Cetylpyridinium bromide-based oil-in-water microemulsions as a medium for hydrolysis of esters of phosphorus acids in the presence of primary amines

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High-resolution ^{1}H NMR technique with Fourier-transform and pulsed-gradient spin-echo was used to study the structure of oil-in-water microemulsions based on cetylpyridinium bromide. The sizes of microdrops and the distribution of components between the disperse and continuous phases were found. It was shown for the hydrolytic decomposition of *O,O*-bis-(*p*-nitrophenyl) methyl phosphonate in the presence of amines that the microemulsion medium can affect both the rate and mechanism of hydrolysis. The reaction rate constants depend on the structure of microdrops.

Key words: microemulsions, cetylpyridinium bromide, structure, ^{1}H NMR spectroscopy, diffusion, kinetics, hydrolysis, amines, *O,O*-bis-(*p*-nitrophenyl) methyl phosphonate.

Detergent microemulsions (ME) are thermodynamically stable, self-organizing, macroscopically uniform dispersions with aqueous and hydrocarbon phases separated by the surfactant and co-surfactant molecules.[1] Diverse properties of ME forced the appearance of many studies of their structure and dynamic properties by physical methods.[1—3] At the same time, the high solubilizing ability of ME and developed interface, which provides an efficient contact between the reactants with different solubilities in the aqueous and organic media, stipulate an interest in these systems as microreactors for chemical processes.[4—6] However, authors rarely consider a relationship between the structural parameters of ME and properties of ME as reaction media. In addition, the majority of authors deal with the oil-in-water ME.

In this work, we studied the properties of oil-in-water ME to reveal the interrelation between the structure of microaggregates and their influence on the rate and mechanism of the reactions in them. The kinetics of hydrolytic cleavage of esters of tetracoordinate phosphorus in the presence of amines in ME based on cetylpyridinium bromide (CPB) was studied, and the effect of solubilized reactants on the parameters of the systems under study was considered.

Experimental

Solvents and amines were purified by standard procedures. Samples of CPB were twice precipitated with diethyl ether from an ethanolic solution. The substrate *O,O*-(bis-*p*-nitrophenyl) methyl phosphonate (**1**) was synthesized and purified by the previously published procedure.[7]

Microemulsions were optimized in composition according to the published data[6]: the molar ratio surfactant : co-surfactant (CPB : Bu^nOH) was 1 : 5, the fraction of hydrocarbon (*n*-hexane) was 10% of the total weight of the hydrophobic core, and the ratio between the dispersed and dispersion (aqueous) phases was variable.

High-resolution ^{1}H NMR spectroscopy technique with Fourier-transform and pulsed-gradient spin-echo was used for structural studies. Measurements were performed on a Tesla BS 587A modified NMR spectrometer at a proton resonance frequency of 80 MHz. The spectrometer was supplied with a block of the magnetic field pulse gradient, which made it possible to create the field gradient up to 50 G cm^{-1}. The application of this equipment and some methodical approaches to the study of ME have previously been described[8] in detail. Proton spectra and diffusion coefficients were measured at 30 °C. In the ME studied in this work by NMR spectroscopy, the bulk phase was water containing 98% (v/v) D_2O and 2% bidistilled water (H_2O). The error of determination of diffusion coefficients did not exceed 4%.

The reaction kinetics was studied spectrophotometrically on a Specord UV-VIS instrument in thermostatted cells. The reaction was monitored by a change in the optical density of solutions at λ = 400 nm (formation of the *p*-nitrophenolate anion). The initial concentration of the substrate was $5 \cdot 10^{-5}$ mol L^{-1}, conversion >90%, an equimolar amount of the *p*-nitrophenolate anion was formed when the hydrolysis of **1** ceased. The fact that this is precisely hydrolysis rather than aminolysis, which occurs in the ME studied during the cleavage of **1** in the presence of amines, was confirmed by ^{31}P NMR

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(Bruker MSL with a working frequency of 161.97 MHz): the chemical shift of the reaction product of 22.3 ppm is characteristic of the *O*-(*p*-nitrophenyl) methyl monophosphonate.

The apparent rate constants of the pseudo-first order (k_{app}) were found from the plot $\log(D_\infty - D_\tau) = -0.434k_{app}\tau + \text{const}$, where D_τ and D_∞ are the absorbances of solutions at the instant τ and after the end of the reaction, respectively. The k_{app} values were calculated by the least-squares method. The rate constants of the second order (k_2) were calculated in the linear region of the plot k_{app} *vs.* amine concentration (C_{am}) by the equation $k_2 = (k_{app} - k_0)/C_{am}\alpha$, where k_0 is the rate constant of alkaline hydrolysis of the substrate determined as a section cut on the ordinate at the specified pH in ME, and α is the fraction of the neutral (reactive) form of amine under the conditions of kinetic experiment. The error of determination of k_2 was $\leq$5%. The α value was found by potentiometric titration of amine solutions with hydrochloric acid.

Results and Discussion

High-resolution ^{1}H NMR technique with Fourier-transform and pulsed-gradient spin-echo makes it possible to determine the diffusion decays of individual lines in the spectra of ME and find the diffusion coefficients (D) of the components of a mixture, which provides an information on the structure of solutions under study.[8,9]

In this work, we studied the structure of oil-in-water ME consisting of water, CPB, Bu^{n}OH, and *n*-hexane, which have already been used previously as a reaction medium.[10] The ratios of components for some studied ME are presented in Table 1.

The ^{1}H NMR spectrum of the ME is complex due to the superposition of lines from various components of the system. However, we can distinguish individual lines from protons of the pyridine ring of CPB (9.07, 8.73, and 8.24 ppm), H_2O (4.80 ppm), CH_2 group of Bu^{n}OH in the α-position to the OH group (3.63 ppm), as well as lines from $(CH_2)_n$ (1.3 ppm) and Me (0.9 ppm) with contributions from protons of CPB, Bu^{n}OH, and *n*-hexane. To measure the diffusion coefficients of the components of ME, we chose the most intense lines in the ^{1}H NMR spectrum. The obtained diffusion coefficients of the components of ME are presented in Table 1.

When the surfactant concentration in ME much exceeds the critical concentration of micelle formation, its diffusion is close to that of microdrops: $D_{surf} \approx D_{drop}$.[11,12] Thus, we can estimate the effective radius of a microdrop (R) using D by the Stokes—Einstein equation

$$D = kT/6\pi\eta R, \quad (1)$$

where η is the medium viscosity. The equation in this form can be used only for dilute systems. Therefore, we used ME in a wide range of concentrations of the dispersed phase (ϕ). The experimental data for the diffusion coefficients of a microdrop are shown by points in Fig. 1. Interpolating the experimental plot $D = f(\phi)$ by the correlation $D = D_0(1 - 2\phi)$ obtained for rigid spherical particles,[13] we can find the diffusion coefficients of a microdrop D_0 at infinite dilution. Using the viscosity value for heavy water, we found the radius (3.7 nm) of microdrops in the system. The experimental data coincide with the theoretical curve only below some concentration of the dispersed phase. In more concentrated ME, an apparent decrease in the microdrop size is observed, which is a consequence of an additional mechanism of diffusion of individual surfactant molecules over the cluster surface from microdrops.[14]

In the oil-in-water ME, hydrocarbon, which forms the nonpolar core, and co-surfactant participate along with the surfactant in microdrop formation. Our data on diffusion indicate that the diffusion decay of the signal from protons of $(CH_2)_n$ *n*-hexane, and CPB are not separated, which corresponds to their motion within the same structural aggregate. However, the diffusion coefficients of Bu^{n}OH determined by the individual line from protons of its α-CH_2 group exceed substantially D_{drop}, which can be a result of the partial presence of Bu^{n}OH in the volume phase of ME. Under the assumption of fast (in the framework of the NMR time scale) exchange between two states for the measured diffusion coefficient of butanol D_{Bu}, we can write

$$D_{Bu} = p_b D_{drop} + (1 - p_b) D_{Bu}^{free}, \quad (2)$$

where p_b is the relative fraction of Bu^{n}OH in the bound state, *i.e.*, in the composition of a microdrop. To obtain

Table 1. Volume fraction of the dispersed phase (ϕ), weight composition (mol.%), and diffusion coefficients (D/m^2 s^{-1}) of the components in microemulsions

Component, coefficient	Composition (%) at ϕ				
	0.055	0.11	0.22	0.27	0.38
CPB	2.38	4.75	9.5	11.8	16.7
Bu^{n}OH	2.23	4.55	9.1	11.3	16.1
He	0.5	1.0	2.0	2.6	3.7
H_2O	94.89	89.7	79.4	74.3	63.5
$D_{CPB} \cdot 10^{-11}$	5.43	4.75	3.54	4.49	7.83
$D_{Bu} \cdot 10^{-9}$	0.67	0.59	0.46	0.43	0.34
$D_w \cdot 10^{-9}$	2.16	1.97	1.74	1.55	1.35

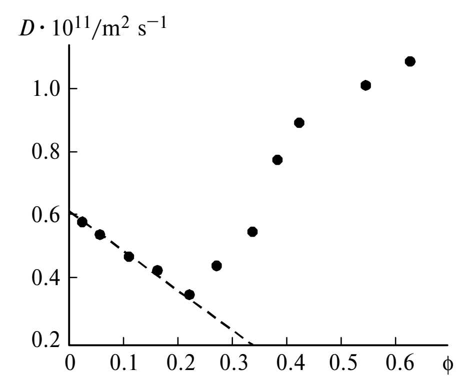

Fig. 1. Experimental diffusion coefficients at different fractions of the dispersed phase. The theoretical plot $D = D_0(1 - 2\phi)$ is shown by dotted line.

the diffusivity of Bu^nOH in the dispersion phase ($D_{Bu}{}^{free}$ = 0.69 · 10^{-9} m^2 s^{-1}), we determined its diffusion in an aqueous-butanolic mixture and took into account the effect of hindrances for the Bu^nOH molecules from microdrops in the real ME.[15] It was shown for ME with ϕ = 0.22 (ME-1) that the microdrops retain in their composition only some part of Bu^nOH of the total amount contained in the system: p_b = 0.34. Similar analysis of water diffusion in ME-1 ($D_w{}^{free}$ = 1.86 · 10^{-9} m^2 s^{-1}) showed that a part of water is present in the composition of the microdrop (p_b = 0.065), most likely, due to the interaction of water with the polar surface of microaggregates.

The introduction of organic additives, in particular, amines, affects the ME structure. It is known that these compounds can act as co-surfactants,[16,17] which assumes the possibility of competition between amines and Bu^nOH in the surface layer of the drop of the studied ME. We studied the influence of hydrophobic alkylamines on the ME structure. These alkylamines are capable of distributing among the oil drop and aqueous phase. The structural studies were carried out for ME-1, which is sufficiently dilute and does not exhibit the cluster formation effect. This system possesses a high solubility, which makes it possible to introduce various amines (up to *n*-octadecylamine) in high concentrations. Under the experimental conditions, we failed to separate individual lines of long-chain amines in the ^{1}H NMR spectra. The results of analysis of the diffusion data by Eqs. (1) and (2) are presented in Fig. 2, which suggests that the amines can be classified into two groups by their influence on the ME structure. The first group (*n*-butyl- and *n*-octylamine) is characterized by a ~15% decrease in the radius of the microaggregates as compared to the reference, and the relative fraction of Bu^nOH in the microdrop structure increases. Beginning from *n*-decylamine, the microdrop radius increases noticeably, and Bu^nOH and water are displaced from its composition to the dispersion phase (see Fig. 2). Probably, the hydrophobic amines are incorporated into the microdrop, resulting in some increase in its sizes.

Phosphonate cleavage in aqueous solutions occurs as neutral and alkaline hydrolysis. In addition, the general basic mechanism of catalysis, whose efficiency is determined by the amine basicity, can take place.[18,19]

$$\underset{\mathbf{1}}{MeP(O)(OC_6H_4NO_2\text{-}p)_2} + H_2O\cdot H_2NR + 3\,H_2O \longrightarrow MeP(O)(OC_6H_4NO_2\text{-}p)O^- + {}^-OC_6H_4NO_2\text{-}p + 2\,H_3O^+ + H_2O\cdot H_2NR$$

The plots of the apparent rate constants (k_{app}) *vs.* amine concentration are linear. Amines capable of self-association or amines in surfactant solutions exhibit the micellar catalytic effect resulting in the violation of the Brönsted functions.[19,20]

Unlike micellar media,[20] in detergent CPB-based ME, the plots of k_{app} *vs.* content of amines with different hydrophobicity for the hydrolysis of **1** are linear (Fig. 3). In the studied interval of amine concentrations

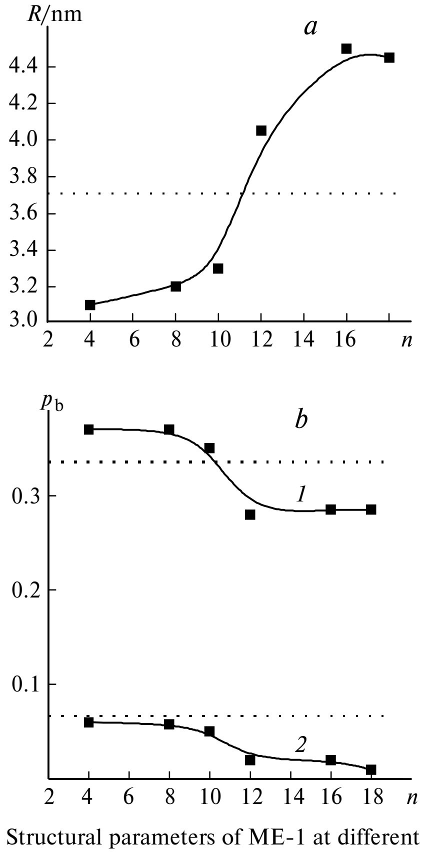

Fig. 2. Structural parameters of ME-1 at different lengths of the hydrocarbon radical of amine (*n*): *a*, radius of microdrops; *b*, relative fractions of Bu^nOH (*1*) and H_2O (*2*) in the composition of microdrops. The corresponding values of the parameters in the absence of amines are shown by dotted lines.

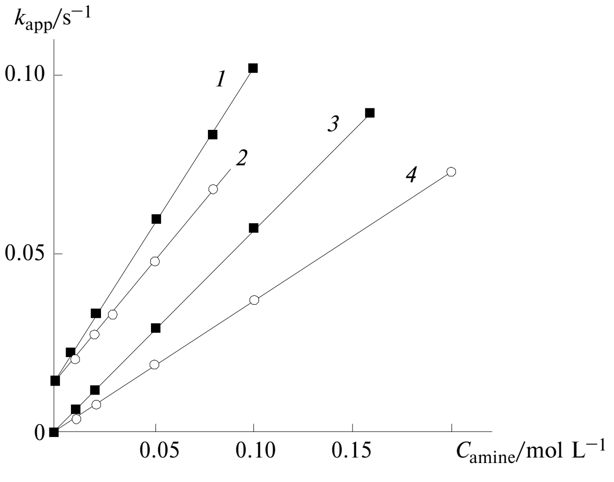

Fig. 3. Apparent rate constant of hydrolysis (k_{app}) of **1** at different amine concentrations in ME-1 (25 °C); *n*-octylamine: *1*, α = 1.0 (pH 10.3); *2*, α = 0.7 (pH 9.4); *n*-cetylamine: *3*, α = 1.0 (pH 10.3); *4*, α = 0.69 (pH 9.4).

Table 2. Rate constants (k_2/L mol^{-1} s^{-1}) of hydrolysis of **1** and activation parameters of the reaction (E/kJ L mol^{-1}, log$A$), the molar fraction of the neutral form of amine (α)

Amine	α		T /°C	k_2	E	log$A$
	pH 9.4	pH 10.3				
n-Butylamine	0.2	0.56	25	1.30		
			32	1.80	31.8	5.7
			43	2.41		
n-Octylamine	0.68	0.95	25	0.85		
n-Decylamine	0.69	1.0	25	0.55		
			32	0.70	27.8	4.6
			43	1.03		
n-Dodecylamine	0.695	1.0	25	0.56		
n-Cetylamine	0.70	1.0	25	0.55		
			32	0.65	26.4	4.4
			43	1.00		
n-Octadecylamine	0.70	1.0	25	0.55		

Note. At 25 °C the k_2 values were determined in the pH interval from 9.0 to 10.3 and the amine concentration region below 0.2 mol L^{-1}; at 32 and 43 °C the k_2 values were found in the same region of amine concentrations (pH 10.3); at this pH the contribution of alkaline hydrolysis (k_0) at 25, 32, and 42 °C is 0.015, 0.019, and 0.029 s^{-1}, respectively.

≤0.2 mol L^{-1}, all amines, regardless of the length of the hydrocarbon radical, exhibit linear plots. The second-order rate constants (k_2) and activation parameters of hydrolysis of compound **1** in ME-1 are presented in Table 2. *n*-Butylamine and *n*-octylamine in ME-1 are stronger general basic catalysts than their hydrophobic homologs. It is known that chemical reactions in microemulsions occur, as a rule, inside or in the surface layer of the microdrop.[6] Probably, the displacement of water by hydrophobic amines from the surface layer separates the nucleophile and substrate to decrease the hydrolysis rate constant with an elongation of the chain of the hydrocarbon radical. Hydrolysis of **1** in ME-1 is

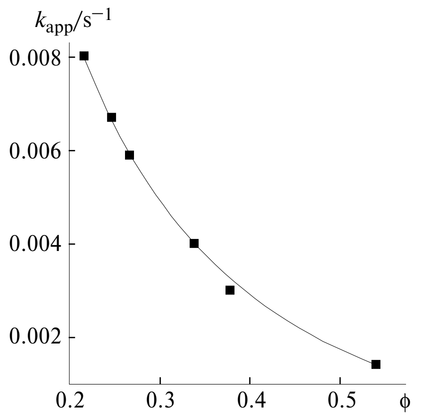

Fig. 4. Apparent rate constant of hydrolysis of **1** in the presence of *n*-cetylamine at different fractions of a dispersed phase in ME (C_{am} = 0.05 mol L^{-1}, 25 °C).

characterized by somewhat lower activation energy than that in water.[19] The E_a value decreases as the hydrocarbon length of the amine radical lengthens (see Table 2).

An increase in the volume of the aqueous phase in ME enlarges the interfacial boundary surface.[6] This provides the efficient contact of reactants and acceleration of processes at the boundary and in the near-boundary layer, which increases the apparent rate constant of hydrolysis of **1** (Fig. 4).

In micellar solutions of CPB, when compound **1** undergoes hydrolysis in the presence of amines, the ratio of contributions of alkaline hydrolysis and hydrolysis catalyzed by the general basic mechanism, as well as the micellar catalytic effect, depend on the amine hydrophobicity.[20] In the microemulsions studied, the length of the hydrocarbon radical of the nucleophile does not affect substantially the ratio of contributions of these two processes. The fraction of the general basic mechanism of catalysis is high, increases, and becomes predominant when the amine concentration increases and the pH of the medium decreases (see Fig. 3). However, amine hydrophobicity affects the hydrolysis rate. The hydrolysis rate constant depends on the composition of microdrops, in particular, on the presence of bound water in their surface layer. The content of bound water is determined by the length of the hydrocarbon radical of the solubilized amine.

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