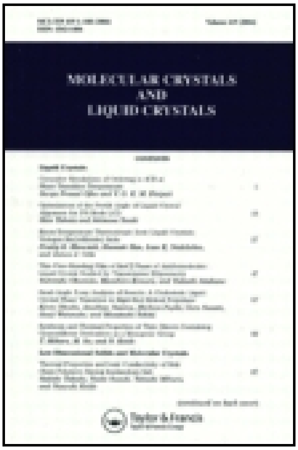

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Micellar, Liquid Crystalline and Polymer Systems Based on Surfactant and Polyethylene Imine as Nanoreactors for the Transfer of Phosphoryl Group

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Micellar, Liquid Crystalline and Polymer Systems Based on Surfactant and Polyethylene Imine as Nanoreactors for the Transfer of Phosphoryl Group

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In the kinetic study of the hydrolysis of p-nitrophenyl alkyl chloromethylphosphonates and p-nitrophenyl diphenyl phosphate in the cationic surfactant-polyethylene imine-water system the dependence of the catalytic effect of the system on the nature of surfactants and substrates and the surfactant-polyethylene imine ratio was found. An appearance of liotropic mesophase in the surfactant -polymer solutions results in alteration in the reactivity of the substrates.

Keywords: kinetics; surfactant; polymer; liquid crystal

INTRODUCTION

In our earlier studies [1-3] the influence of direct and reverse micelles, microemulsions and liquid crystals on the rate of nucleophilic substitution reactions of phosphorus acid esters has been investigated.

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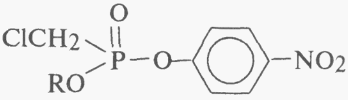
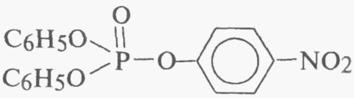
Solutions of surfactants considered as biomimetic structures acting via 'guest-host' mechanism [4] attract a wide attention. At the same time macromolecular nature of proteins encourages an interest in the catalytic systems based on synthetic polymers [5,6]. It can be assumed that the use of the micellar solutions of polymer as reaction media can result in new additional effects. Whereas the reactivity in micelles is widely studied, the effects of polyelectrolytes and the mixed surfactant-polymer systems on the reaction rate are scarcely examined.

In the present work the hydrolysis of p-nitrophenyl alkyl chloromethylphosphonates (**1**,**2**) and p-nitrophenyl diphenyl phosphate (**3**) in the aqueous solutions of polyethylene imine (PEI), micellar solutions of cetyl trimethylammonium bromide (CTAB) and cetyl dimethylethylammonium bromide (CDAB) and mixed surfactant-polymer solutions has been studied. At present, solution behavior of the mixed surfactant-polymer systems attracts a wide attention [7-9]. Nevertheless there is rather scare information on the nature of interactions in such complex solutions, which become still more complicated when reagents are added. Since conductometric methods are intensively employed for the study of surfactant-polymer interactions [9], we have examined the structural behavior of the systems used as the reaction medium by means of conductivity measurements.



1,2



3

R= C_2H_5 (**1**); n-C_6H_{13} (**2**)

EXPERIMENTAL

Substrates **1-3** were prepared according to the previously reported procedure [10]. The surfactant CTAB and CDAB were from "Sigma", PEI of branched structure (molecular weight 30000, Aldrich) was obtained commercially. Solutions were made up in double-distilled water. The reaction was controlled by monitoring the p-nitrophenolate absorption at 400 nm. The spectrophotometer "Specord M-400" equipped with temperature-controlled cell holders was employed. The initial substrate concentration was $5\cdot10^{-5}$ M. The observed rate constants (k_{obs}) were determined from D vs. t dependencies: $\ln(D_\infty - D) = -k_{obs}t + \text{const}$, where D and D_∞ are the optical density of the micellar solutions at the moment *t* and after competition of the reaction, respectively. The k_{obs} values were calculated using the weighted least-squares computing methods. Each value of k_{obs} is the mean of at least three independent determinations differing by 5%. The electrical conductivity was measured using a conductivity meter CDM-2d (Denmark). Small-angle neutron scattering experiments (SANS) were carried out with YuMO instrument based on time-of-flight spectrometer located at the IBR-2 at the Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia. The main principles and details of the experimental procedure were described in [11]. Sample-to-detector distance was 10.5 m and the q-range was 0.01-0.4 A^{-1}. Flux on the sample was about $6\cdot10^6$ n/s cm^2. The intensities from circular one-dimensional detector were corrected by subtracting of the background. The same procedure was used for correction of incoherent scattering. The solution was placed into into quartz-glass Hellma cells of 1 and 2 mm useful thickness. The data treatment included model fitting of the experimental results, using the mean-least-square methods.

The kinetic data for the PEI solutions were treated in terms of equation 1, which is often used in the case of fermentative and micellar catalysis [12]

$$k_{obs} = \frac{k_w + k_m K'_S C}{1 + K'_S C} \qquad (1)$$

where k_w and k_m (s^{-1}) are the pseudo-first rate constants in the aqueous and micellar phase respectively, K'_S (M^{-1}) is the binding constant of the substrate, C (M) is the PEI concentration below the critical aggregation concentration (*cac*).

The kinetic data for the systems based on surfactants were treated in terms of the pseudo phase model using equation (2) [13]

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

where k'_{obs} ($M^{-1}s^{-1}$) is the second order rate constant obtained by division of the observed pseudo first rate constant k_{obs} by the total nucleophile concentration; $k_{2,w}$ and $k_{2,m}$ ($M^{-1}s^{-1}$) are the second order rate constants in the aqueous and micellar phases, respectively; K_s and K_{Nu} (M^{-1}) are the substrate and nucleophile binding constants; V is the molar volume of the surfactant assumed equal to 0.3 M^{-1}; C is the surfactant concentration below the *cmc*. Problems and approximations involved in this formalism have been discussed earlier [13].

RESULTS AND DISCUSSION

For the purpose of comparing before the kinetics in the mixed surfactant-PEI systems the hydrolysis of the substrates in the PEI solutions as well as in water with no catalytic additives was examined. In unbuffered water, PEI solutions are basic, and the pH of aqueous solutions containing PEI at the concentrations used in the experiment, is higher than 9.0. At these conditions the basic hydrolysis of the substrates occurs. An increase in the alkyl chain length of the substrates results in a decrease in their reactivity due to increase in the stearic hindrance at the electrophilic phosphorus atom [14] (the values of $k_{2,w}$ are equal to 4.0, 3.0 and 0.32 $M^{-1}s^{-1}$ for **1** ,**2** and **3** respectively).

It has been found in our earlier studies [15] that in the presence of PEI the general basic catalysis of phosphorus acid esters occurs. In aqueous solutions, PEI is partly protonated depending on pH. Cationic centres formed result in a decrease in the basicity of amine due to induction effects and electrostatic interactions. The catalysis of the hydrolysis is fulfilled by the uncharged amino groups activating the water molecules. In addition, cationic centres because of their electrostatic interactions with hydroxide-ions can increase the contribution of the alkali hydrolysis to the observed rate constant. The observed rate constant of the hydrolysis in the PEI aqueous solutions for the substrate **1** is higher than that for **2** (Figure 1), while as it has been shown [3,16], in cationic micelles there observed an increase in the reactivity with the substrate hydrophobicity. The PEI catalyzed hydrolysis of **3** has still lower rate than **1** and **2**. Unlike the short-chain homologues, which demonstrate a linear k_{obs} vs. [amine] plot [17] the dependence of the observed rate constant on the [PEI] has a non-linear form typical of the fermentative

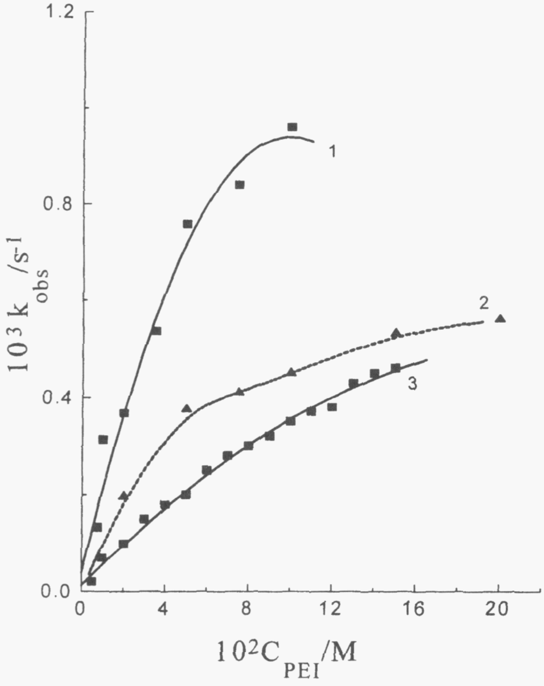


FIGURE 1. The observed rate constant of hydrolysis of **1-3** in the PEI-water system as a function of the PEI concentration.

and micellar catalysis. The non-linear k_{obs} vs. [PEI] plot can be considered as a kinetic argument in favor of the hypothesis that the aggregation of the PEI occurs, which is confirmed by the conductivity data for the PEI solutions (Figure 2, b). The value of the *cac* detected as a turning point in the 'conductivity' vs. [PEI] plot is equal to 0.01 M. Kinetic data for the hydrolysis in the presence of PEI, presented in Figure 1, demonstrate a (5-36)-fold acceleration for the phosphonate **1,** a (5-20)-fold acceleration for **2** and up to 100-fold acceleration of the reaction for the phosphate **3** compared to reaction in water, depending on the PEI concentration. The kinetic data were treated in terms of eqn.1, and the values of $k_m = 1.07 \cdot 10^{-3}$ s^{-1} , $K'_S = 50$ M^{-1} (for **1**),

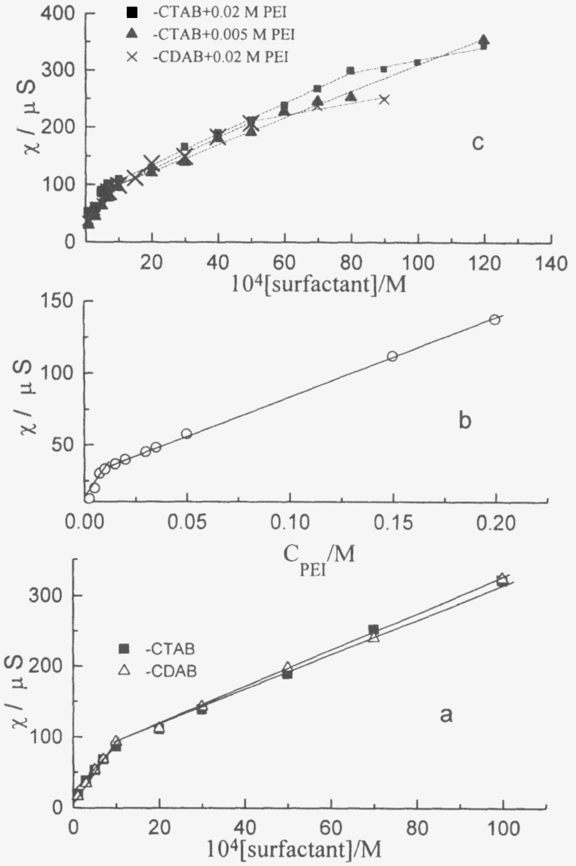


FIGURE 2. The conductivity of the surfactant - water system as a function of the surfactant concentration. (a). The conductivity of the PEI-water system as a function of the PEI concentration. (b) The conductivity of the surfactant - PEI - water system as a function of the surfactant concentration. (c).

$k_m = 6.33 \cdot 10^{-4}$ s^{-1}, $K'_S = 48$ M^{-1} (for **2**), $k_m = 5.0 \cdot 10^{-4}$ s^{-1}, $K'_S = 46.4$ M^{-1} (for **3**) were calculated. The quite low values of K'_S are probably due to low degree of aggregation of PEI. Kinetic data for **1-3** in the mixed surfactant-PEI solutions are shown in Figures 3-5. The surfactant-PEI ratio considerably influences the reactivity of the substrates. At the fixed PEI concentration equal to 0.02 M a substantial increase in the observed rate constant of **1** occurs, which is almost unchanged both prior and after this PEI concentration (see Figure 3). In the Figure 2 the conductometric data for the individual and mixed systems based on

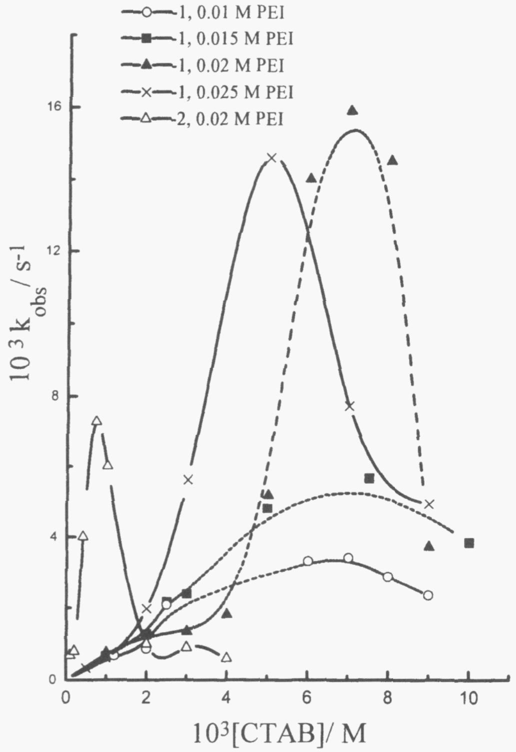


FIGURE 3. The observed rate constant of hydrolysis of **1** and **2** in the CTAB-PEI-water system as a function of the CTAB concentration.

surfactant and PEI are presented. As can be seen in Figure 2, in the individual surfactant and PEI· solutions an aggregation occurs, which can be identified as the break points in the 'conductivity' *vs*. [surfactant] or [PEI] plots. There is one break point only in the individual surfactant and PEI solutions, which is treated as the *cmc* for CTAB and CDAB direct micelles and as the *cac* for the PEI solutions. When [PEI] is lower than 0.2 M an identical behavior is observed in the mixed surfactant-PEI system, i.e. one break point only is revealed, whereas at the [PEI] fixed at values equal to 0.2 M, the second break point appears. According to the literature [9] the first break point in the mixed surfactant-polymer systems called as *cac*, marks the concentration at which small micelle-like aggregates of surfactant bound to the polymer begin to form. The second break point above the *cac* is taken to be the polymer saturation point (*psp*), where the saturation of the polymer with surfactant occurs. Apparently, a sharp increase in the reactivity in the mixed system at the 0.2 M mentioned above reflects a change in the structural behavior occurring in the mixed systems in the presence of 0.2 M of the PEI.

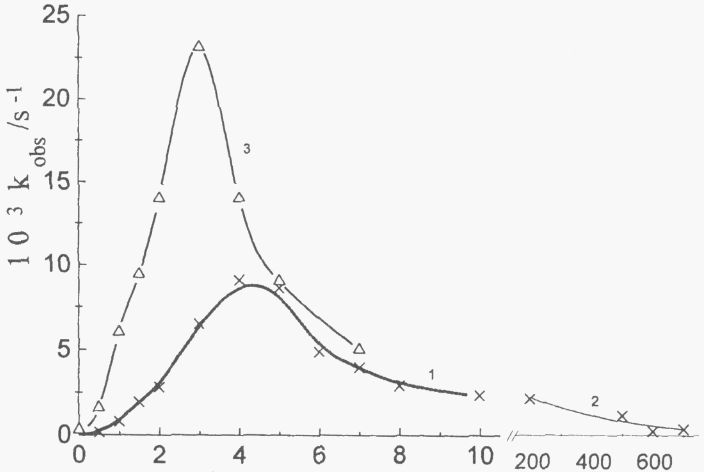


FIGURE 4. The observed rate constant of hydrolysis of **1** (1) and **2** (3) in the CDAB-PEI-water system as a function of the CDAB concentration at the 0.02 M of PEI in the micellar (1,3) and liquid crystalline (2) phases.

TABLE 1. Kinetic data for the individual and mixed systems treated in terms of the pseudo phase model

System	(k_{obs}/k_w) max	K_S/ M^{-1}	K_{Nu} / M^{-1}	k_{2m}/ $M^{-1}s^{-1}$	F_K^*	F_M^*
1 (CTAB+ 0.01 M PEI)	12.5	422	100	0.0025	149	0.08
1 (CTAB+ 0.015 M PEI)	14.2	1670	95	0.0018	207	0.07
1 (CTAB+ 0.02 M PEI)	21	1922	251	0.0011	451	0.05
2 (CTAB+ 0.02 M PEI)	11.5	3070	270	0.00037	535	0.01
3 (CTAB+ 0.02 M PEI)	14.3	2700	432	0.000063	900	0.013
1 (CDAB+ 0.02 M PEI)	24.7	1040	460	0.00057	554	0.03
2 (CDAB+ 0.02 M PEI)	36.5	2290	535	0.00078	811	0.03
3 (CDAB+ 0.02 M PEI)	16.6	5420	260	0.000142	584	0.03

*The F_c and F_m values are calculated using modified form of eqn.2: $\left({}^{k_{obs}}\!/_{k_w}\right)_{max} = \frac{k_{2,m}}{k_{2,w}} \times \frac{K_S K_{Nu}}{V(\sqrt{K_S} + \sqrt{K_{Nu}})^2}$. The term on the left expressed as the ratio between the pseudo first rate constants in the micellar system and water describes the maximum acceleration of the reaction. The first term on the right is associated with the influence of the micellar microenvironment (F_m) and the second term reflects concentrating the reagents in micelles (F_c).

We have studied the structural characteristics of micelles in the CTAB-PEI-water system by the SANS method. At low concentration of CTAB (0.002M) there exist spherical micelles in the CTAB-water system. The addition of PEI stimulates the sphere-rod micellar transition, and the semiaxes of the micelle become aqual to 25 A^o and 55 A^o. In addition, we defined the shape of the micelles on finishing the reaction. The products of the reaction of **2** increase the semiaxes of cylindrical micelles to 33A^o, while the products of the reaction of **1** has no influence on the structural characteristics.

As can be seen in Figure 3-5, the substrate nature and the structure of the surfactant head group markedly influence the reaction rate. The reactivity of **1** in the mixed CDAB-PEI-water system is twice lower, than that in the CTAB-PEI-water system, while k_{obs} for **2** is by 3-fold higher in the CDAB based system. Based on the data in Table 1, the conclusion can be made that concentrating the reagents is mainly responsible for the catalysis in the surfactant-PEI-water system (F_c ranged within the limits 150-800 depending on the PEI concentration, see Table 1), whereas a microenvironment exerts a negative effect resulting in the reduction of the reaction rate in comparison with water by factor of 12-100 depending on the PEI concentration (see Table 1). As a result, a maximum 40-fold acceleration of the reaction in study is observed. When the CTAB-PEI ratio is increased compensatory changes in the binding constants of the reagents and the $k_{2,m}$ values occur. For the more hydrophobic substrate **2** the higher K_S values were obtained in the case of both the surfactants, this fact as well as the higher $k_{2,m}$ value for **2** compared to **1** in the CDAB-PEI-water system are responsible for the higher reactivity of **1** in the CDAB based system. The opposite is true in the CTAB-PEI-water system because of the higher $k_{2,m}$ value in the case of **1** compared to **2**.

It has been shown in earlier study [16] that above 0.1 M CDAB in aqueous solution metastable liquid crystalline mesophase forms and above 0.4 M a stable hexagonal phase (E-phase) appears. In the Figure 4 (the curve 2) the kinetic data for the hydrolysis of **1** in the E-phase of the ternary CDAB-PEI-water system are represented. A decrease of the k_{obs} value with ordering in the solution behaviour is observed.

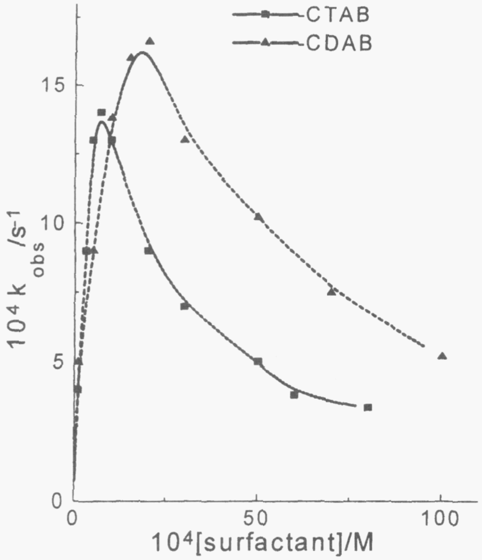


FIGURE 5. The observed rate constant of hydrolysis of **3** in the surfactant-PEI-water system as a function of the surfactant concentration at the 0.02 M of PEI.

The reactivity of phosphate **3** in the mixed surfactant-polymer systems is shown in Figure 5. The observed rate constants of **3** are much lower than those for **1,2**. Nevertheless, the micellar rate effect for each of the substrates studied is almost identical.

Thus, the catalysis in the mixed polymer-micellar systems is mainly determined by the concentrating factor, while a microenvironment makes a negative contribution to the micellar rate effect. The reactivity depends on the nature of surfactant, substrate and the surfactant-polymer ratio.

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