

# Factors Determining the Catalytic Activity of the Mixed Micellar System Cetyltrimethylammonium Bromide–Brij-35 in the Hydrolysis of a Phosphonic Acid Ester

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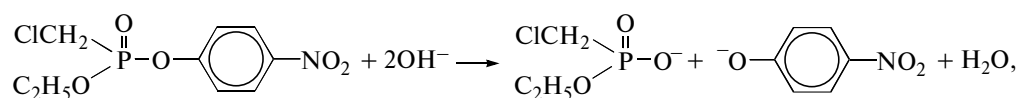
**Abstract**—The micellization and surface properties, Stern layer micropolarity, and catalytic action of the cetyltrimethylammonium bromide–Brij-35 system in the alkaline hydrolysis of *O*-ethyl *O*-*p*-nitrophenyl chloromethylphosphonate have been investigated at different proportions of the constituent surfactants. This system has unique, invertible catalytic properties ranging from acceleration of the hydrolysis reaction by more than one order of magnitude to strong inhibition of this reaction and even termination of the reaction at certain proportions of the surfactants. The factors in the changes of the catalytic effect under variation of the surfactant ratio are micropolarity in the reaction zone and surface potential. A likely cause of the termination of the process is the shift of the reaction zone from the surface layer to the micelle core, where the environment is less polar.

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In recent years, there has been increasing theoretical and practical interest in mixed surfactant-based micellar systems [1–5]. This is primarily due to the uncommon physicochemical and mechanical and other properties shown by these mixed compositions. Furthermore, these compositions are cheaper and less sensitive to the purity of their components than individual solutions. The mixed micellar systems are of both fundamental and practical interest. The mixed solutions differ in their properties (critical micelle concentration (CMC), aggregation number, solubilizing capacity) from the individual solutions of their constituent surfactants [2, 6–9]. This makes it possible to attain the required parameters of the micellar system by varying its composition. In most cases, mixed micellar systems are superior to individual compounds since the composition of the mixture can be optimized for each particular case. Although the number of publications on mixed micellization, including studies using theoretical and semiempirical approaches, has increased in the last 2–3 years, the basic features of the

functioning of binary surfactant systems still need a more profound consideration. The reactivity of compounds in mixed systems remains a poorly explored area [10–17].

Earlier, we studied the micellization properties and catalytic effects of binary micellar systems based on the cationic surfactant cetyltrimethylammonium bromide (CTAB). The following nonionic surfactants were examined as the second component: polyethylene glycol(~9) monotetradecyl ether [18], polyethylene glycol(10) oleyl ether (Brij-97) (C<sub>14</sub>E<sub>9</sub>) [19], and polyethylene glycol(10) mono-4-isooctylphenyl ether [20, 21]. These surfactants differ in their hydrophilic–lipophylic balance (HLB). The present work continues this series of studies, dealing with the CTAB–Brij-35 binary system. Its main purpose is to estimate the catalytic activity of the system in the alkaline hydrolysis of *O*-ethyl *O*-*p*-nitrophenyl chloromethylphosphonate (**1**),



and to study the micellization and surface properties and micropolarity of the system, which are the properties determining the efficiency of the catalytic process.

When selecting objects for our study, we took into account the following circumstances. Firstly, we considered the HLB of surfactants. The nonionic surfactants examined in our earlier works [18, 19] were dominated by a hydrophobic moiety. In this study, we chose to examine the surfactant Brij-35, whose polyoxyethylene chain has 32 units and is much longer than the hydrocarbon radical, which consists of 12 methylene groups. Brij-35 has one of the largest HLB values in the Brij family, namely, 16.9 (as compared to HLB = 12.4 for Brij-97). Secondly, we took into consideration the fact that CTAB and Brij-35 are the surfactants most widely used in research and development. The third circumstance that determined our choice was that, in our earlier studies [18, 19], we examined binary mixtures in which only one component (CTAB) was catalytically active in the alkaline hydrolysis of phosphonate **1**, while the other (nonionic) component was catalytically inactive. By contrast, the individual micelles of both surfactants examined here can exert an effect on this model reaction. The effects of these surfactants are opposite: CTAB accelerates and Brij-35 slows down the alkaline hydrolysis of the substrate. For this reason, it was expected that the catalytic effect of the mixed micelles would vary in a wide range. Fourthly, we chose the alkaline hydrolysis of an ester of a tetracoordinated phosphorus acid (reaction (I)) as the model reaction for the reason that such esters are environmental toxicants and the problem of their decomposition in natural aqueous media is a present-day challenge [22, 23].

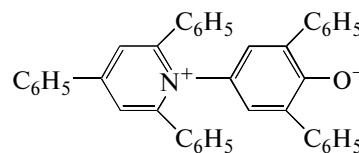
## EXPERIMENTAL

Compound (**1**) was synthesized via a patented procedure [24]. CTAB and Brij-35 were purchased from Sigma-Aldrich.

The hydrolysis kinetics was studied spectrophotometrically on a Specord M-400 spectrophotometer by recording the absorbance due to the *p*-nitrophenolate ion at a 10- to 30-fold excess of alkali over the substrate. Apparent rate constants ( $k_{app}$ ) were derived from the relationship  $\ln(A_{\infty} - A) = -k_{app}t + \text{const}$ , where  $A$  and  $A_{\infty}$  are the absorbances of the solution at the point in time  $t$  and after the completion of the reaction, respectively.  $k_{app}$  was calculated by weighted least squares; the arithmetic mean of three measurements differing by at most 5% were used in the calculation.

Surface tension was measured by the Du Nouy ring method [19] at 25°C.

The solvatochromic probe  $E_T(30)$  (Serva),



was used as received. The absorption spectra of the probe in solution were recorded on a Hewlett-Packard HP-8452A spectrophotometer. The empirical parameter  $E_T$  (kcal/mol) was calculated via the formula  $E_T = (2.859 \times 10^{-3}) \nu$ , where  $\nu$  is the frequency at which the maximum of the electron transfer band occurs. The initial solution of the reagent ( $1 \times 10^{-3}$  mol/L) was prepared by dissolving a precisely weighed sample in an aqueous alkali. The probe concentration in the micellar systems was  $1 \times 10^{-4}$  mol/L.

## THEORY

Micellization in solutions of binary surfactant systems is largely determined by the structure of the surfactants, namely, the nature of their head groups and the length of their hydrocarbon tails. The composition of the mixed micelles of ionic and nonionic surfactants may differ significantly from the composition of the solution. A number of thermodynamic theories have been developed and several semiempirical models suggested for quantitative description of the properties of mixed micellar solutions. In the case of perfect mixing, the quantitative characteristics of surfactant solutions, such as CMC, the composition of micellar aggregates, and the concentration of the monomer form of amphiphilic molecules, can be predicted using the following equation [25]:

$$\frac{1}{C^*} = \frac{\alpha_1}{C_1} + \frac{\alpha_2}{C_2}, \quad (1)$$

where  $\alpha_1$  and  $\alpha_2$  are, respectively, the mole fractions of the ionic and nonionic surfactants in the solution, and  $C^*$ ,  $C_1$ , and  $C_2$  are the CMC values for the mixed system and ionic and nonionic surfactants, respectively. This theory adequately describes the behavior of mixed solutions of almost ideally miscible surfactants belonging to the same homological series. However, it poorly predicts the properties of solutions of surfactants with different heads. A semiempirical model based on regular solution theory [26] is widely used for these systems. The nonideality of the mixture in this model is taken into account by introducing, into Eq. (1), the surfactant activity coefficients ( $f_1$  and  $f_2$ ) and the parameter accounting for surfactant-surfactant interaction in mixed aggregates ( $\beta$ ):

$$f_1 = \exp \beta \times (1 - x_1)^2, \quad (2)$$

$$f_2 = \exp \beta \times x_1^2, \quad (3)$$

where  $x_1$  is the mole fraction of the ionic surfactant in the mixed micelles, which can be calculated by iteratively solving the equation

## Colloidal properties of the CTAB–Brij-35 system

| $\alpha_1$ | $\Gamma_{\max} \times 10^6$ ,<br>mol/m <sup>2</sup> | $A_{\min}$ , nm <sup>2</sup> | $\pi_{\text{CMC}}$ , mN/m | $-\Delta G_m$ ,<br>kJ/mol | $-\Delta G_{\text{ad}}$ ,<br>kJ/mol | CMC,<br>mmol/L | Degree of binding<br>of counterions |
|------------|---|------------------------------|---------------------------|---------------------------|-------------------------------------|----------------|-------------------------------------|
| 0          | 1.60  | 1.04                         | 35.3                      | 20.0                      | 42.1                                | 0.31           | —                                   |
| 0.10       | 1.23  | 1.35                         | 33.3                      | 21.4                      | 48.6                                | 0.31           | 0.11                                |
| 0.26       | 1.34  | 1.24                         | 35.8                      | 22.1                      | 48.8                                | 0.33           | 0.15                                |
| 0.40       | 1.59  | 1.04                         | 32.6                      | 24.1                      | 44.6                                | 0.35           | 0.22                                |
| 0.77       | 1.90  | 0.87                         | 32.0                      | 30.8                      | 47.6                                | 0.52           | 0.62                                |
| 0.90       | 2.36  | 0.70                         | 34.0                      | 33.2                      | 47.6                                | 0.67           | 0.80                                |
| 1.0        | 3.14  | 0.53                         | 20.3                      | 31.5                      | 38.0                                | 0.85           | 0.82                                |

$$\frac{x_1^2 \ln\left(\frac{a_1 C^*}{x_1 C_1}\right)}{(1-x_1)^2 \ln\left(\frac{(1-a_1)C^*}{(1-x_1)C_2}\right)} = 1. \quad (4)$$

The mathematical apparatus used in these calculations was detailed by Rubingh [26]. The parameter  $\beta$  can be calculated via the equation

$$\beta = \frac{\ln\left(\frac{a_1 C^*}{x_1 C_1}\right)}{(1-x_1)^2}. \quad (5)$$

This parameter accounts for the deviation of the system from the ideal mixture state and for the character of the interaction between surfactant monomers in the mixed micelles. A negative value of  $\beta$  implies that there are attractive forces, while a positive value of this parameters means the domination of repulsive forces between different surfactant molecules. An increase in the absolute value of  $\beta$  indicates an increasing deviation of the micellar system from the ideal mixture state.

The composition of the micellar aggregates is a function of the total surfactant concentration and can be calculated as

$$x_1 = \frac{-(C_{\text{Surf}} - \Delta) + \sqrt{(C_{\text{Surf}} - \Delta)^2 + 4\alpha_1 C_{\text{Surf}} \Delta}}{2\Delta}, \quad (6)$$

where  $\Delta = f_2 C_2 - f_1 C_1$ .

The Gibbs adsorption equation [27] provides means to calculate the maximum amount adsorbed,  $\Gamma_{\max}$  (mol/m<sup>2</sup>):

$$\Gamma_{\max} = \frac{1}{4.61RT} \lim_{C \rightarrow \text{CMC}} \frac{d\pi}{d \log C}, \quad (7)$$

where  $\pi$  (mN/m) is the surface tension equal to the difference between the surface tension of the solvent and that of the solution at a given surfactant concentration ( $\pi = \gamma_0 - \gamma$ ) and  $R$  is the gas constant (8.31 J mol<sup>-1</sup> K<sup>-1</sup>). The minimum surface area of the surfactant molecule ( $A_{\min}$ , nm<sup>2</sup>), free energy of micellization ( $\Delta G_m$ , kJ/mol), and standard free energy of adsorption ( $\Delta G_{\text{ad}}$ , kJ/mol), were calculated using the following formulas [28, 29]:

$$A_{\min} = 10^{18} / (N \Gamma_{\max}) \quad (8)$$

( $N$  is Avogadro's number),

$$\Delta G_m = (1 + g) RT \ln(\text{CMC}) \quad (9)$$

( $g$  is the degree of counterion binding determined from surface tension isotherms.

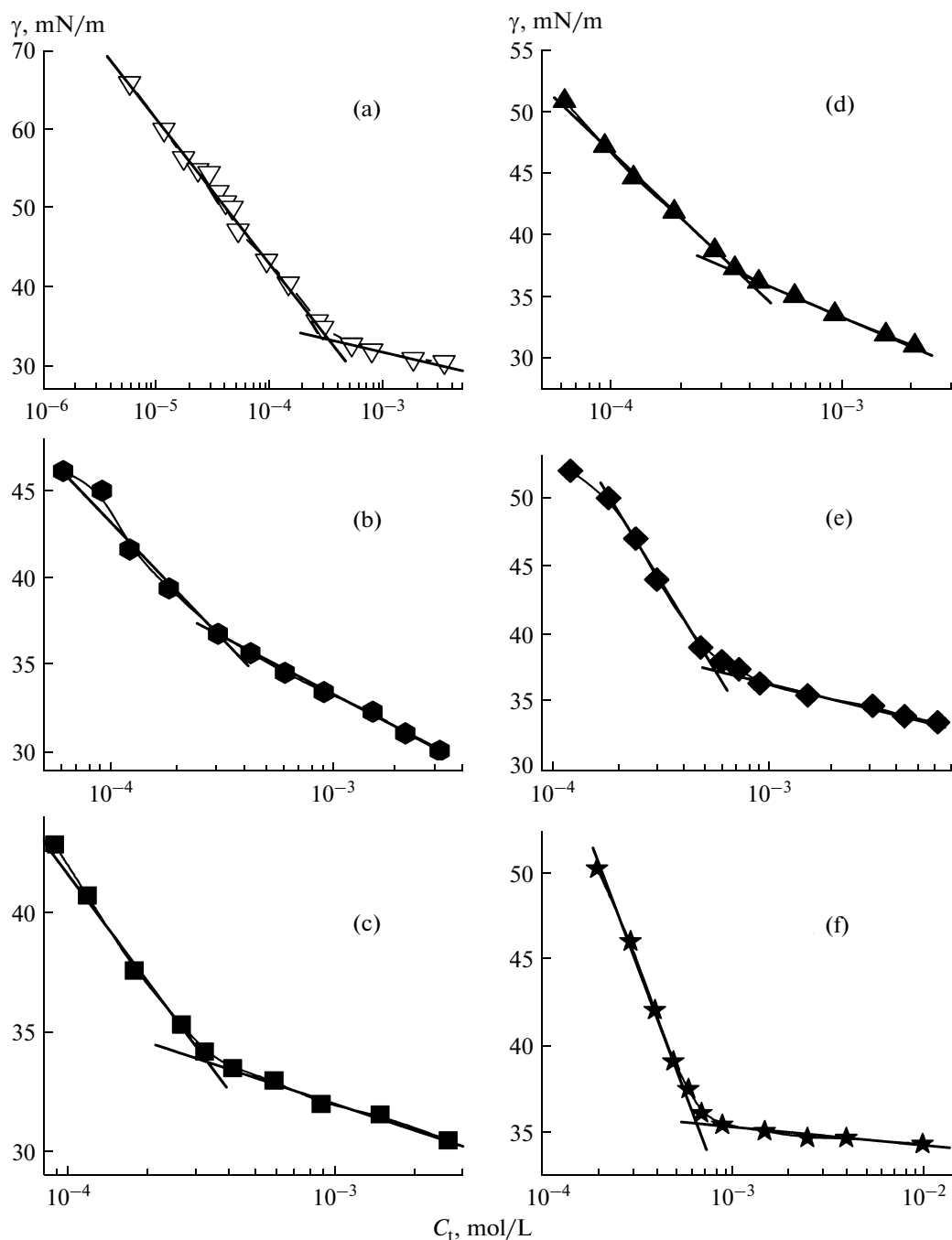
$$\Delta G_{\text{ad}} = \Delta G_m - (\pi_{\text{CMC}} / \Gamma_{\max}). \quad (10)$$

## RESULTS AND DISCUSSION

The major factors in the efficiency of micellar catalysis are reactant concentration and the change in the microenvironment of the reactants as a result of their passage from the bulk phase to nanosized aggregates. Therefore, the most important characteristics of micellar catalytic systems include quantitative parameters of the aggregates and micropolarity in the reaction zone. In this work, we will consider various aspects of the physicochemical behavior of the CTAB–Brij-35 system, including its surface and micellization properties, micropolarity in the surface layer, and catalytic effect. All parts of this work were carried out within a single methodological approach: any property was investigated as a function of the proportions of the ionic and nonionic surfactants. Hereafter, the molar ratio of the surfactants is expressed in terms of the mole fraction of the ionic surfactant in the solution ( $\alpha_1$ ).

*Surface and Micellization Properties of the CTAB–Brij-35 System*

Figure 1 shows surface tension isotherms for the CTAB–Brij-35 system at different surfactant ratios  $\alpha_1$ . The table lists the CMC values for the mixtures corresponding to the kink points in the  $\gamma$  versus  $\log C_1$  curves and the parameters characterizing surfactant adsorption at the water/air interface. For Brij-35,  $\Gamma_{\max}$  is smaller than for CTAB (table). This can be due to the fact that, in the case of Brij-35, the balance of molecular interactions controlling both adsorption and micellization is favorable for micellization, while in the case of CTAB, adsorption is hampered by the Coulomb repulsion between the head groups to a lesser extent than aggregation is. Conversely, the large

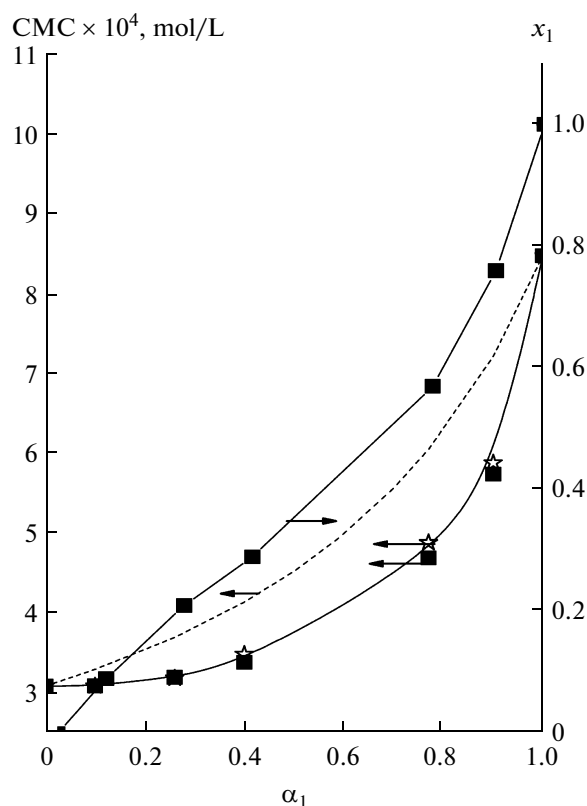


**Fig. 1.** Surface tension isotherms for micellar CTAB–Brij-35 solutions at 25°C and cationic-to-nonionic surfactant ratios of  $\alpha_1 =$  (a) 0, (b) 0.10, (c) 0.26, (d) 0.40, (e) 0.77, and (f) 0.90.

volume of the heads of Brij-35, which contains 23 ethylene glycol units, obviously offers more serious steric hindrance to adsorption than it does to micellization.

The data presented in the table suggest that, as the proportion of the nonionic surfactant in the mixture is decreased, the maximum amount of surfactant adsorbed increases and the packing of surfactant molecules in the surface layer becomes denser. Deviation from this monotonic trend is observed only on passing

from the individual Brij-35 solution to the mixed system with  $\alpha_1 = 0.1$ . As was mentioned above, surfactant adsorption at the water/air interface depends on two counteracting factors, namely, molecular interaction and the tendency of the surfactants to micellization. At  $\alpha_1 = 0.1$ , owing to the synergetic effect, the CMC values for the mixture and for Brij-35 alone are identical. However, the introduction of charged head groups leads to Coulomb repulsion between them, to a looser



**Fig. 2.** CMC for the mixed micellar system CTAB–Brij-35 and the mole fraction of CTAB in the mixed aggregates ( $x_1$ ) as a function of  $\alpha_1$ . The points represent experimental data. The dashed line represents the data calculated using the perfect mixing model. The solid line represents the data calculated using Eqs. (2)–(4).

packing (an increase in  $A_{\min}$ ), and to a decrease in the maximum amount adsorbed relative to the individual Brij-35 solution.

The table also lists the  $\Delta G_m$  and  $\Delta G_{ad}$  values calculated from surface tension isotherms with the degree of binding of surfactant counterions taken into account [30]. In this connection,  $\Delta G_m$  and  $\Delta G_{ad}$  acquire additional informativity. For ionic surfactant–nonionic surfactant binary systems at small  $\alpha_1$  values, a low degree of counterion binding can cause an “artificial” decrease in the absolute values of  $\Delta G_m$  and  $\Delta G_{ad}$  and distort the way they vary with the composition of the system. Nevertheless, the data presented in the table provide insight into the thermodynamic behavior of the mixed solution and are in good agreement with the order of magnitude of the values known from the literature and with the earlier revealed regularities [28, 29].

Tensiometric CMC data were analyzed within the pseudophase separation model. Figure 2 presents experimental CMC data and those calculated using the perfect mixing model (Eq. (1)) and regular solution theory in the pseudophase approximation (Eqs. (2)–(4)). Clearly, the behavior of the system deviates from the behavior that would be observed in the case of

perfect mixing. In the pseudophase separation mode, the extent of this deviation is characterized by the surfactant interaction parameter  $\beta$ . An analysis of the experimental data using original software implementing iterative solution of Eq. (5) has made it possible to calculate the value of  $\beta$ , which turned out to be  $-1.1$ . The negative value of  $\beta$  is evidence that an synergetic effect occurs in the binary surfactant solution; that is, there is attraction between surfactant molecules that results in the formation of mixed aggregates.

A comparison of these data to the data obtained earlier for the CTAB– $C_{14}E_9$  ( $\beta = -4.5$ ) and CTAB–Brij-97 ( $\beta = -2.5$ ) systems suggests that a negative deviation from the behavior of ideal mixtures takes place in all cases; however, the extents of this deviation are different. In the systems involving  $C_{14}E_9$  and Brij-97, both the head groups and the hydrocarbon tails of the nonionic surfactants are approximately equal in size. These tails differ from the tail of CTAB by only two methylene groups. The difference between the  $\beta$  values for these systems is likely due to the presence of an unsaturated moiety in the Brij-97 molecule. Here, the value of  $\beta$  can be affected both by the change in the molecular interactions and by the change in the geometry of the hydrocarbon radical: the Brij-97 molecule contains a  $sp^2$ -hybridized carbon atom, and such fragments are typically more loosely packed. The decrease in the absolute value of  $\beta$  on passing to the CTAB–Brij-35 system is likely due to the fact that the affinity between the ionic and nonionic surfactants in this pair is lower than in the pairs studied earlier [18, 19]. The difference between the surfactant affinities arises from the marked difference in the sizes of hydrocarbon tails and head groups between CTAB and Brij-35.

As is clear from Fig. 2, the CMC values calculated via Eqs. (1)–(3) within the pseudophase separation model with  $\beta = -1.1$  are in good agreement with experimental data.

Equation (6) makes it possible to estimate the mole fraction of either component of the binary solution ( $x_1$  and  $x_2$ ) in the mixed micelles in the CMC region. The results of this estimation are presented in Fig. 2, from which it follows that the mixed aggregates are enriched with the nonionic component. As the total surfactant concentration is raised, the concentrations of either component in the solution and in the mixed aggregates are equalized. As is shown in Fig. 3,  $x_1$  increases with an increasing total surfactant concentration, approaching the  $\alpha_1$  value.

Using Eq. (6), we calculated the composition of the mixed micelles. The variation of the activity of the ionic component with the proportions of the surfactants makes it possible to estimate the surface potential ( $\psi$ ) of mixed systems [31]:

$$\frac{d|\Psi|}{d \log a} = 59.16 \text{ mV}, \quad (11)$$

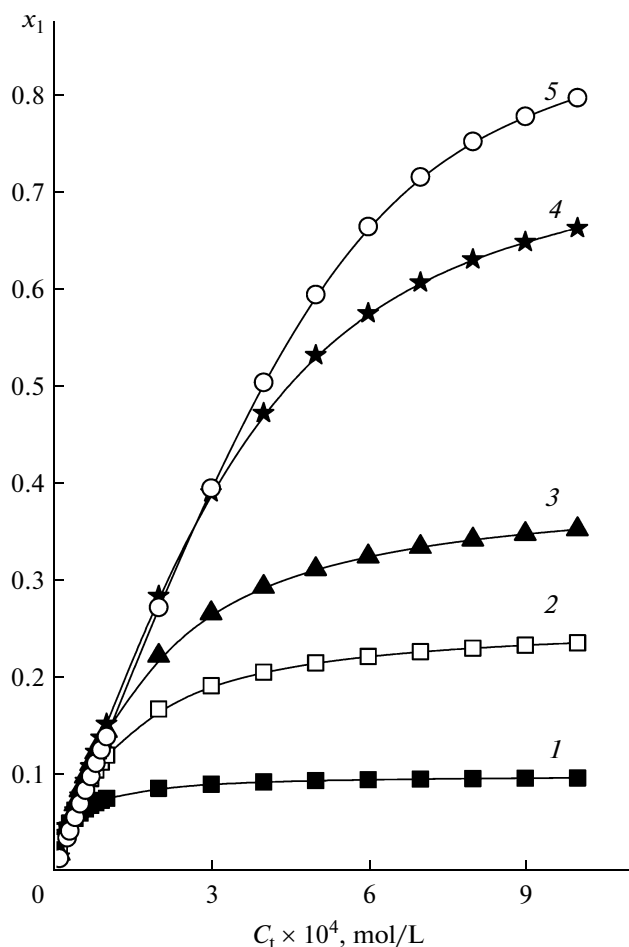


Fig. 3. Mole fraction of CTAB monomers in the mixed aggregates ( $x_1$ ) as a function of the total surfactant concentration ( $C_t$ ) at  $\alpha_1 =$  (1) 0.10, (2) 0.26, (3) 0.40, (4) 0.77, and (5) 0.90.

where  $a$  is the activity of the ionic monomer in the aqueous solution. The results of this calculation are plotted in Fig. 4. Clearly, as the mole fraction of the ionic surfactant decreases, the surface potential, which plays the key role in ion–molecule reactions in micellar media, decreases nonlinearly.

#### Catalytic Activity

Design of catalytic systems is among the most popular applications of micellar solutions. Use of mixed micelles opens up ample opportunities for controlling reaction rates in a wide range by varying the nature, concentration, and proportions of surfactants. In individual micellar solutions of CTAB, the rate of the alkaline hydrolysis of phosphonate **1** is higher than in water by a factor of 10–100, depending on reaction conditions (pH, alkali concentration, and ionic strength). Conversely, the rate of this reaction in Brij-35 micelles is three times lower. In this work, we aimed at evaluating the catalytic effect attained at various proportions of the surfactants and at determining the

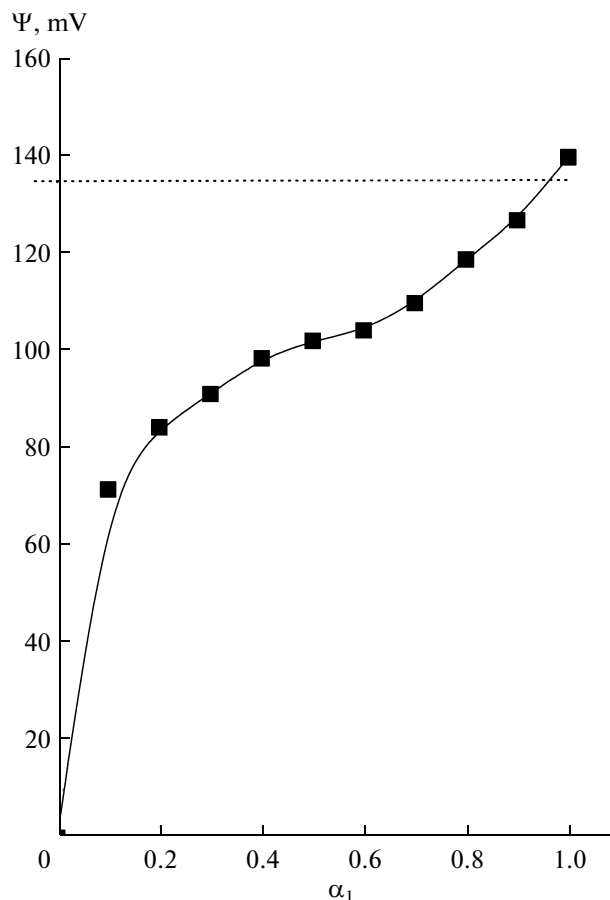
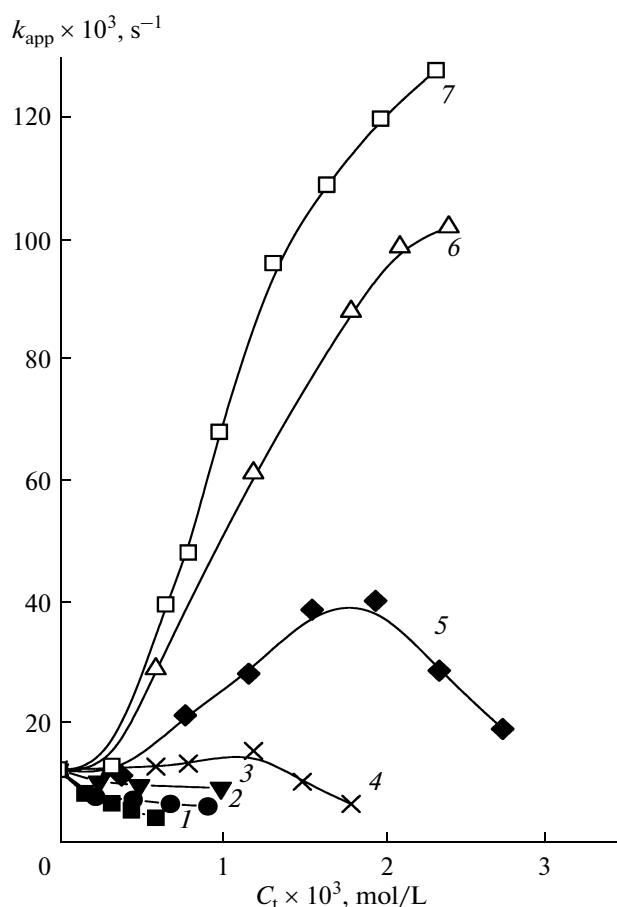


Fig. 4. Variation of the surface potential of the mixed micelles with the composition of the system. The dashed line indicates the surface potential of individual CTAB micelles.

contributions from different factors to this effect at the qualitative level. It is for this purpose that we optimized the kinetic experiment, measured micropolarity using the solvatochromic probe, and analyzed the UV–Vis spectra of *p*-nitrophenol, one of the reaction products.

The kinetics of the alkaline hydrolysis of phosphonate **1** was investigated at a NaOH concentration of 0.003 mol/L. At this alkali concentration, the observed reaction rates were comparable and convenient to measure irrespective of whether the reaction was accelerated or slowed down. In Fig. 5, we plot the apparent hydrolysis rate constant (which has the same physical meaning as the specific rate of the process) as a function of the total surfactant concentration.

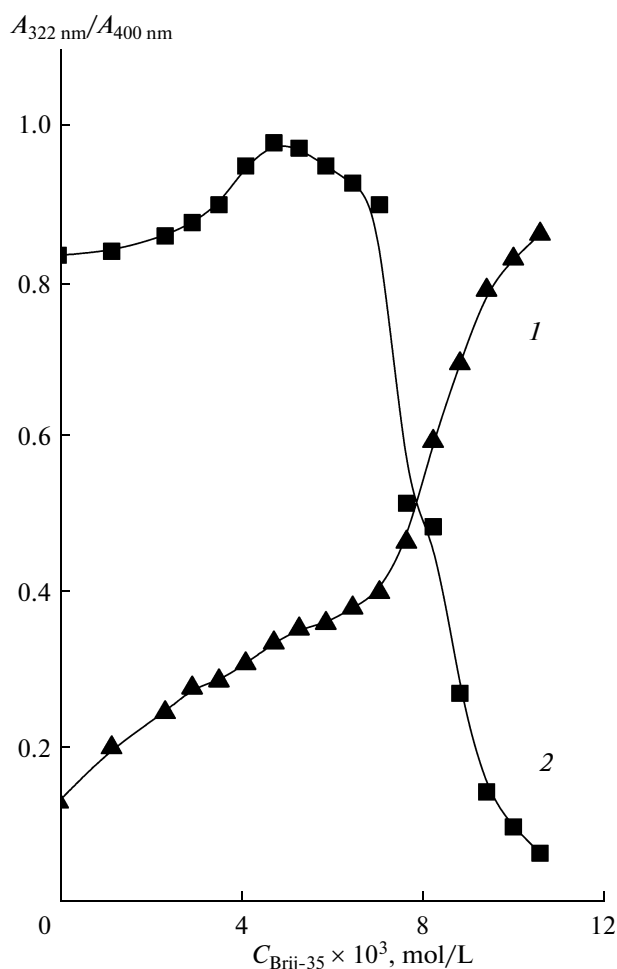
These data suggest that this binary system can change the specific rate of the process in an extraordinarily wide range. At  $\alpha_1 = 0.5$ –1.0, the rate constant increases with an increasing surfactant concentration: if it is compared to the rate constant in aqueous solution, the acceleration factor will be as large as 10. At



**Fig. 5.** Apparent rate constant of the alkaline hydrolysis of compound **1** in the mixed micellar system CTAB–Brij-35 as a function of the total surfactant concentration at  $\alpha_1 =$  (1) 0.10, (2) 0.26, (3) 0.40, (4) 0.50, (5) 0.77, (6) 0.85, and (7) 0.90. The NaOH concentration is 0.003 mol/L; 25°C.

$\alpha_1 = 0-0.4$ , an increase in the surfactant concentration slows down the process. At small  $\alpha_1$  values and a certain Brij-35 concentration, the reaction ceases. Not only does absorption at  $\lambda = 400$  nm fades away as this takes place, but also no changes in light absorption by the solution occur over the next 2 months. In view of this, we carried out a spectroscopic kinetic study involving the reaction product *p*-nitrophenol and the solvatochromic probe  $E_T30$ .

It is shown in Fig. 6 how the absorbance  $A_{max}$  of *p*-nitrophenol varies with the Brij-35 concentration. The  $pK_a$  value of phenol in water is 7.14. The absorption spectrum of the neutral and dissociated phenol species has a peak at 322 and 400 nm, respectively. At an alkali concentration of 0.003 mol/L, *p*-nitrophenol is completely dissociated. The alkaline hydrolysis reaction occurs in the Stern layer of the micelles. The micropolarity of this layer is sufficiently high for *p*-nitrophenol dissociation, so the reaction was monitored as the variation of the absorbance of the solution at 400 nm. The data presented in Fig. 6 demonstrate



**Fig. 6.** Absorbance of the (1) neutral *p*-nitrophenol species (322 nm) and (2) *p*-nitrophenolate anion (400 nm) as a function of the Brij-35 concentration at 25°C.

that, as the Brij-35 concentration is increased, the absorbance of the solution at 400 nm decreases and that at 322 nm increases. This is evidence that the effective  $pK_a$  value of *p*-nitrophenol increases, apparently because of the changes in the microenvironment of the compound.

The study of micropolarity in the surface layer of the micelles using the solvatochromic probe  $E_T30$  (Fig. 7) demonstrated that, as the total surfactant concentration is increased,  $E_T$  decreases, and this can be the cause of the decrease in the acidity of *p*-nitrophenol. However, the value of microenvironment polarity in the surface layer, which is indicated by the probe, remains similar to the polarity of alcohols. Therefore, the disappearance of the absorption by the solution at 400 nm, observed in our kinetic experiment at small  $\alpha_1$  values and a total surfactant concentration of about 0.001 mol/L, is not due to the changes in micropolarity in the surface layer. It can be hypothesized that the reaction zone shifts from the surface layer to the micelle core, where the environment is less polar.

Thus, the changes in the rate of the alkaline hydrolysis of phosphonate **1** in the CTAB–Brij-36 binary system under variation of the proportions of its constituent surfactants are determined by the simultaneous effects of a number of factors.

(1) Since the individual micellar systems CTAB and Brij-35 exert opposite effects on the reaction rate, it is to be expected that the catalytic effect will decrease with a decreasing proportion of CTAB.

(2) The decrease in the positive surface potential caused by a decrease in  $\alpha_1$  must weaken the Coulomb attraction between the hydroxide ion and the micelle, thus decelerating the reaction.

(3) The decrease in the degree of counterion binding caused by a decrease in  $\alpha_1$  must increase the number of charged groups. It is likely that this contribution is completely or partly taken into account in paragraph 2.

(4) The decrease in microenvironment polarity (Fig. 7) must be favorable for ion–molecule reactions, according to Ingold and Hughes's theory [32].

Additional information about the factors determining the catalytic effect could be provided by kinetic simulations using the pseudophase model. However, in this study it was impossible to carry out a systematic quantitative analysis of kinetic data within a single model. Part of the  $k_{app}$  versus  $C_{surf}$  data pertaining to the inhibition region ( $\alpha_1 = 0–0.4$ ) could be analyzed using the unimolecular reaction model. However, at a certain surfactant concentration, the  $k_{app}$  versus  $C_{surf}$  curves break because of the complete termination of the process. The kinetic curves obtained at  $\alpha_1 = 0.5–1.0$  should be analyzed using the second-order reaction model. In order to elucidate the contributions from different factors to the catalytic effect, we analyzed the dependence of  $k_{app}$  on  $C_{surf}$  at  $\alpha_1 = 0.77$  using the pseudophase approach. This kinetic model was detailed in earlier publications [19, 33]. The equation for the apparent second-order rate constant is

$$k'_{app} = \frac{k_{2,w} + \frac{k_{2,m}}{V} K_S K_{Nu} C}{(1 + K_S C)(1 + K_{Nu} C)}, \quad (12)$$

where  $k'_{app}$  is the second-order rate constant obtained by dividing  $k_{app}$  by the total nucleophile concentration;  $k_{2,w}$  and  $k_{2,m}$  are the second-order rate constants for the aqueous and micellar phases, respectively;  $K_S$  and  $K_{Nu}$  are the substrate and nucleophile binding constants, respectively;  $V$  is the molar volume of the surfactant; and  $C$  is the total surfactant concentration minus CMC. Earlier [19], we analyzed the applicability of this equation to mixed systems and presented examples of calculation of the binding constants and surfactant molar volume for different proportions of the constituent surfactants. The modified form of Eq. (12),

$$\left( \frac{k_{app}}{k_w} \right)_{max} = \frac{k_{2,m}}{k_{2,w}} \times \frac{K_S K_{Nu}}{V(\sqrt{K_S} + \sqrt{K_{Nu}})^2}, \quad (13)$$

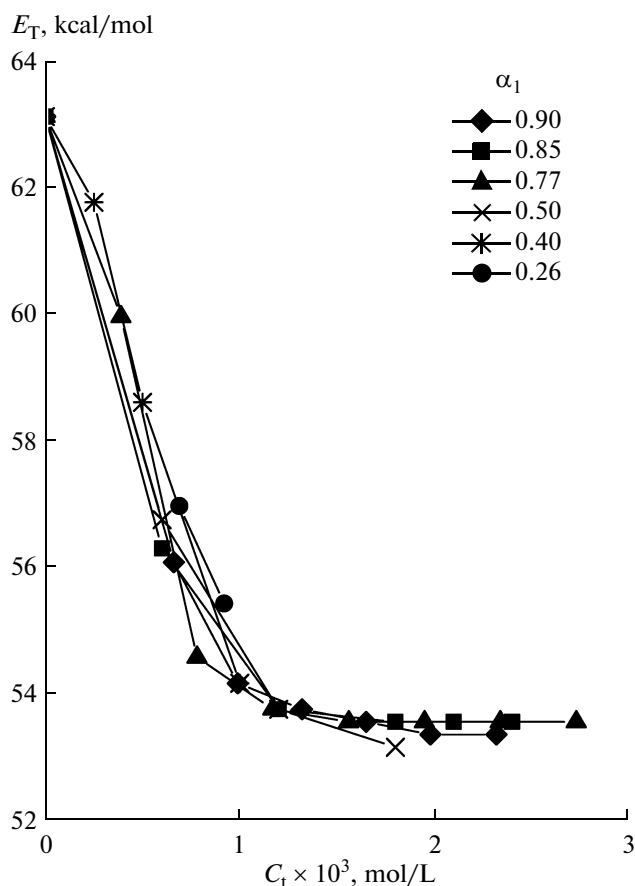


Fig. 7. Parameter  $E^T$  of the mixed micellar system CTAB–Brij-35 as a function of the total surfactant concentration.

where the first factor on the right-hand side ( $F_m$ ) characterizes the effect of the change in the microenvironment of the reactants upon their passage from the aqueous phase into the micellar phase and the second factor ( $F_c$ ) characterizes the effect of reactant concentration in the micelles, provides a quantitative estimate for the contribution from the different factors to the micellar effect.

By fitting the kinetic data for  $\alpha_1 = 0.77$  to Eq. (12), we obtained the following values:  $K_S = 5900$  L/mol,  $K_{OH} = 170$  L/mol, and  $k_m = 0.097$  s $^{-1}$  (here,  $k_m = k_{2,m}/V$ ). The true value of the second-order rate constant depends on the molar volume of the surfactants. For the ionic and nonionic surfactants, we used  $V_1 = 0.3$  L/mol and  $V_2 = 0.51$  L/mol, respectively. These values disregard the volume of water in the hydration shells of the surfactants. From these data, the rate constant of the second-order reaction in the micellar pseudophase was calculated to be  $k_{2,m} = 0.05$  L mol $^{-1}$  s $^{-1}$ . Thus, we observed a decrease in reactivity that is typically shown by phosphorus acid esters as the reaction zone passes into the micelles. Using Eq. (13), we calculated the contributions from the concentration and micellar environment factors to the catalytic effect. At

$k_{2,m} = 0.05 \text{ L mol}^{-1} \text{ s}^{-1}$ ,  $F_m = 0.012$  and  $F_c = 310$ . Therefore, the major contribution to the acceleration of the reaction by the CTAB–Brij-35 mixed micelles is made by the reactant concentration factor, while the micellar environment exerts an adverse effect, decelerating the reaction by a factor of 80 relative to the same reaction in aqueous solution. The net effect at  $\alpha_1 = 0.77$  in terms of the  $k_{app}/k_w$  ratio is 3.7.

Thus, the CTAB–Brij-35 system produces a unique, invertible effect ranging from acceleration of the reaction by more than one order of magnitude to strong inhibition of this reaction and even termination of the reaction at certain proportions of the two surfactants. A likely cause of the termination of the process is the shift of the reaction zone to the micelle core, where the environment is less polar. The data obtained in this study characterize the surface and micellization properties of the binary system and the micropolarity of the surface layer. The mixed solutions show synergism characterized by an interaction parameter of  $\beta = -1.1$ .

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