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Wetting effect of aqueous binary mixed solutions of cationic and nonionic surfactants

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Wetting of low-energy solid surfaces (polymers, hydrophobized glass) with aqueous solutions of binary mixtures of cationic and nonionic surfactants was investigated at molar fractions of the cationic surfactant of 0.2, 0.5, and 0.8. In a narrow concentration range, the non-additive effect of wetting was observed: wetting of the solid surfaces with solutions of the mixtures is better than that would be expected from the additive behavior of the components. The magnitude of the effect depends on the surface energy of the solid substrate, total surfactant concentration in a mixture, and molar fraction of the cationic component. The wetting effect of surfactant mixtures with respect to low-energy solid surfaces can be predicted using the surface tension isotherms.

Key words: wetting, surfactants, binary surfactant mixtures, non-additivity.

Components of surfactant mixtures exert a non-additive effect on different physicochemical properties of dispersed systems. Reinforcement (synergism) and weakening (antagonism) of the surfactant effect in a mixture compared to the effects of individual components are known. The non-additive influence of surfactants in mixtures is commonly related to an excessive interaction between molecules (ions) of components of a mixture, and its measure is the interaction parameter β.[1—3] For the excessive (compared to the same molecules or ions) attraction, synergism is observed, *i.e.* some property in a mixture is achieved at lower surfactant concentrations than in solutions of individual components.[1]

Many bulk and surface properties of solutions of binary mixtures of surfactants (surface tension, micelle formation, solubilization) are well studied.[1—8] The behavior of mixtures at the solution—solid interface, in particular, adsorption of components from solutions on the solid surface,[9—14] has been studied to a less extent. At the same time, little attention has been given to the wetting of solids with solutions of surfactant mixtures, although the contact angle value is known to depend on the total concentration and ratio of components in the mixture.[6,15,16] The use of surfactant mixtures for wetting control can be promising, the more so, the methods and approaches describing the behavior of surfactant mixtures at different interfaces have been proposed presently.[3,14,17]

According to the Young law, the equilibrium contact angle θ is given by

$$\cos\theta = (\sigma_{sv} - \sigma_{sl})/\sigma_{lv}, \qquad (1)$$

where σ_{sv} and σ_{sl} are the specific free surface energies of solid at the interfaces with the gas and wetting liquid, respectively; σ_{lv} is the surface tension of the liquid. According to the Young law, on analyzing the behavior of surfactant mixtures during wetting of solids, one should take into account the possibility of the non-additive behavior of components of a mixture during their adsorption at three interfaces, *viz*., solid—gas, solid—solution, and solution—gas. The non-additive behavior of components of mixtures during adsorption at different interfaces[3,7,9—11,18] suggests that the synergetic or antagonistic effects are also possible on wetting solid surfaces with solutions of surfactant mixtures.

The purpose of this work is to study regularities of wetting of low-energy solids with aqueous binary mixed solutions of cationic and nonionic surfactants and to prove effects caused by the non-additive behavior of components of the mixtures. The choice of low-energy surfaces is motivated by the absence of specific interactions of molecules (ions) with the solid surface during adsorption under wetting conditions (for low-energy surfaces σ_{sv} = const with a change in the surfactant concentration in the aqueous phase).[19] A mixture of cationic and nonionic surfactants was chosen because of an increased interest in studying the properties of mixtures in which one

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of the components is a nonionic surfactant with a sufficiently long polyoxyethylene chain.[1] Among mixtures of surfactants of different types, the mixture of cationic and nonionic surfactants is characterized by the lowest parameters of interaction of molecules and ions of components in mixed adsorption layers at the solution—air interface and in the bulk solution.[1,3] Therefore, it is easier to interpret the results obtained for wetting of low-energy solid surfaces with solutions of mixtures of cationic and nonionic surfactants.

Experimental

Mixtures of the nonionic surfactant, *viz.*, Triton X-100 (TX-100), and cationic surfactant cetyltrimethylammonium bromide (CTAB) (Serva, 99.8%) were studied. The molar fraction of the cationic surfactant in mixtures (α) was 0.2, 0.5, and 0.8. The region of studied concentrations of individual surfactants (c) and the total surfactant concentration in a mixture (c_{tot}) were 10^{-8}—10^{-2} mol L^{-1}, and the pH of solutions was 6.5.

Teflon, polystyrene, and hydrophobized glass were used as solid substrates (all samples were in the form of plates). Hydrophobized glass was prepared by storing glass plates in dimethyldichlorosilane vapor for 24 h followed by washing with chloroform. The surfaces of the materials were cleaned according to known procedures.[20] Samples were characterized by the advancing (θ_a) and receding (θ_r) contact angles of water (Table 1), which agree well with published data.[21] A small hysteresis of the contact angles $\Delta\theta = (\theta_a - \theta_r)$ indicates that the solid surfaces are rather uniform.

The contact angles θ were determined goniometrically under the advancing (when a drop of water or solution was supported on the solid surface) and receding conditions (when an air bubble approached the surface of a sample immersed in a solution). The volume of the drop (bubble) was 0.01 mL. Measurements were carried out in a closed chamber at an intrval of 3—5 min after the drop or bubble was supported. The values obtained for the contact angles are close to equilibrium, because θ remained unchanged during measurements for 30 min. The accuracy of contact angle measuring was ±1°, and the root-mean-square deviation was ±2° (from the results of 3—6 measurements). All experiments were carried out at 20 °C.

The surface tension of solutions (σ_{lv}) of surfactants and their mixtures was determined by the Wilhelmy method (equilibration of an aluminum plate). For water at 20 °C σ_{lv} = 72.4±0.5 mN m^{-1}. For solutions of individual surfactants and their mixtures, the root-mean-square deviation ranged from ±0.5 to ±2 mN m^{-1} (from the results of 3—5 measurements).

Table 1. Contact advancing (θ_a) and receding (θ_r) angles for water on solid substrates

Substrate	σ_{sv}/mJ m^{-2}	θ_a	θ_r
		deg	
Polystyrene	44—46	86	84
Hydrophobized glass	21—24	104	103
Teflon	18—20	117	106

The amount of adsorbed surfactant at the polystyrene—solution interface was determined by the methods of Quartz Crystal Microbalance (QCM)[22] and radioactive indicators (RI) using a tritium label and liquid scintillation spectrometry for measuring radioactivity.[23] Tritium-labeled TX-100 (^{3}H-TX-100) was obtained by the thermal activation of tritium,[24] and the radiochemical purity of the labeled sample was ≥96%.

We developed a new procedure including a combination of the QCM and RI methods to determine the contribution of individual surfactants to the total amount of adsorbed substance from mixed solutions on polystyrene. This procedure can be used for measuring the amount adsorbed on the surface of any adsorbent, which is readily soluble in an organic solvent (a basis of a scintillator) and can be supported on the surface of a quartz resonator (sensor of a microbalance) as a thin film. The toluene-based scintillator was used in this work.

The procedure of measurements was as follows. The intrinsic resonator frequency f_0 was determined first, then a polystyrene film was supported on the resonator surface from a 0.5% toluene solution, and the frequency of resonator oscillations f_1 was measured. We calculated the thickness of the supported film (~200 nm) from the $\Delta f = f_1 - f_0$ difference taking into account the polystyrene density.[22] Then the resonator was stored for 30 min in a solution of a surfactant mixture in which one of the components (TX-100) contained the tritium label. After drying, the frequency of resonator oscillations f_2 was measured. The change in the oscillation frequency of the microbalance sensor ($\Delta f = f_2 - f_1$) makes it possible to calculate the total amount of the surfactant adsorbed from solutions of the mixtures on polystyrene (Γ) by the equation

$$\Gamma = \Delta m/S = -\Delta f/C_f, \qquad (2)$$

where Δm is the change in the weight of the substance (g), C_f is the weight sensitivity coefficient dependent on the piezoquartz properties, and S is the area of the working surface of the resonator.[22] Resonators of the AT cut (with silver electrodes) with the intrinsic frequency f_0 = 5 MHz for which $C_f = 2.27 \cdot 10^{-6} f_0^2$ = 56.75 Hz cm^2 g^{-1} were used. The amount adsorbed (Γ) was calculated by the equation

$$\Gamma = -1.76 \cdot 10^{-8} \Delta f, \qquad (3)$$

where Δf is the change in the frequency of resonator oscillations due to the surfactant adsorption on its surface.[22]

Then the polystyrene film with the adsorption layer of the surfactant was dissolved in toluene, and its radioactivity was measured on a liquid scintillation spectrometer (Mark III).[23] The amount of the labeled component (^{3}H-TX-100) adsorbed was calculated by the equation

$$^*\Gamma = I/(\varepsilon A_{sp} 2S), \qquad (4)$$

where ε is the efficiency of detection, A_{sp} is the specific radioactivity of the labeled surfactant, and S is the area of the working surface of the resonator.

The amount of CTAB adsorbed was calculated from the difference of the amount adsorbed determined by the QCM and RI methods. Correctness of this calculation method was confirmed by the fact that the amounts adsorbed of TX-100 on the polystyrene surface, which were obtained by the PM and RI

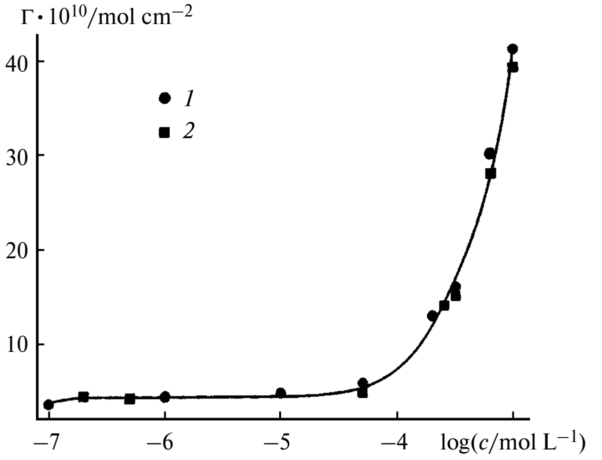

Fig. 1. Adsorption isotherms of TX-100 on the polystyrene surface obtained by the PM (*1*) and RI (*2*) methods.

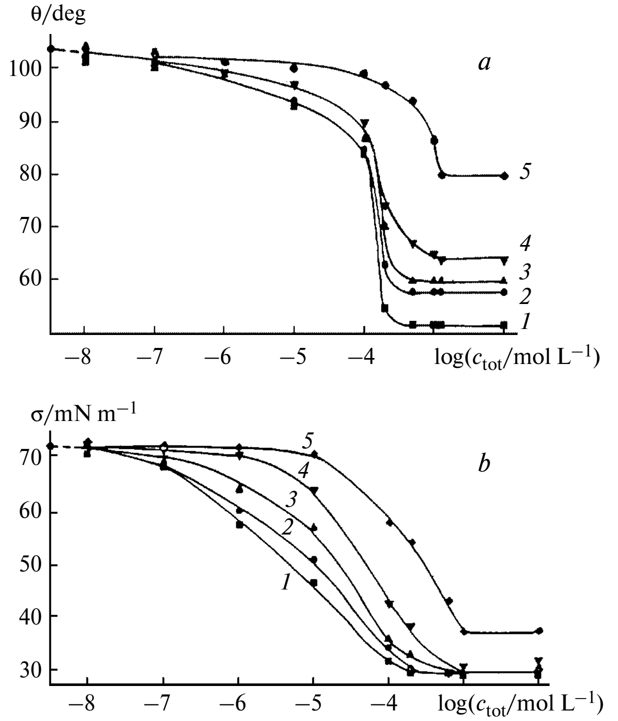

Fig. 2. Isotherms of advancing contact angles on hydrophobized glass (*a*) and surface tension (*b*) for solutions of TX-100 (*1*), TX-100—CTAB mixtures at the molar fraction of α = 0.2 (*2*), 0.5 (*3*), and 0.8 (*4*), and CTAB (*5*).

methods, coincided within the determination accuracy limits (7—10%) (Fig. 1).

The modification of solid substrates by adsorption layers of binary mixtures of surfactants was also studied. Samples were stored in solutions of mixtures for 30 min and then dried, and the advancing contact angles of water drops (θ_w) on the modified surface were measured. The degree of modification of solid substrates (φ) was calculated on the basis of the theory of wetting of heterogeneous surfaces using the Cassier—Baxter equation[25]

$$\cos\theta_w = \varphi\cos\theta_1 + (1 - \varphi)\cos\theta_2, \qquad (5)$$

where θ_2 and θ_1 are the advancing contact angles of water on the initial and completely modified surfaces, respectively. The coverage of the surface with the adsorption layer $\varphi(c)$ can thus be estimated, and the relative amounts of the mixed surfactant solutions adsorbed on different substrates can be compared.[26]

When a water drop is supported on the modified surface, the surfactants adsorbed on the polymer film can be dissolved in the drop. The calculations showed that the surfactant concentration in the aqueous phase was $\leq 10^{-6}$ mol L^{-1} provided that the adsorption layer for the formed by compact monolayer coverage of the solid surface was completely consumed by the drop. The presence of the surfactant in this concentration can decrease the surface tension of water by 4—10%, depending on the content of TX-100 in a mixture. For these solutions, the contact angles on the hydrophobic surface change insignificantly and do not virtually differ from the contact angles of water. Thus, the modification method allows a sufficiently reliable estimation of the relative amount of the surfactant adsorbed (coverage of the surface $\varphi(c)$ with the adsorption layer).

Results and Discussion

The isotherms of advancing contact angles on hydrophobized glass (*a*) and surface tension (*b*) for solutions of TX-100, CTAB, and their mixtures are shown in Fig. 2. The contact angle isotherms $\theta = f(c_{tot})$ of solutions of the surfactant mixtures and individual components have three characteristic regions. The region of low concentrations exhibits an insignificant decrease in the contact angles. The contact angles decrease with an increase in the concentration, and at concentrations higher than the critical micelle concentration (CMC) the θ value remains unchanged (see Fig. 2, *a*). Such isotherms were obtained for all solution—solid substrate systems studied. In the entire region of concentrations studied, wetting of the solid substrates with solutions of TX-100 and TX-100—CTAB mixtures is better than that for solutions of CTAB (see Fig. 2, *a*), TX-100 possesses the highest wetting efficiency, and the efficiency of the wetting action of the mixtures decreases with an increase in the molar fraction of the cationic surfactant.

The wetting isotherms of the low-energy substrates with solutions of the surfactants and their mixtures are similar to the surface tension isotherms: the contact angles and surface tension of solutions change in parallel with an increase in the surfactant concentration (see Fig. 2). The critical micelle concentrations of solutions of individual surfactants and their mixtures determined from the isotherms $\theta = f(c_{tot})$ and $\sigma_{lv} = f(c_{tot})$ are close (Table 2) and agree with published data.[8,21,27]

Analysis of the wetting $\theta = f(c_{tot})$ and surface tension $\sigma_{lv} = f(c)$ isotherms of solutions of individual surfactants and their mixtures showed that TX-100 and CTAB in a mixture exhibited no synergism with respect to wetting

Table 2. Critical micelle concentrations (CMC) of solutions of TX-100, CTAB, and their mixtures derived from the surface tension $\sigma_{lv}(c_{tot})$ and wetting $\theta(c_{tot})$ isotherms

α	$\mathrm{CMC} \cdot 10^4/\mathrm{mol\ L^{-1}}$			
	Published data		Experiment	
	Magnitude	Ref.	$\sigma_{lv}(c_{tot})$	$\theta(c_{tot})$
0	2.4; 3.2	21	2.4	2.5
0.2	3.2	8	2.6	2.8
0.5	3.8	8	3.1	3.5
0.8	4.9	8	4.4	4.3
1	8.0; 10.0	21	9.0	9.1

and a surface tension decrease in the whole region of concentrations studied and ratios of components (see Fig. 2).

The influence of the ratio and surfactant concentration on the contact angle is illustrated by the $\cos\theta = f(\alpha)$ plots (Fig. 3, *a*). These plots are linear in the region of low total concentrations of the surfactants ($c_{tot} = 10^{-8}$—10^{-5} mol L^{-1}). The linear $\cos\theta = f(\alpha)$ plot indicates the additive contribution of the components of the mixture to the contact angle values. A deviation from the linear plot (Fig. 3, *a*) is observed in the concentration region corresponding to micelle formation in solutions of the surfactants and their mixtures ($c_{tot} = 10^{-4}$—10^{-3} mol L^{-1}). This shows that in this concentration interval wetting of the solid substrates with solutions of the mixtures is better than it could be expected for the additive effect of the components.

The $\sigma_{lv} = f(\alpha)$ plots are linear in the region of low surfactant concentrations and characterized by the negative deviation from linearity in the interval $c_{tot} = 10^{-4}$—10^{-2} mol L^{-1} (Fig. 3, *b*). Thus, the concentration intervals corresponding to the linear and non-linear regions of the curves coincide for the $\cos\theta = f(\alpha)$ and $\sigma_{lv} = f(\alpha)$ plots.

On going from solutions of CTAB ($\alpha = 1$) to solutions of the mixtures ($\alpha = 0.8$), the contact angles and surface tension of the solutions decrease most dramatically. The further increase in the molar fraction of TX-100 in solutions of the mixtures ($\alpha = 0.8$—0.5) slightly decreases the contact angles and surface tension, and at $\alpha \le 0.5$ these values change slightly. The deviation of the $\cos\theta = f(\alpha)$ and $\sigma_{lv} = f(\alpha)$ plots from linearity can be related to the non-additive effect of the components of the mixture and a change in the activity coefficient of the surfactant in a solution. Nevertheless, changes in the activity coefficients alone could not produce the linear $\cos\theta = f(\alpha)$ plot at $c_{tot} = 10^{-2}$ mol L^{-1} (see Fig. 3, *a*, curve *9*).

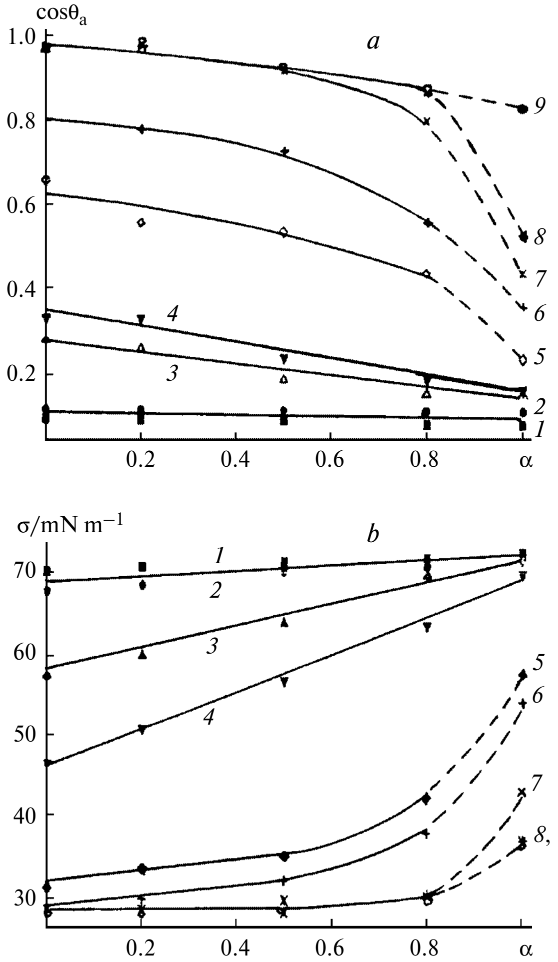

Fig. 3. Plots of cosines of advancing contact angles (θ_a) of solutions of TX-100—CTAB mixtures on polystyrene (*a*) and surface tension of these solutions (σ) (*b*) *vs.* molar fraction of CTAB (α) at different total surfactant concentrations: $c_{tot} = 10^{-8}$ (*1*), 10^{-7} (*2*), 10^{-6} (*3*), 10^{-5} (*4*), 10^{-4} (*5*), $2 \cdot 10^{-4}$ (*6*), $6 \cdot 10^{-4}$ (*7*), 10^{-3} (*8*), and 10^{-2} mol L^{-1} (*9*).

In order to examine the behavior of a surfactant at the solution—air interface, we used the Rosen approach[3] based on the theory of regular solutions. This approach makes it possible to calculate the interaction parameters β^σ for molecules and ions of components of a mixture and the composition of the mixed adsorption layer at the solution—air interface. The calculations were carried out by the equations

$$\beta^\sigma = \ln[\alpha c_{12}{}^\sigma/(X^\sigma c^\sigma{}_1)]/(1 - X^\sigma)^2, \qquad (6)$$

$$\frac{(X^\sigma)^2 \ln[\alpha c_{12}^\sigma/(X^\sigma c_{12}^\sigma)}{(1 - X^\sigma)^2 \ln\{(1 - \alpha)c_{12}^\sigma \,/\, [(1 - X^\sigma)c_2^\sigma]\}} = 1, \qquad (7)$$

where $c_1{}^\sigma$, $c_2{}^\sigma$, and $c_{12}{}^\sigma$ are the concentrations of solutions of individual components and a mixture necessary for decreasing the surface tension to a desired value[3,7,8]; α and X^σ are the molar fractions of CTAB in the bulk solution and in the mixed adsorption layer at the solution—air interface, respectively.[3,7,8] The β^σ and X^σ values were calculated by Eqs. (6) and (7) using the experimental c_1^{σ}, c_2^{σ}, and c_{12}^{σ} values. The β^{σ} and X^{σ} values calculated for the saturated adsorption layers at σ_{lv} = 37.5 mN m^{-1} are presented below as an example.

α	$-\beta^{\sigma}$	X^{σ}
0.2	1.2	0.16
0.5	1.3	0.34
0.8	1.5	0.54

The β^{σ} and X^{σ} values obtained agree with the published data.[8] Our calculations show that, at c_{tot} = 10^{-4}—10^{-2} mol L^{-1} corresponding to the saturated adsorption layers at the solution—air interface, only the first of two synergism conditions formulated by Rosen[3]

1) $\beta^{\sigma} < 0$, 2) $|\ln(c_1^{\sigma}/c_2^{\sigma})| < |\beta^{\sigma}|$,

is fulfilled. The second condition is not fulfilled, because for a TX-100—CTAB mixture $|\ln(c_1^{\sigma}/c_2^{\sigma})| = 1.2$.

The low negative values of the interaction parameter indicate a weak excessive attraction of molecules and ions of the components of the mixture in the mixed adsorption layer. The calculation by Eqs. (6) and (7) shows that the mixed adsorption layer at the solution—air interface is enriched in TX-100, which has a higher surface activity.

Thus, the negative deviation from the ideal behavior is observed for mixed surfactant solutions of TX-100—CTAB at the aqueous solution—air interface: the surface tension of mixed surfactants is lower than that expected from the additive effect of the components. The concentration interval corresponding to the non-additive behavior of the components of the mixture at the solution—air interface coincides with the interval of concentrations at which the non-additive wetting effect is observed (see Fig. 3).

Approaches to analysis of the wetting effect of solutions of surfactant mixtures and criteria that allow the estimation of the deviation from the additive behavior of components of mixtures during wetting are not virtually developed so far.[28] Let us consider the possibility of this estimation.

For the additive behavior of components, the contact angle θ of a solution of the mixture on the solid substrate is determined by the equation

$$\cos\theta = \alpha\cos\theta_1 + (1 - \alpha)\cos\theta_2, \qquad (8)$$

where θ_1 and θ_2 are the contact angles of solutions of individual components, and α is the molar fraction of the cationic surfactant in the mixture. It is assumed that the ratio of components in the mixed adsorption layers at the solution—air and solution—solid surface interfaces is the same and equal to the volume ratio. For all solid substrates studied, the contact angle values calculated by Eq. (8) agree well with the experimental values in the region of low concentrations c_{tot} = 10^{-8}—10^{-5} mol L^{-1}. The contact angles of solutions of the mixtures at c_{tot} = 10^{-7}, 10^{-5} mol L^{-1} (on Teflon) are presented in Table 3.

Table 3. Experimental and calculated contact angles (θ) of solutions of TX-100—CTAB mixtures on Teflon

c_{tot} /mol L^{-1}	α	θ/deg		
		Experiment	Calculation	
			by Eq. (8)	by Eq. (9)
10^{-7}	0.2	113	112	114
	0.5	113	113	114
	0.8	114	114	115
10^{-5}	0.2	104	105	103
	0.5	108	108	109
	0.8	109	110	113
$2\cdot10^{-4}$	0.2	79	78	80
	0.5	80	93	89
	0.8	86	97	104
10^{-3}	0.2	56	60	68
	0.5	65	73	72
	0.8	77	86	76

In the region of concentrations corresponding to micelle formation in solutions of the surfactants and their mixtures, the calculated contact angles exceed the experimental values (see Table 3).

According to the Young law (1), the non-additivity of the wetting effect of mixed solutions can be caused by a stronger decrease in the surface tension σ_{lv} and interfacial surface energy σ_{sl} than by a decrease due to the additive effect of the components. This means that the composition of the mixed adsorption layers at the solution—air and solution—solid interfaces differs from that of the volume phase. This discrepancy results in the difference in the experimental and calculated values of contact angles.

Based on the experimental values of surface tension σ_{lv}^{exp}, we can calculate the contact angles taking into account the inconsistency of the adsorption layer composition at the solution—air interface to the ratio of the components in the bulk solution

$$\cos\theta = \{\sigma_{sv} - [\alpha\sigma_{sl}^{(1)} + (1 - \alpha)\sigma_{sl}^{(2)}]\}/\sigma_{lv}^{exp}, \qquad (9)$$

where $\sigma_{sl}^{(1)}$ and $\sigma_{sl}^{(2)}$ are the interfacial energies at the solid—solution interface for individual components calculated by the Antonov rule.[21] Equation (9) is a consequence of the Young law under the condition σ_{sv} = const.[19] The experimental values of surface tension of solutions of the mixtures and contact angles of individual surfactant solutions and the reference values of the surface energy of the substrates (see Table 1) were used for calculations. A possible negative contribution of the components of the mixture during adsorption at the solid surface—solution interface was ignored.

The contact angles calculated by Eq. (9) agree well with the experimental values in the concentration interval c_{tot} = 10^{-8}—10^{-5} mol L^{-1} (see Table 3), whereas at c_{tot} = 10^{-4}—10^{-3} mol L^{-1} they exceed the experimental values. Therefore, the non-additive wetting effect of the components of the mixture is caused by their non-additive behavior not only at the solution—air interface but also at the solution—solid interface. These results were obtained for both the advancing and receding contact angles for all low-energy substrates used.

This conclusion is confirmed by measurements of the amounts of TX-100 and CTAB adsorbed from solutions of the mixtures on polystyrene: in the concentration region $c_{tot} = 10^{-7}$—10^{-4} mol L^{-1} the amount of CTAB adsorbed increases in the presence of TX-100 (Fig. 4). The amount of TX-100 adsorbed in the region of $c_{tot} = 10^{-7}$—$2 \cdot 10^{-5}$ mol L^{-1} decreases with addition of CTAB (Fig. 5). In the region of $c_{tot} = 10^{-4}$—10^{-3} mol L^{-1} corresponding to the appearance of the non-additive effect for polystyrene wetting, the amount of TX-100 adsorbed increases in the presence of CTAB, and the presence of TX-100 exerts no substantial effect on CTAB adsorption.

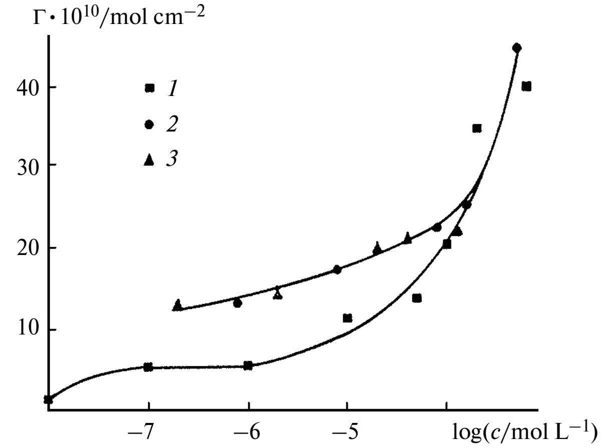

Fig. 4. Adsorption isotherms of CTAB from individual solutions (*1*) and TX-100—CTAB mixtures at the molar fraction of CTAB α = 0.2 (*2*) and 0.8 (*3*) on the polystyrene surface.

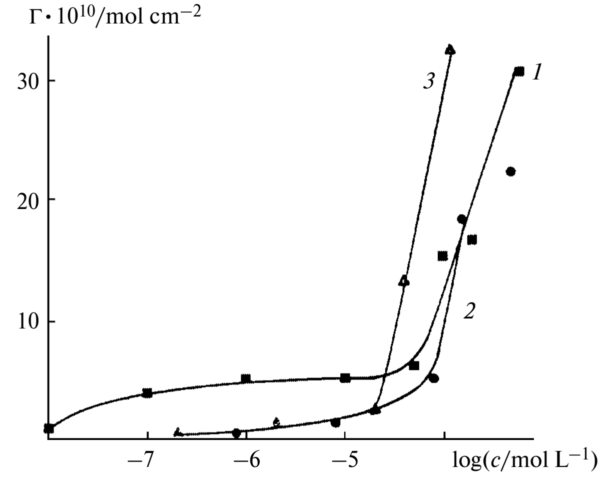

Fig. 5. Adsorption isotherms of TX-100 from individual solutions (*1*) and TX-100—CTAB mixtures at the molar fraction of CTAB α = 0.2 (*2*) and 0.8 (*3*) on the polystyrene surface.

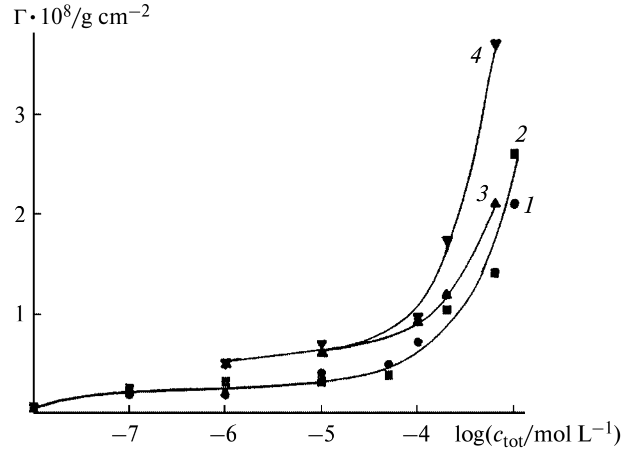

Fig. 6. Adsorption of CTAB (*1*) and TX-100 (*2*) from individual solutions and the total amount adsorbed from TX-100—CTAB mixtures at the molar fraction of CTAB α = 0.2 (*3*) and 0.8 (*4*) on polystyrene.

The results obtained by the QCM method show that the total amount of TX-100 and CTAB adsorbed from mixed solutions on polystyrene exceeds their amounts adsorbed from individual solutions (Fig. 6). Thus, adsorption of surfactants at the polystyrene—solution interface leads to synergism, which does not result, however, in wetting synergism. Only the negative deviation from the additive wetting effect of the components is observed. Therefore, the behavior of the components at the solution—air interface is a factor determining the wetting effect of the mixtures.

The measurements of the total amount adsorbed in combination with measurements of the amounts of individual surfactants adsorbed from solutions of the mixtures made it possible to calculate the composition of the mixed adsorption layer at the solution—polystyrene using Eqs. (3) and (4).

Under the conditions when the non-additive effect of the wetting action of solutions of the mixtures was the most pronounced (α = 0.8, $c_{tot} = 6 \cdot 10^{-4}$ mol L^{-1}), the mixed adsorption layer is enriched in TX-100 as at the solution—air interface (Table 4).

The measurements of the amounts of the surfactants adsorbed from solutions of the mixtures showed that in the concentration interval corresponding to micelle formation in solutions of the individual and mixed surfactant solutions ($c_{tot} \geq 2 \cdot 10^{-4}$ mol L^{-1}) the composition of the mixed adsorption layers at the solid—solution interface differs from the composition of the bulk phase (see Table 4). Therefore, Eqs. (8) and (9) can be used for the calculation of the contact angles only in the region of $c_{tot} \leq$ CMC. The presented calculations of the contact angles by Eqs. (8) and (9) are not rigid, because they were

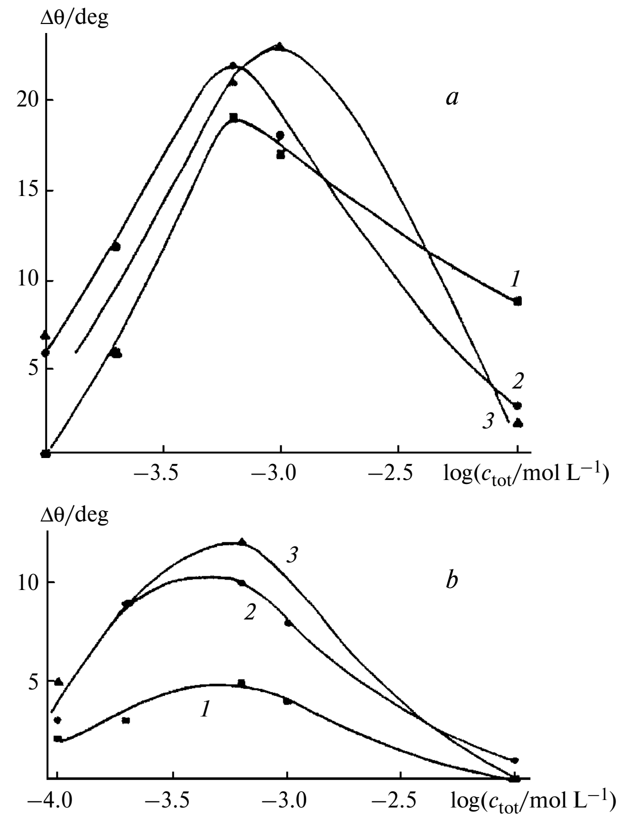

Fig. 7. Plots of the non-additive wetting effect (Δθ) *vs.* total concentration (c_{tot}) for solutions of TX-100—CTAB mixtures on polystyrene (*a*) and Teflon (*b*) at the molar fraction of CTAB $\alpha = 0.2$ (*1*), 0.5 (*2*), and 0.8 (*3*).

performed using the concentrations of the surfactants rather than their activities.[29] More exact calculations require the knowledge of the activities of individual surfactants in a solution and also the determination of their changes upon mixing.

The difference of the experimental and calculated contact angles $\Delta\theta = \theta_{calc} - \theta_{exp}$ (the θ_{calc} values were calculated by Eq. (8)) can be used as a characteristic of the deviation of the behavior of components of the mixture from additivity .

As can be seen from the data in Fig. 7, the magnitude of the non-additive effect for wetting (Δθ) increases with an increase in the molar fraction of the cationic surfactant (in the interval of $\alpha = 0.2$—0.8) and the surface energy of the solid substrate. The $\Delta\theta = f(\log c_{tot})$ plot has an extreme character with a maximum at the concentration near the CMC of a CTAB solution (see Fig. 7). The maximum Δθ value is 13, 18, and 23° for Teflon, hydrophobized glass, and polystyrene, respectively.

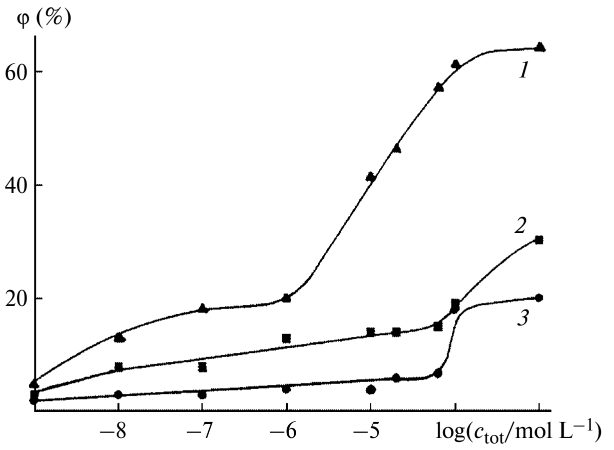

Fig. 8. Plots of the degree of hydrophilization (φ) of polystyrene (*1*), Teflon (*2*), and hydrophobized glass (*3*) *vs.* total surfactant concentration in a mixture (c_{tot}) with modification by solutions of a TX-100—CTAB mixture (molar fraction of CTAB $\alpha = 0.8$).

The enhancement of the non-additive wetting effect with an increase in the surface energy of the solid substrate is caused, most likely, by an increase in the combined adsorption of the surfactant at the solid surface—solution interface. This conclusion is confirmed by the data on the modification of the solid surfaces with solutions of the mixtures. The coverage (φ) of the polystyrene surface with the mixed adsorption layer is higher than those for Teflon and hydrophobized glass (Fig. 8).

The results obtained show that for the low-energy surfaces in the narrow region of concentrations corresponding to micelle formation in surfactant solutions and their mixtures the efficiency of the wetting action observed for the surfactant mixtures is higher than that expected for the additive behavior of the components. This is caused by an enhanced content of the nonionic surfactant (TX-100) in the mixed adsorption layers at the solution—air and solution—solid interfaces. The effect can be predicted on the basis of the surface tension isotherms of the corresponding mixed solutions of the cationic and nonionic surfactants.

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