

Hydrolysis of phosphorus acid esters in the sodium bis(2-ethylhexyl)sulfosuccinate—*n*-nonane—polyethylene glycol—water supramolecular system before and after the percolation threshold

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The kinetics of alkaline hydrolysis of *O*-ethyl *O*-*p*-nitrophenyl chloromethylphosphonate in a sodium bis(2-ethylhexyl)sulfosuccinate—*n*-nonane—polyethylene glycol—water reverse micellar system was studied in a wide range of concentrations of the surfactant and water. The sign of the catalytic effect of micelles is inverted in the presence of the polymer. A sharp change in the apparent rate constant of hydrolysis of the phosphonate was found in a region of the temperature percolation threshold.

Key words: reverse micelles, microemulsions, polyethylene glycol, percolation, kinetics, hydrolysis, phosphorus acid esters, pseudo-phase model.

Investigation of the reaction kinetics in self-organized systems is a rapidly developed scientific area.^{1,2} Wide possibilities for direct control of rates of various processes are provided by reverse micellar systems^{3,4} consisting of three regions of different polarity: nanosized aqueous cores, nonpolar macrophase of an organic solvent (oil), and separating interfacial monolayer of a surfactant (Surf).^{5,6} A specific feature of the surface layer, whose thickness is determined, on the average, by the hydrocarbon radical length of Surf, is a sharp gradient of the medium polarity on going from the aqueous core to the oil phase of the organic solvent. The properties of water in the core of a reverse micelle are also unusual, because they depend on the mole ratio $W = [\text{H}_2\text{O}]/[\text{Surf}]$.^{7,8} Water in the core exists, most likely, in two states. At $W < 10$ –12 all H_2O molecules are bound to the charged head groups of the Surf and their counterions, and the properties of this hydrate-structured water differ strongly from those of normal water. At higher W water with the three-dimensional hydrogen bonding lattice appears in the center of the core. Its properties are similar to those of bulk water. The polarity gradient of the interfacial layer and two states of water in reverse micelles make it possible to govern the localization of the reactants and, hence, their reactivity by changing the component ratio.

Additional possibilities for controlling reaction constants in water/oil microemulsions are given by the struc-

tural factor, *i.e.*, change in the shape and size of the aggregates and, as a consequence, microenvironment of the reactants and their distribution between different microregions. Since the continuous phase in reverse micelles is formed by the nonpolar organic liquid, its conductivity is low and determined by exchange of ions formed due to the dissociation of the head groups of ionic surfactants between reverse micelles during their thermal motion. Under certain conditions, the conductivity of such systems increases sharply by several orders of magnitude.⁹ This phenomenon named electrical percolation is caused by cluster formation of reverse micelles and charge motion within the extended clusters.¹⁰ We have shown¹¹ that the reaction rates before and after the percolation threshold can differ substantially: the processes can be accelerated or retarded by inducing the cluster formation of microemulsion drops.

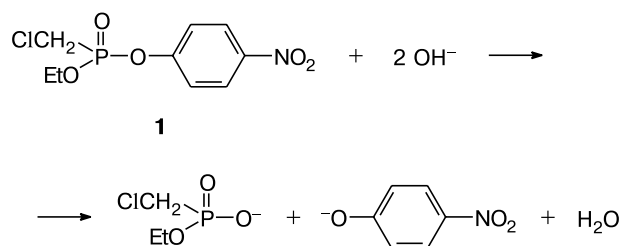
In this work, we continued to study the factors determining the catalytic effect of reverse microemulsions using as an example a system sodium bis(2-ethylhexyl)sulfosuccinate (Aerosol OT, AOT)—*n*-nonane—water—polyethylene glycol (PEG) with molecular weight 10 000. The introduction of the polymer allows a wider use of the structural factor of catalysis, because it enhances the probability of formation of new catalytic complexes involving reactants and components of the micellar system. A different influence of cluster formation of microemulsion

drops in the presence of the polymer on the reactivity of compounds can be expected.

Polymer-modified reverse micellar systems are poorly studied, and virtually no data on their catalytic properties are available. It is known^{12–16} that, depending on the nature and concentration of macromolecules, their localization and structure of combined Surf–polymer aggregates can differ considerably. A series of studies indicates that the structural characteristics of reverse micelles remain unchanged in the presence of hydrophilic polymers, *i.e.*, macromolecules are dissolved in the aqueous core.¹² A change in the micelle size in the presence of polymers was found in some studies. In particular, an increase in the size of reverse micelles upon the addition of small polymer additives followed by a decrease in the particle radius with its increasing concentration has been shown.¹³ According to published data,¹⁴ the structure and properties of polymer-colloidal complexes formed are determined by the size ratio of the polymer to microemulsion drop, *i.e.*, by the molecular weight and concentration of the polymer and the W parameter of the reverse systems.

We have previously¹⁷ obtained data characterizing the physicochemical properties and catalytic effect of Surf–polyelectrolyte compositions in reactions of nucleophilic substitution at the phosphorus atom. The catalytic effect of a reverse micellar system AOT–decane–water was studied in the region of reverse systems during alkaline hydrolysis of several esters of phosphorus acids. The change in the reactivity of the compounds above the percolation threshold has been found for the first time.^{11,18} In addition, we studied¹⁹ structural rearrangements of the AOT–*n*-nonane–water system in the presence of PEG, determined temperatures of the percolation threshold (T_p), and discussed the

Scheme 1



mechanism of inducing percolation transitions. In the AOT–*n*-nonane–PEG–water system, the radius of the aqueous core of micellar aggregates varies in an interval of 2–4 nm and the inertia radius of the polymer is ~3 nm.¹⁹ These data show that the polymer sizes are close to those of the aqueous core of micellar particles. The estimate of the stoichiometric composition of the combined structures indicates that the number of micelles per macromolecule changes from 0.5 to 50 depending on the W value and PEG concentration.¹⁹ Based on the aforesaid, one can expect that in the AOT–*n*-nonane–PEG–water system under study the forms of self-organization shown in Fig. 1 are preferential.

The task of this work is to study the effect of polymer on the catalytic effect of the AOT-based reverse micellar system and cluster formation of micellar particles on the kinetics of substrate hydrolysis in the absence and presence of PEG. For this purpose, we studied in parallel experiments the conductivity of the AOT–*n*-nonane–PEG–water system and kinetics of alkaline hydrolysis of *O*-ethyl *O*-*p*-nitrophenyl chloromethylphosphonate (**1**) (Scheme 1) in the temperature interval covering the region before and after the percolation threshold.

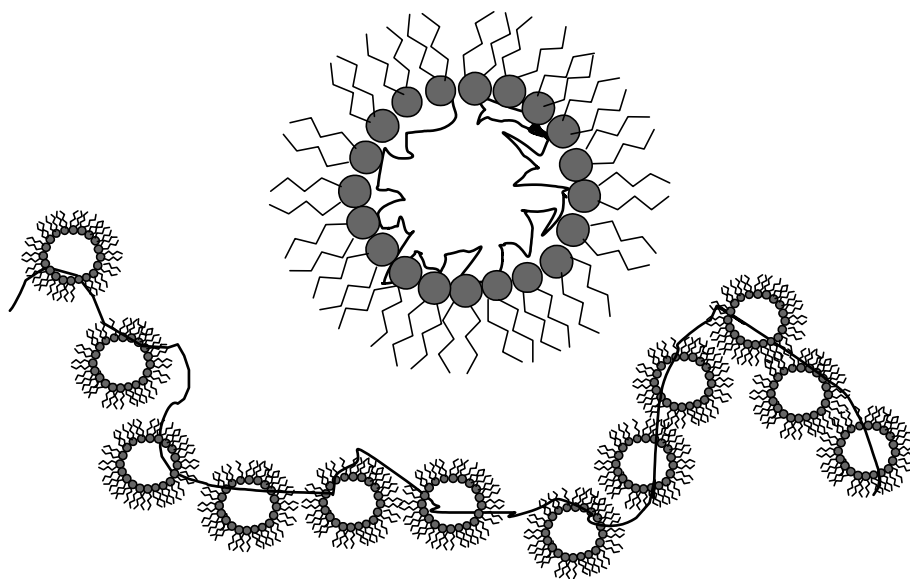


Fig. 1. Preferential forms of self-organization in the AOT–*n*-nonane–PEG–water system under study.

Phosphorus acid esters were chosen, because they are biologically active and widely used as pesticides, medical products, etc. Therefore, the problem of their hydrolytic stability is practically significant. The phosphoryl group transfer plays an important role in biocycles of highest organisms. In addition, this reaction is widely used in aqueous media in the absence of surfactants and in individual micellar solutions,² which allows correct estimation of the contribution of different components to the catalytic effect of more complicated micellar systems to be made.

Experimental

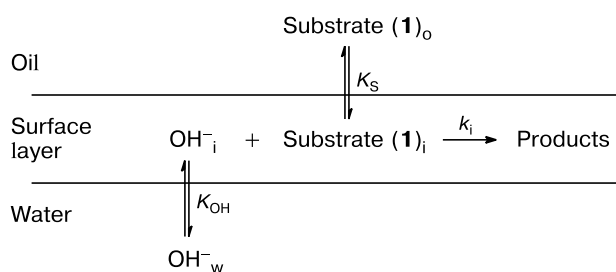
Compound **1** was synthesized according to a known procedure²⁰; AOT (Sigma) was used without preliminary purification. Reverse micellar systems were prepared by the addition of a specified amount of water to an AOT solution in *n*-nonane of specified concentration and vigorous shaking of the mixture until a transparent solution was formed. The mole ratios of the components of the system, viz., $W = [\text{H}_2\text{O}]/[\text{AOT}]$ and $Z = [n\text{-nonane}]/[\text{AOT}]$, were varied in the intervals 9.8–37.6 and 5–22, respectively. Micellar solutions were always optically homogeneous and, according to the phase diagram of AOT,²¹ corresponded to the region of reverse micellar systems.

Conductivity was measured with an OK 102/1 conductometer (Radelkis, Hungary) on a frequencies of 80 Hz and 3 kHz in a temperature-controlled planar-parallel cell. The temperature was maintained constant with an accuracy of ± 0.2 °C.

IR spectra were recorded on a Vector 22 FT-IR spectrometer (Bruker) with a resolution of 4 cm^{-1} . The spectra of solutions were detected in a region of 1000–4000 cm^{-1} in a fluorite cell with a thickness of 0.07 mm at 20 °C. The AOT concentration was maintained at a level of 0.07 mol L^{-1} , and the PEG concentration was 0.1 mol L^{-1} .

The hydrolysis kinetics was studied spectrophotometrically on a Specord M-400 instrument from a change in the absorption of the leaving group anion in the pseudo-first order regime. We have previously shown² that the alkaline hydrolysis of phosphonic esters occurs in the surface layer of the water/oil microemulsions (Scheme 2; indices "o," "w," and "i" indicate the oil phase, aqueous phase, and interface, respectively), whose amphiphilic properties provide the affinity to both reactants: hydrophobic substrate and hydrophilic nucleophile.

Scheme 2



Kinetic data for the reactions in ternary reverse systems were analyzed in the framework of the pseudo-phase model,²² according to which the reactants are distributed between the phases

and the reaction occurs in one or several pseudo-phases. For the reactions that occur in the surface layer, when one of the reactants (substrate) is distributed between the oil phase and surfactant monolayer and the second reactant (hydroxide ion) is distributed between the surface layer and water (see Scheme 2), the equation for the apparent rate constant (k_{app}) has the form²²

$$k_{\text{app}} = (k_i K_S K_{\text{OH}} [\text{OH}]_{\text{tot}}) / \{(K_S + Z)(K_{\text{OH}} + W)[\text{AOT}]\}, \quad (1)$$

where k_i/s^{-1} is the rate constants in terms of the nucleophile concentration expressed as the mole ratio $[\text{OH}]/[\text{AOT}]$; K_S is the partition constant of the substrate (S) between the oil phase and surfactant; K_{OH} is the partition constant of the hydroxide ion between the aqueous phase and surfactant; $[\text{OH}]_{\text{tot}}/\text{mol L}^{-1}$ is the total concentration of the OH⁻ ions. The k_i constant is related to the traditional constants of the pseudo-first (k_i'/s^{-1}) and second ($k_{2,i}/\text{L mol}^{-1} \text{s}^{-1}$) orders through the following correlations:

$$k_i' = k_i([\text{OH}]/[\text{AOT}]),$$

$$k_{2,i} = k_i V,$$

where V is the molar volume of the surfactant. The K_S and K_{OH} constants are represented by

$$K_S = ([S]_i[n\text{-C}_9\text{H}_{20}]) / ([S]_o[\text{AOT}]),$$

$$K_{\text{OH}} = ([\text{OH}]_i[\text{H}_2\text{O}]) / ([\text{OH}]_w[\text{AOT}]).$$

The main assumptions and approximations used in the pseudo-phase model were considered earlier.²³ The linearized form of Eq. (1)

$$1/(k_{\text{app}}[\text{AOT}]) = (K_{\text{OH}} + W)/(k_i K_{\text{OH}}[\text{OH}]) + \{(K_{\text{OH}} + W)/(k_i K_S K_{\text{OH}}[\text{OH}])\}Z \quad (2)$$

makes it possible to calculate the K_S , K_{OH} , and k_i values.

As can be seen from Eq. (2), the binding constant of the substrate K_S can easily be determined from the $1/(k_{\text{app}}[\text{AOT}])$ — Z plot as the ratio of the section cut in the ordinate to its slope. This model assumes that the K_S value remains unchanged when W is varied.

Results and Discussion

It can be assumed that the effect of the polymer on the rate of the model reaction depends on the polymer localization. Probably, the effect of PEG is maximum when it is solubilized near the surface layer, because this can result in a change in the physical properties of the interfacial zone where hydrolysis occurs and affect the binding of the reactants by the nanoaggregates.

The AOT—*n*-nonane—PEG—water micellar system was studied by FT-IR spectroscopy. The characteristic frequencies of reverse micellar solutions at different water contents and their assignment to functional groups are given in Table 1. Special attention is given to the change in the characteristic bands of AOT forming the interphase layer and water that forms the core of the particles upon the introduction of the polymer and variation of the W parameter (Fig. 2). As already mentioned,^{7,8} water in reverse micelles and microemulsions can exist in different

Table 1. Vibrational frequencies (cm^{-1}) of some functional groups in the IR spectra of the AOT—*n*-nonane—water system in the absence and presence of PEG at different $W = [\text{H}_2\text{O}]/[\text{AOT}]$

Vibration ²⁴	No PEG			$C_{\text{PEG}} = 0.1 \text{ mol L}^{-1}$		
	$W = 5$	$W = 10$	$W = 20$	$W = 5$	$W = 10$	$W = 20$
$\nu(\text{OH})$	3474	3462	3424	3451	3448	3423
$\delta_{\text{as}}(\text{CH}_3)$, $\delta(\text{CH}_2)$	1466	1466	1466	1466	1466	1466
$\delta_{\text{s}}(\text{CH}_3)$	1378	1378	1378	1378	1378	1378
$\nu(\text{C}=\text{O})$	1737	1737	1737	1737	1736	1736
$\delta(\text{OH})$	1640	1640	1639	1641	1643	1644

states: hydrate water (bound water) and bulk (free) water localized in the center of the core. The bulk water is accepted to appear at $W > 12$. As follows from the data shown in Fig. 2, the frequency of the band of the OH group ($\nu(\text{OH})$) depends on the W value: it decreases from 3487 to 3419 cm^{-1} with the W increase in the 1–20 interval, and then the dependence reaches saturation. This shift agrees with the thesis on different states of water in a reverse microemulsion. At low W values water exists in the bound state, and the $\nu(\text{OH})$ values differ from those for the absorption band of normal water. With an increase in the content of the latter in the system, bulk water appears in the center of the core, which is reflected by the shift of the $\nu(\text{OH})$ band and achievement of a plateau by the $\nu(\text{OH})$ — W plot.

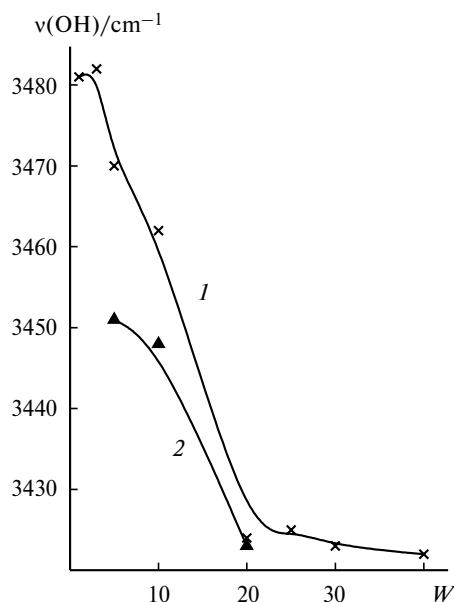


Fig. 2. Plots of the frequency of stretching vibrations of water ($\nu(\text{OH})$) in the IR spectrum of the AOT—*n*-nonane—water reverse micellar system vs. W parameter in the absence (1) and presence of PEG (2) ($C_{\text{PEG}} = 0.1 \text{ mol L}^{-1}$, $C_{\text{AOT}} = 0.07 \text{ mol L}^{-1}$).

In the presence of PEG, the characteristic frequencies of the functional groups of AOT change slightly (see Table 1). The main spectral changes concern the $\nu(\text{OH})$ — W plot. In particular, the range of changing the $\nu(\text{OH})$ values before reaching the plateau, covering the region of bound water, becomes narrower (see Fig. 2). Probably, this fact confirms that PEG is localized near the head AOT groups, where mainly bound water exists. These data agree with an assumption on PEG dissolution in the aqueous core of water/oil microemulsions.¹²

We also studied the kinetics of alkaline hydrolysis of phosphonate **1** in a wide range of concentrations of AOT, PEG, and water (parameter W controlling the size of the aqueous core). Continuing investigation of the role of the structural factor in micellar catalysis, we studied the effect of percolation transitions on the reactivity of the substrate. The kinetic data for the alkaline hydrolysis of phosphonate **1** in the AOT—*n*-nonane—PEG—water system at different AOT concentrations are presented in Fig. 3.

The basic kinetic tendencies (decrease in k_{app} with an increase in the concentrations of the surfactant and water) found earlier^{2,8,25,26} for the kinetic dependences of alkaline hydrolysis of phosphorus acid esters in the three-component micellar systems are retained in the presence of PEG. According to the data presented in Fig. 4, the character of the effect depends on the polymer concentration: at small PEG additives (0.02 – 0.05 mol L^{-1}) k_{app} somewhat decreases, and the further increase in the PEG

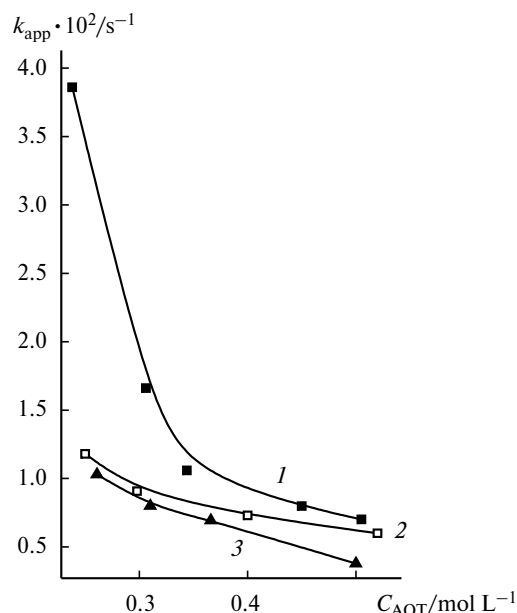


Fig. 3. Plots of the apparent rate constant of alkaline hydrolysis of phosphonate **1** (k_{app}) in the AOT—*n*-nonane—PEG—water system vs. AOT concentration (C_{AOT}) at $W = 9.8$ (1), 15.1 (2), and 20.0 (3) ($C_{\text{PEG}} = 0.02 \text{ mol L}^{-1}$, $C_{\text{NaOH}} = 0.01 \text{ mol L}^{-1}$, 25°C).

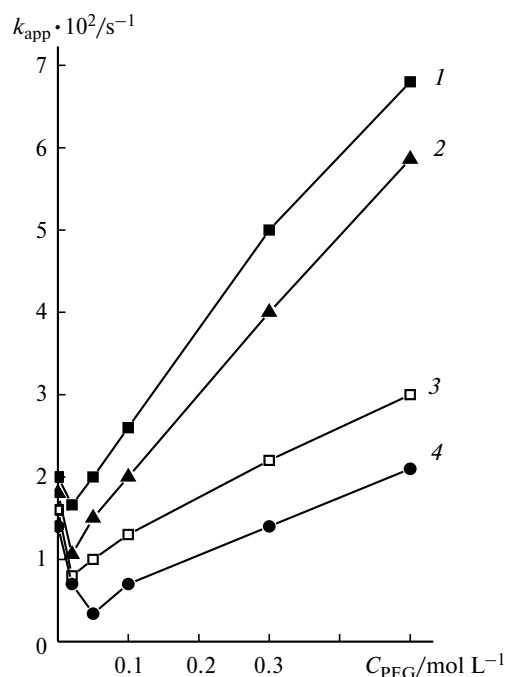


Fig. 4. Plots of the apparent rate constant of alkaline hydrolysis of phosphonate **1** (k_{app}) in the AOT–*n*-nonane–PEG–water system vs. PEG concentration (C_{PEG}) at $C_{AOT} = 0.26$ (1), 0.37 (2), 0.45 (3), and 0.50 mol L^{−1} (4) ($C_{NaOH} = 0.01$ mol L^{−1}, $W = 15.1$, 25 °C).

concentrations results in a considerable increase in the rate constant. The sign of the effect changes: transition from inhibition of the reaction to its catalysis occurs. Structural organization of the system changes, most likely, with an increase in the concentration of macromolecules, which modifies the surface layer and affects the reactivity of compounds. Perhaps, transitions between the structures shown in Fig. 1 are observed in this case.

Additional information on the polymer effect on the kinetics of the process was obtained by the graphical analysis of the kinetic data presented in Fig. 3 using Eq. (2) (Fig. 5). Although linearity is fulfilled in the $1/(k_{app}C_{AOT})$ – Z coordinates, Eq. (1) does not obey in the presence of the polymer. This is indicated by the negative slope of the sections and different in absolute values b/a ratios that characterize the binding constant of the substrate (Table 2). The most probable explanation is that the reaction zone changes in the presence of the polymer and distribution of the reactants shown in Scheme 2 is not invariant. In the presence of the polymer, the reaction in the surface layer makes no determining contribution to the apparent rate constant, which is indicated by unfulfilled Eq. (1). Inversion of the sign of the catalytic effect (see Fig. 4) is also related, most likely, to a change in the nature of aggregates in the presence of macromolecules and, as a consequence, to a change in the distribution of the reactants between different pseudo-phases.

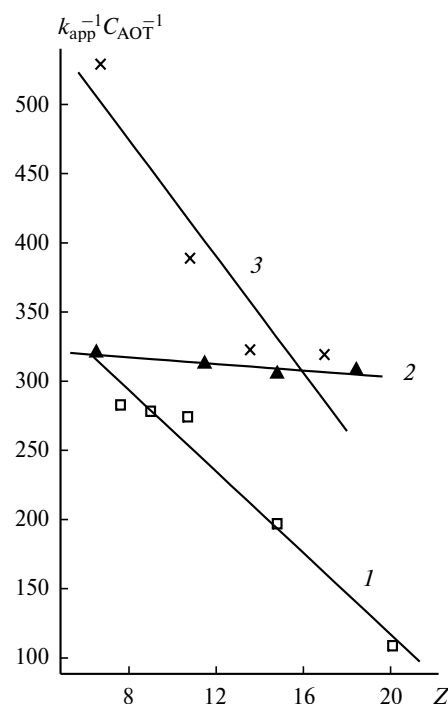


Fig. 5. Kinetic data presented in Fig. 3 linearized in the coordinates of Eq. (2) for $W = 9.8$ (1), 15.1 (2), and 20.0 (3).

The kinetics of alkaline hydrolysis of phosphonate **1** was studied in a wide temperature range. The kinetic data are shown in Fig. 6, *a* and *b* in the coordinates of the Arrhenius equation in the AOT–*n*-nonane–PEG–water system at different water contents and unchanged concentrations of AOT (0.35–0.45 mol L^{−1}) and PEG. In molecular solutions this plot is linear, and its slope determines the activation energy of the process. As shown previously,^{11,18} in the AOT–alkane–water reverse systems, the slope of the Arrhenius dependence changes sharply at some temperature T_{cr} dependent of the composition of the system. When the temperature rises to T_{cr} , the typical shape of the plots is observed in the absence of PEG: linear increase in the rate constant with temperature. A decrease in the slope or a negative slope of the plots is observed above T_{cr} . The sharp change in the reactivity of phosphorus acid esters above the percolation threshold is

Table 2. Analysis of the kinetic data obtained at different temperatures using Eqs (1) and (2)

W	$T = 25\text{ °C}$			$T = 40\text{ °C}$		
	a	b	K_S	a	b	K_S
9.8	411.0	−14.7	−28.0	3335	−163.4	−20.4
15.1	326.8	−1.1	−297	246	10.8	22.8
20.0	642.6	−21.0	−30.6	2910	−147.2	−19.8

Note. a is the section cut in the ordinate; b is the slope of the section (for the graphical solution of Eq. (2)).

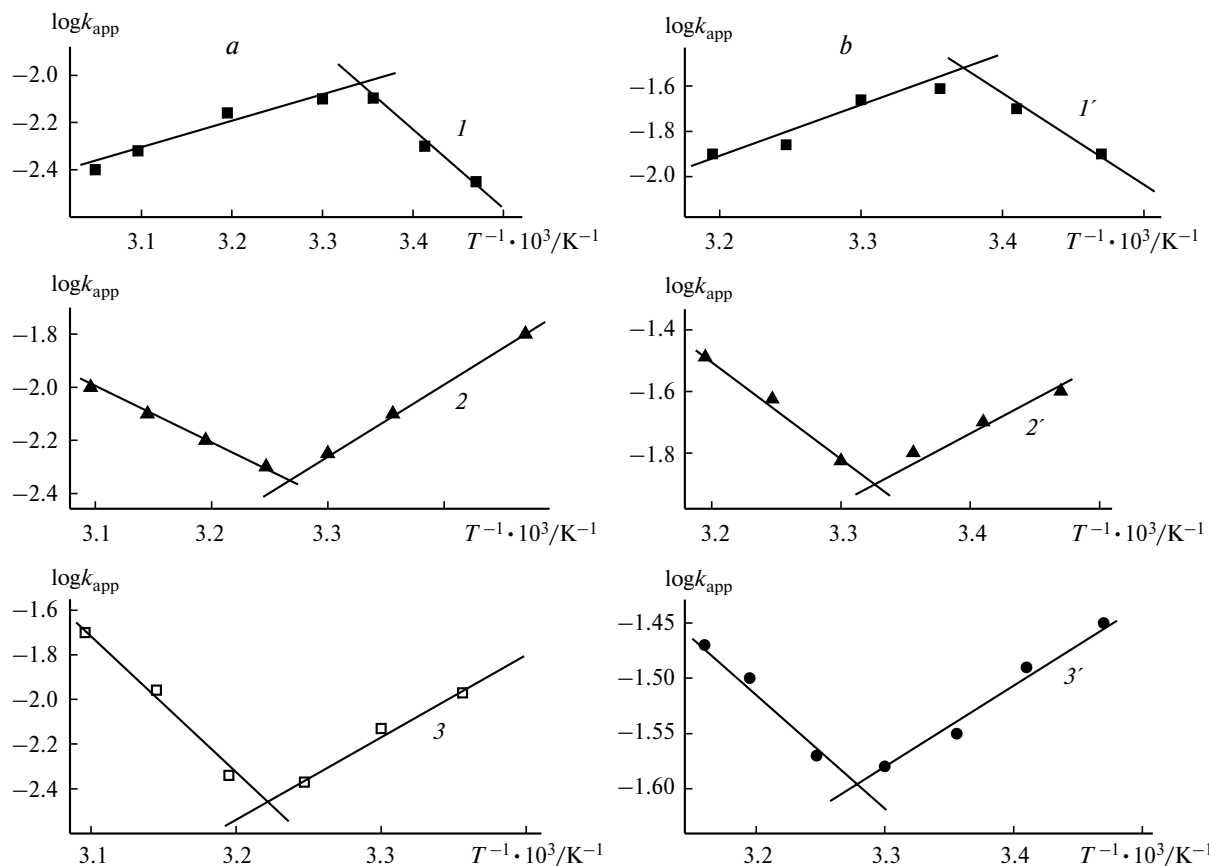


Fig. 6. Arrhenius plots of the apparent rate constant of alkaline hydrolysis of phosphonate **1** (k_{app}) in the AOT–*n*-nonane–PEG–water system at $C_{\text{PEG}} = 0.02$ (a) and 0.5 mol L^{-1} (b) and $W = 9.8$ (1, 1'), 15.1 (2, 2'), and 20.0 (3, 3') ($C_{\text{NaOH}} = 0.01 \text{ mol L}^{-1}$).

caused by a change in localization of the reactants due to the cluster formation of microemulsion drops, in particular, by the migration of the reaction zone to the region with a decreased microscopic polarity. Similarly, a break at T_{cr} is observed in the $\log k_{\text{app}} - 1/T$ plots (see Fig. 6); however, only at $W = 9.8$ the run of the plots coincides with that observed earlier in the absence of PEG. At $W = 15.1$ and 20.0 the typical Arrhenius dependence is fulfilled only above T_{cr} , and below this value the rate constant decreases with the temperature rise. Comparison of the T_{cr} values (see Fig. 6, a and b) and the temperature of percolation threshold (Table 3) shows that they are

close. Identical character of the T_{cr} and T_{p} values has been found previously¹⁸ for the AOT–alkane–water systems, which suggested a relationship between the reactivity of the compounds and cluster formation of reverse particles that causes the percolation phenomenon. The results obtained in the present work confirm this conclusion. Moreover, the quantitative data¹³ on the percolation transition in the water/oil microemulsions suggest that the preferential formation of combined structures according to the type presented in Fig. 1 (bottom) can induce cluster formation and the percolation transition in the system in the presence of the polymer. In other words, PEG can affect significantly the catalytic effect of reverse micelles due to both the formation of new Surf–polymer combined structures and promotion of cluster formation of microemulsion drops.

Analysis of the data presented in Fig. 6, a and b, shows that in the presence of the polymer at $W > 10$ tendencies for changing k_{app} with temperature change for opposite tendencies, *i.e.*, additives of macromolecules exert a substantial effect on the kinetics of hydrolysis of phosphonate **1** in the AOT-based reverse systems. This confirms the formation of combined structures in which the redistribution of reactants between pseudo-phases differs

Table 3. Values of T_{p} (conductometric data) and T_{cr} for the alkaline hydrolysis of phosphonate **1** in the AOT–*n*-nonane–PEG–water reverse micellar system (for experimental conditions, see Fig. 6, a)

W	$T_{\text{p}}/^{\circ}\text{C}$ at $C_{\text{PEG}}/\text{mol L}^{-1}$			$T_{\text{cr}}/^{\circ}\text{C}$ at $C_{\text{PEG}}/\text{mol L}^{-1}$		
	0	0.02	0.5	0	0.02	0.5
9.8	26	25	25	25	26	26
15.1	35	33.5	28	32	33	28.5
20.0	37	37	32	36	36.5	32

from that in individual microemulsions drops. Taking into account that the apparent rate constant k_{app} in reverse micelles depends, generally in a complicated way, on the contribution of the reaction in different microscopic regions, *i.e.*, on the partition of compounds and their reactivity in this microenvironment, the plots in Fig. 6, *a* and *b*, can be explained as follows. When the temperature rises, the reactants reallocate between different nanoregions due to cluster formation. This change in localization decreases the apparent rate constant of substrate hydrolysis due to a change in the microenvironment or a decrease in the partition coefficients of the reactants.¹⁸ This inhibition effect competes with the tendency for increasing the reactivity with the temperature rise typical of molecular solutions. Probably, at $W = 9.8$ and temperatures below T_{cr} the normal temperature effect of reaction acceleration predominates (see Fig. 6, *a* and *b*), and above this temperature coinciding with the percolation threshold prevailing is the inhibition effect caused by cluster formation. To the contrary, at $W = 15.1$ and 20.0 before the percolation threshold the change in the structural characteristics of the system and related relocation of the reactants exert the decisive effect on their reactivity, and above T_{cr} the normal increase in k_{app} with temperature is observed. The specific behavior of the AOT–*n*-nonane–PEG–water system at $W = 9.8$ is caused, most likely, by the fact that for this composition normal bulk water is absent from the reverse micelles and only water in hydrate shells of the head AOT groups is observed. Therefore, the localization of the polymer and reactants and their redistribution upon cluster formation can substantially differ from those occurring at higher W values, when the microemulsion particles are formed.

More detailed investigation of the hydrolysis kinetics of phosphonate **1** at $C_{\text{PEG}} = 0.02 \text{ mol L}^{-1}$ in the form of the $k_{\text{app}}-C_{\text{AOT}}$ plot at 40°C , *i.e.*, above the percolation threshold, is presented in Fig. 7. Comparison with the kinetic data at 25°C (see Fig. 3) suggests the following. At $W = 9.8$, despite the temperature increase from 25 to 40°C , the reaction rate decreases by 2.5–5 times depending on the surfactant concentration. The point corresponding to 40°C (see Fig. 6, *a*) lies in the descending line, *i.e.*, in this case the structural factor of the temperature dependence preventing unfavorable changes in the microenvironment of the reactants is predominant. At $W = 15.1$ and 20.0 the apparent rate constant decreases slightly or remains constant when the temperature increases to 40°C . These cases concern the ascending line (see Fig. 6, *a*), and mutual compensation of two effects is observed: temperature activation of the chemical reaction and unfavorable structural changes of the system in the microenvironment of the reactants. As a whole, the kinetic tendencies are retained with the temperature rise: k_{app} decreases with an increase in the surfactant concentration and parameter W . The exception is the region of

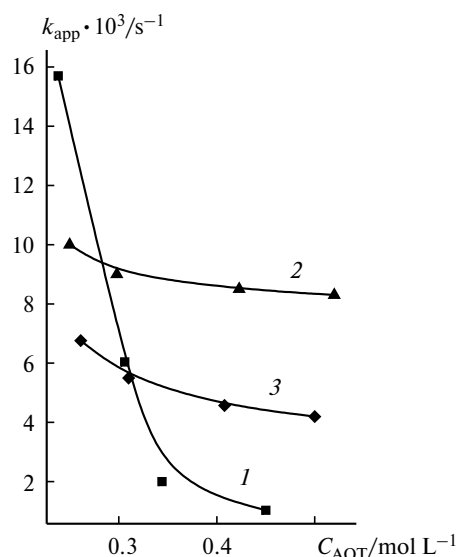


Fig. 7. Plots of the apparent rate constant of alkaline hydrolysis of phosphonate **1** (k_{app}) in the AOT–*n*-nonane–PEG–water system vs. AOT concentration (C_{AOT}) at $W = 9.8$ (1), 15.1 (2), and 20.0 (3) ($C_{\text{PEG}} = 0.02 \text{ mol L}^{-1}$, $C_{\text{NaOH}} = 0.01 \text{ mol L}^{-1}$, 40°C).

high surfactant concentrations at $W = 9.8$ for which lower k_{app} values than those for $W = 15.1$ and 20.0 are observed.

Additional information on the effect of the polymer on the kinetics of the process was obtained by the graphical analysis of the kinetic data presented in Fig. 7 using Eqs (1) and (2) (Fig. 8). Although linearity is fulfilled in the $1/(k_{\text{app}}[\text{AOT}])$ – Z coordinates, in the presence of the polymer Eq. (1) obeys neither before nor after the percolation threshold. This is indicated by the negative slope of the sections and different in absolute values b/a ratios that characterize the binding constant of the substrate (see Table 2). The most probable explanation is a change in the distribution of the reactants between the pseudo-phases in the presence of the polymer. Perhaps, in this case the substrate is distributed between all pseudo-phases and the contribution of the reactions in the aqueous core increases, *i.e.*, the results of analysis confirm the change in the properties of the nanoaggregates caused by the formation of Surf–polymer complexes.

Thus, our study demonstrated a possibility of direct controlling the rate of chemical reactions using reverse micellar systems as nanoreactors. The concentration and temperature regimes of the reaction should be mentioned among tools controlling the process rate. Varying concentrations of all components of the reverse system, we found a wide range of changes in the catalytic effect from inhibition of the reaction to its acceleration. An additional factor affecting the reaction rate is related to the induction of cluster formation in the system when the activation energy of substrate hydrolysis changes sharply in the point of the temperature percolation threshold. In

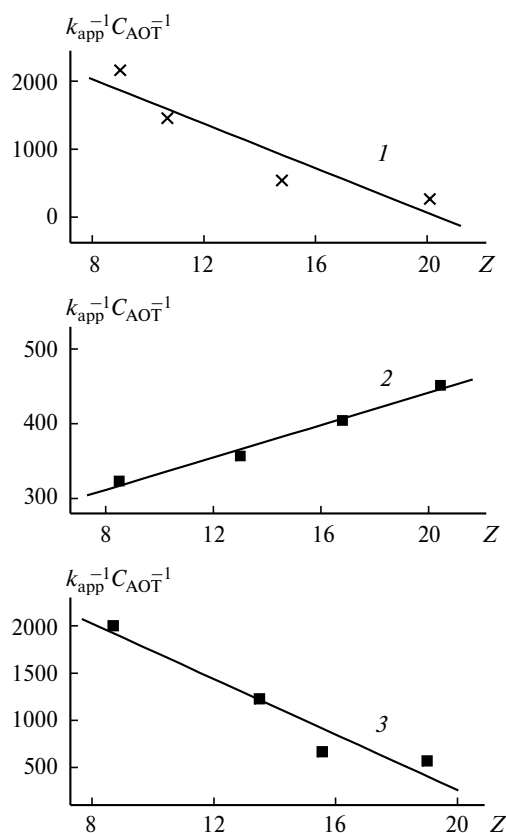


Fig. 8. Kinetic data presented in Fig. 7 linearized in the coordinates of Eq. (2) for $W = 9.8$ (1), 15.1 (2), and 20.0 (3).

the presence of polyethylene glycol, the reactants are relocated between the microphases of the microemulsion and the reaction zone migrates, which is indicated by the quantitative analysis of the data in the framework of the pseudo-phase model.

It should be emphasized in conclusion that investigations of the reactivity of compounds in organized solutions are simulated by their resemblance to enzymatic systems. In the present work, we showed that the use of polycomponent supramolecular ensembles as catalytic systems increases their similarity with biocatalysts that are characterized by a complicated multivariant matched mechanism of catalytic effect combining elements of homogeneous, micellar, and polymeric catalyses.

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