Catalysis of nucleophilic substitution reactions in supramolecular systems*

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The factors determining the catalytic effect of supramolecular systems on the nucleophilic substitution reactions are analyzed. The role of the structural and phase transitions of nanoaggregates in the catalytic mechanism are determined. The substrate specificity is shown for different structures of the supramolecular composition.

Key words: supramolecular systems, catalysis, kinetics, nucleophilic substitution.

Control of the reactivity of compounds is one of the fundamental problems of chemical science. Scientific achievements in different areas of organic and physical chemistry should be concentrated to solve this problem. Unlike homogeneous catalytic processes, supramolecular catalysis assumes different principles of the catalytic effect based on the model of the most efficient (biocatalytic) mechanism of functioning.[1—4] A high efficiency of enzymes is a result of the concerted effect of different factors. Depending on the ratio of components, supramolecular structures of different morphological types, including direct and reverse micelles, microemulsions, vesicles, and liquid crystals, can be formed in organized systems. Structural and phase transitions of the nanostructures can substantially affect the rate and mechanism of the processes. The role of the structural factor in supramolecular catalysis is a poorly studied aspect.

The main principles of catalysis in self-organizing systems based on surfactants are related to the formation of nanoregions with specific characteristics. They make it possible to create gradients of polarity and concentrations of solubilized reactants, which allows their reactivity to be purposefully changed.[1—7] An additional tool including new self-organization mechanisms is the use of modifying additives (metal ions,[8] electrolytes,[9—13] cosurfactants,[14—16] calixarenes,[17] polymers,[18—23] and others). This tool provides considerable variations in concentration boundaries of formation and shapes of nanoparticles, induces sharp changes in the properties of the system, and allows control of their catalytic activity to perform in a wide range.

To predict the catalytic effect of self-organizing systems, it is necessary to establish the factors influencing a change in the rate of chemical reactions in nanoaggregates. The principles determining the catalytic effect of these systems were formulated on the basis of results of studying the reactivity of esters of phosphorus-containing and carboxylic acids in direct and reverse micelles, microemulsions, and liquid crystals.

1. Influence of reactant concentrating and micellar microenvironment on the reactivity of compounds

Quantitative analysis of kinetic data in micellar solutions was performed for the first time for monomolecular and bimolecular reactions inhibited by micelles or occurring in the pseudo-first-order regime.[4] Equation (1) used for these reactions is similar to the Michaelis—Menten equation, which is widely used in enzymatic catalysis and assumes the formation of a substrate—micelle catalytic complex.

$$k_{obs} = \frac{k_0 + k_m K'_S C}{1 + K'_S C}, \quad (1)$$

where k_{obs} is the observed rate constant of the pseudo-first order; k_0 and k_m (s^{-1}) are the first-order rate constants in the bulk and micellar phases, respectively; K'_S ($L\ mol^{-1}$) is the reduced binding constant of a substrate with micelles; C is the surfactant concentration minus the critical micellization concentration (CMC).

The physicochemical foundations of micellar catalysis and quantitative estimation of the main factors responsible for a change in the rate in organized solutions of surfactants have been formulated earlier.[1,24] It is assumed in the framework of the pseudo-phase approach that a micellar solution consists of the micellar and bulk pseudo-phases between which reactants are distributed. In the general case, the reaction occurs in both pseudo-phases.

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For a bimolecular reaction of nucleophilic substitution, the expression of the observed second-order rate constant (k'_{obs}) takes the form:

$$k'_{obs} = \frac{k_{2,0} + (k_{2,m}/V) K_S K_{Nu} C}{(1 + K_S C)(1 + K_{Nu} C)}, \quad (2)$$

where $k_{2,0}$ and $k_{2,m}$ (L mol^{-1} s^{-1}) are the second-order rate constants in the aqueous and micellar pseudo-phases, respectively; K_S and K_{Nu} (L mol^{-1}) are the binding constants for the substrate and nucleophile; V is the molar volume of the surfactant; C is the surfactant concentration minus the CMC.

This kinetic model makes it possible to estimate quantitatively the factors determining the micellar effect and to describe the maximum acceleration, which is equal to the ratio of k_{obs} to k_0, by the following expression:

$$(k_{obs}/k_0)_{max} = \frac{k_{2,m}}{k_{2,0}} \frac{K_S K_{Nu}}{V(\sqrt{K_S} + \sqrt{K_{Nu}})^2}. \quad (3)$$

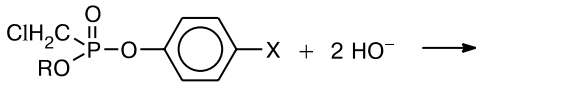
The first term in the right part (F_m) characterizes the influence of changing the microenvironment of reactants when the reaction is transferred from the bulk to micellar phase, and the second term (F_c) characterizes the effect of concentrating reactants in micelles. Similarly to enzymatic processes, effects of microenvironment (medium effect) and concentrating (cage effect) can provide high efficiency and selectivity of catalysis in supramolecular systems. Since micelles are grouped with nanodimensional particles, the F_c term plays an enormous role providing an increase in local concentrations of reactants by several orders of magnitude during solubilization.

Different modifications of the pseudo-phase model and their application for quantitative analysis of the kinetics of bimolecular reactions are generalized in the reviews.[2,3] In these comprehensive studies covering a wide scope of ion-molecular reactions, the authors confirm the previously predicted[1] conclusion about a predominant positive contribution of the concentrating factor to the micellar effect and a negative influence of the factor of micellar environment.

The systematic study of the kinetics of nucleophilic substitution of phosphorus acid esters in aqueous and organic solutions of ionic surfactants with different structures shows that the above-mentioned tendency for decreasing the reactivity on going from the bulk to micellar pseudo-phase is characteristic only of systems with efficient binding of reactants, *i.e.*, for reactions of hydrophobic compounds in aqueous solutions of surfactants with a high micelle-forming ability. In this case, the kinetic k_{obs}—C_{surf} plots have a pronounced maximum. The most part of kinetic data systematized in the reviews[2,3] were obtained for these reactions.

In fact, the study of the alkaline hydrolysis of chloromethyl phosphonates **1**—**11** (Scheme 1) in aqueous micellar solutions of cationic surfactants cetyltrimethylammonium bromide (CTAB)[25,26] and cetylpyridinium bromide (CPB)[27] showed that the concentrating effect reaches two orders of magnitude, while the reaction transfer to a micellar microenvironment decreases considerably the reactivity of the phosphonates (Table 1). For instance, F_c = 766 and F_m = 0.14 were obtained for the alkaline hydrolysis of **4** in CPB micelles. This implies that the calculated binding constants allow one to expect more than 700-fold acceleration of the reaction due to the effect of reactant concentrating. The rate constant in the micellar phase ($k_{2,m}$) decreases simultaneously by almost 7 times compared to that of the reaction in water. A combination of these effects results in the observed 100-fold acceleration of the reaction (see Table 1).

Scheme 1



	X	R		X	R
1	NO_2	Et	**7**	Et	Et
2	NO_2	Bu^n	**8**	Bu^n	Et
3	NO_2	n-C_6H_{13}	**9**	n-C_8H_{17}	Et
4	NO_2	n-C_8H_{17}	**10**	*iso*-$C_{12}H_{25}$	Et
5	Br	Et	**11**	H	n-C_6H_{13}

On going from CTAB and CPB micelles (CMC 0.00085 mol L^{-1}) to dodecylpyridinium bromide (DDPB) (CMC 0.018 mol L^{-1}), the F_m value for compound **1** increases considerably, which is accompanied by the replacement of the extreme type of the k_{obs}—C_{surf} plot by a kinetic curve reaching a plateau.[26] At the same time, a maximum in the kinetic curve and the negative influence of the micellar microenvironment (F_m < 1) are retained for more hydrophobic phosphonate **3** in a micellar solution of DDPB.

The study of the solvolysis kinetics of *p*-nitrophenyl bis(chloromethyl) phosphinate (**12**) in direct micelles of sodium dodecyl sulfate (SDS) in ethylene glycol showed that the ratio of contributions from the F_c and F_m terms in these systems differs from that in aqueous micellar solutions, namely, the predominant positive influence of the micellar microenvironment factor on the catalytic effect is observed (see Table 1).[31,32] A similar result was obtained for the system SDS—ethylene glycol—lanthanum(III) salt by studying the solvolysis kinetics of substrate **12**.[8] In these solutions, the efficiency of micelle

Table 1. Results of quantitative analysis of the kinetic data using Eq. (2)

Surfactant/nucleophile/medium	Substrate	$k_{2,0}$	$k_{2,m}$	K_S	K_{Nu}	$(k_{obs}/k_0)_{max}$	F_c	F_m	$F_c \cdot F_m$	Refs
		L mol^{-1} s^{-1}		L mol^{-1}						
CPB/0.0005*M* NaOH/H_2O	**1**	4.0	0.78	2020	80	35	187	0.19	36	27
	2	3.56	1.07	3000	115	75	265	0.30	80	27
	3	3.26	0.62	4720	307	105	650	0.19	125	27
	4	2.68	0.38	7600	337	95	766	0.14	109	27
CTAB/0.0005*M* NaOH/H_2O	**1**	4.0	0.1	1190	145	7.0	266	0.026	6.5	26
CTAB/0.001*M* NaOH/H_2O	**1**	4.0	0.055	1775	240	7.5	432	0.014	6	25, 26
	5	0.55	0.016	945	135	5.5	240	0.028	6.3	25, 26
	6	0.24	0.01	400	90	5	144	0.042	6	25, 26
	7	0.19	0.0098	800	75	7	146	0.053	7.7	25, 26
	8	0.16	0.0082	1675	87	9	190	0.051	9.8	25, 26
	9	0.12	0.0043	2350	350	22	604	0.037	22.5	25, 26
	10	0.08	0.0031	1490	470	24	640	0.039	24.9	25, 26
	11	0.12	0.014	2795	365	74.2	657	0.117	77	25, 26
CPB/AMP-1/borate buffer	**1**	0.036	0.011	290	35	20	64	0.3	20	29
	17	0.22	0.0035	5000	330	12	696	0.016	11.1	28
CPB/AMP-2/borate buffer	**17**	0.26	0.0042	5300	310	11	670	0.016	10.7	28
CPB/AMP-3/borate buffer	**17**	0.20	0.0041	5560	440	15	885	0.020	16	28
CPB/AMP-5/borate buffer	**1**	0.05	0.020	870	30	31	64	0.4	28.4	29
PM/*n*-hexylamine/toluene	**1**	0.0069	0.029	5.2	2.3	11.5	2.7	4.2	11.4	30
	2	0.0054	0.020	6.7	2.4	11.6	3.1	3.7	11.6	30
	3	0.0049	0.033	8.2	1.2	13.3	2.1	6.7	14.2	30
	4	0.0040	0.025	21.0	1.2	17.6	2.5	6.3	16.0	30

formation is much lower than that in aqueous solutions (CMC of SDS in ethylene glycol is 0.18 mol L^{-1}, and that in water is 0.0083 mol L^{-1}), and the micelles formed have low aggregation numbers, a loosen structure, and a low solubilizing ability (the binding constants of the substrates are two orders of magnitude lower than those in aqueous solutions).[31—34]

A tendency for decreasing the contribution from the concentrating factor and for increasing the contribution from the micellar microenvironment factor observed for direct micelles on going to systems with less hydrophobic reactants and less efficient micelle formation, which is caused by the structure of a surfactant or the nature of a solvent, is also retained for reverse nonaqueous solutions of surfactants. The analysis of the kinetic data for aminolysis of phosphonates **1—4** in the polyethylene glycol-600—monolaurate (PM) reverse system in the framework of the pseudo-phase model showed that both factors make positive contributions to the micellar effect, and $F_m > F_c$ (see Table 1).[30,35] In nonaqueous nonpolar solvents, micelle formation has a different nature than that in aqueous solutions where the main moving factor is a hydrophobic effect, which causes a high cooperativity of the process. In nonaqueous reverse systems, micelle formation occurs due to dispersion interactions and is accompanied by the formation of small surfactant aggregates with low binding constants of reactants.[36—39]

The mechanism of changing the reactivity in direct micelles was analyzed in the study.[26] An unfavorable influence of the micellar microenvironment contradicts the Ingold—Hughes rule,[40] according to which a decrease in the polarity on going from the aqueous to micellar phase should assist ion-molecular reactions, because the latter are characterized by some charge delocalization in the transition state compared to that in the initial state. The kinetics of alkaline hydrolysis of substrates **1** and **3** in micellar solutions of DDPB was measured at different temperatures, and the activation parameters of the reaction (activation enthalpy and activation entropy) were calculated in the absence of a surfactant (ΔH_0, ΔS_0) and in the micellar pseudo-phase (ΔH_m, ΔS_m). The transfer of ion-molecular reactions from water to the less polar pseudo-phase is accompanied by some decrease in the activation enthalpy (from 46.2 to 39.3 kJ mol^{-1} for **1** and from 40.8 to 30.0 kJ mol^{-1} for **3**), *i.e.*, occurs according to the Ingold—Hughes rule for both substrates. At the same time, the transition from dilute aqueous solutions of reactants to concentrated solutions in the micellar pseudo-phase is accompanied by a decrease in the activation entropy by 22 J mol^{-1} K^{-1} for **1** and 45.6 J mol^{-1} K^{-1} for **3**, probably, due to losses of the entropy of mixing, a decrease in the degree of reactant mobility, a change in their orientation, *etc.* In the case of the reaction of substrate **1**, changes in the activation enthalpy and activation entropy are mutually compensated, and the reactivity is almost the same in both pseudo-phases. An increase in the concentrating effect for phosphonate **3** results in more considerable losses of the activation entropy, which exceed

quantitatively the gain in the activation enthalpy and is expressed in the apparent violation of the Ingold—Hughes concept. Thus, entropy control of changing the reactivity of compounds takes place in micellar systems.[26]

2. Role of the structural factor in supramolecular catalytic systems

Before 1990s, the main direction of studies in the area of micellar catalysis was the accumulation and generalization of kinetic data and improvement of model concepts. The pseudo-phase ion-exchange model,[3] the approaches based on the Poisson—Bolzmann equations,[41] and the Langmuir isotherms[42] found a wide use for the interpretation of the kinetics of ion-molecular reactions in direct micelles. Various modifications of the pseudo-phase model have later been developed for reverse micellar systems.[43,44] A substantial gap in these studies is the absence of data on the influence of structural factors on the efficiency of catalysis. Taking this into account, we performed a series of studies aimed at establishing an interrelation between the structure of the nanoaggregates and their activity.

2.1. Influence of the "sphere—rod" micellar transitions of direct micelles on the reactivity of compounds

Nucleophilic substitution reactions of carboxylic and phosphorus esters are accelerated by cationic micelles.[1—5] Catalysis is induced by the solubilization of hydrophobic substrates in the surface layer of micelles, where nucleophilic ions are also concentrated due to the Coulomb attraction to the positively charged micellar surface. The introduction of electrolytes into the system decreases the surface potential and catalytic effect. However, in addition to trivial inhibition, electrolytes can exert an indirect effect on the reaction rate in micellar solutions of surfactants. An increase in the concentration of surfactant counterions in a micellar solution decreases the CMC and increases the size of micelles.[45] Near the CMC micelles are spherical, and their radius does not exceed the length of an extended surfactant molecule. The shape and size of micelles are determined by a combination of geometrical and energy criteria and, therefore, a contradiction between these criteria appears during growth of spherical micelles at a certain concentration of counterions. The energy and geometrical factors become more favorable for cylindrical aggregates, providing almost unrestricted possibilities of micelle elongation, and the "sphere—rod" micellar transition occurs, which was experimentally confirmed by quasi-elastic light scattering, small-angle neutron scattering, viscosimetry, and other methods.[45] The "sphere—rod" micellar transition can analytically be found from a break in the plot "property"—"logarithm of salt concentration." A change in the structural characteristics can affect the reactivity of compounds in micelles.

To check this assumption, we carried out a kinetic experiment for the alkaline hydrolysis of phosphonate **1**. Cationic surfactants with different chain lengths and structures of the head group were used (decylpyridinium chloride (DPC), DDPB, CPB, and CTAB[9—13]), as well as a repeated series of organic and inorganic electrolytes. Three different processes have been studied earlier[46]: alkaline hydrolysis of two substrates, *viz.*, bis(*p*-nitrophenyl) methyl phosphonate (**13**) and *p*-nitrophenyl acetate (**14**), and acid-base dissociation of *p*-nitroanilide of bis(chloromethyl)phosphinic acid in a micellar solution of CTAB. The analysis of the kinetic data in the semilogarithmic coordinates (Fig. 1) revealed a critical concentration of electrolytes corresponding to the break in the k_{obs}—logC_{NaX} plots. It is found that the same order of changing the activity of counterions is true for all processes and surfactants studied: $F^- < Cl^- < Br^- \approx NO_2^- <$ $< OTs^- <$ salicylate $(Sal)^-$. The concentration value in the break point C_{cr} depends on the surfactant nature: the C_{cr} value shifts to the region of lower concentrations for surfactants with a greater number of methylene units. For instance, in the case of the bromide ion, C_{cr} is 1.0, 0.5, 0.02, and 0.04 mol L^{-1} for DPC, DDPB, CPB, and CTAB, respectively.[13] This is likely related to different characters of micelle formation in solutions of the surfactants listed. The critical micelle concentration decreases in the series DPC > DDPB > CPB ≈ CTAB, and the CMC of each subsequent surfactant is 5—8 times lower than that of the previous surfactant. Therefore, the concentration in a micellar solution of DPC near the CMC is much higher than that of DDPC and CPB, and a higher concentration of electrolytes is needed to the partial neutralization of the charge of the head groups of DPC.[13] The same C_{cr} values for the Sal^- ion were obtained in the case of CTAB and CPB micelles, which indicates that critical concentrations concern the micelle formation process rather than the kinetics, because the reactivities of **1** in micellar solutions of CTAB and CPB differ strongly,[26] while micelle formation is characterized by rather close CMC values. The coinciding C_{cr} values were found for each counterion in CTAB micelles for the above-listed processes of hydrolysis and acid-base dissociation.[46] This also implies that C_{cr} depends only on the counterion and surfactant nature and is independent of the type of the process, *i.e.*, it is a characteristic of a surfactant for each particular counterion.

When comparing the C_{cr} values of CTAB and CPB micelles found by physical methods and C_{cr} determined in kinetic experiments, these parameters were found to coincide. In addition, a special study of the problem of correlation of the structural factor and catalytic effect

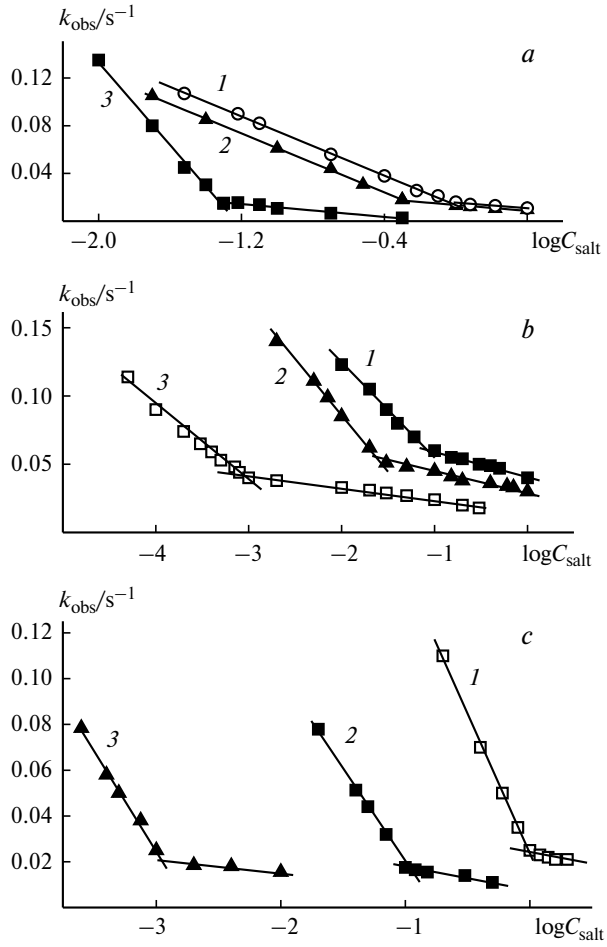


Fig. 1. Plots of the observed rate constant of alkaline hydrolysis of **1** in micellar solutions of cationic surfactants: (*a*, *b*) *vs.* logarithm of the electrolyte concentration in micellar solutions of DDPB (*a*) and CPB (*b*) in the presence of NaCl (*1*), NaBr (*2*), and NaSal (*3*); *c*, in micellar solutions of DPC in the presence of NaBr (*1*) and NaSal (*2*) and in micellar solutions of CTAB in the presence of NaSal (*3*).

was carried out for DDPB micelles.[11,12] The catalytic properties and structural behavior of the system in the presence of sodium salicylate (NaSal) were studied in parallel experiments. The analysis of the kinetic data for the alkaline hydrolysis of **1** in the semilogarithmic coordinates revealed the critical concentration of NaSal to be ~0.05 mol L^{-1} corresponding to the break in the k_{obs}—$\log C_{NaX}$ plot.

The size and shape of micelles were determined by high-resolution pulsed-field gradient ^1H NMR spectroscopy from the self-diffusion coefficients of DDPB. The ratio of axes of a micelle was calculated in the approximation of a micelle by a prolate ellipsoid of revolution in a region of long particle radius, which was determined by the Stokes—Einstein equation. It was established that an increase in the concentration of the salicylate ion changes the shape of aggregates from spherical to sphere-cylindrical; in a concentration region of 0.05 mol L^{-1}, the shape becomes cylindrical.[11]

Asymmetrization of micelles was also studied by ESR from a change in the correlation time of paramagnetic probe rotation (τ).[12] When the NaSal concentration increases to 0.05 mol L^{-1}, τ increases, after which the mobility of the probe remains unchanged. The increase in τ, which reflects an increase in the packing density of surfactant monomers, can be interpreted as an increase in the relative fraction of DDPB molecules in the cylindrical part of micelles, *i.e.*, as the "sphere—rod" micellar transition. Thus, the data on self-diffusion NMR and ESR indicate a structural rearrangement of DDPB micelles in a NaSal concentration region of ~0.05 mol L^{-1}, which corresponds to the concentration of the Sal ions at which the reactivity of compound **1** changes sharply according to the data of kinetic experiment.[11,12]

We have recently[9—13] shown that, unlike k_{obs}, the surface potential of micelles Ψ decreases monotonically with an increase in the concentration of counterions. This means that the presence of critical concentrations in the plots (see Fig. 1) is not a consequence of the trivial inhibition of phosphonate hydrolysis related to the neutralization of the micelle charge. At the same time, an interesting fact should be mentioned. Although the C_{cr} values of inorganic counterions for the same surfactant differ, they correspond to the same surface potential value. For instance, in CPB micelles, the C_{cr} values for Cl^- and Br^- ions are 0.1 and 0.02 mol L^{-1}, which corresponds to Ψ values of 123 and 124 mV.[9,10] In DDPB micelles, C_{cr} for Cl^- and Br^- ions are 1.0 and 0.5 mol L^{-1}, which corresponds to Ψ 73 and 71 mV.[12]

Thus, the data presented make it possible to relate rather reasonably the breaks in the k_{obs}—$\log C_{NaX}$ plots (see Fig. 1) to the "sphere—rod" micellar transitions and conclude that the structures of surfactant aggregates affects the reactivity of compounds.

2.2. Influence of cluster formation of reverse micelles on the reactivity of compounds

Reverse micellar systems are characterized by a phenomenon of electric percolation,[47] which manifests itself as a sharp increase in the electric conductivity of the system by 3—4 orders of magnitude. As a rule, the conductivity of reverse micellar solutions of surfactants is controlled by the Stokes transport of surfactant monomers or micellar particles, *i.e.*, water droplets stabilized by a surfactant monolayer. When the temperature or volume fraction of the dispersed phase increases, "infinite" clusters are formed and change the conductivity mechanism: the Stokes process is replaced by the transfer of charge carriers along chains of droplets that formed. The studies of percolating ionic and nonionic reverse systems

by different methods allowed the conclusion to be drawn that the conductivity increase is not related to the "jump" of monomers of ionic surfactants from one droplet into another or to the formation of bicontinuum systems. According to the commonly accepted model, percolation is caused by the ion exchange of the water core during temporal confluence of droplets in dynamic cluster formation.[48] This process is reversible from the viewpoint of effects of the temperature and composition. The percolation transition characterized by temperatures of the percolation threshold T_p or the critical volume fraction x_p manifests the properties of a phase transition of the second order (the thermal capacity and specific volume change with temperature), which indicates that the phenomenon observed is a phase transition.

We studied[49–51] the influence of this phenomenon on the reactivity of **1** in the sodium bis(2-ethylhexyl)sulfosuccinate (AOT)—*n*-decane—water reverse micellar system with variation of the parameters Z = [decane]/[AOT] (concentration in mol L^{-1}) and W = $[H_2O]$/[AOT] (concentration in mol L^{-1}). Based on the data on the conductivity of solutions, we determined the percolation threshold temperatures T_p and chose conditions for measuring the kinetics of alkaline hydrolysis of **1** at different temperatures before and after the percolation threshold. The $\log k_{obs}$—$1/T$ plots at different W values are presented in Fig. 2. Unlike the reaction in the absence of a surfactant, in reverse systems the slope of the Arrhenius plot changes at a certain temperature T_{cr}. At W = 26.6 above T_{cr}, the slope decreases, *i.e.*, the activation energy decreases, and at W = 20.0 and 15.1, k_{obs} decreases with the temperature increase. The T_{cr} values coincide with the percolation threshold temperature.[50]

Evidently, the change in the slope of the Arrhenius plot is caused by clusterization of reverse micelles, although it is not probably related directly to the acceleration of dynamic processes due to cluster formation of reverse micelles. This influence would be characteristic of very fast reactions, whose rate is controlled by diffusion of reactants. The alkaline hydrolysis of phosphonate **1** is not grouped with such reactions and, therefore, the main prerequisite of the pseudo-phase model should be fulfilled: the dissociation of monomers in micelles, exchange of reactants between phases, and other dynamic processes occur with a much higher rate that the reaction under study and exert no effect on its kinetics.[1–3] It can be assumed that some characteristics of the micellar environment of reactants (micropolarity, surface potential, and others), which affect the reactivity of the substrate, can change due to cluster formation and exchange of the water contents between micelles. The preliminary study of the absorption spectra of **1** and products of its hydrolysis showed that above the T_{cr} temperature the localization of these compounds is displaced, in fact, to a less polar microenvironment.

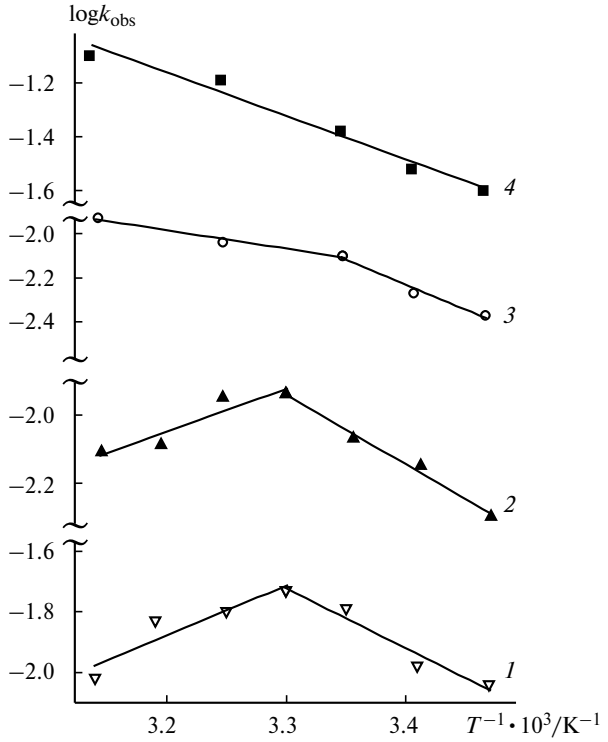


Fig. 2. Arrhenius plots of the observed rate constant of alkaline hydrolysis of **1** in the AOT—decane—water reverse micellar system at different W (C_{NaOH} = 0.01 mol L^{-1}, C_{AOT} = 0.42 mol L^{-1}): 15.1 (*1*), 20.0 (*2*), and 26.6 (*3*); *4*, water.

2.3. Influence of micelle—liquid crystals phase transitions on the catalytic effect of supramolecular systems

As shown above, the "sphere—rod" micellar transitions induced by electrolytes have a noticeable effect on the reactivity of compounds. Cylindrical micelles are also formed in the absence of electrolytes with an increase in the surfactant concentration.[45] In concentrated solutions of some surfactants, the solution is further ordered, which is characterized by a transition from isotropic micellar systems to anisotropic liquid-crystalline (LC) liomesophases. It is of interest to compare the reaction kinetics in the micellar and LC concentration regions of organized solutions. Publications on this theme are rare and, hence, worth of attention. The authors of several studies showed the formation of lamellar and hexagonal LC mesophases in the systems *n*-decylammonium chloride—*n*-decylamine—water,[52] SDS—water,[53] cetyldimethylethylammonium bromide (CDAB)—water,[54,55] CDAB—polyethyleneimine—water,[20] and CTAB—*n*-hexylamine—water (with additives of NaOH and KF).[56] The LC structures formed have a specific effect on the rate and direction of nucleophilic substitution in phosphorus esters. In the *n*-decylammonium chloride—*n*-decylamine—water

and CTAB—*n*-hexylamine—water systems, the nucleophilic attack at the phosphorus atom in *p*-nitrophenyl dimethyl thiophosphate (**15**) is virtually inhibited, and the substrate is dealkylated.[52,56] The addition of NaOH to the CTAB—*n*-hexylamine—water system changes the direction of nucleophilic attack from the carbon atom to phosphorus, and in the LC structures CTAB—*n*-hexylamine—water—KF both processes occur[56]: dealkylation and dephosphorylation of substrate **15**.

The transition from a micellar solution to the LC mesophase can result in the change in the mechanism of the process and also a sharp change in the reaction rate. It is known that cylindrical micelles are building blocks of one of the most often observed mesomorphic species: hexagonal LC liomesophase (E-phase).[46] The stable hexagonal LC mesophase (E-phase) is shown[19,20,54,55] to be formed in the CDAB—water and CDAB—polyethyleneimine—water systems. The studies of aqueous solutions of CDAB by small-angle neutron scattering showed[55] that in an interval of surfactant concentrations of 0.001—0.005 mol L^{-1} the system contains spherical micelles, whose radius is 25 Å. At a surfactant concentration close to 0.1 mol L^{-1}, the shape of micelles is most adequately described by a "rigid" rod with a radius of 21 Å and a length of 65 Å. Optical anisotropy was found by polarization microscopy in solutions of CDAB beginning from a concentration of 0.1 mol L^{-1}, and at a surfactant concentration of 0.4 mol L^{-1} a texture is formed, which is characteristic of hexagonal packing of cylindrical micelles, *i.e.*, the formation of the E-phase is observed.[53] A kinetic experiment provided data for the hydrolysis of substrates **1**, **15**, and *O*-*p*-nitrophenyl-*O*-ethyl ethyl phosphonate (**16**) in micellar solutions of CDAB and under the conditions of E-phase formation. The observed rate constants of hydrolysis of compounds **15** and **16** decreases approximately 20-fold with an increase in the degree of ordering of the solution, and for substrate **15** catalysis in the micellar phase is replaced by inhibition in a region of the LC mesophase.[54,55]

The structural factor in micellar catalysis concerns finer mechanisms of action on the catalytic effect compared to the concentrating and microenvironment factors. The variation of the reactivity by inducing the structural and phase rearrangements of nanoaggregates provides wide possibilities for purposeful control of the rate and mechanism of chemical reactions in supramolecular systems. Studies of this problem showed that both the micelle—liquid crystals phase transition and changes in a solution preceding LC mesophase formation (polymorphism and polydispersity of micellar particles in a region of high surfactant concentrations, enhancement of intermicellar interactions, and formation of meshes and a spatial network) can affect the reaction kinetics.

We studied[14] the reactivity of phosphonate **1** in a mixed micellar system based on CTAB and polyethylene glycol (~9) monoalkyl ethyl (~14) (PEM) in a region preceding the formation of LC mesophases. In the $(HO(CH_2CH_2O)_nCOC_mH_{2n+1}$ ($n \approx 9$, $m \approx 14$), PEM)—water system, an L_β lamellar phase (gel phase) is formed. This phase retains stability in rather wide temperature and concentration intervals.[14] The gel phase formed in a PEM—water system was established to retain also in a PEM—CTAB—water system in a wide interval of surfactant ratios (up to $\alpha_1 = 0.67$, where α_1 is the molar fraction of CTAB in a solution). In a region of high surfactant concentrations preceding liomesophase formation, the kinetic k_{obs}—C_{surf} plots were obtained at the fixed CTAB—PEM molar ratio $\alpha_1 = 0.50$ and a fixed concentration of one of the surfactants. Micellar solutions of CTAB exhibit a 20-fold acceleration of the alkaline hydrolysis of **1** compared to water, and nonionic PEM micelles exert no effect on the process rate. In a mixed micellar solution, the catalysis efficiency decreases up to 14 times. On going to a region of high surfactant concentrations, the catalysis efficiency decreases further, and the sign of the micellar effect changes at a concentration of a nonionogenic surfactant higher than 0.2 mol L^{-1}.[14]

A similar qualitative change in the reactivity of compounds in a region of high surfactant concentrations preceding the formation of the hexagonal LC liomesophase was observed for the system SDS—ethylene glycol—lanthanum salt. It was shown[8] that SDS forms with the La^{3+} salts the surfactant $La(C_{12}H_{25}OSO_3)_3$ (lanthanum tris(dodecyl sulfate)). Types of mesophases were identified[8] by observing textures in a polarization microscope, and phase transitions of lanthanum tris(dodecyl sulfate) with ethylene glycol were studied. The kinetics of solvolysis of **12** was studied in a SDS solution in ethylene glycol at an SDS—La^{3+} ratio of 3 : 1 in a micellar region of the solution and at high concentrations of SDS. It was found that the 3 : 1 SDS—La^{3+} composition possesses a pronounced catalytic effect (more than two orders of magnitude), which increases by more than order of magnitude at an SDS concentration higher than 0.6 mol L^{-1}.[8]

The array of these data suggests with a high probability an interrelation between the reactivity of compounds in highly organized media and structural changes in the region preceding the formation of liomesophases.

3. Manifestation of the substrate specificity in supramolecular catalytic systems

An important feature of biocatalysis is the substrate specificity manifesting itself in a high selectivity of enzyme effect toward both compounds of different classes (functional specificity) and inside homological series. Highly organized media are classified with biomimetic structures modeling the main principles of biocatalysts functioning, including a high selectivity.[57]

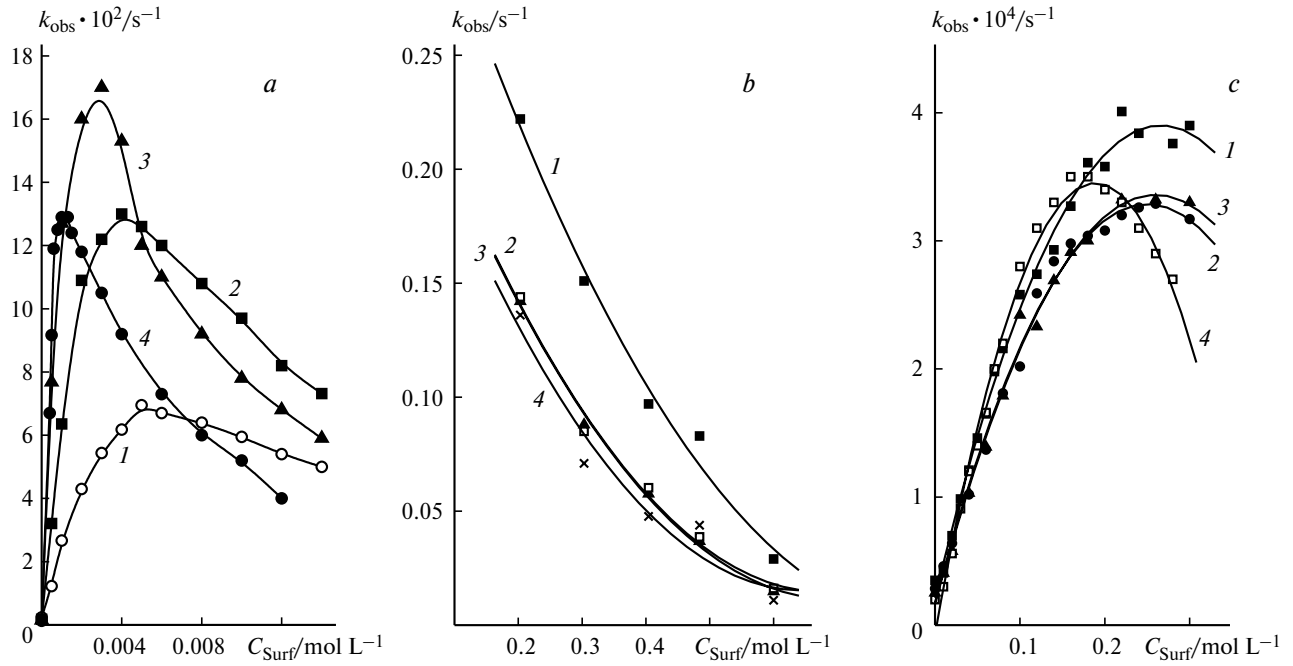


Fig. 3. Plots of the observed rate constant of nucleophilic substitution of phosphonates **1** (*1*), **2** (*2*), **3** (*3*), and **4** (*4*) *vs.* surfactant concentration in direct micellar solutions of CPB (25 °C, 0.0005 mol L^{-1} NaOH) (*a*), SDS—hexanol—water reverse micellar systems (25 °C, $W = 22.8$, 0.002 mol L^{-1} NaOH) (*b*) and the PM—toluene system (40 °C, 0.05 mol L^{-1} *n*-hexylamine) (*c*).

The substrate specificity was studied[27,29,35,36,56—62] for supramolecular systems in catalysis of nucleophilic substitution of *O*-alkyl-*O*-*p*-nitrophenyl chloromethyl phosphonates (**1**—**4**) with variation of a substituent at the reaction center. Micellar systems of different morphological types were considered: direct CPB and CTAB micelles, a ternary reverse micellar system SDS—*n*-hexanol—water (alkaline hydrolysis), and reverse PM micelles in toluene (the reaction with *n*-hexylamine) (Fig. 3).

In the absence of a surfactant, the reactivity of substrates **1**—**4** toward an OH^- ion in water somewhat decreases with the elongation of the radical in the alkoxy group (see Table 1), which is probably related to steric hindrance of the attack of the hydroxide ion. The observed rate constant of the pseudo-first order for the aminolysis of phosphonates **1**—**4** in toluene in the absence of a surfactant is nonlinear and described by the equation

$$k_{obs} = k_1 C_A + k_2 C_A^2,$$

where C_A is the concentration of *n*-hexylamine. The constant k_2 can be attributed to the catalytic process involving the second amine molecule. The substrate structure exerts almost no effect on the process rate.

Direct cationic micelles consist of a nonpolar core formed by hydrocarbon surfactant chains and a Stern polar layer including head groups of the surfactant, some of which are linked with counterions.[64] The reaction of alkaline hydrolysis under study (Scheme 1) is assumed to occur in the micelle core, *i.e.*, in the region adjacent to the head groups of the surfactant. In micellar solutions of CPB, the alkaline hydrolysis of substrates **1**—**4** is accelerated and the catalytic effect $(k_{obs}/k_0)_{max}$ varies in an interval of 35—105; k_{obs} increases with the elongation of the alkyl radical in the series: **1** < **2** ≈ **4** < **3** (see Fig. 3).[27] The reactivity increases due to an increase in the concentrating factor (F_c) in an interval of 190—800 on going to more hydrophobic substrates (see Table 1). When the reaction is transferred from the aqueous to micellar phase, a change in the microenvironment of reactants exerts an unfavorable effect on the process rate ($F_m < 1$), decreasing the catalytic effect.

It is of interest that the nature of the head group of cationic micelles affects the acceleration of alkaline hydrolysis (see Table 1). For substrate **1**, the acceleration in CPB and CTAB micelles is 35 and 7.0, respectively.[26] The structures of the head group and counterions manifest themselves to a great extent in aqueous solutions of ionic surfactants, which is mentioned in several publications.[21,26,65] The study of the catalytic effect of the compositions based on polyethyleneimine and cationic surfactants CTAB, CDAB, and cetyl-(2-hydroxyethyl)dimethylammonium bromide (CHAB) in the hydrolysis of *p*-nitrophenyl diphenyl phosphate (**17**) showed[21] that the concentrating factor, reaching three orders of magnitude in the case of CHAB, contributes mainly to the micellar effect of the system. The micellar microenvironment for all surfactants has a negative effect; however, this is pre-

cisely the 60-fold increase in the F_m factor which determines the change in the micellar effect in the series CTAB < CDAB < CHAB.[21]

In the reverse micellar system SDS—*n*-hexanol—water, the reaction involving hydrophobic substrates **1**—**4** and **16** and the hydrophilic OH^- ion occurs in the surface layer of the surfactant, whose amphiphilic properties provide affinity to both reactants.[58,59] The reaction is accelerated to 40 times compared to that in water. An increase in the hydrophobicity of the alkyl group affects the catalytic effect only on going from substrate **1** to **2**, whereas k_{obs} for substrates **2**—**4** is virtually the same (see Fig. 3).[61]

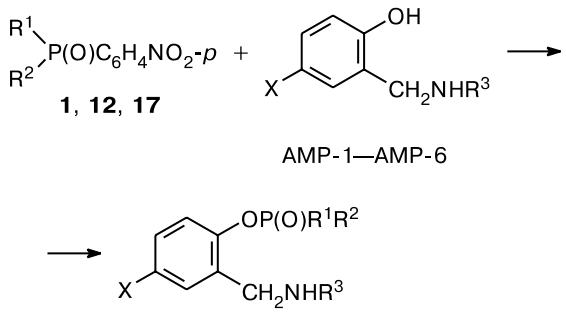
In the above-described reverse micellar system AOT—*n*-decane—water in the series of substrates **1**—**3**, alkaline hydrolysis is inhibited to five times compared to the reaction in water.[62,63] Kinetic measurements were carried out with a wide variation of the composition of the reverse system, including cluster formation of nanoparticles. As earlier,[50] the pseudo-phase model was established to be adequate under these conditions, which made it possible to estimate bimolecular constants of the alkaline hydrolysis rate in the interphase layer, *i.e.*, in the reaction zone ($k_{2,i}$), and binding constants of the reactants. The calculated data obtained indicate that alkaline hydrolysis is inhibited in this system due to a decrease in the reactivity of phosphonates when the reaction is transferred from the aqueous to micellar medium ($k_{2,i} < k_{2,0}$). The reactivity of phosphonates **1**—**4** also changes on going from **1** to **2**, and the further increase in the hydrophobicity does not change the reaction rate.

In reverse PM micelles in toluene, the reaction of substrates **1**—**4** with *n*-hexylamine is accelerated by more than an order of magnitude.[30,35] As in the absence of a surfactant, k_{obs} is almost independent of the hydrophobicity of the substrate (see Fig. 3). Both factors of concentrating and micellar microenvironment of reactants make positive contributions to the micellar effect (see Table 1). The binding constants of the substrate and nucleophile are much lower than those in direct cationic micelles and somewhat increase with an increase in the hydrophobicity of compounds. At the same time, it should be mentioned that the substitution of the *O*-alkyl group by *O*-phenyl has a dramatic effect on the rate of the process. The study of the reactions of *O*-*p*-nitrophenyl-*O*-phenyl chloromethyl phosphonate with several aliphatic amines found[36] the acceleration of the reaction in the PM—toluene reverse system to four orders of magnitude.

The studies allow one to conclude that the manifestation of the substrate specificity depends on the type of a micellar system. Direct CPB micelles have a differentiating effect on the reactivity of compounds **1**—**4**, while in reverse micelles based on SDS, AOT, and PM the reactivity depends weakly on the hydrophobicity of substrates. This is related to different mechanisms of catalytic effect of micelles of different types: the factor of reactant concentrating plays the main role in catalysis by direct micelles, while in reverse micelles the micellar microenvironment of reactants makes a substantial contribution to the catalytic effect.

Probably, it should be noted that the variation of the hydrophobicity of the substituent, which is remote from the reaction center, in the reactant exerts a negligible effect on both the binding of the reactant by micelles and a tendency for changing the bimolecular reaction rate constant in water and in the micellar pseudo-phase. This conclusion was drawn as a result of studying the reactions of substrate **17** with 2-aminomethylphenols (AMP) in aqueous micellar solutions of CPB. In aqueous systems, the product of substrate phenolysis formed in the first step (Scheme 2) is hydrolyzed to form the corresponding acid. It is shown that the F_c and F_m factors remain almost unchanged with the elongation of the alkyl substituent at the nitrogen atom in the series AMP-1, AMP-2, and AMP-3 (see Table 1).[28] Similar results were obtained in direct CPB micelles for the reaction of **1** with AMP-1 and AMP-5 (see Table 1), *i.e.*, the substitution of hydrogen in the *para*-position of the benzyl group of AMP by the *n*-butyl group exerts either no significant effect on the catalytic effect of CPB micelles.[29]

Scheme 2



Compound	R^1	R^2	AMP	X	R^3
1	OEt	$ClCH_2$	AMP-1	H	Me
12	$ClCH_2$	$ClCH_2$	AMP-2	H	Et
17	OPh	OPh	AMP-3	H	Pr^n
			AMP-4	Cl	Me
			AMP-5	Bu^n	Me
			AMP-6	*iso*-C_9H_{19}	Me

Unlike direct micelles, the study of the phenolysis of phosphinate **12** with AMP-1, AMP-4, and AMP-6 in reverse PM micelles in toluene showed that the catalytic effect depends on the nucleophile structure and decreases in the series of substituents *iso*-C_9H_{19} < H < Cl.[66] The authors established an increase in the efficiency of catalysis in the region of structural rearrangement of reverse aggregates at high surfactant concentrations. In this process, the hydrophobicity of a substituent plays a negative role as in the described above aminolysis of *O*-*p*-nitro-

phenyl-*O*-phenyl chloromethyl phosphonate, where the decrease in the catalytic effect with an increase in the hydrophobicity of amine was observed.[36]

The substantial change found for the nature of the catalytic effect in aqueous and nonaqueous media stimulates further studies in this area. To consider in more detail the problem of substrate specificity, we enlarged the scope of reactants and studied the reactivity of phosphonates **1** and **5—10** with variation of the structure of the leaving group in reverse SDS and AOT micelles and direct CTAB micelles.[25,26,61—63]

In the absence of a surfactant, the alkaline hydrolysis rate decreases substantially in the series of substrates **1**, **5**, and **6**, which is related to weakening of the electron-acceptor properties of the X substituent destabilizing the leaving group (see Table 1). For substrates **7—10**, a smoother decrease in the reactivity is observed due to some increase in the positive inductive effect of the X substituent and enhancement of steric strain at the pentacoordinate phosphorus atom in the transition state.

In a micellar solution of CTAB, the alkaline hydrolysis of compounds **1** and **5—10** is accelerated to 25 times. The k_{obs} value decreases with weakening of the electron-acceptor effect of the X substituent in the series of substrates **1**, **5**, and **6**. The order of changing the reactivity of substrates **7—10** is opposite to the tendency observed in water: the maximum k_{obs} value was found for substrate **9** (X = *n*-C_8H_{17}), and substrates **6** and **7** (X = H, Et) are characterized by minimum k_{obs}. As a whole, the influence of substituents changes as follows: NO_2 > Br > *n*-C_8H_{17} > > *iso*-$C_{12}H_{25}$ > Bu^n ≈ Et ≈ H.[25] The main reason for the acceleration of alkaline hydrolysis of substrates **1** and **5—10** is a local increase in the concentration of compounds in CTAB micelles (see Table 1).[25,26]

Variation of the nature of the leaving group in phosphonates made it possible to estimate quantitatively the ratio between the second-order rate constants in the aqueous and micellar pseudo-phases and the observed rate constant of alkaline hydrolysis in a micellar solution of CTAB. Similar information in the literature is lacking, if any, although it could elucidate the mechanism of the effect of micelles. A linear correlation found[26] between the second-order rate constants in the aqueous ($k_{2,0}$) and micellar ($k_{2,m}$) pseudo-phases for substrates **1** and **5—10** indicates, most likely, that the reaction mechanism remains unchanged when the reaction is transferred from the aqueous to micellar phase. At the same time, a correlation of the observed rate constant (k'_{obs}) and rate constant in water is observed only in the series of substrates **1**, **5—8** and is violated for phosphonates **9** and **10** (Fig. 4). The latter is explained by a sharp increase in the concentrating effect (F_c ≈ 600—650) with an increase in the hydrophobicity of the substituent in phosphonates **9** and **10** compared to **6—8** (F_c = 150—190) (see Table 1). Thus, the structure—reactivity correlation in the series of substrates **1**, **6—8** in a micellar solution is the same as that for the reaction in molecular solutions and is determined mainly by electron and steric properties of the X substituent. In the case of substrates **9** and **10**, a considerable contribution is made by the specifics of micellar solution, in particular, the micelle—reactant interaction of the "guest—host" type. In this series, the leading role belongs to the hydrophobic effect of the substituent rather than its electron and steric characteristics.[26]

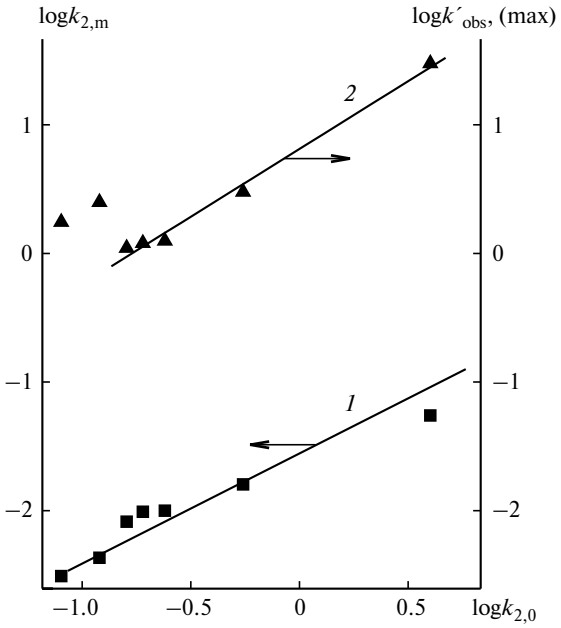


Fig. 4. Correlations between the second-order rate constants of alkaline hydrolysis of substrates **1** and **5—10** in micellar and aqueous pseudo-phases (*1*); observed rate constant and the rate constant in water (*2*), CTAB, 25 °C: (*1*) $\log k_{2,m} = 0.69\log k_{2,0} - 1.62$ (R = 0.98, n = 7) and (*2*) $\log k'_{obs} = 1.05\log k_{2,0} + 0.81$ (R = 0.99, n = 5).

For alkaline hydrolysis in the AOT—*n*-decane—water reverse micellar system, the influence of the substituent in the leaving group occurs as follows. The substitution of the nitro group by the less negative Br atom decreases k_{obs} by more than an order of magnitude, and the further decrease in the electronegativity of X (replacement of the Br atom by H atom) exerts no effect on the reactivity. An increase in the hydrophobicity of the X substituent has an effect only on going from **6** to **7**, and an elongation of the alkyl radical in the series of substrates **7—10** does not influence k_{obs}.[62,63]

It is of interest that in the AOT—*n*-decane—water system in the series of phosphonates **1** and **5—10**, the inhibition of alkaline hydrolysis ($k_{obs}/k_0 < 1$) is gradually replaced by equalizing the rates of the process in water and the micellar system ($k_{obs}/k_0 \approx 1$) in the case of substrates **9** and **10**. In addition, substrates **1**, **5**, and **6** (X = NO_2, Br, H) exhibit the retention of the tendency for decreasing k_{obs} with an increase in the surfactant con-

centration and water content, while for compounds **7**—**10** (X = Et, Bu^n, *n*-C_8H_{17}, *iso*-$C_{12}H_{25}$) k_{obs} is independent of the AOT concentration at a constant W.[63]

Unlike the reverse micellar system AOT—*n*-decane—water, the SDS—*n*-hexanol—water system manifests catalysis of the alkaline hydrolysis of esters **1** and **5**—**10**.[25,61] The catalytic effect changes in the series of X substituents as follows: $NO_2 > Br > H > Et \approx Bu^n \approx$ $\approx$ *n*-$C_8H_{17} \approx$ *iso*-$C_{12}H_{25}$.[61] A noticeable decrease in the reaction rate of phosphonate hydrolysis was observed in the series **1**, **5**, and **6**. The reactivity of substrates **6**—**10** in reverse SDS micelles differs from their behavior in water. In micellar solutions, k_{obs} for substrates **6** and **7** differ substantially and the reaction rate constants of phosphonates **7**—**10** are almost the same, while in water $k_{2,0}$ decreases smoothly with an elongation of the alkyl radical in the *para*-position of the leaving group. When *n*-hexanol is replaced by more polar *n*-butanol, the observed rate constant of alkaline hydrolysis decreases.[67] A comparative study of the micropolarity and catalytic effect of the reverse micellar system SDS—*n*-alkanol—water in the alkaline hydrolysis of **16** showed that the observed rate constant decreases with an increase in the microsopic polarity in the reaction zone. Therefore, it cannot be excluded that this is precisely the increase in the microenvironment polarity that decreases the reactivity of phosphonate **16** on going from *n*-hexanol to *n*-butanol.[67]

Thus, we can conclude that in direct micellar systems the factor of hydrophobicity of compounds plays a significant role. It provides better binding of reactants by micelles and favors an increase in the observed rate constant. In reverse micellar systems, a change in the microenvironment of reactants in the micellar pseudo-phase plays a great role, and the micellar effect is mainly related to a change in the true rate constant in micelles.

The results obtained indicate that catalysis in supramolecular systems is an efficient tool for purposeful control of the reactivity of compounds and the mechanism of their interaction. In addition to the concentrating effect and influence of the medium as the main components of the catalytic effect, there are structural factors providing a finer control of the catalytic mechanism, which enlarges substantially possibilities of supramolecular catalysis in the fundamental and practical aspects.

4. Catalytic and structural properties of microemulsions based on cationic surfactants and long-chain amines

Detergent microemulsions are thermodynamically stable, self-organizing, and macroscopically homogeneous dispersions with aqueous and hydrocarbon phases stabilized by surfactant molecules and cosurfactants (as a rule, low-molecular alcohols).[68,69] The high solubilizing ability and unusually developed interface surface, which provides efficient contact between the reagents with different solubility in aqueous and organic media, cause an interest in these systems as microreactors for various chemical processes.[70,71] Microemulsions differ from their precursors (micellar solutions) by a large size of aggregates, a high surfactant concentration in the system, and a considerable volume of the dispersed phase (more than 10%). Cosurfactants play an important role in the dynamic structure of microemulsions: a cosurfactant is localized in the interphase layer of a microdroplet and thus decreases its surface potential ψ. Based on the data on the kinetics of alkaline hydrolysis of carboxylic and phosphorus esters using the approaches proposed,[72] the authors determined the effective potentials in direct microemulsions based on cationic surfactants (CSurf). In these systems, they are 30—40 mV, *i.e.*, by 50—100 mV lower than those in micellar solutions.[73,74] The surface potential is a parameter characterizing a microemulsion as a reaction medium, because it determines the strength and role of Coulomb interactions during solubilization of reactants. This is precisely the surface potential that exerts a determining effect on the shift of acid-base equilibria related to the selective solubilizing ability toward neutral and ionic species of compounds. This was clearly demonstrated for a change in the basicity of *n*-cetylamine in direct microemulsions based on CPB, Brij-97, and SDS.[74] The higher the surface potential of a microdroplet, the larger the amount of the neutral species of amine present in the system, which reflects, in turn, its reactivity.

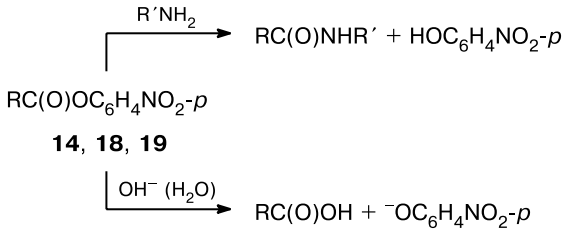
The influence of aggregation of different types in surfactant solutions (micelles, microemulsions) on the reactivity of organic compounds can be demonstrated by cleavage of esters in the presence of primary aliphatic amines. In this case, mixed systems can be formed containing microaggregates functionalized by the incorporation of long-chain amines into surfactant micelles. They are sensitive to a change in the pH of the medium and the ratio of components of the system and are capable of substrate binding in the prereaction step and entering into chemical reaction with the substrate, thus modeling the behavior of enzymes.[75—78]

Several characteristic parameters of the system, which confirm the formation of CSurf—amine microaggregates of a mixed type, were determined by independent physical methods (tensimetry, conductometry, high-resolution pulsed-field gradient ^1H NMR spectroscopy, and spin probe ESR).[79—82] For instance, for direct micellar solutions and microemulsions containing CSurf and long-chain amine, the diffusion motion of these components of the system inside a single structural aggregate was unambiguously shown by NMR. This method makes it possible to estimate the hydrodynamic radius (R) of microaggregates formed. In micellar solutions of CPB, R is equal to 3 nm and increases by approximately 15% when minor (less than 0.02 mol L^{-1}) additives of long-chain

amines (C_{10}—C_{18}) are introduced. In a region of high concentrations of CPB and amine, the mixed aggregates can be enlarged and rearranged. For example, for the CPB—*n*-decylamine system (C_{CPB} = 0.05 mol L^{-1}), a sharp increase in the hydrodynamic radius of a micelle (to 15 nm) is observed for an amine concentration higher than 0.02 mol L^{-1}.[76] Structural rearrangements in the system change the packing density of molecules forming the surface layer of a micelle. This is observed by ESR, which detects an increase in the correlation time of a paramagnetic probe solubilized in the surface layer of a micelle. It was also shown by this method that the critical amine concentration corresponding to structural rearrangement depends on the length of the hydrocarbon radical of the amine: the critical concentration of amine changes from 0.005 to 0.03 mol L^{-1} on going from *n*-dodecylamine to *n*-octylamine.[83]

In direct and reverse microemulsions based on cationic surfactants, the introduction of long-chain amines also increases the packing density of molecules in the interphase layer and the aggregate size. For instance, in the CPB—*n*-butanol—*n*-hexane—water system, the addition of 0.1 mol L^{-1} *n*-dodecylamine to direct microemulsions changes the *R* value (according to the self-diffusion NMR data) from 4.5 to 5 nm, whereas in reverse microemulsions *R* changes from 3.2 to 4.5 nm.[79] In this case, as shown by the analysis of the diffusion coefficients of the components of the system, amine partially displaces butanol and water from a microdroplet to the bulk, thus changing the composition, flexibility, and polarity of the interphase layer.[79,82]

In aqueous micellar solutions and microemulsions, the main process of cleavage of carboxylic esters is aminolysis. In addition to aminolysis, alkaline and neutral hydrolyses can occur, whose contributions are low. However, their value should be controlled in experiments in microheterogeneous systems.



R = Me (**14**), *n*-C_7H_{15} (**18**), *n*-$C_{11}H_{23}$ (**19**)
R´ = Alk

Long-chain amines in aqueous solutions are prone to self-association,[76,77,84] decreasing substantially their basicity and increasing nucleophilicity compared to the short-chain analogs. In the presence of a surfactant, the system is rearranged and mixed aggregates are formed. The latter possess qualitatively new properties. In micellar solutions and microemulsions based on CSurf, the

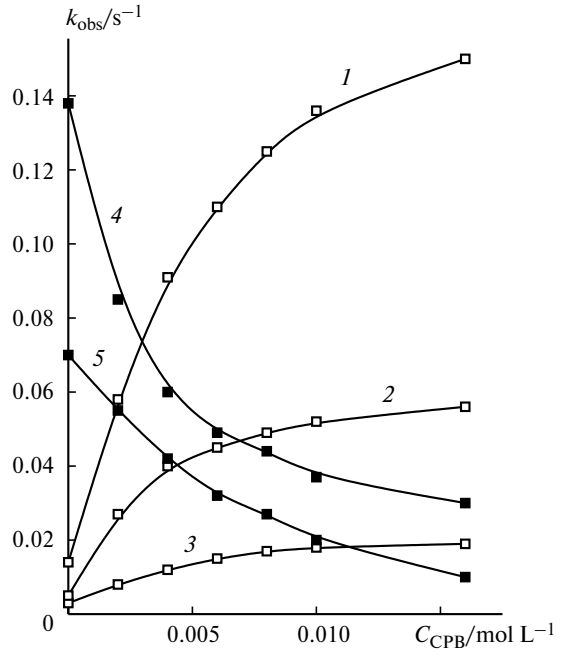


Fig. 5. Plots of the observed rate constants (k_{obs}) of the reactions of carboxylates with *n*-decylamine (DA) *vs.* CPB concentration (pH 9.4, 25 °C): *p*-nitrophenyl acetate, C_{AM}/mol L^{-1}: 0.005 (*1*), 0.0025 (*2*), and 0.001 (*3*); *p*-nitrophenyl caprylate, C_{AM}/mol L^{-1}: 0.005 (*4*) and 0.0025 (*5*).

shift of pK_a of amines increases the amount of their reactive neutral species and the rate of processes involving the amines. For instance, a considerable acceleration of the reactions (to 70 times) in mixed micelles CPB—*n*-decylamine was detected for the aminolysis of acetate **14**.[75,83] However, the reaction rate decreases strongly (Fig. 5) for hydrophobic substrates *p*-nitrophenyl caprylate (**18**) and *p*-nitrophenyl laurate (**19**) in these systems. The inhibition of the reactions of esters **18** and **19** with *n*-decylamine by CPB micelles contradicts the increase in the neutral species of amine. Probably, the addition of CSurf to the *n*-decylamine—water system containing highly active aggregates, whose formation also involves a hydrophobic substrate,[77,85] induces the rearrangement of micelles and formation of a new multicomponent highly organized mixed system involving a surfactant. In this case, neutral decylamine and substrate molecules included in this system can be separated or unfavorably oriented, which impedes their interaction and results in the inhibition of the process. The inhibition of the reaction can also be related to the fact that it occurs in the low-polarity region of a micelle and, in this case, the transition state of the S_N2 process can be destabilized. It should be noted that reactions of nonmicelle-forming amines (*n*-butylamine, *n*-heptylamine) in solutions of CPB are accelerated by approximately two orders of magnitude for both substrates **14** and **18**. In addition, the contribution of alkaline hydrolysis becomes noticeable

for these amines in the presence of CSurf.[75] Thus, the CSurf—amine—water systems exhibit a pronounced substrate specificity toward *p*-nitrophenyl carboxylates, which is related to structural rearrangements of CSurf micelles in the presence of hydrophobic amines.

In direct CSurf-based microemulsions, no substrate specificity for carboxylates is observed in the presence of amines. For instance, in CTAB (or CPB)—*n*-butanol—*n*-hexane—water systems at different ratios of the components in the microemulsion, the activity of ester **14** is higher than those of **18** and **19** regardless of the hydrocarbon radical length in amine, and the hydrophobicity of the nucleophile affects slightly the process rate (Table 2).[78,86] In the microemulsions studied, the dependence of k_{obs} on the amine concentration is linear. This linearity is not violated even for *n*-decylamine prone to micelle formation in aqueous solutions. The value of intercept in the kinetic plots characterizing the contribution of alkaline hydrolysis to the overall process rate is low; however, this contribution should be taken into account for low amine concentrations and high pH of the medium. The study of the kinetics of aminolysis and hydrolysis of carboxylic esters at different temperatures showed that the first process is characterized by a low activation energy (16.7—29.3 kJ mol^{-1}), whereas the second process has a much higher activation energy (71.1—83.6 kJ mol^{-1}). Therefore, in microemulsions, the temperature, along with the concentration of nucleophiles and pH, can be an important parameter determining the direction of the process of substrate cleavage.

The study of the kinetics of aminolysis of carboxylates in microemulstion CTAB-based systems with variation of the water to hydrocarbon (*n*-hexane) ratio in a wide range found an increase in k_{obs} on going from reverse to direct microemulsions (see Table 2).[82] Taking into account that low-polarity long-chain amines are insoluble in water, we estimated the second-order rate constants in the nonaqueous phase of microemulsions ($k_{2,\varphi}$) from the concentration plots of k_{obs} using the equation $k_{2,\varphi} = (1 - \varphi)k_{obs}/C_{am}$, where φ is the volume fraction of water in the system. These constants make it possible to take into account the influence of the concentrating factor on the process rate and reflect a change in the microenvironment in the reaction zone (medium factor). The resulting $k_{2,\varphi.}$ values (see Table 2) are rather close for different types of microemulsions, *i.e.*, probably, the reaction occurs in regions with the same micropolarity regardless of the microemulsion structure. The second-order rate constants (k_2) of aminolysis of the esters under study in nonpolar *n*-hexane and low-polarity *n*-butanol are much lower than $k_{2,\varphi}$ in microemulsions.[73,82] This allows us to assert that the chemical reaction zone in microemulsions is the polar interphase layer and shifts to the oily or aqueous phase depending on the hydrophobicity of reactants. This can be indicated, *e.g.*, by an increase in the $k_{2,\varphi}$ values for the aminolysis of acetate **14** on going from *n*-cetylamine to *n*-hexylamine (see Table 2).

The influence of a change in the medium dispersity on the mechanism of the process can be illustrated by the hydrolytic cleavage of phosphorus esters, in particular, phosphonate **13**, in the presence of amines. The cleavage of these esters in aqueous solutions occurs as hydrolysis catalyzed according to the general basic mechanism of catalysis, whose efficiency is determined by the basicity of amine.[4,86] In addition, alkaline hydrolysis can occur.

$$MeP(O)(OC_6H_4NO_2\text{-}p)_2 + H_2O \cdot H_2NR + 3\ H_2O \longrightarrow$$
$$\longrightarrow MeP(O)(OC_6H_4NO_2\text{-}p)O^- +$$
$$+\ {}^-OC_6H_4NO_2\text{-}p + 2\ H_3O^+ + H_2O \cdot H_2NR$$

R = Alk.

We can expect that both processes would be accelerated in aqueous micellar solutions containing CPB and long-chain amine. This is caused, first of all, by the fact that the substrate and amine are solubilized by micelles due to hydrophobic interactions. In addition to this, OH^- ions are concentrated on the positively charged micellar surface (the surface potential for CPB micelles is

Table 2. Observed rate constants of the reactions of carboxylates **14** and **19** with *n*-alkylamines (amine concentration 0.04 mol L^{-1}, 25 °C) and the second-order rate constants of aminolysis in the nonaqueous phase in CTAB-based microemulsions at different volume fractions of water (φ) in the system

Amine	k_{obs}/s^{-1} ($k_{2,\varphi}$/L mol^{-1} s^{-1})					
	φ = 0.14		φ = 0.30		φ = 0.74	
	14	**19**	**14**	**19**	**14**	**19**
Hexylamine	0.059 (1.27)	0.0027 (0.058)	0.068 (1.15)	0.0035 (0.06)	0.203 (1.27)	0.0144 (0.090)
Octylamine	0.0496 (1.066)	0.0023 (0.0495)	0.065 (1.10)	0.0036 (0.061)	0.192 (1.2)	0.0141 (0.088)
Decylamine	0.045 (0.968)	0.00248 (0.0533)	0.055 (0.935)	0.0033 (0.056)	0.18 (1.125)	0.013 (0.081)
Cetylamine	0.645 (0.03)	0.06 (0.0028)	0.647 (0.0381)	0.097 (0.0039)	0.73 (0.177)	0.0663 (0.0106)

Note. k_2 (L mol^{-1} s^{-1}) of aminolysis of acetate **14** in *n*-hexane: 0.018 (hexylamine) and 0.02 (cetylamine); in *n*-butanol: 0.28 (hexylamine) and 0.33 (cetylamine).

Table 3. Micellar parameters of hydrolysis of **13** in a CPB medium in the presence of primary *n*-alkylamines (AM) (25 °C)

Nucleophile	C_{AM} /mol L^{-1}	pH	K'_S /L mol^{-1}	CMC* /mol L^{-1}	k_m /s^{-1}	k_m/k_0**
Butylamine	0.005	10.4	330	0.001	0.185	30
	0.01	10.4	300	0.0011	0.197	32
Octylamine	0.0025	9.4	195	0.0001	0.0306	77
	0.005	9.4	267	0.0002	0.0329	82
	0.01	9.4	364	0.0001	0.0385	96
	0.02	9.4	350	0.0001	0.0407	98
	0.005	10.4	310	0.0003	0.20	35
Decylamine***	0.0010	9.4	80	0.0001	0.060	150
	0.0018	9.4	92	0.0001	0.0826	206
	0.0025	9.4	87	0.00007	0.121	300
NaOH		10.4	330	0.0006	0.20	36

* For CPB, the CMC is 0.00085 mol L^{-1}.
** k_0 is the observed rate constant of alkaline hydrolysis at a specified pH in the absence of a surfactant.
*** In the absence of CPB at pH 9.4 for decylamine, K'_S = 46 L mol^{-1}, the CMC is 0.001 mol L^{-1}, and k_m = 0.21 s^{-1}.

130—140 mV)[75] due to the electrostatic attraction. The observed rate constant values obtained for the hydrolysis of ester **13** in the presence of *n*-octylamine in aqueous solutions of CPB at pH 9.4 depend slightly on the amine content in the reaction medium (Table 3).[76] This favors that alkaline hydrolysis is prevailing under these conditions and the amine acts as a buffer only. The rate of cleavage of **13** in micellar solutions of CPB in the presence of *n*-decylamine, where mixed aggregates with a high catalytic effect are formed, depends substantially on the amine concentration (see Table 3). This suggests that the contribution of general basic catalysis is rather high in this case.

The kinetic data obtained for the cleavage of substrate **13** were analyzed in the framework of the pseudo-phase model of micellar catalysis using Eq. (1). This model is also successfully used for mixed micelles.[87] The results of calculations presented in Table 3 show that long-chain amines facilitate the micelle formation of CPB decreasing the CMC, which is characteristic of the formation of mixed micellar aggregates.[88] Despite low K'_S values of substrate **13** in the presence of *n*-decylamine, the efficiency of micellar catalysis (k_m/k_0) is approximately fourfold higher than that for *n*-octylamine (see Table 3). It should be emphasized once more that alkaline hydrolysis can occur along with general basic catalysis in micellar solutions of CPB for the cleavage of phosphorus esters. Therefore, the values of rate constants in the micellar phase are effective. The close k_m values for *n*-butylamine and *n*-octylamine at pH 10.4 and k_m of alkaline hydrolysis at the same pH correspond to the assumption that the process proceeds, in this case, *via* almost single direction: micelle-catalyzed alkaline hydrolysis of **13**.

The study of the hydrolysis of substrate **13** in the presence of amines in direct CPB-based microemulsions showed that the plots of k_{obs} *vs.* concentration of amines with different structures are linear with a high slope,[80,89] which indicates a low contribution of alkaline hydrolysis. The surface potential of the CPB-based microemulsion is 35 mV.[73] This is precisely the parameter much lower for this system than for a micellar solution of CPB, which is responsible for concentrating of hydroxide ions near the microdroplet surface and determines the alkaline hydrolysis rate of the substrate. In a microemulsion for the process studied, the contribution of the general basic mechanism of catalysis turned out to be high: it increased and became predominant with an increase in the amine concentration and a decrease in the pH of the medium. The surface potential also affects the acid-base equilibrium constants and determines the fraction of the neutral (reactive) species of amine. The second-order rate constants of hydrolysis of substrate **13**, catalyzed by the general basic mechanism, were calculated taking into account the fraction of the neutral species of amine (α) and are presented in Table 4.

The hydrophobicity of a nucleophile in microemulsions has no substantial effect on the mechanism of the process under study. However, hydrolysis in the presence of *n*-butylamine and *n*-octylamine occurs more rapidly than in the presence of their more hydrophobic homologs. This can be explained by different effects of amines on the structure of microemulsion droplets, namely, displacement of water from the surface layer by long-chain amines.[79] Since chemical processes in microemulsions occur inside a droplet or in its surface layer, water displacement results in the separation of a nucleophile, which is water activated by amine, and a substrate. This separation reflects in a decrease in the hydrolysis rate with an elongation of the hydrocarbon radical chain of amine.

Thus, in micellar solutions of CSurf for the hydrolysis of phosphorus esters in the presence of amines, the ratio of contributions of alkaline hydrolysis and hydrolysis cata-

Table 4. Rate constants of hydrolysis (k_2) of **13** in the presence of *n*-alkylamines in a direct CPB-based microemulsion (25 °C)

Amine	α at pH		k_2/L mol^{-1} s^{-1}
	9.4	10.4	
Butylamine	0.20	0.56	1.30
Octylamine	0.68	0.95	0.85
Decylamine	0.69	1.0	0.55
Dodecylamine	0.70	1.0	0.56
Cetylamine	0.70	1.0	0.55
Octadecylamine	0.70	1.0	0.55

Note. α is the fraction of the neutral species of amine; k_2 were determined in the pH interval from 9.0 to 10.4 and for the amine concentration from 0.001 to 0.2 mol L^{-1}.

lyzed by the general basic mechanism and the micellar catalytic effect depend on the hydrophobicity of amines. In microemulsions, the contribution from the general basic mechanism of catalysis is high, and its value is determined by the amine concentration, pH of the medium, surface potential, and distribution of components of the system between the extended and dispersed phases.

Based on the above-presented material, we can conclude the following. Supramolecular catalytic systems provide broad possibilities for control of the mechanism and rates of chemical reactions. An information obtained by the systematic study of the physical and catalytic properties of self-organizing solutions of surfactants showed a variety of species formed in these systems, which possess a specific catalytic effect. The purposeful inducing of structural and phase transitions between these species is an efficient tool for the variation of the reactivity of compounds. In addition, different manifestations of the catalytic effect in supramolecular systems depending on the nature of substrates create wide challenges for design of highly selective compositions. Additional prospects in this direction are related to the functionalization of micelles and microemulsions by the formation of multicomponent supramolecular systems including ingredients with nucleophilic activity or manifesting their inherent catalytic effect.

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