bulk solution (at equilibrium, $\mu_1^s = \mu_1^\beta$); therefore

$$\mu_1^{s0} - \mu_1^{\beta 0} = RT \ln \alpha f_1 c_{12} - RT \ln f_1^s x_1^s + \gamma_{12} A_1 \ . \tag{11}$$

For an aqueous solution of pure surfactant 1 giving a surface tension γ_1^0, Eq. (11) reduces to

$$\left(\mu_1^{s0} - \mu_1^{\beta 0}\right)^0 = RT \ln f_1 c_1^0 + \gamma_1^0 A_1^0 \ , \tag{12}$$

where the superscript 0 refers to values for pure surfactant 1. Combining Eqs. (11) and (12) yields

$$\gamma_{12} A_1 - \gamma_1^0 A_1^0 = RT \ln\left[\frac{f_1^s x_1^s f_1^0 c_1^0}{\alpha f_1 c_{12}}\right] \ , \tag{13}$$

According to the definition of x_1^s in Eq. (9), the mole fraction of the solvent is included ($x_1^s + x_2^s + x_{H_2O}^s = 1$), whereas in Eqs. (1)–(6), it is not ($x_1^s + x_2^s = 1$). The difference between the two x_1^s, however, decreases with increasing surfactant adsorption and approaches zero at saturation. $x_{\mathrm{H_2O}}^{\mathrm{s}}$ can then be neglected with respect to the mole fractions of surfactants [26]. Equation (13) may therefore be combined with nonideal theory. According to Ref. [20], Eq. (1) is tenable when the condition

$$\gamma_{12} = \gamma_1^0 \tag{14}$$

is met. Now, we obtain (since $f_1/f_1^0 \sim 1$)

$$\ln\left(\frac{f_1^{\mathrm{s}} x_1^{\mathrm{s}} c_1^0}{\alpha c_{12}}\right) = 0\ . \tag{15}$$

Combining Eqs. (13)–(15) leads to

$$\gamma_{12}(A_1 - A_1^0) = 0\ . \tag{16}$$

Since γ_{12} can never be zero

$$A_1 = A_1^0 \tag{17}$$

and similarly

$$A_2 = A_2^0\ , \tag{18}$$

which means that the partial molar area of surfactant *i* in the mixed monolayer is the same as that in its pure monolayer giving the same surface tension. According to the nonideal theory [21], Eq. (1) implies that the surface tension of a binary surfactant solution of total concentration c_{12} and global mole fraction α of surfactant 1 is equivalent to that of a solution of pure surfactant 1 at a concentration c_1^0. Thus, the surface tension equation for pure surfactant solutions may be used to predict the surface tension of an aqueous binary mixture. Now, the surface tension reduction $(\gamma_0 - \gamma)$ or surface pressure, π, of a pure surfactant solution can usually be well predicted by the Szyszkowski equation

$$\gamma_0 - \gamma = \pi = nRT\Gamma^{\infty}\ln(1 + Kc) \tag{19}$$

which arises from the combination [27] of the Langmuir adsorption equation

$$\Gamma = \Gamma^{\infty}\frac{Kc}{1 + Kc} \tag{20}$$

with the Gibbs adsorption equation

$$\mathrm{d}\gamma = nRT\Gamma\mathrm{d}(\ln c)\ , \tag{21}$$

where γ_0 is the surface tension of the solvent, Γ and Γ^{∞} are the surface concentration and the saturated surface concentration (Gibbs surface excess), respectively, of the surface-active solute, *n* is the number of particles per molecule of surfactant whose concentration varies with the surfactant concentration, *c* (for a nonionic surfactant, $n = 1$) and *K* is a constant. From Eqs. (1), (14) and (19), the surface tension of a binary nonionic mixture reads

$$\gamma_0 - \gamma_{12} = RT\Gamma_1^{\infty}\ln\left(1 + \frac{K_1 \alpha c_{12}}{f_1^{\mathrm{s}} x_1^{\mathrm{s}}}\right) \tag{22}$$

and similarly

$$\gamma_0 - \gamma_{12} = RT\Gamma_2^{\infty}\ln\left(1 + \frac{K_2(1-\alpha)c_{12}}{f_2^{\mathrm{s}}(1 - x_1^{\mathrm{s}})}\right) \tag{23}$$

The constants $\Gamma_1^{\infty}, \Gamma_2^{\infty}, K_1$ and K_2 can be obtained by fitting Eq. (19) to experimental $\gamma - \log c$ data for pure surfactants 1 and 2, respectively; x_1^{s}, f_1^{s}, f_2^{s} and β^{s}, which do not change for a given α, can be calculated from Eqs. (3)–(6) based on a group of data, c_1^0, c_2^0 and c_{12}, obtained from a single surface tension measurement of a mixture solution (total concentration lower than the mixed cmc) and $\gamma - \log c$ curves of pure surfactants 1 and 2. For a given binary system, when α is changed, x_1^{s}, f_1^{s} and f_2^{s} change correspondingly, but β^{s} is constant. For constant c_1^0 and c_2^0 but different α values, x_1^{s} can be obtained by solving the following relationship numerically:

$$x_1^{\mathrm{s}} = \frac{\alpha(1 - x_1^{\mathrm{s}})c_2^0\exp[\beta^{\mathrm{s}}(x_1^{\mathrm{s}})^2]}{(1-\alpha)c_1^0\exp[\beta^{\mathrm{s}}(1 - x_1^{\mathrm{s}})^2]} \tag{24}$$

which comes from the combination of Eqs. (1), (2), (5) and (6). Thus, the surface tension of a nonionic binary mixture in the whole composition range can be predicted by Eq. (22) or Eq. (23).

For binary ionic/nonionic or ionic/ionic mixtures, only the surface-active ions are considered, and, since the surface phase is electrically neutral, the net charge transfer is zero and terms for surface potential difference are not required [20]. Therefore, with the appropriate selection of *n* and in the absence of excess counterion, the above equations, which are still applicable, become

$$\gamma_0 - \gamma_{12} = n_1 RT\Gamma_1^{\infty}\ln\left(1 + \frac{K_1 \alpha c_{12}}{f_1^{\mathrm{s}} x_1^{\mathrm{s}}}\right) \tag{25}$$

$$\gamma_0 - \gamma_{12} = n_2 RT\Gamma_2^{\infty}\ln\left(1 + \frac{K_2(1-\alpha)c_{12}}{f_2^{\mathrm{s}}(1 - x_1^{\mathrm{s}})}\right)\ . \tag{26}$$

For the anionic/cationic surfactant systems investigated (1-1 ionic surfactants, anionic species taken as surfactant 1) Eqs. (25) and (26) take the forms

$$\gamma_0 - \gamma_{12} = 2RT\Gamma_{\mathrm{R}-}^{\infty}\ln\left(1 + \frac{K_1 \alpha c_{12}}{f_1^{\mathrm{s}} x_1^{\mathrm{s}}}\right) \tag{27}$$

$$\gamma_0 - \gamma_{12} = 2RT\Gamma_{\mathrm{R}+}^{\infty}\ln\left(1 + \frac{K_2(1-\alpha)c_{12}}{f_2^{\mathrm{s}}(1 - x_1^{\mathrm{s}})}\right)\ . \tag{28}$$

$\Gamma_{\mathrm{R}-}^{\infty}$ and $\Gamma_{\mathrm{R}+}^{\infty}$ are the saturation surface concentrations of pure anionic and cationic surfactant, respectively. Combining Eqs. (27) and (28), the surface tension equation for an anionic/cationic binary mixture reads

$$\gamma_0 - \gamma_{12} = RT\left[\Gamma_{\mathrm{R}-}^{\infty}\ln\left(1 + \frac{K_1 \alpha c_{12}}{f_1^{\mathrm{s}} x_1^{\mathrm{s}}}\right) + \Gamma_{\mathrm{R}+}^{\infty}\ln\left(1 + \frac{K_2(1-\alpha)c_{12}}{f_2^{\mathrm{s}}(1 - x_1^{\mathrm{s}})}\right)\right]\ . \tag{29}$$

When equal excess concentrations of counterions are added to pure or mixed solutions, the ionic strength is constant for all the solutions and the activity coefficients of surfactants in the bulk phase are therefore constant at a given temperature. Thus, Eq. (29) becomes

$$\gamma_0 - \gamma_{12} = RT\left[\Gamma^{\infty}_{\mathrm{R-}} \ln\left(1 + \frac{K_1 \alpha f_1 c_{12}}{f_1^{\mathrm{s}} x_1^{\mathrm{s}}}\right) + \Gamma^{\infty}_{\mathrm{R+}} \ln\left(1 + \frac{K_2(1-\alpha) f_2 c_{12}}{f_2^{\mathrm{s}}(1 - x_1^{\mathrm{s}})}\right)\right] \quad . \qquad (30)$$

In fact, K_1 and f_1 (or K_2 and f_2, respectively) can be combined. These two new constants are obtained directly from the $\gamma - \log c$ curves of individual surfactant systems in the presence of excess counterions.

Experimental

TADPS containing about 2 ethylene oxide units was a liquid sample kindly provided by SEPPIC (commercial name Montelane LT 4088, about 30% active matter). It is a mixture of various surfactant species with different hydrophobic chain lengths, different numbers of ethylene oxide units (mainly 1–4) and a small amount of residual alcohol. As a compromise, an average molar mass of 547 (M_{TADPS}) was assumed. Now, TADPS is derived from a fatty-alcohol mixture whose hydroxyl value corresponds to a molar mass of 197 (60–66% C_{12}, 21–25% C_{14} and 10–12% C_{16}); so M_{TADPS} may have been overestimated by about 6%. A shallow minimum appeared in the surface tension curves of aqueous solutions of TADPS near the cmc, or, in other words, a gentle surface tension increase was observed beyond the cmc (Fig. 1): this is probably due to the presence of several surface-active species. However, this commercial sample was used as received. DTABr and CTABr from Aldrich were used as received as no minima in the surface tension curves were found near their cmc (Figs. 1, 2). The active matter percentages of the surfactants used measured by titration against Hyamine 1622 or sodium dodecyl sulfate by the two-phase mixed indicator method [28] are shown in Table 1.

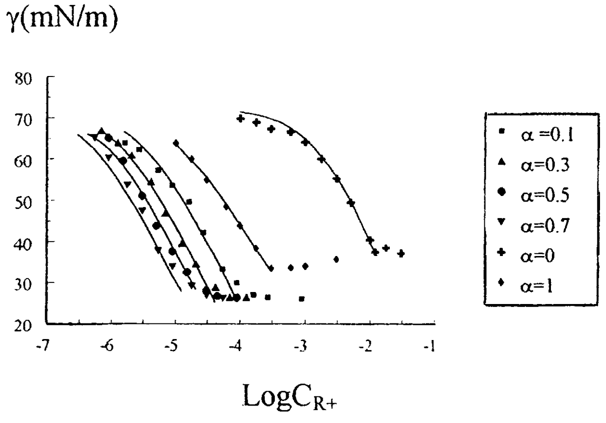

Fig. 1 Surface tension of triethanolammonium dodecylpolyloxyethylene sulfate (*TADPS*) dodecyltrimethylammonium bromide (*DTABr*) solutions at 25 °C. *Symbols*: experimental values; *solid lines*: predictions using Eq. (29) with parameters of Table 4. For pure TADPS ($\alpha = 1$), $\log c_{\mathrm{R+}}$ should read $\log c_{\mathrm{R-}}$. Parameters for one surface tension measurement: $c_1^0 = 4.5 \times 10^{-5}$ M, $c_2^0 = 4.27 \times 10^{-3}$ M, $c_{12} = 6.0 \times 10^{-6}$ M, $\alpha = 0.5$, $\gamma = 51.5$ mN m^{-1}, $\beta^{\mathrm{s}} = -16.05$

Surface tensions were measured to ±0.1 mN m^{-1} by means of the Du Noüy ring technique with a LAUDA TD1 tensiometer at 25 ° ± 0.2 °C: a constant surface tension value was reached after 10–30 min for pure surfactant solutions and after 2.5–3 h for binary mixtures (equilibration time recommended, for instance, by Lucassen-Reynders et al. [15]). Bidistilled water was used throughout ($\gamma = 72.3$ mN m^{-1} at 25 ° ± 0.2 °C).

Results and discussion

The $\gamma - \log c_{\mathrm{R}}$ data for "pure" surfactants and for mixtures of TADPS with DTABr and CTABr are reported in Figs. 1 and 2. As regards TADPS (Fig. 1), only the straight portion of the Gibbs isotherm is shown: it spans an order of magnitude on the concentration scale, which means a constant excess surface concentration over this concentration range, as explained by Schott [29]. The coordinates of the breakpoint (cmc and γ_{cmc} values) are not close to those of pure sodium dodecyldioxyethylene sulfate, which shows both a higher cmc by an order of magnitude and a higher surface tension at the cmc [30, 31]. In fact, the effect of the counterion may not be critical [32], but, above all, that of the longer hydrophobic chains, reinforced by the mixture effect, is likely to be responsible for these discrepancies.

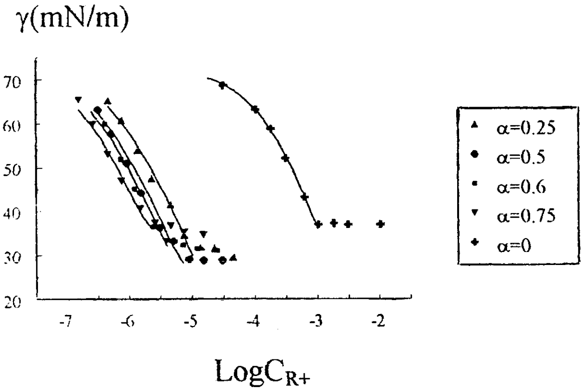

Fig. 2 Surface tension of TADPS hexadecyltrimethylammonium bromide (*CTABr*) solutions at 25 °C. *Symbols*: experimental values; *solid lines*: predictions using Eq. (29) with parameters of Table 4. Parameters for one surface tension measurement: $c_1^0 = 1.32 \times 10^{-5}$ M, $c_2^0 = 1.0 \times 10^{-4}$ M, $c_{12} = 6.0 \times 10^{-7}$ M, $\alpha = 0.5$, $\gamma = 63.2$ mN m^{-1}, $\beta^{\mathrm{s}} = -16.17$

Table 1 Active matter percentage of surfactants used: Triethanolammonium dodecylpolyoxyethylene sulfate (*TADPS*), dodecyltrimethylammonium bromide (*DTABr*) and hexadecyltrimethylammonium bromide (*CTABr*)

Surfactant	TADPS	DTABr	CTABr
Active matter (%)	31.6	99.4	99.8

x_1^s and β^s calculated according to the nonideal adsorption theory are shown in Tables 2 and 3. The great negative β^s values in Table 2 indicate a strong synergism in the surface tension reduction efficiency. For each mixed system, although β^s decreases a little with increasing surface pressure, it can be taken as constant in a wide range of mixing ratios (-15.78 ± 0.48 for $\alpha = 0.1 - 0.7$, -16.44 ± 0.40 for $\alpha = 0.25 - 0.75$ for TADPS with DTABr and CTABr, respectively). Thus, although TADPS is not a single surfactant, it behaves as a pure one when mixed with another surfactant, showing a definite β^s value. In fact, the monomer distribution in such a commercial surfactant is constant below the cmc, and only above the cmc (i.e. beyond the range considered in the discussion of mixed adsorption) does this distribution change because the more surface-active species enters the micelle preferentially [33]. This implies that the nonideal theory is also applicable to binary systems where at least one component is a "homogeneous" mixture (i.e. containing homologues with different chain lengths and/or various numbers of ethylene oxide units). On the other hand, the average values of β^s for these mixed systems indicate that the interaction between the two surfactants increases with alkyl chain length [5].

After Eqs. (17) and (18) the nonideal adsorption theory assumes that the molar area of a surfactant in a mixed monolayer is the same as in its pure monolayer. Gu and Rosen [34], however, showed that this reference might not be appropriate for binary systems with strong interactions ($\beta^s < -5$). Therefore, since in some anionic/cationic systems the difference between the calculated β^s values at low and high surface pressure can exceed 15%, they suggested modifying the nonideal adsorption theory, taking into account the difference between the surfactant molar areas in pure and mixed monolayers. Now, this phenomenon has not been observed in the present work. Furthermore, the required modifications would make it difficult to derive such a simple surface tension equation for binary surfactant mixtures.

The surface tensions of pure and mixed surfactant solutions calculated using the Szyszkowski Eqs. (19) and (29), respectively (parameters in Table 4), are illustrated in Figs. 1 and 2 together with the experimental values. For each system, the x_1^s and β^s values used in the prediction are calculated from one surface tension measurement on a mixed solution. The variations of x_1^s as a function of α are illustrated in Fig. 3. The results show that the Szyszkowski equation fits the experimental values very well for individual surfactant solutions. For binary systems, surface tension prediction by Eq. (29) is successful within experimental uncertainty, but at higher surface pressures (near γ_{cmc} of individual surfactant solutions) the values predicted by Eq. (27) or Eq. (28) begin to deviate from the experimental ones. According to Gu and Rosen [34], the molar area of a surfactant in a mixed monolayer, A_1, may not be exactly the same as in the "pure" monolayer, A_1^0, at higher

Table 2 Surface properties of the TADPS(1)/DTABr(2) system at 25 °C: composition of the adsorption layer and the interaction parameter (β^s). α is overall mole fraction of surfactant 1 with respect to the total surfactant concentration x_1^s is the mole fraction of surfactant 1 in the adsorbed layer and π is the surface pressure. Average $\beta^s = -15.78 \pm 0.48$

α	0.1		0.3		0.5		0.7	
π (mN m^{-1})	x_1^s	β^s	x_1^s	β^s	x_1^s	β^s	x_1^s	β^s
10	0.561	−16.1	0.604	−15.5	0.633	−14.8	0.658	−14.8
15	0.567	−15.8	0.606	−15.6	0.632	−15.4	0.660	−15.0
20	0.566	−15.5	0.604	−15.8	0.628	−15.7	0.655	−15.4
25	0.564	−15.6	0.599	−16.0	0.622	−16.1	0.648	−15.9
30	0.558	−15.7	0.594	−16.1	0.616	−16.2	0.640	−16.1
35	0.555	−15.9	0.591	−16.3	0.612	−16.5	0.635	−16.4

Table 3 Surface properties of the TADPS(1)/CTABr(2) system at 25 °C. Average $\beta^s = -16.44 \pm 0.40$

a	0.25		0.5		0.6		0.75	
π (mN m^{-1})	x_1^s	β^s	x_1^s	β^s	x_1^s	β^s	x_1^s	β^s
10	0.529	−16.0	0.559	−16.1	0.572	−15.7	0.592	−15.7
15	0.529	−16.2	0.559	−16.5	0.571	−16.0	0.591	−15.9
20	0.528	−16.5	0.556	−16.3	0.568	−16.4	0.588	−16.1
25	0.523	−16.6	0.552	−17.0	0.563	−16.6	0.582	−16.6
30	0.516	−16.6	0.545	−17.2	0.556	−16.8	0.575	−16.6
35	0.510	−16.5	0.538	−17.1	0.549	−16.9	0.568	−16.6

Table 4 Parameters for surface tension prediction

Mixtures	TADPS/DTABr	TADPS/CTABr
Γ^x_{R-} (mol cm^{-2})	2.20×10^{-10}	2.20×10^{-10}
K_1	1.20×10^5	1.20×10^5
Γ^n_{R+} (mol cm^{-2})	3.52×10^{-10}	3.69×10^{-10}
K_2	5.32×10^2	6.30×10^3
β^s	−16.05	−16.17

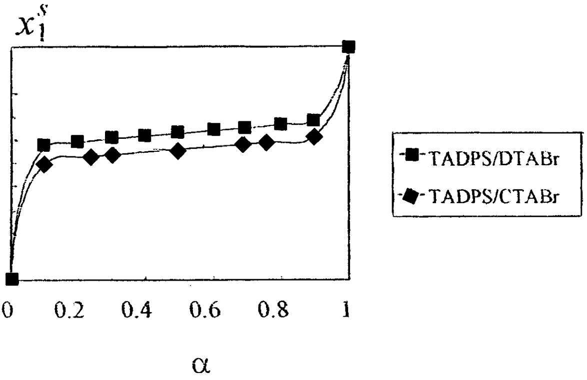

Fig. 3 Dependence of anionic/cationic mixed monolayer composition on bulk composition at 25 °C, calculated using Eq. (24)

surface pressure, for the systems studied. As indicated by a lower Γ^∞_{R-} value (Table 4), A_1^0 for TADPS is much larger than A_2^0 for the cationics, which show higher Γ^∞_{R+} values, and so, with increasing surface pressure, the differences between A_1^0 and A_1 and A_2^0 and A_2 appear in opposite directions. Thus, since Eq. (29) is the average of Eqs. (27) and (28), the deviations may well cancel each other. Anyway, the most useful mixed surfactant systems are ionic/nonionic ones, whose β^s values are less negative ($\beta^s > -5$). Even with more strongly interacting systems (e.g. anionic/cationic), addition of excess inorganic electrolytes greatly decreases β^s absolute values. It is thus expected that the surface tension equations developed in this paper apply to a large range of systems.

Tables 2 and 3 and Fig. 3 also show that x_1^s changes with mixing ratio and that the composition at the air/solution interface is not equimolar but slightly asymmetric in a wide range of compositions. Usually, for mixtures of anionic/cationic surfactants with similar surface activity, the surface phase is an equimolar mixture [1, 15, 35], whereas for mixtures of surfactants with different surface activities, the mole fraction of the more surface-active species is larger in the surface phase [6, 7, 9, 35]. Now, the surface activities of the species considered here range in the order TADPS > CTABr > DTABr; so, TADPS has priority in surface adsorption and the asymmetry in the surface phase composition intensifies with increasing surface activity difference

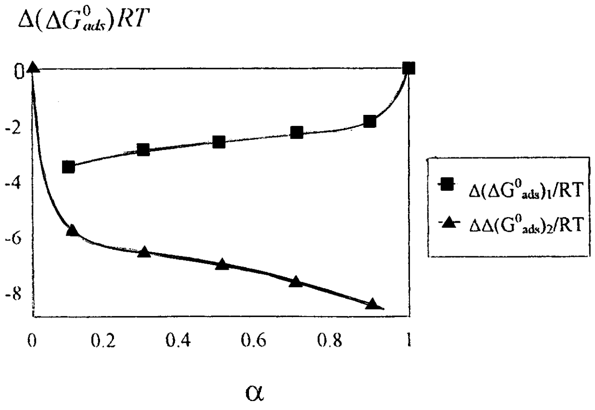

Fig. 4 Difference between the free adsorption energies of TADPS (■) and DTABr (▲) in mixed and pure monolayers

between anionic and cationic surfactants, as illustrated in Fig. 3.

The strong synergism shown by anionic/cationic mixtures in the surface tension reduction efficiency can be explained by the great decrease in the adsorption free energy, ΔG^0_{ads}, of each surfactant. For nonionic surfactants, ΔG^0_{ads}, can be calculated using the relationship [27]

$$\Delta G^0_{ads} = -RT \ln \omega K \ , \tag{31}$$

where ω is the molar concentration of water at temperature T and K is the constant in the Szyszkowski equation. For a binary mixture, Eq. (22) can be written

$$\gamma_0 - \gamma_{12} = RT\Gamma_1^\infty(1 + K_1'\alpha c_{12}) \ , \tag{32}$$

where

$$K_1 = K_1/f_1^s x_1^s \ . \tag{33}$$

Thus, the difference between the adsorption free energies in the mixed and in the pure monolayer is

$$\begin{aligned}\Delta(\Delta G^0_{ads})_1 &= -RT\ln(\omega K_1') + RT\ln(\omega K_1) \\ &= RT\ln f_1^s x_1^s = RT[\ln x_1^s + \beta^s(1 - x_1^s)^2] \ ,\end{aligned} \tag{34}$$

For ionic surfactants, Eq. (31) is not exact because of the presence of Coulombic energy, but Eq. (34) is acceptable with the assumption that, in the difference $\Delta(\Delta G^0_{ads})$, the Coulombic energy terms cancel each other [27]. Similarly

$$\Delta(\Delta G^0_{ads})_2 = RT[\ln(1 - x_1^s) + \beta^s(x_1^s)^2] \ . \tag{35}$$

Since x_1^s and $(1 - x_1^s)$ are always smaller than 1 and $(x_1^s)^2$ and $(1 - x_1^s)^2$ are always positive, when $\beta^s < 0, \Delta(\Delta G^0_{ads})$ must be negative. For instance, the variations of $\Delta(\Delta G^0_{ads})_i$ for the TADPS/DTABr system are represented in Fig. 4. This figure deserves two comments: firstly, the absolute value of $\Delta(\Delta G^0_{ads})_i$ increases when the mixture becomes poorer in surfactant i; secondly, the surfactant with the lower surface activity shows a larger difference in adsorption free energy. This is reasonable since, if the anionic/cationic mixed monolayer has a nearly equimolar composition, the higher the difference in surface activity or the lower the mole fraction in the mixed solution, the larger the difference in adsorption between mixed and pure monolayers.

Another interpretation for the strong synergism in the surface tension reduction efficiency is the remarkable decrease in the area occupied by the surfactant hydrocarbon chains, or the more compact arrangement of the latter in the mixed monolayer. Remembering the equalities (Eqs. 17, 18) and considering that the monolayer should be electrically neutral, one must assume that, in an anionic/cationic mixed monolayer, surface-active ions replace partly (nonequimolar monolayer) or completely (equimolar monolayer) the counterion of the other (oppositely charged) surfactant. Thus, the area occupied by each hydrocarbon chain is greatly reduced and, in the particular case of an equimolar monolayer, is reduced to half that occupied in a pure monolayer. This interpretation can also be drawn from the analysis of the $\gamma - \log c$ curves (Figs. 1 and 2). The Gibbs equation for a pure surfactant solution can be expressed as

$$-\mathrm{d}\gamma = \Sigma\Gamma_i^0 \mathrm{d}\mu_i^0 = RT\Sigma\Gamma_i^0 \mathrm{d}\ln c_i^0 = 2RT\Gamma_\mathrm{R} \mathrm{d}\ln c_\mathrm{R}^0 \ , \quad (36)$$

whereas for anionic/cationic systems at a fixed α, the mixed monolayer has an almost equimolar composition and the adsorption of inorganic ions can be neglected. The Gibbs equation then becomes

$$\begin{aligned} -\mathrm{d}\gamma &= RT\Sigma\Gamma_i \mathrm{d}\ln c_i \sim RT(\Gamma_{\mathrm{R}-} + \Gamma_{\mathrm{R}+}) \mathrm{d}\ln c_{\mathrm{R}+} \\ &= RT(\Gamma_{\mathrm{R}-} + \Gamma_{\mathrm{R}+}) \mathrm{d}\ln c_{\mathrm{R}-} \ . \quad (37) \end{aligned}$$

From Figs. 1 and 2 it is obvious that, at a given surface pressure, the slope of the Gibbs isotherm is generally larger for a mixture $(-\mathrm{d}\gamma/\mathrm{d}\ln c_{\mathrm{R}+})$ than for a pure solution $(-\mathrm{d}\gamma/\mathrm{d}\ln c_\mathrm{R}^0)$. The sum $(\Gamma_{\mathrm{R}-} + \Gamma_{\mathrm{R}+})$ is accordingly larger than $2\Gamma_\mathrm{R}^0$. If x_1^s is taken to be 0.5 and Γ_R^0 is assumed to be the average of $\Gamma_{\mathrm{R}-} + \Gamma_{\mathrm{R}+}$, the results agree quite well with Eqs. (17) and (18), i.e. the total adsorption of the hydrocarbon chains doubles in a mixed monolayer with respect to pure monolayers. These predictions totally agree with the results of Lucassen-Reynders et al. [15].

Conclusions

1. The adsorption behavior of the two systems studied (TADPS/DTABr and TADPS/CTABr) can be well described by the extended nonideal theory of mixed adsorption. The large negative interaction parameters (from −15.8 to −16.4) show that the strong synergism in the surface tension reduction efficiency increases with the alkyl chain length of the cationic surfactant.

2. The surface tension of anionic/cationic binary solutions can be predicted by an equation derived from the Szyszkowski equation combined with nonideal adsorption theory. Good agreement is obtained between predicted and experimental values.

3. The composition of the mixed monolayer is mixing-ratio dependent and is asymmetric. For equimolar mixtures ($\alpha = 0.5$), the mole fraction of the more surface-active component is larger.

4. The strong synergism in the surface tension reduction efficiency in these systems can be interpreted by the more negative adsorption free energy of each surfactant and the smaller area occupied by each hydrocarbon chain in the mixed monolayer.

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