Supramolecular systems based on poly(ethyleneimines) and calix[4]resorcinarenes with alkylphosphonate fragments. Aggregation and catalytic activity

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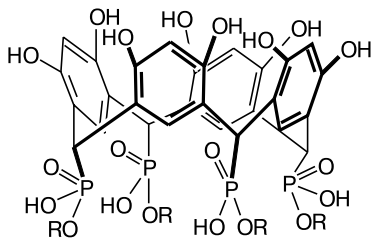
Aggregation in poly(ethylenimine)—calix[4]resorcinarene—water—DMF systems was studied by the methods of conductometry and dynamic light scattering. The sizes (radii) of the aggregates formed and the critical micelle concentrations were determined. The catalytic activity for these systems in the hydrolisys of phosphorus acid esters was shown.

Key words: poly(ethyleneimines), calix[4]resorcinarenes, aggregation, catalysis, phosphorus acid esters, hydrolysis, phosphonates.

Many publications are devoted to investigation of the properties of mixed solutions of polymers (polyelectrolytes) with amphiphilic compounds, for example, with ionogenic surfactants (Surf).[1—4] In these systems, combined associates are formed due to noncovalent interactions (electrostatic, hydrophobic, hydrogen, and others) of the amphiphile with the polymer macromolecule. The study of the properties of mixed compositions makes it possible to model and understand the nature of intermolecular interactions of biopolymers (proteins) with lipids in biomembranes and the mechanisms of their functioning.[5—7] At the same time, nanostructured polymeric systems are of practical significance, because they are used as flocculants, mediators of biologically active substances, nanoreactors for various chemical processes, *etc.* Aggregates of different shape and size are formed and structural and phase transformations occur due to the selection of the structures of amphiphiles and polymers (polyelectrolytes) and their ratio and concentration in mixed systems, which determine their specific properties, including the catalytic ones.

In the present work, polyelectrolyte—calix[4]resorcinarene—water—DMF (30 vol.%) compositions were studied as nanoreactors of hydrolysis of phosphorus acid esters. Phosphorylated calix[4]resorcinarenes (PCR) **1** and **2** containing the alkylphosphonate fragments at the lower rim of the molecule in the *cone* conformation were used.

Calixarenes are macrocyclic compounds synthesized by the condensation of phenols and aldehydes of different structure.[8] They contain hydrophobic cavities that allow them to act as receptors binding molecules with certain sizes and polarity to form host—guest complexes (molecular recognition).



1, **2**

R = Et (**1**), Pr (**2**)

Depending on the conformation, amphiphilic calix[*n*]arenes form aggregates of different structure of the type of micelles or lamellas.[9—12] The critical micelle concentrations (CMC) depend on the length of the hydrocarbon radicals and the number of aromatic rings (*n*) in a calixarenes molecule. It is known[13] that functionalized calixarenes, similarly to natural detergents, can incorporate into micelles and bilayers formed by other amphiphiles. It has previously been found[14] by conductometry that PCR aggregate in a water—DMF (30 vol.%) medium at high pH (PCR : NaOH = 1 : 8) with CMC = $4 \cdot 10^{-4}$ mol L^{-1}. We showed by tensiometry that the PCR under study at neutral pH values possess surface activity affected by the hydrophobicity of the R radical in calixarene (CMC = $1.3 \cdot 10^{-4}$ and $8 \cdot 10^{-5}$ mol L^{-1} for PCR **1** and **2**, respectively) (Fig. 1). The radii of the PCR aggregates ($4 \cdot 10^{-4}$ mol L^{-1}) determined by the light scattering method are 100—103 nm.

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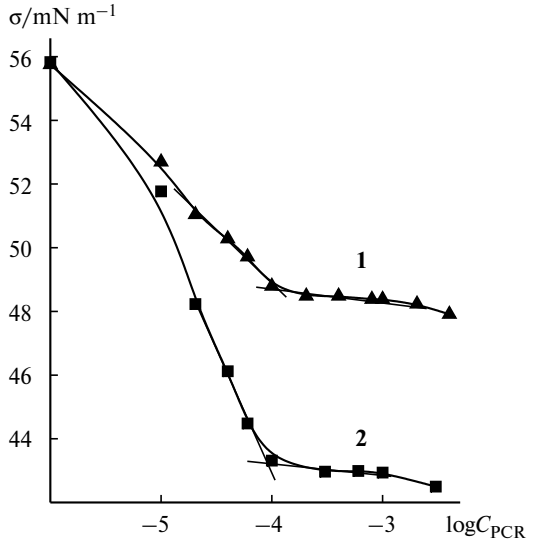


Fig. 1. Surface tension isotherms (σ) of solutions of PCR **1** and **2** at their different concentrations (C_{PCR}) (water—DMF (30 vol.%), 25 °C).

Linear and branched water-soluble poly(ethyleneimines) (PEI) were used as polyelectrolytes in this work.

Experimental

4-Nitrophenyl bis(chloromethyl)phosphinate (**3**) and bis(4-nitrophenyl) methylphosphonate (**4**) were synthesized using known procedures.[15] Samples of branched PEI (Fluka) with the molecular weights 10000 (PEI_{10}) and 800 ($PEI_{0.8}$), linear PEI with the molecular weight 5000 ($LPEI_5$), and the PEI_{10} sample modified by $C_{12}H_{25}$ groups (12-PEI_{10}) were used. The latter were synthesized according to a described procedure[16] by the reaction of PEI_{10} with dodecyl bromide. The alkylated polymer isolated from the organic layer was evacuated by heating to a constant weight and characterized by IR and ^{1}H NMR spectroscopy. The molecular weight of the monomeric unit of PEI was determined by potentiometric titration on a pH-150MA instrument.

Calix[4]resorcinarenes **1** and **2** containing the alkylphosphonate groups were synthesized according to a described procedure.[17] The structures and compositions of the compounds were confirmed by ^{1}H NMR, ^{31}P NMR, and IR spectroscopy, MALDI-TOF mass spectrometry, and elemental analysis data.

The kinetics of hydrolysis of 4-nitrophenyl esters of tetracoordinate phosphorus acids was studied by spectrophotometry on a Specord UV—VIS instrument at the initial substrate concentrations $5\cdot10^{-5}$—$1\cdot10^{-4}$ mol L^{-1} and different pH values. The course of the reaction was monitored by a change in the absorbance of the solutions (A) at 400 nm (formation of the 4-nitrophenoxide anion). The conversion was >90%. The observed rate constants of the first-order reaction (k_{obs}/s^{-1}) was calculated using the regression method by the equation

$$\ln(A_\infty - A_t) = -0.434k_{obs}t + \text{const}, \quad (1)$$

where A_∞ and A_t are the absorbances at the reaction cessation and at the time t, respectively.

Data on the electrical conductance of micellar solutions were obtained on a CDM-2d conductometer (Denmark). The conductance of bidistilled water, which was used for preparing solutions of the reactants, was accepted as zero. The surface tension was determined by the ring detachment method on a Du Nouy tensiometer.

The effective hydrodynamic radius of the aggregates (R_{eff}) was determined on a Photocor Complex instrument for dynamic and static light scattering. The radiation source was a He—He gas laser with a power of 10 mW and a wavelength of 633 nm. The effective radii of the aggregates were calculated from the diffusion coefficients using the Stokes—Einstein equation for spherical particles of the same size taking into account the viscosity of the solutions under study.

For each system, the hydrodynamic radius was determined as the arithmetic mean from the data of ten measurements. The measurement error was ≤10%.

The kinematic viscosity of solutions was determined using a VPZh-1 capillary glass viscosimeter (internal diameter of the capillary 0.54 mm, viscosimeter constant 0.01162 mm^2 s^{-2}). The measurements were carried out in a temperature-controlled vessel at 25±0.2 °C.

The kinetic dependences were analyzed in terms of the equation of the pseudo-phase model of micellar catalysis[18]

$$k_{obs} = [k_w + k_m K_S(C_{Surf} - CMC)]/ /[1 + K_S(C_{Surf} - CMC)], \quad (2)$$

where k_{obs} is the observed rate constant of the first-order reaction (s^{-1}); k_w and k_m are the reaction rate constants in the solvent bulk and in the micellar phase (s^{-1}), respectively; K_S is the binding constant of the substrate and micelle (L mol^{-1}); C_{Surf} is the surfactant concentration (mol L^{-1}).

Results and Discussion

We found by conductometry that in a water—DMF (30 vol.%) medium at critical association concentrations (CAC) poly(ethyleneimines) form aggregates. It should be noted that the conductometric curves for the polyelectrolytes studied contain two breaks: at $(0.8—4)\cdot10^{-3}$ (CAC_1) and $(0.9—1)\cdot10^{-2}$ mol L^{-1} (CAC_2) (Table 1).

Table 1. Critical association concentrations (CAC) of poly(ethyleneimines) in a water—DMF (30 vol.%) medium in the absence and presence of PCR **1** (30 °C)

PEI	$C_{PCR}\cdot10^4$	$CAC_1\cdot10^3$	$CAC_2\cdot10^2$
	mol L^{-1}		
PEI_{10}	—	4.0	1.0
PEI_{10}	2.7	0.9	1.3
12-PEI_{10}	—	2.4*	0.96
12-PEI_{10}	4.0**	1.0	0.9
$PEI_{0.8}$	—	0.8	0.95
$PEI_{0.8}$	4.0	1.85	1.5
$LPEI_5$	—	2.0	0.9

* According to the viscosimetry data, $2\cdot10^{-3}$ mol L^{-1}.
** For PCR **2**.

The molecular weight of the electrolyte and the presence of long-chain alkyl radicals in the macromolecule affect the CAC_1 values, and the CAC_2 values are close for all PEI samples under study (see Table 1).

Probably, aggregation of PEI first occurs inside one macromolecule (intrapolymer interactions) involving the N...HN hydrogen bonds, whereas for 12-PEI_{10} the aggregation first involved strong hydrophobic interactions. The CAC_2 values in the PEI—water—DMF systems characterize structural rearrangements of the aggregates, which involves, evidently, several polyelectrolyte macromolecules (interpolymer interactions). This can change the sizes and properties of the polymeric associates. We found by light scattering that the PEI concentration affects the radius size: for 12-PEI_{10} R_{eff} = 88 and 106 nm at concentrations of 0.01 and 0.02 mol L^{-1}, respectively. Note that in a water—DMF medium the sizes of the PEI aggregates are much larger than those in water. For instance, the effective radius of 12-PEI_{10} (0.02 mol L^{-1}) in water is 72 nm and that in a water—DMF medium is 106 nm. The presence of DMF in the system should decrease the dissociation of the acidic groups of PCR capable, probably, of forming complexes with DMF, although, as shown earlier,[19] the interaction of phosphorus acids with water is energetically more favorable than that with DMF.

For 12-PEI_{10} some increase in the CAC is observed in a water—DMF medium (see Table 1) compared to an aqueous solution, where $CAC_1 = 1.8 \cdot 10^{-3}$ mol L^{-1} and $CAC_2 = 8 \cdot 10^{-3}$ mol L^{-1}. It is most likely that the CAC values decrease in an aqueous medium, because the hydrophobic interactions that are more pronounced in water participate primarily in the formation of the polymer associate 12-PEI_{10}. Interestingly, for PEI_{10} the aggregation occurs in water at high concentrations (0.01 mol L^{-1}), although CAC_1 and CAC_2 are determined for PEI_{10} in the presence of DMF (see Table 1). It is known[20] that DMF favors the destruction of the water structure due to the arrangement of its Me groups in cavities of the tetrahedral framework of water, which can affect the solvation of the nitrogen atoms of PEI and its aggregation properties. Note that the CAC_1 value for $LPEI_5$ in a water—DMF medium differs strongly from CAC_1 for branched PEI, but structural rearrangements in these samples occur at virtually equal concentrations (CAC_2) (see Table 1). The conductometric curves for $PEI_{0.8}$ in water also exhibit two breaks (at $1.1 \cdot 10^{-3}$ and $1.6 \cdot 10^{-3}$ mol L^{-1}).

It is known[21,22] that the properties of mixed polymer—amphiphile compositions (viscosity, surface activity, electrical conductance, aggregation numbers of the amphiphile, size of the polymer globule, and others) change compared to the properties of the systems based on individual components. We found that in the presence of PCR in a water—DMF medium the CAC_1 values for the PEI samples (except for $PEI_{0.8}$) decrease. According to published data,[21,23] this indicates in favor of the formation of combined aggregates (polyelectrolyte complexes with calix[4]resorcinarenes) in PEI—PCR—water—DMF systems. The plots of the electrical conductivity *vs.* 12-PEI_{10} concentration in the absence and presence of PCR are shown in Fig. 2 as an example.

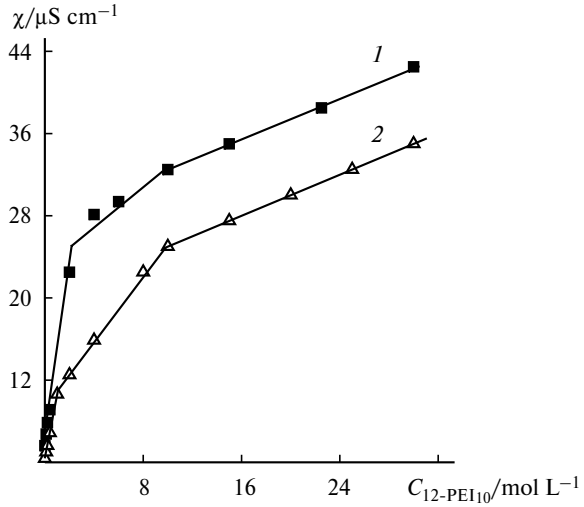


Fig. 2. Plots of the electrical conductance (χ) *vs.* 12-PEI_{10} concentration ($C_{12\text{-}PEI_{10}}$) in the absence (*1*) and presence of PCR **2** (*2*) (water—DMF (30 vol.%), 30 °C).

The formation of the mixed nanostructures confirms the sharp increase in the radii of the 12-PEI_{10} aggregates (0.01 mol L^{-1}) from 88 to 138 nm in the presence of PCR **1** ($4 \cdot 10^{-4}$ mol L^{-1}) in a water—DMF medium, which was determined by us using the light scattering method.

Several publications on studying self-assembling in aqueous systems based on PEI and anionic surfactants are available.[24—26] Aggregation manner in these compositions varies depending on the pH of the medium and the molecular weight and structure of the polyelectrolyte.

The main intermolecular interactions in the PEI—PCR—water—DMF systems are electrostatic interactions and hydrogen bonds of the N...HN and OH...N types, whereas hydrophobic binding is substantial for the compositions based on 12-PEI_{10}. Contributions of noncovalent interactions depend on the pH of the medium, because they change the ratio of charged and free nitrogen atoms of the polyelectrolyte and the number of anions of the alkylphosphonate fragments. This should unambiguously affect the aggregation properties of the systems under study. The fraction of the free amino groups in PEI (α) at different pH values of the medium and in the presence or absence of PCR was determined by potentiometric titration of the samples of the PEI studied in a water—DMF medium using the Henderson—Hasselbach equation[27] (Table 2). The presence of PCR exerts a weak effect on the α value. At high pH values poly(ethyleneimines) are almost neutral polymers (see Table 2), because the fraction of the charged amino groups ($1 - \alpha$) is

Table 2. Fraction of the free amino groups (α) in the PEI samples (0.02 mol L^{-1}) in a water—DMF (30 vol.%) medium at different pH values (30 °C)

pH	PEI_{10}	$PEI_{0.8}$	$LPEI_5$	12-PEI_{10}*	12-PEI_{10}—PCR **1****
9.5	0.92	0.99	—	0.92 (0.96)	0.95
9.0	0.84	0.94	0.96	0.87 (0.92)	0.89
8.5	0.75	0.87	0.81	0.77 (0.79)	0.81
8.0	0.64	0.77	0.69	0.64 (0.67)	0.71
7.5	0.5	0.64	0.57	0.51 (0.56)	0.58
7.0	0.4	0.49	0.46	0.39 (0.41)	0.45
6.5	0.31	0.35	0.36	0.27 (0.3)	0.31
6.0	0.23	0.26	0.23	0.17 (0.25)	0.23
5.5	0.15	0.16	0.13	0.09 (0.14)	0.14
5.0	0.08	0.07	0.03	0.016 (0.07)	0.05

* The value for C_{PEI} = 0.01 mol L^{-1} is given in parentheses.
** C_{PEI} = 0.01 mol L^{-1}, $C_{PCR} = 4 \cdot 10^{-4}$ mol L^{-1}.

insignificant: for instance, at pH 9.5 it is 0.05—0.08, which agrees with literature data.[26]

A PEI macromolecule (Fig. 3, *a*) or globule (Fig. 3, *b*) can be considered as a soluble polymer matrix (scaffold) on which a PCR molecule "sits down," approaching to the polyelectrolyte by its lower rim containing the alkylphosphonate fragments that bind to the nitrogen atoms of PEI.

Probably, the mixed PEI_{10}—PCR and 12-PEI_{10}—PCR aggregates have different structures. A 12-PEI_{10} macromolecule contains rather high number of long-chain radicals arranged closely to each other and in rather low concentration ($CAC_1 \approx 2 \cdot 10^{-3}$ mol L^{-1}) it forms a polymer ball, whose formation involves the hydrophobic fragments of the macromolecule. The aggregation of PEI_{10} in a water—DMF medium begins at a higher concentration (see Table 1) involving N...HN hydrogen bonds. In this case, R_{eff} in a water—DMF medium for 12-PEI_{10} is much longer than that for PEI_{10} (106 and 4 nm, respectively (C_{PEI} = 0.02 mol L^{-1})). Therefore, it can be assumed that PCR interacts with PEI_{10} as shown in Fig. 3, *a*, and the interaction with 12-PEI_{10} occurs as shown in Fig. 3, *b*. At the same time, the large size of the PCR aggregates ($R_{eff} \approx 100$ nm) assumes that for the formation of combined structures the calixarene nanoaggregate can serve as a scaffold on which the supramolecular catalyst is formed. A probability of threading PCR on the PEI macromolecules according to the type of pseudorotaxane formation[28] cannot be rejected; however, this requires additional proofs.

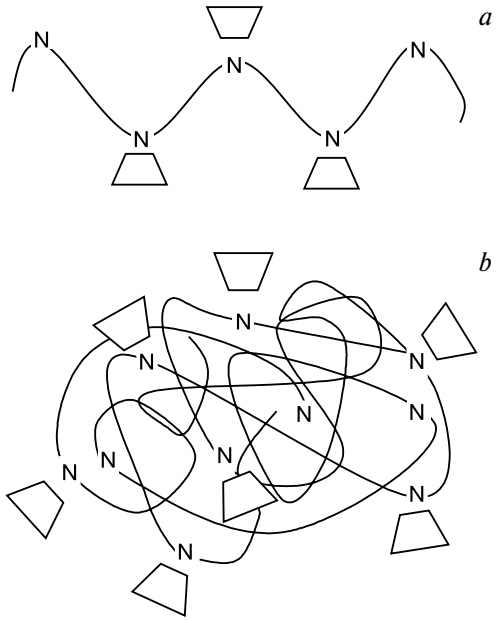
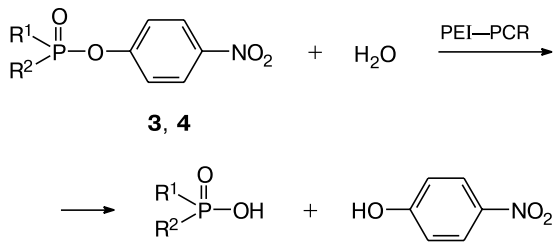


Fig. 3. Interactions in the PEI—PCR system involving the PEI macromolecule (*a*) or globule (*b*).

It is known[14,29—32] that aqueous and aqueous-organic compositions based on calixarenes manifest catalytic activity in processes of ester bond cleavage in esters of phosphorus and carboxylic acids. The weak catalytic effect of PCR on the hydrolysis of phosphorus acid esters in aqueous-alcohol media was shown, whereas in aqueous DMF virtually no catalytic activity of these compounds is observed.[33] The catalytic effect of the PEI—water compositions in the hydrolysis of phosphorus acid esters was described,[34—37] including for PEI_{10} and $LPEI_5$.[35,37] However, in a water—DMF medium the catalytic activity of PEI has not been studied earlier.

In the present work, the catalytic effect of the PEI—water—DMF and PEI—PCR—water—DMF (30 vol.%) systems on the hydrolysis of 4-nitrophenyl bis(chloromethyl)phosphinate (**3**) and bis(4-nitrophenyl) methylphosphonate (**4**) (Scheme 1) was studied.

Scheme 1



$R^1 = R^2 = CH_2Cl$ (**3**); R^1 = Me, R^2 = 4-$O_2NC_6H_4O$ (**4**)

The plots of the observed rate constants for hydrolysis of substrates **3** and **4** *vs.* pH of the medium in the PEI—water—DMF and PEI—PCR—water—DMF systems are shown in Figs 4 and 5. The catalytic activities of PEI_{10} and PEI_5 are equal, and 12-PEI_{10} catalyzes the hydrolysis of the esters considered by ~7—10 times more rapidly (see Fig. 4). It is known[37] that PEI catalyze this

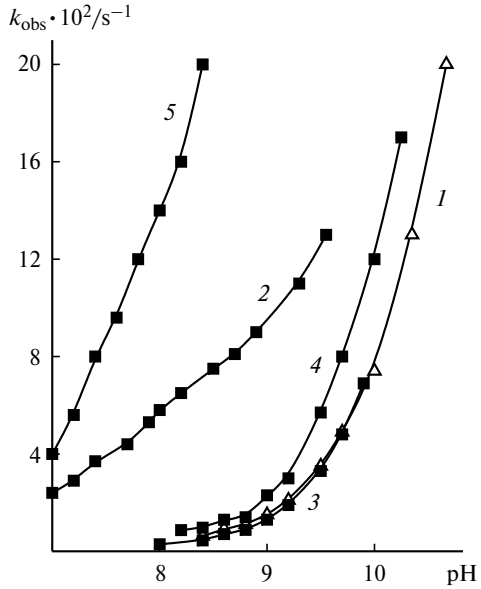


Fig. 4. Plots of the observed rate constant of hydrolysis of phosphinate **3** (k_{obs}) *vs.* pH for PEI_{10} (*1*), 12-PEI_{10} (*2*), $LPEI_5$ (*3*), PEI_{10}—PCR **2** (*4*), and 12-PEI_{10}—PCR **1** (*5*) (water—DMF (30 vol.%), C_{PEI} = 0.02 (*1*, *3*, *4*) and 0.01 mol L^{-1} (*2*, *5*), $C_{PCR} = 4 \cdot 10^{-4}$ mol L^{-1}, 30 °C).

process *via* the general basic mechanism. The presence of PCR exerts a weak effect on the catalytic activity of PEI_{10}; however, the acceleration values (k_{obs}/k_0) in the systems based on 12-PEI_{10} and PCR are much higher than those in the absence of the latter (Fig. 6).

In the presence of PCR in an aqueous-organic system based on 12-PEI_{10}, the plots $k_{obs} = f(pH)$ shift considerably toward lower pH values (see Fig. 4), which makes it possible to use these catalytic compositions under mild conditions at pH 7—8, where the acceleration of hydrolysis achieves three orders of magnitude (see Figs 5 and 6). It should be noted that the 12-PEI_{10}—PCR—water—DMF system manifests some selectivity toward substrates of different structure. For instance, at pH 7—8 the acceleration value for phosphonate **4** (see Fig. 5) is by ~3—5 times higher than that for phosphinate **3** (see Fig. 6).

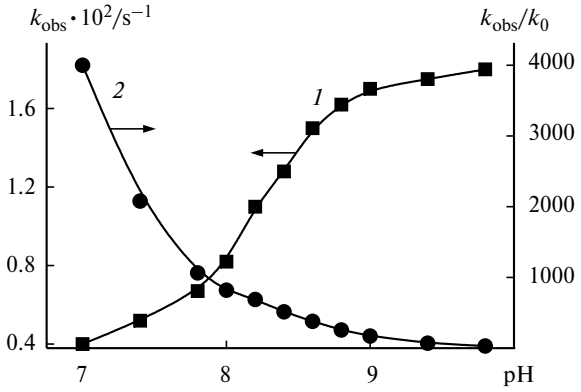


Fig. 5. Plots of the observed rate constant of hydrolysis of phosphonate **4** (k_{obs}) in the 12-PEI_{10}—PCR **2**—water—DMF (30 vol.%) system (*1*) and the acceleration value (k_{obs}/k_0) (*2*) *vs.* pH ($C_{PCR} = 4.0 \cdot 10^{-4}$ mol L^{-1}, $C_{PEI} = 0.01$ mol L^{-1}, 30 °C).

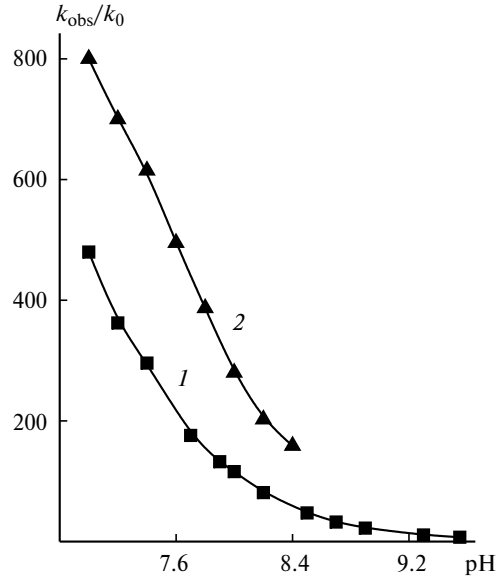


Fig. 6. Plots of the acceleration value of the hydrolysis of phosphinate **3** (k_{obs}/k_0) *vs.* pH in a water—DMF (30 vol.%) medium for 12-PEI_{10} (*1*) and 12-PEI_{10}—PCR **1** (*2*) (C_{PCR} = $4.0 \cdot 10^{-4}$ mol L^{-1}, $C_{PEI} = 0.01$ mol L^{-1}, 30 °C).

The study of the plot of k_{obs} *vs.* PEI concentration in the absence and presence of PCR showed that the kinetic profiles are nonlinear and reach a plateau (Figs 7 and 8).

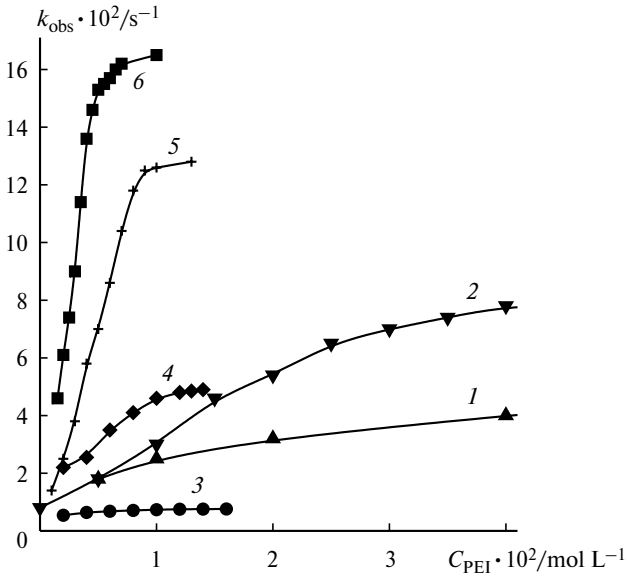


Fig. 7. Plots of the observed rate constant of hydrolysis of phosphinate **3** (k_{obs}) *vs.* PEI concentration (C_{PEI}) for PEI_{10} (*1*), PEI_{10}—PCR **1** (*2*), $PEI_{0.8}$—PCR **2** (*3*, *4*), 12-PEI_{10} (*5*), and 12-PEI_{10}—PCR **2** (*6*) at pH 9.5 (*1*, *2*, *5*), 8 (*3*, *6*), and 9 (*4*) ($C_{PCR} = 2.7 \cdot 10^{-4}$ (*2*—*4*) and $4 \cdot 10^{-4}$ mol L^{-1} (*6*), water—DMF (30 vol.%), 30 °C).

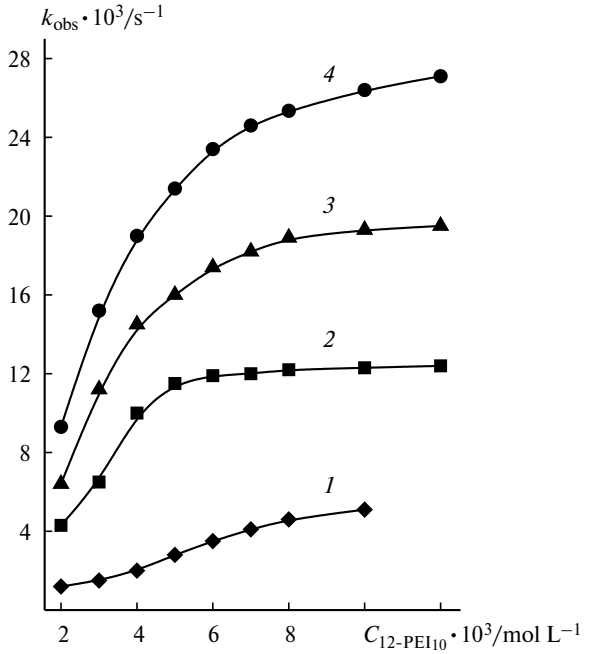


Fig. 8. Plots of the observed rate constant of hydrolysis of phosphonate **4** (k_{obs}) *vs.* 12-PEI_{10} concentration ($C_{12\text{-}PEI_{10}}$) in the absence (*1*) and presence of PCR **2** (*2—4*) at 30 (*1*, *2*), 40 (*3*), and 50 °C (*4*) ($C_{PCR} = 4 \cdot 10^{-4}$ mol L^{-1}, water—DMF (30 vol.%), pH 8).

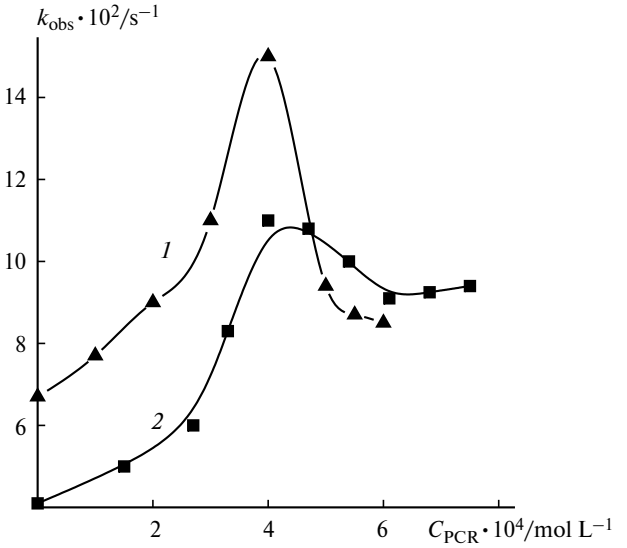


Fig. 9. Plots of the observed rate constant of hydrolysis of phosphinate **3** (k_{obs}) *vs.* PCR **1** concentration in the presence of $PEI_{0.8}$ (*1*) and PEI_{10} (*2*) (C_{PEI} = 0.02 mol L^{-1}, pH 9.5, 30 °C).

This assumes the primary binding of the substrate by mixed PEI—PCR aggregates according to the host—guest type similarly to the formation of enzyme—substrate complexes,[38] which precedes the reaction itself. The plots of k_{obs} of hydrolysis of substrate **3** *vs.* PCR concentration in the presence of constant amounts of PEI_{10} and $PEI_{0.8}$ (0.02 mol L^{-1}) have also nonlinear profiles with maxima at $C_{PCR} \approx (4—4.5) \cdot 10^{-4}$ mol L^{-1} (PEI : PCR ≈ 45—50) (Fig. 9). Usually in surfactant—PEI systems the C_{PEI}/C_{Surf} ratio in the point of maximum in the $k_{obs} = f(C_{Surf})$ plots at the PEI content equal to 0.02 mol L^{-1} is significantly lower, being ~3—6 for phosphorus acid esters of different structure.[34,36] In a water—DMF medium PCR has no catalytic activity in the hydrolysis of phosphorus acid esters[33] but in the presence of PCR the catalytic effect of PEI_{10} and $PEI_{0.8}$ increase by ~2—2.5 times (see Fig. 9). This confirms the formation of combined PEI—PCR structures with the higher catalytic activity than that of the polyethyleneimine aggregates.

The kinetic curves $k_{obs} = f(C_{PEI})$ were processed using Eq. (2) for the pseudo-phase model of micellar catalysis,[18] which is used successfully for polymeric and nanostructured polymeric systems.[34,36,39,40] The obtained parameters (k_m, K_S, and CMC) are given in Table 3.

Table 3. Parameters of hydrolysis of substrates **3** and **4** in PEI—water—DMF (30 vol.%) and PEI—PCR **2**—water—DMF (30 vol.%) systems at different pH and *T* values calculated by Eq. (2)

Substrate	PEI	$C_{PCR} \cdot 10^4$ /mol L^{-1}	pH	*T* /°C	k_m /s^{-1}	K_S /L mol^{-1}	CMC $\cdot 10^3$ /mol L^{-1}	k_m/k_0*
3	PEI_{10}	—	9.5	25	0.071	55	29	4.4
3	PEI_{10}	2.7**	9.5	30	0.11	53	3.4	6.3
3	12-PEI_{10}	—	9.5	30	0.31	89	2.2	19.4
3	12-PEI_{10}	4.0	8.0	30	0.22	490	1.1	367
3	$PEI_{0.8}$	2.7	8.0	30	0.008	950	1.0	14.5
3	$PEI_{0.8}$	2.7	9.0	30	0.063	280	2.2	11.5
4	12-PEI_{10}	—	8.0	30	0.0089	190	2.5	990
4	12-PEI_{10}	4.0	8.0	30	0.014	1400	2.4	1560
4	12-PEI_{10}	4.0	8.0	40	0.023	730	1.5	2560
4	12-PEI_{10}	4.0	8.0	50	0.032	550	1.3	3560

* k_0 is the rate constant of the noncatalytic process at the corresponding pH.
** For PCR **1**.

As can be seen from the data in Table 3, substrate **4** under similar conditions (pH 8, 30 °C) is much stronger bound by the 12-PEI_{10}—PCR aggregate (K_S = 1400 L mol^{-1}) than substrate **3** (K_S = 490 L mol^{-1}), which affects the acceleration of the hydrolysis reaction (1560 and 367 times, respectively). The binding constants for substrate **3** decrease with the pH increase (for example, for the system based on $PEI_{0.8}$ and PCR it decreases from 950 (pH 8) to 280 L mol^{-1} (pH 9)), *i.e.*, with a decrease in the fraction of the protonated nitrogen atoms ($1 - \alpha$) from 0.23 to 0.06 (see Table 2). Evidently, the protonated nitrogen atoms of PEI on the surface of polymer-colloidal globule participate only in the binding of phosphorus acid esters similarly to micelles of cationic surfactants. In the presence of PCR, the CMC values for PEI_{10} determined by the kinetic method decrease considerably (see Table 3), which agrees with the conductometric data (see Table 1). For 12-PEI_{10} these values are close to CAC_1 (conductometric method). At the same time, it should be mentioned that the CMC determined by the kinetic and conductometric methods can differ, because the presence of the substrate in the reaction medium can affect the aggregation properties of the system.[22]

The effective activation parameters of the hydrolysis of substrate **4** in the 12-PEI_{10}—PCR—water—DMF system were calculated from the kinetic plots $k_{obs} = f(C_{PEI})$ at different temperatures (see Fig. 8). The effective activation parameters, contributed from the reaction in the solution bulk, aggregation processes, and the reaction on the surface of the supramolecular associate, depend on the 12-PEI_{10} concentration. The sharp decrease in the activation energy (E_a) to 25 kJ mol^{-1} is observed, most likely, in the region of formation of the 12-PEI_{10}—PCR complexes at the polymer concentration ~$(4—6) \cdot 10^{-3}$ mol L^{-1} (C_{PEI} : $C_{PCR} \approx 10—15$) (Fig. 10), *i.e.*, at the 12-PEI_{10} content higher than CAC_1 (see Table 1). It can be assumed that CAC_1 corresponds to the onset of formation of the polymeric ball (matrix) with which the PCR molecules then interact (formation of combined aggregates). It should be mentioned that for the systems based on hydrophobic 12-PEI_{10} the C_{PEI} : C_{PCR} ratio equal to 10—15 is considerably lower than that for PEI_{10} and $PEI_{0.8}$ (C_{PEI} : $C_{PCR} \approx 45—50$, see Fig. 9). The activation energy of the reaction in the mixed 12-PEI_{10}—PCR aggregates calculated from the k_m values at different temperatures (see Table 3) is 33.7 kJ mol^{-1}.

To conclude, in the water—DMF systems based on poly(ethyleneimines) and calix[4]resorcinarenes containing the alkylphosphonate fragments at the lower rim of the molecule, the combined polymer-colloidal structures are formed due to various noncovalent interactions (electrostatic, hydrogen, hydrophobic, and others). The high catalytic activity of these systems in hydrolysis of phosphorus acid esters (acceleration by 10^3 and more times at pH 7—8) and the dependences of the catalytic effect on the substrate structure (selectivity), molecular weight and structure of the polyelectrolyte, pH of the medium, and temperature were shown.

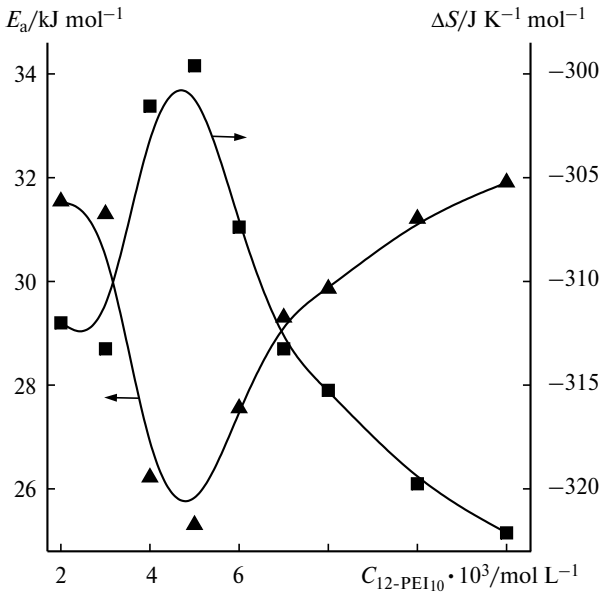


Fig. 10. Plots of the activation parameters of hydrolysis of substrate **4** (E_a and ΔS) in the 12-PEI_{10}—PCR **2**—water—DMF (30 vol.%) system *vs.* polyelectrolyte concentration ($C_{12\text{-}PEI_{10}}$).

Investigations of the structural organization of polymer—amphiphile complexes provide new routes for the design of nanostructured polymeric systems for the purpose of developing materials with predicted properties, including the catalytic ones.

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