Mixed micelles of cetyltrimethylammonium bromide and poly(ethylene glycol)-600 monolaurate as catalysts of polyethylenimine phosphorylation in chloroform

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Micelle formation in a cetyltrimethylammonium bromide—poly(ethylene glycol)-600 monolaurate—chloroform system in the absence and presence of hydroxybenzylated polyethylenimines (PEI) was studied by dielcometric titration, NMR self-diffusion, light scattering, and kinetic methods. A catalytic effect of mixed micelles on the reaction of 4-nitrophenylbis(chloromethyl)phosphinate with PEI was shown. The catalytic effect depends on the degree of substitution of PEI and composition of a surfactant mixture.

Key words: surfactant, mixed micelles, catalysis, polyethylenimine, phosphorylation, complex.

Mixtures of surfactants are often used in detergent, cosmetic, pharmaceutical, and other compositions.[1] Mixed systems are of interest because of their ability to enhance metal extraction[2] and act as media for biocatalytic reactions[3] or catalysts of chemical processes.[4] Therefore, it is necessary to study the properties of mixed micellar systems. The most part of works[1,5—7] in this area concern aqueous solutions of surfactants. It is known that reverse micellar systems, including those of the mixed type, can act as nanoreactors for the synthesis of practically important compounds.[8,9]

In the present work, we studied the micelle formation in a mixture of cationic (cetyltrimethylammonium bromide, CTAB) and nonionogenic (poly(ethylene glycol)-600 monolaurate, PM) surfactants in chloroform and the effect of reverse micelles on the reaction of 4-nitrophenylbis(chloromethyl)phosphinate (NCP) with branched polyethylenimines (PEI) containing 2-hydroxybenzyl substituents at the secondary and tertiary nitrogen atoms: $CH_2C_6H_4OH$-2 (PEI-1) and $CH_2C_6H_3$(OH-2)(*i*-C_9H_{19}-5) (PEI-2—PEI-4). The degree of substitution (the number of substituted fragments per unsubstituted PEI fragment) for PEI-1, PEI-2, PEI-3, and PEI-4 was 0.3, 0.12, 0.16, and 0.3, respectively.

Experimental

Cetyltrimethylammonium bromide (Sigma) was purified by recrystallization from an acetone—ethanol mixture, PM (Ferak) was used without preliminary purification, and NCP was synthesized using an earlier described procedure.[10] Samples of hydroxybenzylated PEI were prepared by refluxing branched PEI (M 10 000) with 2-dimethylaminomethylphenol or 2-dimethylaminomethyl(4-isononyl)phenol (transamination reaction) on reflux for 5—10 h in *p*-xylene followed by removal of volatiles and evacuation at 150 °C to constant weight. A sample of the initial PEI (Aldrich) was used as received. The molecular weight of monomeric units of PEI was determined by potentiometric titration.[11] Prior to use chloroform was purified by a standard method.[12]

The reaction kinetics was studied spectrophotometrically under pseudo-molecular conditions on a Specord UV—Vis spectrophotometer. Reaction rate constants were determined by the first-order equation. The substrate concentration in kinetic experiments was $5 \cdot 10^{-5}$—$2 \cdot 10^{-4}$ mol L^{-1}. The PEI concentration (mol L^{-1}) was calculated from the molecular weight of the monomeric unit.

^{31}P NMR spectra were recorded on a Bruker MSL-400 instrument (162 MHz) using H_3PO_4 as external standard. The concentration NCP and PEI at the beginning of the reaction was 0.02—0.03 and 0.1—0.3 mol L^{-1}, respectively.

Dielcometric titration was carried out by an earlier described procedure.[13] The dielectric constant of solutions (ε) was determined on a setup consisting of an E12-I instrument working by the beat method and a measurement cell (temperature-controlled condenser).[14] The orientational polarization was calculated by the equation

$$P_{or}^{exp} = 3 \cdot 10^3 C^{-1}[(\varepsilon_{12} - \varepsilon_1)(\varepsilon_1 + 2)^{-2} - (n_{12}^2 - n_1^2)(n_1^2 + 2)^{-1}],$$

where C is the concentration of the dilute (mol L^{-1}), n is the refraction index, and indices 12 and 1 concern the solution and

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solvent, respectively. Refraction indices were measured on an IRF-23 refractometer.

Self-diffusion aggregates of surfactants in $CDCl_3$ were measured according to a procedure of 2D diffusion ordered spectroscopy (2D DOSY)[15] on a Bruker Avance-600 NMR spectrometer with the 5-mm *z*-gradient inversion sensor.

Sizes of aggregates were determined on a PhotoCor Complex photon correlation spectrometer of dynamic and static light scattering. A He—Ne gas laser (power 10 mW, wavelength 633 nm) served as the laser radiation source. Signals were analyzed with a one-plate multichannel correlating device connected with the IBM PC-compatible computer. The light scattering angle was 90°.

Viscosimetric measurements were carried out on an Ubellohde viscometer using a temperature-controlled cell.

Results and Discussion

Micelle formation in solutions of CTAB and PM was studied by dielcometric titration, NMR self-diffusion, light scattering, and kinetic methods.

The dependences of the dielectric constant and orientational polarization in mixed CTAB—PM (5 : 1, mol) solutions on the total surfactant concentration in chloroform are presented in Figs 1 and 2. In the absence and presence of PEI-2, the characteristic curves (see Fig. 1) contain inflections at $(2—3.5)\cdot10^{-3}$ and $2.5\cdot10^{-3}$ mol L^{-1}, respectively, which can be explained[16] by a change in the aggregate state of the solutions caused by the formation of reverse micelles or polymer-colloidal structures. The inflections at $1.3\cdot10^{-2}$ and $1.6\cdot10^{-2}$ mol L^{-1} are probably caused by the change in their shape with the growth of the aggregate volume. The concentration plots of P_{or}^{exp} also contain inflections in the regions of total concentrations of $(2—6)\cdot10^{-3}$ and $(1—1.7)\cdot10^{-2}$ mol L^{-1} (see Fig. 2).

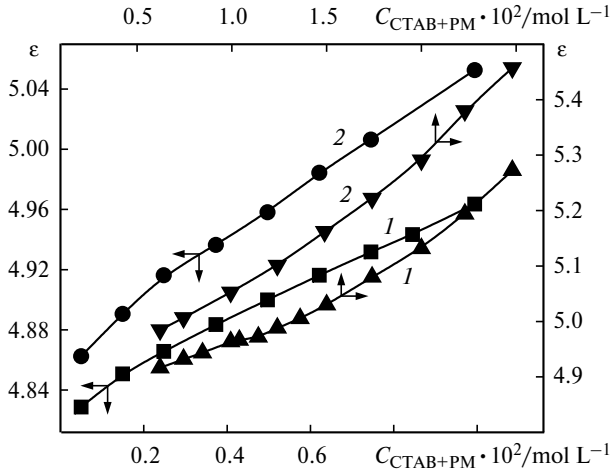


Fig. 1. Dependences of the dielectric constant of CTAB—PM (5 : 1, mol) solutions in chloroform in the absence (*1*) and presence of 0.01 *M* PEI-2 (*2*) on the total surfactant concentration at 20 °C.

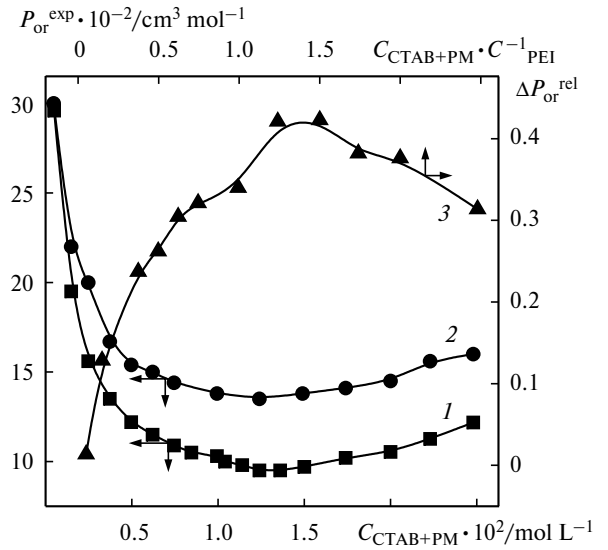


Fig. 2. Orientational polarization in CTAB—PM (5 : 1, mol) solutions in the absence (*1*) and presence of 0.01 *M* PEI-2 (*2*) and the dependence of the relative increase in the orientational polarization on the ratio of the total surfactant concentration to the PEI concentration (*3*) at 20 °C.

The data obtained by NMR self-diffusion of mixed solutions of CTAB and PM with the surfactant mole ratio 5 : 1 indicate in favor of assumptions about the change in the micelle size. The self-diffusion coefficient of formed aggregates decreases with an increase in the total surfactant concentration (Fig. 3).

It is known[17] that in the spherical approximation one of the main characteristics of micelles, their radii, can be estimated by the Stokes—Einstein equation

$$D_M = kT/(6\pi\eta R_M), \qquad (1)$$

where D_M is the self-diffusion coefficient of micelles, η is the viscosity of the medium, k is the Boltzmann constant, and R_M is the radius of micelles.

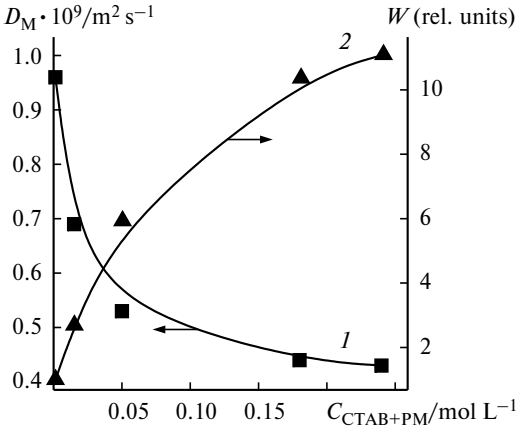


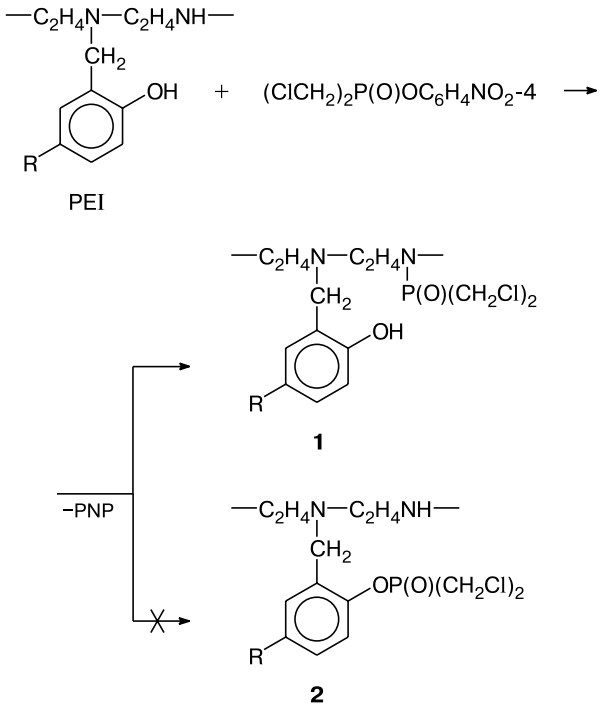
Fig. 3. Self-diffusion coefficient (*1*) and the change in the volume of micellar CTAB—PM (5 : 1, mol) aggregates (*2*) in the region of total surfactant concentrations of 0.0012—0.24 mol L^{-1} at 30 °C.

For the calculation of R_M of mixed micelles it was assumed that at the minimum total surfactant concentration the viscosity of the solution is equal to the solvent viscosity. A correction to the change in the viscosity of solutions with a higher surfactant content was applied by the multiplication of the experimentally determined D_M values by the extent of decreasing the self-diffusion coefficient of chloroform with an increase in the total surfactant concentration. In the range of total concentrations from 0.0012 to 0.24 mol L^{-1} at 30 °C R_M increases from 0.79 to 0.97 nm. An 11-fold increase in the volume of mixed micelles (W) corresponds to this change (see Fig. 3), and the sharp decrease in the self-diffusion coefficients and the increase in the aggregate volume start already at low surfactant concentrations. It can be assumed that this character of changing the volume of micelles provide the rearrangement of their structure.

The results obtained by NMR self-diffusion agree with the light scattering data. The effective radius of aggregates formed in a solution of a mixture of CTAB (0.2 mol L^{-1}) and PM (0.04 mol L^{-1}) in chloroform at 25 °C was calculated by Eq. (1) and equals 0.9 nm. In this case, the viscosity of a surfactant solution determined by viscosimetry was used in calculations of R_M.

In addition to structural studies of CTAB—PM solutions in chloroform, we studied the effect of mixed micelles on the phosphorylation of hydroxybenzylated PEI.

Scheme 1



R = H (PEI-1), *i*-C_9H_{19} (PEI-2—PEI-4)

The formation of *p*-nitrophenol (PNP) during the reaction was detected spectrophotometrically by the appearance of absorption bands at 310—320 and 390—440 nm. The reaction affords the phosphorylation products (**1**) at the N—H bonds of the substrate (Scheme 1). The ^{31}P NMR signals with δ_P +22.7, +22.9, +22.3, and +23.9 correspond to these products, which is characteristic of amidophosphinates.[18] The ^{31}P NMR spectra of the substrate in $CHCl_3$ and in CTAB (0.2 mol L^{-1})—PM (0.04 mol L^{-1}) mixture exhibit signals with δ_P +39.5 and +40.1. Note that when the process proceeds at the second possible reaction center, namely, the phenolic hydroxyl of the hydroxybenzyl substituent, the signal at δ ~38 in the ^{31}P NMR spectrum would correspond to the phosphorylation product (**2**).[19]

In mixed micellar solutions of CTAB (0.2 mol L^{-1}) and PM (0.04 mol L^{-1}) the reaction products of PEI-1 and PEI-4 are characterized by signals with δ_P +22.7 and +22.8, *i.e.*, the transition of the reactants from the solvent bulk to the micellar phase exerts no effect on the direction of PEI phosphorylation.

In the absence of a surfactant, the dependence of the apparent rate constant (k_{app}) of the reaction of NCP with PEI-1, PEI-2, PEI-3, and PEI-4 on the PEI concentration is described by the equation

$$k_{app,0} = k_{2,0} \cdot C_{PEI},$$

where at 25 °C the $k_{2,0}$ value is equal to 0.85, 0.16, 0.33, and 0.66 L mol^{-1} s^{-1}, respectively.

A polymer—micelle complex can be formed in a CTAB—PM—PEI—chloroform system. It is known that the formation of the complexes can reflect the physical properties of the solutions and the chemical behavior of the polymer.[20—22] The dielcometric plot of the relative increase in the orientational polarization of mixed micellar solutions in the presence and absence of PEI-2 ($\Delta P_{or}^{rel} = \Delta P_{or}^{exp}/P_{or}^{CTAB+PM}$, where $\Delta P_{or}^{exp} = P_{or}^{PEI+CTAB+PM} - P_{or}^{CTAB+PM}$) *vs.* ratio of the surfactant and PEI concentrations (see Fig. 2) exhibits an increase in ΔP_{or}^{rel} with passing through the maximum and, beginning from the concentration ratio $C_{CTAB+PM}/C_{PEI} = 1.5$, a decrease in the ΔP_{or}^{rel} value. The latter can be explained by the interaction of the polymer with surfactant aggregates. In addition, since the maximum $C_{CTAB+PM}/C_{PEI}$ ratio is not high, we can assume that low CTAB and PM concentrations in the solution the polymer interacts with surfactant aggregates of low degree of association.

Binding of the polymer and substrate with mixed CTAB—PM micelles increases k_{app} of PEI phosphorylation (Fig. 4). The experiments were carried at both the unchanged mole ratio of the cationic and nonionogenic surfactants (5 : 1) and constant PM concentration (0.01 mol L^{-1}) and an increasing CTAB content in the

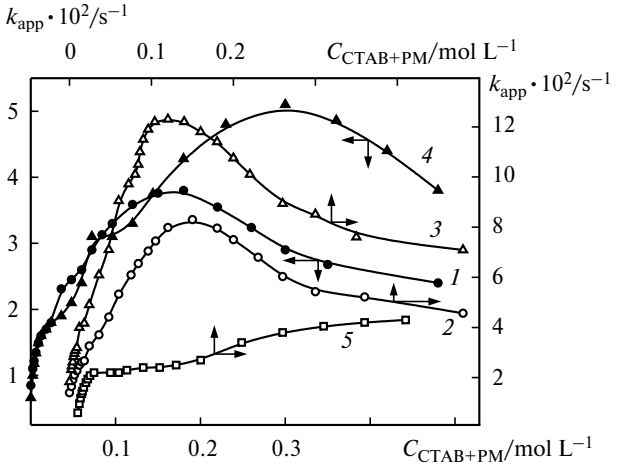


Fig. 4. Dependences of the apparent rate constant of the phosphorylation of PEI-1 (*1—3*), PEI-4 (*4*), and PEI-3 (*5*) in mixed micellar CTAB—PM (5 : 1, mol) (*1—4*) and CTAB—PM (0.01 mol L^{-1}) (*5*) solutions in chloroform on the total surfactant concentration at 25 (*1*, *4*, *5*), 40 (*2*), and 50 °C (*3*); C_{PEI} = 0.01 mol L^{-1}.

system (see Fig. 4). In the both cases, the concentration plots of k_{app} of the reaction are stepped. For instance, at 25 °C for PEI-1 in regions of total surfactant concentrations 0.02—0.03 and 0.05—0.07 mol L^{-1} a tendency of reaching a plateau is observed, while at 0.16—0.17 mol L^{-1} the plot passes through the maximum value. In the case of PEI-4, the character of these features remains unchanged but they occur at higher surfactant concentrations: 0.03—0.04, 0.07—0.11, and 0.3 mol L^{-1}, respectively.

At the constant PM concentration in the studied concentration range, the increase in the total surfactant content does not result in the extreme shape of the plot at high concentration but is accompanied by its gradual increase with a tendency of reaching a plateau (see Fig. 4). The stepped character of the dependence can be related to the rearrangement of the structure of mixed aggregates formed in the system, which favors an increase in k_{app} of the process. According to the pseudo-phase model of micellar catalysis, the plots pass through a maximum due to the diffusion of the reactants, which are solubilized in the micellar pseudo-phase, with an increase in the number of aggregates in the solution.[23] In our case, the tendency of passing through a maximum is observed only when the PM content in the solution increases and can be associated with an unfavorable influence of this component of the system on the process under study.[24]

Since the obtained concentration plots of k_{app} are stepped and particular regions of the plots, which correspond presumably to aggregates of the same type, has different shapes (with reaching a plateau and passing through a maximum), Eqs. (2)[25] and (3),[26] respectively, were used for quantitative description of these regions

$$k_{app} = (k_m K_s C_{surf} + k_0)/(1 + K_s C_{surf}), \quad (2)$$

where k_m (s^{-1}) and k_0 (s^{-1}) are the rate constants of a first-order reaction in the micellar phase and in the solvent bulk, respectively; K_s (L mol^{-1}) is the binding constant of the substrate with surfactant micelles; C_{surf} (mol L^{-1}) is the total surfactant concentration in the solution minus the critical micelle formation concentration (C_{mc});

$$k_{2,app} = \frac{k_{2,0} + (k_{2,m}V^{-1})K_s K_{Nu} C_{surf}}{(1 + K_s C_{surf})(1 + K_{Nu} C_{surf})}, \quad (3)$$

where $k_{2,app}$ (L mol^{-1} min^{-1}) is the apparent second-order rate constant obtained by the division of k_{app} into the nucleophile concentration; $k_{2,0}$ and $k_{2,m}$ (L mol^{-1} min^{-1}) are the second-order rate constants in the solvent bulk and micellar pseudo-phase, respectively; V (L mol^{-1}) is the mole volume of the surfactant; K_s and K_{Nu} (L mol^{-1}) are the binding constants of the substrate and nucleophile, respectively, with micelles.

The data presented in Tables 1 and 2 show that the values of k_m and binding constants of the reactants depend on the temperature, region of surfactant concentrations, and, in some cases, on the PEI structure. For instance, in CTAB—PM (5 : 1, mol) solutions the temperature increase is accompanied by an increase in k_m of the reaction (see Tables 1 and 2) and a decrease in K_{Nu} (see Table 2). The binding constant of the substrate in the region of low surfactant concentration somewhat decreases with the temperature increase (see Table 1). However, at high $C_{CTAB+PM}$ increases strongly (see Table 2). This leads to a situation when at 25 °C the K_s value decreases (by more than an order of magnitude) with an increase in the surfactant concentration. whereas at 50 °C K_s becomes twice as large (see Tables 1 and 2). The dependences of K_s on the temperature and surfactant concentration can be related to structural changes in the system and the relative decrease (or increase) in the polarity of their microenvironment in the micellar phase. This assumption is favored by the data on a change in the micellar phase polarity in the region of localization of the NH bonds in PEI in CTAB—PM—PEI-1(PEI-4) solutions in chloroform at 25 °C at different surfactant contents. The form of existence of micelle-solubilized PNP served as a measure of polarity of the medium.

In nonaqueous media in the presence of amines, PNP is known to form a complex with a hydrogen bond characterized by an absorption band at 300—330 nm and an ion pair with an absorption band in the visible spectral region.[27,28] In solvents with low dielectric constant (ε = 2—7) the equilibrium is shifted to the formation of the nonionic structure[27] (Scheme 2).

Table 1. Parameters of the micelle-catalyzed phosphorylation of PEI in mixed micellar CTAB—PM solutions in chloroform calculated using Eq. (2)[a]

Surfactant	PEI	Region of total surfactant concentrations /mol L^{-1}	T/°C	$k_0 \cdot 10^2$	$k_m \cdot 10^2$	K_s /L mol^{-1}	C_{mc} /mol L^{-1}	k_m/k_0
				s^{-1}				
CTAB—PM	PEI-1	0—0.024	25	0.85	2.2	104	0.0002	2.6
(5 : 1, mol)			40	1.4	3.6	81	0.00032	2.6
			50	1.8	5.7	74	0.00041	3.2
	PEI-4	0—0.036	25	0.66	2.1	170	0.00055	3.2
CTAB—PM	PEI-3	0.01—0.04	25	0.6[b]	2.5	130	0.01025	4.2 (7.6)[c]
(0.01 mol L^{-1})		0.11—0.41	25	2.4[d]	5.1	9.5	0.14	2.1 (15)[c]

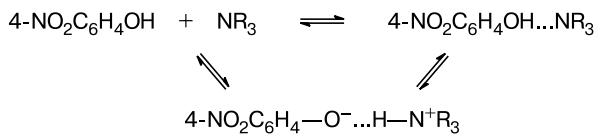
[a] C_{PEI} = 0.01 mol L^{-1}; 25 °C.
[b] The k_{app} value in a 0.01 *M* solution of PM.
[c] Acceleration of the reaction in the micellar phase relative to the process in chloroform (k_0 = 0.0033 s^{-1}).
[d] The k_{app} value at $C_{CTAB+PM}$ = 0.11 mol L^{-1}.

Table 2. Parameters of the micelle-catalyzed phosphorylation of PEI in mixed micellar CTAB—PM (5 : 1, mol) solutions in chloroform calculated using Eq. (3)[a]

PEI	Region of total surfactant concentrations/mol L^{-1}	T /°C	$k_{2,m}$ /L mol^{-1} min^{-1}	K_s	K_{Nu}	$k_{2,max}/k_{2,0}$[b]	C_{mc} /mol L^{-1}
				L mol^{-1}			
PEI-1	0.06—0.48	25	50	8.3	4.1	4.5	0.06
		40	140	25	1.9	5.9	0.073
		50	274	130	1.3	6.7	0.083
PEI-4	0.096—0.48	25	190	3.4	1.5	7.7	0.11

[a] C_{PEI} = 0.01 mol L^{-1}; 25 °C.
[b] Maximum acceleration of the reaction in micellar CTAB—PM solutions relative to the phosphorylation in chloroform.

Scheme 2



The spectrum of PNP in chloroform in the absence of PEI exhibits an absorption band at 310 nm. We have earlier found[29] that in the absence of surfactants in solutions of PEI-1 and PEI-4 an increase in the polymer concentration results in a decrease in the absorbance (D) at 310—330 nm and the appearance and increase in D of the absorption band of the ion pair at 400 nm. At constant PEI concentrations and low total concentrations of CTAB—PM (5 : 1, mol) the absorbance at 400—420 nm increases and that at 320 nm decreases with an increase in the surfactant content in the solution (Fig. 5), *i.e.*, in the region of the initial aggregation of CTAB—PM, PNP and PEI molecules exist in even somewhat more polar microenvironment than in the absence of surfactants. However, with an increase in the total concentration of CTAB and PM the absorbance at 400—420 nm decreases substantially and that at 320 nm (D_{320}) increases. These changes indicate a decrease in relative fraction of the ion pair in the solution, which reflects the fact of decreasing the

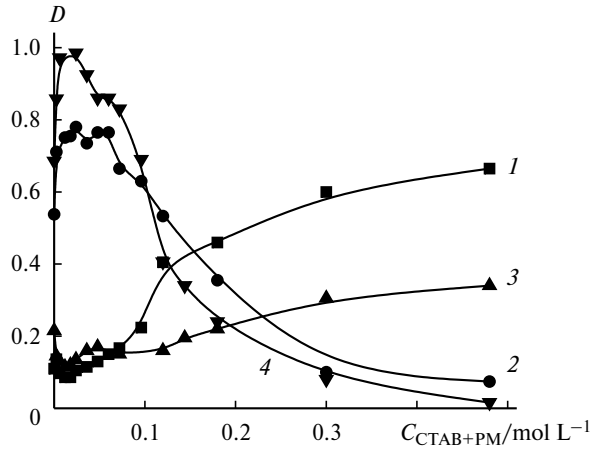


Fig. 5. Dependences of the absorbance of the PNP complexes with PEI-1 (*1*, *2*) and PEI-4 (*3*, *4*) in chloroform at 320 nm (*1*, *3*) and the absorption band maxima of the complexes at 400—420 nm (*2*, *4*) on the total concentration of CTAB and PM (5 : 1, mol) at 25 °C; $C_{PNP} = 5 \cdot 10^{-5}$ mol L^{-1}, C_{PEI} = 0.01 mol L^{-1}, d = 1 cm.

polarity of the microenvironment of the NH groups in PEI linked to the surfactant micelles.

The catalytic effect of micelles, which can be expressed through the $k_m k_0^{-1}$ (see Table 1) or $k_{2,max} k_{2,0}^{-1}$ ratio (see Table 2) depending on the range of the concentrations considered, depends weakly on the temperature and PEI structure.

In the framework of Berezin´s model (see Eq. (3)), the maximum acceleration of the process is described by the equation[26]

$$(k_{app} k_0^{-1})_{max} = \frac{k_{2,m}}{k_{2,0}} \cdot \frac{K_s K_{Nu}}{V(K_s^{0.5} + K_{Nu}^{0.5})^2}, \quad (4)$$

where the first cofactor in the right part reflects the factor of exchange of microenvironment of the reactants on their transition from the solvent to the micellar phase (F_m), and the factor shows the effect of concentrating the reactants in the micellar phase (F_c). In the region of high surfactant concentration in CTAB—PM (5 : 1, mol) solutions at 25 °C, for PEI-4 the F_m value equals unity, and that for PEI-1 is 0.32. This indicates that in the reactions under study the factor of microenvironment exchange exerts no or negative effect on the process. The F_c value for PEI-1 and PEI-4 is 3.3 and 1.3, *i.e.*, the factor of reactant concentrating makes the determining contribution to the catalytic effect of micelles. The temperature increase has no influence on the ratio of the factors. At 40 and 50 °C for PEI-1 the F_m values are 0.4 and 0.45, respectively, and F_c = 2.7 and 2.4.

When considering the catalytic effect of mixed micelles on chemical processes, the dependence of the catalytic activity of aggregates on the quantitative ratio of components of a binary composition is an important aspect.

The observed rate constants of phosphorylation of PEI in mixed micellar CTAB—PM solutions at different mole fractions of the cationic (α_{CTAB}) and nonionogenic (α_{PM}) surfactants are presented in Fig. 6. The presented plots show that an increase in the PM fraction in the solution first results in an increase in k_{app} of the process. However, the catalytic effect of micelles begins to decrease when α_{PM} = 0.2 (C_{CTAB} = 0.05 mol L^{-1}) and 0.024—0.1 (C_{CTAB} = 0.4 mol L^{-1}) are achieved (see Fig. 6 and Table 3). The increase in the PM fraction is also accompanied by a substantial decrease in the absorbance of PNP at 410 and 420 nm and an increase in D_{320} (Fig. 7). This fact indicates a change in the polarity of the reactant microenvironment depending on the relative fraction of surfactants in a CTAB and PM mixture, which can affect both the binding and reactivity of PEI and the substrate and, as a consequence, on the experimentally detected k_{app} value of the process. The catalytic effect of the system in the phosphorylation increases in the series

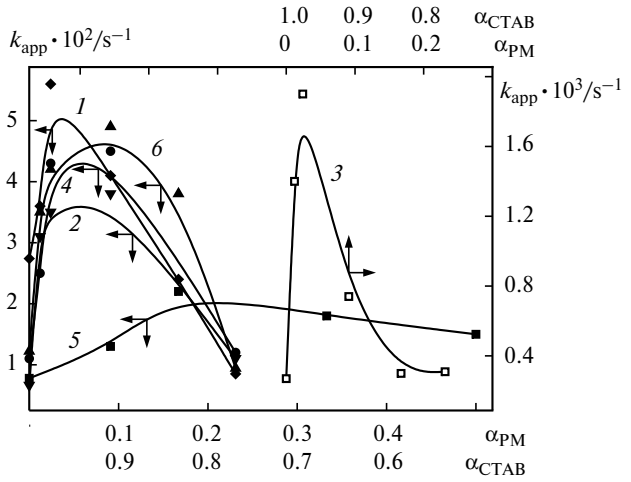


Fig. 6. Dependences of the apparent rate constant of the phosphorylation of PEI-1 (*1*), PEI-2 (*2*, *3*), PEI-3 (*4*, *5*), and PEI-4 (*6*) in mixed micellar CTAB—PM solutions in chloroform on the mole fraction of CTAB and PM in the solution; C_{PEI} = 0.01 (*1*, *2*, *4*—*6*), $5 \cdot 10^{-4}$ mol L^{-1} (*3*); C_{CTAB} = 0.4 (*1*—*4*, *6*), 0.05 mol L^{-1} (*5*); 25 °C.

Table 3. Catalytic effect of mixed CTAB—PM micelles in the phosphorylation of hydroxybenzylated PEI in chloroform at different mole fractions of the content of CTAB and PM in the solution[a]

$C_{CTAB+PM}$ /mol L^{-1}	α_{CTAB}	α_{PM}	$k_{CTAB+PM}/k_0$			
			PEI-1	PEI-2[b]	PEI-3	PEI-4
0.050	1	0	—	—	2.4	—
0.055	0.909	0.091	—	—	3.9	—
0.060	0.833	0.167	—	—	6.7	—
0.075	0.667	0.333	—	—	5.5	—
0.100	0.5	0.5	—	—	4.5	—
0.400	1	0	3.2	4.1 (3.4)	3.3	1.8
0.405	0.988	0.012	4.2	19 (18)	7.6	5.3
0.410	0.976	0.024	6.6	22 (24)	13	6.4
0.440	0.909	0.091	4.8	24 (9.3)	14	7.4
0.480	0.833	0.167	2.8	— (3.8)	—	5.8
0.520	0.769	0.231	1.0	6.9 (3.9)	3.6	1.4

[a] C_{PEI} = 0.01 mol L^{-1}; 25 °C.
[b] The values at $C_{PEI} = 5 \cdot 10^{-4}$ mol L^{-1} are given in parentheses.

PEI-1 < PEI-4 < PEI-3 < PEI-2; the maximum increase in the reaction rate is 24 times (see Table 3).

The apparent activation parameters of the reaction of PEI-1 with PNP in CTAB—PM (5 : 1, mol) in chloroform are given in Table 4. In the whole range of total

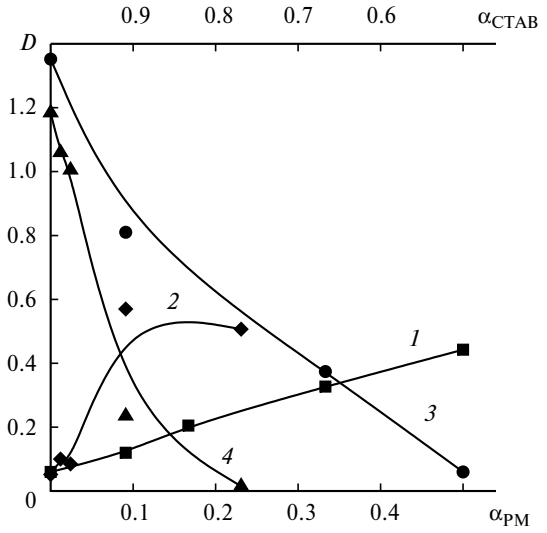


Fig. 7. Dependences of the absorbance of the PNP complexes with PEI-3 in mixed micellar CTAB—PM solutions in chloroform at 320 (*1*, *2*), 410 (*3*), and 420 nm (*4*) on the mole fraction of CTAB and PM in the solution; C_{CTAB} = 0.05 (*1*, *3*), 0.4 mol L^{-1} (*2*, *4*); $C_{PNP} = 5 \cdot 10^{-5}$ mol L^{-1}, C_{PEI} = 0.01 mol L^{-1}; 25 °C, d = 1 cm.

Table 4. Apparent activation energy and entropy of the reaction of PNP with PEI-1 (0.01 mol L^{-1}) in chloroform at different total concentrations of CTAB—PM

$C_{CTAB+PM}$ /mol L^{-1}	$E_{a,app}$ /kJ mol^{-1}	$\Delta S_{app}^{\neq}$ /J mol^{-1} K^{-1}
0	24.7	172
0.006	24.9	167
0.018	28.1	155
0.024	31.9	141
0.048	33.7	133
0.084	38.7	114
0.096	40.8	106
0.120	39.6	110
0.180	35.4	123
0.300	34.2	130
0.480	34.5	130

surfactant concentrations, the activation energies of the process are higher and the activation entropies are lower by the absolute value than those in the absence of surfactants. This indicates that the acceleration of the phosphorylation of PEI in reverse micellar CTAB—PM solutions is caused by the entropy factor. The $E_{a,m}$ and $\Delta S_m^{\neq}$ values calculated from the temperature dependences of the rate constants of the process in the micellar phase in the ranges of total surfactant concentrations 0—0.024 mol L^{-1} (see Table 1) and 0.06—0.48 mol L^{-1} (see Table 2) are equal to 30 kJ mol^{-1}, −150 J mol^{-1} K^{-1} and 54 kJ mol^{-1}, −73 J mol^{-1} K^{-1}, respectively. The values of the activation parameters in both the solvent bulk (see Table 4) and micellar phase correspond to the bimolecular mechanism of nucleophilic substitution.

Thus, binding of hydroxybenzylated PEI and PNP by mixed reverse micelles of the cationic and nonionogenic surfactants (CTAB and PM) accelerates the phosphorylation of PEI by more than an order of magnitude. The catalytic effect of the micelles depends substantially on the ratio of surfactant concentrations in the solutions and is enhanced with a decrease in the degree of substitution of PEI.

References

1. C. C. Ruiz and J. Aguir, *Langmuir*, 2000, **16**, 7946.
2. M. Mashimo, H. Sato, and I. Komasawa, *J. Chem. Eng. Jpn*, 1997, **30**, 712.
3. Y. Yamada, R. Kuboi, and I. Komasawa, *Biotechnol. Prog.*, 1993, **9**, 468.
4. A. J. Rondinone, A. C. S. Samia, and Z. J. Zhang, *J. Phys. Chem. B*, 1999, **103**, 6876.
5. L. Ya. Zakharova, F. G. Valeeva, A. R. Ibragimova, L. A. Kudryavtseva, N. N. Valeev, T. L. Didenko, V. I. Kovalenko, and A. I. Konovalov, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 2019 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 2176].
6. L. Ya. Zakharova, F. G. Valeeva, A. V. Zakharov, A. R. Ibragimova, L. A. Kudryvtseva, and H. E. Harlampidi, *J. Colloid. Interface Sci.*, 2003, **263**, 597.
7. J. A. McDonald and A. R. Rennie, *Langmuir*, 1995, **11**, 1493.
8. M. P. Pileni, *J. Phys. Chem.*, 1993, **97**, 6961.
9. C. L. Chiang, *J. Colloid Interface Sci.*, 2000, **230**, 60.
10. V. E. Bel´skii, L. S. Novikova, L. A. Kudryavtseva, and B. E. Ivanov, *Zh. Obshch. Khim.*, 1978, **48**, 1512 [*J. Gen. Chem. USSR*, 1978, **48** (Engl. Transl.)].
11. A. Arcelli and C. Concilio, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1327.
12. A. J. Gordon and R. A. Ford, *The Chemist´s Companion*, J. Wiley and Sons, New York, 1972.
13. E. N. Gur´yanova, I. P. Gol´dshtein, and I. P. Romm, *Donorno-aktseptornaya svyaz´* [*Donor-Acceptor Bond*], Khimiya, Moscow, 1973, 156 pp. (in Russian).
14. R. Sh. Nigmatullin, M. R. Vyaselev, and V. S. Shatunov, *Zav. Labor.*, 1964, **30**, 500 [*Ind. Lab.*, 1964, **30** (Engl. Transl.)].
15. B. Antalek, *Concepts Magn. Reson.*, 2002, **14**, 225.
16. E. P. Zhil´tsova, A. P. Timosheva, R. A. Shagidullina, A. R. Mustafina, L. A. Kudryavtseva, V. E. Kataev, E. Kh. Kazakova, V. F. Nikolaev, and A. I. Konovalov, *Zh. Obshch. Khim.*, 2001, **71**, 419 [*J. Gen. Chem.*, 2001, **71** (Engl. Transl.)].
17. V. D. Fedotov, Yu. F. Zuev, A. P. Archipov, and Z. Sh. Idiyatullin, *Appl. Magn. Reson.*, 1996, **11**, 7.
18. E. P. Tishkova and L. A. Kudryavtseva, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 280 [*Russ. Chem. Bull.*, 1998, **47**, 273 (Engl. Transl.)].
19. E. P. Zhil´tsova, L. A. Kudryavtseva, A. P. Timosheva, N. I. Kharitonova, and A. I. Konovalov, *Zh. Obshch. Khim.*, 2004, **74**, 687 [*J. Gen. Chem.*, 2004, **74** (Engl. Transl.)].
20. J. C. Brackman and J. B. F. N. Engberts, *Chem. Soc. Rev.*, 1993, **22**, 85.
21. D. Schubel and G. Ilgenfritz, *Langmuir*, 1997, **13**, 4246.

22. F. M. Witte and J. B. F. N. Engberts, *J. Org. Chem*., 1987, **52**, 4767.
23. C. A. Bunton and G. Savelli, *Adv. Phys. Org. Chem*., 1986, **22**, 213.
24. G. A. Garifullina and E. P. Zhil´tsova, in *Struktura i dinamika molekulyarnykh sistem* [*Structure and Dynamics of Molecular Systems*], Kazan Gos. Univ., Kazan, 2004, Issue XI, Part 1, 422 (in Russian).
25. *Adv. Phys. Org. Chem*., Ed. V. Gold, Academic Press, London—New York, 1970, **8**.
26. I. V. Berezin, K. Martinek, and A. K. Yatsimirskii, *Usp. Khim*., 1973, **42**, 1729 [*Russ. Chem. Rev*., 1973, **42** (Engl. Transl.).
27. *Molecular Interactions*, Eds H. Ratajczak and W. J. Orville-Thomas, J. Wiley and Sons, Chichester—New York—Brisbane—Toronto, 1981.
28. H. Baba, A. Matsuyama, and H. Kokubun, *Spectrochim. Acta, Part A*, 1969, **25**, 1709.
29. E. P. Zhil´tsova, G. A. Garifullina, S. S. Lukashenko, and A. P. Timosheva, *Zhidkie kristally i ikh prakticheskoe ispol´zovanie*, 2004, Issue 1, 38 [*Liquid Crystals and Their Application*, 2004 (Engl. Transl.)].

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