ISSN 0027-1314, Moscow University Chemistry Bulletin, 2007, Vol. 62, No. 3, pp. 147–151. © Allerton Press, Inc., 2007.
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Interactions between Nonpolar Surfaces in Mixed Solutions of Cationic and Nonionic Surfactants

N. I. Ivanova, A. M. Parfenova, and E. A. Amelina

Colloid Chemistry Department
e-mail: ini@colloid.chem.msu.ru

Received September 7, 2006

Abstract—The interaction energy between hydrophobic SiO_2 particles in aqueous solutions of a cationic surfactant (dodecylpyridinium bromide, DDPB), a nonionic surfactant (Triton X-100, TX-100), and their mixed solutions was measured as a function of concentration. Synergism has been observed in mixed surfactant solutions: the surfactant concentration required for achieving the set interaction energy in the mixed solutions was lower than in the solutions of the individual surfactants. The molecular interaction parameters in surfactant mixtures were calculated using the Rosen model. Chain–chain interactions between nonionic and cationic surfactants were suggested as the main reason for the synergism.

DOI: 10.3103/S002713140703008X

Surfactants, being diphilic, can be adsorbed at various interfaces, including solid/surfactant solution interfaces. This adsorption can dramatically alter the properties of the interface; it can also affect the wetting of the solid surface and interactions between solid particles in various media, i.e., the stability of disperse systems [1]. Rapid progress has recently been observed in the field of investigation of mixed surfactant systems. This progress is due to the appearance of synergism in mixed solutions of surfactants of different characters: reciprocal enhancement of surfactant effects can occur. Synergism can appear differently: as a decrease in the surface tension at surfactant solution/air interfaces, micelle formation in surfactant solutions, adsorption of surfactants at solution/air interfaces, adsorption of surfactants at solid/surfactant solution interfaces, and others [2].

This work examines the interaction energy between two nonpolar solid surfaces in mixed aqueous solutions of two surfactants (one cationic and the other nonionic) and compares the interactions between cationic and nonionic surfactants at nonpolar solid/surfactant solution and surfactant solution/air interfaces.

EXPERIMENTAL

Dodecylpyridinium bromide (DDPB) was used as the cationic surfactant (hereafter, c-surfactant), and Triton X-100 (TX-100) was used as the nonionic surfactant (hereafter, n-surfactant). Dodecylpyridinium bromide before use was purified by recrystallization from ethyl acetate as described in [3]. The purification was verified by the absence of a minimum on the surface tension isotherm. Triton X-100 (polyoxyethylene glycol *p-tert*-octylphenyl ether with the average degree of ethoxylation equal to 9.5 from Ferak, analytical grade) was used as received.

Mixed aqueous solutions of surfactants were prepared using bidistilled water with the surface tension 72.5 mJ/m^2 and the electrical conductivity (2–3) × 10^{-6} Ω^{-1} cm^{-1}. The n-surfactant mole fraction α was varied as follows: 0, 0.2, 0.4, 0.6, 0.8, and 1.0.

The surface tension of solutions was measured by the Wilhelmi method (using a platinum plate) on a Techniprot BT-5 tensiometer. The measurement accuracy was ±0.5 mJ/m^2.

Test samples to measure cohesive forces were spherical drops, which were obtained from glass capillaries ~1 mm in diameter pulled from a glass pipe. The diameters of the spherical samples determined with a microscope were 1.5–2 mm. Surface methylation was performed by exposure to dimethyldichlorosilane vapor at room temperature for 10 h followed by chloroform rinsing.

The prepared samples were dipped into water and brought in contact with one another; then, the force required for separating them, i.e., the coercive force in water, was measured. Next, a calculated amount of the concentrated surfactant solution was added to water (and then to the solution) without removing the samples. The total amount of the solution was about 100 mL. Samples were exposed without contact for 3 h. After this time, the samples were brought into contact with one another without pressing and kept in contact for 10 s; then, with a detachment force applied, the coercive force (i.e., the force required for breaking particles away from each other) was measured. At least ten replicate experiments were carried out; the mean deviation was within 10%. A magnetoelectric device designed at the Colloid Chemistry Department [4] was

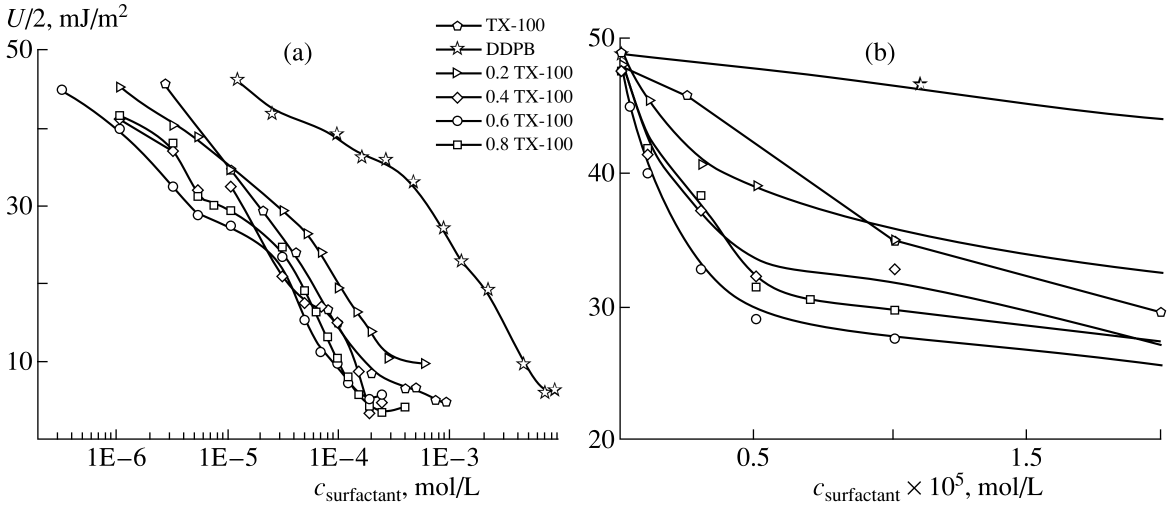

Fig. 1. Panel (a): the interaction energy between two nonpolar solid surfaces vs. the concentration of DDPB, TX-100, and their mixed solutions with the TX-100 mole fraction α equal to 0.2, 0.4, 0.6, and 0.8 of the total surfactant concentration in the solution. Panel (b): the initial portion of the curve.

used to measure coercive forces. The interaction energy *U* was derived from the experimentally measured interaction force *F* using the relationship [5]

$$U = F/\pi r,$$

where *r* is the radius of contacting spherical particles.

The samples chosen for the experiments had the interaction energy in water equal to 48 ± 2 mJ/m^2. All experiments were carried out at room temperature.

RESULTS AND DISCUSSION

It was shown in [6] that the interaction energy for nonpolar solid surfaces equals the doubled specific free energy of these surfaces. For the interaction between nonpolar surfaces in surfactant solutions, the $U/2 = f(c)$ curve is the surface tension isotherm at the nonpolar surface/solution interface [4, 5]. This isotherm can be fitted by the Gibbs equation [7, 8]

$$\Gamma = -\frac{c}{RT}\frac{d(U/2)}{dc}. \tag{1}$$

Here, Γ is the adsorption at the solid/surfactant solution interface, *c* is the surfactant concentration in the solution, *R* is the gas constant, and *T* is temperature.

Figure 1 demonstrates the results of the coercive force measurements in solutions of individual surfactants and their mixtures. We draw the following inferences from the data in Fig. 1: (1) in solutions of individual surfactants, the interaction energy between two nonpolar surfaces decreases more strongly in TX-100 than in DDPB; (2) for the solutions in which the n-surfactant mole fraction is 0.4, 0.6, or 0.8, the $U/2 = f(\log c)$ curve over a wide range of the concentrations lies lower than the analogous curves for DDPB and TX-100, which proves the existence of specific interactions between adsorbate surfactant molecules [2]; and (3) a minimum *U*/2 value is achieved at a certain surfactant concentration, and this value remains unchanged at higher surfactant concentrations.

Evidently, the decrease in the interaction energy between two hydrophobic surfaces in surfactant solutions is due to the absorption of surfactants on the solid surface. Adsorption in this case is due to dispersion forces between the surfactant chain and the nonpolar solid surface [1, 9]. These interactions orient the polar group of the surfactant to the bulk solution, and the surface hydrophilicity will increase with rising surfactant concentration until a saturated adsorbate layer is formed on the solid surface. The concentration at which the saturated adsorbate layer is formed is referred to as the critical admicelle concentration (CAC) [10]. Table 1 lists the maximum adsorption values found from $U/2 = f(c)$.

The concentration at which the saturated adsorbate layer is formed is determined from the break on the $U/2 = f(c)$ curve (Fig. 1a). In an ideal system, the concentration corresponding to CAC for a surfactant mixture (c_{12}) as a function of composition is described by

$$\frac{1}{c_{12}} = \frac{\alpha_1}{c_1^0} + \frac{(1-\alpha)}{c_2^0}, \tag{2}$$

where α_1 is the mole fraction of the n-surfactant in the solution and c_1^0 and c_2^0 are the CACs in TX-100 and DDPB solutions, respectively.

The experimental $c_{12} = f(\alpha_1)$ curve shows a negative deviation from the curve for the ideal system (which is shown by a dashed line). The maximum negative anomaly is observed for $\alpha_1 = 0.6$. Thus, synergism in this case appears as a decreased surfactant concentration providing the maximal adsorption on the solid surface.

According to Rosen's ideas [2], a negative anomaly is caused by the effect of attractive forces between different surfactants; these attractive interactions are characterized by the interaction parameter β:

$$\beta = \frac{E_{11} + E_{22} - E_{12}}{RT}. \qquad (3)$$

Here, E_{11}, E_{22}, and E_{12} are the interaction energies between similar (surfactant 1 or surfactant 2) molecules and E_{12} is the interaction energy between surfactant 1 and surfactant 2 molecules. The interaction parameter at the hydrophobic solid/surfactant solution interface with the formation of a mixed saturated adsorbate layer is calculated from the following equations [9, 11]:

$$\frac{X_1^2 \ln(\alpha_1 c_{12}/X_1 c_1^0)}{(1 - X_1)^2 \ln[(1 - \alpha_1)c_{12}/(1 - X_1)c_2^0]} = 1, \qquad (4)$$

$$\beta^\Gamma = \frac{\ln(\alpha_1 c_{12}/X_1 c_1^0)}{(1 - X_1)^2}. \qquad (5)$$

Here, X_1 is the TX-100 mole fraction in the mixed layer at the solid/surfactant solution interface and c_1^0, c_2^0, and c_{12} are the concentrations required for achieving the ultimately saturated adsorbate layer of TX-100, DDPB, and their mixtures, respectively. Equation (4) is numerically solved for X_1, which is then substituted into Eq. (5) in order to calculate β^Γ, the interaction parameter between surfactant molecules and ions in the adsorbate layer.

The data listed in Table 2 imply that, when $\alpha_1 < 0.6$, the mixed adsorbate layer on the surface is enriched in n-surfactant molecules. Synergism for the formation of a mixed adsorbate layer on solid surfaces is observed over the whole range of the TX-100/DDPB ratios. The absolute value of the maximal anomaly is found in the surfactant mixture with the TX-100 mole fraction equal to 0.6.

An analogue of relationship (1) can be used to describe the formation of a sparse adsorbate layer at the solid/mixed surfactant solution interface. In this case, c_1^0, c_2^0, and c_{12} are, respectively, the TX, DDPB, and mixed surfactant concentrations required for achieving the set $U/2$ value. Example correlations are demonstrated in Fig. 3 for $U/2$ equal to 45 and 40 mJ/m^2. One can see from these curves that the maximum nonideality is also observed for $\alpha_1 = 0.6$. Table 3 lists the compositions of the sparse adsorbate layers calculated for $U/2 = 45$ mJ/m^2. It follows that synergism in the formation of sparse adsorbate layers is greater (β^Γ has a higher absolute value) at low surfactant concentrations, and the adsorbate layers at low α_1 are also enriched in TX-100 molecules. The dominance of the n-surfactant in the adsorbate layer can be due to the higher activity of TX-100 molecules on the solid/surfactant solution

Table 1. Surface activity (G^σ), adsorption activity (G^Γ), maximum adsorption (Γ_m), and surface area (s) per molecule upon the maximum adsorption at surfactant solution/air (L/G) and nonpolar solid/surfactant solution (S/L) interfaces as functions of TX-100 mole fraction (α) in a mixed aqueous solution of surfactants

α	G^σ	G^Γ	Γ_m, 10^{-6} mol/m^2		s, 10^{-20} m^2	
	mJ/(m^2 mol)					
	L/G	S/L	L/G	S/L	L/G	S/L
0	1.4×10^4	2.0×10^5	3.2	4.7	52	35
0.2	4.2×10^5	3.7×10^6	2.8	3.8	59	44
0.4	1.1×10^6	7.9×10^6	3.2	6.2	52	27
0.6	7.7×10^5	1.2×10^7	3.2	3.3	52	51
0.8	1.2×10^6	6.7×10^5	3.6	5.2	48	32
1.0	5.3×10^5	1.4×10^6	2.9	3.4	57	47

Table 2. Interaction parameter β^Γ and TX-100 mole fraction in a saturated mixed adsorbate layer

TX-100 molefraction in the bulk of the mixed surfactant solution	Interaction parameter β^Γ	TX-100 mole fraction in the mixed adsorbate layer
0	–	0
0.2	–6.5	0.6
0.4	–6.8	0.7
0.6	–8.3	0.7
0.8	–5.4	0.8
1	–	1

Table 3. Interaction parameter β^Γ and TX-100 mole fraction in a sparse adsorbate layer for $U/2 = 45$ mJ/m^2

TX-100 mole fraction in the bulk of the mixed surfactant solution	Interaction parameter β^Γ	TX-100 mole fraction in the mixed adsorbate layer
0	–	0
0.2	–6.9	0.5
0.4	–10	0.5
0.6	–11.7	0.6
0.8	–9.8	0.8
1	–	1

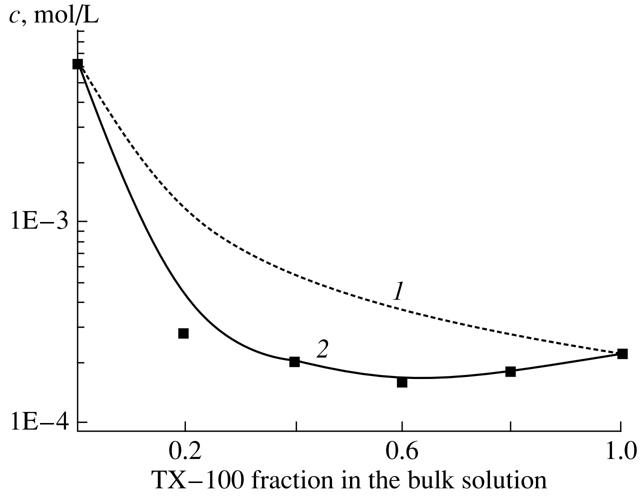

Fig. 2. Concentration required for achieving the maximal adsorption on a solid surface in solutions of DDPB, TX-100, and their mixtures vs. TX-100 mole fraction: (*1*) the curve calculated for the ideal mixture and (*2*) the experimental curve.

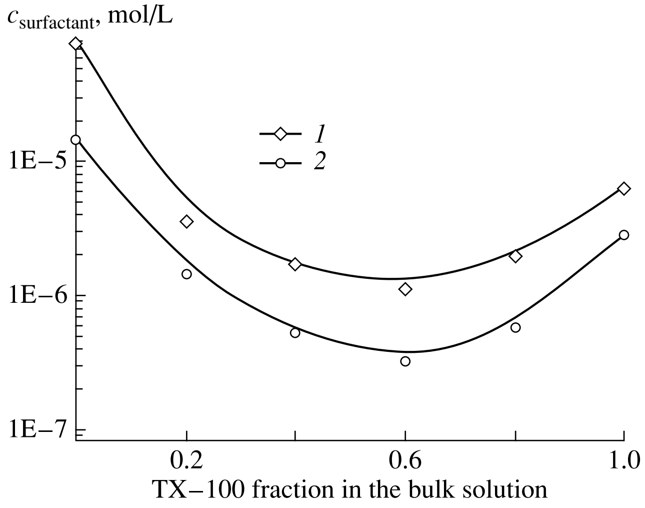

Fig. 3. Concentration of a DDPB + TX-100 mixture required for achieving the set $U/2$ value equal to (*1*) 40 and (*2*) 45 mJ/m^2 vs. TX-100 mole fraction in the solution.

interface compared to the activity of DDPB. The surfactant activity at the nonpolar solid/aqueous surfactant solution interface can be determined, by analogy with the surface activity, as

$$G^{\Gamma} = \lim_{c \to 0}\left(\frac{dU/2}{dc}\right).$$

The adsorption activity of surfactants is a nonmonotonic function of the mixture's composition, and the highest value is observed in the solution with the n-surfactant mole fraction equal to 0.6 (Table 1).

Thus, our experiments show synergism in the adsorption of surfactants on hydrophobic surfaces over the whole range of the DDPB and TX-100 ratios in mixed solutions. Synergism is maximal in mixed solutions with $\alpha_1 = 0.6$. Presumably, chain–chain dispersion interactions between surfactants adsorbed on the nonpolar solid surface are the main reason for the formation of mixed aggregates on the solid surface.

Previously [12], synergism in DDPB/TX-100 mixtures was only manifested as a decrease in the interfacial tension at the mixed surfactant aqueous solution/air interface and was not observed for micelle formation. The mixed adsorbate layer on the aqueous solution/air interface is enriched in n-surfactant molecules, and the maximum absolute value of the interaction parameter between n-surfactant and c-surfactant molecules corresponds to $\alpha_1 = 0.6$.

We should note that the interaction parameters for this TX-100 mole fraction at the nonpolar solid/aqueous surfactant solution interface are close in their absolute values to the interaction parameters at the aqueous surfactant solution/air interface.

Let us compare some properties to characterize adsorption at a mixed surfactant aqueous solution/air interface and a mixed surfactant solution/nonpolar solid interface. From the data listed in Table 1, one can see that the activity at the nonpolar solid/surfactant solution interface is higher than at the surfactant solution/air interface for both individual surfactants and their mixtures. These different activities can arise from the existence of dispersion interactions between surfactant molecules or ions and the nonpolar solid surface. The maximum adsorptions on the solid are also higher, as well as the surface area per molecule in the adsorbate layer is smaller, than at the solution/air interface. These results imply that surfactants are adsorbed on the solid surface as aggregates in agreement with the related literature [13–16].

Having studied the interaction energy between two nonpolar surfaces in solutions of cationic and nonionic surfactants and their mixed solutions, we found that the interaction energy decreases with increasing surfactant concentration to acquire values lower than 10 mJ/m^2. The interaction energies in mixed surfactant solutions are lower than in solutions of the individual surfactants. Having compared the properties of mixed surfactant solutions at aqueous solution/air interfaces and hydrophobic solid/mixed surfactant solution interfaces, we found that synergism in both cases appears over a wide concentration range with the formation of either a saturated mixed adsorbate layer or a sparse adsorbate layer. The compositions of the adsorbate layers at nonpolar solid/mixed surfactant solution interfaces have been calculated using the Rubin–Rosen model; the layers are enriched in the nonionic surfactant. Chain–chain interactions between the nonionic and cationic surfactants with the formation of mixed aggregates are suggested as the main cause of synergism.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 05-03-32555).

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