Structure and Properties of Water–Oil Microemulsions

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Abstract-The parameters determining the structure and properties (surface potential and size of microdrops) of oil-water microemulsions containing various surfactants, and also the distribution of components between the dispersed phase and dispersing medium were determined by the kinetic method and by high-resolution ¹H NMR spectroscopy with a pulse magnetic field gradient.

Microemulsions, i.e., isotropic optically homogeneous dispersions of oil in water or water in oil (by oil is meant a hydrocarbon) are formed spontaneously when a hydrocarbon, water, a surfactant, and a cosurfactant (usually a lower alcohol) are mixed in definite proportions. Thanks to the high solubilizing power of microemulsions and extremely developed interface ensuring an efficient contact between reactants with different solubility in aqueous and organic media, these systems are actively used as media for chemical reactions [1–3]. It is very important to reveal what characteristics of microemulsions determine the rates and direction of chemical reactions in them. This can be done by various physical and physicochemical methods [4, 5].

This work continues and develops our studies on the use of oil-water microemulsions in nucleophilic substitutions [6, 7]. Our goal was to study the properties of direct microemulsions based on various surfactants and to reveal factors affecting chemical processes in these systems.

The features of microemulsions as media for chemical reactions can be evaluated directly by studying the kinetics of chemical reactions, i.e., by measuring the rate constants of processes in these media. This method can also be used for determining physicochemical parameters of microemulsion media, e.g., the surface potential of microdrops [8]. The data on structural features of microemulsions, in particular, on the size of microdrops and phase distribution of system components, are extremely useful for choosing the best microemulsion for performing a particular reaction. Among the diversity of structural methods, our attention was attracted by Fourier-transform ¹H NMR spectroscopy with pulse magnetic field gradient [9], allowing measurement of the diffusion coefficients of microemulsion components.

As reaction media for base hydrolysis of esters [p-nitrophenyl acetate (I) and bis-p-nitrophenyl methylphosphonate (II)], we chose microemulsions with equal volumes of disperse phases but different charges of the microdrop surface. As surfactants we used cationic cetyltrimethylammonium and cetylpyridinium bromides, anionic sodium dodecyl sulfate, and nonionic decaoxyethylated oleyl alcohol (Brij-97). The content of a surfactant in all microemulsions was 5.05 wt %. Apart from a surfactant, the microdrops consist of *n*-hexane (1.97 wt %), which forms a nonpolar core, and *n*-butanol (5.05 wt %). The volume fraction of the disperse phase was 0.13.

The general scheme of base hydrolysis of the esters can be presented as follows.

$$CH_{3}C(O)OC_{6}H_{4}NO_{2} + 2OH^{-} = CH_{3}C(O)O^{-} + {}^{-}OC_{6}H_{4}NO_{2}$$

$$I$$

$$CH_{3}P(O)(OC_{6}H_{4}NO_{2})_{2} + 2OH^{-}$$

$$I$$

$$= CH_{3}P(O)(OC_{6}H_{4}NO_{2})O^{-} + {}^{-}OC_{6}H_{4}NO_{2}$$

Kinetic data describing base hydrolysis of esters **I** and **II** in microemulsions are given in the table and in Fig. 1. It should be taken into account that the esters are localized mainly in oil drops {e.g., the dis-

Surfactant	Ester I		Ester II	
	$k_{2, \varphi}, \ 1 \text{ mol}^{-1} \text{ s}^{-1}$	φ, mV	$k_{2, \varphi}, \ 1 \ \text{mol}^{-1} \ \text{s}^{-1}$	φ, mV
Cetyltrimethylammonium bromide Cetylpyridinium bromide Sodium dodecyl sulfate Brij-97	8.8 9.6 1.1 3.4	24.4 26.6 -29.9 0	29.4 30.0 2.7 9.0	30.4 29.2 -30.9 0

Second-order rate constants $(k_{2,\varphi})$ of base hydrolysis of esters **I** and **II** and surface potential of microdrops (φ) $(C_{OH^-} 0.001-0.01 \text{ M}, 25^{\circ}\text{C})$

tribution factor of ester I between hexane and water is 10.8 [5]}, whereas highly hydrophilic hydroxide ions are concentrated in the dispersion medium. This suggests that the chemical reaction takes place on the interface. Irrespective of the nature of a surfactant which forms a microemulsion, the observed hydrolysis rate constants (k_{obs}) linearly depend on the alkali concentration in the dispersion medium within the entire concentration range studied (Fig. 1), which allows estimation of the second-order rate constants $(k_{2,0})$ of this process (see table). With cationic surfactants, the hydrolysis of esters I and II is accelerated, as compared to aqueous solutions with the same alkali concentration, which is apparently due to the accumulation of negatively charged hydroxide ions near the microdrop surface. The negative charge of the surface in the case of anionic surfactants decelerates this reaction; the microemulsions with nonionic surfactants have no appreciable effect on the hydrolysis rate (Fig. 1).



Fig. 1. Observed rate constant $(25^{\circ}C)$ of hydrolysis of ester **I** (*1*–3) in microemulsions containing (*1*) cetylpyridinium bromide, (2) Brij-97, and (3) sodium dodecyl sulfate and (4) in aqueous solution, as a function of the alkali concentration.

Two components of the effect of microemulsions on the reaction rate can be distinguished: the electrostatic component associated with interaction of hydroxide ions with the charged surface of microdrops and the nonelectrostatic component describing the effect of the medium.

$$\ln k_{2,\phi}(\text{ISA}) = e\phi/k_{\text{B}}T + \ln k_{2,\phi}(\text{NSA}).$$
(1)

Here e is the electron charge; φ , effective surface potential; $k_{\rm B}$, Boltzmann constant; T, absolute temperature; $k_{2,\varphi}(\rm ISA)$ and $k_{2,\varphi}(\rm NSA)$, second-order rate constants determined in microemulsions with ionic and nonionic surfactants, taking into account the phase volume. As nonionic surfactant, we used Brij-97.

From the kinetic data on base hydrolysis of **I**, using Eq. (1), we determined the effective surface potentials in microemulsions containing ionic surfactants (see table). The potentials in these systems are less by 50–100 mV (in absolute values) than in micellar solutions [10–12]. This is due to the presence of neutral butanol molecules in the surface layer of microdrops. The coincidence of φ values obtained in the experiments with esters **I** and **II** suggests that the location of these substrates in microdrops is similar.

The surface potential is an important parameter describing microemulsions as reaction media, because it determines the role of Coulombic interactions in solubilization of reactants. Specifically the surface potential exerts a decisive effect on the shift of acidbase equilibria, as it is related to the solubilizing selectivity with respect to neutral and protonated species. We have clearly demonstrated it by the example of cetylamine: the pH of its half-neutralization point is 8.5, 8.7, and 10.9 in microemulsions based on cetylpyridinium bromide, Brij-97, and sodium dodecyl sulfate, respectively. Hence, the higher the microdrop surface potential, the greater the content of the neutral amine species in the system, which, in turn, affects the behavior of amines in chemical processes, in particular, their activity in cleavage of ester bonds [6, 7].



Fig. 2. Diffusion falloffs of signals in the ¹H NMR spectra of microemulsions based on cetylpyridinium bromide: (1) hexane, (2) butanol, and (3) water. (G) Magnetic field gradient.

It should be noted that, although the surface potential is a characteristic parameter of microemulsions, it can be affected by solubilized agents. This may be due to a change in binding of head groups and counterions of a surfactant in a microdrop, and also to redistribution of microemulsion components between the dispersed phase and the dispersion medium under the action of added components.

Information on the distribution of microemulsion components can be obtained by NMR spectroscopy. The combination of high-resolution NMR with the technique of pulse magnetic field gradient makes it possible to determine diffusion falloffs of individual components of microemulsions (Fig. 2) and to compute their diffusion coefficients (*D*).

The procedure of studying distribution of microemulsion components between various phases requires the diffusion coefficients of microdrops to be determined first. As a rule, the diffusion coefficients of a surfactant (D_{SA}) and a drop (D_{drop}) in microemulsions are approximately equal, in contrast to micellar solutions. It is clearly seen from the dependences of D_{SA} on the dispersed phase fraction φ for two microemulsions under study (Fig. 3). As seen from Fig. 3, the concentration dependences of the diffusion behavior of microdrops based on sodium dodecyl sulfate and cetylpyridinium bromide differ essentially. Nevertheless, without analyzing this difference in detail, we can state that these dependences reflect diffusion of hard spherical particles [13, 14], i.e., indeed, $D_{SA} \approx D_{drop}$. The concentration dependences of D_{SA} also allow us to determine by extrapolation the microdrop diffusion coefficient at infinite dilution and to



Fig. 3. Diffusion coefficient of a surfactant as a function of the dispersed phase fraction in microemulsions based on (1) cetylpyridinium bromide and (2) sodium dodecyl sulfate.

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calculate the size of microdrops using the Stokes–Einstein equation. We have determined the radii of microdrops based on cetylpyridinium bromide (3.7 nm) and sodium dodecyl sulfate (2.7 nm).

The fact that butanol, which is added to a microemulsion to stabilize the surface layer, is not completely concentrated in microdrops is seen even from its experimental diffusion coefficients. For a microemulsion with cetylpyridinium bromide, D_{but} is 5.9×10^{-10} m² s⁻¹, and for a microemulsion with sodium dodecyl sulfate, D_{but} is 4.7×10^{-10} m² s⁻¹. These values are greater than the corresponding diffusion coefficients of microdrops (4.8×10^{-11} and 4.9×10^{-11} m² s⁻¹) by almost an order of magnitude. Thus, motion of butanol both in microdrops and in the aqueous dispersion medium contributes to its measured diffusion coefficient. Under the conditions of fast (in the NMR time scale) exchange of butanol between these two states, the observed diffusion coefficient is determined by Eq. (2).

$$D_{\text{but}} = p_{\text{bond}} D_{\text{drop}} + (1 - p_{\text{bond}}) D_{\text{but}}^{\text{free}}.$$
 (2)

Here p_{bond} is the butanol fraction participating in formation of microdrops, and $D_{\text{but}}^{\text{free}} = 7.2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ is the butanol diffusion coefficient in an aqueous medium, as determined in independent measurements. We found that, in the case of microemulsions with cetylpyridinium bromide, only 20% of butanol participates in the dispersed phase formation, and in the case of microemulsions with sodium dodecyl sulfate this fraction is 38%. Compounds I and II and alkali in concentrations used in the kinetic experiments do not affect the diffusion characteristics of the system. However, with a microemulsion based on sodium dodecyl sulfate as example, we found that its components are considerably redistributed at a high alkali content. At C_{OH^-} 0.2 M, the fraction of bound butanol is lowered (29%), and the radius of microdrops decreases (2.2 nm). This should cause an increase in the absolute value of the surface potential and, as a consequence, a decrease in the second-order rate constants of base hydrolysis. Indeed, $k_{2,\varphi}$ for the hydrolysis of **I** in 0.2 N alkali solution appeared to be 0.86 1 mol⁻¹ s⁻¹ (cf. data in table).

Thus, we have demonstrated the possibilities of using the kinetic method and high-resolution ¹H NMR spectroscopy with pulse magnetic field gradient to determine the characteristics (surface potential and size of microdrops) of microemulsions and the distribution of components between the dispersed phase and dispersion medium. These data determine the

structure and properties of oil-water microemulsions used as media for hydrolytic cleavage of ester bonds.

EXPERIMENTAL

The solvents and substrates **I** and **II** were purified by common procedures. Surfactant samples were twice reprecipitated with diethyl ether from ethanol solution.

The reaction kinetics were studied spectrophotometrically with a Specord UV-Vis instrument in temperature-controlled cells. The reaction course was monitored by variation of the optical density of solutions at 400 nm (formation of *p*-nitrophenolate anion). The initial substrate concentration was 5×10^{-5} M, and the conversion exceeded 90%.

We determined the observed pseudo-first-order rate constants $(k_{\rm obs})$ from the relationship $\log(D_{\infty} - D_{\tau}) = -0.434k_{\rm obs}\tau + {\rm const}$, where D_{τ} and D_{∞} are the optical densities of solutions at instant τ and after the reaction completion. The $k_{\rm obs}$ values were calculated using the least-squares technique. The second-order rate constants $(k_{2,\phi})$ were calculated for a linear portion of the dependence of $k_{\rm obs}$ on the alkali concentration in the dispersion medium $(C_{\rm OH})$ by the equation $k_{2,\phi} = k_{\rm obs}/C_{\rm OH}$.

We measured the diffusion coefficients of microemulsion components with a modified Tesla BS-587A high-resolution NMR spectrometer at the proton resonance frequency of 80 MHz. The spectrometer was equipped with a unit of pulse magnetic field gradient, which allows creation of a field gradient of up to 50 G cm⁻¹. The device and experimental procedures used for studying microemulsions are described elsewhere [15, 16]. We recorded the ¹H NMR spectra and measured the diffusion coefficients at 30°C. In microemulsions studied in this work by NMR, we used a dispersion phase consisting of 98 vol % D₂O and 2 vol % double-distilled H₂O.

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