

Catalytic Effect of Multicomponent Supramolecular Systems in Phosphoryl-Group Transfer Reactions

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Abstract—The catalytic effect of the cetyltrimethylammonium bromide–poly(ethylenimine)–water system in the hydrolysis reactions of phosphonic acid esters (an increase in the rate constant by three orders of magnitude) is due to the concentration of reactants in polymer–colloid complexes and changes in their microenvironments. The catalyst efficiency depends on the structures of substrates, surfactants, and polymers.

INTRODUCTION

The catalysis of chemical reactions in organized media occurs in nanoparticles formed in a microheterogeneous solution. The binding of reactants on the surface or within nanoreactors results in a dramatic increase in their local concentrations, a change in the microenvironment, and, as a consequence, a change in the reactivity of compounds [1, 2]. Analogous catalytic effects take place in enzyme systems [3]; therefore, it is of interest to study simpler model systems based on the micellar solutions of surfactants. Aqueous surfactant–polymer systems are promising test materials, which have been little studied [4, 5]. A wide range of practically useful properties of polymer–colloid solutions and the possibility of controlling them purposefully by

varying the composition of the system is an incentive for the development of this line.

Previously, we studied the catalytic effect of the cationic surfactant–poly(ethylenimine) (molecular weight of 30000) (PEI₃₀)–water system in the nucleophilic substitution reactions of the esters of tetracoordinated-phosphorus acids [6, 7]. We found that the acceleration of reaction essentially depends on the nature of the substrate and the surfactant and on the concentration of the polymer. In this work, we studied the physical properties and the catalytic effect of the cetyltrimethylammonium bromide (CTAB)–poly(ethylenimine) (molecular weight of 10000) (PEI₁₀)–water polymer–colloid system in the hydrolysis reactions of phosphonic acid esters **1–4** (scheme).



1—X = NO₂, R = C₂H₅, **2**—X = NO₂, R = n-C₆H₁₃, **3**—R = C₂H₅; X = Br, **4**—R = C₂H₅, X = H.

Scheme.

EXPERIMENTAL

Compounds **1–4** were synthesized in accordance with a published procedure [8]. CTAB (Sigma) and PEI₁₀ (Aldrich) were used. Dielectrometric titration was performed in accordance with a published procedure [9]. The permittivities of solution series were determined using a setup composed of an E12-1 instrument, which works on the principle of beats, and a measuring cell, which was a thermostated capacitor [10]. The kinetics of hydrolysis was studied spectrophotometrically on a Specord M-400 instrument under

pseudo-first-order conditions by monitoring the absorption of the *para*-nitrophenolate anion. The observed rate constants (k_{obs}) were determined from the equation $\ln(A_{\infty} - A) = -k_{\text{obs}}t + \text{const}$, where A and A_{∞} are the absorbances of solutions at the point t in time and after completion of the reaction, respectively. They were calculated using the weighted least-squares method from the arithmetic means of three measurements differing by no more than 5%.

To obtain quantitative data (reactant binding constants and rate constants in nanoaggregates), the $k_{\text{obs}} - C_{\text{surfactant}}$

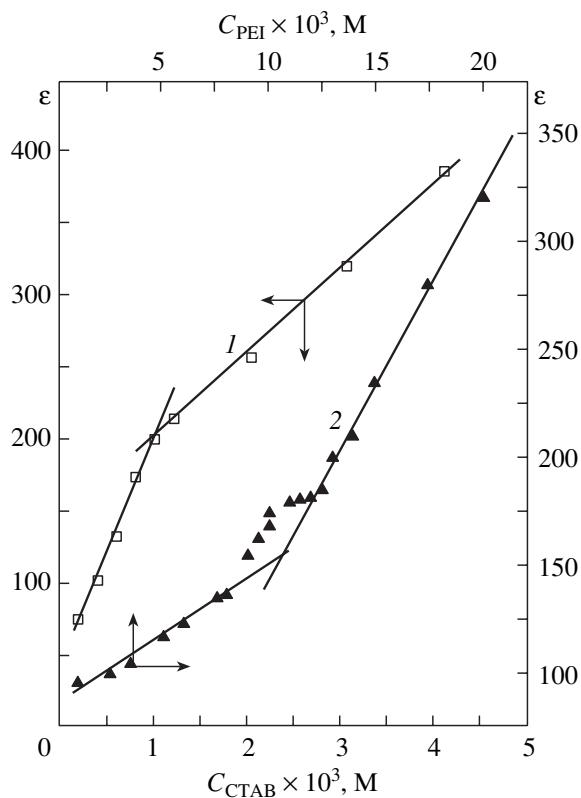


Fig. 1. Permittivity of aqueous (1) CTAB or (2) PEI₁₀ solutions as a function of concentration; $T = 20^\circ\text{C}$.

kinetic relations were analyzed in terms of the pseudophase model using the equations given below.

The following equation, which is applicable to enzymatic and micellar catalysis [2], was used for the analysis of kinetic data obtained in PEI₁₀ solutions:

$$k_{\text{obs}} = \frac{k_{\text{aq}} + k_{\text{mic}} K'_S C}{1 + K'_S C}, \quad (1)$$

where k_{aq} and k_{mic} (s^{-1}) are the pseudo-first-order rate constants in an aqueous phase and a catalytic complex, respectively; K'_S (l/mol) is the reduced binding constant of the substrate; and C is the concentration of an associated surfactant or the polymer.

The kinetic data for the systems containing surfactants were analyzed in terms of the pseudophase model using the equation [1]

$$k'_{\text{obs}} = \frac{k_{2,\text{aq}} + \frac{k_{2,\text{mic}}}{V} K_S K_{\text{Nu}} C}{(1 + K_S C)(1 + K_{\text{Nu}} C)}, \quad (2)$$

where k'_{obs} ($\text{mol}^{-1} \text{s}^{-1}$) is the second-order rate constant obtained by dividing k_{obs} by the total nucleophile concentration; $k_{2,\text{aq}}$ and $k_{2,\text{mic}}$ ($\text{mol}^{-1} \text{s}^{-1}$) are the second-order rate constants in the aqueous and micellar

phases, respectively; K_S and K_{Nu} (l/mol) are the substrate and nucleophile binding constants, respectively; V is the molar volume of the surfactant; and C is the surfactant concentration below the critical micelle concentration (CMC).

The contributions of various factors to the micellar effect can be quantitatively evaluated using the following modified form of Eq. (2):

$$(k_{\text{obs}}/k_w)_{\text{max}} = \frac{k_{2,\text{mic}}}{k_{2,\text{ad}} V} \frac{K_S K_{\text{Nu}}}{(\sqrt{K_S} + \sqrt{K_{\text{Nu}}})^2},$$

where the first term on the right (F_m) characterizes the effect of changes in the reactant microenvironments upon the transfer of the reaction from an aqueous phase to a micellar phase, whereas the second term (F_c) characterizes the effect of concentrating reactants in micelles.

RESULTS AND DISCUSSION

According to published data [11], in mixed aqueous solutions containing a surfactant and a polymer, structures can be formed with the participation of both of the components. A surfactant concentration that corresponds to the onset of combined aggregation is referred to as the critical aggregation concentration (CAC). Above this concentration, small surfactant globules bound to a polymer chain are formed in solution. On reaching the polymer saturation concentration (PSC), free micelles are formed in solution. The identification of combined structures and the concentration boundaries of their occurrence was performed by measuring the physical characteristics of a mixed solution (surface tension, electric conductivity, viscosity, permittivity, etc.) as functions of surfactant concentration at a fixed concentration of the polymer. Figures 1 and 2 demonstrate the results of a dielectrometric experiment for individual solutions of CTAB and PEI₁₀ and for the CTAB-PEI₁₀-water system at $C_{\text{PEI}_{10}} = 0.02$ and 0.2 M .

The permittivity (ϵ) plotted as a function of CTAB or PEI₁₀ concentration exhibited an inflection point at 0.001 or 0.01 M , respectively. For a micellar CTAB solution, the concentration at the inflection point was close to the CMC of 0.00085 M , which was determined using alternative techniques [12]. The value of 0.01 M , which corresponds to the onset of associative processes in a PEI₁₀ solution, is consistent with the value determined by conductometry for an aqueous PEI₃₀ solution [6]. It follows from Fig. 2 that the shape of the ϵ - C_{CTAB} curve for a mixed solution is significantly different from that for individual solutions, and it exhibits two pronounced inflection points, which correspond to CAC and PSC. The values of CAC for both PEI concentrations were close to the CMC of CTAB, whereas the value of PSC somewhat decreased with polyelectrolyte concentration. The examples of both decreasing and increasing concentration regions of the existence of

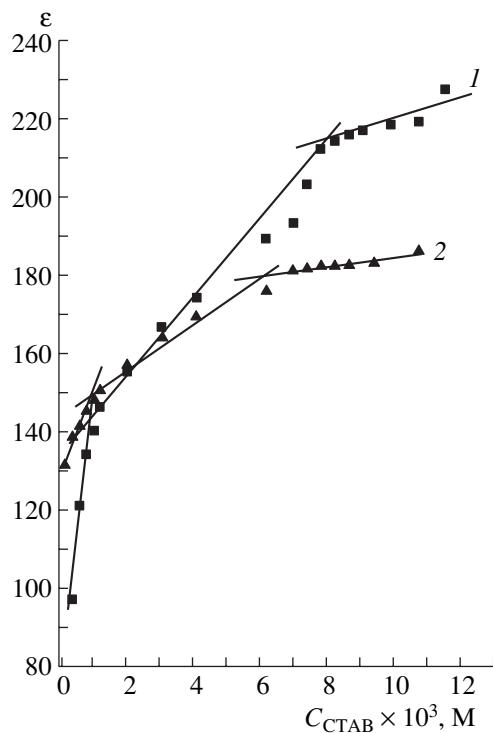


Fig. 2. Permittivity of aqueous CTAB-PEI₁₀ solutions as a function of CTAB concentration at a PEI₁₀ concentration of (1) 0.02 or (2) 0.2 M; $T = 20^\circ\text{C}$.

combined structures with polymer concentration were reported in the literature [13, 14]. Note that the values of PSC in Fig. 2 are close to those obtained previously [6] for the cationic surfactant-PEI₃₀-water systems. It is of interest to follow the stoichiometric composition of surfactant-polymer complexes at the inflection points of curves shown in Fig. 2. The critical point that corresponds to CAC was reached at the molar ratio CTAB/PEI = 1 : 20 or 1 : 200 for 0.02 or 0.2 M PEI, respectively. The critical point that corresponds to PSC was observed at the molar ratio CTAB/PEI = 1 : 2.5 or 1 : 32 for the above polymer concentrations, respectively.

In a kinetic experiment, we studied the reactivity of compounds **1-4** in the CTAB-PEI₁₀-water system at 0.02 M PEI₁₀ as a function of CTAB concentration (Fig. 3). The given data suggest that the maximum value of the observed rate constant in the test substrate series decreased in the order **2** > **1** > **4** > **3**. For comparison, note that k_{obs} for the reaction of alkaline hydrolysis in the absence of surfactants or in a micellar CTAB solution changed in the order **1** > **2** > **3** > **4** or **2** > **1** > **4** > **3**, respectively [15]. The above reactivity orders are different because the electronic and steric factors of substituents at the reaction center are the main controlling factors in an aqueous solution in the absence of the surfactant and the polymer, whereas the binding of reactants by nanoaggregates, which correlates with the

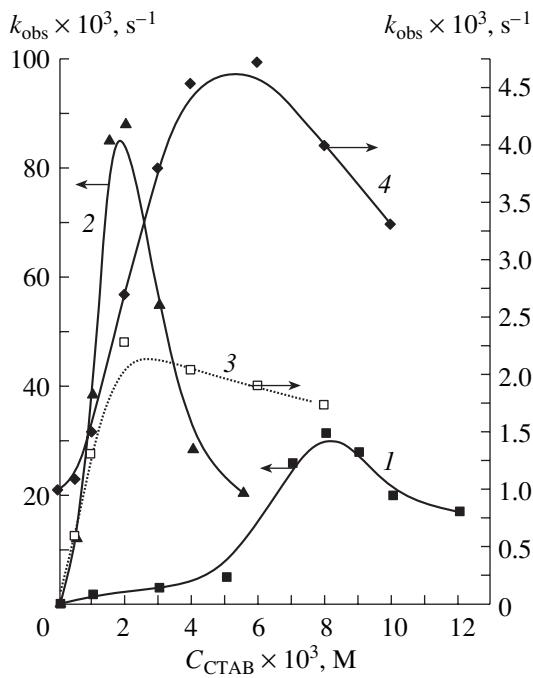


Fig. 3. Observed rate constants of hydrolysis of phosphonates (1) **1**, (2) **2**, (3) **3**, and (4) **4** in the CTAB-PEI₁₀-water system as functions of CTAB concentration at a 0.02 M concentration of PEI₁₀; $T = 30^\circ\text{C}$.

hydrophobicity of compounds, makes a significant contribution to the catalytic effect in organized media.

Figure 4 demonstrates kinetic data for the hydrolysis of substrates **1**, **2**, and **4** in a PEI₁₀ solution. The k_{obs} - $C_{\text{PEI}_{10}}$ relationship for compound **3** was not obtained because of the poor solubility of the substrate. Previously [16, 17], it was found that the base catalysis of the hydrolysis of phosphonic acid esters was observed in the presence of amines, including PEI. The shape of kinetic curves in Fig. 4 is indicative of the formation of a catalytic substrate-polymer complex, and it can be indirect evidence for the aggregation of PEI₁₀ in an aqueous solution; this is consistent with data shown in Fig. 1. The greatest effective rate constant was obtained for compound **1**, whereas phosphonates **2** and **4** exhibited equal activities; however, in the case of **4**, catalysis began at lower polymer concentrations. The quantitative analysis of kinetic data (Fig. 4) with the use of Eq. (1) allowed us to calculate the binding constants (K'_S) and the catalytic pseudo-first-order rate constants (k_{mic}) as follows: $K'_S = 104 \text{ l/mol}$ and $k_{\text{mic}} = 0.0033 \text{ s}^{-1}$ (**1**), $K'_S = 287 \text{ l/mol}$ and $k_{\text{mic}} = 0.0015 \text{ s}^{-1}$ (**2**), and $K'_S = 64 \text{ l/mol}$ and $k_{\text{mic}} = 0.0015 \text{ s}^{-1}$ (**4**). A comparison between the catalytic effects of PEI₁₀ and PEI₃₀ [6] for substrates **1** and **2** indicates that in both cases k_{obs} was higher for phosphonate **1**; however, in general, the

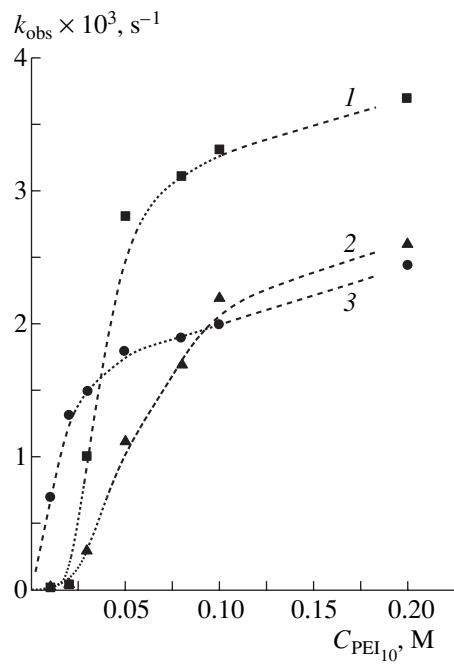


Fig. 4. Observed rate constants of hydrolysis of phosphonates (1) **1**, (2) **2**, and (3) **4** as functions of PEI_{10} concentration in water; $T = 30^\circ\text{C}$.

value of k_{obs} was greater by a factor of 3–4 in the presence of PEI_{10} . Note that changes in reactivity exhibited different tendencies in the individual solutions of CTAB and PEI and in the mixed system (Fig. 3). This is an additional argument for the occurrence of the reaction in catalytic complexes formed by both of the system components.

The plots in Fig. 3 indicate that catalysis of all the test substrates was observed in the CTAB– PEI_{10} –water system, although the catalytic effect significantly depended on the structure of the phosphonate and varied by a factor in the range 4–1500 (see table). The kinetic data were analyzed in terms of the pseudophase approach with the use of Eq. (2); the table summarizes the results of the simulation. According to these data, the inversion of reactivity in the pairs of substrates **1**, **2** and **3**, **4** in the mixed polymer–colloid system, as compared with aqueous alkaline hydrolysis, was due to both a change in the reaction mechanism in the presence of

PEI (a change to basic hydrolysis) and the specific character of catalysis in organized media, the main factor of which is the binding of reactants by nanoaggregates. For substrates **1** and **2**, the effects of substituents in aqueous and micellar phases were equal, as evidenced by a decrease in $k_{2, \text{mic}}$ with increasing hydrocarbon radical at the reaction center. However, in this case, the binding of reactants, including a more hydrophobic substrate, considerably increased; this is the controlling factor in this instance. Previously [6], it was found that in the CTAB– PEI_{30} –water system k_{obs} was lower in the case of substrate **2**, for which a decrease in $k_{2, \text{mic}}$ is not compensated by an increase in the concentration effect. Note that the balance of concentration and micellar microenvironment factors depends not only on the nature of the substrate and the polymer but also on the nature of the surfactant, and the activity of **2** in the cetyltrimethylammonium bromide– PEI_{30} –water system was higher than that of **1** [6].

The reactivity of substrates **3** and **4** toward PEI_{10} in the absence of surfactants was very different: the hydrolysis of phosphonate **3** was practically uncatalyzed by the polymer, whereas the reaction of **4** was accelerated even at low concentrations of PEI_{10} . The above difference is responsible for the rather high catalytic effect of polymer–colloid complexes for **3** and the insignificant effect for **4**. According to data given in the table, phosphonate **3** was effectively bound to nanoaggregates; it exhibited a maximum binding constant in the substrate series. At the same time, the lowest reactivity in a micellar pseudophase was detected for this compound in the test series; this is likely due to its unfavorable localization or orientation. The value of $k_{2, \text{mic}}$ for **3** is lower than those of the other compounds by one order of magnitude.

Thus, we studied the reactivity of a number of phosphonic acid esters in the CTAB– PEI_{10} –water mixed system. We found that the catalytic effect (an increase in the rate constant) in the test substrate series varied over a wide range and was as great as three orders of magnitude in the case of the most hydrophobic phosphonate **2**. The mechanism of the catalytic action includes the binding of reactants in polymer–colloid complexes, the formation of which was supported by the dielectric titration of a mixed solution. A comparison between the experimental results and previous

Results of the quantitative analysis of kinetic data (Fig. 3) in the CTAB–PEI–water system with the use of Eq. (2)

Substrate	$k_{2, \text{aq}}, \text{1 mol}^{-1} \text{s}^{-1}$	$(k_{\text{obs}}/k_{\text{aq}})_{\text{max}}$	$K_S, \text{l/mol}$	$K_{\text{Nu}}, \text{l/mol}$	$k_{2, \text{mic}}, \text{1 mol}^{-1} \text{s}^{-1}$	F_c	F_m
1	0.0025	626	250	220	0.007	195	2.86
2	0.0025	1500	950	320	0.0043	590	1.77
3	0.00027*	420	4600	90	0.0005	230	1.8
4	0.07	4	1690	30	0.004	75	0.06

* Reduced rate constant of alkaline hydrolysis.

data allowed us to conclude that the reactivity of phosphonates and the catalytic effect of a polymer–colloid system significantly depend on the nature of the substrate and the surfactant and on the molecular weight and concentration of the polymer, which affect a balance between concentration and micellar microenvironment factors.

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REFERENCES

1. Berezin, I.V., Martinek, K., and Yatsimirskii, A.K., *Usp. Khim.*, 1973, vol. 42, p. 1729.
2. Fendler, E.J. and Fendler, J.H., *Adv. Phys. Org. Chem.*, 1970, vol. 8, p. 271.
3. Berezin, I.V. and Martinek, K., *Osnovy fizicheskoi khimii fermentativnogo kataliza* (Basics of Physical Chemistry of Enzymatic Catalysis), Moscow: Vysshaya Shkola, 1977.
4. Lindman, B. and Thalberg, K., *Interactions of Surfactants with Polymers and Proteins*, Goddard, E.D. and Ananthapadmanabhan, K.P., Eds., Boca Raton: CRC, 1993, part 5.
5. Goddard, E.D., *Colloids Surf.*, 1986, vol. 19, p. 255.
6. Kudryavtsev, D.B., Bakeeva, R.F., Kudryavtseva, L.A., Zakharova, L.Y., and Sopin, V.F., *Mendeleev Commun.*, 2000, vol. 10, no. 5, p. 202.
7. Bakeeva, R.F., Kudryavtsev, D.B., Zakharova, L.Y., Kudryavtseva, L.A., Raevska, A., and Sopin, V.F., *Mol. Cryst. Liq. Cryst.*, 2001, vol. 367, p. 585.
8. US Patent 2922810.
9. Gur'yanova, E.N., Gol'dshtein, I.P., and Romm, I.P., *Donorno-aktseptornaya svyaz'* (Donor–Acceptor Bond), Moscow: Khimiya, 1973.
10. Nigmatullin, R.Sh., Vyaselev, M.R., and Shatunov, V.S., *Zavod. Lab.*, 1964, no. 30, p. 500.
11. Brackman, J.C. and Engberts, J.B.F.N., *Chem. Soc. Rev.*, 1993, vol. 122, p. 85.
12. Shinoda, K., Nakagava, T., Tamamushi, B., and Isemura, T., *Colloidal Surfactants: Some Physicochemical Properties*, New York: Academic, 1963.
13. Witte, F.M. and Engberts, J.B.F.N., *J. Org. Chem.*, 1987, vol. 52, p. 4767.
14. Hou, Z., Li, Z., and Wang, H., *Colloid Polymer Sci.*, 1999, vol. 277, p. 1011.
15. Shagidullina, R.A., Zakharova, L.Y., Valeeva, F.G., and Kudryavtseva, L.A., *Izv. Akad. Nauk, Ser. Khim.*, 2001, vol. 7, p. 1125.
16. Bakeeva, R.F., Kudryavtseva, L.A., Bel'skii, V.E., and Ivanov, B.E., *Zh. Obshch. Khim.*, 1983, vol. 53, no. 5, p. 1058.
17. Bakeeva, R.F., Fedorov, S.B., Bel'skii, V.E., Kudryavtseva, L.A., and Ivanov, B.E., *Zh. Obshch. Khim.*, 1982, vol. 52, no. 11, p. 2503.