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Supramolecular Catalytic System Triton X-100–Polyethyleneimine–La(III) for Hydrolysis of Phosphonic Acid Esters

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Abstract—The self-organization of systems based on the nonionic surfactant Triton X-100, polyethyleneimine, and lanthanum ions has been investigated. The micellar solutions of Triton-X-100 alone and the Triton-X-100–polyethyleneimine binary systems inhibit the hydrolysis of phosphonic acid esters. The Triton-X-100–polyethyleneimine–La(III) ternary system with a certain component ratio exerts a considerable catalytic effect, raising the rate of the reaction by more than three orders of magnitude relative to the rate of the alkaline hydrolysis of the phosphonates.

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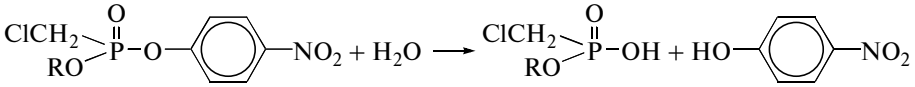
A promising area of present-day catalysis science is design of supramolecular systems that, due to their biomimetic character, can ensure high catalytic activity and selectivity under mild conditions [1–3]. In our earlier works [4–6], we suggested an approach to the design of multicomponent catalytic systems capable of executing a combined catalytic action, including micellar, macromolecular, and homogeneous catalysis. Surfactants of various natures, polymers, and metal ions were used as the components of these systems. In particular, we investigated catalytic systems based on polyethyleneimine (PEI) and a lanthanum salt, modified with the anionic surfactant sodium dodecyl sulfate [4], geminal pyrimidine-containing surfactants [5], and the nonionic surfactant decaethylene glycol monodecyl ether ($C_{12}EO_{10}$) [6]. These systems afforded a considerable catalytic effect, raising the rate of the hydrolysis of phosphorus acid esters by 3–6 orders of magnitude relative to the rate of the alkaline hydrolysis of the same substrates.

Continuing those works, we have designed a new catalytic system based on the nonionic surfactant polyethylene glycol(10) mono(4-isooctylphenyl) ether (Triton X-100). As distinct from the nonionic surfactant $C_{12}EO_{10}$, which is inactive in the hydrolysis of phosphorus acid esters, the aqueous solutions of Triton X-100 slow down the hydrolysis of the substrates. Therefore, by varying the nature and concentrations of components, it is possible to formulate compositions ranging in activity from inhibition to catalysis. For this purpose, we studied, in succession, the catalytic effects of the single-component system Triton X-100, the binary system Triton X-100–PEI, and the ternary system Triton X-100–PEI–La(III) on phosphorus acid ester hydrolysis:



1, 2

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

In addition, the micellization properties of these systems were studied by surface tension measurements and dynamic light scattering.

Phosphoryl group transfer is among the most important biochemical reactions [7]. The esters of phosphorus acids are biologically active compounds widely used as pesticides, medicines, etc. [8]. Therefore, the stability of these substrates is a topical issue. The hydrolysis of phosphorus acid esters in water in the absence of a surfactant and in simple micellar systems has been studied in detail [1–3, 9], so it is a convenient test reaction. The hydrolysis of *p*-nitrophenyl esters occurs through P–OAr bond breaking, yielding *p*-nitrophenol.

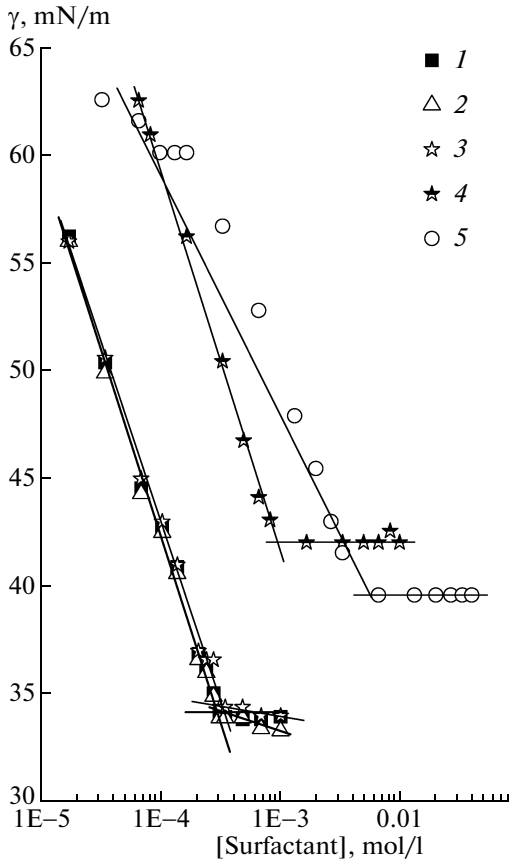


Fig. 1. Surface tension (γ) isotherms for the systems (*1*) Triton X-100–H_2O, (*2*) Triton X-100–PEI–H_2O, (*3*) Triton X-100–PEI–La(III)–H_2O, (*4*) Triton X-100–DMF–H_2O (10 vol % DMF), and (*5*) Triton X-100–DMF–H_2O (30 vol % DMF). [PEI] = 0.05 mol/l; [$La(NO_3)_3$] = 0.008 mol/l; T = 25°C.

EXPERIMENTAL

Compounds **1** and **2** were synthesized using a standard procedure [10]. The components of the catalytic system were Triton X-100 (Sigma), branched PEI (molecular weight of 50000, 50% solution, Aldrich), $La(NO_3)_3 \cdot 6H_2O$ (Aldrich). The PEI molar concentrations specified below refer to the monomer unit.

The hydrolysis kinetics was studied spectrophotometrically on a Specord M-400 spectrophotometer under pseudo-first-order conditions by measuring the absorbance of the *p*-nitrophenolate anion. Apparent rate constants (k_{app}) were determined using the relationship $\ln(A_\infty - A) = -k_{app}t + \text{const}$, where A and A_∞ are the absorbances of the solution at the point in time t and after the completion of the reaction, respectively. These calculations were carried out by the weighted least squares method. The arithmetic mean values of three measurements differing by no more than 5% were involved in the calculations.

Surface tension was measured at 25°C by the Du Nouy ring detachment method.

Particle sizes were determined by the dynamic light scattering method on a Photocor Complex photon correlation spectrometer (Milton Roy, United States) equipped with a 25-mW He–Ne laser (λ = 633 nm). The scattering angle was 90°, and the pulse counting time was 500 s. Before measurements, the samples were filtered through Millipore membrane filters with a pore diameter of 0.45 μm to remove dust. The autocorrelation functions of scattered light intensity fluctuations were measured with a PhotoCor-M 72-channel correlator and were analyzed using the cumulant method and the DynaLS program, which allowed the aggregate size distribution to be estimated.

The kinetic data obtained for the PEI solutions were fitted to Eq. (1), an analogue of the Michaelis–Menten equation, which is widely used in enzyme and micellar catalysis [1] and assumes the formation of a substrate–micelle catalytic complex:

$$k_{app} = \frac{k_w + k_{cat}K_S C}{1 + K_S C}, \quad (1)$$

where k_{app} is the apparent pseudo-first-order rate constant; k_w and k_{cat} are the first-order rate constants of the reaction in water and in the catalytic complex medium, respectively; K_S is the reduced substrate–micelle binding constant; and C is the surfactant concentration minus the critical micelle concentration (CMC).

RESULTS AND DISCUSSION

Self-Organization

According to the literature [11], the mutual affinity of the components in nonionic surfactant–polymer systems is much weaker than that in ionic surfactant–polymer systems. Figure 1 shows the surface tension isotherms from which we derived the CMC values for the Triton X-100 solution, the binary system Triton X-100–PEI, and the ternary system Triton X-100–PEI–La(III). The introduction of the polymer into the solution does not decrease the CMC, which remains equal to 0.00021 mol/l. The absence of a polymer effect on the micellization behavior of a surfactant is conventionally considered to be evidence of weak mutual affinity in the surfactant–polymer pair. The introduction of metal ions into the system exerts only a slight effect on the CMC (Fig. 1).

Addition of solvents that disturb the structure of water diminish the hydrophobic effect [12–14], which plays the key role in the formation of normal phase micelles. We studied the effect of the aprotic solvent dimethylformamide (DMF) on the micellization properties of the surfactant. A comparison of surface tension isotherms for Triton X-100 solutions containing different DMF concentrations (Fig. 1) demonstrates that the addition of 10 and 30 vol % DMF sharply raises the Triton X-100 CMC from 0.00021 to 0.00090 and 0.0048 mol/l, respectively.

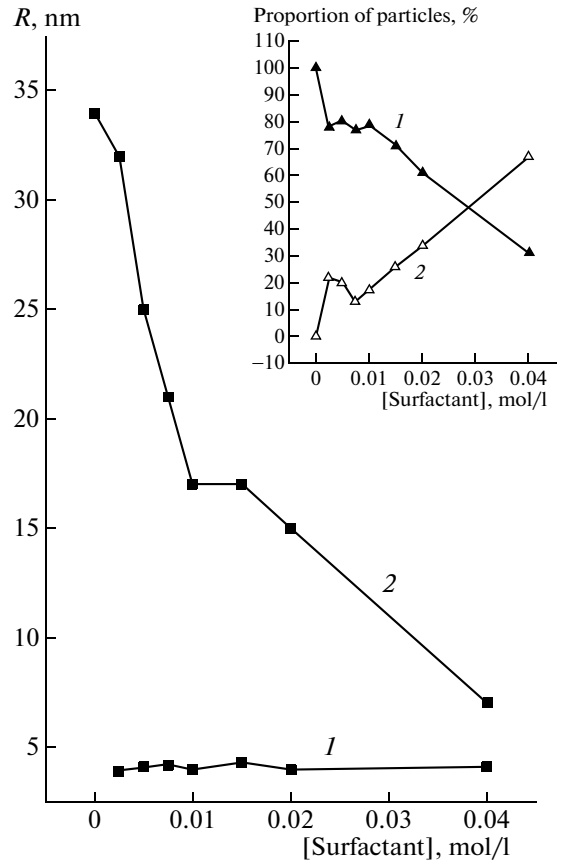


Fig. 2. Average hydrodynamic radius of the particles (R) in the (*1*) Triton X-100 solution and (*2*) Triton X-100–PEI system as a function of the surfactant concentration at 25°C and [PEI] = 0.05 mol/l. Inset: Proportion of particles with a radius of (*1*) 50 ± 5 and (*2*) 4–6 nm as a function of the surfactant concentration in the Triton X-100–PEI system.

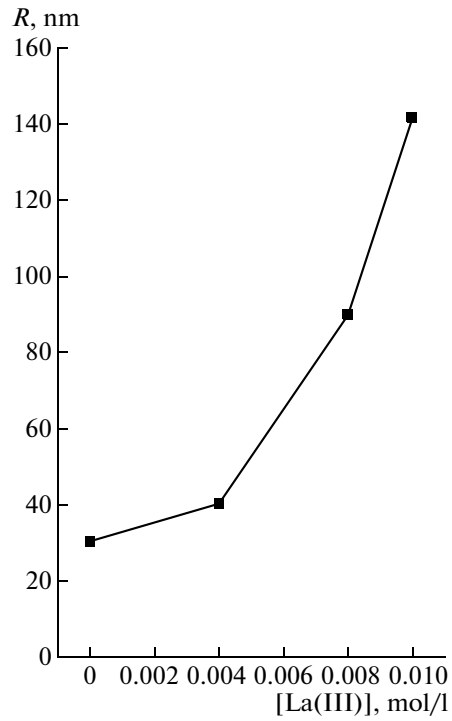


Fig. 3. Average hydrodynamic radius of the particles in the PEI–La(III) system as a function of the lanthanum ion concentration at 25°C and [PEI] = 0.05 mol/l.

The formation of aggregates in systems based on Triton X-100 was proved by dynamic light scattering (Figs. 2, 3). The average hydrodynamic radius of the aggregates in the Triton X-100 solutions is 4 nm. The Triton X-100–PEI system was also investigated by dynamic light scattering. The concentration dependences of the effective hydrodynamic radius of the aggregates measured by the cumulant method (autocorrelation function expansion in two cumulants) are plotted in Fig. 2. The inset in Fig. 2 shows the particle size distribution obtained using the DynaLS program. In the Triton X-100–PEI system, the effective aggregate size decreases from 30 to 7 nm as the surfactant concentration is raised. As is clear from the data presented in the inset in Fig. 2, the binary solutions are polydisperse and contain two types of particles, namely, large particles with an average hydrodynamic radius of 50 ± 5 nm and small particles 4–6 nm in radius. The former can be assumed to be polymer molecules. Their size in the binary system is larger than their size in the solution of the polymer alone. This is likely due to the immobilization of micellar aggregates accompanied by some unfolding of the polymer coil. The small aggregates are apparently free Triton X-100 micelles not bound to a macromolecule. As the surfactant concentration is increased, the number of free micelles increases, resulting in a decrease in effective aggregate size in the binary system. This is in agreement with theory [11], according to which coaggregation via the immobilization of surfactant aggregates on the polymer matrix occurs in surfactant–polymer systems at low surfactant concentrations. Upon the saturation of the macromolecules with micelles, ordinary micelles unbound to the polymer form in the solution.

In the presence of a lanthanum salt, polymeric hydroxo complexes form in the solution according to the following scheme [15]:

$$[La(H_2O)_n]^{3+} \rightleftharpoons [La(H_2O)_{n-k}(OH)_k]^{(3-k)+},$$

where $k = 1–3$, and n can be fairly large, as in typical polymers. As a consequence, a sharp increase in the aggregate size takes place in the systems containing PEI and lanthanum ions (Fig. 3), which is accompanied by gelation and by a decrease in the pH of the solution at high lanthanum salt concentrations.

Catalytic Properties

The hydrolysis kinetics of phosphonates **1** and **2** in aqueous solutions of an alkali and PEI was studied in our earlier works [4, 16]. The second-order rate con-

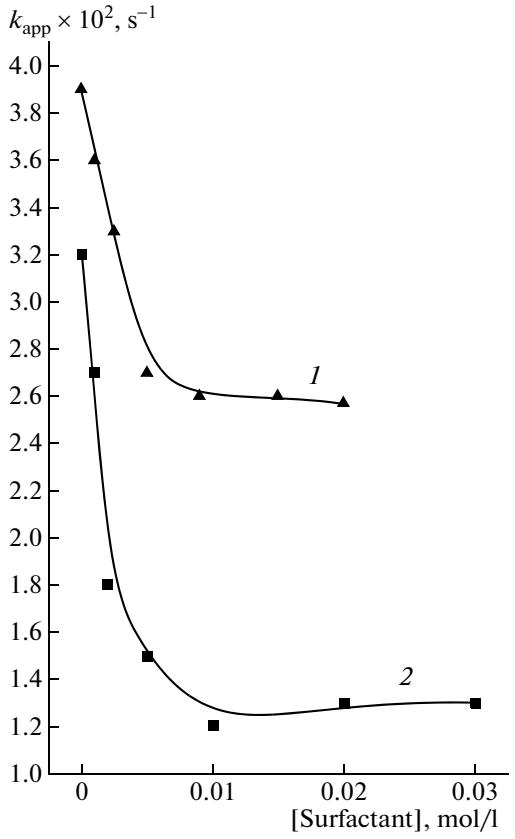


Fig. 4. Apparent rate constant of the alkaline hydrolysis of substrates (*1*) **1** and (*2*) **2** as a function of the Triton X-100 concentration at 25°C and [NaOH] = 0.01 mol/l.

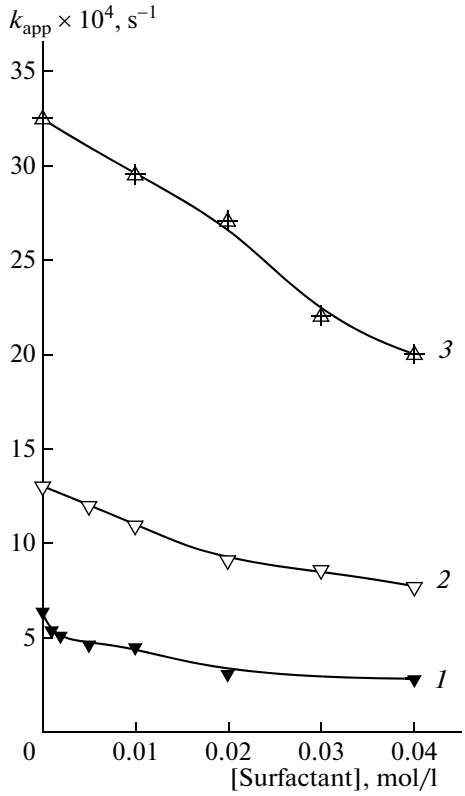


Fig. 5. Apparent rate constant of the hydrolysis of substrate **1** as a function of the Triton X-100 concentration at a constant PEI concentration of (*1*) 0.05, (*2*) 0.1, and (*3*) 0.5 mol/l. $T = 25$°C.

stants of the alkaline hydrolysis of **1** and **2** are 4.0 and 3.0 l mol^{-1} s^{-1}, respectively. In the aqueous solutions containing PEI, general base catalysis takes place and phosphonate **1**, which is less hydrophobic than **2**, is more reactive [16, 17]. Investigation of the hydrolysis of esters with different hydrophobicities in surfactant–polymer systems provides information concerning the contributions from the micellar catalysis and macromolecular catalysis to the overall catalytic effect, which can be characterized by the ratio of the rate constant in the catalytic complex medium to the rate constant in water (k_{cat}/k_w) at a fixed pH. In the case of micellar catalysis, in which the solubilization mechanism of substrate binding takes place, the hydrolysis rate constant usually increases considerably with an increasing hydrophobicity of the substrate. In polymer solutions in which a catalytic substrate–polymer complex forms, the hydrophobicity factor is insignificant [16].

Figures 4–8 plot the apparent rate constant of hydrolysis of the substrates as a function of the concentrations of the components of the supramolecular system. In the aqueous solution of Triton X-100, the alkaline hydrolysis of the phosphonates slows down with an increasing surfactant concentration, and this surfactant effect is greater for the more hydrophobic substrate **2** (Fig. 4). The concentration of hydroxide ions in the polyoxyethylene mantle of the nonionic micelles of Triton X-100 decreases, which is likely due to the strong affinity of these ions for the aqueous pseudophase, and this leads to the separation of the reactants, as in the micelles of anionic surfactants. The hydrolysis of the phosphonates in the aqueous solution of PEI accelerates with an increasing PEI concentration. This is due the contribution from two processes, namely, the binding of the reactants by the macromolecules and general base catalysis by the amino groups [4]. In the Triton X-100–PEI system, the reaction is inhibited ($k_{cat}/k_w < 1$; see the table), and this effect is again more pronounced for the more hydrophobic phosphonate **2** (Figs. 5, 6). As was mentioned above, this is evidence that the micellar effect makes the major contribution to the overall change in the reaction rate. On the whole, the degree of inhibition increases with an increasing PEI concentration. The deceleration of the reaction in the surfactant–PEI systems is an unusual observation. It was demonstrated earlier [4–6] that the hydrolysis of phosphonates **1** and **2** accelerates in similar systems containing surfactants of various natures, including nonionic surfactants [6].

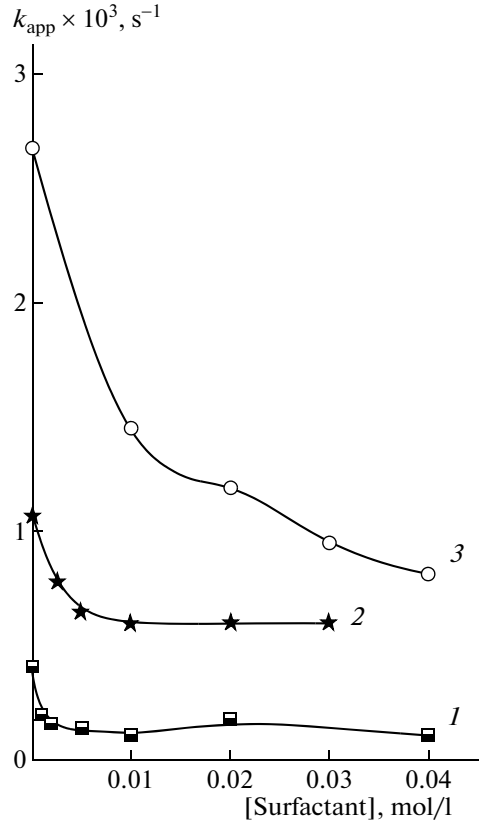


Fig. 6. Apparent rate constant of the hydrolysis of substrate **2** as a function of the Triton X-100 concentration at a constant PEI concentration of (*1*) 0.05, (*2*) 0.1, and (*3*) 0.5 mol/l. $T = 25°C$.

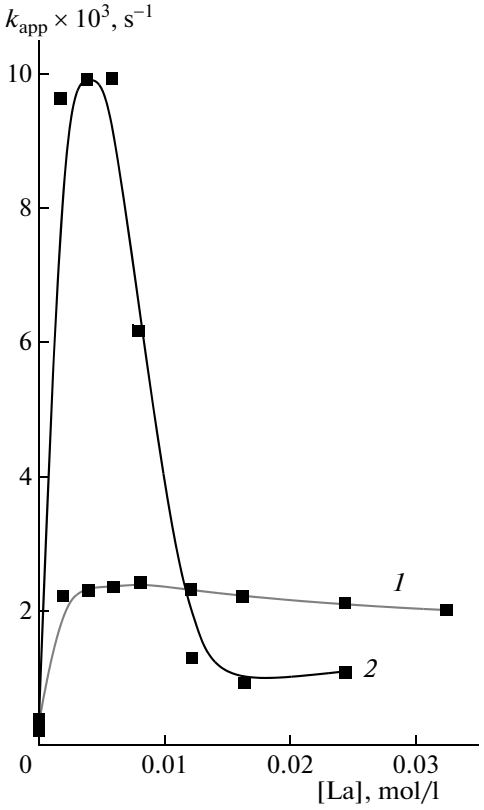


Fig. 7. Apparent rate constant of the hydrolysis of substrates (*1*) **1** and (*2*) **2** in the Triton X-100–PEI–La(III)–H_2O system as a function of the La concentration at constant PEI and Triton X-100 concentrations of 0.05 and 0.005 mol/l, respectively. $T = 25°C$.

The causes of the total suppression of the catalytic action of the amino groups of PEI will be discussed below.

Kinetic data were analyzed within the pseudophase model using Eq. (1). As is clear from the table, the stronger inhibition of the hydrolysis of **2** (threefold decrease in the reaction rate) as compared to the hydrolysis of **1** is due to the larger values of the binding constants of the hydrophobic substrate. The binding constants of the substrates decrease on passing from the Triton X-100 solution to the Triton X-100–PEI systems. In addition, they decrease sharply (by up to two orders of magnitude in the case of **1**) as the PEI concentration is raised (table). This tendency is likely due to the crossover from the more effective, solubilization mechanism of substrate binding in Triton X-100 micelles to the sorption mechanism involving PEI macromolecules in the polymer–colloid systems. However, in the case of **2**, the more hydrophobic phosphonate, the solubilization mechanism makes a considerable contribution to hydrolysis in the presence of the polymer, as is indicated by the fairly large K_S values (table).

Results of quantitative analysis of the kinetic data presented in Fig. 4 within the pseudophase model of micellar catalysis ($T = 25°C$)

System	PEI concentration, mol/l	Substrate	K_S, l/mol	k_{cat}, s^{-1}	k_{cat}/k_w
Triton X-100	0	**1**	240	0.021	0.52
Triton X-100	0	**2**	2100	0.012	0.38
Triton X-100–PEI	0.05	**1**	590	0.00028	0.44
Triton X-100–PEI	0.05	**2**	2500	0.00011	0.27
Triton X-100–PEI	0.1	**1**	18	0.0008	0.60
Triton X-100–PEI	0.1	**2**	540	0.0005	0.47
Triton X-100–PEI	0.5	**1**	19	0.002	0.62
Triton X-100–PEI	0.5	**2**	330	0.0008	0.30

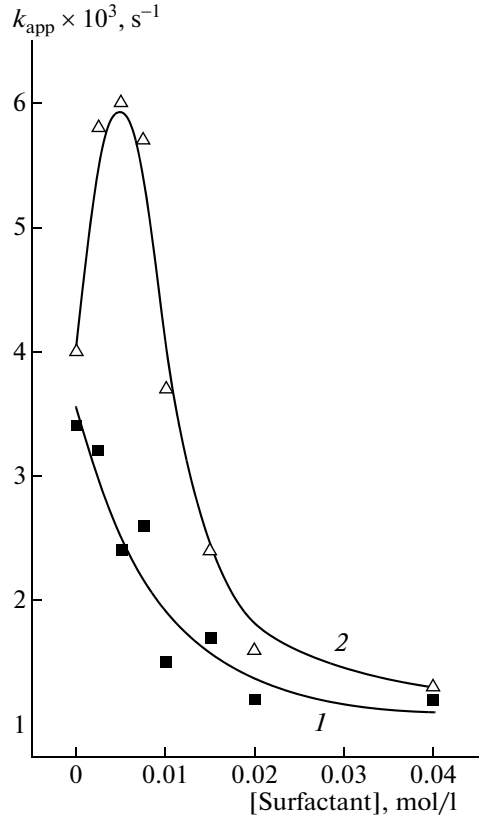


Fig. 8. Apparent rate constant of the hydrolysis of substrates (*1*) **1** and (*2*) **2** in the Triton X-100–PEI–La(III)–H_2O system as a function of the Triton X-100 concentration at constant PEI and $La(NO_3)_3$ concentrations of 0.05 and 0.008 mol/l, respectively. $T = 25°C$.

Taking into account the above quantitative data, we will analyze the uncommon inhibition effect observed in the Triton X-100–PEI system, in contradistinction to the acceleration of the hydrolysis of **1** and **2** in the presence of the nonionic surfactant $C_{12}EO_{10}$ and PEI [6]. Note that, although PEI exerts no effect on the micellization properties of the surfactants (Fig. 1), the existing kinetic data provide indirect evidence in favor of the formation of mixed aggregates involving Triton X-100. This is indicated by the fact that the substrate binding constants for the binary systems are much larger than those for the solution of PEI alone [4], as well as by the pronounced dependence of these constants on the polymer concentration. In the case of separate aggregation, the contribution from substrate binding by the polymer should not have a significant effect on the binding constants. The observed inhibition effect provides further indirect evidence in favor of surfactant aggregation through micelle immobilization on macromolecules. In this case, the slowdown of the reaction in the bound micelles can dominate over the catalytic acceleration of the reaction by the free PEI molecules. It is not impossible that some contribution to the inhibition effect is made by the alkaline hydrolysis of the substrates as a side reaction.

Figures 7 and 8 present the kinetic data obtained for the hydrolysis of the phosphonates in the Triton X-100–PEI–La(III) system. As the lanthanum ion concentration is increased at fixed concentrations of the other components, the apparent rate constant initially increases sharply (by a factor of 4 and 80 for **1** and **2**, respectively) relative to the rate constant for the Triton X-100–PEI binary system (Fig. 7). As the lanthanum ion concentration is further raised, the hydrolysis rate constant of **1** gradually decreases to a constant level, while that of **2**, a more hydrophobic substrate, passes through a maximum. This kind of dependence can be due to the competitive character of component interaction in the system. It is likely that the lanthanum ions saturate the surface layer of the micelles and, as a consequence, there is Coulomb repulsion between the positively charged ions and the protonated groups of PEI. The number of the latter increases as the pH of the solution decreases. This can destabilize the polymer–colloid complexes in which the reaction takes place and cause a decrease in the substrate binding constant.

Based on the above data, we chose a lanthanum nitrate concentration of 0.008 mol/l as the optimum concentration. It is at this concentration that we studied the dependence of the apparent rate constant of phosphonate hydrolysis in the ternary system on the surfactant concentration (Fig. 8). The rate constant for **1**, the less hydrophobic substrate, gradually decreases with an increasing surfactant concentration, while the rate constant for **2** passes through an extremum. However, even for the descending branches of these kinetic curves, the hydrolysis rate is higher than is observed for the solution of PEI alone. As is clear from Figs. 7 and 8, the more hydrophobic substrate **2** is more reactive, indicating that the micellar catalysis makes the dominant contribution to the overall catalytic effect.

Addition of the lanthanum salt reduces the alkalinity of the solution to pH 8. The hydrolysis rate of **1** and **2** in the ternary system is higher than the rate of the alkaline hydrolysis of the same compounds by a factor of 600 and 3000, respectively.

Thus, we investigated the self-organization of the single-component micellar system Triton X-100, the binary system Triton X-100–PEI, and the ternary system Triton X-100–PEI–La(III). Surface tension measurements revealed no change in the CMC on passing from the individual nonionic micelles to the binary or ternary system. The catalytic effect on the hydrolysis of phosphorus acid esters was studied in these systems. Triton X-100 and the Triton X-100–PEI system inhibit phosphonate hydrolysis, reducing the reaction rate by a factor of 3. The ternary system is an effective catalyst acting under mild conditions (25°C, pH 8) and showing substrate specificity toward the more hydrophobic phosphonate. As compared to

alkaline hydrolysis, the hydrolysis of phosphonates **1** and **2** in the Triton X-100–PEI–La(III) system is, respectively, 600 and 3000 times more rapid. The shapes of the kinetic profiles and the quantitative data characterizing the reactivity of the phosphonates in the binary and ternary systems differ from the corresponding hydrolysis characteristics observed for the single-component systems. This is evidence that the reaction occurs in polymer–colloid complexes.

ACKNOWLEDGMENTS

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