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Aggregation Behavior and Catalytic Properties of Systems Based on Aminomethylated Calix[4]resorcinarenes and Poly(ethylene) Imines

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Abstract—Self-assembling in systems poly(ethylene) imine–aminomethylated calix[4]resorcinarene–water–DMF (30 vol%) and catalytic properties of these compositions in hydrolysis of 4-nitrophenylbis (chloromethyl)phosphinate are studied. Critical concentrations of association, aggregates radii, and kinetic parameters of the reaction are established.

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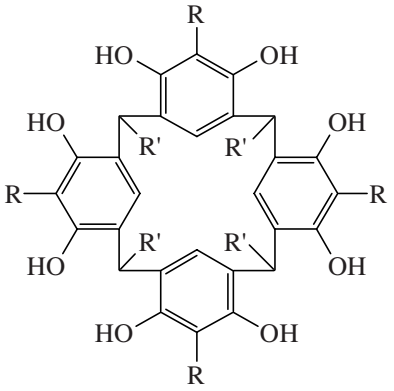
In aqueous and non-aqueous systems of polymer–amphiphilic substance a formation of mixed aggregates (polymer-colloid complexes) occurs. Their composition and structure is defined by the scope of intermolecular interactions of the components [1–3]. Such systems allow elucidation of the mechanisms of biomembranes self-assembling and functioning [4, 5]. On the other hand, the nanostructural polymeric compositions possess a wide range of practical properties due to the formation in the combined aggregates of "intramolecular" micelles [1, 3, 6]. It would be feasible to control the useful properties like catalytic activity through the structure, the ratio and concentration of components of the polymer-colloid system. It seems promising in the development of such catalytic compositions to build up supramolecular ensembles based on the compounds capable of self-organization and (or) containing catalytic centers. It would provide systems possessing complex mechanism of catalytic action similar to biocatalysts.

The purpose of this work is proving the joint aggregation of polyelectrolyte and amphiphile in water–organic systems. Moreover, reactivity of phosphorus acids esters in the nanostructural polymeric compositions, that is, the catalytic properties of such compositions, was poorly studied, and we also aimed to fill this gap.

As the amphiphilic compounds in the system polymer–amphiphile–water–DMF (30 vol %) we used aminomethylated calix[4]resorcinarenes of general formula (**I**), and for comparison also calix[4] resorcinarene with R = H and R = C_9H_{19} (**Ic**).



R = CH_2NEt_2, R′ = C_9H_{19} (**Ia**); R = $CH_2N(CH_3)CH_2CH\cdot(OCH_3)_2$, R′ = C_6H_{13} (**Ib**).

The aminomethylated calix[4]resorcinarenes can be prepared by Mannich reaction from the corresponding calix[4]resorcinarenes, aldehydes and amines. This synthesis has been first reported in [7].

The amphiphilic calixarenes are known to form in water, water–organic, and non-aqueous media supramolecular aggregates of different structures [8–10]. In crystalline form and in chloroform or 2-propanol they

can form dimeric gels or large hexameric capsules of "head-to-head" structure [11–13]. Besides, the calixarenes can be easily built into the aggregates of various morphological types underlain by surfactants [14] resembling models of a ferment molecule fixation in a lipid bilayer of plasmatic membrane [15].

Critical concentrations of micelle formation (CCM) by a calix[4]resorcinarene in the cone conformation [16, 17] depend on the length of hydrocarbon radicals and on the presence of functional groups at the upper or lower rim of the molecule. [8, 9]. It has been shown that aminomethylated calix[4]resorcinarenes are prone to aggregation in water–DMF (30 vol %) medium forming associates with low CCM, e.g, for compound **Ia** CCM = 5×10^{-5} M [9]. We estimated by conductometric method the CCM of calixarene **Ib** in this solution at ~6×10^{-5} M (Fig.1). It is known that the radius of the aggregates of compound **Ia** in water–DMF medium according to the NMR self-diffusion measurement is ~1.7 nm [18].

As a polyelectrolyte component in the studied systems was used poly(ethylene) imine of molecular weight 10000 (**II**) and a sample of the same polymer modified by *n*-$C_{12}H_{25}$ radicals (**IIa**).

Note that the principal biopolymers (proteins and nucleic acids) are typical polyelectrolytes whose conformation and functions are mainly governed by the balance of electrostatic and hydrophobic interactions. Besides, synthetic macromolecules containing functional groups are known to self-associate into complex three-dimensional ensembles opening a way to designing supramolecular nanostructures of various morphological types with specific properties. In this respect the interest to the study of mixed polyelectrolyte–amphiphile ensembles is understandable.

We established by conductometric method that poly (ethylene) imines **II** and **IIa** in the water–DMF (30 vol %) medium form aggregates at critical concentrations of association (CCA). On the conductometry curves there are two bends corresponding to CCA_1 (beginning of aggregation) and CCA_2 (structural rearrangements in the system) (Table 1). The presence of aminomethylated calixarenes results in decreasing the CCA values of poly(ethylene) imines. On Fig.2 plots of electroconductivity against concentration of polyelectrolyte **IIa** are given as an example in the absence and in presence of compound **Ib**. The relatively sharp decrease in the electroconductivity in the presence of calixarene **Ib** should be noted.

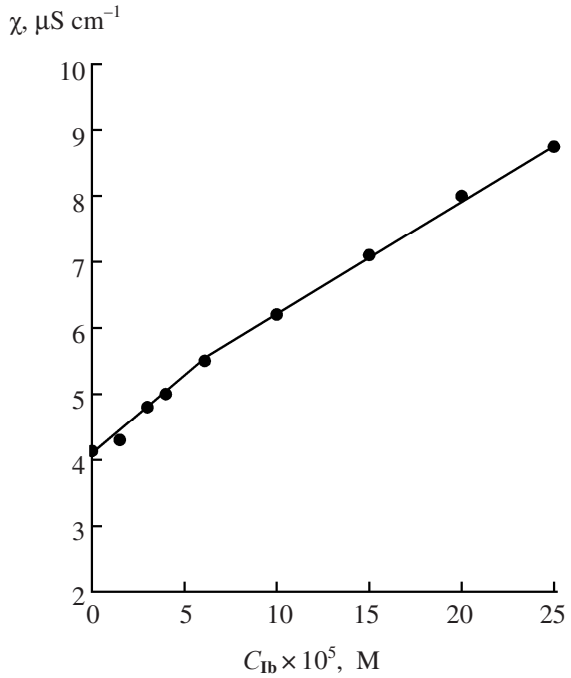


Fig. 1. Plots of electrconductivity vs calixarene **Ib** concentration, water–DMF (30 vol %), 30°C.

The self-association of polymer **II** in water occurs at a high concentration (0.01 M), while in water–DMF medium it starts at a much lower content of polyelectrolyte ($CCA_1 = 4 \times 10^{-3}$ M) (Table 1). Compound **IIa** in water, as shown by conductometry, possesses $CCA_1 = 1.8 \times 10^{-3}$M and $CCA_2 = 0.8 \times 10^{-3}$ M, that is, lower than in water–DMF medium (Table 1). This difference is probably related to the involvement

Table 1. Values of CCA for poly(ethylene) imines in water and water–DMF (30 vol %) in the absence and in the presence of calixarenes **Ia** (27×10^{-4} M) and **Ib** (4×10^{-4}M) measured by conductometry, 30°C

Poly (ethylene) imine	Calixarene	CCA_1, M	CCA_2, M	R_{eff}, nm
II	–	0.0040	0.0100	40[a]
II	**Ia**	0.0010	0.0110	57[a]
IIa	–	0.0024	0.0096	88[b]
IIa	**IIb**	0.0012	0.0090	116[b]

[a] $C_{II} = 0.02$ M; [b] $C_{IIa} = 0.01$ M.

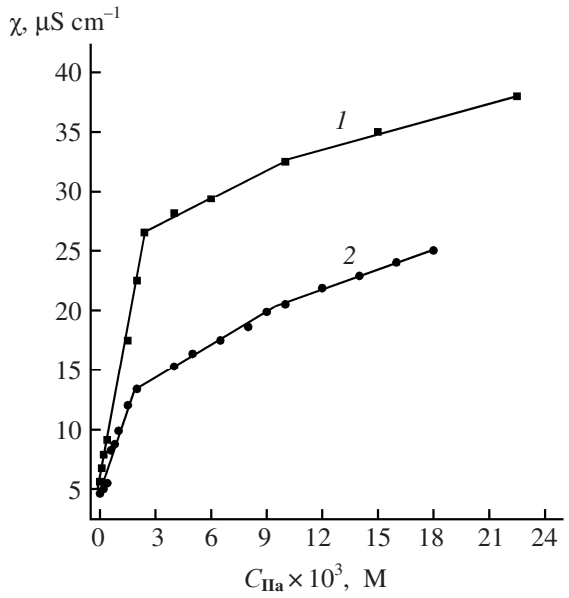


Fig. 2. Plot of electroconductivity vs the poly(ethylene) imine **IIa** concentration in the (*1*) absence and in the (*2*) presence of **Ib** (4×10^{-4} M) (*2*), water–DMF(30 vol %), 30°C.

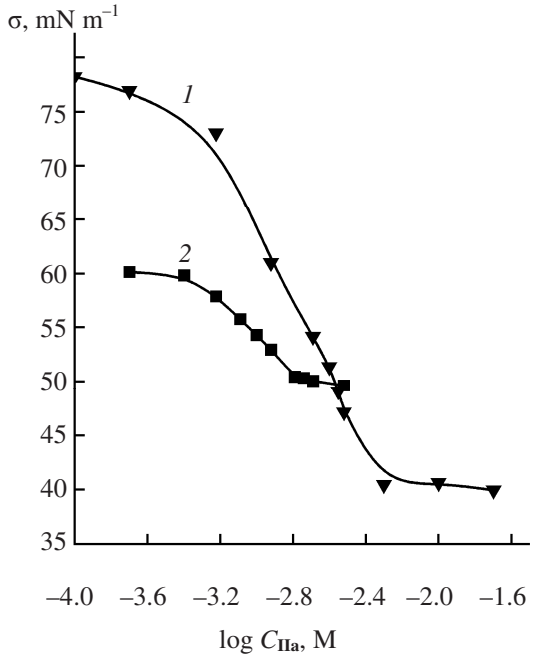


Fig. 3. Isotherms of surface tension of (*1*) poly(ethylene) imine **IIa** in water and (*2*) in water–DMF (30 vol %), 25°C.

of hydrophobic interactions during the association of polymer chains that is much stronger in water. Interestingly, the size of the aggregates of poly(ethylene) imines in water is less than in water–DMF (30 vol %): the effective radius (R_{eff}) of compound **IIa** (0.02 M) in water is 72 nm, in water–DMF system ~106 nm, for compound **II** (0.02M) $R_{eff} \approx 20$ nm (water) and 40 nm (water–DMF). This fact indicates probable participation of DMF molecules in formation of aggregates by >C=O···HN< hydrogen bonds.

The self-association of the studied poly(ethylene) imines proceeds involving the H-bonds between the nitrogen atoms N···HN; their contribution depends on the pH of the medium, namely, on the fraction of free amino groups in the polyelectrolyte (α). From the data of potentiometric titration of poly(ethylene) imines we calculated using Henderson–Hasselbach equations [19] the α values of poly(ethylene) imines at various pH. The α values are weakly affected by the poly(ethylene) imine concentration and by the presence of alkyl substituents in the molecule. For example, at pH 8 and concentration 0.02 M for the studied electrolytes α = 0.60–0.64. Effect of the polymer concentration is weak: for compound **IIa** at pH 8 α = 0.67 (0.01 M) and 0.64 (0.02 M). The addition of calixarenes insignificantly affects the α value of poly(ethylene) imines: for polymer **IIa** (0.01 M) at pH 8 α = 0.67 in the absence of compound **Ia** and 0.70 when concentration of compound **Ia** is 10^{-4} M. At pH 9.5 the fraction of nonprotonated reactive nitrogen atoms in the studied poly(ethylene) imines is high enough: 0.92 to 0.96.

Unlike the polyelectrolyte **II** the hydrophobically modified sample **IIa** shows surface activity both in water and in water–DMF (30 vol %) medium: it decreases surface tension by 35 and 10 units respectively. Figure 3 shows isotherms of surface tension on the water–air boundary for polymer **IIa**: CCA_1 5×10^{-3} M (water) and 1.4×10^{-3} M (water–DMF).

In is presumable that initially the aggregation of poly(ethylene) imines proceeds intramolecularly due to the non-covalent interactions of functional groups in the macromolecule. The value of CCM_2 characterizes structural reorganizations with probable involvement of interpolymeric interactions of the fragments of several macromolecules. Therewith, the aggregates formed after CCA_2 are weakly dissociating (Fig. 2). In the last case the polymer-colloid structures can grow:

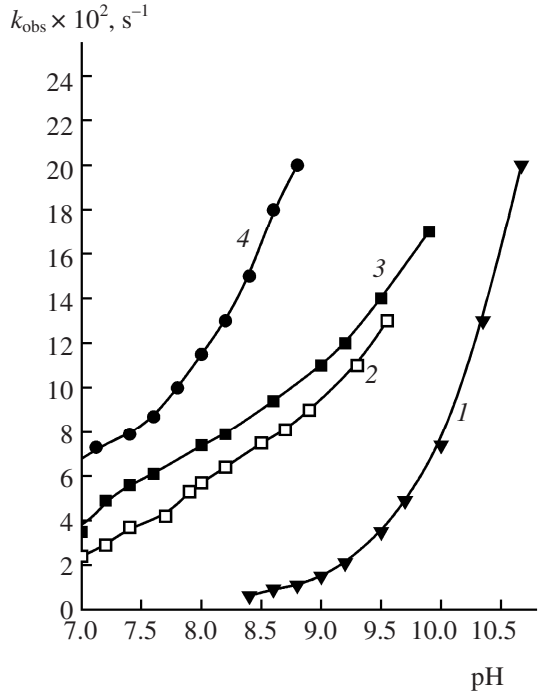


Fig. 4. Plots of the apparent rate constant (k_{app}, s^{-1}) of the hydrolysis of phosphinate **III** vs. pH for systems based on (*1*) **II**, (*2*) **IIa**, (*3*) **IIa–Ia** (2.7×10^{-4} M), and (*4*) **IIa–Ib**(4×10^{-4} M) in water–DMF (30 vol %) medium, C_{II} 0.02 M[1], C_{IIa} 0.01 M, 30°C.

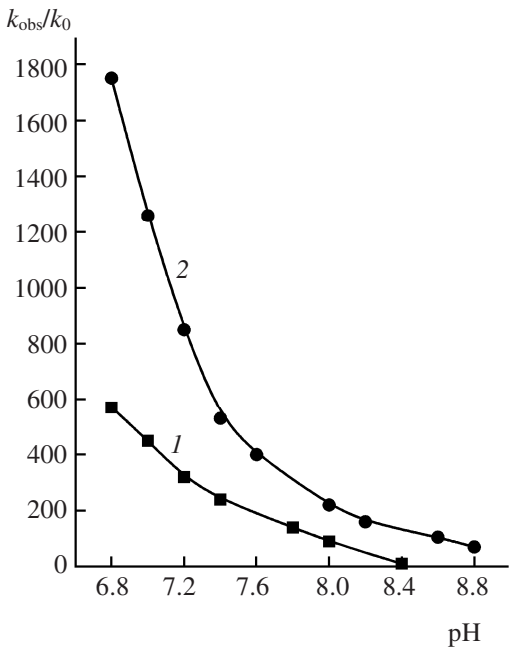


Fig. 5. Plots of acceleration values (k_{app}/k_o) vs pH for systems (*1*) **IIa**–water–DMF (30 vol %) and (2) **IIa–Ib**–water–DMF (30 vol %), C_{II} 0.01 M, C_I 4×10^{-4} M, 30°C.

For example, the size (radius) of the aggregates of compound **IIa** at concentration 0.01 and 0.02 M, consequently, after CCA_2, are 88 and 106 nm, respectively (according to the light scattering measurements).

Decrease in CCA at adding aminomethylated calix[4]resorcinarene to a system based on poly(ethylene) imine (Table 1) according to the data of [20,21] attests the formation of mixed supramolecular aggregates (complexes) which in the compositions based on the compound **II** involve mainly the H-bonds of OH···N and N···HN types, and in the compositions based on compound **IIa**, principally the hydrophobic interactions. Therewith, in the presence of a calixarene the aggregate size is changed significantly, thus also confirming formation of joint nanostructures. For example, in the case of polyelectrolyte **IIa** (0.01M) the radius of polymeric globule in the presence of compound **Ib** (4×10^{-4} M) grows from 88 to 116 nm, while for polyelectrolyte **II** in the presence of calyxarene **Ia** (2.7×10^{-4} M) the radius grows from 40 nm to 57 nm (Table 1). It is presumable that self-organizing poly(ethylene) imines in these systems play the role of water-soluble matrix (platform). Adding amphiphilic calix[4]resorcinarene results in reorganization of micro architecture of the polymeric globule due to H-bonding or formation of hydrophobic bonds (complex formation). This reorganizations can change the properties of the system, in particular, of their catalytic activity.

The catalytic activity in the system poly(ethylene) imine–aminomethylated calix[4]resorcinarene–water–DMF (30 vol%) we studied by an example of hydrolysis of 4-nitrophenyl-bis(chloromethyl)phosphinate (**III**):

$$(C1CH_2)_2P(O)OC_6H_4\text{–}NO_2\text{-}4 + H_2O \rightarrow (C1CH_2)_2P(O)OH + HOC_6H_4\text{–}NO_2\text{-}4.$$

It is known that the compositions calixarene–water–DMF [9, 22–24] and poly(ethylene) imine–water [25–27] display catalytic activity in the hydrolysis of phosphorus acids esters. Fig. 4 shows plots of the apparent rate constant (k_{app}, s^{-1}) versus pH for the

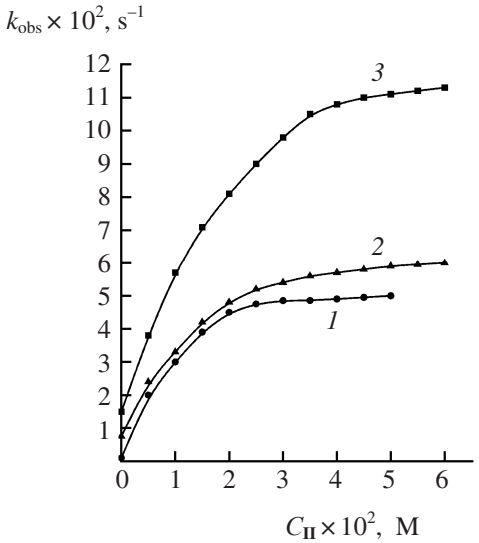


Fig. 6. Plots of the apparent rate constant (k_{app}, s^{-1}) of the hydrolysis of phosphinate **III** vs. the concentration of poly (ethylene) imine **II** in the presence of: (*1*) **Ic** (30°C); (*2*) **Ia** (30°C); (*3*) **Ia** (40°C); water–DMF (30 vol %), pH 9.5.

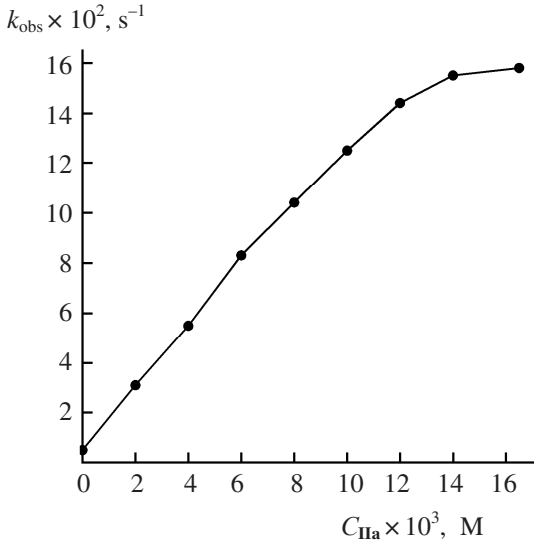


Fig. 7. Plots of the apparent rate constant (k_{app}, s^{-1}) of the hydrolysis of phosphinate **III** vs. the concentration of **IIa** in the presence of compound **Ib** (4×10^{-4} M), water–DMF (30 vol %), pH 8, 30°C.

polylectrolytes **II** and **IIa** in the presence and in the absence of calixarene. The catalytic effect of a system based on compound **IIa** in the presence of calixarene **Ia** is changed insignificantly, and compound **Ib** slightly increases the catalytic activity of this polyelectrolyte. Adding compound **Ib** to the system based on the polyelectrolyte **IIa** shifts the plot $k_{app} = f(pH)$ to lower pH values (Fig.4), therefore this composition exhibits relatively high catalytic effect under mild conditions (pH 7–8). Fig. 5 shows the values of acceleration (k_{app}/k_o) as a function of pH for the **IIa–Ib**–water–DMF and **IIa**–water–DMF systems. Note that acetal substituents at the nitrogen atoms on the upper rim of compound **Ib** probably increase the receptor properties of the calixarene.

It is known that hydrolysis of the phosphorus acids esters in water solutions of poly(ethylene) imine proceeds by the general basic mechanism [25]. In the case of polymer-colloid systems surfactant–poly (ethylene) imine–water the mechanism is the same; for example, in the case of the composition poly(ethylene) imine–sodium dodecylsulfate–water it was confirmed by similarity of activation parameters with those of the system poly(ethylene) imine–water [26].

We showed that the value of deuterium isotopic effect for the compositions poly(ethylene) imine–aminomethylated calix[4]resorcinarene–water–DMF (30 vol %) is ~2 meaning that here the mechanism of catalysis is also general basic, with participation of free amino groups of poly(ethylene) imine which activate water molecules.

Figures 6 and 7 present the plots of k_{app} vs. the concentration of poly(ethylene) imine in the presence of calixarene. Nonlinear appearance of kinetic profiles ended in a plateau indicates pre-reaction ionic binding of the phosphinate by mixed poly(ethylene) imine–calixarene aggregate, like the formation of ferment–substrate complexes at the bioactalysis or the complexes micelle–substrate and polymer–substrate at the micellar and polymeric catalysis, respectively [28, 29]. Therefore we were able to treat kinetic data according to equation (1) corresponding to the pseudophase model of micellar catalysis.

$$k_{obs} = \frac{k_w + k_m K_s (C_{surfactant} - CCM)}{1 + K_s (C_{surfactant} - CCM)}, \qquad (1)$$

where k_{app} is the apparent first order rate constant, s^{-1}; k_w and k_m are the reaction rate constants in bulk solvent and in the micellar phase, respectively, s^{-1}, K_S is the constant of binding between the substrate and the micelle, 1 mol^{-1}, $C_{surfactant}$ is surfactant concentration, M, CCM is critical concentration of micelle formation.

The validity of application of this equation to polymer-colloid systems is known [26, 27, 30]. The results of quantitative treatment are listed in Table 2. It follows from these data that acceleration of the reaction of hydrolysis of substrate **III** in the systems **II–Ia** (**Ic**)–water–DMF (pH 9.5) as compared with the non-catalytic process at the same pH value is 3–3.5-fold despite much larger bonding constants in the presence of compound **Ic** as compared with **Ia**. At lower pH values a significant acceleration of phosphinate **III** hydrolysis can be achieved. For example, in the system **IIa–Ib**–water–DMF the acceleration (k_m/k_o) at pH 8 is 560 times (Table 2), while at pH 7 the value of k_{app}/k_o for the same composition achieves ~1200 times (Fig.5).

Note that functional fragments of the aminomethylated calix[4]resorcinarenes probably are not involved in the catalysis: the catalytic activity of the systems based on compounds **Ia** or **Ic** is practically the same (Table 2) despite the fact that in water–DMF medium the aminomethylated calixarene **Ia** in contrast to Ic is known to catalyze the hydrolysis of phosphorus acids esters [9].

At the same time it should be stressed that a nonlinear dependence of catalytic activity of the system **II–Ia**–water–DMF on the concentration of calixarene **Ia** at the constant content of poly(ethylene) imine **II** is apparent (Fig. 8). Quantitative treatment of these data according to equation (2) provided the following reaction parameters of phosphinate **III** hydrolysis: k_m = 0.133 s^{-1} ; K_s = 2000 l mol^{-1}, CCM = 3.1×10^{-4} M. It can be suggested alternatively that concentration of compound **Ia** affects the size of polymeric globule of the poly(ethylene) imine **II**, and this probably changes the catalytic activity of the formed mixed nanoaggregates. This assumption however requires detailed inspection.

Thus, self-assembling systems containing as "building blocks" poly(ethylene) imines (including hydrophobic ones) and amphiphilic aminomethylated calix[4]resorcinarenes in the water–dimethylform-mide form joint nanoaggregates (of radius 60 to 120 nm) possessing high catalytic activity under mild conditions in the processes of hydrolytic splitting phosphorus acids esters.

EXPERIMENTAL

The substrate 4-nitrophenylbis(chloromethyl)phosphinate (**III**) was prepared by the known procedure [31]. Compound **Ib** was synthesized by reaction of calix[4]resorcinarene with methylaminoacetic aldehyde and formalin in the ratio 1:5:5. The method of two-dimensional 2D-ROESY spectroscopy showed that compound **Ib** had a cone conformation. Calixarene **Ia** was prepared by the known procedure [7]. Structure and composition of aminomethylated calix[4] resorcinarenes was proved by ^1H and ^{13}C NMR spectroscopy and elemental analysis. We used a sample of branched poly(ethylene) imine (**II**) purchased from

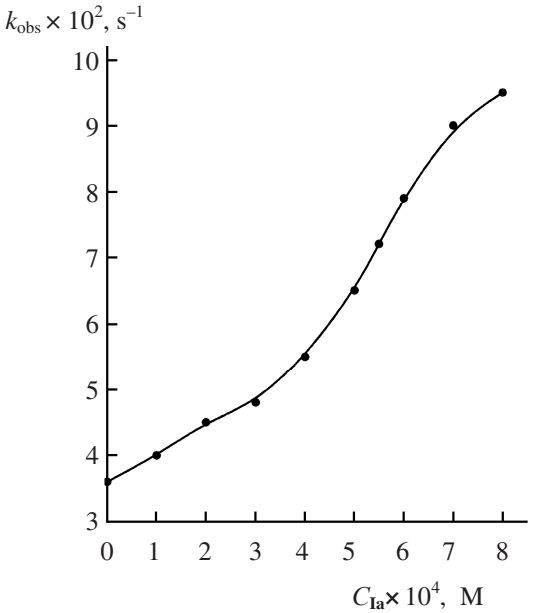


Fig. 8. Plot of the apparent rate constant of hydrolysis of phosphinate **III** vs. the concentration of compound **Ia** in the presence of poly(ethylene) imine **II** (0.02 M), water–DMF (30 vol %), 30°C.

Table 2. Parameters of hydrolysis kinetics of 4-nitrophenylbis(chloromethyl)phosphinate (**III**) in the system poly(ethylene) imine–calixarene–water–DMF (30 vol %), pH 9.5

Polymer	Calixarene	$C_I\times10^4$, M	T, °C	k_m, s^{-1}	K_s, l mol^{-1}	CCM$\times10^4$, M	k_m/k_0 [a]
II	**Ia**	2.7	30	0.064	214	1.4	3.7
II	**Ia**	2.7	40	0.121	262	1.6	3.0
II	**Ic**	2.7	30	0.052	607	1.1	3.0
IIa[b]	**Ib**	4.0	30	0.280	93	1.6	560

[a] k_o is the hydrolysis rate constant of phosphinate **III** in the water–DMF (30 vol %) medium at the corresponding pH value; [b] pH 8.

Fluka of molecular weight 10000 (**II**) and modified hydrophobic sample of **II** with radicals n-$C_{12}H_{25}$ (**IIa**). Poly(ethylene) imine **IIa** was synthesized by procedure in [32] reacting compound **II** with dodecyl bromide, the target alkylated polymer isolated from organic layer was dried under a vacuum to a constant weight and characterized by IR and ^{1}H NMR spectroscopy. Molecular weight of a monomer unit of the poly (ethylene) imines was determined by potentiometric titration on a pH-150MA device: 78 (**II**) and 118 (**IIa**). The fraction of free amino groups (a) in the polyelectrolytes at various pH values was calculated by the Henderson–Hasselbach equation [19].

Hydrolysis kinetics of phosphinate **III** was studied by spectrophotometry on a Specord UV–VIS spectrophotometer at the starting substrate concentration 5×10^{-5}–1×10^{-4} M varying pH values and temperature. The reaction progress was monitored by measuring optical density of solutions at the wave length 400 nm (formation of the 4-nitrophenoxide anion). Conversion was over 90%. The apparent first order rate constants of the reaction (k_{app}, s^{-1}) are calculated by the regression method using equation (2)

$$\ln (D_\infty - D_t) = -0.434k_{app}\times t + \text{const}, \qquad (2)$$

where D_∞ and D_t are the values of optical density at the reaction completion and at the time moment t respectively.

The electroconductivity of micellar solutions was measured on a conductometer CDM-2d (Denmark). The electroconductivity of bidistilled water used for preparation of the reagent solutions was taken as the zero point. The surfactants properties are studied by measuring surface tension isotherms (δ, mN m^{-1}) by the method of ring break-off (Du Noüy). The aggregates effective radii were determined on an instrument for dynamic and static light scattering "Photocor Complex." The light source is a HeNe gas laser of 10 mW power and 633 nm bond length. Micelle effective radii were calculated from the diffusion coefficients according to the Stokes–Einstein equation for spherical particles of equal size accounting for the viscosity of the studied solutions. For each system the hydrodynamic radius was determined by arithmetic averaging of 10 measurements.

Kinematic viscosity of solutions was determined using glass capillary viscometer VPZh-1, internal diameter of the capillary was 0.56 mm, the viscometer constant was 0.009279 mm^2 sec^{-2}. The measuring was carried out in a vessel maintained at constant temperature 25°±0.2°C.

Kinetic plots $k_{app} = f(C_{surfactant})$ were analyzed in keeping with equation (1) of pseudophase model of micellar catalysis [33].

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