Aggregation and catalytic activity of 2-hydroxybenzylated polyethyleneimines in water-organic solutions

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The aggregation of 2-hydroxybenzylated derivatives of polyethyleneimine in a water—DMF medium in the absence and in the presence of cationic surfactants was studied. The catalytic activity of modified polyethyleneimines in hydrolysis of phosphorus acid esters depends on the pH of the medium and increases with the formation of polymer-colloidal complexes. The polymer-colloidal complexes based on surfactants with two hydroxyethyl substituents in the head group have the maximum catalytic activity (increase in the reaction rate by up to three orders of magnitude).

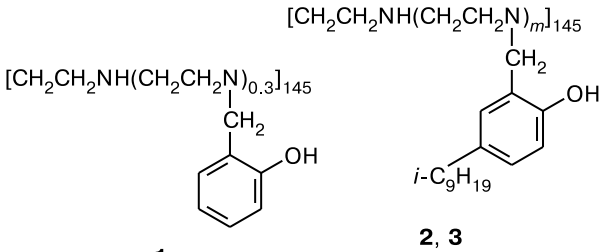
Key words: 2-hydroxybenzylated polyethyleneimines, surfactant, aggregation, catalysis, hydrolysis.

The modern level of technical progress provides the development of new approaches to the solution of problems in the field of catalysis. One of the promising trends is the use of supramolecular systems, whose biomimetic character allows one to achieve high efficiency and selectivity of catalysts under mild conditions.[1—3] A tendency to the development of polycomponent compositions, whose catalytic activity can be controlled by varying the nature and ratio of reactant concentrations, is observed in the recent time.[4,5] Nowadays the study of the properties of polymer-colloidal solutions is an intensely developing area of supramolecular chemistry. Interest to the systems based on surfactants and polymers is defined by their wide application in the production of detergents, oil regeneration, cosmetic industry, *etc.*[6] From the viewpoint of biomimetics, surfactant—polymer systems are models of protein—lipid interactions. Among many polymers, we noticed polyethyleneimines (PEI), which are of practical interest because of their use as corrosion inhibitors, demulsifiers,[7,8] biologically active substances,[7] complexing agents,[9] and carriers of drugs.[10]

It is known that polyethyleneimines can form aggregates in individual solutions, and polymer-colloidal complexes (PCC) are formed in the presence of surfactants.[11,12] In addition, it is shown that PEI and polymer-colloidal complexes based on them act as catalysts of hydrolysis of phosphorus acid esters.[12,13] Many works are devoted to the study of systems consisting of PEI and anionic surfactants (for example, PEI—sodium dodecyl sulfate[13—17]). The works on studying the interactions in systems based on polyethyleneimines (including those hydrophobically modified) and cationic surfactants have appeared in the recent time.[12,18—21] In aqueous solutions of such systems, electrostatic interactions exert an unfavorable effect on the formation of PCC, and combined structures are formed due to ion-dipole and hydrophobic interactions.[18,21]

Modified polyethyleneimines are of certain interest. For instance, additional hydrophobic fragments (benzyl, alkyl) in a PEI molecule enhance their aggregation activity and ability to complex formation toward molecules and ions of low-molecular-weight organic compounds, as well as the catalytic activity in hydrolysis of carboxylic and phosphorus acid esters.[22,23]

In the present work, we investigated the self-organization and catalytic activity of 2-hydroxybenzylated polyethyleneimine derivatives **1**—**3** in an H_2O—DMF (30 vol.% DMF) medium both as individual solutions and as mixed compositions with cationic surfactants.



1 **2**, **3**

m = 0.12 (**2**), 0.16 (**3**)

† Deceased.

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Cetyltrimethylammonium bromide (CTAB) and its 2-hydroxyalkyl derivatives, *viz.*, cetyl(2-hydroxyethyl)-dimethylammonium bromide (CHAB), cetyldi(2-hydroxyethyl)methylammonium bromide (CDHAB), and cetyl(2-hydroxypropyl)dimethylammonium bromide (CPAB), were chosen as cationic surfactants.

Experimental

2-Hydroxybenzylated PEI were synthesized from branched polyethyleneimine (molecular weight 10 000) and 2-dimethylaminomethylphenol or 2-dimethylaminomethyl(4-isononyl)-phenol (transamination reaction) by refluxing the reactants for 5—10 h in *p*-xylene with the removal of volatiles followed by distillation of the solvent and evacuation at 150 °C to a constant weight. The samples synthesized were characterized by IR spectroscopy and ^{1}H NMR spectroscopy. The starting unsubstituted PEI (Fluka) were used without preliminary purification. The molecular weight of the monomeric unit of 2-hydroxybenzylated PEI was determined by potentiometric titration on a pH-150MA instrument, the measurement error being 0.01 pH units. The fraction of free amino groups of polyelectrolytes (α) at different pH values was calculated by the Henderson—Hasselbach equation.[24]

4-Nitrophenylbis(chloromethyl)phosphinate (**4**) was synthesized according to a known procedure.[25] The purity of the substrate was checked by the elemental analysis data and by the correspondence of the rate constants of alkaline hydrolysis and melting points to the literature data.

Cetyltrimethylammonium bromide (Sigma) with the major substance content 99% was used. Cationic surfactants (CHAB, CDHAB, CPAB) were synthesized according to known procedures.[26,27]

The kinetics of hydrolysis of substrate **4** was studied spectrophotometrically on a Specord UV-VIS instrument at different pH values and the initial substrate concentration $5 \cdot 10^{-5}$—$1 \cdot 10^{-4}$ mol L^{-1}. The latter was achieved by the introduction of 2—10 μL of a phosphinate solution in ethanol (0.02 mol L^{-1}) into quartz cells (thickness 0.5 cm, 1.0 cm) containing a solution of PEI or a PEI—surfactant mixture. The reaction course was monitored by a change in the absorbance of solutions at the wavelength 400 nm (formation of the 4-nitrophenolate anion). The apparent (observed) rate constants for the first-order reaction (k_{app}/s^{-1}) were calculated using the regression method by the equation: $\ln(D_\infty - D_t) = -0.434k_{app}t + \text{const}$, where D_∞ and D_t are the absorbance values at the completion of the reaction and at the time moment t.

The kinetic dependences were analyzed in terms of Eq. (1) of the pseudophase model of micellar catalysis[28]:

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

where k_{app}/s^{-1} is the apparent rate constant for the first-order reaction; k_0/s^{-1} and k_m/s^{-1} are the rate constants for the first-order reaction in the solvent bulk and in the micellar phase, respectively; K_b/L mol^{-1} is the binding constant of the substrate with the micelle; C_{Surf}/mol L^{-1} is the surfactant concentration; CMC/mol L^{-1} is the critical micelle concentration.

The specific electroconductivity (χ) of polymer and polymer-colloidal systems was measured on a CDM-2d conductometer (Denmark). The critical association concentrations (CAC) were determined by the break in the plot of the electroconductivity *vs* concentration of a polymer or amphiphilic compound. The electroconductivity of the H_2O—DMF (30 vol.% DMF) solution was accepted to be zero.

The effective hydrodynamic radius (R_H) of aggregates in solution was determined on a Photocor Complex instrument of dynamic and static light scattering. A He—Ne gas laser with a power of 10 mW and a wavelength of 633 nm served as a radiation source. For each system, the hydrodynamic radius was calculated as an arithmetical average of three measurements. The measurement inaccuracy was not higher than 10%.

Results and Discussion

The electroconductivity of 2-hydroxybenzylated PEI **1** and **2** was measured in an H_2O—DMF medium in the absence (Fig. 1) and in the presence (Fig. 2) of CHAB. The conductometric plots have two breaks, which are commonly attributed to the onset of aggregation in the solution (CAC_1) and structural rearrangements in the system (CAC_2).[4] In the absence of a surfactant, the run of the conductometric plots reflects the change in the number of charge carriers formed due to the acid-base interactions of the amino groups of PEI with water. The decrease in the slope of the plots after the start of PEI aggregation and structural rearrangements (see Fig. 1) associated with the formation of intramolecular micelles or intermolecular aggregates is due to a decrease in the accessibility of the amino groups for similar interactions.

In the presence of surfactants, the slope of the conductometric plots after each break increases (see Fig. 2). Per-

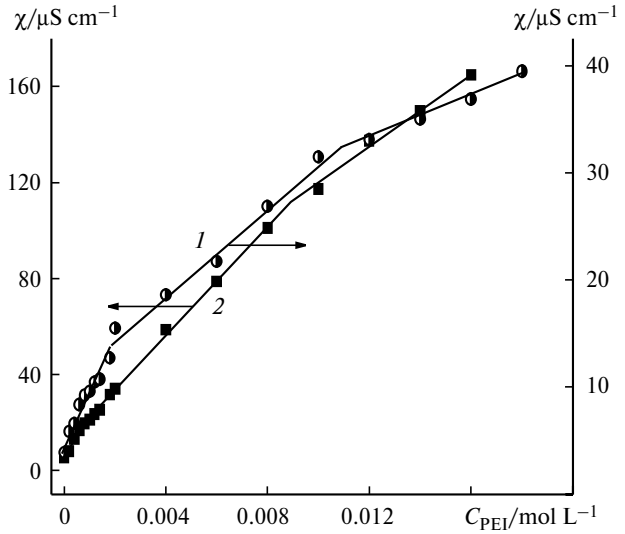


Fig. 1. Plots of the specific electroconductivity (χ) *vs* concentration of PEI **1** (*1*) and **2** (*2*) (H_2O—DMF (hereinafter, 30 vol.% DMF), 30 °C).

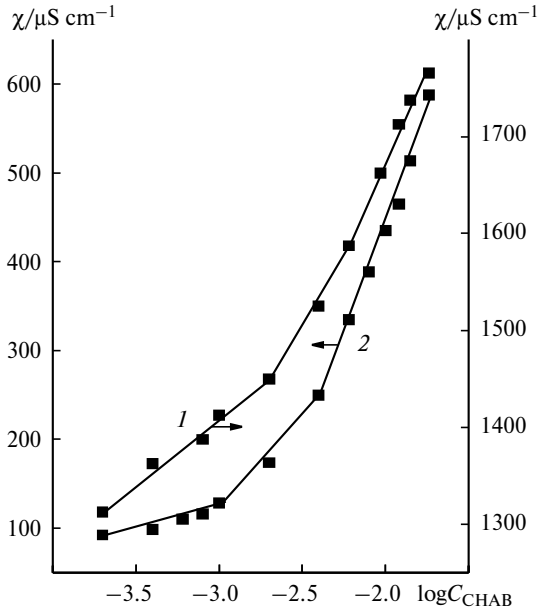


Fig. 2. Plots of the specific electroconductivity (χ) of solutions of PEI **1** (*1*) and **2** (*2*) in the presence of CHAB *vs* surfactant concentration (C_{PEI} = 0.01 mol L^{-1}, H_2O—DMF, 30 °C).

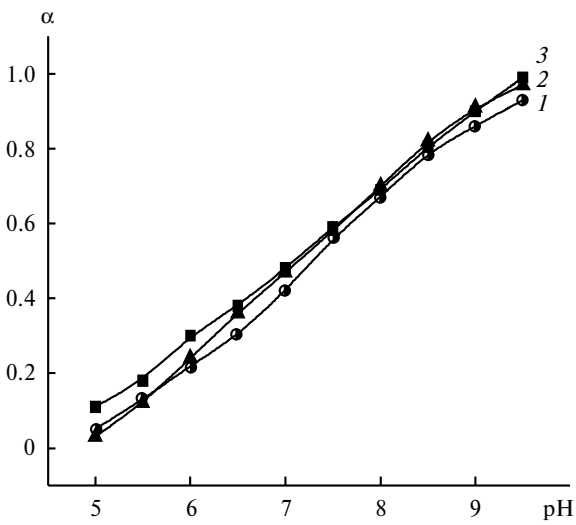


Fig. 3. Plots of the fraction of free amino groups (α) *vs* pH of the medium for solutions of PEI **1** (*1*) and **3** (*2*) and a **1**—CDHAB system (*3*) (C_{PEI} = 0.01 mol L^{-1}, C_{CDHAB} = 0.01 mol L^{-1}, H_2O—DMF, 25 °C).

haps, this is due to a decrease in the degree of binding of surfactant counterions upon the formation of mixed surfactant—polymer ensembles.

It looks likely that at low polymer concentrations aggregation occurs predominantly due to interactions inside one polymer chains (CAC_1), whereas an increase in the concentration increases the probability of bonding between polymer molecules (formation of supramolecular structures) due to hydrophobic interactions and hydrogen bonds (CAC_2). The contribution of hydrogen bonds is determined by the number of free amino groups of the polymer, whose fraction depends on the pH of the medium. The fraction of the free amino groups (α) of PEI **1** and **3** in an H_2O—DMF medium (Fig. 3) was calculated using the Henderson—Hasselbach equation by the potentiometric titration curves. At high pH values, polyethyleneimines are almost neutral polymers. An increase in hydrophobicity of the polymer and the addition of a surfactant exert a weak effect on the α value, although an increase in the fraction of free amino groups could be expected in the presence of cationic surfactants. It is known[29] that the pK_a values of the compounds decrease in cationic micelles.

Another feature of the conductometric plots of surfactant—PEI binary systems is the dependence of the degree of increasing the absolute values of the specific electroconductivity of the solution on the polymer structure. In the absence of a surfactant the electroconductivity is higher in a solution of more hydrophobic PEI **2** compared to a solution of PEI **1** having the same concentration (see Fig. 1). On the contrary, in binary systems a sharper increase in the electroconductivity is observed for the system based on less hydrophobic PEI **1** (see Fig. 2). The dependence on the PEI structure is also observed for the CAC values. In the absence and in the presence of a surfactant, an increase in the hydrophobicity of the polymer facilitates association in the system (Table 1).

The dynamic light scattering method was used to obtain the effective radii of particles of PEI **3** at different concentrations of the polymer in an H_2O—DMF medium at 25 °C. This plot passes through a maximum value of 125 nm at C_{PEI} = 0.03 mol L^{-1}.

C_{PEI}/mol L^{-1}	R_H/nm
0.01	85
0.02	110
0.03	125
0.05	72

Such behavior of the dependence of the effective radius on the concentration was observed for alkylated PEI in chloroform.[30] Interestingly, the sizes of particles of 2-hydroxybenzylated PEI at a concentration of 0.02 mol L^{-1} are much larger than those in the case of the starting branched PEI with the molecular weight 10 000 (R_H = 110

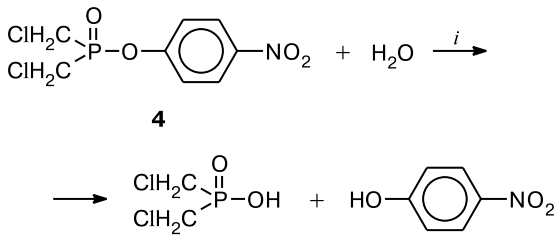
Table 1. Critical association concentrations for 2-hydroxybenzylated PEI in an H_2O—DMF (30 vol.% DMF) medium in the absence and in the presence of CHAB (conductometric method)

PEI, system	$CAC_1 \cdot 10^3$/mol L^{-1}	$CAC_2 \cdot 10^3$/mol L^{-1}
1	1.8	11.0
2	0.8	9.0
1—CHAB	2.0	6.3
2—CHAB	1.0	3.9

and 4 nm,[31] respectively). Probably, this indicates the formation of aggregates by hydrophobic interactions.

The catalytic activity of modified polyethyleneimine—cationic surfactant systems in H_2O—DMF medium was studied for the hydrolysis of 4-nitrophenylbis(chloromethyl)phosphinate (**4**) (Scheme 1).

Scheme 1



i. PEI, H_2O—DMF (30 vol.% DMF).

The plots of the apparent rate constants (k_{app}) for the hydrolysis of substrate **4** in individual solutions of PEI **1** and **2** and in their mixtures with cationic surfactants are shown in Figs 4 and 5. The hydrophobicity of PEI exerts almost no effect on their catalytic activity. The presence of cationic surfactants increases the apparent rate constants and shifts the dependences toward lower pH values, which makes it possible to use these catalytic systems for the acceleration of hydrolysis of *p*-nitrophenylphosphinates under mild conditions (pH 7—8).

The presence of CHAB affects the k_{app} values for PEI **2** more significantly than those for PEI **1**. The plots of the increase in the hydrolysis rate ($k_{app} \cdot k_0^{-1}$) *vs* pH for the systems based on PEI **2** are shown in Fig. 6. An increase in the number of 2-hydroxyethyl fragments in the head groups

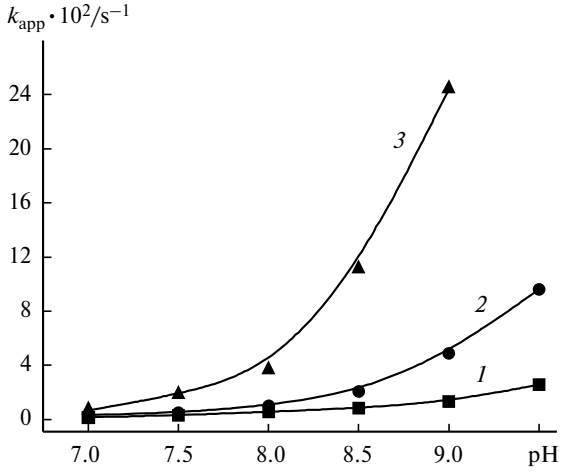


Fig. 4. Plots of the apparent rate constant (k_{app}/s^{-1}) for the hydrolysis of substrate **4** *vs* pH of the medium for PEI **1** (*1*) and **1**—CTAB (*2*) and **1**—CDHAB (*3*) systems (C_{PEI} = 0.01 mol L^{-1}, C_{Surf} = 0.01 mol L^{-1}, H_2O—DMF, 25 °C).

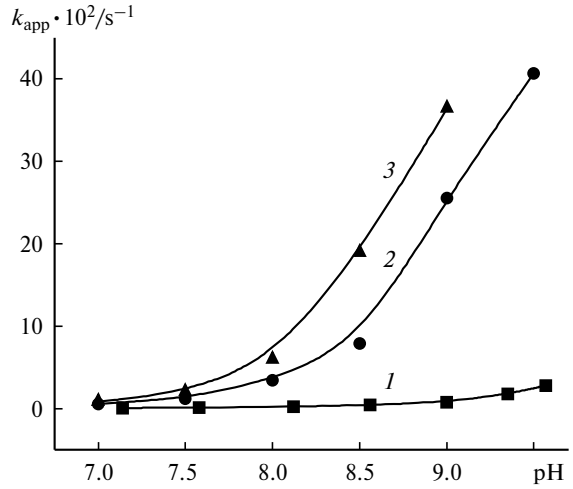


Fig. 5. Plots of the apparent rate constant (k_{app}/s^{-1}) for the hydrolysis of substrate **4** *vs* pH of the medium for PEI **2** (*1*) and **2**—CHAB (*2*) and **2**—CDHAB (*3*) systems (C_{PEI} = 0.01 mol L^{-1}, C_{Surf} = 0.01 mol L^{-1}, H_2O—DMF, 25 °C).

of cationic surfactants enhances the catalytic activity: on going from CHAB to CDHAB, the catalytic effect increases and the reaction in a **2**—CDHAB system at pH 7 is accelerated by approximately 170 times, which can be a consequence of the formation of polymer-colloidal complexes in the systems studied.

It is known that in the presence of PEI the hydrolysis of phosphorus acid esters follows the general basic mechanism.[32] This mechanism was confirmed[20] to retain in polymer-colloidal systems.

The plots of the apparent hydrolysis rate constant *vs* concentration of the cationic surfactants with the variation of different parameters are presented in Figs 7—9. All

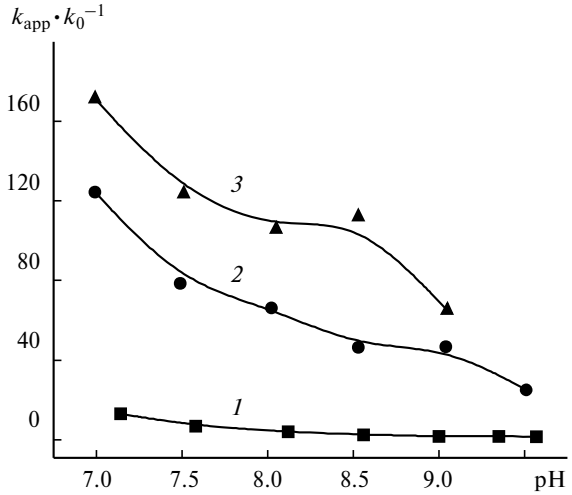


Fig. 6. Plots of the increase in the rate ($k_{app} \cdot k_0^{-1}$) of the hydrolysis of substrate **4** *vs* pH of the medium for PEI **2** (*1*) and **2**—CHAB (*2*) and **2**—CDHAB (*3*) systems (C_{PEI} = 0.01 mol L^{-1}, C_{Surf} = 0.01 mol L^{-1}, H_2O—DMF, 25 °C).

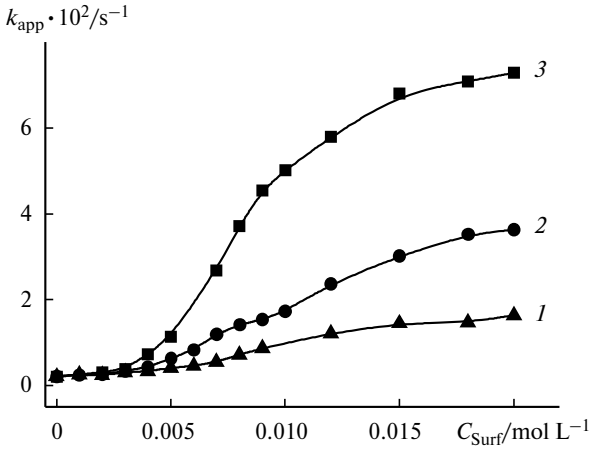


Fig. 7. Plots of the apparent rate constant (k_{app}/s^{-1}) for the hydrolysis of substrate **4** *vs* surfactant concentration (C_{Surf}) for **3**—CPAB (*1*), **3**—CHAB (*2*), and **3**—CDHAB (*3*) systems (C_{PEI} = 0.01 mol L^{-1}, H_2O—DMF, 25 °C).

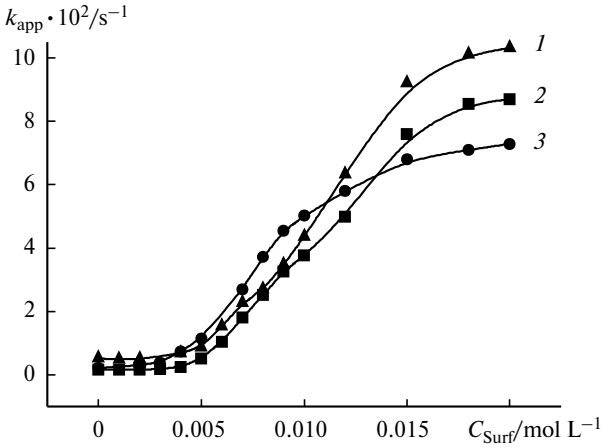


Fig. 8. Plots of the apparent rate constant (k_{app}/s^{-1}) for the hydrolysis of substrate **4** *vs* surfactant concentration (C_{Surf}) in PEI—CDHAB systems for PEI **1** (*1*), **2** (*2*), and **3** (*3*) (C_{PEI} = = 0.01 mol L^{-1}, H_2O—DMF, 25 °C).

kinetic dependences are similar reaching a plateau at some value of concentration. This suggests that the hydrolysis reaction itself is preceded by the primary binding of the substrate by polymer-colloidal aggregates analogously to the formation of enzyme—substrate complexes. The kinetic dependences were analyzed using Eq. (1). The calculation results are listed in Table 2. A comparison of the cationic surfactants with one hydroxyalkyl group shows that CHAB (see Fig. 7) containing the hydroxyethyl fragment is more active than CPAB which has the hydroxypropyl group. Probably, this is due to the steric hindrances to aggregation in the case of bulky hydroxypropyl fragments and, hence, to weakening the aggregate ability for micelle formation and solubilization. The CDHAB is more catalytically active than CHAB, because the presence of two hydroxyalkyl groups creates more possibilities for the formation of polymer-colloidal complexes due to the hydrogen bonding.

As can be seen from the data in Table 2, in the series of the 2-hydroxybenzylated PEI considered, the highest binding constant value was obtained for **2**—CDHAB systems.

Table 2. Parameters of the hydrolysis of 4-nitrophenylbis-(chloromethyl)phosphinate in the polymer-colloidal systems* (pH 8, 25 °C)

System	k_m/s^{-1}	K_b /L mol^{-1}	CMC · 10^3 /mol L^{-1}	$k_m \cdot k_0^{-1}$
1—CDHAB	0.459	18	4.7	920
2—CDHAB	0.089	160	5.4	180
3—CDHAB	0.138	82	3.8	275
3—CHAB	0.037	130	3.7	75
3—CHAB	0.0275	84	4.9	55

* k_0 is the rate constant of the non-catalytic process at pH 8, 25 °C.

However, in this case the acceleration of the reaction is low because of the low hydrolysis rate constant in the polymer-colloidal phase. A comparison of the activity of PEI **1**—**3** with the same surfactant (CDHAB) shows that the highest catalytic effect was obtained for PEI **1** containing no hydrophobic radical in the hydroxybenzyl substituent. The reaction rate in this system increases by more than two orders of magnitude.

We studied the kinetics of hydrolysis of phosphinate **4** in the **3**—CHAB system at different temperatures (see Fig. 9) and calculated the effective activation parameters (activation enthalpy $\Delta H_{eff}^{\neq}$ and activation entropy $\Delta S_{eff}^{\neq}$) as functions of the surfactant concentration (Fig. 10). As can be seen from Fig. 9, the typical behavior of the temperature plots of the rate constant is found in the region below the CMC (region *A*) and when the reaction is en-

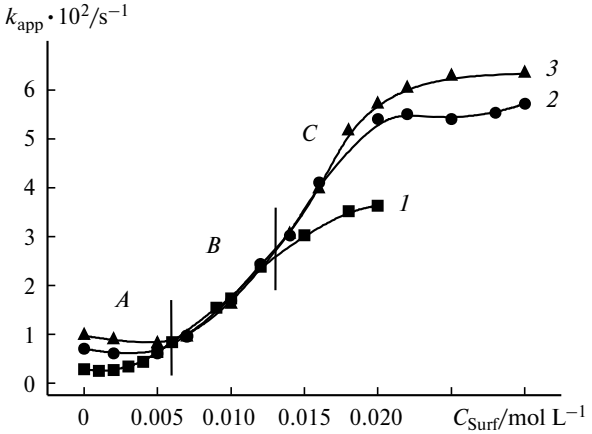


Fig. 9. Plots of the apparent rate constant (k_{app}/s^{-1}) for the hydrolysis of substrate **4** in a PEI **3**—CHAB system *vs* surfactant concentration (C_{Surf}) at 25 (*1*), 40 (*2*), and 50 °C (*3*) (C_{PEI} = = 0.01 mol L^{-1}, H_2O—DMF).

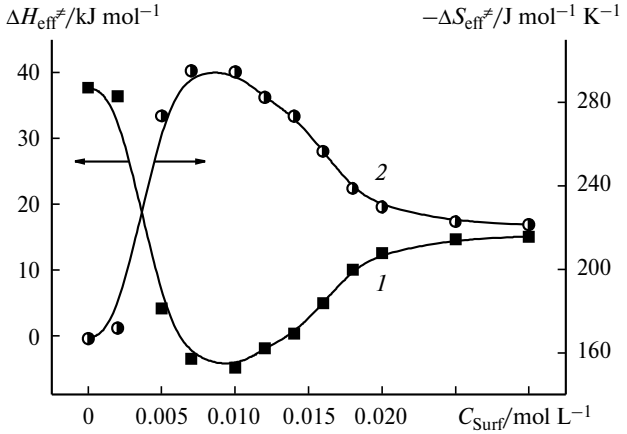


Fig. 10. Plots of the effective activation parameters for the hydrolysis of substrate **4** in a PEI **3**—CHAB system *vs* surfactant concentration (C_{Surf}): $\Delta H_{eff}^{\neq}$ (*1*) and $\Delta S_{eff}^{\neq}$ (*2*).

tirely transferred into micelles (region *C* corresponding to the plateau). In the region of the kinetic dependences (*B*), the rate constants remain unchanged with temperature. This behavior can probably be due to the following reasons. The apparent rate constant reflects the change in the reactivity of substrate **4** with the temperature change in the aqueous and micellar phases, respectively. Region *B* corresponds to the transfer of the reaction from the aqueous to micellar phase and reflects the contribution of different process: the change in the reactivity, micelle-forming properties, and solubilizing activity of the aggregates with temperature. Probably, tendencies for a change in these parameters with the temperature variation can be non-coincident and can mutually compensate each other. This appears as the imaginary absence of a change in the apparent rate constant with the temperature increase.

According to Fig. 10, the compensation character of the change in the parameters $\Delta H_{eff}^{\neq}$ and $\Delta S_{eff}^{\neq}$ is observed with an increase in the surfactant concentration, and region *B* coincides with the minimum values of both activation parameters. As a whole, the transfer of the reaction from the aqueous to micellar phase is accompanied by the favorable change in the activation enthalpy from 38 (in water) to 15 kJ mol^{-1} (in micelles) and a decrease in the activation entropy from -167 to -221 J mol^{-1} K^{-1}. It can be concluded that the increase in the reaction rate is controlled by a change in the effective values of the activation enthalpy.

Thus, 2-hydroxybenzylated PEI and cationic surfactants can form mixed aggregates exerting a catalytic effect on the hydrolysis of phosphorus acid esters in an H_2O—DMF (30 vol.% DMF) medium under mild conditions. The catalytic effect of these systems depends on the structure and concentration of the cationic surfactant, pH of the solution, and temperature. In the series of surfactants considered, the polymer-colloidal systems based on CDHAB possess the highest catalytic activity (an increase in the reaction rate by more than two orders of magnitude).

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