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Adsorptive Modification of Hydrophobic Solid Surfaces by Mixed Surfactant Solutions

A. V. Kostenko and O. A. Soboleva
Department of Colloid Chemistry
e-mail: soboleva@colloid.chem.msu.ru

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Abstract—We studied the reciprocal influence of a nonionic surfactant (triton X-305) and a cationic surfactant (tetradecyltrimethylammonium bromide; TTAB) on their adsorption from aqueous solution on hydrophobic glass, interfacial tension at the solution/solid interface, composition of the mixed adsorption layer, and interaction parameters between surfactant molecules in mixed adsorption layers.

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Studies of the properties of surfactant mixtures are of great applied importance, in particular, in cosmetics and pharmaceuticals, detergents, flotation, chemical industry, coatings, and all other fields of industry where surfactants are used. The behavior of surfactant mixtures in micelle formation and adsorption at aqueous surfactant solution/air interfaces has been studied quite comprehensively. Adsorption of surfactant mixtures on solid adsorbents has been studied much less; the effect of surfactant mixtures on the interfacial energy at solution/solid interfaces is almost unstudied. Intentionally altering the properties of solid surfaces by means of surfactants, one can control the stability of suspensions and sols and regulate wetting, capillary flow, and adhesion.

Our task in this work was to study the effect of mixtures of cationic and nonionic surfactants on the interfacial energy and adsorption at aqueous solution/apolar solid interfaces. We employed a set of techniques including measurements of contact interactions, capillary rise, and adsorption, which gave us sufficient data on the interfacial behavior of surfactant mixtures.

SUBJECTS

We used the following surfactants: cationic tetradecyltrimethylammonium bromide (TTAB) from Merck (with critical micelle concentration CMC = 4×10^{-2} mol/L) and nonionic ethylene glycol *p-tert*-octylphenyl ether (Triton X-305, TX-305) from Ferak Berlin (CMC = 10^{-3} mol/L). Both surfactants were 98% pure. The solutions used in experiments had overall concentrations c of 10^{-6} to 10^{-2} mol/L; the mole fraction of the nonionic surfactant α was 0.5, 0.2, and 0.05. The solutions were prepared by consecutive dilution with distilled water (with electrical conductivity $\kappa = 2 \times 10^{-6}$ S/cm). Experiments were carried out at room temperature: (22–25)°C.

The solid surface used was hydrophobic glass. Fused glass is a molecular smooth surface; when it is made hydrophobic, the resulting surface is chemically stable and has reproducible characteristics [1]. Samples for contact interaction measurements were prepared from newly pulled glass capillaries. Capillary rise experiments employed glass capillaries from the Skhodnya plant with the inner radius $r_0 = (0.30 \pm 0.02)$ mm. All glass samples and capillaries were made hydrophobic by exposure to dimethyldichlorosilane vapor (DMCS, Fluka, 98% pure) at room temperature for 24 h followed by chloroform washing. The specific surface energy σ_{sl} at the sample/water (S/L) interface derived from the results of measurements was (52 ± 3.5) mJ/m^2, which can serve as evidence in favor of the complete hydrophobicity of glass. The water contact angle θ in hydrophobic capillaries was $(105 \pm 0.7)°$. This value is also indicative of an almost complete hydrophobicity of the surface [2, 3].

Surfactant adsorption was studied on quartz sand (Sigma, specific surface area $S_{\text{sp}} = 0.03$ m^2/g). This sand was made hydrophobic by exposure for 48 h to a 2% DMCS solution in chloroform followed by washing with neat chloroform and drying in air.

METHODS

The surface tension σ_{lv} of individual and mixed surfactant solutions was measured by the maximum pressure in the bubble method.

σ_{sl} was determined via contact interaction measurements [1]. Once the attraction strength between convex solid surfaces in a solution, $F(h)$, has been determined, one can calculate the interfacial tension at the solid/liquid interface from

$$\sigma_{sl} = F(h)/2\pi k, \tag{1}$$

where k is a geometric parameter determined by the curvature of contacting surfaces. For two spherical surfaces with different radii (r' and r''), $k = 2r'r''/(r' + r'')$. The radii r' and r'' for each pair of contacting samples were determined with a horizontal microscope. The curvature radius of spherical samples averaged 1 mm.

TX-305 and TTAB adsorption on hydrophobic quartz sand was determined as the decrease in surfactant concentration in solution:

$$\Gamma = (c_0 - c_{\mathrm{eq}})V/(mS_{\mathrm{sp}}), \tag{2}$$

Here, V is solution volume, m is adsorbent weight, and c_0 and c_{eq} are initial and equilibrium concentrations of surfactant solutions.

Spectrophotometry was used to study TX-305 adsorption [4]. Absorption spectra for TX-305 solutions were taken on a Agilent 8453 spectrophotometer (Agilent Technologies).

TTAB adsorption on hydrophobic quartz sand was determined using a tritium label [5, 6]: when labeled TTAB dissolves in water, the radioactivity of the solution is proportional to its concentration. Radioactivity was determined on an LKB-Wallac Rack Beta 1215 liquid scintillation spectrometer. This method makes it possible to determine the initial and equilibrium concentrations of solution from its radioactivity and to calculate adsorption from Eq. (2).

Another way we used to determine the parameters of an adsorption layer at the hydrophobic glass/surfactant solution interface was capillary rise measurements. In finding the simultaneous solution of the Gibbs and Young equations, adsorption at aqueous/low-energy solid interface, Γ_{sl}, can be calculated from

$$\Gamma_{sl} = \frac{c}{nRT}\frac{d(\sigma_{lv}\cos\theta)}{dc}, \tag{3}$$

where θ is contact angle in the hydrophobic glass/surfactant solution/air system, σ_{lv} is surface tension at the surfactant solution/air (L–V) interface, R is universal gas constant, T is absolute temperature, $n = 1$ for nonionic surfactant, and $n = 2$ for cationic surfactant [7–11].

Capillary rise measurements give the product $\sigma_{lv}\cos\theta$ from the capillary rise height H for aqueous surfactant solutions in hydrophobic capillaries with radius r_0:

$$\sigma_{sv}\cos\theta = 1/2Hr_0\rho g. \tag{4}$$

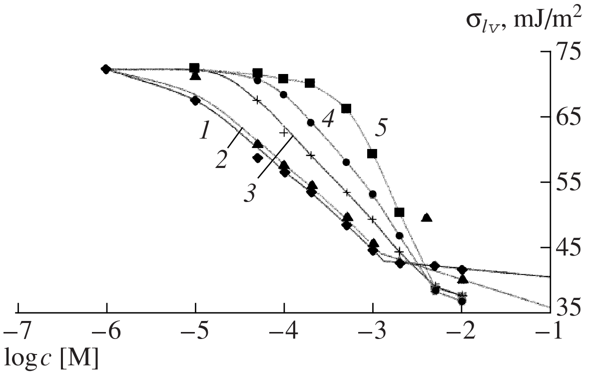

Fig. 1. Surface tension isotherms for (*1*) TX-305 solution, (*5*) TTAB solution, and (*2*–*4*) mixed solutions with the TX-305 mole fraction α = (*2*) 0.5, (*3*) 0.2, and (*4*) 0.05.

Here, ρ is surfactant solution density and g is gravity acceleration. A KM-6 cathetometer was used to measure H and r_0.

RESULTS AND DISCUSSION

Figure 1 displays surface tension isotherms for TTAB, TX-100, and their mixtures. From the surface tension isotherms of the individual surfactants, we calculated surfactant adsorption at the solution/air interface and determined the maximal adsorption $\Gamma_{\max}$, adsorption activity A, and the surface area per surfactant molecule in the saturated adsorption layer, S_l (Table 1). We found that TTAB forms quite close-packed adsorption layers and decreases the surface tension to lower values than TX-305 does. The adsorption activity of TX-305 is far higher than for TTAB. However, the bulky polar group of TX-305 is responsible for the greater surface area per molecule in its saturated adsorption layer and the smaller decrease in surface tension on entering the plateau compared to TTAB.

We used the model from [12, 13] to calculate TX-305 mole fractions, X^{lv}, in adsorption layers at the solution/air interface (Fig. 2) and interaction parameters β_{lv} in them (Table 2). The empty cells in Table 2 refer to the complete displacement of TTAB by TX-305 from the adsorption layer ($X^{lv} = 1$). Calculations show that adsorption layers are enriched in TX-305, with the TX-305 fraction in mixed adsorption layers decreasing

Table 1. Parameters of adsorption layers at solution/air and solution/hydrophobic glass interfaces

Surface	Solution/air		Solution/hydrophobic glass			
			contact interactions		capillary rise	
Surfactant	TX-305	TTAB	TX-305	TTAB	TX-305	TTAB
$\Gamma_{\max}$, mol/m^2	2.8×10^{-6}	3.5×10^{-6}	4.1×10^{-6}	1.9×10^{-6}	2.9×10^{-6}	2.2×10^{-6}
S_1, nm^2	0.60	0.48	0.40	0.87	0.58	0.75
A, L/mol	50805	1269	222820	13480	106329	2524

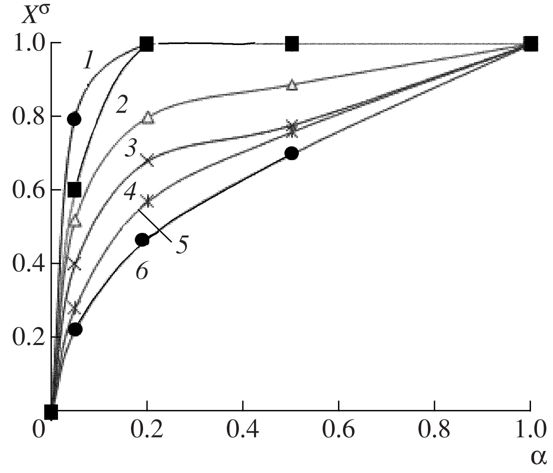

Fig. 2. TX-305 mole fraction in the adsorption layer, X^{lv}, vs. TX-305 mole fraction in solution, α, for σ_{lv} = (*1*) 70, (*2*) 65, (*3*) 60, (*4*) 55, (*5*) 50, and (*6*) 45 mN/m.

with an increase in the total surfactant concentration in solution. The interaction parameters are negative, indicating attraction between the components in adsorption layers. In their absolute values, the interaction parameters are small; that is, attraction between TX-305 and TTAB molecules is very weak.

The effect of surfactant mixtures on the properties of aqueous solution/hydrophobic glass interfaces was studied using data on the strength of contact interactions between methylated glass samples in aqueous surfactant solutions, capillary rise of solutions in hydrophobic capillaries, and surfactant adsorption from individual and mixed solutions.

Contact interaction measurements between molecularly smooth spherical hydrophobic glass samples show that cohesive strength acquires a steady-state value in a period ranging from 24 h for solutions with $c = 10^{-7}$ to 10^{-6} mol/L to 20 min for solutions with $c = 10^{-4}$ mol/L or higher. Figure 3 illustrates the calculations of the interfacial energy σ_{sl} from Eq. (1). These interfacial energy isotherms are typical of micelle-forming surfactants: with increasing surfactant concentration, σ_{sl} first decreases, then acquiring a steady-state value. Interfacial tension acquires a steady-state value far before CMC is reached: the interfacial energy isotherm for TX-305 acquires a steady-state value at a concentration almost one order of magnitude smaller than CMC. For TTAB, the solution concentration at which a steady-state σ_{sl} value is acquired is roughly one-half CMC. This result implies that saturated monolayers appear at the solution/apolar solid interface at lower concentrations than at the solution/air interface.

Table 2. Interaction parameters β_{lv} in TX-305–TTAB mixed adsorption layers at solution/air interface

σ_{lv}, mJ/m^2	β_{lv}		
	α = 0.5	α = 0.2	α = 0.05
70	–	–	0.7
65	–	–	–0.4
60	–1.3	–0.4	–1.1
55	–2.3	–0.6	–0.9
50	–1.2	–0.6	–0.6
45	–1.1	–0.3	–0.7

To quantify the behavior of individual surfactants at solid/solution interfaces, we obtained adsorption isotherms and determined the $\Gamma_{\max}$, S_1, and *A* parameters of adsorption layers using the Gibbs and Langmuir equations (Table 1).

Comparing the parameters of adsorption layers at solution/air and solution/hydrophobic glass interfaces, we find that the adsorption activity *A* of a surfactant at the liquid/solid interface is higher than at the liquid/air interface. Apparently, the rise in adsorption activity is due to the interaction of the hydrocarbon radicals of the surfactant with the solid surface. The adsorption layer appears on a solid surface as follows [14, 15]: First, separate molecules are adsorbed, being oriented parallel to the surface. Then, depending on the surfactant and substrate, a saturated adsorption layer is formed of horizontally oriented surfactant molecules, aggregates, or vertically oriented surfactant molecules. The surface area per molecule in the saturated adsorption layer at the interface with glass for TTAB is near twice than in the layer at the interface with air. Presumably, a monolayer with the dominant horizontal orientation of molecules is formed. For TX-305, the surface area per molecule in the saturated adsorption layer indicates the dominance of the vertical orientation of molecules in the monolayer at the solution/solid interface.

The contact interaction measurement data were compared to the capillary rise data. From the capillary rise heights, the product $\sigma_{lv}\cos\theta$ was determined using Eq. (4) for individual and mixed solutions; surfactant adsorption at the solution/solid interface was calculated from Eq. (3). The results of $\Gamma_{\max}$, S_1, and *A* determinations are compiled in Table 1.

Qualitatively, the characteristics of adsorption layers at the solution/hydrophobic glass interface determined from capillary rise experiments agree with those derived from contact interaction measurements. However, there is a serious quantitative discrepancy in adsorption activities. Contact interaction measurements give higher surface activity than capillary rise measurements. This discrepancy may arise from the kinetics of surfactant adsorption on solids. The adsorption of micelle-forming surfactants on solids is a lengthy process; a steady state is acquired over hours or even days. In contact interaction measurements, a steady state was acquired. The capillary rise height was measured, on the average, every 1 h after the capillary was brought in contact with a surfactant solution.

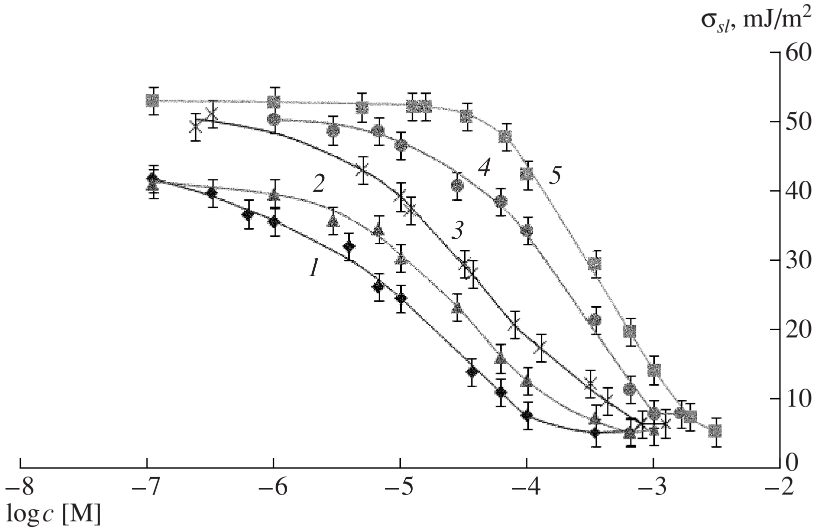

Fig. 3. Interfacial energy isotherms for (*1*) TX-305 solution, (*5*) TTAB solution, and (*2–4*) mixed solutions with the TX-305 mole fraction α = (*2*) 0.5, (*3*) 0.2, and (*4*) 0.05 at the hydrophobic glass interface.

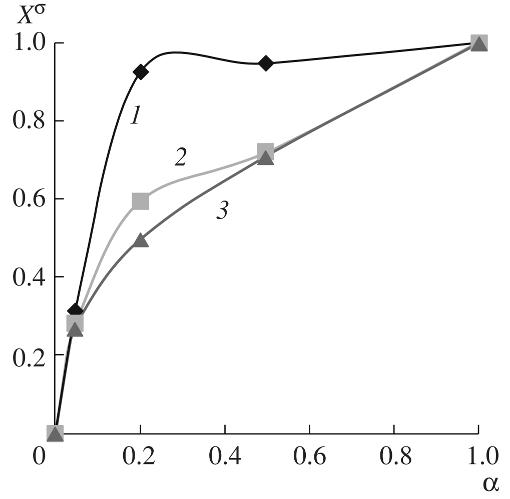

Fig. 4. TX-305 mole fraction in the adsorption layer at solution/hydrophobic glass interface, X^{sl}, vs. TX-305 mole fraction in solution, α, for σ_{sl} = (*1*) 28, (*2*) 23, and (*3*) 18 mJ/m^2.

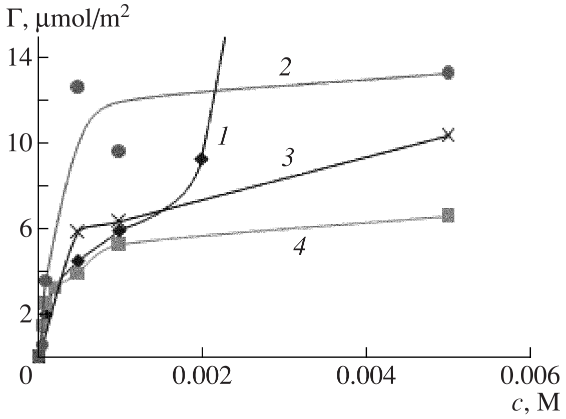

Fig. 5. Total adsorption of (*1*) TX-305, (*4*) TTAB, and (*2*, *3*) their mixtures with the TX-305 mole fraction α = (*2*) 0.5 and (*3*) 0.2 vs. total surfactant concentration in solution.

Adsorption equilibrium was not necessarily achieved over this period, especially for dilute solutions. Another explanation of the different adsorption activities determined by different methods is that the surface energy changes at the air interface upon capillary rise [16]. Near the three-phase contact line, surfactant molecules can transfer either from the liquid/gas interface or from the bulk of the solution to the solid surface in front of the contact interface. As a result, the solid increases its energy and the surface becomes more hydrophilic.

We used the Rosen approach [9] to analyze the behavior of surfactant mixtures at the solution/hydrophobic glass interface. We calculated the TX-305 mole fractions in mixed adsorption layers, X^{sl}, and their interaction parameters β^{sl} (Fig. 4, Table 3). Here, as at the air interface, adsorption layers are enriched in TX-305. The small interaction parameter values signify the existence of a small excess attraction between the components in the adsorption layer.

It is pertinent to compare the adsorption values calculated from the Gibbs equation with direct measurements of surfactant adsorption on hydrophobic quartz glass.

Figure 5 displays the adsorption value derived experimentally from the decrease in surfactant concentration in solution. The calculated and experimentally determined TX-305 adsorption values coincide for $c < 5 \times 10^{-4}$ mol/L. At higher concentrations, the values derived from the decrease in surfactant concentration in solution exceed the values calculated from the Gibbs

Table 3. Interaction parameters β_{sl} in TX-305–TTAB mixed adsorption layers at solution/hydrophobic glass interface

$\sigma_{lv}\cos\theta$, J/m^2	σ_{sl}, J/m^2	β_{sl}		
		$\alpha = 0.5$	$\alpha = 0.2$	$\alpha = 0.05$
–5	28	0	0	0.8
0	23	–2.1	–0.5	–0.1
5	18	–1.2	–1.0	–1.2

equation; when $c >$ CMC, there is a strong increase in adsorption. The increase in TX-305 adsorption in this range of concentrations can arise from surfactant aggregation on the surface. For TTAB, adsorption increases with increasing surfactant concentration to acquire a steady-state value, which approximately coincides with the maximal adsorption at the solution/air interface calculated from the Gibbs equation.

We obtained adsorption values for each component from mixed solutions with the TX-305 mole fraction $\alpha = 0.5$ and 0.2 and calculated the overall adsorption (Fig. 5). In the concentration range from 10^{-4} to 10^{-3} mol/L, the overall adsorption of surfactant mixtures exceeds the adsorption of the individual surfactants; that is, a synergistic effect is observed. Apparently, this effect is caused by excessive interactions between TX-305 and TTAB molecules in adsorption layers; this agrees with the negative interaction parameter values in mixed adsorption layers. Using a complex of methods (contact interaction measurements, capillary rise, tensiometry, spectrophotometry, and radioactive indicators), we determined the reciprocal influence of mixtures of a cationic surfactant (TTAB) and a nonionic surfactant (TX-305) on adsorption and interfacial energy at aqueous solution/hydrophobic glass interfaces. We found that the adsorption activity of the surfactant at the solution/hydrophobic glass interface is higher than at the solution/air interface; interfacial energy acquires a steady-state value at lower concentrations. We observed a synergistic effect at concentrations from 10^{-4} to 10^{-3} mol/L: the adsorption of mixtures exceeds the adsorption of individual surfactants. We used the Rosen model to calculate the interaction parameters and the compositions of mixed adsorption layers at solution/hydrophobic glass interfaces. These adsorption layers are enriched in TX-305, especially at low surfactant concentrations. The small negative values of the interaction parameters signify weak attraction between TTAB and TX-305 in adsorption layers.

REFERENCES

1. Yaminskii, V.V., Pchelin, V.A., Amelina, E.A., and Shchukin, E.D., *Koagulyatsionnye kontakty v dispersnykh sistemakh* (Coagulation Contacts in Disperse Systems), Moscow, 1982.
2. Summ, B.D. and Goryunov, Yu.V., *Fiziko-khimicheskie osnovy smachivaniya i rastekaniya* (Physicochemical Fundamentals of Wetting and Spreading), Moscow, 1976.
3. Fadeev, A.B., Soboleva, O.A., and Summ, B.D., *Kolloidn. Zh.*, 1997, vol. 59, p. 243.
4. Soboleva, O.A., Badun, G.A., and Summ, B.D., *Vestn. Mosk. Univ., Ser. 2: Khim.*, 2007, vol. 48, p. 17.
5. Soboleva, O.A., Yaroslavtsev, A.A., Badun, G.A., and Summ, B.D., *Kolloidn. Zh.*, 2004, vol. 66, p. 525.
6. Soboleva, O.A., Badun, G.A., and Yaroslavtsev, A.A., *Mendeleev Commun.*, 2004, vol. 14, p. 20.
7. Filatov, E.S. and Simonov, E.F., *Fiziko-khimicheskie i yaderno-khimicheskie sposby polucheniya mechenykh organicheskikh soedinenii i ikh identifikatsiya* (Physicochemical and Nuclear-Chemical Processes for Preparation of Labeled Organic Compounds and Their Identification), Moscow, 1987.
8. Dolzhikova, V.D., Goryunov, Yu.V., and Summ, B.D., *Kolloidn. Zh.*, 1982, vol. 44, p. 560.
9. Rosen, M.J. and Gu, B., *Colloid Surf.*, 1987, vol. 23, p. 119.
10. Vogler, E.A., *Langmuir,* 1992, vol. 8, p. 2005.
11. Soboleva, O.A., Dolzhikova, V.D., and Summ, B.D., *Kolloidn. Zh.*, 1996, vol. 58, p. 842.
12. Hohland, P.M. and Rubingh, D.N., *J. Phys. Chem.*, 1983, vol. 83, p. 1984.
13. Rosen, M.J., Molecular Interaction and Synergism in Binary Mixtures of Surfactants, in *Phenomena in Mixed Surfactants System*, Scamehorn, T., Ed., Washington, DC, 1986, p. 144.
14. *Adsorption from Solution on the Solid/Liquid Interface*, Parfitt, G. and Rochester, C., Eds., London: Academic Press, 1983. Translated under the title *Adsorbtsiya iz rastvorov na poverkhnosti tverdykh tel*, Moscow, 1986.
15. *Encyclopedia of Surface and Colloid Science*, Somasundaran, P., Ed., New York/London, 2006.
16. Kumar, N., Garoff, S., and Tilton, R.D., *Langmuir*, 2004, vol. 19, p. 4446.