Catalytic properties of polymer-colloid complexes based on polyethyleneimines and mono- and diquaternized 1,4-diazabicyclo[2.2.2]octane derivatives in the hydrolysis of phosphorus acids esters*

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It is established by spectrophotometry that polyethyleneimines, mono- (MQD) and diquaternized (DQD) hexadecyl derivatives of 1,4-diazabicyclo[2.2.2]octane, and mixed polymer-colloid systems based thereon catalyze the hydrolysis of *p*-nitrophenyl alkyl chloromethylphosphonates. The catalysis efficiency depends on the structures of substrate, 1,4-diazabicyclo-[2.2.2]octane derivatives, and polyethyleneimine, pH of the medium, and the temperature. In the case of MQD, the catalytic effect changes from 20 to 80-fold with an increase in the length of phosphonate alkyl radical from R = OEt to R = OC_6H_{13}; the DQDs exhibit lower catalytic activity compared to the MQD. The most efficient catalysis (up to 90-fold acceleration) is observed for a mixed polyethylene—dicationic surfactant system where the surfactant contains the hydroxyethyl fragment in the head group, which is due to a favorable effect of the micellar microenvironment of reagents.

Key words: polyethyleneimine, 1,4-diazabicyclo[2.2.2]octane, polymer-colloid complex, alkaline hydrolysis, phosphorus acids esters.

Systems based on polymers and surfactants have found a wide application in cosmetic, pharmaceutical, paint-and-varnish, petrochemical, and other fields of industry, and, in recent years, in nanomedicine upon the design of drug and genetic material delivery systems.[1,2] The efficacy of mixed surfactant—polymer compositions is known to be caused by the formation of joint structures or polymer-colloid complexes[3—5] and depends on the surfactant type and the ratio between the system components.[6,7] Earlier,[8,9] we have shown that the use of polymer-colloid systems based on surfactants and polymers (polyethylene glycols, polyethyleimines, block copolymers) makes it possible to control the rate of hydrolysis of phosphorus and carboxylic acids esters and to decrease the concentration of catalytic agents.

Polyethyleneimine is widely used as the gene transfection agent; it is available in commercial forms which possess low toxicity *in vivo*[10,11] and approved themselves in clinical trials.[12] Many recent studies[13] show that the transfection efficiency and the cytotoxicity upon application of polyethyleneimine—DNA complexes depend significantly on the polymer molecular weight[14] and concentration[15], as well as on its chemical modification.[16—20] Polyethyleneimine forms nanoassemblies with naturally occurring polyions, peptides,[21—23] and proteins[24] and is applied for immobilization and stabilization of metal nanoparticles[25—27] and enzymes.[28—31] The nanocatalyst obtained involving polyethyleneimine possess some advantages over conventional ones (low cost, the absence of reducing and stabilizing agents, recoverability, *etc.*).[32,33] There are also successful works on the design of platinum catalysts using polyethyleneimine for fuel cells.[34,35]

Polyethyleneimines are known to catalyze the transfer of acyl and phosphoryl groups.[36—38] In the presence of surfactants[39,40] and amphiphilic cyclophanes,[41,42] polyethyleneimines form polymer-colloid complexes exhibiting catalytic activity in the hydrolysis of carboxylic and phosphorus acid esters.[43,44] In continuation of our studies, in the present work we evaluated the catalytic properties of polyethyleneimine (PEI) and its hydrophobized analog (HPEI) in the absence and in the presence of mono- and dicationic surfactants, *viz.*, mono- and diquaternized 1,4-diazabicyclo[2.2.2]octane hexadecyl derivatives (MQD and DQD, respectively). The cationic surfactants (CSs) under study are known to possess lower toxicity[45] compared to their classical analog, cetyltrimethylammonium bromide. Addition of cationic surfactants with a variable number of cationic centers to the polymer composition will allow one to control the polyfuncitonal properties of the system by optimization of its composition.

* Dedicated to Academician of the Russian Academy of Sciences N. S. Zefirov on occasion of his 80th birthday.

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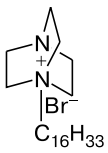
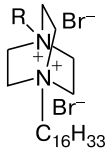


MQD

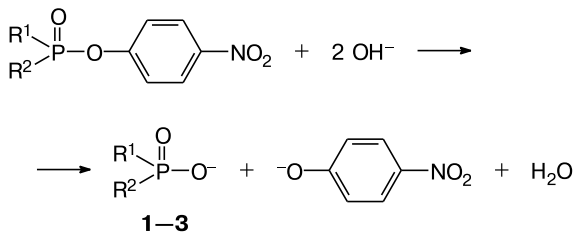


R = Et (DQD-1), C_2H_4OH (DQD-2)

Experimental

HPEI compounds were obtained by the reaction of PEI (the molecular weight is 25000) (Aldrich) with *n*-dodecyl bromide according to the earlier described procedure.[46] Complete characterization of the HPEI sample under study has been given in Ref. 47. The molecular weight of HPEI monomer unit was determined by potentiometric titration, which was found to be efficient. The preparation of MQD from 1,4-diazabicyclo[2.2.2]octane and hexadecyl bromide has been described previously.[49] DQD-1 and DQD-2 were synthesized by quaternization of MQD with 1-bromoethane and 2-bromoethanol, respectively.[50] The substrates, *O*-4-nitrophenyl-*O*-alkyl chloromethylphosphonates (**1**—**3**) (Scheme 1), were prepared according to the procedure described in Refs 51 and 52. The polymer concentration is expressed as the molar concentration of monomer unit, which was calculated based on the data from potentiometric titration of the polymer; it corresponds to the number of its ionic groups capable of undergoing alkylation.

Scheme 1



1—**3**

$R^1 = ClCH_2$, R^2 = OEt (**1**), OBu (**2**), OC_6H_{13} (**3**)

The reaction kinetics was studied on a Specord UV—Vis spectrophotometer in thermostatically controlled cells by the increase in the absorbance of 4-nitrophenolate anion at 400 nm. The apparent rate constants for the reaction (k_{app}, s^{-1}) were determined by the first-order equation (1):

$$\log(D_\infty - D_t) = -0.434k_{app}t + \text{const}, \quad (1)$$

where D_∞ and D_t are the absorbances after completion of the reaction and at a time point t, respectively.

The concentrations of substrates **1**—**3** were $5 \cdot 10^{-5}$—$1 \cdot 10^{-4}$ mol L^{-1}. The parameters of the micelle-catalyzed process were determined by the equations of the pseudophase model of micellar catalysis[53,54] (2) and (3):

$$k_{app} = \frac{k_m K_S (C_{Surf} - CMC) + k_0}{1 + K_S (C_{Surf} - CMC)}, \quad (2)$$

$$k_{2,app} = \frac{k_{2.0} + (k_{2,m}/V) K_S K_{Nu} (C_{Surf} - CMC)}{[1 + K_S (C_{Surf} - CMC)][1 + K_{Nu} (C_{Surf} - CMC)]}, \quad (3)$$

where k_m and k_0 (s^{-1}) are the rate constants in the micellar pseudophase and the bulk of solvent, respectively; C_{Surf} is the surfactant concentration (mol L^{-1}); CMC is the critical micelle concentration (mol L^{-1}); $k_{2,app}$ (L mol^{-1} s^{-1}) is the apparent second-order rate constant obtained upon division of k_{app} by the nucleophile concentration; $k_{2,0}$ and $k_{2,m}$ (L mol^{-1} s^{-1}) are the second-order rate constants in the bulk of solvent and the micellar pseudophase, respectively, V (L mol^{-1}) is the molar volume of surfactant; K_S and K_{Nu} (L mol^{-1}) are the constants for substrate and nucleophile binding to micelles. In terms of the model proposed in Ref. 54 (see Eq. (3)), the maximum acceleration of the process is described by Eq. (4):

$$(k_{app}/k_0)_{max} = \frac{k_{2,m}}{k_0} \cdot \frac{K_S K_{Nu}}{V (K_S^{0.5} + K_{Nu}^{0.5})^2}, \quad (4)$$

where the first multiplier in the right side of the equation reflects the factor of change in the microenviroment of reagents on their going from a solvent to the micellar phase (F_m) and the second multiplier corresponds to the effect of reagents concentrating in the micellar phase (F_c).

All solutions under study were prepared in water purified using a Direct-Q 5 UV system (Millipore S.A.S. 67120 Molsheim, France).

Results and Discussion

Supramolecular systems based on similarly charged surfactants and polyelectrolytes are less studied than polymer-colloid complexes based on surfactants and uncharged polymers. Earlier,[39,41,55,56] we have studied systems based on the weak polyelectrolyte, PEI, and cationic surfactant of different structure. In the case of hydrophobized PEI, complexation is likely defined mainly by the contribution of hydrophobic effect and the reaction of the non-alkylated analog proceeds by the same mechanism as in the case of uncharged polymers, since the portion of protonated amino groups is low at pH ~10 in the absence of a buffer solution. The catalytic activities of the systems based on polyethyleneimines and mono- and diquaternized surfactants were studied by the example of hydrolysis of *O*-4-nitrophenyl-*O*-alkyl chloromethylphosphonates **1**—**3** (see Scheme 1).

Catalytic activity of PEI and HPEI. The reaction kinetics in the presence of PEI was studied by the example of hydrolysis of phosphonate **1**. According to the data obtained earlier,[41] the hydrolysis of phosphorus acids esters in aqueous solutions of PEI proceeds by the mechanism of generally base ligand. Figure 1 shows the apparent rate constant for the hydrolysis of phosphonate **1** as a function of the concentration of polymers for which there was a tendency of coming to plateau in the high concentration range, which is typical of micellar catalyzed reactions[53,54] and suggests binding of the substrate to aggregates. The

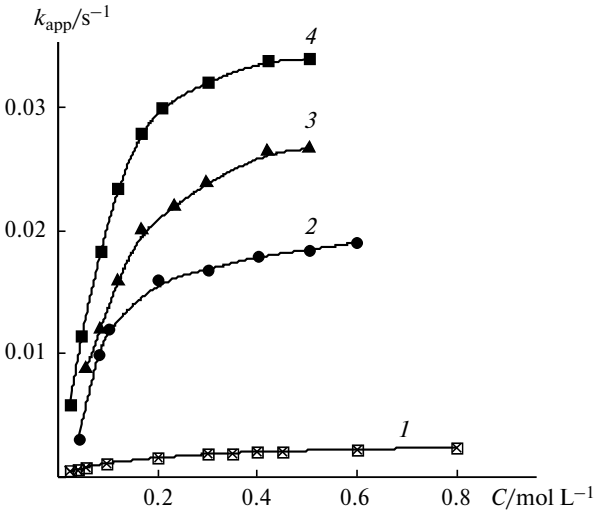


Fig. 1. Apparent rate constant (k_{app}) for the hydrolysis of phosphonate **1** as a function of the concentration of PEI (*1*) and HPEI (*2—4*) at pH = 10.5 (*1*) and 10 (*2—4*) and at T = 25 (*1*, *2*), 35 (*3*), and 45 °C (*4*).

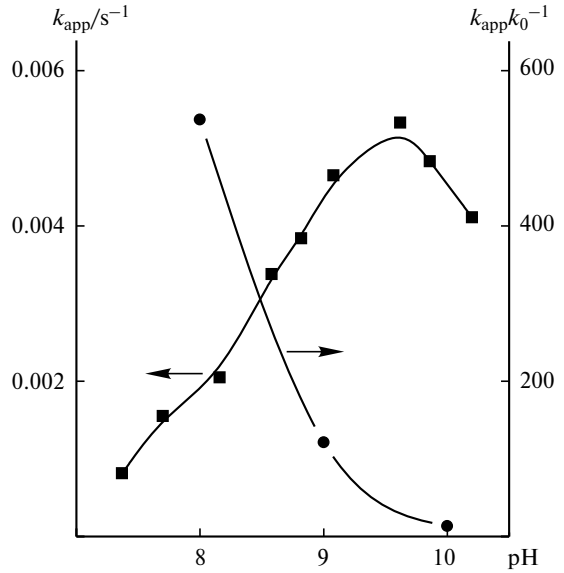


Fig. 2. Apparent rate constant (k_{app}) for the hydrolysis of phosphonate **1** and acceleration ($k_{app}k_0^{-1}$) of this process as a function of pH for the HPEI—water system, C_{HPEI} = 0.1 mol L^{-1}, 25 °C.

analysis of kinetic data in terms of the pseudophase model of micellar catalysis suggests an insignificant acceleration of the reaction $(k_{app}k_0^{-1})_{max}$ in the presence of PEI and a high catalytic effect of HPEI (~60-fold). With increasing the temperature by 20 °C, the reaction in the presence of HPEI is accelerated more than 100-fold (Table 1). The amphiphilic HPEI polymer showing a capability of association in the aqueous medium[55] and creating favorable conditions for binding between the substrate and the nucleophile can catalyze efficiently the reaction under study. It should be noted that the resulting effect for HPEI based on PEI with a molecular weight of 25000 is higher than that for its hydrophobized analog based on PEI with a molecular weight of 10000 studied by us earlier.[56] With a decrease in the pH of solution to 7.5, the catalytic effect increases up to 600-fold (Fig. 2). In the region of neutral and slightly alkaline pH values, there occurs protonation of the amino groups of HPEI nanoaggregates which can bind the hydroxide ions due to the electrostatic interaction, *i.e.*, can increase the contribution of the reagent concentrating factor to the catalytic effect of the system.

Table 1. Parameters for the hydrolysis of substrate **1** in the presence of PEI (pH 10.5) and HPEI (pH 10) in water

System	T/°C	CMC[a] · 10^2 /mol L^{-1}	K_S /L mol^{-1}	k_m · 10^2 /s^{-1}	$k_m k_0^{-1}$[b]
PEI	25	0.47	37.00	0.29	2.2
HPEI	25	3.20	20.00	2.00	57.0
	35	1.90	8.10	3.40	97.0
	45	1.30	0.13	4.10	117.0

[a] Critical micelle concentration.
[b] k_0 is the apparent rate constant for the hydrolysis in the absence of PEI and HPEI at the corresponding pH value.

Catalytic activity of cationic surfactants. The study of hydrolysis in the presence of individual cationic surfactants (Fig. 3) showed that the catalytic effect obtained is comparable in the order of magnitude with the efficiency of systems based on the individual HPEI. The highest catalytic effect (~20-fold) is reached in the case of MQD (Table 2). The change in the structure of the head group of

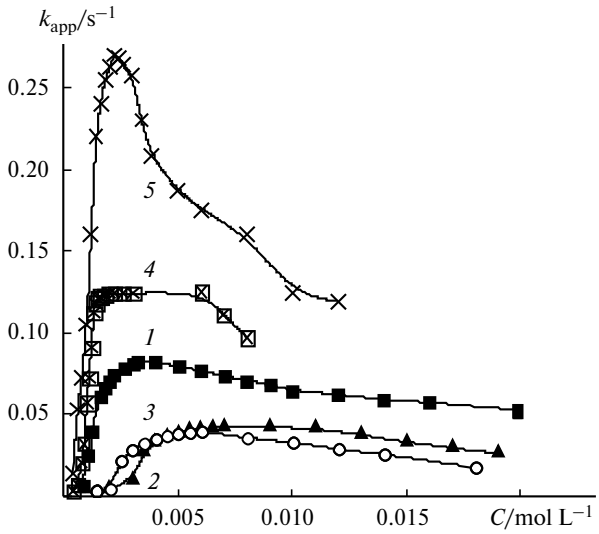


Fig. 3. Apparent rate constant (k_{app}) for the hydrolysis of substrates **1** (*1—3*), **2** (*4*), and **3** (*5*) as a function of the concentrations of MQD (*1*, *4*, *5*), DQD-1 (*2*), and DQD-2 (*3*); C_{NaOH} = 0.001 mol L^{-1}, 25 °C.

Table 2. Parameters for the hydrolysis of substrates **1**—**3** in the presence of cationic surfactants[a] and CS—HPEI[b] at 25 °C

System	Substrate	$k_{2,m}$ /L mol^{-1} s^{-1}	K_S	K_{Nu}	$(k_{app}k_0^{-1})_{max}$[c]	F_m	F_c	CMC[d] /mol L^{-1}
			L mol^{-1}					
MQD	**1**	0.9800	2000	32	20.50	0.240	83	0.00090
	2	0.4800	4570	110	40.60	0.160	270	0.00075
	3	0.5700	9300	180	82.00	0.172	470	0.00110
DQD-1	**1**	0.3200	1500	55	10.60	0.080	130	0.00290
DQD-2	**1**	0.2000	1100	90	9.75	0.050	180	0.00200
PEI—MQD	**1**	0.0066	1300	26	29 (29)[e]	0.430	66	0.00120
PEI—DQD-1	**1**	0.0060	1600	23	23 (56)[e]	0.380	60	0.00330
PEI—DQD-2	**1**	0.0130	600	20	36 (88)[e]	0.870	41	0.00270
HPEI—MQD	**1**	0.0760	1000	1.0	3.8 (53)[e]	0.850	4	0.00150
HPEI—DQD-1	**1**	0.0016	830	60	2.5 (35)[e]	0.020	125	0.00290
HPEI—DQD-2	**1**	0.0054	400	23	2.9 (41)[e]	0.060	50	0.00150

[a] C_{NaOH} = 0.001 mol L^{-1}, CS—PEI pH 10.5, and C_{PEI} = 0.05 mol L^{-1}.
[b] pH 9.5, C_{HPEI} = 0.02 mol L^{-1}.
[c] k_0 is the apparent rate constant for the hydrolysis in the absence of cationic surfactant at the corresponding pH value.
[d] Determined by Eq. (2).
[e] The acceleration of alkaline hydrolysis without catalyst is given in parentheses.

cationic surfactant (the increase in the charge number and introduction of the hydroxyethyl fragment) has an effect on its catalytic activity. The increase in the charge number in the head group of CSs under study affects favorably the value of reagent concentrating factor which increases ~2-fold. However, the acceleration of hydrolysis in the presence of DQD is 2-fold less than that in the case of MQD, which can be due to a significant decrease (3—5-fold) in the factor of change in the microenvironment of solubilized reagents (F_m).

To reveal the substrate specificity, the effect of substrate structure on the catalytic effect of MQD was studied (see Fig. 3, curves *1*, *4*, and *5*). According to the data given in Table 2, the catalytic effect of MQD micelles increases from 20 to 80-fold on going from the less hydrophobic substrate **1** to the more hydrophobic substrate **3**. The resulting effect is caused by the increase in the reagent concentrating factor (F_c) with an increase in the length of substrate alkyl radical.

Catalytic activity of polymer—CS compositions in the hydrolysis of phosphonate 1. According to our previous studies,[55] the mixed polymer-colloid complexes are produced in aqueous solutions of polymer—CS, where the concentration range of their formation depends significantly on the type of cationic surfactant.

The comparison between the catalytic activities of individual compounds and compositions based thereon showed the mixed polymer–CS systems to possess higher catalytic effect compared to their components. The highest catalytic effect is reached in the PEI—DQD-2 system (Fig. 4, see Table 2), where the reaction is accelerated ~90-fold compared to the noncatalyzed reaction. The reagent concentrating factor for the CS—PEI systems changes insignificantly to be 66 for PEI—MQD, 60 for PEI—DQD-1, and 40 for PEI—DQD-2. The factor of micellar microenvironment for the PEI—DQD-2 system is equal to 0.87 which is ~2-fold higher than that for the PEI—MQD and PEI—DQD-1 systems. Thus, the effect obtained is caused by a lower contribution of the nonfavorable factor of reagent micellar microenvironment to the total catalytic effect.

In the case of HPEI—CS composition, the reaction acceleration depends slightly on the CS structure (Fig. 5, see Table 2). In the presence of MQD, the acceleration

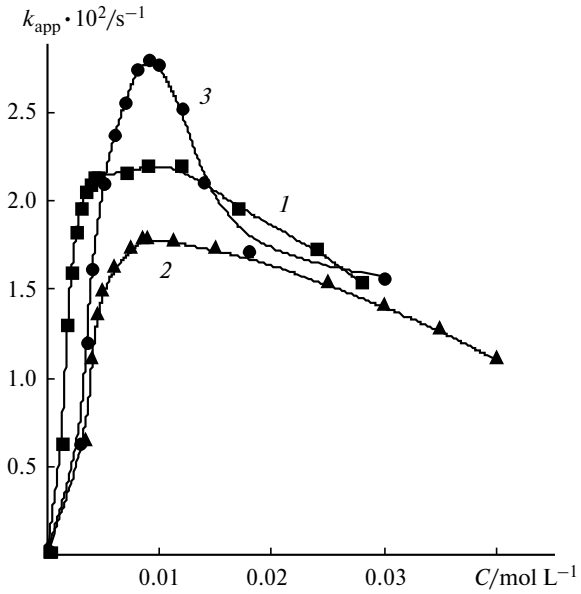


Fig. 4. Apparent rate constant (k_{app}) for the hydrolysis of substrate **1** as a function of the concentration of MQD (*1*), DQD-1 (*2*), and DQD-2 (*3*) in the presence of PEI (0.05 mol L^{-1}), pH 10.5, 25 °C.

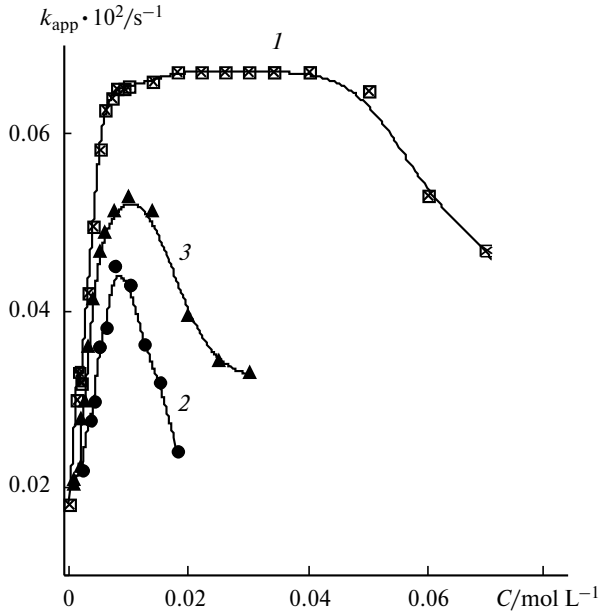


Fig. 5. Apparent rate constant (k_{app}) for the hydrolysis of substrate **1** as a function of the concentration of MQD (*1*), DQD-1 (*2*), and DQD-2 (*3*) in the presence of HPEI (0.02 mol L^{-1}), pH 9.5, 25 °C.

can be caused by a low constant of binding between the nucleophile and the polymer-colloid complex and, in the case of DQD, it is caused by low F_m values.

Thus, new polymer-colloid complexes based on MQD, DQD, and PEI with different hydrophobicities exhibit high catalytic activity in the hydrolysis of phosphorus acid esters. The catalysis efficiency was found to depend on the structures of surfactant, polymer, and substrate, the temperature, and pH of the medium. The systematic data obtained allows one to reveal the structure—property correlation and to optimize the formulation of catalytic compositions.

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