374 Russian Chemical Bulletin, International Edition, Vol. 57, No. 2, pp. 374—382, February, 2008

Supramolecular catalytic systems based on anionic amphiphiles and polyethyleneimine for hydrolytic cleavage of phosphorus ester bonds

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Self-organization in individual and binary systems based on polyethyleneimine (PEI) and amphiphilic sulfonatocalix[4]resorcinarene was studied by conductometry, tensiometry, dynamic light scattering, and ^{1}H NMR spectroscopy. The critical concentrations of micelle formation and aggregate sizes were determined. The enhancement of the catalytic effect on the hydrolysis of *O*-ethyl *O*-*p*-nitrophenyl chloromethylphosphonate was shown in the following series of the systems: PEI—water < PEI—calixarene—water < PEI—calixarene—La^{III}—water.

Key words: amphipilic sulfonatocalix[4]resorcinarenes, polyethyleneimine, lanthanum ions, self-organization, esters of phosphorus acids, hydrolysis, kinetics, supramolecular catalysis.

Supramolecular catalysis is presently being developed in two directions: catalysis in organized media (micelles, microemulsions, vesicles, liquid crystals)[1—5] and catalysis involving inclusion complexes based on cyclodextrins, calixarenes, crown ethers, podands, *etc.*[6,7] The reaction mechanism of such catalysts includes the formation of host—guest complexes, which fact brings together supramolecular catalysis and enzymatic systems. Binding of "guest" reactants creates a specific microenvironment and concentration gradient compared to their state in solution and makes the main contribution to the catalytic effect.

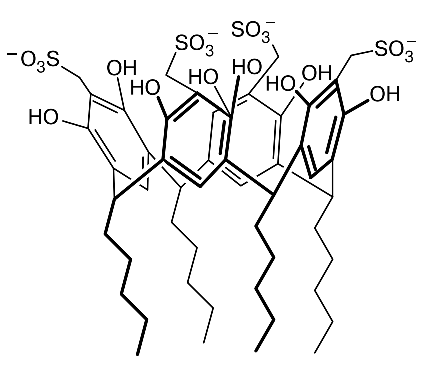
We have previously[8—12] obtained results indicating that the simulation of the polyfunctional mechanism of the enzyme action (using the synthetic supramolecular systems as an example) leads, possibly, to high catalytic effects. In particular, ensembles of the ionic and nonionic surfactants were modified step-by-step using polymers and Ln^{III} compounds,[9—12] which made it possible to form efficient supramolecular catalytic systems for the hydrolytic decomposition of toxic organophosphorus compounds working under mild conditions.[9,11]

In the present work, we applied this methodology to another type of supramolecular catalysts based on cyclophanes. We have previously[13—18] synthesized amphiphilic sulfonatocalix[4]resorcinarenes with four methylsulfonate groups at the upper rim. Their sodium salts exist in solution as tetraanions and are capable of forming inclusion complexes with biologically active compounds, metal complexes, and polyfunctional organic derivatives.

The purpose of the present work is to study self-organization and catalytic activity of the complexes of amphiphilic sulfonatocalix[4]resorcinarene (**1**) containing the pentyl substituent at the lower rim of the molecule with polyethyleneimine (PEI) of branched structure (molecular weight 50 000). We compared the results for compound **1** and a typical anionic surfactant, sodium dodecyl sulfonate (**2**), whose head group is identical in structure to the charged moiety of sulfonatocalixresorcinarene. In addition, we studied the effect of La^{III} on the catalytic effect and hydrolysis of *O*-ethyl *O*-*p*-nitrophenyl chloromethylphosphonate (**3**) (Scheme 1), which has earlier[8] been studied in aqueous and individual micellar solutions.

Each component of the ensembles under study possesses catalytic activity and can participate in self-organization processes. Lanthanide complexes and polyamines are widely known as homogeneous catalysts that are able to accelerate nucleophilic substitution in esters of phosphorus acids *via* the mechanism of electrophilic and general basic catalysis.[19—21] Compounds **1** and **2** are typical supramolecular catalysts capable of solubilizing or inclusively binding reactants to form host—guest complexes,

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 366—373, February, 2008.



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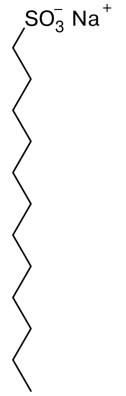

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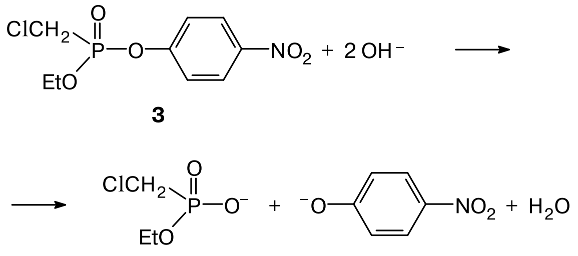
Scheme 1



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changing their local concentrations, properties of the microenvironment, *etc.*

Experimental

Compound **1** was synthesized using a known procedure.[13] Compound **3** was prepared according to a described procedure.[22] Commercial $La(NO_3)_3 \cdot 6H_2O$ (Aldrich), sodium dodecyl sulfonate, and PEI of branched structure with a nominal molecular weight of 50 000 (Sigma) were used. Molar concentrations of PEI are based on a monomeric unit. Twice distilled water was used to prepare all solutions.

The hydrolysis kinetics was studied spectrophotometrically on a Specord M-400 instrument in the pseudo-first order conditions by a change in the absorption of the anion of the leaving group. The apparent rate constants (k_{app}) were determined from the equation

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

where A and A_∞ are the absorbances of the solution at the time moment t and at the end of the reaction. The methods of weighed least squares was used in the calculation, taking into account the arithmetic mean values of three measurements that differ by at most 5%. The conductivity was measured with an Ino Lab conductometer. The surface tension was determined by the ring detachment method with a Du-Nouy tensiometer. The experimental details were described.[23]

Aggregate sizes were determined by the dynamic light scattering (DLS) method on a PhotoCor Complex photon-correlation spectrometer. A He—Ne gas laser with a power of 10 mW and a wavelength of 633 nm served as the laser radiation source. The light scattering angle was 90°, and the pulse accumulation time was several minutes. The signals were analyzed by a one-plate multichannel correlator conjugated with an IBM PC-compatible computer. Experimental data were processed using the method of cumulants included in the program package of the goniometer. The method is based on the expansion of the correlation function to the series including 2—3 cumulants. The first cumulant reflects the aggregate radius, the second cumulant is responsible for polydispersity, and the third one reflects the asymmetric character of particles. The effective radii (R) of PEI and polymer-colloidal structures were calculated from the diffusion coefficients (D) using the Stokes—Einstein equation based on the first cumulant

$$D = kT/6\pi\eta R,$$

where k is the Boltzmann constant, T is the absolute temperature, and η is the solvent viscosity. Prior to measurements solutions were filtered through Millipore filters to remove dust.

NMR experiments were carried out on a Bruker AVANCE-600 instrument. An inverse probe (5 mm) with the maximum magnetic field pulse gradients in the Z axis direction ~50 G cm^{-1} was used for the measurements. Chemical shifts are presented relative to HDO as the internal standard. In experiments on measuring the self-diffusion coefficients with the pulse magnetic field gradient, the increment of the pulse gradient in the interval from 0 to 32 G cm^{-1} was increased by 32 steps. The gradient duration was established to be 4.6 ms; in all cases, the diffusion time Δ was 120 ms. Experiments on diffusion were carried out at least 3 times, and the results were used with the correlation coefficient $\ln(I/I_0)$ and $\gamma^2\delta^2g^2(\Delta - \delta/3) > 0.999$ (I/I_0 is the relative decrease in the NMR signal as a function of the magnetic field pulse gradient; γ is the gyromagnetic ratio for protons; g is the amplitude of pulses of the magnetic field gradient; Δ is the interval between the gradient pulses; δ is the duration of the gradient pulse). All resolved signals were analyzed, and their average values for the molecule were used. In all cases, the root-mean-square error in the determination of the self-diffusion coefficients was at most 5%. The 2D NOESY experiments were carried out with a mixing time of 400 ms using the gradient filtration of signals. The pulse programs for all NMR experiments were taken from the Bruker software library.

Results and Discussion

Investigation of self-organization. The results of the tensimetric study of the aggregation of compounds **1** and **2** in aqueous solutions are presented in Fig. 1. Since the calixarene molecule contains four pentyl substituents at the lower rim, we can *a priori* propose the formation of aggregates of **1** caused by the hydrophobic effect similarly to aqueous solutions of standard surfactants. As can be seen from the data in Fig. 1, the surface tension isotherms of compounds **1** and **2** are identical in shape. The inflection points in the γ—log$C$ plots correspond to the critical micelle formation concentrations (CMC), which differ insignificantly. Analogous results were obtained by

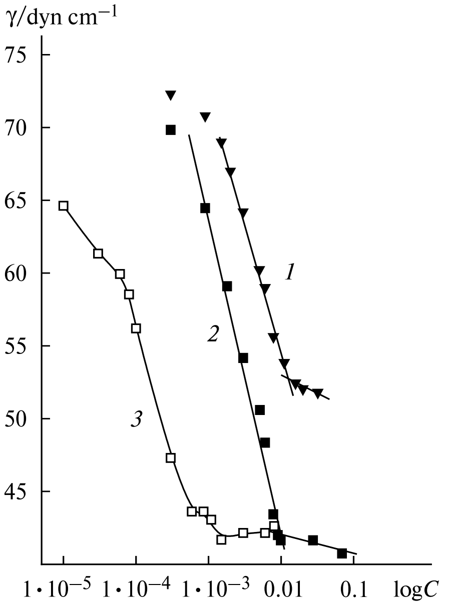


Fig. 1. Surface tension (γ) isotherms for the **1**—H_2O (*1*), **2**—H_2O (*2*), and PEI—**2**—H_2O (*3*) systems at 25 °C (*C* is concentration).

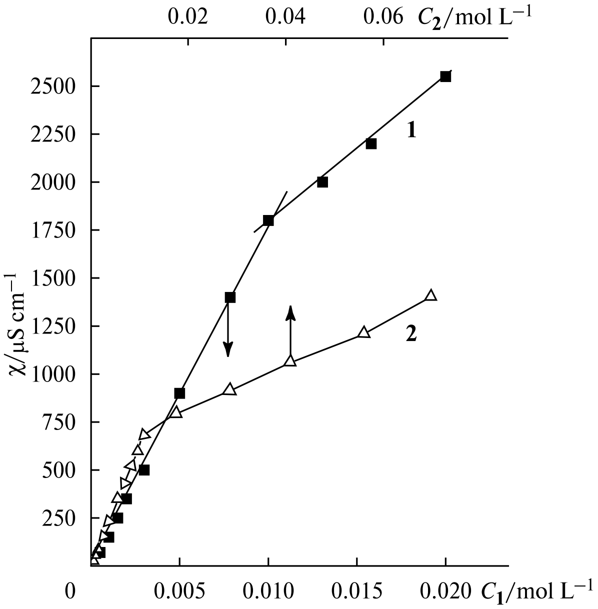


Fig. 2. Conductivity (χ) of aqueous solutions of compounds **1** and **2** *vs* their concentration at 25 °C.

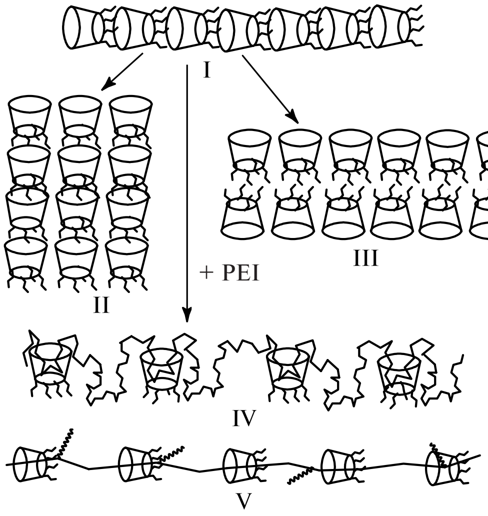
measurements of the conductivity of solutions of compounds **1** and **2** (Fig. 2).

The CMC in a PEI—**2** binary system decreases noticeably, indicating the combined aggregation to form polymer-colloidal complexes. As shown previously by potentiometric titration,[11] pH ~10.5 is maintained in a PEI solution in the absence of a buffer. At this pH value, the macromolecule contains only an insignificant number of protonated amino groups (<1%). Thus, aqueous solutions of PEI are similar in properties to systems based on neutral polymers. According to literature data,[24,25] aggregation in solutions of anionic surfactants and uncharged polymers results in the formation of structures of the "necklace" type presented by micellar aggregates peripherally linked to the macromolecules. The sizes of the aggregates in the PEI—**2** system were determined by the DLS method and are equal to 40 nm, which agrees with the results obtained for the PEI—sodium dodecyl sulfate system.[11]

Self-organization in the PEI—**1** binary system was studied by tensiometry, conductometry, DLS, and NMR spectroscopy. The measurements of the surface tension and conductivity revealed no critical concentrations corresponding to structural rearrangements. This indicates, most likely, a change in the self-organization mode in a binary solution.

Individual solutions of calixarene **1** were studied by the DLS method in the region of dilute solutions (below CMC that was determined tensiometrically) and at high concentrations exceeding the CMC. At the concentration of calixarene **1** equal to 0.004 mol L⁻¹, the average hydrodynamic radius (R_H) is 34 nm, whereas at $C = 0.03$ mol L⁻¹ it increases to ~80 nm. Such a sharp increase in the size, probably, reflects a change in the type of formed aggregates. Taking into account the ^{1}H NMR data, which are discussed below, one can propose the transition from the formation of aggregates of the structural type I in a dilute solution of calixarene to structural organization according to the type II or III (Scheme 2).

Scheme 2



The average hydrodynamic radius of PEI (0.05 *M* solution) determined the DLS method is 30 nm. Aggregates of the same size were observed in the PEI—**1** binary system

(0.05 mol L^{-1} PEI, 0.001 mol L^{-1} **1**). However, in the latter case, polydispersity increased. An analysis of the particle size distribution by the DynaLS program showed the presence of aggregates, whose size corresponded to PEI or was much smaller than that of PEI ($R_H \approx 8$ nm). These aggregates can probably be assigned to the aggregated form of compound **1** (see Scheme 2, structure I).

The self-association of calixarene **1** in aqueous solutions has earlier[26] been studied in detail by various NMR methods. It was shown that associates with an unusual "head-to-tail" packing of calixarene molecules (see Scheme 2, structure I) were formed at the concentrations exceeding 0.001 mol L^{-1}. Binding of the guest molecules (tetramethylammonium or *N*-methylpyridinium), *i.e.*, inclusion of the guest into the complex, increases the aggregation number with the retention of the "head-to-tail" packing of the calixarene molecules.

In the ^{1}H NMR spectra of the PEI—**1** system, the signal of the polymer is strongly broadened and split into two peaks, *i.e.*, the slow exchange in the NMR scale is observed. The signal of free PEI retains its value (δ 2.8), and the signal of the bound polymer appears at δ 0.5. The measurements of the spectra of the PEI—**1** system under the temperature variation conditions proved that the upfield shift was related to the bound polymer (and/or its particular units). When the temperature increases, the upfield signal of PEI shifts to the left (Fig. 3), the intensity of the signal ascribed to the free polymer increases, and the both peaks are narrowed. These changes indicate an increase in the rate of the bound PEI—free PEI exchange and a simultaneous increase in the fraction of the unbound polymer.

The high upfield shift of the signals from PEI ($\Delta\delta = -2.3$) indicates that some polymer regions are included into the calixarene cavity (see Scheme 2). As shown,[27] the formation of inclusion complexes leads to the upfield shift of the signals in the NMR spectra of the guest molecules included into the cavity of the calixarene molecules. Such great shifts caused by aromatic currents of the benzene rings of sulfonatocalix[4]resorcinarene could not be obtained if the polymer would simply cover a calixarene molecule. In this case, the aromatic circular currents of only one aromatic fragment of calixarene would affect a particular region of the polymer chain, and the maximum shift value would not exceed 1.5 ppm (see Ref. 28). The observed upfield shift could appear only under the action of all aromatic rings of calixarene when a polymer molecule is deeply included into its cavity. This is indicated by the 2D NOESY spectra containing the cross-peaks of PEI with both protons of the pentyl substituents and the CH_2SO_3 groups of calixarene (Fig. 4). This asserts reliably that the macromolecule does not cover the pentyl substituents, otherwise the influence of the aromatic fragments of calixarene **1** would be minimum.

Additional data can be extracted from measurements of the self-diffusion coefficients (D_S) using the Fourier transform pulsed-gradient spint-echo (FT-PGSE) NMR technique (Table 1). With an increase in the calixarene concentration in the PEI—**1** binary system, its D_S values first decrease sharply and by the order of magnitude approach D_S for the polymer, indicating that calixarene **1** is completely bound. Then a sharp increase in D_S is ob-

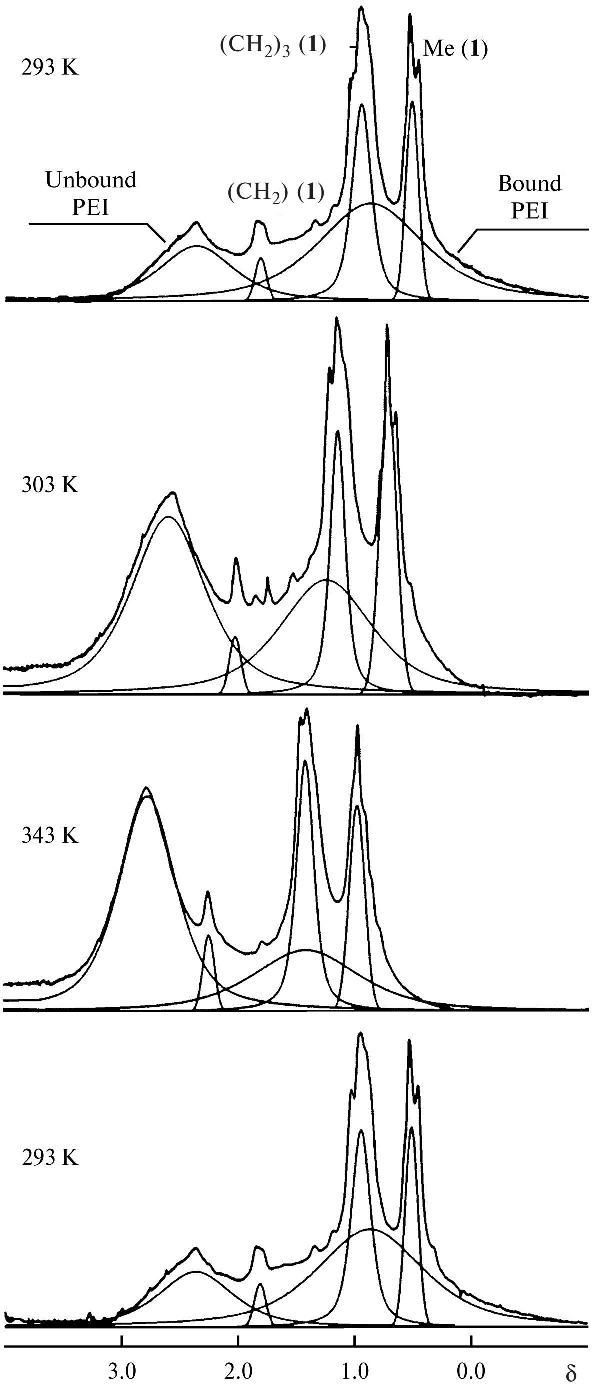


Fig. 3. Change in the shape of the ^{1}H NMR spectra of the PEI—**1** system with the temperature increase. The deconvolution peaks are given below the real spectra.

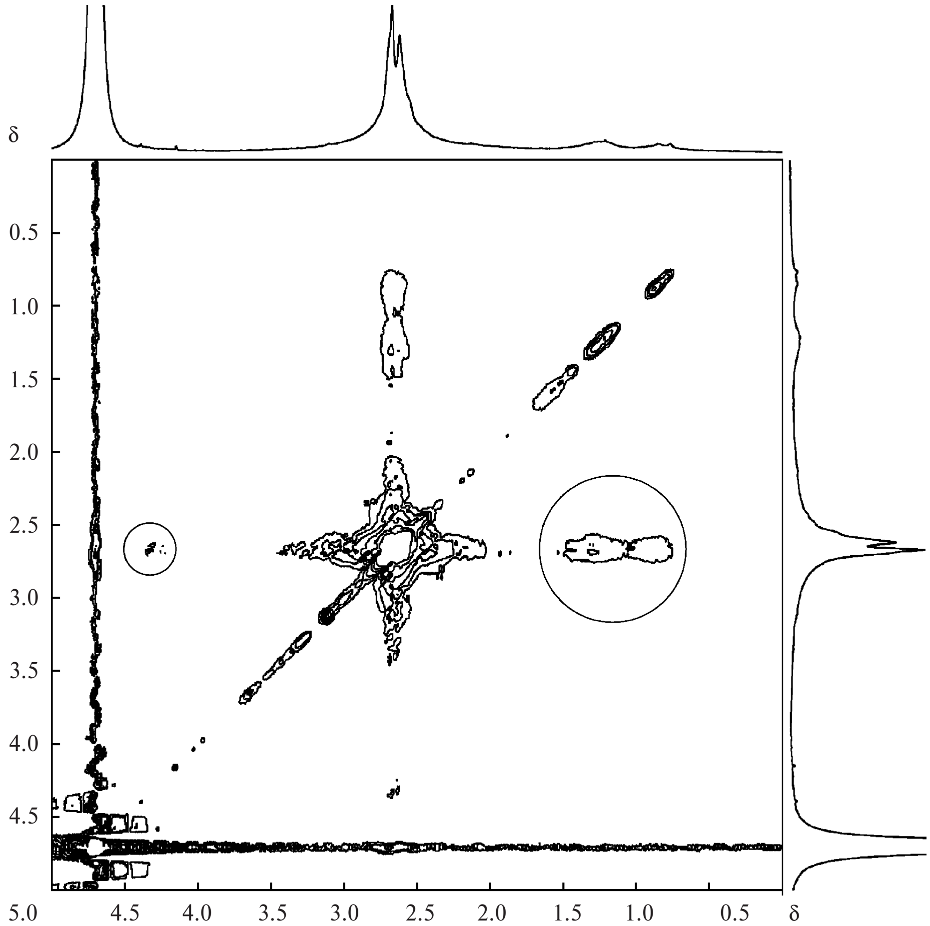


Fig. 4. 2D NOESY spectrum of the PEI—**1** system. Cross-peaks between PEI and protons of the CH_2SO_3 group are designated by the small circle, and those between PEI and protons of the pentyl substituent in **1** are shown by the large circle; $C_{PEI} = 0.05$ mol L^{-1}, $C_1 =$ 0.001 mol L^{-1}.

served up to the value virtually equal to D_S for free calixarene, *i.e.*, free calixarene **1** appears, whose signal is detected in the spectrum. The effect observed is due to the fact that the signals of bound calixarene **1** are strongly broadened and have a low absolute (non-integral) intensity, whereas the narrower signals of free calixarene give the main contribution in calculation. The calculation of the self-diffusion coefficients by the integral intensities of signals is impossible in this case, because the base line of the spectrum is distorted by strongly broadened lines of the polymer. Nevertheless, it can be concluded that the inflection point in the concentration dependence of D_S (in an interval of concentrations of **1** of (1—20) • 10^{-3} mol L^{-1} at a fixed polymer concentration of 0.05 mol L^{-1}) corresponds to the stoichiometry of the PEI—**1** aggregates. Thus, for equilibrium stoichiometry ~30 units of PEI or 20 units of the main chain fall on one molecule of compound **1**, if the ratio of the primary, secondary, and tertiary amino groups, being ~1 : 2 : 1, is taken into account.

Table 1. Self-diffusion coefficients (D_S) in PEI—**1** binary aqueous solutions at the fixed PEI concentration 50 mmol L^{-1}

C_1/mmol L^{-1}	$D_S \cdot 10^{-10}$/$m^2 s^{-1}$	
	PEI	**1**
0.5	0.68	1.49
1	0.74	1.28
2	1.24	3.39
5	1.22	3.20

Note. For an individual solution of PEI $D_S = 0.44 \cdot 10^{-10}$ $m^2 s^{-1}$, and for free calixarene **1** $D_S = 3.26 \cdot 10^{-10}$ $m^2 s^{-1}$ (see Ref. 24).

Based on the results of studying aqueous solutions of the PEI—**1** system by a complex of methods, we can propose the following scheme of self-organization. According to published data,[26] the "head-to-tail" aggregates (see Scheme 2, structure I) are formed in an individual solution of **1** at low concentrations (below the CMC). At high concentrations (above the CMC), they form pile structures (II) or layers of the "tail-to-tail" type (structure III), which is best consistent with the large sizes of the aggregates obtained by the DLS method. The addition of PEI results, probably, in the destruction of intrinsic aggregates of compound **1** and the formation of mixed structures of the type IV (see Scheme 2). According to the ^{1}H NMR data, supramolecular ensembles can be formed according to the type of pseudopolyrotaxanes (see Scheme 2, structure V).[29]

A more precise scheme of self-organization can be constructed after additional studies.

Kinetics of hydrolysis of phosphonate 3. The kinetics of hydrolysis of phosphorus acid esters in solutions of polyethyleneimines with different molecular weights has been studied previously.[11,30,31] In the presence of amines, including polymeric amines, the hydrolysis of esters of phosphorus acids is catalyzed *via* the general basic mechanism.[19] The pH plots of the hydrolysis of substrate **3** in individual and binary PEI-based systems are shown in Fig. 5. An increase in the rate was observed at pH 9.5 in an individual solution of PEI. The concentration of the unprotonated PEI amino groups involving in catalysis of the general basic hydrolysis increases in this pH region. In strongly alkaline solutions, it is probable that the alkaline hydrolysis of the substrates would contribute to the rate constant. As can be seen from the data shown in Fig. 5, the addition of calixarene sharply increases the apparent rate constant and shifts the kinetic dependences to the region of lower pH values. Thus, the PEI—**1** binary system manifests a higher catalytic activity under mild conditions.

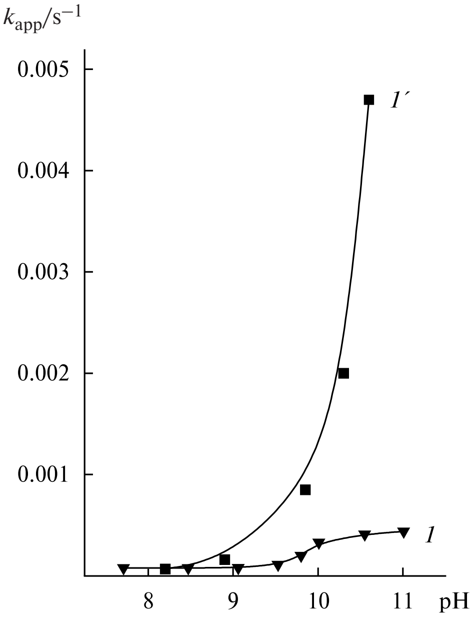


Fig. 5. Plots of the apparent rate constant for hydrolysis of phosphonate **3** (k_{app}) in an individual solution of PEI (*1*) and in the PEI—**1** binary system (*1′*) *vs* pH (C_1 = 0.001 mol L^{-1}, C_{PEI} = 0.05 mol L^{-1}, 25 °C).

The plots of the apparent rate constant for the hydrolysis of substrate **3** in the PEI—**1** binary system *vs* concentration of calixarene or polymer at a fixed concentration of another component are shown in Figs 6 and 7. The data for the PEI—**1** system are presented for

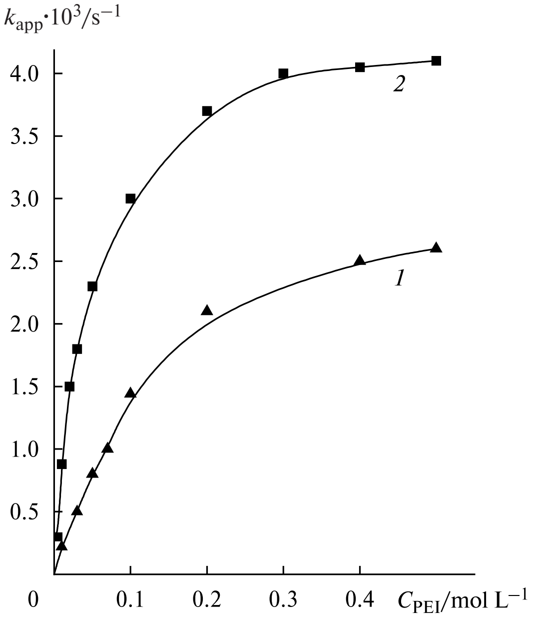


Fig. 6. Plots of the apparent rate constant for hydrolysis of phosphonate **3** (k_{app}) in an individual solution of PEI (*1*) and in the PEI—**1** binary system (*2*) *vs* PEI concentration (C_1 = 0.0001 mol L^{-1}, 25 °C).

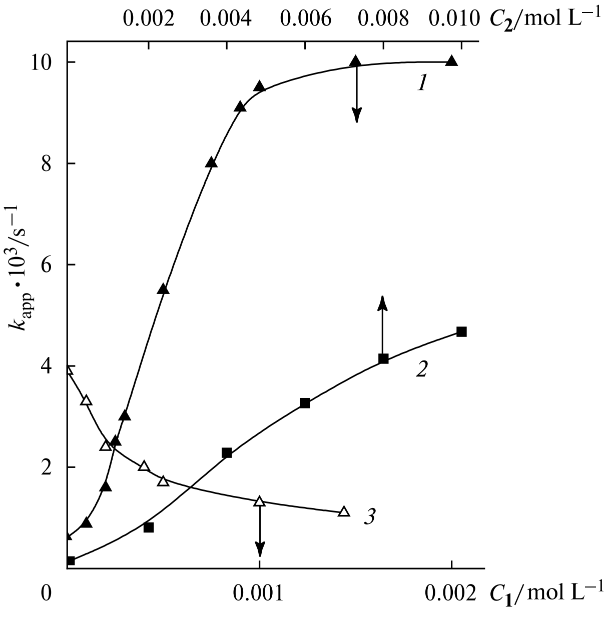


Fig. 7. Plots of the apparent rate constant for hydrolysis of phosphonate **3** (k_{app}) in PEI—**1** (*1*) and PEI—**2** (*2*) binary solutions and in the PEI—**1**—La^{III} ternary system (*3*) *vs* amphiphile concentration (C_{PEI} = 0.05 mol L^{-1}, $C_{La^{III}}$ = 0.008 mol L^{-1}, 25 °C).

comparison. An increase in the polymer or amphiphile concentration results in a nonlinear increase in the apparent rate constant, and the plots reach a plateau in the region of high concentrations (see Figs 6 and 7). This type of kinetic curves is characteristic of reactions preceded by an equilibrium process, such as the formation of a catalytic complex according to the host—guest principle. In this case, the apparent rate constant is described by the equation[1]

$$k_{\text{app}} = (k_0 + k_{\text{cat}}K'_{\text{S}}C)/(1 + K'_{\text{S}}C), \quad (1)$$

where k_{app} is the apparent pseudo-first rate constant; k_0 and k_{cat} are the pseudo-first rate constants in solution and in the catalytic complex, respectively; K'_{S} is the reduced binding constant of the substrate; C is the concentration of the polymer or amphiphile in the composition of the catalytic complex.

An analysis of the kinetic dependences shown in Figs 6 and 7 using Eq. (1) makes it possible to estimate the critical concentrations of PEI and **1** corresponding to the beginning of the catalytic effect, which coincides, as a rule, with the beginning of aggregation in solution, and to determine the binding constants of the substrate with the polymer and aggregated amphiphile (surfactant or calixarene) in individual or binary systems. As can be seen from the data in Table 2, the addition of **1** to a solution of PEI sharply decreases the critical concentration of PEI corresponding to the catalysis onset (in Table 2 this parameter is designated as CMC by analogy to micellar solutions). In addition, the binding constant increases more than by 4 times upon the introduction of compound **1**.

According to the kinetic data (see Fig. 7 and Table 2), the CMC values for calixarene **1** are considerably lower than the CMC determined tensiometrically (see Fig. 1). Taking into account the absence of a pronounced surface activity in the binary system and the ^{1}H NMR data, we can assume the following. Probably, not only aggregates of compound **1** formed at the CMC equal to 0.011 mol L^{-1} (according to the data of tensiometry) can be catalytically active, but the complexes of PEI and compound **1** in the monomeric form can also be active in catalysis. The binding constant calculated by the analysis of the kinetic curves (see Fig. 7) and reflecting the binding of phosphonate **3** by the calixarene-based structures is 134 L mol^{-1}. This is much higher than the binding constants determined for PEI by the analysis of the kinetic data in the k_{app}—C_{PEI} coordinates (see Fig. 6 and Table 2). The higher K_{S} value for calixarene can be due to a change in the mechanism of reactant binding: transition from complex formation according to the type of multicenter binding with a macromolecule to the solubilization mechanism, which is indirect evidence for the participation of the aggregated form of **1** in catalysis. The same is indicated by similarity of the binding constants for calixarene and micelles of **2**, which are characterized by reactant solubilization. It is important that in the PEI—**1** system the k_{cat} rate constant is significantly higher than that in the PEI—**2** system (see Table 2).

The introduction of La$^{\text{III}}$ into the PEI—**1** system increases the rate constant and catalytic effect (Figs 7 and 8). In addition, in a ternary system the pH of the solution decreases by 2—3 units due to the hydrolysis of the lanthanum salt, and catalysis occurs under milder conditions (pH ~8.5). At the same time, the apparent rate constant for phosphonate hydrolysis decreases with an increase in the calixarene concentration in the PEI—**1**—La$^{\text{III}}$ system (see Fig. 7), although an opposite tendency is observed in the absence of lanthanum ions: the PEI—**1** behaves as a typical supramolecular catalyst. This transition from catalysis to inhibition can be caused by various factors. If catalysis occurs in polymer—calixarene complexes, whose formation involves the electrostatic and inclusive interactions of the components, then the multicharge La$^{\text{III}}$ ions capable of efficiently binding with **1** [15] would neutralize the potential of the upper rim of calixarene weakening its interaction with PEI. The acceleration values in the binary and ternary systems with respect to hydrolysis in an individual solution of PEI or with respect to the alkaline hydrolysis of phosphonate **3** are presented in Fig. 8. It should be mentioned that the efficiency of the PEI—**1**—La$^{\text{III}}$ ternary system is higher even compared to the catalytic process effected by PEI, despite the decrease

Table 2. Results of the analysis of the kinetic data using Eq. (1)

System	k_{app}/k_0	CMC/mol L^{-1}			K'_{S} /L mol^{-1}	k_{cat}/s^{-1}
		Kinetics	Tensiometry	Conductometry		
PEI—H$_2$O (see Fig. 6)	7[a]	0.024	—	—	5	0.0036
PEI—**1**—H$_2$O (see Fig. 6)	15[a]	0.0029	—	—	23	0.0043
PEI—**1**—H$_2$O (see Fig. 7)	19[b]	0.00007	0.011	0.01	134	0.06
PEI—**2** (see Fig. 7)	12[b]	0.0013	0.0009, 0.0085[c]	0.009[c]	115	0.009

[a] k_0 corresponds to the rate constant of alkaline hydrolysis at pH 10.

[b] k_0 corresponds to the hydrolysis rate constant in an individual solution of PEI.

[c] The CMC values of individual solutions of compound **2**.

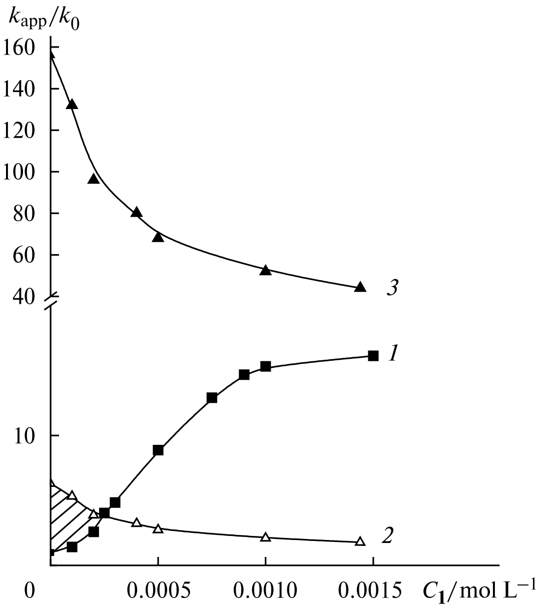


Fig. 8. Plots of the catalytic effect (k_{app}/k_0) of the PEI—**1** system in the hydrolysis of phosphonate **3** in the absence (*1*) and presence (*2*, *3*) of the La^{III} ions *vs* concentration of compound **1** (25 °C); k_0 corresponds to the hydrolysis rate constant in an individual solution of PEI (*1*, *2*); k_0 corresponds to the rate constant of alkaline hydrolysis at pH 8 (*3*).

in the rate constant in a specific interval of calixarene concentrations (hatched section in Fig. 8). Taking into account the decrease in the pH of the solution, we can say that the catalytic effect in the presence of the La^{III} ions is more than 2 orders of magnitude compared to the alkaline hydrolysis of substrate **3** (see Fig. 8).

Thus, in the present study, we determined the critical micelle formation concentrations and aggregate sizes in the individual and binary systems based on polyethyleneimine and amphiphilic sulfonatocalix[4]resorcinarene. The kinetics of hydrolysis of phosphonate **3** was studied in the series of the PEI—water, PEI—calixarene—water, and PEI—calixarene—La^{III}—water systems. The ternary catalytic system, which represents lanthanum ions immobilized on the supramolecular platform, provides a complex mechanism of catalysis (catalytic effect is more than two orders of magnitude) including the contribution of the general basic, electrophilic, and supramolecular catalyses.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos 05-03-32558a and 06-03-32189).

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Received May 31, 2007