Influence of the Fluoride Ion on the Aggregation and Catalytic Properties of Micellar Solutions of Cetyltrimethylammonium Bromide

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Abstract—The influence of the fluoride ion on the aggregation behavior and catalytic properties of neutral and alkaline aqueous solutions of cetyltrimethylammonium bromide in nucleophilic substitution reactions of phosphorus acid esters was studied by tensiometry, small-angle neutron scattering, and UV spectrophotometry. The critical micelle concentrations and the radii, aggregation numbers, and shape of micelles forming in these systems, as well as the kinetic parameters of the nucleophilic substitution reactions of phosphorus acid esters, were determined.

INTRODUCTION

The influence of inorganic salts on the structural rearrangements and catalytic properties of micellar solutions of surfactants is of obvious interest because the salt effect and surface potential (Ψ) should be estimated in order to interpret kinetic data.

Extensive data concerning the changes in the properties of micellar aggregates in the presence of inorganic and organic electrolytes have been accumulated [1–9]. However, the data available on the effect of the structural rearrangements of micelles on nucleophilic substitution reactions of phosphorus acid esters are scarce [3–6]. The effect of electrolytes on micellization is usually considered in terms of their binding to the micellar surface, which reduces the surface potential. According to the theory of colloid stability, the surface potential is an important factor preventing micelle destruction [10]. A decrease in the surface potential of the micelles of cationic surfactants in the presence of electrolytes violates the energy balance of the forces involved in micellization, namely, the hydrophobic interaction, which favors surfactant association, and the unfavorable electrostatic repulsion between the likely charged head groups. This results in a decrease in the critical micelle concentration (CMC) and Ψ, a decrease in the radius of the spherical micelles, and an increase in their aggregation number.

A sphere $\longrightarrow$ cylinder micellar structural transition can take place in the system at a certain electrolyte concentration [2, 3]. The weaker the electrostatic repulsion between the surfactant molecules in spherical micelles, the lower the thermodynamic stability of the micelles. Accordingly, the rearrangement of micelles into nonspherical structures occurs at low electrolyte concentrations. The addition of electrolytes to surfactant solutions is a method of initiating the growth of micellar aggregates, the formation of long flexible micelles, and the formation of lyotropic liquid-crystal mesophases.
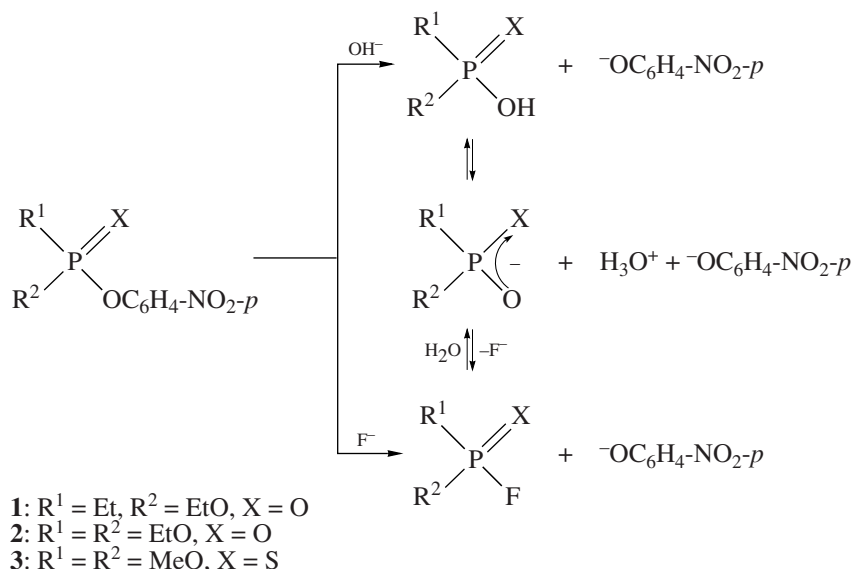
In the investigation of the salt effect in micellar catalysis, electrostatic and ion-exchange models were developed for data interpretation [11]. The electrostatic approach assumes that an increase in the electrolyte concentration reduces the potential of the micellar surface, giving rise to attraction or repulsion of the counterions. The ion-exchange model takes into account both the electrostatic interaction of the counterions with the surface of the surfactant micelles and the nature of the counterions themselves. These models are not in conflict. The effect of counterions on the catalytic activity of micelles increases in the following order [12]: $F^- < OH^- < CO_3^{2-} < Cl^- < Br \approx NO_3$. Organic counterions exert a stronger effect on the properties of surfactant solutions and induce sphere $\longrightarrow$ cylinder micellar transitions at low concentrations [13].

The reactivity of compounds in nanostructured systems is determined by the surface potential of the micelles [3, 4, 13]. A possible cause of the changes in the reactivity of reactants in nucleophilic substitution is that, as the counterion concentration increases, the sur-

face charge of the cationic surfactant micelles decreases, implying a weakening of the electrostatic interaction between the nucleophile and the charged micellar surface on which the chemical process occurs. At the same time, the extent of binding of counterions increases with a decrease in Ψ, which probably exerts an adverse effect on the solubilization of the substrate, causing its displacement from the micellar surface and its separation from the nucleophile. Which of the possi-

bilities occurs will depend on the reactant structure [3, 4].

In this work, we describe nucleophilic substitution reactions in O-4-nitrophenyl-O-ethyl ethylphosphonate (**1**), O-4-nitrophenyl-O,O-diethyl phosphate (**2**), and O-4-nitrophenyl-O,O-dimethyl thiophosphate (**3**) that occur in micellar systems of cetyltrimethylammonium bromide (CTAB) containing fluoride or hydroxide ions or their mixture (scheme).

1: R^1 = Et, R^2 = EtO, X = O
2: R^1 = R^2 = EtO, X = O
3: R^1 = R^2 = MeO, X = S

Scheme.

It was found earlier that inorganic indifferent counterions (Cl$^-$, Br$^-$) exerting an electrolyte effect on the alkaline hydrolysis of phosphorus acid esters produce an inhibiting effect in micellar solutions of cationic surfactants [3, 4, 6, 12]. Reactive electrolytes (reactants), such as potassium fluoride and sodium hydroxide, can efficiently affect both the aggregation and catalytic properties of micellar systems. The joint effect of these ions on the phosphoryl transfer reaction also seems interesting. The hydroxide and fluoride ions are known to be reactive in direct nucleophilic substitution, attacking the phosphorus atom of the substrate [14] (scheme). Note that the hydroxide ion is much more reactive than the fluoride ion [15, 16].

EXPERIMENTAL

The hydrolysis kinetics of 4-nitrophenyl esters of the acids of tetracoordinated phosphorus (**1–3**) was studied spectrophotometrically using a Specord UV-Vis instrument at initial substrate concentrations of 5×10^{-5} to 1×10^{-4} mol/l. The reaction (4-nitrophenolate anion formation) was monitored as the absorbance of the solution at a wavelength of 400 nm. The substrate conversion exceeded 90%. Apparent first-order rate constants (k_{app}) were calculated by the regression method using the equation

$$\ln(D_\infty - D_t) = -k_{app}t + \text{const},$$

where D_∞ and D_t are the absorbances measured upon the completion of the reaction and at the point in time t, respectively.

The surface tension was determined by the ring method with a Du Nouy tensiometer.

The small-angle neutron scattering (SANS) method was used to determine the characteristic parameters of micelles (radius, shape, aggregation number). Neutron scattering curves were obtained on a YuMO small-angle scattering setup (two-detector version) [17, 18] using a high-efficiency neutron pulse source (IBR-2 reactor). Samples were placed in cells (Hellma) with a working thickness of 2 mm and were kept in a thermostat at 30°C [19].

The shape of scattering associates (micelles) was determined by Porod invariant and Guinier plot analyses [20, 21], as well by simulation using the FITTER program package (developed at the Joint Institute for Nuclear Research) [22].

Kinetic data were processed using the pseudophase model equation of micellar catalysis [23]:

$$k_{app} = \frac{k_w + k_m K_s([\text{Surf}] - \text{CMC})}{1 + K_s([\text{Surf}] - \text{CMC})}, \quad (1)$$

where k_{app} is the apparent first-order rate constant (s^{-1}); k_w and k_m are the reaction rate constants (s^{-1}) in the solvent bulk and in the micellar phase, respectively; K_s is the substrate–micelle binding constant (l/mol); [Surf] is the surfactant concentration (mol/l); and CMC is the critical micelle concentration (mol/l).

RESULTS AND DISCUSSION

The aggregation of CTAB in water begins at CMC = 8.4×10^{-4} mol/l. As was demonstrated by tensiometry, the introduction of potassium fluoride into a micellar solution results in a decrease in the CMC (Table 1). The surface tension (σ) isotherms for CTAB in the presence of different KF concentrations are shown in Fig. 1. The CMC value depends nonlinearly on the fluoride ion concentration (Fig. 2). The dynamics of the decrease in the CMC of CTAB with an increase in the KF concentration (Table 1) is very similar to what was observed for the aggregation of cetylpyridinium bromide micelles in the presence of NaCl or KBr [3, 4].

The surface potentials of the CTAB micelles are listed in Table 1. They were calculated using the equality $d\Psi/d \log CMC = 59.16$ mV [24]. The plot of Ψ versus the fluoride ion concentration is nonlinear and has an inflection at [KF] ≈ 0.115 mol/l, like the CMC = f[KF] plot (Fig. 2).

The spatial characteristics of the CTAB micelles at different KF concentrations were studied by SANS in the following systems:

I, CTAB (0.0047 mol/l) + D$_2$O,

IIa, CTAB (0.0047 mol/l)
+ KF (0.005 mol/l) + D$_2$O,

IIb, CTAB (0.0047 mol/l)
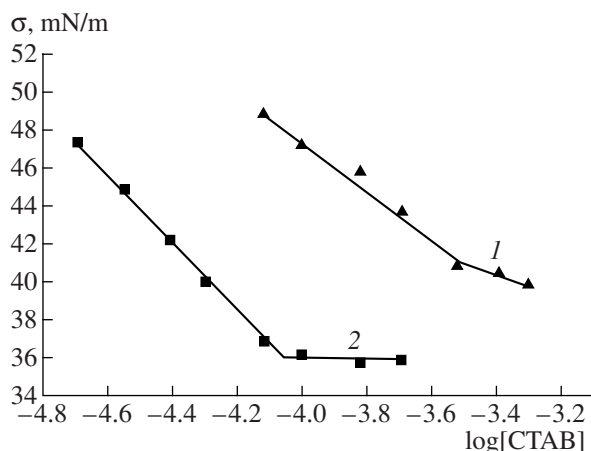+ KF (0.05 mol/l) + D$_2$O,

IIc, CTAB (0.0047 mol/l)

Table 1. CMC and surface potential data for CTAB in the presence of KF

[KF], mol/l	CMC $\times 10^4$, mol/l	Ψ, mV	[KF], mol/l	CMC $\times 10^4$, mol/l	Ψ, mV
0	8.4	140	0.2	1.56	97
0.005	7.2	136	0.3	1.4	94
0.05	3.2	115	0.4	1.2	90
0.1	1.8	99.5	0.5	0.9	83

+ KF (0.5 mol/l) + D$_2$O,

IIIa, CTAB (0.002 mol/l)

+ KF (0.05 mol/l) + D$_2$O,

IIIb, CTAB (0.002 mol/l)

+ KF (0.5 mol/l) + D$_2$O,

IVa, CTAB (0.0047 mol/l)

+ KF (0.005 mol/l) + NaOD (0.1 mol/l) + D$_2$O,

IVb, CTAB (0.0047 mol/l)

+ KF (0.05 mol/l) + NaOD (0.1 mol/l) + D$_2$O,

IVc, CTAB (0.0047 mol/l)

+ KF (0.5 mol/l) + D$_2$O + NaOD (0.1 mol/l).

Fig. 1. Surface tension isotherms for CTAB in the presence of (*1*) 0.05 and (*2*) 0.5 M KF at 25°C.
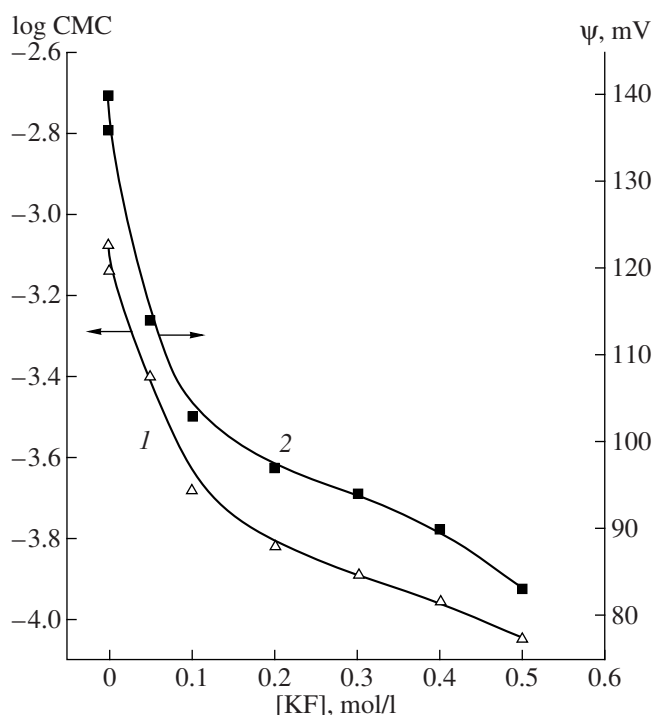

Fig. 2. (*1*) CMC and (*2*) the surface potential of the CTAB micelles versus the KF concentration.
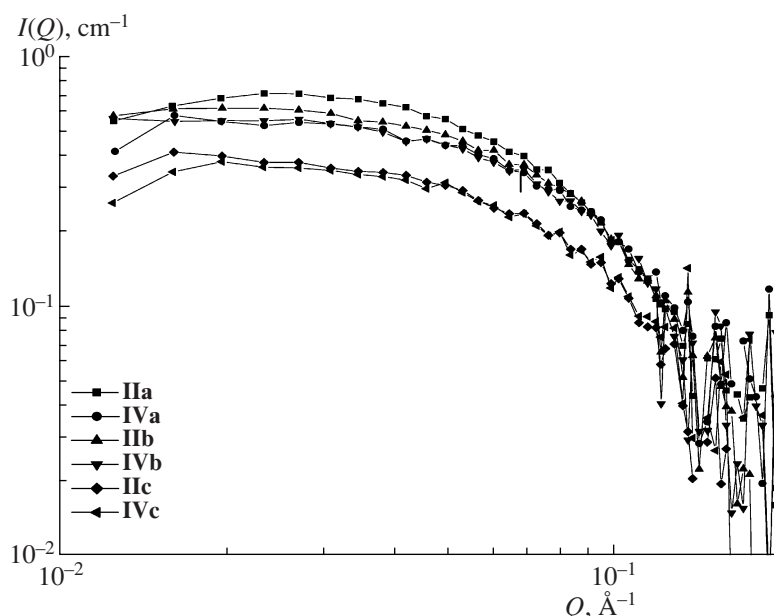
Fig. 3. Neutron scattering curves for the systems CTAB (0.0047 mol/l) + KF + D_2O and CTAB (0.0047 mol/l) + KF + NaOD + D_2O.

The plots of the intensity of the scattering vector I versus the scattering vector itself (Q) in systems **I–IV** are shown in Figs. 3 and 4. The character of the neutron scattering curves makes it possible to elucidate the structural changes that occur in the scattering systems (micelles). The construction of the Guinier plot in terms of the scattering density indicates the presence of a linear portion in the $\ln I(Q) = f(Q^2)$ curves for systems **I** and **II**, pointing to the globular shape of the scattering particles [20]. The gyration radii (R_g) were calculated from the slope of this plot (Table 2).
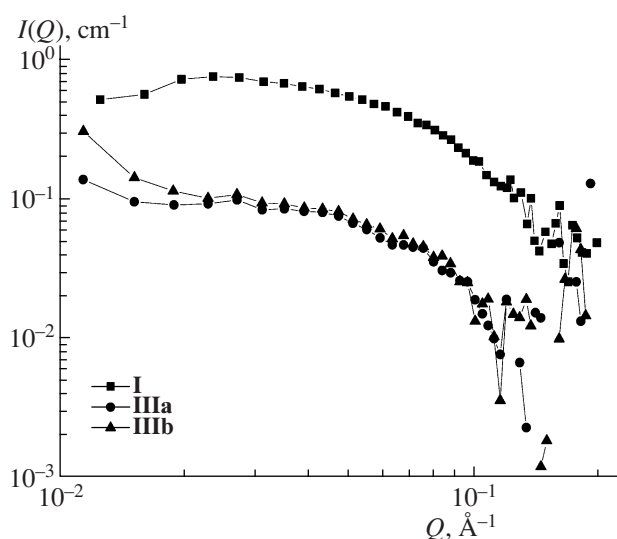

Fig. 4. Neutron scattering curves for the systems CTAB (0.002 mol/l) + KF + D_2O and CTAB (0.0047 mol/l) + D_2O.

For homogeneous noninteracting particles as the scattering object, the Porod invariant Q^* is the area under the scattering curve multiplied by the squared scattering vector. The Q^* value is proportional to the total volume of the scattering particles multiplied by the density of their scattering; i.e., it is proportional to the "scattering mass."

The second way of determining the geometric characteristics is by fitting the SANS curves to an appropriate model using the FITTER program [22]. The most appropriate model of a particle is a sphere for systems **I** and **II** and a cylinder for systems **III** and **IV**. The micelle radii determined by this method (parameter a) and the lengths of cylindrical aggregates (b) are given in Table 2. The gyration radii calculated by the formulas

$$R_g^2 = \frac{3}{5}R^2 \text{ (sphere)}$$

$$\text{and } R_g^2 = \frac{R^2 + R^2}{4} + \frac{h^2}{12} \text{ (cylinder)} \tag{2}$$

(where R is the particle radius a and h is the particle length b) are close to the radii R_g derived from the Guinier plots.

The following formula was used to determine the particle volume V_p:

$$V_p = \frac{2\pi^2 I(0)}{Q^*}, \tag{3}$$

where $I(0)$ is the cross section of scattering to the zero angle and Q^* is the Porod invariant.

Table 2. Characteristic parameters of micelles

System	$Q^* \times 10^{18}$, Å^{-3}	a, Å	b, Å	R_g, Å	R'_g, Å	$I(0)$	$V_p \times 10^{-3}$, Å^3	N
I	9.5	27.2 ± 2.7	–	21.2	20.7	0.74	152	124
IIa	7.0	26.8 ± 2.7	–	20.7	20.3	0.69	189	135
IIb	8.5	24.9 ± 2.4	–	19.3	19.5	0.63	146	169
IIc	6.3	23.6 ± 2.3	–	18.3	18.8	0.41	128	190
IIIa	1.6	22.0 ± 2.0	40.6 ± 3.7	22.5	23.4	0.10	127	232
IIIb	1.7	22.0 ± 2.0	55.8 ± 4.6	22.8	22.1	0.11	131	239
IVa	8.6	17.4 ± 1.4	49.9 ± 3.5	18.9	18.5	0.56	129	235
IVb	8.5	18.1 ± 1.6	48.5 ± 3.2	18.9	18.8	0.56	133	243

The aggregation number N was determined by the formula

$$N = \frac{V_p}{V_n}, \qquad (4)$$

where $V_n = 672.24$ Å is the volume of the nonpolar part of the surfactant molecule.

In systems **II**, the middle chord, R_g, and R'_g of the aggregates decrease with an increase in the KF concentration, indicating CTAB micelle compression. Micelle compression in the presence of the fluoride ion is also confirmed by analysis of the parameter a. The semiaxis, i.e., the radius a, decreases from 27.3 (system **I**) to 23.6 Å (system **IIc**) with an increase in the KF concentration. According to published data, the radius of CTAB micelles is 26–35 Å [25, 26].

Because of the low concentration, no interaction occurs between CTAB micelles in the presence of KF, as is indicated by the absence of diffraction peaks in the neutron scattering curves (Figs. 3, 4). The aggregation number of the CTAB micelles in systems **II** (Table 2) calculated using Eq. (4) increases from 124 in the absence of KF to 190 in the presence of 0.5 M KF, which is typical of micellar systems containing electrolytes.

Note that the radius a of the spherical CTAB micelles (at a CTAB concentration of 0.0047 mol/l) in the presence of KF depends linearly on the CMC:

$$\text{CMC} \times 10^{-4} = 2.06a - 47.75$$

(here, the number of measurements is $n = 5$, the correlation factor is $r = 0.996$, and the standard deviation is $s = 0.35$).

Composition **III** with a low CTAB content (0.002 mol/l) (Fig. 4) and compositions **IV** (Fig. 3) in the presence of 0.05–0.5 M KF are characterized by large aggregation numbers of $N \approx 230$–240 (Table 2), which are characteristic of cylindrical micelles [27].

Large aggregation numbers of CTAB ($N = 235$–245) are observed in solutions containing KF and NaOH. The radius a of a CTAB micelle in the presence of 0.1 M NaOH is 23.4 Å (sphere). The addition of KF to alkaline micellar systems induces a structural micellar transition favoring the formation of rodlike (cylindrical) CTAB micelles with $a \approx 17$–18 Å and $b \approx 48$–50 Å (Table 2).

In an aqueous medium, the apparent rate constant of phosphorus acid ester cleavage (k_{app}) depends linearly on the NaOH or KF concentration. In an aqueous solution containing both fluoride and hydroxide ions, this constant is the sum of the rate constants of alkaline hydrolysis and the reaction with the fluoride ion ($k_{app} = k_{OH^-} + k_{F^-}$) and again depends linearly on the KF concentration ([NaOH] = 0.1 mol/l).

In micellar media, an increase in the KF concentration should adversely affect the rate of the reaction between the fluoride ion and the phosphorus acid ester because KF can serve as both a reactant and an electrolyte and can reduce the surface potential of the surfactant micelles (Table 1). We have demonstrated that, with an increase in the KF concentration, the apparent rate constant of the reaction between substrate **1** and KF in micellar CTAB solutions first increases nonlinearly and then plateaus. The dependence of k_{app} on [CTAB] for substrate **3** in the presence of 0.5 M KF is presented as an example in Fig. 5. Based on the kinetic data obtained for the reactions of substrates **1**–**3** using Eq. (1), we determined the parameters of the reaction of KF with phosphorus acid esters in CTAB solutions (rate constant in the micellar phase, k_m; binding constant of the substrate, K_s; CMC). The results are presented in Table 3.

The binding constant of substrate **1** decreases from 226 to 105 l/mol as the KF concentration increases to 0.5 mol/l (Table 3). Probably, this can be explained by the change in the properties of the micellar aggregate surface (reaction zone) due to the sharp decrease in Ψ (Table 1). The k_m values depend nonlinearly on [KF] because the electrolyte effect of KF comes into play at a certain potassium fluoride concentration to reduce the reactivity of the substrates. Note that the CTAB micellar systems in the reaction of the fluoride ion with the phosphorus acid esters show substrate specificity: the
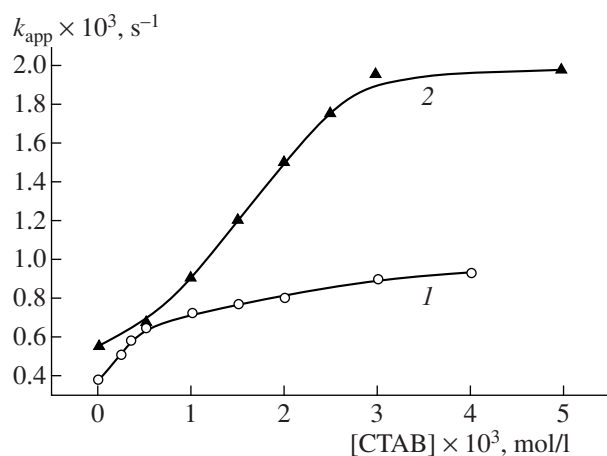
$k_{app} \times 10^3$, s^{-1}

Fig. 5. Apparent rate constant of the reaction of substrate **3** versus the CTAB concentration in the presence of (*1*) 0.5 M KF and (*2*) a mixture of 0.1 M NaOH with 0.5 M KF at 30°C.
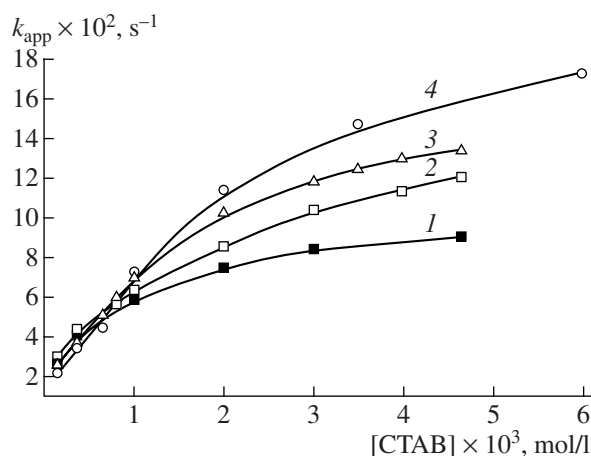
$k_{app} \times 10^2$, s^{-1}

Fig. 6. Apparent rate constant of the reaction of substrate **1** versus the CTAB concentration at 30°C and [KF] = (*1*) 0, (*2*) 0.5, (*3*) 0.004, (*4*) and 0.05 mol/l; [NaOH] = 0.1 mol/l.

greatest acceleration is observed in the reaction involving phosphate **2** (Table 3).

As the hydroxide ion concentration increases, the apparent rate constants of phosphorus acid ester alkaline hydrolyses in micellar solutions of cationic surfactants first increase nonlinearly and then plateau [28]. At low concentrations, hydroxide ions displace the indifferent counterions of the cationic surfactant from the Stern layer. The alkali begins to manifest the electrolytic effect as its concentration increases, and the micellar charge is gradually neutralized (a decrease in Ψ takes place). The introduction of KF into an alkaline micellar solution of CTAB increases k_{app}, which reaches its maximum at [KF] = 0.05 mol/l.

The dependence of the apparent rate constant of the reaction of substrate **1** on the detergent concentration in the system CTAB + NaOH + KF + water is shown in Fig. 6. Similar plots for the reaction of substrate **3** are presented in Fig. 5. Fitting the kinetic data to Eq. (1) made it possible to determine the parameters of the reactions involving substrates **1**–**3**, which are collected in Table 4. The reaction rate constant in the micellar medium of the CTAB + NaOH + KF + water system at [KF] = 0.05 mol/l exceeds the overall rate of the same reaction in the aqueous medium by a factor of ~15 for

substrate **1** and by a factor of 195 for phosphate **2**. Thus, pronounced substrate specificity is observed in the micellar systems containing NaOH and KF. At high fluoride concentrations ([KF] = 0.5 mol/l), the cleavage rate of substrates **1**–**3** in the micellar alkaline media is lower (Table 4) because an increase in the salt concentration reduces the micellar surface potential (Table 1). This exerts an adverse effect on phosphoryl group transfer reactions [3, 4]. The reaction acceleration in terms of the k_m/k_0 ratio is about 4–5 at [KF] = 0.5 mol/l for all three substrates.

However, the replacement of indifferent counterions by reactive counterions (OH$^-$ and F$^-$) in the Stern layer and an increase in the concentration of the latter speed up the process. The competition between the electrolyte and catalytic effects in the micellar system results in a nonadditive change in the rates of the processes involving the hydroxide and fluoride ions in the reactions of substrates **1**–**3** that occur in micellar solutions of CTAB. The introduction of KF, unlike the introduction of KBr or NaCl, leads to the compression of micelles, and the addition of an alkali stimulates the sphere $\longrightarrow$ cylinder transition.

Table 3. Parameters of the micelle-catalyzed cleavage reactions of substrates **1**–**3** in the CTAB + KF + water system at 30°C

Substrate	[KF], mol/l	$k_0 \times 10^3$, s^{-1}	$k_m \times 10^2$, s^{-1}	K_s, l/mol	CMC $\times 10^4$, mol/l	k_m/k_0
1	0.005	0.07	0.212	226	5.04	30
	0.05	0.49	2.83	420	1.49	57
	0.50	6.08	19.45	105	0.97	32
2	0.50	0.15	2.45	129	3.0	162
3	0.50	0.38	0.087	3362	1.00	2.3

Note: k_0 is the rate constant of the reaction between the substrate and the fluoride ion in the absence of a surfactant.

Table 4. Parameters of the micelle-catalyzed cleavage reactions of substrates **1–3** in the CTAB + NaOH (0.1 mol/l) + KF + water system at 30°C

Substrate	[KF], mol/l	$k_0 \times 10^3$, s^{-1}	$k_m \times 10^2$, s^{-1}	K_s, l/mol	CMC $\times 10^4$, mol/l	k_m/k_0
1	0	15.53	9.94	1500	1.07	6.4
	0.005	15.60	26.61	298	0.31	17
	0.05	16.02	23.02	323	1.06	14.4
	0.50	21.61	10.80	1220	2.87	5
2	0	1.14	0.74	1223	3.20	6.5
	0.05	1.80	35.1	40	5.40	195
	0.50	2.27	0.885	1029	2.70	3.9
3	0.50	0.55	0.247	962	7.80	4.5

Note: Here k_0 is the overall rate constant of alkaline hydrolysis and the reaction between the substrate and the fluoride ion in the absence of CTAB.

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