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# Micellization Properties and the Catalytic Effect of the Aqueous Cetyltrimethylammonium Bromide–Triton X-100 Binary System in Nucleophilic Substitution in Esters of Phosphorus Acids

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**Abstract**—The aggregation properties and catalytic effect of the cetyltrimethylammonium bromide-Triton X-100 binary system in nucleophilic substitution in esters of phosphorus acids are studied in the region of normal micelles and oil/water microemulsions. In the presence of phenol, the dissociation of *O*-alkyl-*O*-*para*-nitrophenyl chloromethyl phosphonates is up to 200 times more rapid than the same reaction in water. The efficiency of catalysis depends on the molar ratio of the surfactants and is determined by several factors: concentration, changes in the microenvironment of the reactants, and the shift of the p$K_a$ of phenol.

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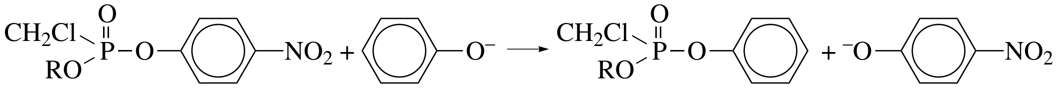
## INTRODUCTION

The present work continues a series of studies of the aggregation behavior and catalytic effect of mixed micellar solutions of surfactants in nucleophilic substitution in esters of phosphorus acids [1, 2]. Interest in self-organizing solutions of surfactants, in particular, mixed systems, is considerably increasing [3]. The use of a surfactant mixture instead of individual compounds allows one to purposefully change the properties of related materials, to adjust the properties of surfactant solutions to specific tasks, to reduce the cost of products, etc.

In the present work, we studied the micellization properties and catalytic effect of the cetyltrimethylammonium bromide (CTAB)–polyethylene glycol(10) mono-4-isooctylphenyl ether (Triton X-100) binary system in the region of normal micelles and oil/water microemulsions. The interaction of *O*-alkyl-*O*-*para*-nitrophenyl chloromethyl phosphonates with phenol in alkaline media (see scheme) was studied as a model reaction:



R = $C_2H_5$ (**1**), $C_6H_{13}$ (**2**)

**Scheme.**

## EXPERIMENTAL

Commercial CTAB and Triton X-100 (Sigma), both ~99% pure, were used in the experiments. Aqueous micellar solutions and microemulsions with an aqueous phase volume fraction of $\phi = 0.87$ were used as the reaction medium. Hydrocarbon (*n*-hexane, 1.97 wt %), which formed a nonpolar core, and a cosurfactant (*n*-butanol, 5.05 wt %) were involved in the formation of microdrops along with the surfactant (5.05 wt %). Compounds **1** and **2** were synthesized according to standard procedures [4]. The kinetics of ester bond dissociation was studied spectrophotometrically on a Specord M-400 spectrophotometer under pseudo-first-order conditions by measuring the light absorption due to the *para*-nitrophenoxide anion at 400 nm. The pH value of solutions was maintained using a borate buffer. At the beginning of the reaction, the substrate concentration was $5 \times 10^{-5}$ mol/l and the phenol concentration was 0.01 mol/l. Rate constants ($k_{obs}$) were derived from the $\ln(A_\infty - A) = -k_{obs}t + \text{const}$ plot, where $A$ and $A_\infty$ are the absorbances of the solution at the moment $t$ and after the end of the reaction, respectively. The constants were calculated by weighed least squares, using the

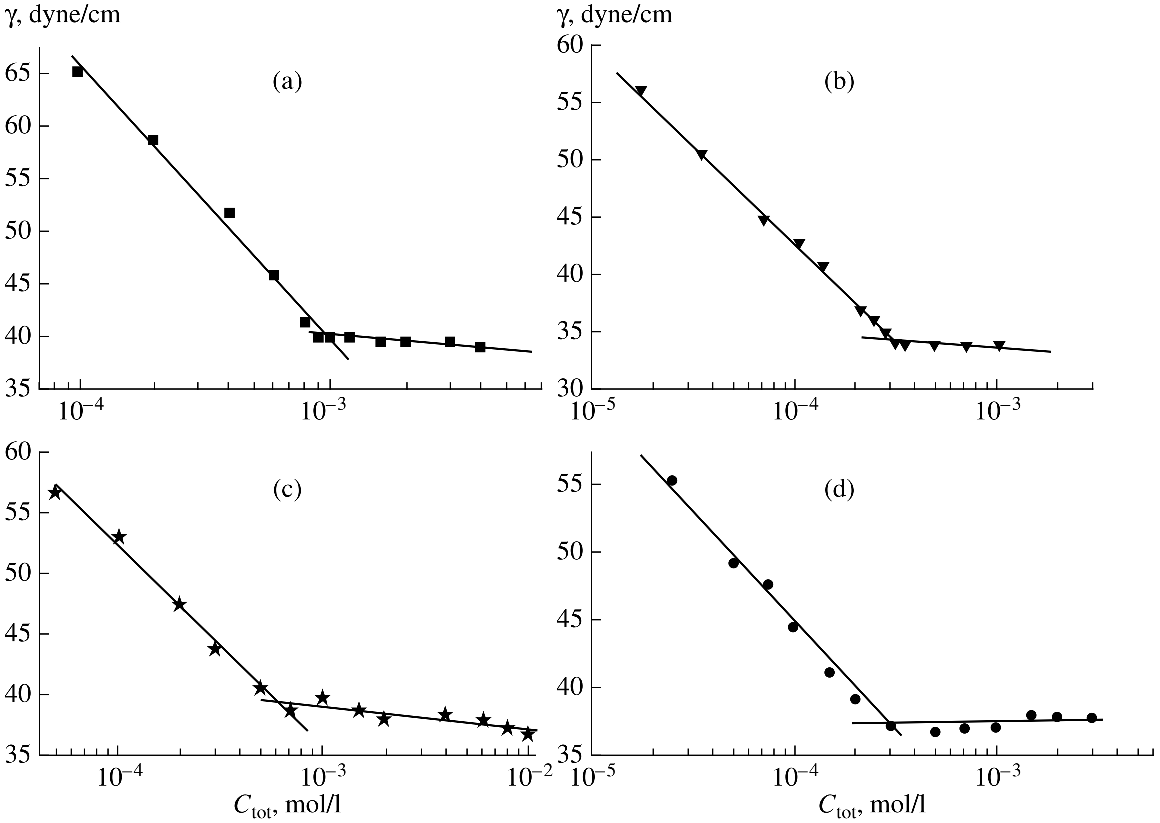


**Fig. 1.** Water–air interfacial tension for binary CTAB–Triton X-100 surfactant solutions as a function of the total surfactant concentration ($C_{tot}$) at $T = 25°C$ for various mole fractions of CTAB: $\alpha_1$ = (a) 1, (b) 0, (c) 0.9, and (d) 0.5.

arithmetic mean of three measurements differing by at most 5%. The surface tension was determined by the ring detachment method on a Du Nouy tensimeter [5] at 25°C. The acid–base properties of phenol were studied spectrophotometrically by measuring the absorption due to the ionized and neutral forms at different pH values. p$K_a$ was calculated using the Henderson–Hasselbach equation [6].

## RESULTS AND DISCUSSION

The micellization properties of binary solutions at different molar ratios of the ionic and nonionic surfactants were studied by measuring the water–air interfacial tension. The results of measurements for the individual and mixed systems are presented in Fig. 1. The critical micelle concentrations (CMC) data calculated for the ideal mixing model [7] are presented in Fig. 2:

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

where $\alpha_1$ and $\alpha_2$ are the mole fractions of the ionic and nonionic surfactants, respectively, in the solution; $C^*$, $C_1$, and $C_2$ are the CMC values for the mixed system, ionic surfactant, and nonionic surfactant, respectively.

As can be seen from these data, the experimental CMC data show a negative deviation from the ideal mixing behavior (synergetic effect). Note that, as compared to the deviations observed for the binary solutions CTAB–$C_{14}E_9$ [1] and CTAB–Brij-97 [2], the deviation for the CTAB–Triton X-100 system is smaller. This is probably caused by the fact that the micellization capacity of the individual surfactants in the CTAB–Triton X-100 pair is low as compared to that of the earlier studied systems.

Using the CMC data for the mixed solutions, we estimated the surface potential of the aggregates using the equation [8]

$$d/\Psi I/d\log a_1 = 59.16 \text{ mV}, \qquad (2)$$

where $a_1$ is the activity of the free monomers of the ionic surfactants in the mixed micellar solution, calculated in the framework of regular solution theory [9].

The surface potential $\psi$ as a function of the surfactant ratio is plotted in Fig. 2. The $\psi$ value decreases smoothly with a decrease in the CTAB mole fraction $\alpha_1$. The charge of the micelle surface plays an important role when micelles are used as nanoreactors, determining, to a great extent, the sign and value of the catalytic effect [10]. In addition, the variation of the surface potential in mixed systems is of independent interest. The shift of the p$K_a$ of ionic compounds in micellar solutions, which is caused, to a great extent, by the electrostatic contribution [10], is also significant. We found spectrophotometrically that the p$K_a$ of phenol is 9.95 in water, 9.3 in 0.01 M CTAB, and 10.3 in 0.01 M Triton X-100. These data indicate that the acidic properties of phenol are enhanced in a micellar CTAB solution and are somewhat weakened in a Triton X-100 solution as compared to water.

We measured the kinetics of the reactions of phosphonates **1** and **2** with phenol (pH 9.2) in mixed CTAB–Triton X-100 micellar solutions at different surfactant ratios (Figs. 3, 4). The phenolysis reactions of phosphonates in a borate buffer in the absence of a surfactant and in CTAB solutions were studied previously [11, 12]. It was shown that alkaline hydrolysis and the reaction of the substrates with borate anions make an insignificant contribution to the observed rate constant.

The contribution from alkaline hydrolysis to the observed rate constant is smaller in the CTAB-enriched mixed systems than in aqueous solution. Firstly, the p$K_a$ of phenol is lower in micellar systems based on cationic surfactants. Secondly, preferential adsorption occurs on the micelle surface of the hydrophobic phenoxide ions, as distinct from highly hydrophilic inorganic anions [13]. Probably, as the nonionic surfactant content increases, these two effects (increase in p$K_a$ and the preferential binding of the phenoxide ion by micelles) compensate each other and the contribution from hydrolysis is higher than that observed in an aqueous solution.

In a micellar CTAB solution containing phenol at pH 9.2, the dissociation of substrates **1** and **2** is, respectively, 80 and 220 times more rapid than the same process in aqueous solution (Tables 1, 2). Individual micelles of Triton X-100 insignificantly inhibit the process, which is possibly due to the shift of the p$K_a$ of phenol and a decrease in the proportion of the reactive phenoxide form. The dependences of the observed rate constant on the total surfactant concentration at various surfactant ratios for the reactions of phosphonates **1** and **2** with phenol in a borate buffer are plotted in Figs. 3a and 4. The kinetic data for the reaction in a CTAB solution in the absence of a buffer are presented in Fig. 3b.

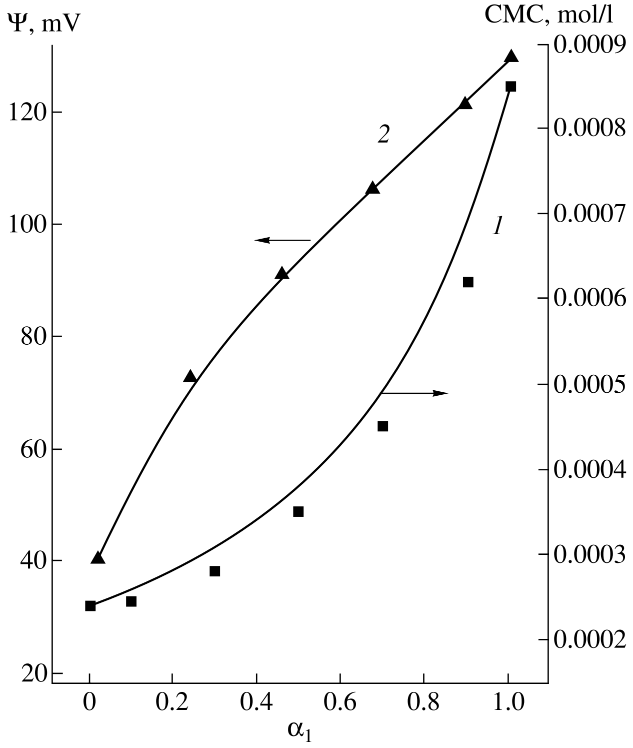


**Fig. 2.** (*1*) CMC for the mixed CTAB–Triton X-100 micellar solutions calculated using the ideal mixing model (solid line) and determined tensimetrically (points) and (*2*) the surface potential of the mixed CTAB–Triton X-100 micelles versus the mole fraction of CTAB in the solution.

The data obtained were analyzed in the framework of the pseudophase approach using the equation [10]

$$k'_{\text{obs}} = \frac{k_{2,\text{w}} + (k_{2,\text{m}}/V)K_{\text{S}}K_{\text{Nu}}C}{(1+K_{\text{S}}C)(1+K_{\text{Nu}}C)}, \quad (3)$$

where $k'_{\text{obs}}$ (l mol$^{-1}$ s$^{-1}$) is the second-order rate constant obtained by the division of $k_{\text{obs}}$ by the total phenol concentration; $k_{2,\text{w}}$ and $k_{2,\text{m}}$ (l mol$^{-1}$ s$^{-1}$) are the second-order rate constants in the aqueous and micellar phases, respectively; $K_{\text{S}}$ and $K_{\text{Nu}}$ (l/mol) are the binding constants of the substrate and phenol, respectively; $V$ is the

**Table 1.** Results of the quantitative analysis of the kinetic data (Fig. 3) in terms of Eq. (3)

| $\alpha_1$ | $k_{\text{obs}}/k_{\text{w}}$ | $k_{2,\text{m}}$, l mol$^{-1}$ s$^{-1}$ | $K_{\text{S}}$, l/mol | $K_{\text{Nu}}$, l/mol | $F_{\text{c}}$ | $F_{\text{m}}$ | $F_{\text{c}} \times F_{\text{m}}$ |
|---|---|---|---|---|---|---|---|
| 1.0 | 79 | 0.083 | 119 | 38 | 51 | 1.4 | 74 |
| 0.9 | 59 | 0.064 | 190 | 35 | 49 | 1.1 | 54 |
| 0.7 | 38 | 0.040 | 102 | 45 | 54 | 0.70 | 38 |
| 0.5 | 20 | 0.030 | 152 | 23 | 40 | 0.50 | 20 |
| 0.3 | 7.5 | 0.008 | 341 | 25 | 55 | 0.14 | 7.8 |
| 0.1 | 3.5 | 0.003 | 612 | 30 | 68 | 0.06 | 4 |

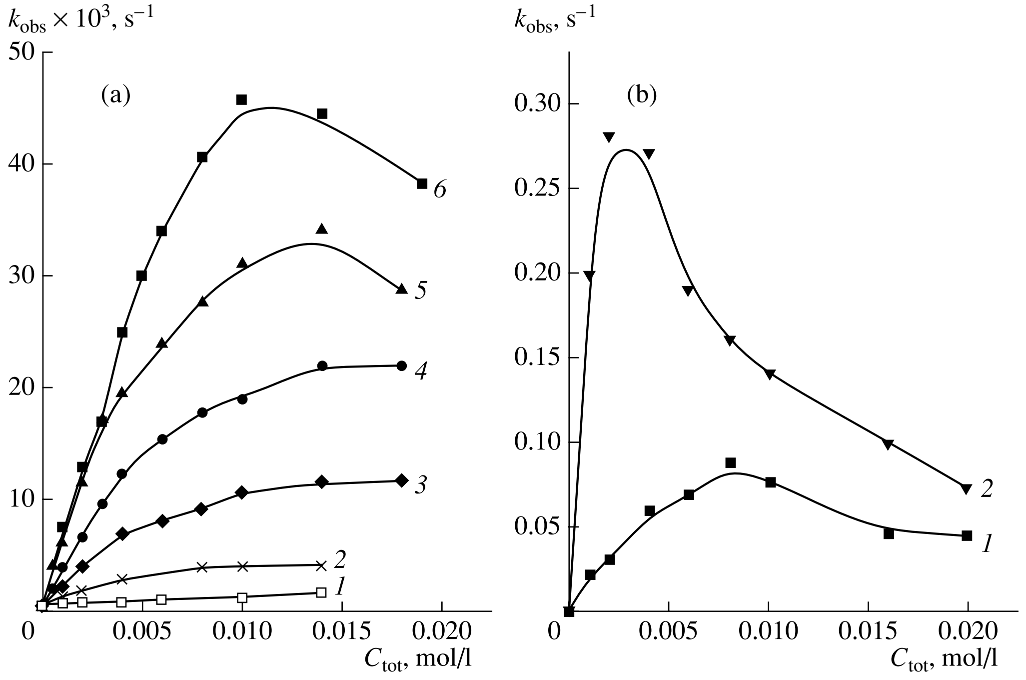


**Fig. 3.** Rate constants observed for (a) the reaction of phosphonate **1** with phenol in the CTAB–Triton X-100 system at $\alpha_1$ = (*1*) 0.1, (*2*) 0.3, (*3*) 0.5, (*4*) 0.7, (*5*) 0.9, and (*6*) 1.0 (borate buffer (pH 9.2), $T$ = 25°C) and (b) the reactions of phosphonates (*1*) **1** and (*2*) **2** with phenol in a micellar solution of CTAB ($C_{phenol} = C_{NaOH}$ = 0.004 mol/l) versus the total surfactant concentration.

molar volume of the surfactant; and $C$ is the total surfactant concentration minus CMC. The applicability of this equation to mixed systems was analyzed, and examples for the calculation of the binding constants and molar volume of the surfactant at their different ratios were presented [1, 2].

Use of the modified form of Eq. (3), specifically, $(k_{obs}/k_w)_{max} = \frac{k_{2,m}}{k_{2,w}}\frac{K_S K_{Nu}}{V(\sqrt{K_S}+\sqrt{K_{Nu}})^2}$, in which the first factor on the right-hand side ($F_m$) characterizes the effect of the variation of the microenvironment of the reactants upon the transfer of the reaction from the aqueous phase to the micellar phase and the second factor ($F_c$) accounts for the effect of the concentrating of the reactants in micelles, makes it possible to quantitatively estimate different factors in the micellar effect.

As was mentioned earlier for the alkaline hydrolysis of phosphonates [14], a higher catalytic effect is observed for hydrophobic substrates in micellar solutions of cationic surfactants. The results presented in Figs. 3a and 4 also confirm this tendency. This is caused by higher binding constants of phosphonate **2**, whereas the second-order rate constants in the micellar pseudophase and in the aqueous solution are higher for phosphonate **1** (Tables 1, 2). For both substrates, the main contribution to the catalytic effect is from the concentrating factor; this situation is typical of aqueous micellar solutions [10, 15]. However, at $\alpha_1$ = 1.0, the factor of the micellar environment is $F_m > 1$; i.e., the micellar microenvironment exerts a favorable effect on

**Table 2.** Results of the quantitative analysis of the kinetic data (Fig. 4) in terms of Eq. (3)

| $\alpha_1$ | $k_{obs}/k_w$ | $k_{2,m}$, l mol$^{-1}$ s$^{-1}$ | $K_S$, l/mol | $K_{Nu}$, l/mol | $F_c$ | $F_m$ | $F_c \times F_m$ |
|---|---|---|---|---|---|---|---|
| 1.0 | 228 | 0.070 | 1923 | 70 | 164 | 1.4 | 222 |
| 0.9 | 199 | 0.050 | 958 | 83 | 191 | 1.0 | 187 |
| 0.7 | 126 | 0.037 | 854 | 86 | 165 | 0.75 | 123 |
| 0.5 | 64 | 0.032 | 1150 | 48 | 110 | 0.63 | 70 |
| 0.3 | 30 | 0.009 | 2653 | 74 | 181 | 0.18 | 32 |
| 0.1 | 6 | 0.004 | 226 | 47 | 74.6 | 0.082 | 6 |

the reaction rate. This is not the case for nucleophilic substitution involving hydrophilic ions [10, 14, 15].

The catalytic effect decreases with a decrease in the mole fraction of CTAB in the mixed aggregates (Figs. 3a, 4; Tables 1, 2). The speedup of nucleophilic substitution in cationic micelles is mainly caused by the electrostatic attraction of the nucleophile to the micelle surface. It would be assumed that the decrease in the efficiency of catalysis with a decrease in the CTAB fraction in mixed aggregates is due to the drop of the surface potential (Fig. 2) and, hence, to a decrease in the binding constant of the nucleophile. This is not true, as follows from the data presented in Tables 1 and 2. The concentrating factor changes insignificantly with a change in the micelle composition for both phosphonates, and the decrease in the catalytic effect is due to the fact that the second-order rate constant in the micellar pseudophase gradually decreases with increasing fraction of the nonionic surfactant. Thus, in this case, as in the CTAB–$C_{14}E_9$ and CTAB–Brij-97 systems [1, 2], the change in the catalytic effect caused by the variation of the solution composition is controlled by the micellar microenvironmental factor, i.e., the changes in the properties of the microenvironment upon the transfer of the reactants from the aqueous solution to the micelles. Note that, unlike the catalytic effect in the systems based on $C_{14}E_9$ and Brij-97, the catalytic effect in the mixed CTAB–Triton X-100 solution decreases monotonically with decreasing CTAB fraction. Analysis of the data listed in Tables 1 and 2 suggests that the binding constants of both reactants change nonmonotonically as the surfactant ratio is varied. This is probably due to the complicated dependence of the binding constants on the properties of the mixed aggregates in the case of several alternative factors simultaneously affecting the solubilization of the reactants. These factors (changes in the micelle composition, surface potential, and p$K_a$ shift) can exert opposite effects and vary nonmonotonically with the variation of the surfactant ratio. A similar kinetic behavior was observed [16] while investigating the catalytic effect of the sodium dodecyl sulfate–Brij-35 mixed micellar system on the alkaline hydrolysis of phosphonate **1**.

The dissociation kinetics of esters **1** and **2** was also studied in microemulsions based on the surfactant mixture in the absence and in the presence of phenol at pH 9.6. The data presented in Fig. 5 show that the rate constants observed for the substrates in the absence of phenol differ only slightly and hydrophobic ester **2** is somewhat more reactive. $k_{obs}$ gradually increases with increasing CTAB fraction in both the microemulsion system and the micellar solutions. This can be explained by an increase in the microdrop charge, which enhances the ability of the system to concentrate nucleophilic ions at the interface.

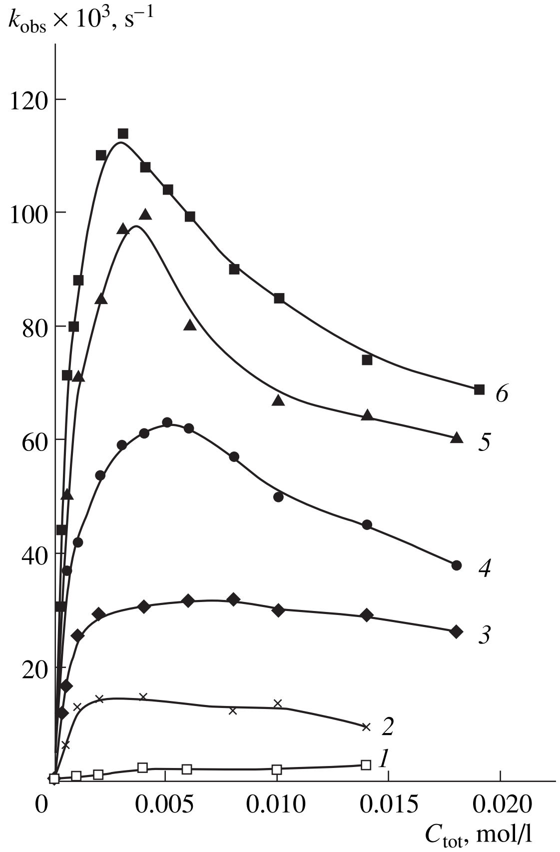


**Fig. 4.** Observed rate constant of the reaction of phosphonate **2** with phenol in a CTAB–Triton X-100–water system as a function of the total surfactant concentration for various mole fractions of CTAB: $\alpha_1$ = (*1*) 0.1, (*2*) 0.3, (*3*) 0.5, (*4*) 0.7, (*5*) 0.9, and (*6*) 1.0; borate buffer (pH 9.2), $T$ = 25°C.

Using the kinetic data for the alkaline hydrolysis of ester **1**, we determined, using Eq. (4), the surface potential for a microdrop at various ionic-to-nonionic surfactant ratios in the microemulsion:

$$\ln k_{2,\phi}(\mathrm{ISurf}) = e\psi/k_B T + \ln k_{2,\phi}(\mathrm{NSurf}), \qquad (4)$$

where $e$ is the electron charge, $\psi$ is the effective surface potential, $k_B$ is the Boltzmann constant, $T$ is absolute temperature, and $k_{2,\phi}$(ISurf) and $k_{2,\phi}$(NSurf) are the second-order rate constants determined for microemulsions based on the ionic and nonionic surfactants taking into account the phase volume [17]. If the volume of the dispersed phase remains unchanged, $k_{2,\phi}$ can be replaced with $k_{obs}$. The data presented in Table 3 show that, in normal CTAB-based microemulsions, the surface potential is substantially lower due to the presence of cosurfactant molecules (*n*-butanol) in the interphase layer than that in micellar solutions. Accordingly, the changes in $\Psi$ upon the addition of Triton X-100 to the system will not be very sharp.

The surface potential change induces a change in the solubilization properties of the microdrop, in particular, in its ability to selectively sorb different forms of compounds involved in acid–base equilibria. This is reflected by the change in the p$K_a$ of phenol (Table 3).

**Table 3.** Surface potential of the drops of the oil/water microemulsion (CTAB–Triton X-100–butanol–hexane–water), the p$K_a$ of phenol, and the second-order rate constants of the phenolysis of esters **1** and **2** at various ratios of CTAB to Triton X-100 in the microemulsion

| CTAB content of the mixed microemulsion, wt % | ψ, mV | p$K_a$ of phenol | $k_2$, l mol$^{-1}$ s$^{-1}$ (phenolysis of ester **1**) | $k_2$, l mol$^{-1}$ s$^{-1}$ (phenolysis of ester **2**) |
|---|---|---|---|---|
| 100 | 38.0 | 9.8 | 0.41 | 0.85 |
| 65 | 35.6 | 9.8 | 0.38 | 0.85 |
| 50 | 35.0 | 9.85 | 0.40 | 0.81 |
| 25 | 28.2 | 10.0 | 0.42 | 0.77 |
| 10 | 19.0 | 10.1 | 0.42 | 0.42 |
| 0 | 0 | 10.2 | 0.45 | 0.25 |

Passing from the microemulsion based on Triton X-100 to the CTAB-containing microemulsion is accompanied by a decrease in the p$K_a$ of phenol, i.e., an increase in the fraction of its anionic form (reactive during phenolysis) at a specified pH value. This fact, along with the effect of the medium on the reactivity of the reacting species (hydroxide and phenoxide ions), contributes to the observed dissociation rate constant of the phosphonates in the presence of phenols (Fig. 5). The dependence of $k_{obs}$ on the phenoxide ion concentration is linear, which makes it possible to estimate the second-order rate constant of phenolysis ($k_2$) from the equation $k_2 = (k_{obs} - k_0)/[PhO^-]$, where $k_0$ is the pseudo-first-order rate constant of alkaline hydrolysis. It should be emphasized that the $k_2$ value takes into account the effect of the medium on p$K_a$ of phenol at different ratios of the ionic and nonionic surfactants in the system. The data presented in Table 3 indicate a change in the reactivity of the phenoxide anion toward the substrates at different compositions of the medium. Hydrophobic substrate **2**, which is localized in the oil drop, is more sensitive to changes in the microenvironment than phosphonate **1**. This is manifested as a decrease in $k_2$ with an increase in the proportion of the nonionic surfactant in the system. Probably, the phenolysis of substrate **1** also occurs partially in the bulk aqueous medium and the change in the $k_2$ values is not so pronounced.

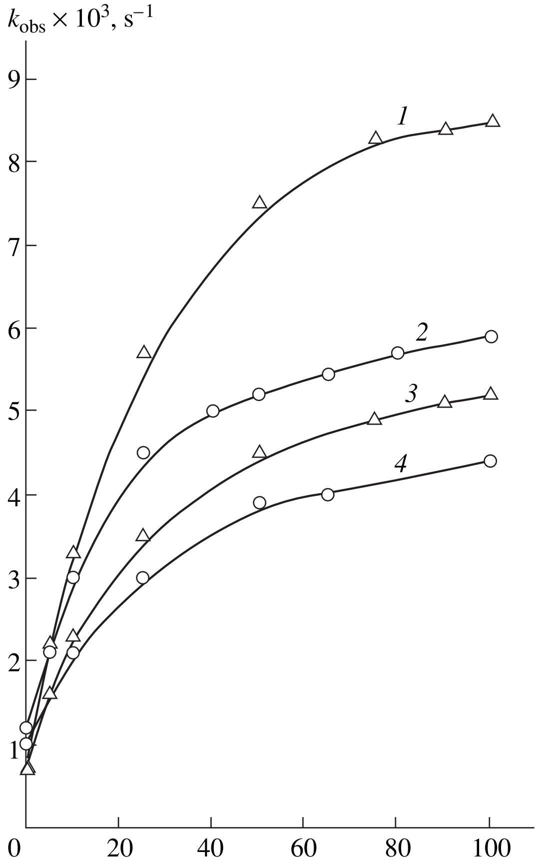


**Fig. 5.** Observed dissociation rate constant of the phosphonates (*2*, *4*) **1** and (*1*, *3*) **2** in the CTAB–Triton X-100 system at pH 9.6 (buffer solution based on sodium tetraborate and alkali) for (*1* and *2*) $C_{phenol} = 0.01$ mol/l and (*3* and *4*) without phenol; $T = 25°C$.

Thus, the micellization properties and catalytic effect of the CTAB–Triton X-100 binary system in the phenolysis of esters of phosphonic acid were studied. The formation of mixed aggregates in the solution was found. In mixed micellar systems, the reaction is up to 200 times more rapid than the reaction in aqueous solution due to the concentrating effect, the changes in the microenvironment of the reactants, and the shift of the p$K_a$ of phenol. The catalytic effect is stronger for more hydrophobic phosphonates and decreases with decreasing fraction of the cationic surfactant.

## ACKNOWLEDGMENTS

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