Sodium dodecyl sulfate—polyethyleneimine—water system. Self-organization and catalytic activity

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Concentration boundaries within which polymer—colloid structures exist in a sodium dodecyl sulfate—polyethyleneimine—water system were determined. The catalytic effect of this composition was found for the hydrolysis of phosphonic acid esters. The found acceleration of hydrolysis up to 25-fold is caused by reagent concentrating in a catalytic complex.

Key words: phosphorus acid esters, hydrolysis, kinetics, surfactant—polymer complex, sodium dodecyl sulfate, polyethyleneimine, pseudo-phase model.

Mixed systems surfactant-polymer are objects of a promising interdisciplinary scientific area that attract great researchers' interest.¹⁻⁶ The development of this avenue of investigation is stimulated by a wide scope of practically useful properties of mixed solutions and a possibility of their purposeful control by the variation of the component ratio in the system. In addition, the study of regularities of the formation of polymolecular ensembles extends potentialities of self-assembly modelling in biological systems. The main goal of fundamental studies of aqueous surfactant-polymer solutions is to prove the combined aggregation, find concentration boundaries for the existence of mixed structures, estimate their stability, and characterize the nature of intermolecular interactions. The reactivity of compounds in mixed polymer-colloid systems is poorly studied and, therefore, is one of the main tasks of the present work.

We have previously^{7,8} studied the physical and catalytic properties of polymer—colloid systems based on the cationic surfactant cetyltrimethylammonium bromide (CTAB) and polyethyleneimine (PEI). Different points of view about the possible cooperative binding of cationic surfactants with nonionic and likely charged polymers can be found in the literature.⁹ The published results^{7,8} favor the hypothesis on the self-organization and formation of supramolecular structures in the CTAB—PEI system. These structures efficiently catalyze the hydrolysis of phosphorus esters. Taking into account that the electrostatic interaction contributes unfavorably to the free energy of formation of complexes of the likely charged surfactant and polymeric species, it should be assumed that combined aggregates are formed in these systems mainly due to hydrophobic interactions. To gain more comprehensive information on the contribution from different types of intermolecular interactions in the surfactant—polymer systems, we continued to study the catalytic properties of PEI-based compositions, using an unlikely charged surfactant, sodium dodecyl sulfate (SDS). The hydrolysis of phosphonates **1–3** was studied as a model process (Scheme 1).



Compounds 1-3 were synthesized by a known procedure.¹⁰ Sodium dodecyl sulfate (Sigma) and branched PEI (Aldrich, molecular weight 30000) containing the primary, secondary, and tertiary nitrogen atoms in a ratio of 1:2:1 were used. Molar concentrations of PEI presented in the work are based on the

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monomeric unit. The hydrolysis kinetics was studied by spectrophotometry on a Specord M-400 instrument in the pseudo-first regime from a change in the absorbance of the leaving group anion. The apparent rate constants (k_{app}) were determined from the plot $\ln(A_{\infty} - A) = -k_{app}t + \text{const}$, where A and A_{∞} are the absorbance of the solution at the time moment t and at the end of the reaction, respectively. The weighed least-squares method was used, and average arithmetical values of three measurements differed by at most 5% were taken into account. The conductivity was measured on a CDM-2-d conductometer (Denmark). The surface tension was determined by the Wilhelmy ring method.¹¹ The degree of protonation of the polymer was estimated by the potentiometric titration of a PEI solution on a pH-340 instrument, using a 0.1 M aqueous solution of HCl as titrant.

The equilibrium surfactant concentration was measured by the potentiometric method using an EM-Vg-01 modified industrial heterogeneous membrane electrode selective to a dodecyl sulfate ion. The calomel electrode (Crytur, type 102) was used as the reference electrode. All measurements were carried out at 298 K in a temperature-controlled cell, whose design allowed potentiometric and viscosimetric measurements to be carried out simultaneously. The electrode function was fulfilled in the whole interval of surfactant concentrations under study. The slope ratio of the electromotive force plot *vs.* surfactant concentration $E = f(-\log c_{surf})$ in the region below the critical micelle concentration (CMC) of sodium dodecyl sulfate was (58±4)/pc_{surf} mV for SDS. All potentiometric measurements were carried out on an M-120 potentiometer (Microtechna) with an accuracy of ±1 mV at 25 °C. For experimental details, see Ref. 5.

The hydrodynamic behavior of macromolecules in solution was concluded from viscosimetric data. The viscosities of PEI solutions and their mixtures with surfactants were measured on a VPZh-1 Ubbelohde-type viscosimeter with a capillary diameter of 0.54 mm. The error for measurements of viscosity was at most 1%.

Kinetic data were analyzed in the framework of the pseudophase model using the equation 12

$$k'_{\rm app} = \frac{k_{2,\rm w} + (k_{2,\rm m}/V)K_{\rm S}K_{\rm Nu}C}{(1+K_{\rm S}C)(1+K_{\rm Nu}C)},$$
(1)

where k'_{app} (L mol⁻¹ s⁻¹) is the second-order rate constant obtained by the division of k_{app} into the overall nucleophile concentration; $k_{2,w}$ and $k_{2,m}$ (L mol⁻¹ s⁻¹) are the second-order rate constants in the aqueous and micellar phases, respectively; K_S and K_{Nu} (L mol⁻¹) are the binding constants of the substrate and nucleophile, respectively; V is the molar volume of the surfactant; and C is the surfactant concentration minus the critical association concentration.

The use of the modified form of Eq. (1) to express the catalytic effect, which is equal to the ratio of the apparent rate constant and the first-order reaction rate constant in an aqueous solution of PEI in the absence of SDS, makes it possible to estimate quantitatively the contribution of different factors to the micellar effect

$$(k_{app}/k_w)_{max} = F_m \cdot F_c, \tag{2}$$

$$F_{\rm m} = \frac{k_{2,\rm m}}{k_{2,\rm w}}, \qquad F_{\rm c} = \frac{K_{\rm S}K_{\rm Nu}}{V(\sqrt{K_{\rm S}} + \sqrt{K_{\rm Nu}})^2}.$$

The first term in the right part (F_m) of Eq. (2) characterizes a change in the microenvironment of reagents when the reaction is transferred from the aqueous to micellar phase, and the second term (F_c) determines the effect of reagent concentrating in aggregates.

Results and Discussion

To estimate the self-organization in the SDS-PEI-water system, we studied the conductometric properties of solution as a function of the surfactant concentration at different unchanged concentrations of the polyelectrolyte. The concentration plots of the conductivity (χ) for several PEI concentrations are presented in Fig. 1 as an example. In these plots, three linear regions are observed with breaks in the points C_1 and C_2 . In this case, the plot of conductivity vs. surfactant concentration¹¹ is assumed to be linear with breaks in the points corresponding to the formation of aggregates.^{13–15} Table 1 contains the critical concentrations and characteristics of the linear regions calculated by the equation y = ax + b, where a is the slope of the plot, and b is the section cut in the ordinate. As can be seen from the analysis, the emphasized sections are linear with a good correlation coefficient ($R \ge 0.99$). This confirms that three regions were substantially isolated in the plots for mixed surfactant-polymer systems, unlike individual micellar solutions of surfactants. Perhaps, this choice is somewhat arbitrary at a PEI concentration of 0.01 mol L^{-1} for which a and b are close in the B and C sections (see Table 1). In this case, probably, we cannot exclude that at such a low concentration of the polymer its influence on the selforganization process is insignificant and the micellization process does not involve macromolecules and is characterized by only one break in the C_1 point (CMC). The corresponding linearization of the data of the conductometric dependence with the isolation of two linear re-



Fig. 1. Conductivity (χ) of aqueous SDS—PEI solutions *vs.* SDS concentration at different PEI concentrations (25 °C): 0.2 (*I*), 0.1 (*2*), 0.02 (*3*), and 0 mol L⁻¹ (*4*).

Table 1. Conductivity in the SDS—PEI—water system vs. surfactant concentration: the critical concentrations C_1 and C_2 , slope (a) of the linear sections A, B, and C, and the section cut in the ordinate (b) by the A, B, and C sections (see Fig. 1; A corresponds to the lower concentration C_1 ; B, in the concentration interval C_1 – C_2 ; C, higher than the C_2 concentration)

$C_{\rm PEI}$	<i>C</i> ₁	<i>C</i> ₂	А			В			С		
	mol L ⁻¹		b	а	<i>R</i> (<i>n</i>)*	b	а	R(n)	b	а	R(n)
0**	0.0085 (CMC)	_	1.656	19.03	0.997 (5)	578.1	18055	0.997 (6)			
0.01	0.0048	0.01	31.70	125206	0.999 (4)	623	29796	0.97 (3)	687	24665	0.997 (6)
0.01**	0.0048	_	31.70	125206	0.999 (4)	681	24735	0.998 (9)			
0.02	0.0051	0.014	51.0	124607	0.994 (5)	466.1	49530	0.991 (4)	765.3	27550	0.991 (6)
0.05	0.0074	0.0155	49.58	124043	0.995 (6)	335.6	86430	0.994 (4)	1136	31662	0.991 (8)
0.1	0.008	0.02	72.14	124333	0.994 (4)	566.6	60569	0.9999 (3)	1230	29875	0.99999 (4)
0.2	0.016	0.035	133.8	115046	0.997 (9)	1205	50619	0.995 (5)	2406	17133	0.995 (4)

* R is the correlation coefficient, and n is the number of points in the section.

** Section B above the C_1 concentration.

gions indicates a small increase in the correlation coefficient (see Table 1).

This type of conductometric plots (see Fig. 1) is characteristic of a wide scope of polymer—colloid systems, including compositions based on anionic surfactants containing uncharged polymers and polyelectrolytes.^{13–15} According to the current concepts, depending on the polymer and surfactant types, complex nanostructures can form in solution, and their composition and structure are determined by all intermolecular interactions between a macromolecule and surfactant. Typical structures are shown in Fig. 2. The C_1 concentration, which is named the critical association concentration, corresponds to the onset of combined aggregation of surfactant and polymer molecules at which small friable surfactant aggregates are formed in solution. They are peripherally bound to the macromolecules. In the case of rather long flexible polymers, polymeric chains undergo globulization with inclusion of surfactant aggregates (see Fig. 2). The formation of combined structures continues up to the surfactant concentration equal to C_2 , which is named the polymer saturation concentration, after which usual micelles unbound to the polymer are formed in solution along with the polymer—colloid complexes.^{2,9}



Fig. 2. Nanostructures of the intrapolymeric (a, b) and interpolymeric (c) types.

The interaction of polyelectrolytes with unlikely charged surfactants,16-22 including self-organization in the PEI-based systems, $^{18-22}$ has a complex character. The structure of supramolecular systems is determined by the mutual influence of components in the surfactant/polyelectrolyte pair, molecular weight, flexibility, branching, and concentration regime of a polyelectrolyte solution. According to the commonly accepted point of view, the cooperative interaction with formation of nanostructures also can occur in the surfactant-polyelectrolyte system (see Fig. 2). The polymer-colloid complexes that formed can be intrapolymeric (involving one polymeric chain) or interpolymeric (involving several macromolecules). However, in some works researchers prove the non-cooperative interaction of the polyion with an oppositely charged surfactant. According to the known data,²² the first step is non-cooperative binding to form stoichiometric surfactant-polymer complexes. The next, cooperative step is accompanied by the formation of intrapolymeric micelles with low aggregation numbers at a surfactant concentration much lower than the CMC. As a result, the formation of the polymer-colloid complexes can be accompanied^{17,22} by a change in the macromolecule conformation and morphology of surfactant aggregates. Taking into account that PEI is a weak polyelectrolyte, we decided to use the polymer-colloid complexes presented in Fig. 2 as model structures for data interpretation.

When PEI additives were introduced into a surfactant solution, the conductivity increased (see Fig. 1) and continued to increase with an increase in the polymer concentration. This is caused by the fact that in an aqueous solution without a buffer (pH 9–10) PEI is a weak electrolyte and introduces the intrinsic contribution to the conductivity of the system. The C_1 and C_2 values increase with an increase in the polyelectrolyte concentration (see Table 1). Different tendencies for changing these critical surfactant concentrations were observed.^{14,15} In our case, as in the works,^{14,15} there is a tendency for extending the area where combined structures exist (designated by the C_1 and C_2 concentrations) with an increase in the polymer concentration. It should be noted that the interpretation of the conductometric results is not final: different explanations of the anomalous change in the conductivity in SDS-PEI solutions can be found in the literature.^{21,22} Therefore, this problem requires an additional study.

Although the catalytic effect of mixed surfactant—polymer solutions is mainly manifested at surfactant concentrations higher than the CMC and is caused by reaction transfer from an aqueous solution to mixed aggregates, we studied the physical properties of the solution in a wide interval of surfactant concentrations lower and higher than the CMC to reveal the motive forces of catalysis and characterize intermolecular interactions that occur in the catalytic complex. The viscosity isotherm of



Fig. 3. *a.* Isotherms of the reduced viscosity of PEI solutions with different concentrations: 0.0073 (1), 0.0365 (2), and 0.073 mol L^{-1} in the presence of SDS (25 °C). *b.* Reduced viscosity of PEI solutions *vs.* polyelectrolyte concentration.

PEI solutions, being the plot of the reduced viscosity η_{sp}/C_{PEI} vs. polymer concentration, is presented in Fig. 3. An increase in η_{sp}/C_{PEI} with the dilution of a polymer solution is a characteristic manifestation of the effect of polyelectrolyte swelling caused by the enhancement of the Coulomb repulsion of likely charged polymeric segments with a decrease in the ionic strength of the solution during dilution. The results of viscosimetric analysis of PEI solutions with different concentrations in the presence of SDS are presented in Fig. 3. It is known that the addition of a surfactant to a polyelectrolyte solution gives different types of plots of the specific viscosity vs. surfactant concentration. As a rule, for the oppositely charged surfactant, the effect is high compared to an uncharged or likely charged surfactant. Based on an insignificant change in the viscosity of the studied PEI samples, one should expect a weak interaction between SDS and PEI upon surfactant addition. A potentiometric study carried out using the electrodes selective toward a dodecyl sulfate ion showed that this is not true. The isotherms of dodecyl



Fig. 4. Degree of binding of dodecyl sulfate ions in PEI solutions with different concentrations *vs.* logarithm of the SDS concentration in the SDS—PEI—water system: 0.0073 (1), 0.073 (2), and 0.0365 mol L^{-1} (3).

sulfate ion binding in PEI solutions with different concentrations are shown in Fig. 4. They represent the plots of degree of binding B vs. surfactant concentration, where B is determined as a ratio of the molar concentration of the bound surfactant to its analytical concentration in solution. The B values never become lower than 0.95, even at low SDS concentrations, i.e., the surfactant molecules introduced into a PEI solution are bound almost completely. For the likely charged polyelectrolyte and surfactant, B do not usually exceed 0.6-0.7.5 High degrees of binding at a weak change in the hydrodynamic properties assume a considerable contribution of hydrophobic interactions to self-organization. This assertion is favored by the fact that PEI in an aqueous solution without buffer and salt additives is a weak polycation. The highest degree of binding (>0.99) was observed for a solution with the lowest PEI content (0.0073 mol L^{-1}). At this concentration, a PEI macromolecule takes the most unfolded conformation due to the effect of polyelectrolyte swelling, which is indicated by the viscous flow data (see Fig. 3). Therefore, the PEI concentration of this order provides the best accessibility of surfactant binding sites for polymeric chains. It cannot be excluded that a certain contribution to the enhancement of the SDS-PEI interaction is made by a change in the fraction of PEI-PEI cross-linking interactions with dilution of the polyelectrolyte solution.

To reveal a reason for the high affinity of PEI to SDS and the efficiency of the catalytic effect of SDS—PEI—water compositions, we measured the surface tension of the solutions at the air interface. The surface tension isotherms of the studied mixtures and SDS solution obtained by the Wilhelmy plate method are given in Fig. 5. We found that the polymer—colloid complexes that formed exhibit surfactant properties, so that already at low surfactant concentrations the surface tension at the liquid—air interface decreases sharply. This behavior is characteristic of the dense interphase packing of comb-



Fig. 5. Surface tension isotherms of the SDS—PEI—water system at different PEI concentrations (25 °C): 0 (*I*), 0.1 (*2*), and 0.2 mol L^{-1} (*3*).

shaped copolymers. The addition of a surfactant enhances this effect, so that the γ values become lower than those for an SDS solution without PEI. Note that, when the CMC of the surfactant is achieved, the surface tension of SDS—PEI—water mixtures increases but remains lower than that for a micellar surfactant solution. The latter is probably due to the desorption of some surfactant ions that are unbound to PEI from the liquid—air interface to the solution bulk during micellization. The researchers^{2,16} examined the adsorption properties of polymer—colloid solutions and proposed theoretical models of the surface behavior for different surfactant—polymer pairs. The type of the plots (see Fig. 5) is characteristic^{2,16} of weakly charged polyelectrolytes at their fairly high concentration in solution.

Before kinetic studies, we estimated the change in the pH of the system under experimental conditions. As known, PEI in an aqueous solution is involved in the acidbase equilibrium due to a lone electron pair (Scheme 2, a), increasing the pH to 9–10. At this pH some amino groups (5%) exist²³ in the protonated form. As can be seen

Scheme 2

$$(-CH_2CH_2NH-)_n + H_2O \iff$$
$$\iff (-CH_2CH_2NH-)_n - H^+ + OH^-, \qquad (a)$$

$$(-CH_2CH_2NH-)_n + H_2O + C_{12}H_{25}OSO_3Na \iff$$

 $\iff (-CH_2CH_2NH-)_n - H^+/C_{12}H_{25}OSO_3^- + NaOH,$

$$(-CH_{2}CH_{2}NH-)_{n}-H^{+}/OH^{-}+C_{12}H_{25}OSO_{3}Na \iff (-CH_{2}CH_{2}NH-)_{n}-H^{+}/C_{12}H_{25}OSO_{3}^{-}+NaOH.$$
(b)



Fig. 6. Plot of the pH of aqueous SDS—PEI solutions *vs.* SDS concentration at different PEI concentrations: 0.2 (*1*), 0.05 (*2*), 0.1 mol L^{-1} (*3*).

(Fig. 6), in the presence of SDS, the pH of the solution increases with an increase in the surfactant concentration. Although we did not carry out special exact studies, a comparison of the data in Figs 1 and 6 shows that the region of a sharp pH change coincides with the interval of SDS concentrations in which combined structures are formed, according to the conductometric data. These changes in the pH of the solution confirm convincingly that the surfactant and polymer molecules interact, probably, *via* Scheme 2, b.¹³

We estimated the fraction of protonated PEI groups (α) by variation of pH of the solution and polymer concentration using potentiometric titration (Table 2). The data presented show that already at pH 8.5 the fraction of protonated groups is close to 0.10, while in the kinetic experiment (at pH 9–10) without a buffer the α value is rather insignificant, which agrees with the published data presented above (5%).²³ In an SDS solution, with an increase in the pH, the degree of protonation is still lower.

Table 2. Degree of protonation of PEI (α) at different pH and concentrations of the polymer

C _{PEI}		α at pH								
/mol L^{-1}	5.5	6.0	6.5	7.0	7.5	8.0	8.5			
0.01	0.83 0.86	0.67 0.72	0.56 0.56	0.39 0.44	0.24 0.34	0.17 0.14	0.09			
0.02 0.03	0.83 0.88	0.72 0.80	0.61	0.50 0.56	0.33 0.39	0.24 0.28	0.11 0.17			

However, one should take into account a possibility of the pK_a shift in the polymer—colloid complexes. The data obtained agree well with the results of viscosimetric and conductometric studies in which PEI demonstrates the behavior of an uncharged polymer rather than polyelectrolyte. Analysis of a possible effect of the concentration of hydroxide ions formed by Scheme 2 on the results of conductometric experiments showed¹³ that the absolute values of specific conductivity corrected by the pH change exceed insignificantly the experimental data and the C_1 and C_2 critical concentrations are independent of the pH of solution.

In kinetic experiments, we studied the reactivity of phosphonates 1-3 (see Scheme 1) in the SDS-PEI-water system. We have earlier found the general base catalysis of hydrolysis of phosphorus esters in the presence of PEI.²⁴ The reaction is catalyzed by uncharged amino groups involved in the activation of a water molecule. Due to the electrostatic interaction with hydroxide ions, the protonated amino groups can enhance the contribution of alkaline hydrolysis of substrates to the apparent rate constant.

We have shown^{7,8} that, unlike short-chain polyamines (analogs of PEI),²⁵ the plot of apparent rate constant *vs.* PEI concentration is nonlinear and S-shaped, which is characteristic of enzymatic and micellar catalysis. The apparent rate constant in PEI solutions for substrate 1 is higher than those for substrates 2 and 3, which corresponds to the behavior of these substrates in aqueous alkaline solutions.²⁶ However, according to our data,²⁷ the reactivity increased with an increase in the substrate hydrophobicity in micellar solutions of cationic surfactants.

In the SDS-PEI-water system, hydrolysis is accelerated compared to an aqueous solution of PEI (Fig. 7), and the reactivity of the substrates decreases in the series 1 > 2 > 3, *i.e.*, the same tendency is fulfilled as in water and an aqueous PEI solution. Under the experimental conditions, the catalytic effect for these substrates, which is equal to the ratio of the apparent reaction rate constant in the surfactant-PEI system to the rate constant in an aqueous solution at the same pH, is 21, 13, and 8 times, respectively. It is important that the shape of the kinetic plots and quantitative data characterizing the reactivity of the substrates in the SDS-PEI-water system differ substantially from the earlier obtained values for individual SDS-water and PEI-water systems,7,28 which confirms that the reaction occurs in the polymer-colloid complexes.

The kinetic data were analyzed using Eq. (1) under the assumption that the reaction is transferred from the aqueous pseudo-phase to the polymer—colloid aggregates (Table 3). There are published examples of the successful use of the Michaelis—Menten equation, which is normally applied to enzymatic catalysis, for the simulation of kinetic data in polymeric colloidal solutions.^{29,30} The pre-



Fig. 7. Apparent hydrolysis rate constant for substrates 1–3 in the SDS–PEI–water system *vs.* SDS concentration in the absence of a buffer (1, 3; 2, 2; and 3, 1) and for substrate 1 in the presence of the methylmorpholine buffer (4); $C_{\text{PEI}} = 0.1 \text{ mol } \text{L}^{-1}$, 45 °C.

dominant contribution to the catalytic effect belongs to the effect of reactant concentrating in the polymer—colloid aggregates (see Table 3), whereas a change in the microenvironment of reactant exerts an unfavorable influence on the reactivity. The enhancement of the negative influence of the microenvironment is a reason for a decrease in the hydrolysis rate in the series of substrates 1-3, despite the simultaneous increase in the concentrating factor.

For substrate 1, we studied the hydrolysis kinetics at different temperatures (Fig. 8) and calculated the activation parameters of reaction in different microphases (see

Table 3. Quantitative analysis of the kinetic data for the hydrolysis of compounds 1-3 in the SDS-PEI-water system using Eq. (1)

Com-	• <i>T</i>	K _S	<i>K</i> _{Nu}	$k_{2,m} \cdot 10^4$	F _m	Fc	$F_m \cdot F_c$
po- /°C und		L mol ⁻¹		/L (mol s) ⁻			
1	25	3627	73	5.2	0.13	187	25
1	35	1804	56	14.2	0.13	134	17
1	45	935	83	23	0.13	163	21
1	55	254	82	47	0.125	111	14
2	45	629	183	5.5	0.051	257	13
3	45	424	117	2.6	0.049	168	8

Note. $\Delta H_{\rm w} = 56.6 \text{ kJ mol}^{-1}$, $\Delta S_{\rm w} = -100.3 \text{ J mol}^{-1} \text{ K}^{-1}$, $\Delta H_{\rm m} = 55.2 \text{ kJ mol}^{-1}$, and $\Delta S_{\rm m} = -121.7 \text{ J mol}^{-1} \text{ K}^{-1}$.



Fig. 8. Apparent hydrolysis rate constant of 1 in the SDS-PEI-water system vs. SDS concentration at different temperatures, $C_{\text{PEI}} = 0.1 \text{ mol } \text{L}^{-1}$: 55 (1), 45 (2), 35 (3), and 25 °C (4).

Table 3). For the aqueous pseudo-phase, we obtained the activation enthalpies $\Delta H_{\rm w} = 56.6$ kJ mol⁻¹ and activation entropies $\Delta S_{\rm w} = -100.3$ J mol⁻¹ K⁻¹. These data agree with the expected values for the bimolecular reaction.³¹ The activation parameters for reaction in the catalytic complex (see Table 3) differ insignificantly from those presented above. We can conclude that the reaction mechanism remains unchanged when the reaction transfers from the aqueous pseudo-phase to the polymer-colloid aggregates, *i.e.*, general base catalysis of hydrolysis of the substrate occurs. To exclude completely the hypothesis on reaction acceleration with an increase in the SDS concentration due to a significant contribution of alkaline hydrolysis of substrates at an elevated pH, we studied the hydrolysis kinetics of substrate 1 at constant pH 7.8 in a methylmorpholine buffer. As can be seen from the data in Fig. 8, the catalytic effect, whose value is equal to the effect of the system without a buffer, is also observed in this case. It should also be taken into account that the nucleophilic attack of hydroxide ions is impeded because of their electrostatic repulsion from the negatively charged surface of the SDS aggregates.

On the contrary to the inhibition of hydrolysis in an individual micellar solution of anionic surfactants at high pH,²⁸ the observed acceleration of the reaction in the polymer—colloid system under study can be explained when assuming that the general basic mechanism of catalysis is retained and the contribution of alkaline hydrolysis as an alternative or parallel reaction route is negligible.



Fig. 9. Apparent hydrolysis rate constant of **1** in the SDS—PEI—water system *vs.* logarithm of the PEI concentration at different SDS concentrations (45 °C): 0.01 (*a*), 0.0005 (*b*), and 0.001 mol $L^{-1}(c)$.

One of the priority tasks of our study of the reactivity of phosphorus esters in organized media is the elucidation of a relation between the structure of nanoaggregates and their catalytic effect. We have studied³² the influence of electrolyte-induced micellar rearrangements on the hydrolysis rate of phosphorus esters. Therefore, it was of interest to carry out a similar study in the presence of a polyelectrolyte. According to the previously developed methodology,³³ we analyzed the kinetic plots in the semilogarithmic coordinates k_{app} -log C_{PEI} at three fixed SDS concentrations in the interval below and above the CMC. The reactivity of substrate 1 changed dramatically at $0.007-0.008 \text{ mol } L^{-1} \text{ PEI}$ (Fig. 9). The absence of a break in the plot obtained at an SDS concentration of 0.001 mol L^{-1} can be related to the fact that at PEI concentrations lower than 0.01 mol L^{-1} homogeneity in this system was violated, which impeded to study this concentration interval. Probably, at specific SDS to PEI ratios, stoichiometric complexes are formed^{2,22} followed by their resolubilization with the further increase in the SDS concentration.

Unlike micellar sphere—cylinder transitions under the action of organic and inorganic electrolytes, the break in the plots (see Fig. 9) is not, probably, caused by changes in the morphology of surfactant aggregates induced by the electrolytic effect of PEI. At least two arguments in favor of this assumption are known. First, the change in the rate constant was observed in the region above the CMC and also at low SDS concentrations. Second, we have previously^{7,8} observed the sharp change in the conductivity and dielectric constant of a PEI solution at a concentration of 0.01 mol L⁻¹, which is rather close to the PEI concentration in the break points (see Fig. 9). Therefore, it seems reasonable to assume that the change in k_{app} is caused by structural rearrangements of the intrinsic polyelectrolyte.

Thus, in this work we used different physicochemical methods to study self-organization in the SDS—PEI—water system and determined the concentration boundaries within which polymer—colloid structures exist. Hydrophobic interactions contribute substantially to these structures. In parallel we studied the catalytic effect of this composition in the hydrolysis of phosphonates 1—3. Analysis of the kinetic data suggested that the reaction mechanism is retained when the process is transferred from the aqueous pseudo-phase to polymer—colloid complexes, which is confirmed by the close activation parameters in the microphases.

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