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Dicationic Surfactant Based Catalytic Systems for Alkaline Hydrolysis of Phosphonic Acid Esters

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Abstract—Use of aqueous micellar solutions of dicationic surfactants with the general formula $[R(CH_3)_2N(CH_2)_6N(CH_3)_2R]^{2+}2Br^-$ (R = n-$C_{10}H_{21}$ to n-$C_{16}H_{33}$) as the reaction medium for the alkaline hydrolysis of phosphonic acid esters has revealed a strong catalytic effect of the surfactants, which can increase the reaction rate by two orders of magnitude. This effect depends on the surfactant structure, shows itself at low surfactant concentrations, and is substrate-specific. The effect of the micelles on the phosphonate hydrolysis rate is largely determined by the hydrophobicity factor.

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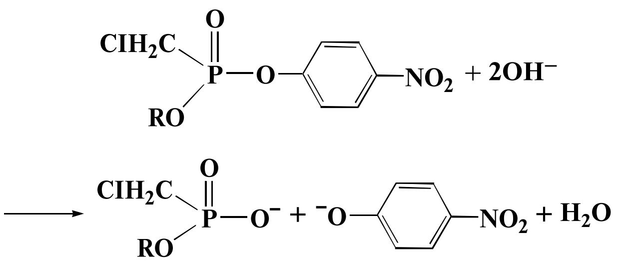
Surfactant-based supramolecular systems have found wide application in present-day technologies, including production of catalysts, mesoporous materials, protective coatings, lubricants, cosmetics, and drugs [1–4]. The hydrophobic moiety and positively charged head groups in the structure of cationic surfactants allow them to incorporate into lipid bilayers and to readily interact with intracellular membranes, phosphate groups of nucleic acids, and other negatively charged biological substances, making them usable in development of nonviral vectors, drug and diagnostic agent transporters, and antimicrobial drugs [5–8]. Cationic surfactants are traditionally used in micellar catalysis for decomposition of organophosphorus environmental toxicants and neurotoxins [9–12]. The wide variety of practically important properties of cationic surfactant based supramolecular systems (high complexing power, strong capacity for affecting chemical processes, biological activity, etc.) makes these substances promising in respect of many performance parameters.

Dicationic (gemini) surfactants consist of two amphiphilic hydrocarbon radicals and two head groups linked by a spacer group, which can be either hydrophilic or hydrophobic and either flexible or rigid [13–16]. These surfactants have better properties than their conventional (monocationic) counterparts. In particular, their critical micelle concentration (CMC) is lower than that of the corresponding monocationic surfactants by one order of magnitude (or by a still greater factor). They more effectively reduce the surface tension of water and exert a stronger solubilizing effect. The most comprehensively studied gemini surfactants are compounds of the alkanediyl-α,ω-bis(alkyldimethylammonium) series, whose structure is often designated *m*-*s*-*m*, where *m* and *s* are the numbers of carbon atoms in the alkyl and spacer groups, respectively. For these surfactants, the CMC, degree of ionization, and degree of aggregation have been measured and micellization thermodynamics, interfacial behavior, and the structure and rheology of their aqueous solutions have been investigated. In recent years, there have been many publications, including reviews [17–20], dealing with the aggregation behavior of alkylammonium gemini surfactants. The possibility of employing these surfactants as a reaction medium has received much less attention [21–25]. Nevertheless, the high surface potential and considerable solubilization capacity of the micellar solutions of these gemini surfactants suggest that they can exert a strong effect on chemical processes, particularly on those involving charged nucleophiles.

The purpose of this work is to estimate the effectiveness and selectivity of micellar solutions of a series of dicationic surfactants whose spacer group consists of six methylene units: $[R(CH_3)_2N(CH_2)_6N(CH_3)_2R]^{2+}2Br^-$, where R = n-$C_{10}H_{21}$ (10-6-10), n-$C_{12}H_{25}$ (12-6-12), n-$C_{14}H_{29}$ (14-6-14), and n-$C_{16}H_{33}$ (16-6-16). These surfactants are used as the reaction medium in hydrolytic processes. The catalytic activity of the micellar systems was studied in the hydrolysis of phosphonic acid esters (PAEs). The general scheme of this process is



R = C_2H_5 (**1**), *n*-C_4H_9 (**2**), *n*-C_6H_{13} (**3**)

The properties of these surfactants will be compared with the properties of similar monomeric cationic surfactants.

EXPERIMENTAL

The gemini surfactants were synthesized by reacting *N*,*N*,*N*',*N*'-tetramethyl-1,6-hexamethylenediamine with alkyl bromides in acetone, and the products were twice recrystallized from ethanol [23]. The *para*-nitrophenyl esters of alklylchloromethylphosphonic acids (**1–3**) were synthesized as described in [26]. The structures of the resulting compounds were identified by elemental analysis and IR and NMR spectroscopy. Commercial monomeric surfactants (99%, Sigma) were used in the experiments.

The surface properties of the surfactants were studied by the Du Nouy ring method using a Kruss tensiometer at 25°C. The CMC value was determined as the intersection point of the linear segments of surface tension isotherms. The bromide ion concentration (C_{Br^-}) in surfactant solutions was determined using a bromide-selective electrode on an I-160MI ion meter. The counterion binding constant (β) was calculated as

$$\beta = \frac{C_S - nC_{\mathrm{Br}^-}}{C_S - \mathrm{CMC}}, \qquad (1)$$

where C_S is the surfactant concentration. The coefficient n for monocationic and dicationic surfactants is 1 and 0.5, respectively.

Aggregate size data for dicationic surfactants in aqueous solution were obtained by the dynamic light scattering method on a Malvern Instruments Zetasizer Nano spectrometer (He–Ne laser, 633 nm). The solution to be examined was filtered through Millipore filters with a pore diameter of 0.4 μm. Aggregate size measurements were performed at least three times for each sample.

The kinetics of the alkaline hydrolysis of the *para*-nitrophenyl phosphonates was studied spectrophotometrically in a 0.001 M sodium hydroxide solution in temperature-controlled cuvettes on a Specord UV-VIS spectrophotometer. The process (*para*-nitrphenolate ion formation) was monitored by measuring the absorbance of the solution at a wavelength of 400 nm. The initial substrate concentration was (2–5) × 10^{-5} mol/L. The substrate conversion was over 90%. The apparent pseudo-first-order constant (k_{app}) was determined using the relationship $\log(D_\infty - D_\tau) = -0.434k_{\mathrm{app}}\tau +$ const, where D_τ and D_∞ are the absorbance of the solution at the point in time τ and after the completion of the reaction, respectively. Numerical values of k_{app} were calculated by least squares.

RESULTS AND DISCUSSION

The aggregation behavior of *m*-6-*m* gemini surfactants in aqueous solutions has been investigated rather extensively. At the same time, admixtures, for example, strong electrolytes are known to alter the properties of micellar solutions [27–29]. In our kinetic study of the alkaline hydrolysis of PAEs, the role of admixtures could be played by the reactants themselves. Low substrate concentrations of (2–5) × 10^{-5} mol/L were used in the experiments, while the alkali concentration was rather high (0.001 mol/L) and, in some cases, was higher than the surfactant concentration. According to existing views, the introduction of an electrolyte increases the concentration of surfactant counterions, and this is favorable for partial neutralization of the surface charge of the micelles and reduces the destabilizing effect of the repulsion between like-charged head groups. This can lead to a decrease in the surface potential of the system and in CMC, to an increase in the aggregation number, and to changes in micelle size and shape. In view of this, before performing kinetic experiments, we studied the micellization of the gemini surfactants in the presence of a nucleophile.

Using the tensiometric method, we measured CMC in aqueous and aqueous alkali solutions of the *m*-6-*m* surfactants (Table 1). The alkali facilitates micellization: the higher the alkali concentration, the lower the CMC and the narrower the concentration range in which the true solution turns into a micellar solution (the greater the slope of the surface tension isotherm). This point is illustrated in Fig. 1 for the 16-6-16 compound. Note that this compound is characterized by two CMC values: the first one corresponds to the formation of spherical micelles, and the second (near 0.001 mol/L) is attributed to a change in the aggregate shape [30]. The addition of an alkali exerts a marked effect on CMC_1 and a much weaker effect on CMC_2. For the homologues with a shorter hydrocarbon radical, the second critical point was not observed in the concentration range examined. The alkali-induced decrease in CMC was detected poten-

Table 1. CMC data for the dicationic surfactants in aqueous and aqueous alkali solutions at 25°C

Surfactant	C_{NaOH}, mol/L	CMC, mol/L	
		tensiometry	potentiometry
10-6-10	0	0.0060	
	0.001	0.0057	
	0.01	0.0052	
12-6-12	0	0.0011	0.00108
	0.001	0.0010	0.00103
	0.01	0.00093	0.00095
	0.1	0.00088	0.00090
14-6-14	0	0.00014	0.00013
	0.001	0.00013	0.00012
	0.01	0.00010	0.00010
16-6-16*	0	0.000044	
	0.001	0.000021	
	0.01	0.000010	

* The CMC of this surfactant is at the lower detection limit of the bromide-selective electrode, making it difficult to obtain reliable potentiometric data.

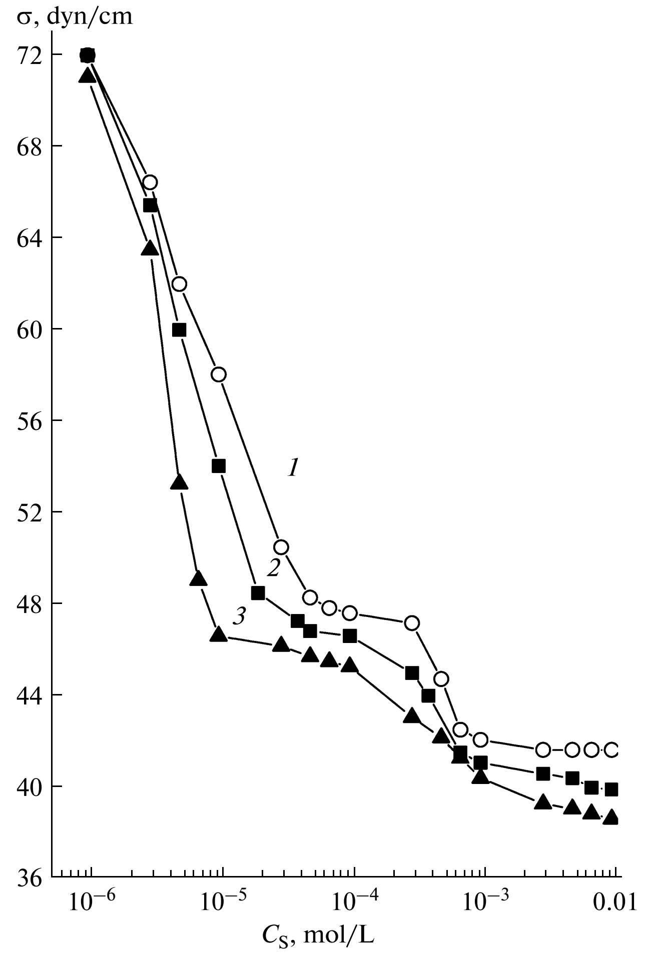


Fig. 1. Surface tensions isotherms for the 16-6-16 surfactant in (*1*) water and (*2*, *3*) aqueous alkali solutions at NaOH concentrations of (*2*) 0.001 and (*3*) 0.01 mol/L at 25°C.

tiometrically with a bromide-selective electrode (Table 1). Using this method and formula (1), it is possible to estimate, from the change in the slope of the potentiometric curve, the effect of alkali on the counterion binding constant β. By way of example, we present potentiometric data for the 12-6-12 compound (Fig. 2). At NaOH concentrations of 0, 0.001, 0.01, and 0.1 mol/L, β = 0.71, 0.67, 0.62, and 0.58, respectively. Thus, as the alkali concentration in the micellar solution is raised, the binding of bromide ions weakens, as is indicated by their passing from the Stern layer into the bulk phase. Note that the hydroxide ion is much more hydrophilic than the bromide ion, which has a larger ionic radius and a lower charge density. The ion exchange coefficient calculated using the pseudophase ion exchange model is $K_{\mathrm{Br/OH}} > 10$ [31], suggesting that the bromide ions have a much higher affinity for the micelle surface and will not be displaced from the Stern layer by the more hydrophilic hydroxide ions. However, under our experimental conditions, part of the bromide ions is likely replaced because of the large hydroxide ion concentration gradient.

The dynamic light scattering method makes it possible to see how an alkali affects the aggregate size. It was demonstrated by the example of aqueous solutions of the 16-6-16 compound (Fig. 3) that the hydrodynamic diameter of the micelles (*D*) increases as the alkali concentration is raised. Here, the alkali serves as a strong electrolyte partially neutralizing the surface charge of the micelles. The weakening of the Coulomb repulsion between the head groups of the surfactant reduces CMC and increases the micelle size. Thus, the

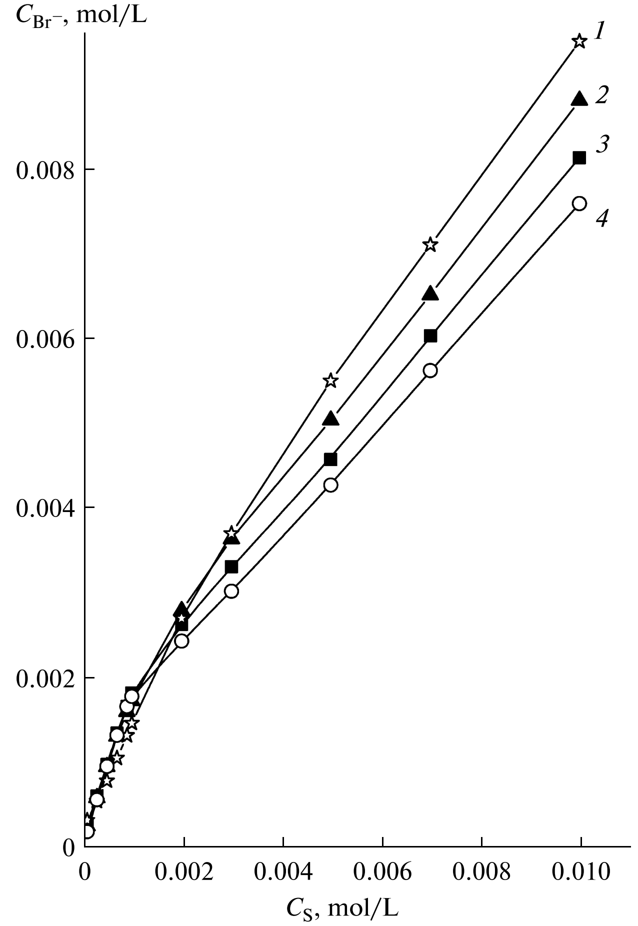


Fig. 2. Potentiometric data obtained with a bromide-selective electrode for the 12-6-12 surfactant in aqueous solutions at NaOH concentrations of (*1*) 0, (*2*) 0.001, (*3*) 0.01, and (*4*) 0.1 mol/L at 25°C.

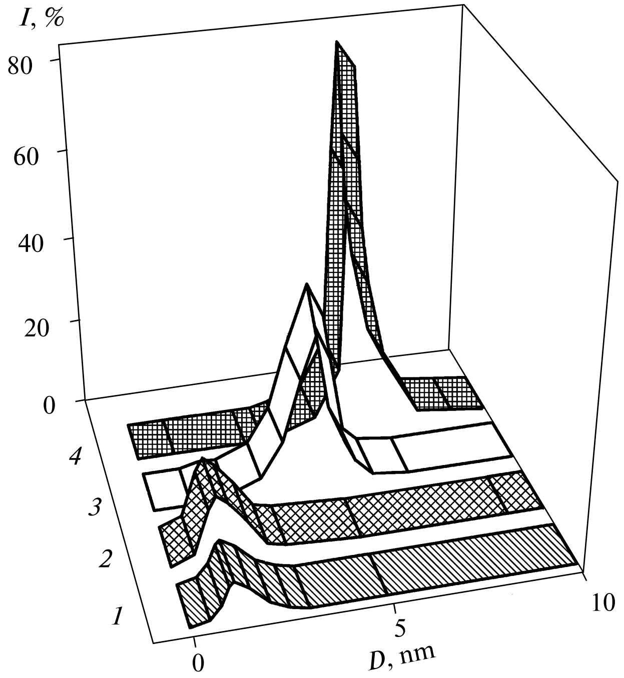


Fig. 3. Micelle size distribution (intensity *I*) versus diameter (*D*) for the 16-6-16 surfactant in aqueous solutions at NaOH concentrations of (*1*) 0, (*2*) 0.001, (*3*) 0.01, and (*4*) 0.1 mol/L; $C_S = 0.005$ mol/L; 25°C.

addition of an alkali or another strong electrolyte to the dicationic surfactant solutions changes the aggregation parameters of the system, and at a high electrolyte concentration these changes can be quite significant.

Micellar solutions of the dicationic surfactants were used as the reaction medium for the alkaline hydrolysis of *para*-nitrophenyl phosphonates differing in their hydrophilic–lipophilic balance. Figures 4–6 show how the apparent rate constant of the hydrolysis of esters **1**–**3** depends on the surfactant structure and concentration. The presence of an extremum in the apparent rate constant versus surfactant concentration curve is typical of micelle-catalyzed processes and is evidence of a high surfactant affinity of the substrate, which shows itself at a certain substrate-to-surfactant ratio [32]. It follows from these kinetic data that the dicationic surfactants are catalytically very active and their strongest catalytic effect is observed at substantially lower concentrations than in the case of their monocationic analogues (compare compound 16-6-16 and CTAB; Figs. 5, 6). By correlating the aggregation data with the results of the kinetic experiment, one can see that the maximum acceleration of the hydrolysis reaction is observed at concentrations slightly above the CMC_1 point, where spherical micelles exist. Note that the way in which the micelles affect the phosphonate hydrolysis rate is largely determined by the hydrophobicity factor. The catalytic effect increases with an increasing length of the alkyl radical of the surfactant, and the largest (nearly threefold) increase in the hydrolysis rate is observed for hydrophobic phosphonate **3** on passing from 10-6-10 to 12-6-12.On passing to the tetradecyl and hexadecyl analogues, the chain length effects become similar. The systems examined here show pronounced substrate specificity: in the presence of any dicationic surfactant, the strongest surfactant effect is attained for the most hydrophobic substrate **3**. This can be explained in terms of substrate distribution between the micelle and the bulk phase: the stronger the substrate–micelle binding, the larger the extent to which the hydroxide ion concentrates at the positively charged surface of the micelle, and this markedly speeds up the process. This substrate specificity is also observed for systems containing monocationic surfactants, but it is less pronounced in that case. For substrates **1**, **2**, and **3**, the largest increase in the reaction

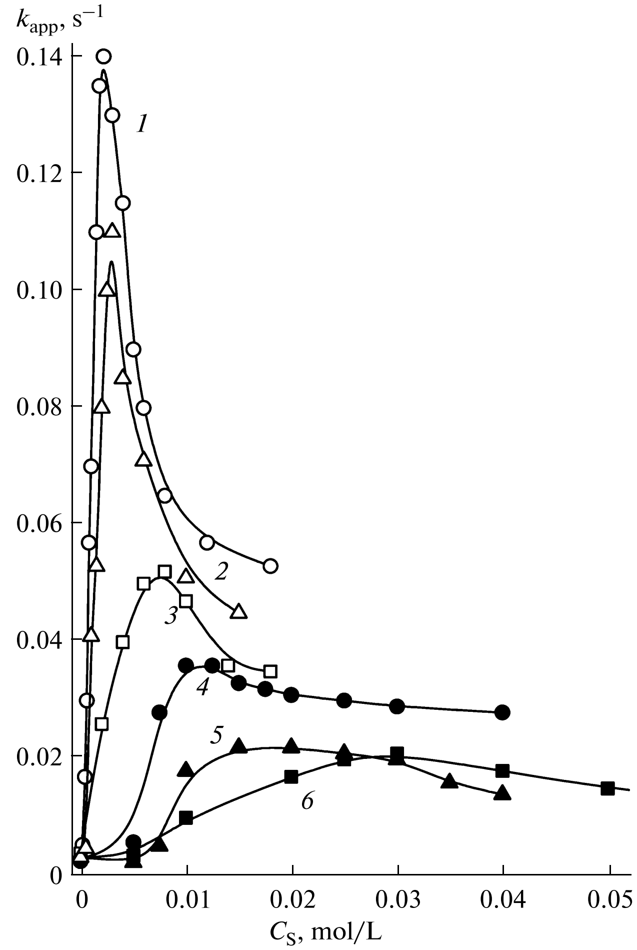


Fig. 4. Apparent rate constant of the alkaline hydrolysis of phosphonates (*1*, *4*) **3**, (*2*, *5*) **2**, and (*3*, *6*) **1** as a function of the concentration of surfactants (*1–3*) 12-6-12 and (*4–6*) 10-6-10; C_{NaOH} = 0.001 mol/L; 25°C.

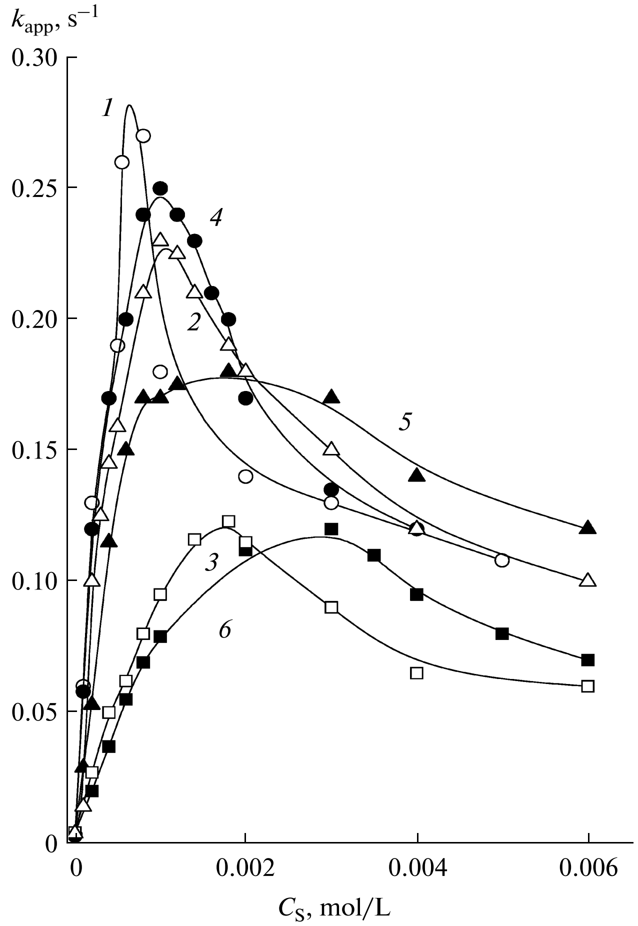


Fig. 5. Apparent rate constant of the alkaline hydrolysis of phosphonates (*1*, *4*) **3**, (*2*, *5*) **2**, and (*3*, *6*) **1** as a function of the concentration of surfactants (*1–3*) 16-6-16 and (*4–6*) 14-6-14; C_{NaOH} = 0.001 mol/L; 25°C.

rate due to the presence of 16-6-16 amounts to a factor of 30, 61, and 97, respectively, while CTAB increases the reaction rate by a factor of at most 25, 39, and 47, respectively.

For gaining quantitative information concerning the factors underlying the action of the dicationic surfactants, the kinetic data plotted in Figs. 4–6 were analyzed in terms of the pseudophase model of micellar catalysis [32]:

$$k'_{app} = \frac{k_{2,0} + \frac{k_{2,m}}{V} K_{sub} K_{OH} C_S}{(1 + K_{sub} C_S)(1 + K_{OH} C_S)}, \qquad (2)$$

where k'_{app} (L mol^{-1} s^{-1}) is the apparent second-order rate constant obtained by dividing k_{app} by the nucleophile concentration; $k_{2,0}$ and $k_{2,m}$ (L mol^{-1} s^{-1}) are the second-order rate constants for the solvent bulk and micellar pseudophase, respectively; V (L/mol) is the molar volume of the surfactant; and K_{sub} and K_{OH} (L/mol) are the phosphonate– and nucleophile–micelle binding constants.

The parameters of micelle-catalyzed phosphonate hydrolysis calculated via Eq. (2) are listed in Table 2. These data indicate that the phosphonate–micelle binding constant K_{sub} increases with increasing substrate hydrophobicity and with an increasing length of the hydrophobic radical in the dicationic surfactant. This is accompanied by an increase in the alkaline hydrolysis rate constant, and the largest increase in the hydrolysis rate is observed for substrate **3** in the 16-6-16 solution. In the case of the 10-6-10 surfactant, the binding constants of substrates **1–3** are small and practically equal and alkaline hydrolysis is accelerated to a small extent. This may be due to this surfactant form-

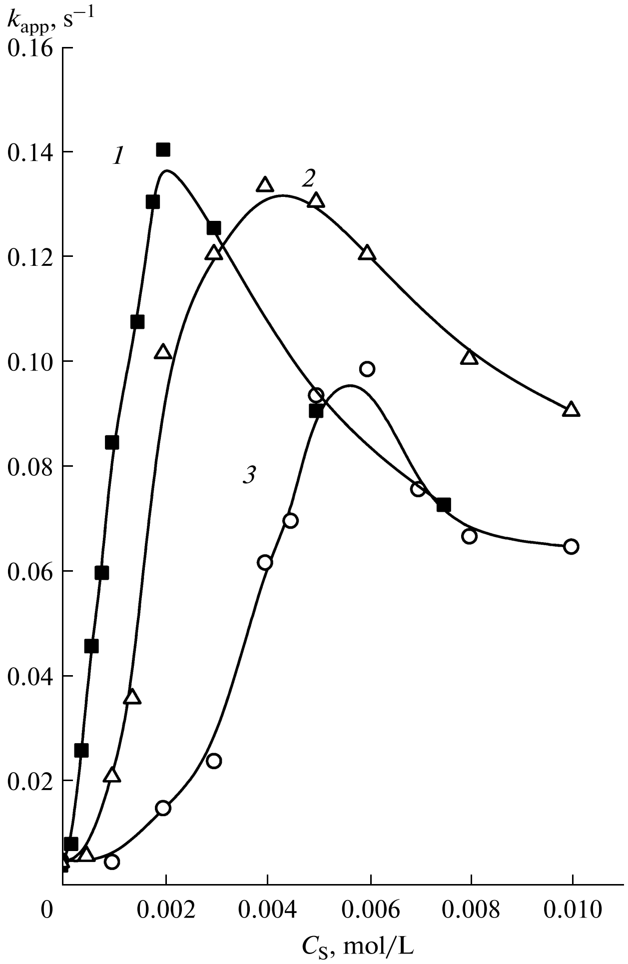


Fig. 6. Apparent rate constant of the alkaline hydrolysis of phosphonates (*1*) **3**, (*2*) **2**, and (*3*) **1** as a function of CTAB concentration; C_{NaOH} = 0.001 mol/L; 25°C.

ing small aggregates having only a weak solubilizing capacity.

In the pseudophase model, the maximum acceleration of hydrolysis is given by the equation

$$\left(k_{app}/k_0\right)_{max} = \frac{k_{2,m}}{k_{2,0}} \times \frac{K_{sub}K_{OH}}{V\left(\sqrt{K_{sub}} + \sqrt{K_{OH}}\right)^2}, \qquad (3)$$

where the first multiplier on the right-hand side is the microenvironmental factor for reactants, which accounts for the changes in their microenvironment (micropolarity, solvation shell, etc.) upon their passage from the solvent into the micellar phase (F_m), and the second multiplier is the concentration factor (F_c), which accounts for the local increase in the reactant concentration as a result of their solubilization in the micellar phase, whose volume is much smaller than the solvent volume.

It is clear from the data presented in Table 2 that the acceleration of the reaction is mainly due to the factor F_c, which increases the hydrolysis rate by more than two orders of magnitude. The microenvironmental factor in this case is <1; that is, it reduces the reaction rate. The higher the hydrophobicity of the substrate, the lower the polarity of the micelle part in which it localizes and the stronger the adverse effect of the microenvironment. The concentrating of the hydroxide ion at a positively charged micelle is primarily governed by the surface potential of the micelle (Ψ), which is higher for dicationic surfactants than for their monocationic counterparts [33], and so is the F_c value.

Thus, aqueous micellar solutions of the alkyldimethylammonium dicationic surfactants with a hexamethylene spacer used as reaction medium for the alkaline hydrolysis of *para*-nitrophenyl phosphonates display a strong catalytic effect, increasing the reaction rate by up to two orders of magnitude. This effect depends on the surfactant structure, arises from the concentrating of the reactants in the micellar phase,

Table 2. Characteristics of the alkaline hydrolysis of phosphonates **1**–**3** catalyzed by the dicationic surfactants in 0.001 M NaOH solutions at 25°C

Substrate	$k_{2,m}$, L mol^{-1} s^{-1}	K_{sub}, L/mol	K_{OH}, L/mol	$(k_{app}/k_0)_{max}$	F_m	F_c	$F_m \times F_c$
10-6-10							
3	0.43	421	46	12	0.143	87	12.4
2	0.66	545	16	8	0.182	45	8.2
1	0.93	758	8	7	0.232	23	5.3
12-6-12							
3	0.18	4273	411	54	0.060	798	48.0
2	0.23	3204	201	33	0.064	429	27.4
1	0.65	3674	28	13	0.163	79	12.9
14-6-14							
3	0.25	11291	219	86	0.085	982	83.5
2	0.54	4535	135	47	0.143	328	46.9
1	0.33	3135	187	30	0.081	353	28.6
16-6-16							
3	0.28	16313	366	97	0.087	922	90.0
2	0.27	5661	398	61	0.071	829	58.9
1	0.16	3517	391	30	0.039	734	28.2
CTAB							
3	0.26	2415	2733	47	0.085	509	43.3
2	0.43	2181	157	39	0.119	325	38.6
1	0.25	1536	234	25	0.062	403	24.8

shows itself at low surfactant concentrations, and is characterized by pronounced substrate specificity.

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