Phosphorylation of alkylated poly(ethyleneimine) in chloroform in the presence of cetyltrimethylammonium bromide and calix[4]resorcinarene

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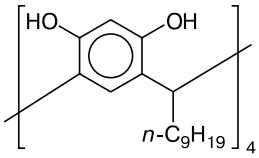
The phosphorylation of alkylated poly(ethyleneimine) with 4-nitrophenyl bis(chloromethyl)phosphinate in chloroform in the presence of cetyltrimethylammonium bromide (CTAB), calix[4]resorcinarene (CR), or their mixture was studied by UV spectrophotometry. The catalytic effect of CTAB and CR on the process of polymer phosphorylation was shown to depend on the concentration of the surfactant and poly(ethyleneimine) in solution. The catalytic effect of the system is ascribed to the formation of poly(ethyleneimine)—CTAB, poly(ethyleneimine)—CR, and poly(ethyleneimine)—CTAB—CR mixed aggregates. Their existence was confirmed by the methods of light scattering and UV spectroscopy.

Key words: poly(ethyleneimine), phosphorylation, phosphinic esters, surfactants, calixresorcinarenes, catalysis, micelle formation.

One of the methods for controlling rates and mechanisms of chemical processes is the use of supramolecular systems based on surfactants (Surf) in which supermolecular structures of various degree of organization can be formed: direct and reverse micelles, microemulsions, vesicles, and liquid crystals. The main principles of catalysis in these systems are related to the formation of nanoregions with specific characteristics, which makes it possible to create the gradients of polarity and concentrations of solubilized reactants, which allows ruling their reactivity to perform.[1] The presence of additives capable of forming complexes with surfactants and affecting self-association processes in the systems can serve as an additional tool for controlling their catalytic activity. Additives that can recognize chemical compounds and aggregation are of special interest. Among them are polymers and calixarenes prone to non-covalent interactions and characterized by the high concentration of functional groups.

Phosphorylated poly(ethyleneimines) are known to be practically valuable compounds. They are used as extracting agents for uranium ions[2] and efficient proton mediators.[3] Therefore, the search for new methods of their synthesis is urgent. The use of supramolecular catalytic systems can be one of the methods for solving this problem.

In the present work, we studied the kinetics and mechanism of the reaction of alkylated poly(ethyleneimine) **1** with 4-nitrophenyl bis(chloromethyl)phosphinate (**2**) in chloroform in the absence and presence of cetyltrimethylammonium bromide (CTAB) as a micelle-forming surfactant and alkylated calix[4]resorcinarene (CR).



CR

Branched poly(ethyleneimine) containing the *n*-tetradecyl substituents with the molecular weight of the monomeric unit equal to 150 was used as polymer **1**. The degree of substitution in this compound, *i.e.*, number of substituted fragments of **1** per one unsubstituted group of the polymer, was 0.3.

Results and Discussion

The mechanism of nucleophilic substitution in phosphinate **2** was determined using the data obtained by UV spectrophotometry and ^{31}P NMR spectroscopy. The liberation of 4-nitrophenol (**3**) detected in solutions of polymer **1** containing no additives indicates the formation of phosphorylated poly(ethyleneimine) **4** (Scheme 1). The existence of the latter is confirmed by the results of ^{31}P NMR spectroscopy. Compound **4** is characterized by the signal at δ 23.7, which corresponds to the products of

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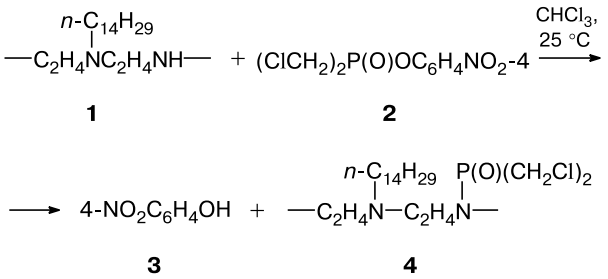
phosphorylation to the N—H bonds[4] (starting phosphinate **2** in chloroform exhibits the signal at δ 39.5).

Scheme 1



In the **1**—CR and **1**—CR—CTAB systems in chloroform, the presence of a macrocycle with the OH groups reactive toward the phosphinate does not change the direction of nucleophilic substitution: the products of the reaction with phosphinate **2** in the indicated systems have ^{31}P NMR signals at δ 22.3 and 24.8, respectively. The reaction products of the phosphinate with calixarene would be characterized by the signal at δ 38.4.[5,6]

The plot of the observed rate constant (k_{obs}/s^{-1}) of the reaction of poly(ethyleneimine) **1** with phosphinate **2** in chloroform *vs.* polymer concentration is nonlinear (Fig. 1, curve *1*) and described by the equation

$$k_{obs} = k_1 C_{\mathbf{1}} + k_2 C_{\mathbf{1}}^2, \quad (1)$$

where k_1 = 0.08 L mol^{-1} s^{-1} and k_2 = 0.76 L^2 mol^{-2} s^{-1} at 25 °C.

The presence of the square term is characteristic of the aminolysis of phosphorus acid esters in nonaqueous media and can be attributed to the co-assistance of the second amine molecule to the nucleophilic substitution in the phosphorus substrate.[7] A certain influence on the process can be exerted also by the self-association of the polymer, which was proved by dielcometric titration and light scattering. The concentration plots of the orientational polarization have breaks in concentration regions of $5 \cdot 10^{-5}$—$4 \cdot 10^{-4}$ and $5 \cdot 10^{-3}$—$1.2 \cdot 10^{-2}$ mol L^{-1} (Fig. 2) indicating, according to known data,[5] the formation of aggregates **1** in chloroform. Structural transformations in the systems continue to occur at a higher content of polymer **1** in solution. It was found by the light scattering method that the change in the polymer concentration from 0.04 to 0.055 mol L^{-1} increases, in the spherical shape approximation, the effective radii of the aggregates (R_{eff}) grow from 7 to 43 nm. An increase in the poly(ethyleneimine) content to 0.1 mol L^{-1} is accompanied by a decrease in R_{eff} to 33 nm. The formation of associates capable of binding and concentrating the phosphinate, *i.e.*, acting as micellar catalysts, should result in reaching a plateau by the concentration plots of k_{obs}.[8] The retention of the square character of Eq. (1) can be due to a large contribution of the catalytic co-assistance of the amino groups in polymer **1** to its phosphorylation and/or to the favorable effect of the change in the aggregate structure.

In the presence of CTAB, the phosphorylation of polymer **1** is accelerated by up to 7 times (Fig. 3, Table 1), which can be a consequence of polymer-colloidal catalysis.[9] It is known[10—12] that a polymer—micelle complex can be formed in solutions containing a surfactant and polymer. Numerous works devoted to this problem consider the mechanism of consecutive structural transformations in the systems. A complex of the polymer with the aggregated surfactant is formed when the detergent concentration increases and reaches the critical association concentration (CAC). Mixed structures continue to form until the concentration polymer saturation is

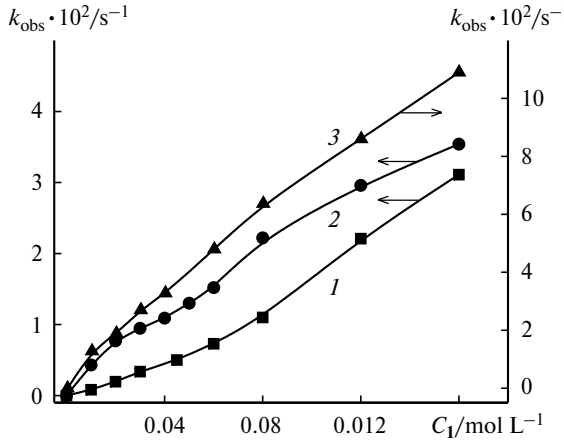


Fig. 1. Plots of the observed rate constant (k_{obs}) of the reaction of polymer **1** with phosphinate **2** in chloroform in the absence of additives (*1*) and in the presence of CR (*2*) and CR—CTAB (*3*) *vs.* polymer concentration ($C_{\mathbf{1}}$) ($C_{CR} = 2 \cdot 10^{-4}$ mol L^{-1}, C_{CTAB} = 0.1 mol L^{-1}, 25 °C).

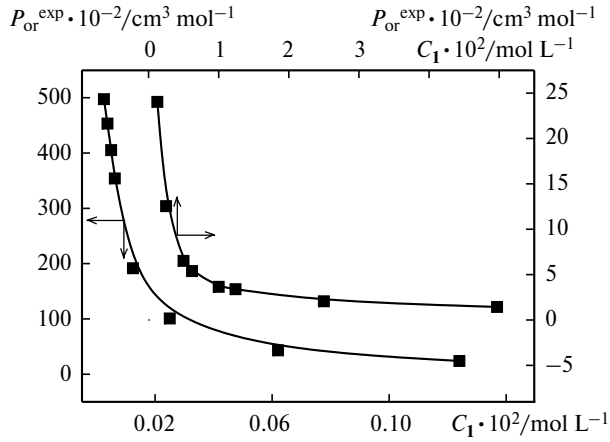


Fig. 2. Orientational polarization (P_{or}^{exp}) of solutions of polymer **1** in chloroform at 20 °C.

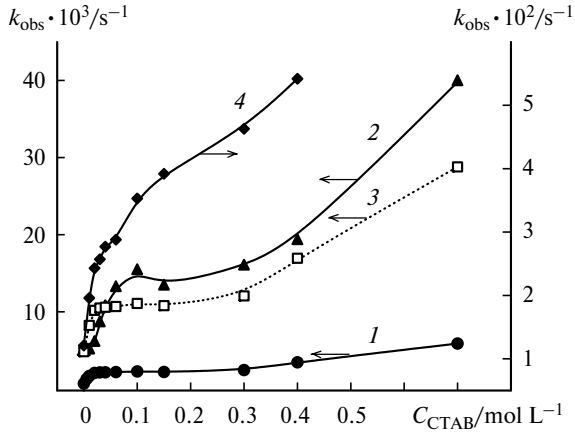


Fig. 3. Plots of the observed rate constant (k_{obs}) of the reaction of polymer **1** with phosphinate **2** in CTAB solutions in chloroform in the absence (*1*) and presence of CR (*2—4*) *vs.* CTAB concentration (C_{CTAB}) at 25 °C ($C_{\mathbf{1}}$ = 0.01 (*1—3*) and 0.05 mol L^{-1} (*4*), $C_{CR} = 2 \cdot 10^{-4}$ mol L^{-1}). Experiment is shown by *1*, *2*, and *4*; calculation is *3*.

achieved, after which micellar surfactant aggregates unbound to the polymer chain can exist in solution in parallel with the polymer-colloidal complex (PCC).[10] The formation of the PCC in the **1**—CTAB—chloroform systems under study is indicated by the data obtained by light scattering. The effective radius of aggregates of **1** (0.05 mol L^{-1}) in chloroform at 25 °C is 58 nm. The radius of CTAB micelles is small. For instance, in solutions of CTAB (0.2 mol L^{-1}) in chloroform at 30 °C the radius is 0.8 nm.[13] In the mixed **1** (0.05 mol L^{-1})—CTAB (0.3 mol L^{-1}) system, the R_{eff} value increases to 88 nm, which corresponds to an increase in the polymer aggregate volume by approximately 3.5 times.

In the **1**—CR and **1**—CTAB—CR systems, the presence of the latter favors the phosphorylation rate of the polymer (see Figs 1 and 3). For example, in the **1**—CR ($2 \cdot 10^{-4}$ mol L^{-1})—chloroform system, the acceleration of this reaction by calixarene achieved 6 times and can be due to the formation of a polymer complex with the macrocycle. Its existence in the absence and presence of CTAB was proved by the methods of UV spectroscopy and light scattering. According to available data,[14] the absorption bands in the UV spectra of calixarenes that form complexes with amines undergo a bathochromic shift. The absorption band of CR ($5 \cdot 10^{-5}$ mol L^{-1}) in chloroform at 285 nm (25 °C) in the presence of polymer **1** ($5 \cdot 10^{-3}$ mol L^{-1}) shifts to higher wavelengths (290.4 nm), *i.e.*, by 5.4 nm. In the CR ($5 \cdot 10^{-5}$ mol L^{-1})—**1** ($5 \cdot 10^{-3}$ mol L^{-1})—CTAB ($5 \cdot 10^{-2}$ mol L^{-1}) system, the shift of the absorption band of CR (293.4 nm) relative to the absorption band in the CR ($5 \cdot 10^{-5}$ mol L^{-1})—CTAB ($5 \cdot 10^{-2}$ mol L^{-1}) solutions (287.6 nm) is 5.8 nm. In addition, according to the results of dynamic light scattering, the effective radius of the aggregates formed in the **1** (0.05 mol L^{-1})—CR (10^{-3} mol L^{-1})—chloroform system is 70 nm, *i.e.*, the volume of poly(ethyleneimine) associates in the presence of calixarene increases by 1.7 times. A weaker effect of the CR on the sizes of the polymer associates compared to that of CTAB can be due to the fact that the micelles of the latter threaded on the polymer matrix perform the binding function for the polymer chains,[15] thus favoring interpolymeric association in the system. In the **1**—CR complexes this phenomenon occurs, most likely, to a less extent.

In the polycomponent **1**—CR—CTAB—chloroform system, the phosphorylation of the polymer is accelerated more strongly: by up to 45 times (see Fig. 3 and Table 1). In the initial region of the k_{obs} plot *vs.* CTAB concentration the calculated overall effect of the surfactant and calixarene is higher than the experimental value, whereas the synergetic effect occurs with an increase in the CTAB content (see Table 1 and Fig. 3).

Table 1. Catalytic effect of CTAB on the reaction of polymer **1** with phosphinate **2** in chloroform in the absence and presence of CR ($C_{CR} = 2 \cdot 10^{-4}$ mol L^{-1})

C_{CTAB} /mol L^{-1}	$C_{\mathbf{1}} = 0.01$ mol L^{-1}			$C_{\mathbf{1}} = 0.05$ mol L^{-1}
	k_{obs}(**1**—CTAB)$\cdot$ $\cdot[k_{obs}(\mathbf{1})]^{-1}$	$\{k_{obs}$(**1**—CTAB—CR)$\cdot$ $\cdot[k_{obs}(\mathbf{1})]^{-1}\}_{exp}$	$\{k_{obs}$(**1**—CTAB—CR)$\cdot$ $\cdot[k_{obs}(\mathbf{1})]^{-1}\}_{calc}$	$\{k_{obs}$(**1**—CTAB—CR)$\cdot$ $\cdot[k_{obs}(\mathbf{1})]^{-1}\}_{exp}$
0	1.0	5.5	4.9	2.1
0.01	1.9	5.7	9.4	3.3
0.02	2.4	6.8	12	4.1
0.04	2.5	12	12	4.7
0.06	2.5	15	12	4.9
0.1	2.6	17	13	6.0
0.3	2.8	18	14	7.8
0.4	3.9	22	19	9.2
0.7	6.7	45	33	—

Note. k_{obs} are the observed rate constants of the reaction under study in **1**—CTAB and **1**—CTAB—CR systems.

Thus, the CTAB effect on the phosphorylation of alkylated poly(ethyleneimine) in chloroform in the absence and presence of calixarene can be a consequence of the transfer of substrate **2** from the solvent bulk into the mixed polymer—surfactant and polymer—surfactant—calixarene aggregates. In this case, the phosphinate is concentrated in the PCC and the microenvironment of the reactants (the substrate and reaction centers of the polymer) changes. The latter fact is indicated by the increase in the absorbance at 400 nm (A_{400}) of the ion pair of polyamine with 4-nitrophenol liberating during the reaction in solutions of CTAB (Fig. 4) and higher A_{400} values of the ion pair in the **1**—CR—CTAB solutions compared to those of the **1**—CR solutions (Fig. 5). It is known[16] that in nonaqueous media the ion pairs of amines with 4-nitrophenol are equilibrated with formed by them complexes containing a hydrogen bond, and the increase in the medium polarity shifts this equilibrium toward ion pairs.

Note that in the plots (see Fig. 3) after the increase in k_{obs} with an increase in the surfactant concentration, which is characteristic of micelle-catalyzed processes, the rate constants of phosphorylation of polymer **1** increase additionally in the region of high CTAB concentrations followed by reaching a plateau. This is related, most likely, to structural rearrangements in the system. Therefore, the concentration curves were processed using the below presented equation corresponding to the pseudo-phase model of micellar catalysis[17] for the surfactant concentrations not higher than 0.1—0.15 mol L^{-1}

$$k_{obs} = [k_{m,Surf}K_{S,Surf}(C_{Surf} - CAC) + k_0]/ \\ /[1 + K_{S,Surf}(C_{Surf} - CAC)], \quad (2)$$

where $k_{m,Surf}$ is the reaction rate constant in the polymer-colloidal phase, $K_{S,Surf}$ is the binding constant of the substrate with the aggregates, C_{Surf} is the surfactant concentration, and k_0 is the reaction rate constant in the solvent bulk.

The parameters of the catalyzed reactions calculated using Eq. (2) are given in Table 2. It can be seen from the presented data that in the presence of calixarene the $k_{m,Surf}$ and CAC values increase and $K_{S,Surf}$ decreases. An increase in the polymer concentration in solutions of CTAB and CR is accompanied by an increase in $k_{m,Surf}$ and $K_{S,Surf}$ and a decrease in the CAC. The catalytic effect of the system ($k_{m,Surf} \cdot k_0^{-1}$) decreases. The dependence of the combined catalytic effect of the surfactant and calixarene on the poly(ethyleneimine) content also affects the dependence of k_{obs} of polymer **1** phosphorylation on the polymer concentration in the **1**—CR ($2 \cdot 10^{-4}$ mol L^{-1})—CTAB (10^{-1} mol L^{-1}) system (see Fig. 1; Table 3). The strongest acceleration of the process (by up to 16 times) is observed at low concentrations of **1**. This can be due to a change in the shape of the concentration dependence upon the addition of calixarene and

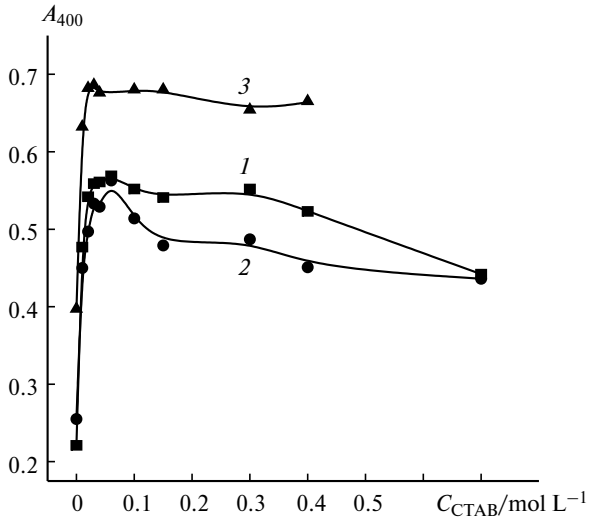


Fig. 4. Plots of the absorbance at 400 nm (A_{400}) of the ion pair of 4-nitrophenol (**3**) with polymer **1** in CTAB solutions in chloroform in the absence (*1*) and presence of CR (*2*, *3*) *vs.* CTAB concentration (C_{CTAB}) ($C_{\mathbf{1}} = 10^{-2}$ (*1*, *2*) and $5 \cdot 10^{-2}$ mol L^{-1} (*3*), $C_{CR} = 2 \cdot 10^{-4}$ mol L^{-1}, $C_{\mathbf{3}} = 5 \cdot 10^{-5}$ mol L^{-1}, 25 °C, $d = 1$ cm).

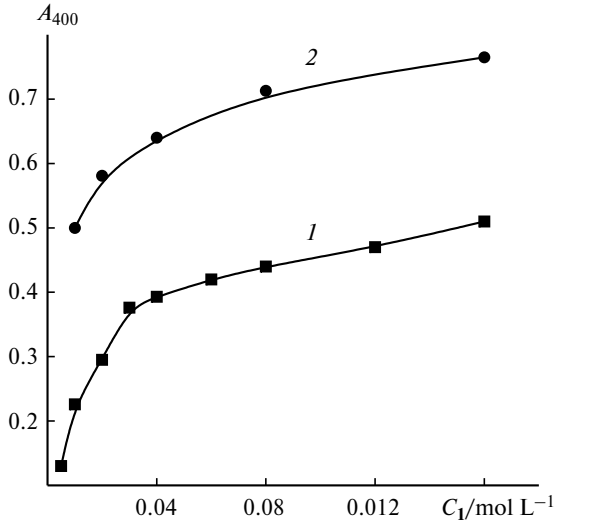


Fig. 5. Plots of the absorbance at 400 nm (A_{400}) of the ion pair of 4-nitrophenol (**3**) with polymer **1** in CR solutions in chloroform in the absence (*1*) and presence of CTAB (*2*) *vs.* polymer concentration ($C_{\mathbf{1}}$) ($C_{CR} = 2 \cdot 10^{-4}$ mol L^{-1}, $C_{CTAB} = 4 \cdot 10^{-4}$ mol L^{-1}, $C_{\mathbf{3}} = 5 \cdot 10^{-5}$ mol L^{-1}, 25 °C, $d = 1$ cm).

CTAB to a solution of poly(ethyleneimine). In the absence of additives, the dependence of k_{obs} on $C_{\mathbf{1}}$ has a square character (see Eq. (1)), whereas in the presence of CR and CTAB the favorable effect of the mixed associates that obeys the laws of micellar catalysts becomes prevailing. Table 4 represents the parameters of the micelle-catalyzed process calculated by the equation for the initial regions of the concentration plots of the mixed systems

Table 2. Parameters calculated by Eq. (2) for the reaction of polymer **1** with phosphinate **2** in CTAB solutions in chloroform in the absence and presence of CR (25 °C)

C_1	C_{CR}	$k_{m,Surf} \cdot 10^2$	$K_{S,Surf}$	CAC · 10^3	$k_0 \cdot 10^4$	$k_{m,Surf} \cdot k_0^{-1}$
mol L^{-1}		/s^{-1}	/L mol^{-1}	/mol L^{-1}	/s^{-1}	
0.01	—	0.24	180	1.9	8.8	2.7
0.01	0.0002	1.6	56	18	48	3.3 (18)*
0.05	0.0002	3.3	80	2.8	120	2.8 (5.6)*

* The catalytic effect on the process in the absence of CTAB and CR is given in parentheses.

Table 3. Catalytic effect of the **1**—CR ($2 \cdot 10^{-4}$ mol L^{-1})—CTAB (0.1 mol L^{-1})—chloroform system on he phosphorylation of polymer **1** at 25 °C

C_1 /mol L^{-1}	k_{obs}(**1**—CTAB—CR) · · $[k_{obs}(\mathbf{1})]^{-1}$	k_{obs}(**1**—CTAB—CR) · · $[k_{obs}$(CTAB—CR)$]^{-1}$
0.01	16	27200
0.02	9.7	40200
0.03	8.0	57400
0.06	6.6	102000
0.08	5.8	136000
0.12	3.9	183000
0.16	3.5	232000

(with the lowest contribution of a possible catalytic effect of free amino groups and structural changes in the system)

$$k_{obs} = [k_{m,\mathbf{1}} K_{S,\mathbf{1}} (C_{\mathbf{1}} - CMC) + k_0] / [1 + K_{S,\mathbf{1}} (C_{\mathbf{1}} - CMC)], \quad (3)$$

where $k_{m,\mathbf{1}}$ and k_0 are the reaction rate constants in the micellar phase and in the solvent bulk, respectively; $K_{S,\mathbf{1}}$ is the binding rate constant of the substrate with the polymer associates; CMC is the critical micelle concentration.

The presence of the surfactant in the solution decreases $K_{S,\mathbf{1}}$ and increases the $k_{m,\mathbf{1}}$ value and catalytic effect of the system ($k_{m,\mathbf{1}} \cdot k_0^{-1}$). It should be noted that the initial point of the concentration plots for the mixed systems (see Fig. 1) corresponds to the reaction of the phosphinate with the macrocycle. For instance, the observed rate constant of the reaction of CR ($2 \cdot 10^{-4}$ mol L^{-1}) with phosphinate **2** in a CTAB solution (0.1 mol L^{-1}) at 25 °C is $4.7 \cdot 10^{-7}$ s^{-1}, and the resulting effect of the polycomponent system on the phosphorylation of polymer **1** in the considered range of polymer concentrations is $2.7 \cdot 10^4$—$2.3 \cdot 10^5$ times (see Table 3) while that in the polymer-colloidal phase is $5.5 \cdot 10^5$ times (see Table 4).

Table 4. Calculated by Eq. (3) parameters of the reaction of polymer **1** with phosphinate **2** in chloroform in the presence of CR ($2 \cdot 10^{-4}$ mol L^{-1}) and CTAB (0.1 mol L^{-1}) at 25 °C

System	$k_{m,\mathbf{1}} \cdot 10^2$ /s^{-1}	$K_{S,\mathbf{1}}$ /L mol^{-1}	CMC · 10^3 /mol L^{-1}	$k_0 \cdot 10^6$ /s^{-1}	$k_{m,\mathbf{1}} \cdot k_0^{-1}$
1—CR	4.4	9.2	0.045	0.3*	147000
1—CR—CTAB	26	4.1	0.052	0.47**	553000

* The k_{obs} value for the reaction CR + **2** at 50 °C.
** The k_{obs} value for the reaction CR + **2** in a CTAB solution (0.1 mol L^{-1}) at 25 °C.

Thus, in the polycomponent alkylated poly(ethyleneimine)—cetyltrimethylammonium bromide—calixarene—chloroform system, poly(ethyleneimine) acts as a nucleophilic agent toward the phosphinate and CTAB and calixarene are catalyzing additives. The catalytic effect of the surfactant and macrocycle on the process of polymer phosphorylation increases with an increase in the CTAB content in the solution and a decrease in the polymer concentration.

Experimental

Polymer **1** was synthesized by the reaction of branched poly(ethyleneimine) (molecular weight 10000) with tetradecyl bromide according to a known procedure.[18] The molecular weight of the monomeric units was determined by potentiometric titration.[19,20] Phosphinate **2** and CR were synthesized as described previously.[21,22] Cetyltrimethylammonium bromide (Sigma) was recrystallized from an acetone—ethanol mixture. Prior to use chloroform was purified by a standard procedure.[23]

The kinetics of the reactions was studied by UV spectrophotometry from an increase in the absorbances of 4-nitrophenol at 310—345 and 400 nm on a Specord UV-Vis spectrophotometer in temperature-controlled quartz cells (25 °C). The reaction rate constants were determined from the first-order equation. The polymer concentration (mol L^{-1}) was calculated from the molecular weight of the monomeric unit. In kinetic experiments, the concentrations of the reactants and surfactant were varied within 0.01—0.16 (**1**), $5 \cdot 10^{-5}$—$2 \cdot 10^{-4}$ (**2**), and 0.005—0.7 mol L^{-1} (CTAB). The CR concentration was $2 \cdot 10^{-4}$ mol L^{-1}.

The ^{31}P NMR spectra of the products of poly(ethyleneimine) phosphorylation (without their isolation) formed in **1**—**2**, **1**—**2**—CR (0.01 mol L^{-1}), and **1**—**2**—CR ($2 \cdot 10^{-4}$ mol L^{-1})—CTAB (0.2 mol L^{-1}) solutions in chloroform were recorded on a Bruker MSL-400 instrument (162 MHz) relative to the external standard (H_3PO_4). At the beginning of the reac-

tion, the concentration of phosphinate **2** was 0.02 mol L^{-1}, and that of polymer **1** was 0.3 (without additives) and 0.1 mol L^{-1} (in the presence of CR and CTAB).

The sizes of the aggregates were determined on a PhotoCor Complex photon correlation spectrometer for dynamic and static light scattering. The laser radiation source was a He—Ne gas laser with a power of 10 mW and a wavelength of 633 nm. The signals were analyzed using a single-plate multichannel correlator conjugated with an IBM PC-compatible computer. The light scattering angle was 90°.

The viscosity of solutions was determined on a VPZh-2 capillary viscosimeter (capillary diameter 0.56 mm) using a temperature-controlled cell.

Dielcometric titration was carried out according to a described procedure.[24] The orientational polarization (P_{or}^{exp}) was calculated by the equation

$$P_{or}^{exp} = 3 \cdot 10^3 \cdot C^{-1}[(\varepsilon_{12} - \varepsilon_1)/(\varepsilon_1 + 2)^2 - (n_{12}^2 - n_1^2)/(n_1^2 + 2)],$$

where C is the concentration of the dissolved compound (mol L^{-1}); ε is the dielectric constant, n is the refraction index; indices 12 and 1 concern the solution and solvent, respectively. The ε values of solutions were determined on a setup consisting of an E12-I instrument, which operates in the beating mode, and a measuring cell representing a temperature-controlled capacitor.[25] The refraction indices were measured on an IRPh-23 refractometer. The determination error P_{or}^{exp} did not exceed 1%.

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