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OF SURFACE PHENOMENA

Mutual Influence of Tweens and Dodecyl Pyridinium Chloride upon Their Joint Adsorption on a Surface of Paraffin

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Abstract—The mutual influence of Tweens (Tween-20, Tween-40, Tween-60, Tween-80) and dodecyl pyridinium chloride (DDPC) upon their joint adsorption on the paraffin surface is studied using different molar ratios of components in a bulk aqueous solution. It is shown that both synergistic and antagonistic effects are observed upon the adsorption of cationic and nonionic surfactants from the mixed solutions. The compositions of mixed adsorption layers and the parameters of intermolecular interaction between surfactants of different natures are calculated. A possible mechanism is proposed for the adsorption process.

Keywords: adsorption, surfactant, paraffin.
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INTRODUCTION

An important line of modern colloid chemistry is the study of the properties of mixtures of surface-active agents (surfactants). The study of surfactant mixtures is, on the one hand, of considerable theoretical interest; on the other hand, such systems are widely used in a variety of applications (e.g., for stabilizing disperse systems and in creating synthetic detergents, cosmetics, and pharmaceuticals) [1, 2].

Of particular practical importance are studies of the adsorption of surfactant mixtures on solid surfaces. At the same time, this problem is relatively new and patterns of the effect mixture compositions have on their adsorption from solutions have yet to be established. There are now a considerable number of works devoted to studying mixtures of anionic surfactants and nonionic surfactants at different interfaces [3, 4]. Less studied are patterns of the adsorption of mixtures of cationic surfactants and nonionic surfactants from aqueous solutions on solid surfaces [5, 6].

As is well known, the adsorption of surfactants from mixed solutions depends on the adsorption activity of each of the components, relative to a specific adsorbent. Among the factors affecting adsorption activity and the behavior of a mixture during adsorption at a liquid–solid interface are the chemical nature of the adsorbent and the components of the mixture; the interactions between surfactant molecules of different natures, both on the surface of the adsorbent and in the bulk solution; and the pH of the medium [7, 8].

In this work, we assess the mutual influence of Tweens and DDPC upon their joint adsorption, determine the composition of a mixed adsorption layer, and compare the obtained data to the results from calculations using the Rosen model. Our analysis is based on results from determining the adsorption of nonionic surfactant mixtures (Tweens) and cationic surfactants (DDPC) from aqueous solutions on low-energy surfaces of paraffin via the concentration difference method.

EXPERIMENTAL

Our objects of study were DDPC cationic surfactant (Fluka, pure), and nonionic surfactants Tween-20 (polyoxyethylene sorbitan monolaurate), Tween-40 (polyoxyethylene sorbitan monopalmitate), Tween-60 (polyoxyethylene sorbitan monostearate), and Tween-80 (polyoxyethylene sorbitan monooleate) from Acros Organics (analytical grade).

Mixed Tween–DDPC systems were studied in concentration limits of $(1.5–5.0) \times 10^{-5}$ mol/dm^3. Molar ratios *n* of Tween in solution were 0.2, 0.5, and 0.8. Solutions were prepared using distilled water with electroconductivity 2×10^{-3} S/cm and pH 5.3.

Adsorption of the surfactant was conducted using 25 cm^3 of individual and mixed solutions with 0.005 g of adsorbent under stirring for 40 min (the time needed to reach adsorption equilibrium in the systems) at 293 K in a Julabo MC-4 thermostat that allowed us to maintain the desired temperature with precision of up to 0.001 K. A 1% aqueous suspension of paraffin, obtained via ultrasonic dispersion of the latter using a UZG 13-01/22 unit with a frequency of 22 kHz in distilled water heated to 353 K for 2 min, was

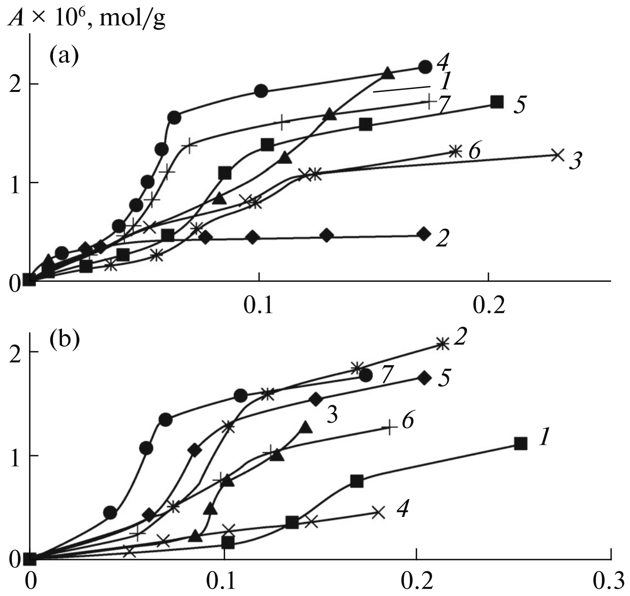

Fig. 1. Sorption isotherms: (a) Tween-40 from (*1*) individual and mixed solutions with DDPC with *n*(Tween) (*2*) 0.2, (*3*) 0.5, and (*4*) 0.8 and total adsorption of the mixture Tween-40–DDPC with *n*(Tween) (*5*) 0.2, (*6*) 0.5 and (*7*) 0.8 on a surface of paraffin; (b) DDPC from (*1*) individual and mixed solutions with Tween-40 with *n*(Tween) (*2*) 0.2, (*3*) 0.5, (*4*) 0.8 and total adsorption of the mixture Tween-40–DDPC with *n*(Tween) (*5*) 0.2, (*6*) 0.5, (*7*) 0.8 on a surface of paraffin.

used as our adsorbent. Dispersion analysis of suspensions formed upon dispersal was performed using an IBI-11 microscope equipped with a hemocytometer grid and a photo adaptor [9]. Dispersion analysis showed that the suspension particles were spherical and similar in size. The average radius of the particles was 2×10^{-5} m. The specific surface area of the paraffin particles, calculated according to the formula

$$S_{\text{sp}} = \frac{S}{V\rho} = \frac{3}{r\rho},$$

where S, V, ρ, r are the surface, volume, density, and average particle size, respectively, was equal to 0.2 m^2/g.

Adsorption (A, mol/g) was calculated using the formula

$$A = \frac{C_0 - C_{\text{eq}}}{m}V, \qquad (1)$$

where C_0 is the initial concentration of surfactant; C_{eq} is the equilibrium concentration of surfactant; m is the mass of the adsorbent; and V is the volume of the sample.

Our analysis of the solutions according to the residual content of Tweens and DDPC before and after adsorption was performed via photocolorimetry following the standard procedures in [10, 11], respectively.

RESULTS AND DISCUSSION

The adsorption isotherms of Tweens and DDPC from both their individual [12] and their mixed aqueous solutions (Fig. 1) on the surface of the paraffin have a shape close to those of the Giles classification's L-type isotherms of according [13]. The driving force behind the studied nonionic and cationic surfactants from mixed solutions on the surface is the electrostatic interaction of polar groups of the surfactant with negatively charged particles of paraffin. Nonspecific dispersion and hydrophobic interactions between the surface of the paraffin and hydrocarbon radicals of the surfactant also cannot be excluded. Adsorption increases along with the concentration of Tweens and DDPC in the mixed solutions, due not only to the adsorption of specific molecules and ions of the studied surfactants but also of their mixed associates.

Our studies showed that the adsorption of mixtures of Tweens and DDPC from aqueous solutions on a solid surface depends on both the structure of the surfactant and the composition of the mixed solution.

To clarify the effect the composition of a mixed solution has on the adsorption of Tweens and DDPC on a surface of paraffin, we analyzed the adsorption values for each component of the mixture at different ratios of nonionic surfactant and cationic surfactant in the solution at two concentrations (0.05×10^{-5} and 0.15×10^{-5} mol/dm^3). The dependences between the adsorption of Tween-20, Tween-40, Tween-60, Tween-80, and DDPC from mixed solutions on surfaces of paraffin and the mixture composition are shown in Fig. 2.

Adsorption of Tween-20 at all molar ratios of mixture components, Tween-40 at *n*(Tween-40) = 0.2 and 0.5, and Tween-60 at *n*(Tween-60) = 0.2 from the mixed solutions with DDPC are less than their adsorption from individual solutions on surfaces of paraffin. The exception is Tween-80, whose adsorption from the mixture with DDPC on the solid surface was greater than from the individual solution over the range of component molar ratios.

Adsorption of DDPC from mixed solutions with Tween-20 and Tween-40 exceeds its adsorption from the individual solution at *n*(Tween) = 0.2 and 0.5. In the mixtures with Tween-60 and Tween-80, DDPC adsorption is higher at all molar ratios of the surfactant in the mixed solution (Figs. 2c, 2d).

As can be seen from Fig. 2, the observed dependences of adsorption for both Tweens and DDPC on mixture composition at low (0.05×10^{-5} mol/dm^3) and high (0.15×10^{-5} mol/dm^3) concentrations of the mixed solution are similar.

From the above, it follows that both synergistic and antagonistic effects are observed upon the adsorption

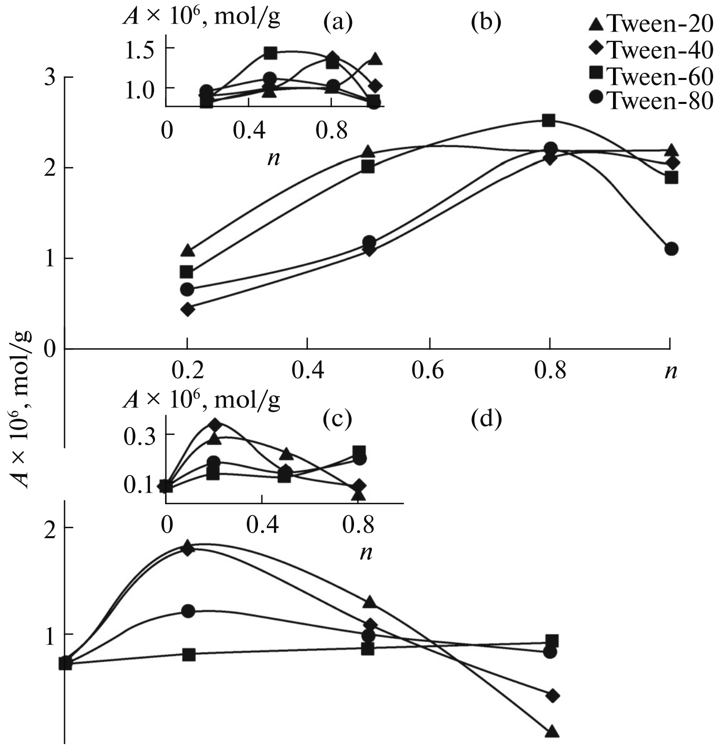

Fig. 2. Dependences of the adsorption of (a, b) Tweens and (c, d) DDPC from mixed solutions on a surface of paraffin on the composition of the mixture (a, c) $C_p = 0.05 \times 10^{-5}$ mol/dm^3; (b, d) $C_p = 0.15 \times 10^{-5}$ mol/dm^3.

of Tweens and DDPC from the mixed solutions. These appear when there is a rise or a drop in the adsorption of the components from binary solutions, respectively, compared to their adsorption from individual solutions.

We may in this case assume that the adsorption of the surfactant from the mixture is of a competitive nature. From the studied nonionic surfactants, Tween-20 containing the shortest hydrocarbon radical in its molecule is better adsorbed from an individual solution on a surface of paraffin. Upon the adsorption of Tween-20 from mixed solutions with DDPC, strong competition for localization sites on the surface of the paraffin thus occurs, and an antagonistic effect is observed at all molar ratios of the components in the solution. The situation is similar upon the adsorption of Tween-40 from mixed solutions with DDPC, but a synergistic effect appears at high contents of Tween-40 in binary mixtures with DDPC. For Tween-60, a synergistic effect is already observed at a stoichiometric ratio of the components in the solution; for Tween-80, it is seen over the whole range of surfactant mole ratios. In transitioning from a series between Tween-20 to Tween-80, the adsorption of certain molecules falls, and the interactions between the hydrocarbon radicals of cationic and nonionic surfactants with the adsorbent and with each other begin to dominate with the formation of associates on the surface of paraffin, thereby increasing the adsorption.

Assuming from the data on the adsorption of surfactants from individual solutions that additivity applies here, the values of total adsorption were calculated according to the formula $A_{\text{calc}} = nA_{\text{Tw}} + (1 - n)A_{\text{DDPC}}$. The experimental and calculated values of adsorption of Tweens and DDPC were analyzed at the same set value of the equilibrium concentration of surfactant in the individual and mixed solutions ($C_{\text{eq}} = 0.15 \times 10^{-5}$ mol/dm^3).

As can be seen from Table 1, for mixtures of Tween-20 and Tween-40 with DDPC, there is positive deviation from ideality at all molar ratios of surfactant in the binary solutions ($A_{\text{exp}} < A_{\text{calc}}$). Mixed systems Tween-60–DDPC and Tween-80–DDPC show negative deviation from ideal behavior ($A_{\text{exp}} > A_{\text{calc}}$) throughout the range of component molar ratios. The data presented in Table 1 are consistent with those on adsorption isotherms of both Tweens and DDPC on paraffin and confirm the effects observed in hybrid systems are synergism and antagonism with respect to the adsorption of the studied surfactants on a solid surface.

If we assume that the binary system is ideal, the ratio between the experimental and calculated values of the concentrations needed to achieve close to max-

Table 1. Total adsorption of a surfactant on a surface of paraffin prepared from mixed solutions containing Tween and DDPC ($C_{\mathrm{eq}} = 0.15 \times 10^{-5}$ mol/dm^3)

n(Tween)	$A \times 10^6$, mol/g (experiment)	$A \times 10^6$, mol/g (calculation)
	Tween-20–DDPC	
0	1.70	–
0.2	1.79	1.89
0.5	1.74	2.19
0.8	1.58	2.48
1	2.68	–
	Tween-40–DDPC	
0	1.70	–
0.2	1.72	1.76
0.5	1.76	1.85
0.8	1.85	1.93
1	1.99	–
	Tween-60–DDPC	
0	1.70	–
0.2	1.75	1.74
0.5	1.98	1.89
0.8	2.01	1.94
1	1.88	–
	Tween-80–DDPC	
0	1.70	–
0.2	1.83	1.59
0.5	1.71	1.43
0.8	1.94	1.28
1	1.17	–

Table 2. Composition of mixed layers of adsorption and parameters of interaction between molecules of a surfactant on a surface of paraffin, calculated using the Rosen approach ($A = 1.5 \times 10^{-6}$ mol/g)

n(Tween)	χ^{T}	$-\beta^{\mathrm{T}}$
	Tween-20–DDPC	
0.2	0.69	6.2
0.5	0.78	8.6
0.8	0.92	14.3
	Tween-40–DDPC	
0.2	0.68	6.5
0.5	0.51	5.8
0.8	0.94	15.1
	Tween-60–DDPC	
0.2	0.67	6.3
0.5	0.77	8.4
0.8	0.84	11.6
	Tween-80–DDPC	
0.2	0.69	6.1
0.5	0.69	6.5
0.8	0.87	12.4

imum adsorption ($A_{\to\max}$) on a solid surface and the composition of the mixed solution is [14]

$$\frac{1}{C_{12}} = \frac{n}{C_1} + \frac{1-n}{C_2}, \tag{2}$$

where C_1, C_2, and C_{12} are the concentrations needed to achieve necessary for close to maximum adsorption on a surface of paraffin, determined using sorption isotherms of surfactants from individual and mixed solutions, respectively; and n is the molar ratio of Tween in the bulk solution.

The values of total concentration C_{12} needed to achieve close to maximum adsorption for the Tween-80–DDPC system on a surface of paraffin, determined using adsorption isotherms of surfactants from binary solutions over the range of mixture component mole ratios are less than the calculated values, demonstrating the synergistic effect the action of the studied surfactants has upon their adsorption on paraffin and is consistent with the data from adsorption isotherms. In other words, there is a negative deviation from the ideal state for mixed system Tween-80–DDPC (Fig. 3).

A similar analysis could be performed only for mixed system Tween-80–DDPC, since $A_{\to\max}$ was not achieved for the studied mixtures at all molar ratios of DDPC with Tween-20, Tween-40, and Tween-60 upon their adsorption from binary mixtures on surfaces of paraffin, relative to the values of the adsorption of nonionic surfactants from individual solutions.

The nonadditive behavior in the mixed systems of cationic and nonionic surfactants can be explained by the specific interaction between the components of the mixture in the bulk solution, i.e., the ability to form guest–host systems among the cationic and nonionic surfactants due to ion-dipole (electrostatic) interaction and hydrogen bonds between the oxyethylene chains of the nonionic surfactant molecules and polar groups of cationic surfactants while the hydrophobic interactions between the hydrocarbon chains give stability to their associates [15].

Since paraffin is nonpolar substance with an energetically homogeneous surface, the possibility of using the Rosen approach to calculate the composition of the mixed adsorption layer χ^T and parameter of intermolecular interaction β^T was suggested in [16].

$$\frac{(\chi^T)^2}{(1-\chi^T)^2}\frac{\ln\left[nC_{12}/C_1\chi^T\right]}{\ln\left[(1-n)C_{12}/C_2(1-\chi^T)\right]} = 1, \tag{3}$$

$$\beta^T = \frac{\ln\left[nC_{12}/\chi^T C_1\right]}{(1-\chi^T)^2}, \tag{4}$$

where n and χ^T are the molar fractions of Tween in the bulk solution and adsorption layer on a surface of paraffin, respectively; β^T is the parameter of interaction between adsorbed molecules; C_1, C_2, and C_{12} are the

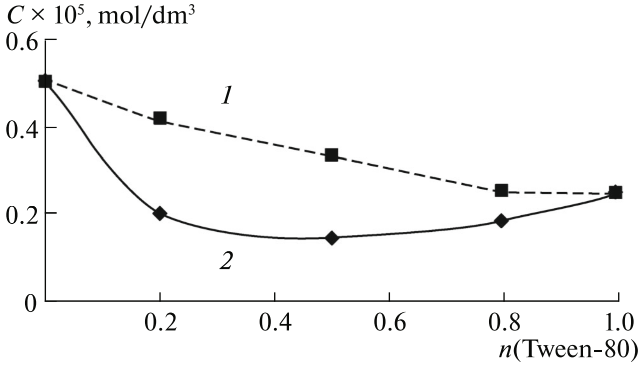

Fig. 3. Dependence of the concentration required to attain near maximum adsorption on a surface of paraffin in individual and binary solutions of Tween–DDPC on molar fraction of Tween-80: (*1*) calculated data; (*2*) experimental data.

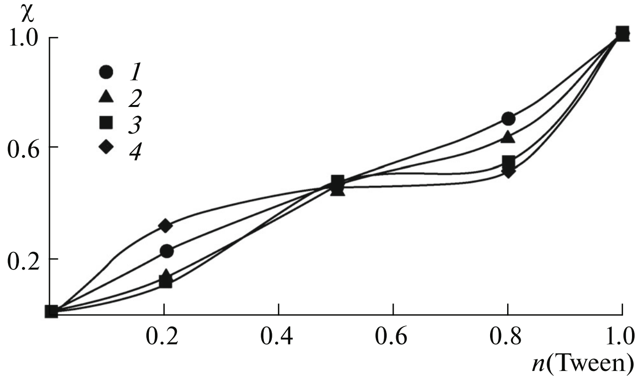

Fig. 4. Dependences of the molar fraction of (*1*) Tween-60, (*2*) Tween-40, (*3*) Tween-80, and (*4*) Tween-20 (χ) in an adsorption layer formed on a surface of paraffin on the composition of the solution at a concentration of $C_{eq} = 0.05 \times 10^{-5}$ mol/dm^3.

concentrations determined from experimental sorption isotherms of surfactants from individual and mixed solutions, respectively.

The calculated parameters of intermolecular interaction β^T and the composition of the adsorption layer at the interface between the binary surfactant–paraffin aqueous solution are shown in Table 2. The negative values of interaction parameter β^T indicate the mutual attraction of Tween and DDPC molecules in the mixed adsorption layer. This result is consistent with the literature data, according to which the interaction parameter between the cationic and nonionic surfactant in mixed adsorption layers and micelles is negative [16]. Our values for the mixed adsorption layer, obtained using the Rosen approach, are consistent with the calculated values on the experimental adsorption isotherms, but only for Tween mole fractions of 0.2–0.5 (Fig. 4, Table 2). For the studied Tween–DDPC systems with 0.8 mole fractions of nonionic surfactant, the values calculated for the composition of the mixed adsorption layer on the surface of the paraffin are exaggerated, excluding the possibility of using the Rosen approach in this case. This was also established in studying the adsorption of mixtures of nonionic, anionic, and cationic surfactants at the liquid–solid interface [9, 17], due likely due to small experimental errors.

Calculations for the composition of the mixed adsorption layer showed that at $C_{eq} = 0.05 \times 10^{-5}$ mol/dm^3, a mixed adsorption layer with composed mainly of cationic surfactants forms on a surface of paraffin at stoichiometric and high contents of DDPC in binary solutions. The content of Tween in a mixed adsorption layer on a paraffin surface is equal to the content of DDPC in the layer when *n* (Tween) > 0.5 in the binary solution (Fig. 4). The molar contents of Tween-20, Tween-40, Tween-60, and Tween-80 in the adsorption layer are the same only when they are in equimolar ratios with DDPC in the bulk of the mixed solution.

At high concentrations ($C_{eq} = 0.2 \times 10^{-5}$ mol/dm^3) and stoichiometric ratios of the components in the binary mixture, the mole fractions of Tweens and DDPC in a mixed adsorption layer on a surface of paraffin are same. An increase in the content of Tweens in the solution increases their mole fraction in the paraffin adsorption layer by a factor of 1.2.

CONCLUSIONS

The adsorption of Tweens and DDPC on surfaces of paraffin was studied experimentally in mixed solutions at different molar contents of the surfactant, and the effect each component had on the mixture was established upon their adsorption. It was shown that upon the adsorption of nonionic surfactants and cationic surfactants from binary solutions, both synergistic and antagonistic effects are observed in the systems, due likely to the competitive mechanism of adsorption on a solid surface of paraffin that we propose. The negative effect adding DDPC to the solution had on the adsorption of Tweens with small hydrocarbon radicals in their molecules (Tween-20 and Tween-40) on a surface of paraffin was established. For Tween-60 and Tween-80, the effect was positive. This positive effect was due to the higher adsorption values of nonionic surfactants from mixed solutions with cationic surfactants, relative to those of individual solutions, and the drop in the values of the concentrations needed to achieve close to maximum adsorption on a surface of paraffin for the Tween-80–DDPC mixed system. The positive effect a nonionic surfactant has on the adsorption of DDPC on a surface of paraffin was also established. It is apparent from the higher values of the adsorption of cationic surfactants from mixtures with Tween, relative to its adsorption from individual solutions. Based on our analysis of the adsorption isotherms of the studied surfactants and in terms of the Rosen approach, the probable structure of the adsorbed layers formed on a solid surface and the parameters of intermolecular interaction between surfactants of different natures on paraffin were calculated.

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