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

A. B. Mirgorodskaya, a* L. A. Kudryavtseva, a Yu. F. Zuev, b B. Z. Idiyatullin, b and V. D. Fedotov b

a A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center of the Russian Academy of Sciences, 8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation. Fax: +7 (843 2) 75 2253, E-mail: vos@iopc.kcn.ru. b Kazan Institute of Biochemistry and Biophysics, Kazan Research Center of the Russian Academy of Sciences, p/b 30 420503 Kazan, Russian Federation.

High-resolution 1H 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, 1H 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. Diverse properties of ME forced the appearance of many studies of their structure and dynamic properties by physical methods. 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. 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 (I) was synthesized and purified by the previously published procedure. Microemulsions were optimized in composition according to the published data: the molar ratio surfactant: co-surfactant (CPB: Bu4OH) 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 1H 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 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) D2O and 2% distilled water (H2O). The error of determination of diffusion coefficients did not exceed 4%.

The reaction kinetics was studied spectrophotometrically on a Spectord 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 · 10 -3 mol L -1, conversion >90%, an equimolar amount of the p-nitrophenolate anion was formed when the hydrolysis of I ceased. The fact that this is precisely hydrolysis rather than aminolysis, which occurs in the ME studied during the cleavage of I in the presence of amines, was confirmed by 31P NMR.
(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 \( k_{\text{app}} \) were found from the plot \( \log(D_u - D_i) = -0.434k_{\text{app}} + \text{const. \[11,12\]} \) where \( D_u \) and \( D_i \) are the absorbances of solutions at the instant \( t \) and after the end of the reaction, respectively. The \( k_{\text{app}} \) 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 \( k_{\text{app}} \) vs. amine concentration \( (C_{\text{am}}) \) by the equation \( k_2 = (k_{\text{app}} - k_0)/C_{\text{am0}} \), 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 \( C_{\text{am0}} \) 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 \( \alpha \) 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\(^\text{u}\)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), \( \text{H}_2\text{O} \) (8.80 ppm), \( \text{CH}_2 \) group of Bu\(^\text{u}\)OH in the \( \alpha \)-position to the OH group (3.63 ppm), as well as lines from \( (\text{CH}_2)_n \) (1.3 ppm) and Me (0.9 ppm) with contributions from protons of CPB, Bu\(^\text{u}\)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 forma-

\[ D = kT/6\eta R, \]

where \( \eta \) 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 (\( \phi \)). 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 \( (\text{CH}_2)_n \) \( n \)-hexane, and CPB are not separated, which corresponds to their motion within the same structural aggregate. However, the diffusion coefficients of Bu\(^\text{u}\)OH determined by the individual line from protons of its \( \alpha \)-CH\(_2\) group exceed substantially \( D_\text{drop} \), which can be a result of the partial presence of Bu\(^\text{u}\)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 \( D_\text{Bu} \), we can write

\[ D_\text{Bu} = p_0D_\text{drop} + (1 - p_0)D_\text{Bu free}, \]

where \( p_0 \) is the relative fraction of Bu\(^\text{u}\)OH in the bound state, i.e., in the composition of a microdrop. To obtain

![Graph](image-url)