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Regulation of the Rate of Hydrolysis of Phosphorus Acid Esters in Organized Systems Based on Amphiphilic Pyrimidinophanes

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Abstract—The aggregation and catalytic activity of supramolecular systems based on new macrocyclic dimeric surfactants (pyrimidinophanes) was studied both in the absence and in the presence of polyethyleneimine (PEI). It was found that the critical micelle concentrations measured by tensiometry were independent of the structure of surfactants. The morphology of aggregates was responsible for various characters of the catalytic effects of pyrimidinophanes in the hydrolysis of phosphonic acid esters. A less hydrophobic pyrimidinophane exhibited a typical effect of cationic surfactants to accelerate the reaction both in the absence and in the presence of PEI. Unlike cationic micelles, a heminal-type pyrimidinophane exhibited an anomalous behavior: it had no effect on the rates of hydrolysis of the substrates and did not inhibit the hydrolysis. Upon the addition of lanthanum ions, the catalytic activity of dimeric surfactants increased. The overall catalytic effect due to the action of supramolecular systems based on pyrimidinophanes, PEI, and lanthanum ions can increase the rates of hydrolysis of the substrates by three orders of magnitude, as compared with that of alkaline hydrolysis.

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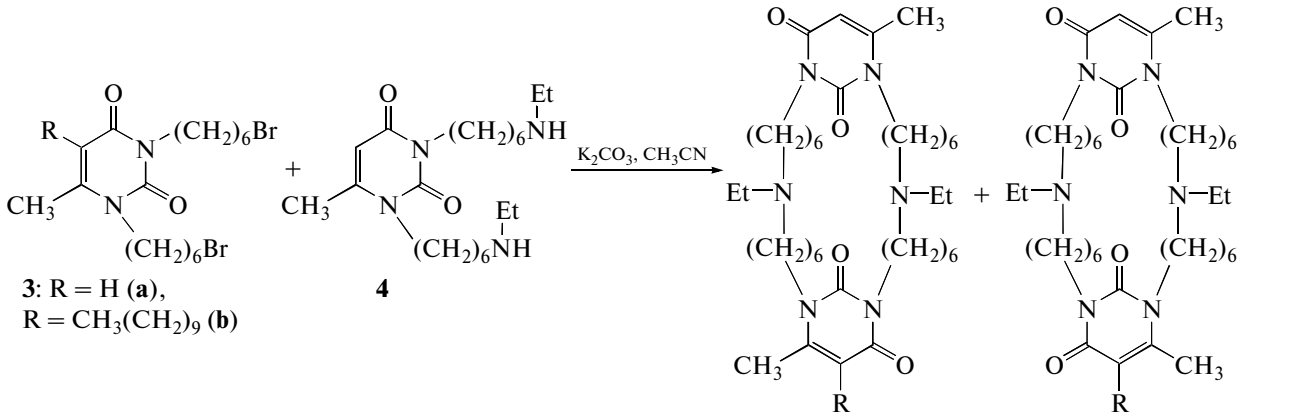
INTRODUCTION

The organized solutions of surfactants are widely used [1]. One of the most important areas in the basic and applied studies of the solutions of practically important amphiphilic compounds is the study of their catalytic effects [2–4]. A search for new building blocks for the formation of noncovalently bound nanosized aggregates (nanoreactors) is a problem of considerable current interest. Previously, we described the synthesis and aggregation and catalytic activity of amphiphilic compounds from a new class—dimeric pyrimidine-containing surfactants [5–7].

In this work, we studied the self-organization of new amphiphilic pyrimidinophanes (APPs) with different hydrophobicities obtained by quaternizing the bridging N atoms of pyrimidinophane isomers **5a,b** and **6a,b** synthesized according to Scheme 1 and the catalytic effects produced by them in the hydrolysis of phosphonic acid esters **1** and **2** (Scheme 2).



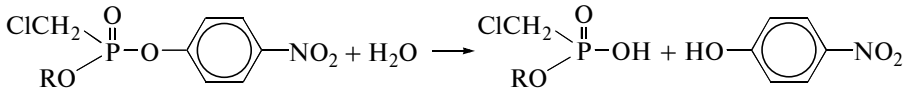
3: R = H (**a**), R = $CH_3(CH_2)_9$ (**b**)

4

R = H (**5a**), R = $CH_3(CH_2)_9$ (**6a**)

R = H (**5b**), R = $CH_3(CH_2)_9$ (**6b**)

Scheme 1.

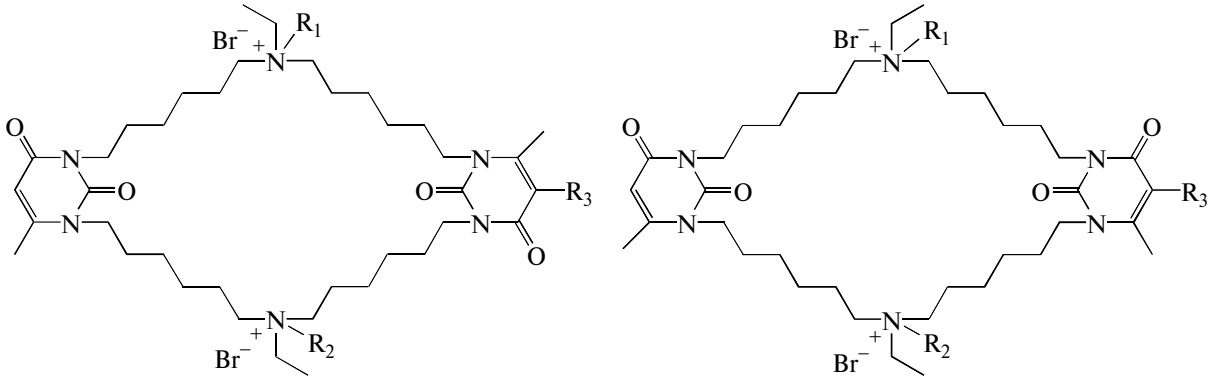


1, **2**

$R = C_2H_5$ (**1**), $R = n\text{-}C_6H_{13}$ (**2**)

Scheme 2.

Compounds APP-1 and APP-2 are the mixtures of isomeric pyrimidinophanes, which differ from each other in the mutual arrangement of C(4)=O groups (*trans* and *cis* isomers) at different pyrimidine rings:



APP-1: $R_1 = R_2 = C_2H_5$; $R_3 = n\text{-}C_{10}H_{21}$
APP-2: $R_1 = R_2 = n\text{-}C_{10}H_{21}$; $R_3 = H$

In the development of catalytic systems, we used chemically different polyethyleneimines (PEIs) [8, 9], which can bind reagents with the formation of a catalytic complex and accelerate the hydrolysis of substrates by a basic mechanism [10]. In this context, we studied the self-organization of APP/PEI binary systems. The third ingredient was La(III) ions, which are an electrophilic catalyst of phosphonate hydrolysis [11].

EXPERIMENTAL

Amphiphilic pyrimidinophanes APP-1 and APP-2 were synthesized in accordance with a previously described procedure [12, 13]. At the first stage, the interaction of 1,3-bis(6-bromohexyl)-6-methyluracil (**3a**) or 1,3-bis(6-bromohexyl)-5-decyl-6-methyluracil (**3b**) with 1,3-bis(6-ethylaminohexyl)-6-methyluracil (**4**) resulted in the mixtures of isomeric pyrimidinophanes **5a** and **5b** or **6a** and **6b** with the *trans* or *cis* arrangement of C(4)=O groups at different pyrimidine rings, respectively, in 17% yield (Scheme 1). We failed to separate the pairs of isomeric macrocycles into individual compounds; therefore, we used their mixtures in the subsequent experiments. At the second stage, amphiphilic pyrimidinophanes APP-2 were synthesized by the quaternization of bridging N atoms in macrocyclic compounds **5a** and **5b** with *n*-decyl bromide ($Br(CH_2)_9CH_3$), whereas amphiphilic pyrimidinophanes APP-1 were synthesized by the quaternization of bridging N atoms in macrocyclic compounds **6a** and **6b** with ethyl bromide ($BrCH_2CH_3$).

The *para*-nitrophenyl esters of alkylchloromethylphosphonic acids, where alkyl is ethyl (**1**) or hexyl (**2**), were synthesized in accordance with a published procedure [14]. Commercial PEI with a branched structure (molecular weight of 50000; 50% solution) and $La(NO_3)_3 \cdot 6H_2O$ (both from Aldrich) were used. The molar concentrations of PEI specified below are given on a monomer unit basis. The kinetics of hydrolysis as a pseudo-first-order reaction was studied by spectrophotometry on a Specord M-400 instrument; the course of the reaction was monitored by measuring the absorbance of the *para*-nitrophenolate anion. The observed rate constants (k_{obs}) were determined from the relation $\ln(A_\infty - A_t) = -k_{obs}t + \text{const}$, where A_t and A_∞ are the absorbances of the solution at the point t in time and after completion of the reaction, respectively. The weighted least-squares method was used for calculations taking into account the arithmetic mean values of the results of three measurements, which differed by no more than 5%. Surface tension was determined by the anchor-ring method using a du Nouy tensiometer at 25°C.

The NMR spectra were measured on a Bruker Avance-600 spectrometer (600 MHz). Tetramethylsilane and the sodium salt of 3-(trimethylsilyl)-2,2,3,3-d_4-propionic acid were used as internal standards in CD_3CN and D_2O, respectively.

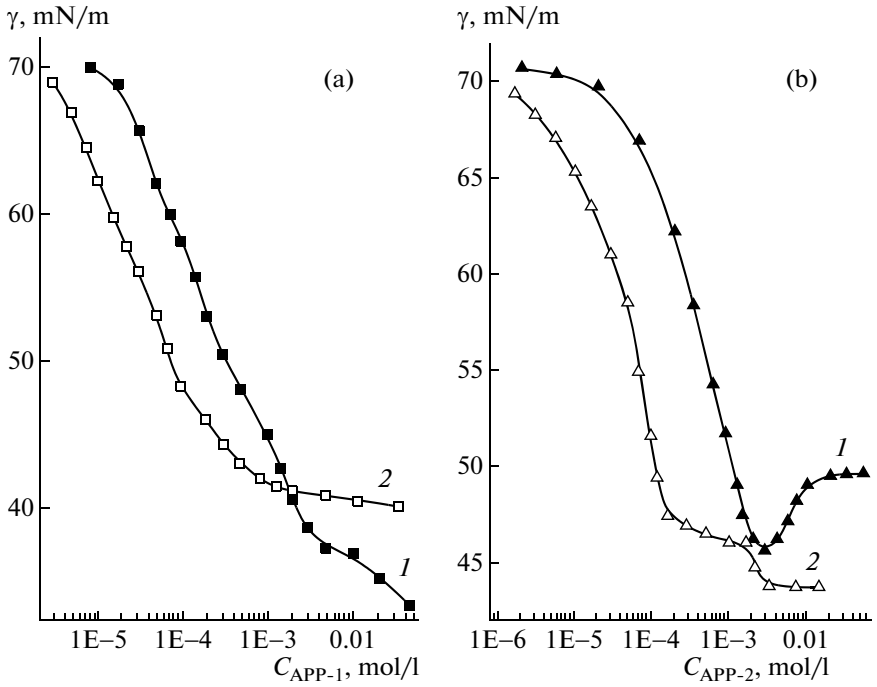


Fig. 1. Surface tension isotherms of the aqueous solutions of (a) APP-1 and (b) APP-2 at 25°C (*1*) in the absence and (*2*) in the presence of PEI.

RESULTS AND DISCUSSION

Self-Organization of Amphiphilic Pyrimidinophanes

Figure 1 shows the isotherms of surface tension (γ) for the individual solutions of amphiphilic pyrimidinophanes and the APP/PEI binary systems. Table 1 summarizes critical micelle concentrations (CMCs). It is well known that the hydrophobicity of molecules has the most significant effect on the CMCs of surfactants [1]. On this basis, it would be expected that the CMC of heminal analog APP-1 (two decyl radicals) is lower than that of bolaform surfactant APP-1 (one decyl radical). However, their CMCs were found the same. It is likely that, if a dodecyl radical occurs in an uracil fragment, the hydrophobicity of this radical and the hydrophobicity of hexamethylene chains in the ring are added. The decyl radical of APP-1 molecules forms the basis of a nonpolar nucleus of aggregates by drawing the hydrophobic regions of a spacer into micelles. In the case of APP-2, it is likely that individual spacer fragments occur near the surface of aggregates to produce steric hindrances for micelle formation and to loose the packing of micelles. Upon the addition of PEI, the CMCs in both of the systems decreased by an order of magnitude (Fig. 1, Table 1); this suggests the formation of mixed aggregates with the polymer.

The use of the Gibbs adsorption equation [15] allows us to calculate the maximum adsorption Γ_{max}:

$$\Gamma_{max} = \frac{1}{2.3nRT}\lim_{C\to CMC}(d\pi/d\log C_{surfactant}), \qquad (1)$$

where π is the surface pressure, which is equal to the difference between solvent and solution surface tensions at a specified surfactant concentration ($\pi = \gamma_0 - \gamma$); R is the gas constant; and $C_{surfactant}$ is the surfactant concentration. The constant is $n = 2$ in the case of ionic surfactants containing a monovalent micelle-forming

Table 1. Characteristics of APP-1, APP-2, and the APP/PEI binary systems

System	$\Gamma_{max} \times 10^6$, mol/m^2	CMC × 10^3, mol/l	A_{min}, nm^2	π_{CMC}, mN/m	$-\Delta G_m$, kJ/mol	$-\Delta G_{ads}$, kJ/mol
APP-1	0.936	3	1.77	24.75	28.8	54.2
APP-1/PEI	0.954	0.2	1.74	22.58	35.2	58.9
APP-2	0.773	3	2.15	31.72	21.6	62.6
APP-2/PEI	0.755	0.3	2.20	26.75	33.3	68.7

Note: Γ_{max} is the maximum adsorption; A_{min} is the minimum surface area per surfactant molecule; π_{CMC} is the surface tension at CMC; ΔG_m is the free energy of micelle formation; and ΔG_{ads} is the standard free energy of adsorption.

ion and a monovalent counterion or 3 in the case of dimeric surfactants containing a divalent micelle-forming ion and two monovalent counterions. The minimum surface area per surfactant molecule (A_{min}), the free energy of micelle formation (ΔG_m), and the standard free energy of adsorption (ΔG_{ads}) were calculated from the following equations:

$$A_{min} = 10^{18}/N\Gamma_{max}, \quad (2)$$

where N is the Avogadro number;

$$\Delta G_m = (1 + g)RT\ln(CMC), \quad (3)$$

where g is the degree of binding of counterions, which was found from surface tension isotherms [16]; and

$$\Delta G_{ads} = \Delta G_m - (\pi_{CMC}/\Gamma_{max}). \quad (4)$$

Table 1 summarizes the results of calculations. Note that the values of limiting adsorption and minimum surface area are much different from the parameters characteristic of classical cationic surfactants. For example, the values of $\Gamma_{max} = 3.1 \times 10^{-6}$ mol/m^2 and $A_{min} = 0.53$ nm^2 were obtained for the solutions of cetyltrimethylammonium bromide (CTAB) [17]. As can be seen in Table 1, the values of A_{min} for APP-1 and APP-2 are higher than that for CTAB by factors of 3 and 4, respectively. It is likely that this large discrepancy is explained by not only a difference between the CMCs of these surfactants but also the peculiarity of molecular packing. Adsorption parameters depend on the structure of surfactants: APP-1 is characterized by smaller surface areas per head group, as compared with those of APP-2. This fact supports the above assumption on a looser packing of APP-2 molecules. The additives of PEI have almost no effect on the values of Γ_{max} and A_{min} (Table 1).

Catalytic Effect

We performed catalytic experiments in which we measured the catalytic effect produced by the presence of supramolecular systems in the hydrolysis reactions of phosphonates **1** and **2**. These two substrates were chosen because the hydrophobicity factors of reagents play a key role in micellar catalysis. A more significant catalytic effect was observed in reactions with the participation of more hydrophobic substrates; this fact is explained by the effective solubilization of them by micelles [2–4]. Deviations from this regularity form the basis for assumptions concerning the possible contribution of other catalysis mechanisms. The form of the concentration dependence of the observed rate constant of bimolecular reactions in micellar systems depends on the nature of reactants and the efficiency of their interaction with micelles. If both of the reactants are efficiently bound to micelles, the dependence of k_{obs} on $C_{surfactant}$ passes through a maximum. A decrease in the rate constant in the region of high surfactant concentrations was due to the effect of reactant dilution as the concentration of micelles was increased [2]. An analysis of kinetic data in the case that k_{obs} is an extremal function of $C_{surfactant}$ was performed in terms of a pseudophase model using the equation [2]

$$k'_{obs} = \frac{k_{2,w} + k_{2,m}/V\, K_S K_{OH} C_{surfactant}}{(1 + K_S C_{surfactant})(1 + K_{OH} C_{surfactant})}, \quad (5)$$

where k'_{obs} is the observed second-order rate constant, which was obtained by dividing k_{obs} by the total nucleophile concentration; $k_{2,w}$ and $k_{2,m}$ (l mol^{-1} s^{-1}) are the second-order rate constants in aqueous and micellar phases, respectively; K_S and K_{OH} (l/mol) are the constants of substrate and hydroxide ion binding, respectively; V is the molar volume of the surfactant; and $C_{surfactant}$ is the concentration of the surfactant minus the CMS.

In the case that the process is inhibited and for pseudo-first-order reactions (when the dependence of k_{obs} on $C_{surfactant}$ flattens out), the following equation can be applied, which is widely used in micellar catalysis [2] and implies the formation of a catalytic substrate–micelle complex:

$$k_{obs} = \frac{k_w + k_{Cat} K'_S C_{surfactant}}{1 + K'_S C_{surfactant}}, \quad (6)$$

where k_{obs} is the observed pseudo-first-order rate constant; k_w and k_{Cat} are the first-order rate constants in water and the catalytic complex, respectively; and K'_S (l/mol) is the reduced constant of substrate binding to micelles.

Pseudophase model propositions are also used in Eq. (6); however, the binding of only one reactant by micelles is taken into consideration. Strictly speaking, it can be applied to unimolecular reactions. However, on the inhibition of the process on in the reaction performed in an excess of a reactant, the rate of bimolecular reaction also depends on only the constant of substrate binding. In this work, we used Eq. (6) in the cases of the inhibition of the hydrolysis of phosphonates in micellar systems or polymer–colloid complexes.

The alkaline hydrolysis of the substrates was studied in the individual solutions of surfactants. Figure 2 shows the concentration dependence of the observed rate constant of hydrolysis of hydrophobic phosphonate **2**. The effects of APP-1 and APP-2 micelles on the rate of reaction were essentially different. In a solution of APP-1, the reaction was accelerated ($k_{obs}/k_w \approx 5.5$); this is typical of cationic micelles and can be explained by the attraction of hydroxide ions to the positively charged surface of aggregates [2]. In an individual solution of APP-2, the rate of hydrolysis of phosphonates remained unchanged. This anomalous effect can be due to the following reasons: First, it is believed that the solubilizing ability of aggregates toward the substrate is weak; this is very likely because an analysis of surface tension isotherms suggests a

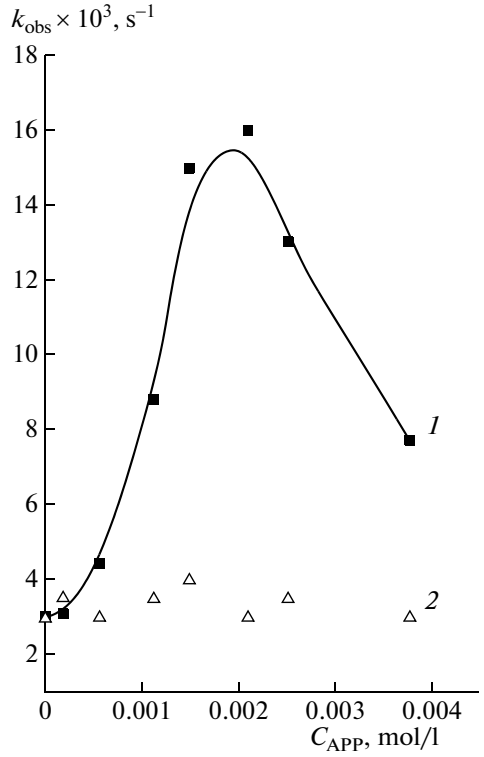


Fig. 2. Dependence of the observed rate constant of alkaline hydrolysis of phosphonate **2** on surfactant concentration in the solutions of (*1*) APP-1 and (*2*) APP-2. C_{NaOH} = 0.001 mol/l; temperature, 25°C.

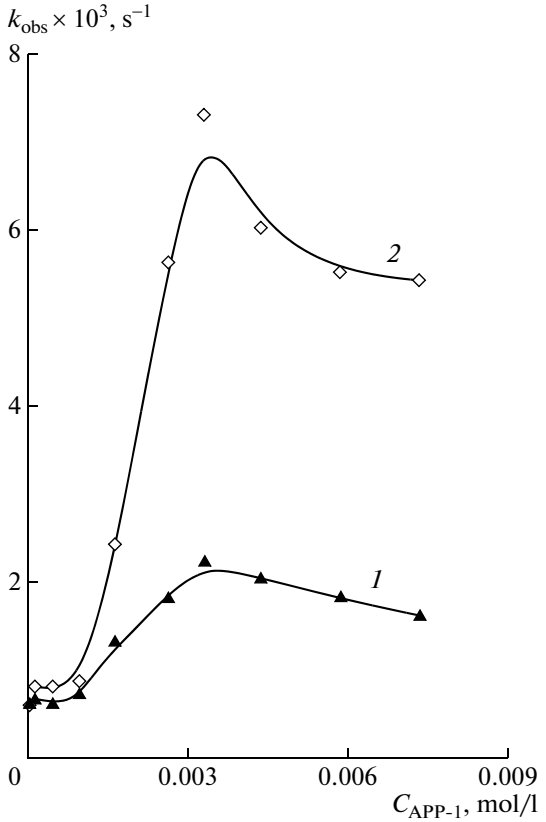


Fig. 3. Dependence of the observed rate constant of alkaline hydrolysis of phosphonates (*1*) **1** and (*2*) **2** on surfactant concentration in the APP-1/PEI system. C_{PEI} = 0.05 mol/l; temperature, 25°C.

loose packing of aggregates. These aggregates have low aggregation numbers and weak solubilizing ability. In this case, the reaction in water makes the main contribution to the observed rate constant and the micellar effect is absent. Second, the charge of micelles can be compensated because of a high degree of binding of counterions. As a result, hydroxide ions become weakly bound to micelles; this may result in the absence of the effect of surfactants or in a weak inhibition of the reaction.

Figure 3 shows the results of a kinetic study of the hydrolysis of phosphonates **1** and **2** in the APP-1/PEI binary system. An acceleration of the hydrolysis of both of the substrates was observed; the catalytic effects (k_{obs}/k_w) were ~3.5 and 10 in the reactions with the participation of phosphonates **1** and **2**, respectively. The fact that the hydrolysis of a more hydrophobic phosphonate was accelerated more strongly is typical of reactions of this kind, and it suggests a considerable contribution of micellar catalysis to the overall effect. Kinetic data shown in Figs. 2 and 3 were analyzed in terms of a pseudophase model with the use of Eq. (5). According to the results given in Table 2, the reagent concentration factor makes the main contribution to the catalytic effect in an individual solution of APP-1 and the APP-1/PEI system, whereas the

Table 2. Results of the quantitative analysis (performed with the use of Eq. (5)) of kinetic data obtained in the study of the hydrolysis of phosphonates **1** and **2** in systems based on APP-1

System	Substrate	$k_{2,w}$, l mol^{-1} s^{-1}	$(k_{obs}/k_w)_{max}$	K_S, l/mol	K_{OH}, l/mol	$k_{2,m}$, l mol^{-1} s^{-1}	F_c	F_m	$F_c \times F_m$
APP-1	**2**	3.0	4.6	4360	450	0.025	855	0.006	5.3
APP-1/PEI	**1**	0.012	12.0	1441	95	0.00024	205	0.023	4.7
APP-1/PEI	**2**	0.012	4.1	1015	12	0.004	34	0.36	12.0

microenvironment factor has a negative effect. These factors were estimated using the expression

$$(k_{obs}/k_w)_{max} = \frac{k_{2,m}}{k_{2,w}} \times \frac{K_S K_{OH}}{V(\sqrt{K_S} + \sqrt{K_{OH}})^2}, \quad (7)$$

in which the multiplicand in the right-hand side of the equation reflects the effect of the micellar microenvironment on reactivity (F_m) and the multiplier reflects the effect of reagent concentration in micelles (F_c). The values of $F_m < 1$ suggest a negative effect of this factor.

At the same time, note that the effect of reagent concentration in an individual solution is much stronger than that in a binary system because of greater binding constants of both of the reactants in the absence of PEI. It is likely that the stronger binding of a nucleophile in an individual solution of APP-1 is explained by the fact that the hydroxide ion, which is effectively attracted to the positively charged surface of cationic micelles (ion–ion interactions), acts as a nucleophilic reagent in the alkaline hydrolysis of phosphonates in the absence of PEI. In the APP-1/PEI binary system, activated water, which occurs in the solvate shells of head groups (ion–dipole interactions), is a nucleophile. Approximately the same values of the binding constants of phosphonates **1** and **2** in the binary system are indirect evidence for a change from the solubilization binding of substrates by micelles to the less effective binding in polymer–colloid aggregates. It is likely that, in this case, the catalytic acceleration of the hydrolysis reaction with the participation of a polymer (the binding of reactants in a polymer coil and the activation of water molecules by amino groups) plays an important role. Unlike the solubilization mechanism of substrate binding, which is characterized by high binding constants (which increase considerably with the hydrophobicity of compounds), much lower binding constants, which depend only slightly on the hydrophobicity of substrates, correspond to the formation of the substrate–PEI complex. The stronger catalytic effect characteristic of phosphonate **2** is due to an increase in the microenvironment factor.

The addition of lanthanum ions considerably decreases the pH of solution because of the formation of hydroxo complexes (Fig. 4, inset). Although the electrophilic activity of cations decreases because of the formation of these complexes, the rate of hydrolysis of phosphonate **2** in the presence of lanthanum ions increases by a factor of 5 as the surfactant concentration is increased (Fig. 4). The overall effect of the catalytic acceleration of the hydrolysis of substrate **2** in the APP-1/PEI/La(III) ternary system is as high as three orders of magnitude, as compared with the alkaline hydrolysis of the phosphonate at pH 8.0.

The kinetics of hydrolysis of phosphonate **1** was also studied in the APP-2/PEI system (Fig. 5). The reaction was inhibited, and the rate of reaction

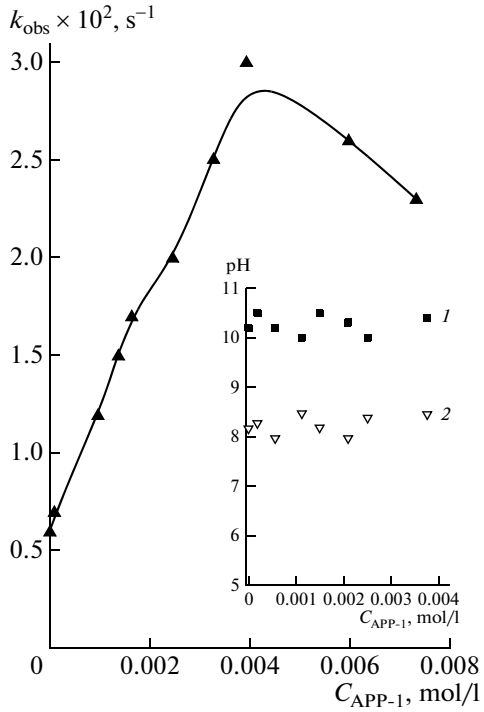


Fig. 4. Dependence of the observed rate constant of alkaline hydrolysis of phosphonate **2** on surfactant concentration in the APP-1/PEI/La(III) system. $C_{PEI} = 0.05$ mol/l; $C_{La(III)} = 0.008$ mol/l; temperature, 25°C. Inset: pH in the (*1*) APP-1/PEI binary system and (*2*) APP-1/PEI/La(III) ternary system as a function of surfactant concentration.

decreased by a factor of 2. A rare effect was observed when, on the contrary, the formation of combined structures with the participation of components potentially capable of catalyzing the process resulted in an inhibiting effect. This observation serves as an additional example of an anomalous effect of systems containing APP-2 on the reaction of hydrolysis. A similar anomalous effect was observed above in the study of the alkaline hydrolysis of the substrate (Fig. 2). The kinetic data obtained in polycomponent systems based on APP-2 were analyzed in terms of the pseudophase model with the use of Eq. (6) (Table 3). The effective binding of the substrate was observed in the APP-2/PEI system; therefore, as well as in the systems based on APP-1, the inhibition of the process can be due to an unfavorable effect of the microenvironment. However, the high binding constant (K_S = 4915 l/mol) allowed us to hypothesize that the reason for inhibition can be the separation of reactants, that is, the localization of the substrate in the nonpolar nuclei of micelles, which contain no water.

It is well known that synergetic effects are frequently observed with the use of binary surfactant solutions. Thus, we studied systems based on APP-2 with the additives of anionic and nonionic surfactants: sodium dodecyl sulfate (SDS) and Triton X-100, respectively (Fig. 5). The individual solutions of SDS

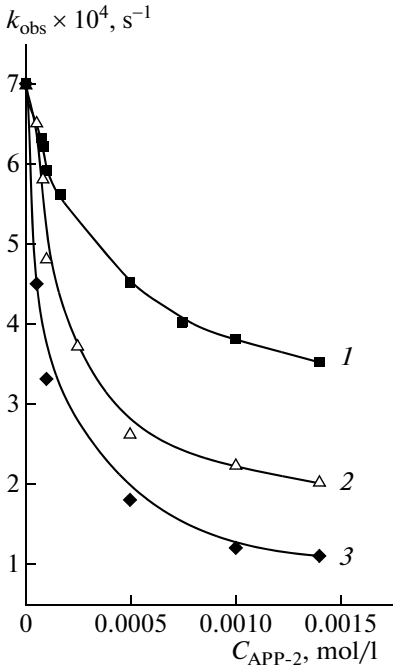


Fig. 5. Dependence of the observed rate constant of hydrolysis of phosphonate **1** in the (*1*) APP-2/PEI, (*2*) APP-2/PEI/SDS, and (*3*) APP-2/PEI/Triton X-100 systems on the concentration of APP-2. $C_{PEI} = 0.05$ mol/l; temperature, 25°C.

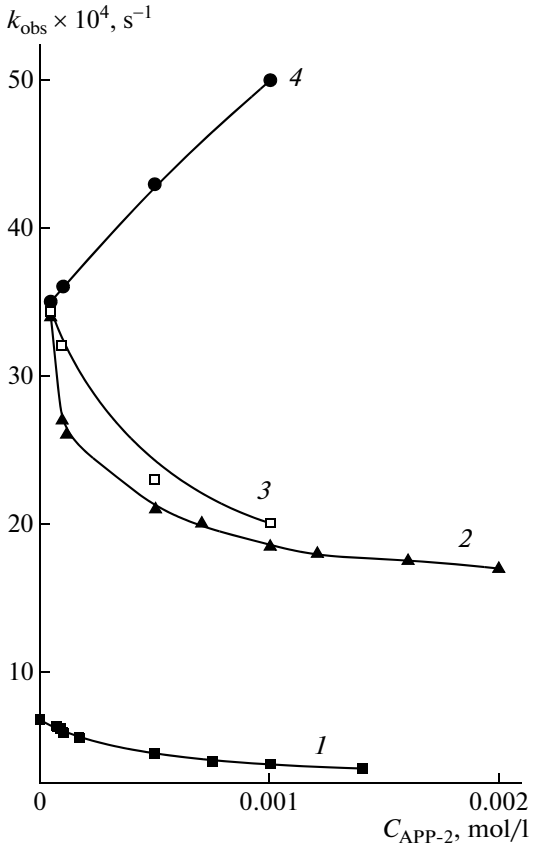


Fig. 6. Dependence of the observed rate constant of hydrolysis of phosphonate **1** in the (*1*) APP-2/PEI, (*2*) APP-2/PEI/La, (*3*) APP-2/PEI/SDS/La, and (*4*) APP-2/PEI/Triton X-100/La systems on the concentration of APP-2. $C_{PEI} = 0.05$ mol/l; $C_{La(III)} = 0.008$ mol/l; temperature, 25°C.

and Triton X-100 inhibit the alkaline hydrolysis of phosphonate **1** [18, 19]. Previously, we found that the hydrolysis was accelerated in the SDS/PEI binary system [9]; on the contrary, it was inhibited in the system with Triton X-100. As can be seen in Fig. 5, the rate of hydrolysis decreased by factors of 3.5 and 7 in the mixed APP-2/SDS/PEI system and the APP-2/Triton X-100/PEI system, respectively. Thus, in both cases, the catalytic effect of PEI was suppressed. This change from catalysis to inhibition upon replacing PEI with the surfactant/PEI system may be considered as an indirect argument for the formation of mixed surfactant–PEI aggregates. According to data given in Table 3, the inhibiting effect increased symbatically with an increase in substrate binding constants in the following order of systems: APP-2/PEI < APP-2/SDS/PEI < APP-2/Triton X-100/PEI. Thus, this is consistent with the hypothesis of a negative effect of the micellar microenvironment of reactivity in combination with the effect of reagent separation.

Table 3. Results of the quantitative analysis (performed with the use of Eq. (6)) of kinetic data obtained in the study of the hydrolysis of phosphonate **1** in systems based on APP-2

System	$k_{Cat} \times 10^3$, s^{-1}	K_S, l/mol	k_{Cat}/k_w
APP-2/PEI	0.33	4915	0.49
APP-2/PEI/SDS	0.13	7000	0.18
APP-2/PEI/Triton X-100	0.096	17000	0.14
APP-2/PEI/La	1.8	16330	0.51
APP-2/PEI/SDS/La	1.4	2685	0.40
APP-2/PEI/Triton X-100/La	9.8	330	2.8

The addition of La(III) ions to a solution of PEI resulted in an increase in the rate constant of hydrolysis of phosphonate **1** by a factor of 7 and in a decrease in the pH of solution to 8–8.5. As can be seen in Fig. 6, the rate constant somewhat decreased in the APP-2/PEI/La(III) system as the pyrimidinophane concentration was increased. However, in general, this system was highly efficient and accelerated the reaction, as compared with the alkaline hydrolysis of the phosphonate (at pH 8) by a factor of 500–900 depending on the concentration of APP-2. We studied the kinetics of hydrolysis of phosphonate **1** in polycomponent systems including the APP-2/surfactant binary

system of amphiphilic compounds as structure-forming components, a polymer component (PEI), and La(III) ions, which exhibit a homogeneous catalytic effect. We found that the dependence of reaction rate constants on the concentration of APP-2 was different in the APP-2/PEI/SDS/La and APP-2/PEI/Triton X-100/La four-component systems. As $C_{APP\text{-}2}$ was increased in the system containing an SDS additive, k_{obs} decreased by a factor of 1.5, whereas in increased by the above factor in the system with a Triton X-100 additive (Fig. 6). It is believed that, in the latter case, aggregates of a new type based on mixed surfactant (APP-2 + Triton X-100) micelles immobilized on a PEI matrix were formed in the system; they accelerated the reaction mainly by the action of PEI amino groups and La(III) ions.

An analysis of kinetic data with the use of Eq. (6) (Table 3) suggests that the inhibition of the hydrolysis of phosphonate **1** with increasing surfactant concentrations in the APP-2/PEI/La(III) and APP-2/PEI/SDS/La(III) system may be of the same nature as in the absence of La(III) ions; that is, it was due to the effective binding of the substrate and the occurrence of the reaction in an unfavorable environment within micelles. The inhibiting effect in these systems increased with binding constants. A considerable (by one or two orders of magnitude) decrease in the substrate binding constant in the APP-2/Triton X-100/PEI/La(III) system was noted; it was accompanied by a change from inhibition to the catalytic acceleration of reaction. This provides support to the above hypothesis that PEI makes the predominant contribution to the catalytic effect of this system.

Thus, we studied the aggregation and catalytic activity of supramolecular systems based on new macrocyclic dimeric surfactants (pyrimidinophanes) in the absence and in the presence of PEI. The structures of surfactants and difference in their hydrophobicity have no effect on the micelle-forming activity of compounds (their CMCs are equal); however, they affect the parameters of adsorption at the water–air interface. This allows us to hypothesize that the molecular packing of APP-2 aggregates is looser. It is likely that the catalytic effects of pyrimidinophanes in the hydrolysis of phosphonic acid esters are different due to the morphology peculiarities of APP-1 and APP-2 aggregates. APP-1 exerts a typical effect of cationic surfactants to accelerate the reaction both in the absence and in the presence of PEI. APP-2 has an anomalous effect on the rate of hydrolysis of the substrates; thus, its behavior is different from the behavior of cationic micelles. An individual solution of APP-2 has no effect on the rate of hydrolysis of phosphonates, whereas the APP-2/PEI binary systems inhibit the reaction. Upon the addition of lanthanum ions, the catalytic activity of systems based on APP-1 increases, and a change from inhibition to the catalytic acceleration of the reaction is observed in the systems based on APP-2. Because of the overall catalytic effect due to the action of supramolecular systems based on pyrimidinophanes, PEI, and lanthanum ions, the rate of reaction can increase by three orders of magnitude, as compared to the rate of alkaline hydrolysis of the substrates.

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