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HIGHLY ORGANIZED CATALYTIC SYSTEMS

Catalytic Properties of Microheterogeneous Systems Based on Cationic Surfactants in Transesterification Processes

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Abstract—The kinetic parameters of the transesterification processes of carboxylic acid esters under the action of alkylphenolates in aqueous micellar solutions of cetyltrimethylammonium bromide (CTAB) are found. The observed catalytic effect is due to a complex mechanism of the solvent effect, which includes a shift of acid–base equilibria in the nucleophile and the formation of mixed CTAB/alkylphenol micelles. The dynamic structure of these aggregates (size, diffusion mobility, and molecular packing density in a surface layer) has been characterized by spin-probe EPR spectroscopy and high-resolution pulsed-field gradient ^{1}H NMR spectroscopy.

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INTRODUCTION

Complex biochemical processes, including the most important energy-trapping reactions such as ester bond cleavage, oxidative phosphorylation, and photosynthesis, occur in highly organized structures such as cell membranes. Microheterogeneous systems based on surfactants (micellar solutions and microemulsions) can serve as the simplest models of cell membranes [1]. The study of factors affecting the reactivity of substances solubilized by systems of this kind provides an opportunity to exert target-oriented effects on the vital functions of biological objects and to develop highly efficient biomimetic systems that exhibit catalytic properties in chemical processes.

The aim of this work was to study the decomposition of esters under the action of anionic alkylphenol species in microheterogeneous media, namely, in the micellar solutions of the cationic surfactant cetyltrimethylammonium bromide (CTAB), and to determine structural factors responsible for the catalytic effect of the test system. Phenolates, which exhibit high nucleophilicity, are low-basicity compounds; for this reason, they are active under mild conditions [2, 3]. Moreover, the interest in phenol compounds is a result of their considerable practical importance for chemical syntheses; the use of them as starting materials for the manufacture of surfactants, stabilizers, additives, and extraction systems; and their physiological activity [4, 5]. Thus, phenols, including phenols containing hydrophobic moieties, incorporating in a cell membrane, can change its conductivity to cause metabolic disturbances and, occasionally, cell death.

EXPERIMENTAL

Commercial CTAB (Sigma) of ~99% purity was used in this study. Twice-distilled water was used for preparing solutions. Phenols and carboxylic acid esters from Fluka were purified using standard procedures.

The acid–base properties of phenols were studied by spectrophotometry using a Specord UV–VIS instrument. The absorption of radiation by the ionized and unionized forms of phenols was measured at various pH values (in buffer solutions and 0.1 M NaOH).

Reaction kinetics were studied by spectrophotometry in thermostated cells on the above instrument. The reaction was monitored by measuring changes in the absorbance of solutions at a wavelength of 400 nm (the formation of the *para*-nitrophenolate ion). The initial substrate concentration was 5×10^{-5} mol/l, and the conversion was higher than 90%. Apparent pseudo-first-order rate constants (k_a) were determined from the relation $\log(A_\infty - A_\tau) = -0.434k_a\tau + \text{const}$, where A_τ and A_∞ are the absorbances of solutions at point τ in time and after completion of the reaction, respectively. The numerical values of k_a were calculated using the least-squares technique.

The EPR spectra were recorded on an RE 1306 spectrometer equipped with a temperature attachment and coupled to a computer. 4-(2-*n*-Undecyl-3-oxyl-4,4-dimethyloxazolidinyl)butyric acid, which is capable of embedding in micelles because of its amphiphilic properties, was used as a spin probe. The conditions of measurements have been described elsewhere [6].

Table 1. The values of pK_a for alkylphenols in aqueous and micellar solutions*

Alkylphenol	In water		In a solution of CTAB	
	pK_a	λ, nm	pK_a	λ, nm
Phenol	9.95	286	9.30	289
4-*n*-Butylphenol	10.10	287	9.50	291
4-Isononylphenol	10.25	289	9.85	299

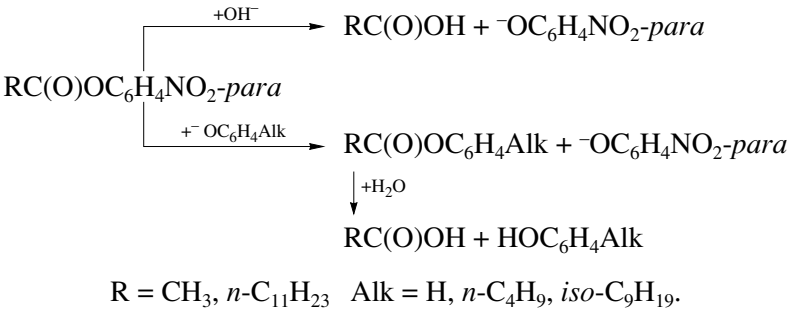
Note: [CTAB] = 0.005 mol/l; 20°C.

* In Triton X-100, the values of pK_a for phenol and 4-isononylphenol are equal to 10.3 and 10.9, respectively.

Self-diffusion coefficients were measured with the use of a modified Tesla BS 587A high-resolution NMR spectrometer at a proton resonance frequency of 80 MHz. The spectrometer was equipped with a pulsed-field gradient unit, which allowed us to produce magnetic field gradients to 0.5 T/m. The use of this instrumentation for studying surfactant solutions was described in detail previously [7, 8]. The measurements were performed at 30°C in solutions prepared with the use of deuterated water (Aldrich, 99.9%) and the deuterated alkali NaOD.

RESULTS AND DISCUSSION

The reactions of *para*-nitrophenyl esters of carboxylic acids with phenols occur in alkaline media as nucleophilic substitution at the carboxyl group [9, 10]. In this case, two processes of transesterification (phenolysis) and alkaline hydrolysis occur. The ratio between the contributions of these two reactions to the apparent rate constant of decomposition primarily depends on the concentration of attacking nucleophilic species (hydroxide and phenolate ions) and the effects of micellar surfactant solutions on both of the processes.



The concentration of anionic phenol species depends on the values of pK_a of these compounds and on the given value of pH in the medium. It is well known that acid–base equilibria are shifted in aqueous micellar surfactant solutions. The acid properties of compounds increase in cationic micelles, whereas the proton affinity decreases in anionic surfactants. This is due to the selective solubilizing ability of micelles toward the acidic and basic forms of compounds. For ionic surfactants, the shift of equilibrium is determined by the surface potential of the micelle [11, 12].

In this work, we studied the acid–base properties of phenols using UV spectroscopy. Based on data on the absorption of radiation by phenolate species at various pH, we calculated the expected value of pK_a (p$K_{a(obs)}$) using the Henderson–Hesselbach equation [13]

$$pK_{a(obs)} = pH + \log([\text{phenol}]/[\text{phenolate}]). \quad (1)$$

Note that the absorption band maximum of 4-isononylphenolate containing a hydrophobic fragment underwent a bathochromic shift (10 nm) on going from aqueous solutions to CTAB solutions because of changes in the microenvironment of the substance upon its solubilization in micelle cores. In the case of unsubstituted phenols, only a small shift of the phenolate absorption band was observed (Table 1). Table 1 summarizes the dissociation constants measured. These data indicate that the value of pK_a for 4-isononylphenol is higher than that for phenol in both water and a CTAB solution. This can be a consequence of the positive induction effect of an alkyl substituent on the hydroxyl dissociation constant. However, it should be remembered that, in the case of unsubstituted phenol, electrostatic interactions with micelles are the main factor responsible for the shift of pK_a (ΔpK). In the case of 4-isononylphenol, hydrophobic interactions manifest themselves. These hydrophobic interactions are responsible for the binding of both ionic and nonionic forms of the compound to micelles, and in doing so they exert an effect against Coulomb forces to decrease ΔpK. These hydrophobic interactions are responsible for an increase in the pK_a of alkylphenols in the micellar solutions of nonionic surfactants, for example, Triton X-100, which has a stronger effect on

4-isononylphenol than on its unsubstituted analog (see note to Table 1).

The *para*-nitrophenyl esters studied in this work differ in hydrophobic properties: the oil–water distribution constants of *para*-nitrophenyl acetate (PNPA) and *para*-nitrophenyl laurate (PNPL) are equal to 10.8 and 205.4, respectively [14]. It is believed that laurate is localized in the oil core of the micelle, whereas acetate occurs near the surface layer. This, as well as the hydrophilic–lipophilic properties of a nucleophile, is reflected in the effect of surfactants on the rates of processes with the participation of the above esters.

To evaluate adequately the contributions of alkaline hydrolysis and phenolysis, we initially studied the kinetics of the alkali hydrolysis of PNPA and PNPL in micellar solutions of CTAB at pH 10.0. It can be seen in Fig. 1 that the micellar catalytic effects observed in reactions with the participation of these esters are essentially different. Thus, the hydrolysis of PNPA was accelerated by a factor no greater than 4, whereas the hydrolysis of PNPL was accelerated by more than two orders of magnitude. It is well known that laurate self-association occurs in aqueous solutions to result in the shielding of substrate active sites and, consequently, the anomalously low reactivity of laurate, as compared with acetate, in alkaline hydrolysis processes in aqueous media [15]. In micellar solutions, this can be explained by the deshielding (i.e., the segregation of molecules and the unfolding of globular associates) of hydrophobic PNPA upon embedding in a CTAB-based micelle to make the substrate accessible to a nucleophilic attack. The substrate binding constant (K_s) can serve as a quantitative characteristic of the interaction of the substrate with a micelle. This constant is obtained in an analysis of experimental kinetic data in terms of a pseudophase model of micellar catalysis in accordance with the equation [16]

$$k_a = \frac{k_m K_s C_{surf} + k_0}{1 + K_s C_{surf}}, \qquad (2)$$

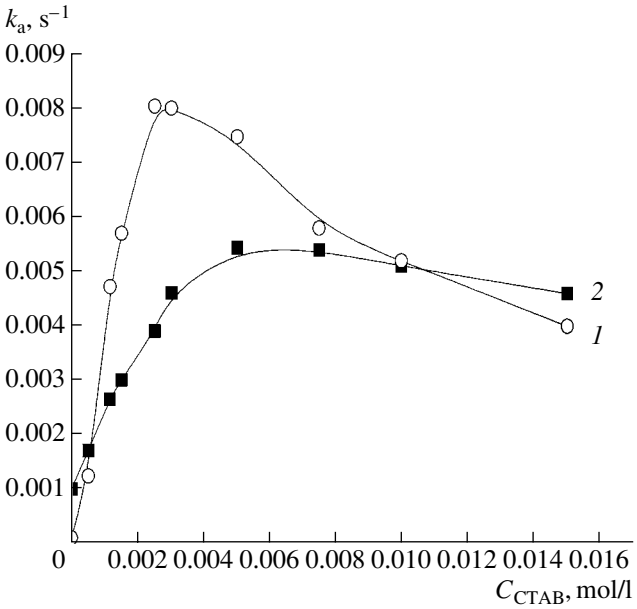


Fig. 1. Dependence of the apparent rate constants of the alkali hydrolysis of (*1*) PNPL and (*2*) PNPA on CTAB concentration (pH 10.0; 25°C).

where C_{surf} is the surfactant concentration corrected for the critical micelle concentration (CMC); k_0 and k_m are the rate constants in an aqueous medium and a micellar phase, respectively.

The results of calculations given in Table 2 indicate that PNPL was bound to the micelle much stronger than PNPA. The similarity of the values of k_m for the alkaline hydrolysis of the test substrates manifested itself in a decreased difference between the behaviors of carboxylic acid esters with different hydrophilic–lipophilic properties in reactions that occurred in micellar CTAB solutions.

An analysis of kinetic data for the reaction of PNPA ester-bond cleavage in micellar CTAB solutions in the presence of phenols indicates that the contribution of

Table 2. Parameters of the micelle-catalyzed transesterification reaction of PNPA in weakly alkaline CTAB solutions (pH 10.0)

Alkylphenol	Phenol concentration, mol/l	k_0, s^{-1}	k_m, s^{-1}	K_s, l/mol	CMC, mol/l	k_m/k_0
With no additives (alkaline hydrolysis)	0	0.001	0.0073	450	0.00026	7.3
Phenol	0.0020	0.0017	0.055	4700	0.00055	3.2
4-*n*-Butylphenol	0.0020	0.0015	0.062	4950	0.00053	41
4-Isononylphenol	0.0020	0.0012	0.076	5900	0.00035	63
	0.0024	0.0014	0.097	6100	0.00036	69

Note: The parameters of the alkaline hydrolysis of PNPL were the following: $k_0 = 0.00004$ s^{-1}; $k_m = 0.011$ s^{-1}; $K_s = 1100$ l/mol; CMC = 0.00044 mol/l (according to Fig. 1); the k_m/k_0 ratio characterizes the catalytic effect.

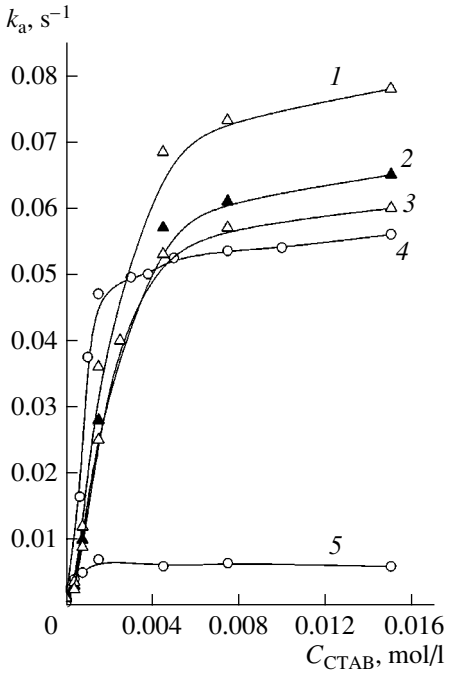


Fig. 2. Dependence of the apparent rate constant of PNPA decomposition on CTAB concentration (pH 10.0; 25°C): (*1*) 4-isononylphenol (0.0024 mol/l), (*2*) 4-isononylphenol (0.0020 mol/l), (*3*) *n*-butylphenol (0.0020 mol/l), (*4*) phenol (0.0020 mol/l), or (*5*) in the absence of phenol.

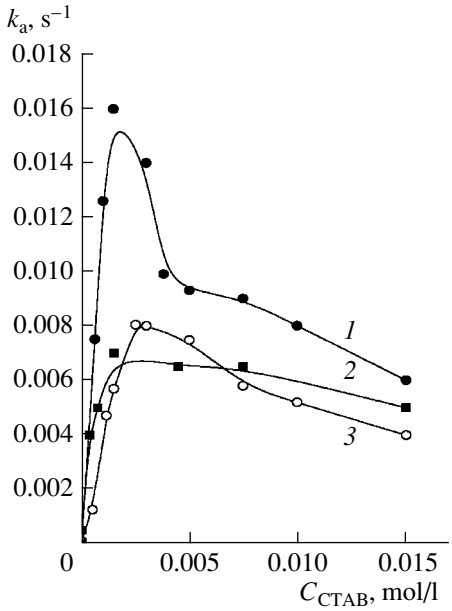


Fig. 3. Dependence of the apparent rate constant of PNPL decomposition on CTAB concentration (pH 10.0; 25°C): (*1*) phenol (0.0020 mol/l), (*2*) 4-isononylphenol (0.0020 mol/l), or (*3*) in the absence of phenol.

alkali hydrolysis to the overall rate of the process was negligibly small at pH 10.0 and a phenol concentration of 0.0020 mol/l (Fig. 2). From a comparison between the values of pK_a under these conditions, it follows that the fractions of reactive phenolate species in the systems with unsubstituted phenol and 4-isononylphenol were 0.5 and 0.35, respectively. The apparent rate constant of reaction depends on nucleophile concentration. The activity of test compounds should be compared at equal concentrations of reactive species. This took place, for example, at a phenol concentration of 0.0020 mol/l and a 4-isononylphenol concentration of 0.0024 mol/l: in this case, the concentrations of the phenolate forms of both of the compounds in a CTAB solution at pH 10.0 were the same and equal to 0.001 mol/l. It can be seen in Fig. 2 that 4-isononylphenol was more active than its unsubstituted analog in the reaction with PNPA, and the micellar catalytic effect in this case was as high as almost two orders of magnitude.

The apparent rate constants of PNPL cleavage in micellar CTAB solutions at pH 10.0 in the presence of alkylphenols were lower that the corresponding constants for PNPA by a factor of 5–10 (see Figs. 2 and 3). The presence of unsubstituted phenol in a concentration of 0.0020 mol/l doubled the value of k_a for the reaction of PNPL cleavage, as compared with the corresponding value for alkaline hydrolysis. 4-Isononylphenol (0.0020 mol/l) did not give such an increase (Fig. 3). This fact suggests that the alkaline hydrolysis of PNPL in a micellar CTAB solution is a predominant process in the cleavage of ester bonds in the presence of phenolates and the resulting catalytic effect was primarily due to an acceleration of this process. Thus, substrate specificity manifested itself in the test system. This substrate specificity depends on the localization, orientation, polarity, and hydrophilic properties of reactants.

Based on the experimental data shown in Fig. 2, we found some parameters of the micelle-catalyzed transesterification of PNPA with the use of Eq. (1) (Table 2). It is likely that the solubilization of alkylphenols by CTAB micelles changed the structure and composition of an aggregate to improve the binding of this ester at a prereaction step. The highest values of K_s are characteristic of 4-isononylphenol. This compound also exerted the greatest catalytic effect in the reaction of PNPA: the process was accelerated by a factor of about 70.

The experimental kinetic data suggest that the introduction of an alkylphenol into a CTAB solution affects the micelle structure and the strength of this effect depends on the localization site of the solubilized additive in the system. We can assume that phenol, which is sufficiently hydrophilic, adsorbed in the surface Stern layer does not disturb the packing density of surfactant molecules in the micelle core, whereas 4-isononylphenol, which is prone to self-association especially in the anionic form, can form mixed aggregates with the cationic surfactant. The properties of these mixed aggregates are qualitatively different from those of individual micelles.

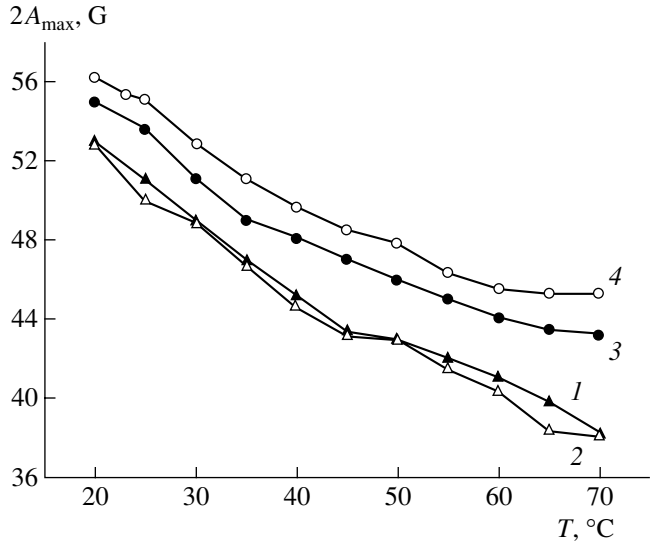


Fig. 4. The temperature dependence of maximum hyperfine splitting in the EPR spectra of micellar solutions ([CTAB] = 0.01 mol/l): (*1*) CTAB at pH 8.7, (*2*) the same at pH 13.0, (*3*) CTAB with the addition of 4-isononylphenol (0.0020 mol/l) at pH 8.7, and (*4*) the same at pH 13.0.

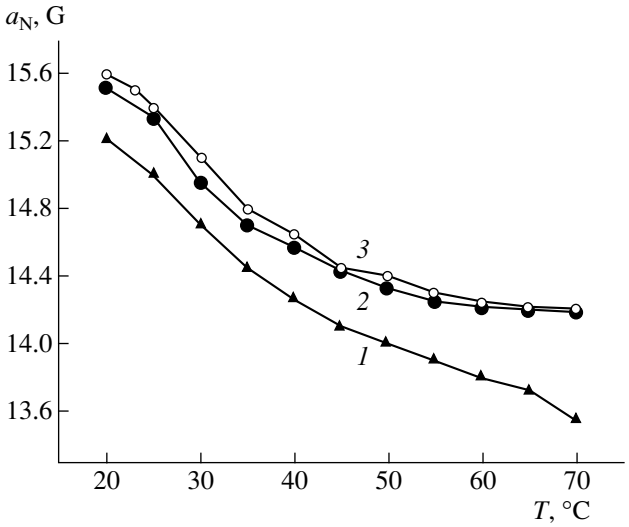


Fig. 5. The temperature dependence of isotropic hyperfine splitting constants for micellar solutions ([CTAB] = 0.01 mol/l): (*1*) CTAB at pH 8.7, (*2*) CTAB with the addition of 4-isononylphenol (0.0020 mol/l) at pH 8.7, and (*3*) the same at pH 13.0.

In this work, we demonstrated the formation of mixed CTAB/4-isononylphenol aggregates using independent physical techniques: spin-probe EPR spectroscopy and high-resolution pulsed-field gradient ^{1}H NMR spectroscopy. The former technique allowed us to monitor changes in the packing density of the hydrocarbon radicals of the surfactant in a micelle, and the latter technique allowed us to determine the size and mobility of micellar aggregates.

The EPR spectra of spin probes in CTAB solutions both in the absence and in the presence of alkylphenols contained external broad hyperfine-structure peaks. This fact suggests that the correlation times of rotation of paramagnetic centers were longer than 10^{-9} s. Because these movements are slow (on an EPR-spectroscopic scale), the maximum hyperfine splitting of spectra ($2A_{max}$) was used in the analysis of spectra. This parameter is sensitive to the amplitude and frequency (correlation time) of rotation of a spin-labeled fragment of probes [17]. The lower the frequency of rotation of a paramagnetic probe fragment, that is, the greater limitations experienced by this rotating fragment, the higher the value of $2A_{max}$. Figure 4 shows the temperature dependence of $2A_{max}$ for the initial micellar solution and a system modified with 4-isononylphenol at pH 8.7 and 13.0.

The EPR data indicate that the packing density of CTAB molecules in a micelle in the absence of phenol is practically independent of the pH of solution. In this case, it is likely that not only interactions between the hydrophobic fragments of CTAB molecules but also the electrostatic interactions of the head groups of this surfactant remain unchanged. The electrostatic interactions essentially depend on exchange equilibrium between bromide and hydroxide ions in the Stern layer. The addition of 4-isononylphenol to the micellar system resulted in an increase in $2A_{max}$; in this case, the phenolate species exerted a stronger effect on this parameter (Fig. 4). It is believed that primarily hydrophobic interactions are the driving forces of the formation of mixed CTAB/4-isononylphenol micelles. The hydrocarbon radicals of 4-isononylphenol molecules are inserted into the micelle core to increase the density of its microstructure, as has also been observed in mixed micelles of other amphiphilic compounds [18]. In the case of phenolate species, the mobility of a spin probe fragment decreased to an even greater extent.

Based on the EPR spectra, we can judge not only the mobility of a spin-labeled probe fragment but also the micropolarity of its environment. The isotropic hyperfine splitting constant (a_N), which characterizes the interaction of the spin of an unpaired electron with the magnetic moment of a nitrogen atomic nucleus, is a magnitude sensitive to changes in this parameter. The higher the polarity of a medium, the higher the value of a_N. It can be seen in Fig. 5 that, regardless of the pH of the medium, the appearance of 4-isononylphenol in micelles was accompanied by an increase in the values of a_N, as compared with a control system, that is, by an increase in polarity in the region of localization of the nitroxyl fragment of the probe. Evidently, this was also a consequence of changes in micelle structure and composition. First, the incorporation of polar 4-isononylphenol molecules (and, especially, 4-isononylphenolate) into CTAB micelles will affect charge distribution in both surface and palisade layers. Second, the hydroxyl groups of phenol can form strong

Table 3. Self-diffusion coefficients and the average hydrodynamic radii of micelles in the starting micellar solutions of CTAB (0.01 mol/l) in the absence and in the presence of 4-isononylphenol (0.0020 mol/l)

System	$D \times 10^{10}$, m^2/s	R, nm
CTAB in D_2O	0.95	2.3
CTAB + 4-isononylphenol in D_2O	0.78	2.8
CTAB in NaOD (pH 11)	1.08	2.1
CTAB + 4-isononylphenol in NaOD (pH 11)	0.87	2.6

hydrogen bonds with water molecules and thereby increase the amount of bound water in the surface layer of a micelle. According to Rusanov [19], each micelle has a layer two to three methylene groups in thickness that is accessible to the penetration of water molecules. The appearance of water in this layer will affect the polarity of the microenvironment of a spin probe fragment localized at the fourth carbon atom of its alkyl chain. If the anionic form of 4-isononylphenol is more prone to the formation of mixed micelles, an increase in the amount of water in this layer should be expected. Indeed, we experimentally found (Fig. 5) an increase in the polarity of the microenvironment of a spin fragment in the presence of the anionic form of 4-isononylphenol, as compared with the neutral species.

The use of high-resolution pulsed-field gradient ^1H NMR spectroscopy for studying the structure of microheterogeneous surfactant solutions allowed us to find diffusion decreases in resonance signals and to determine the self-diffusion coefficients (D) of test system components.

The NMR spectra of the micellar CTAB solutions ([CTAB] = 0.01 mol/l) in the absence and in the presence of 4-isononylphenol up to a concentration of 0.0020 mol/l exhibited well-resolved resonance signals from water protons (4.8 ppm), protons of the CH_3 head groups of CTAB (shifted to the region of 3.43 ppm because of interactions with the positively charged nitrogen atom), and methylene group protons (1.4 ppm) and a less intense signal due to the protons of terminal CH_3 groups (1 ppm). To measure the self-diffusion coefficients of micelles (at [CTAB] $\gg$ CMC, $D_m \approx D_{CTAB}$), we chose the most intense signal in ^1H NMR spectra, namely, a signal due to methylene group protons (Table 3). Unfortunately, in the diffusion mode of measurements, the individual signals due to protons of the phenol ring of 4-isononylphenol were absent from the spectrum. However, a signal from methylene groups (1.4 ppm) included contributions from both CTAB and 4-isononylphenol, which cannot be separated. Thus, the diffusion decay of the signal was single-exponential. This suggests that the self-diffusion coefficients of CTAB and 4-isononylphenol are similar or equal; in this case, this can imply the diffusion migration of both components of a single structural complex. The self-diffusion coefficients found allowed us to determine the average hydrodynamic radius (R) of micelles in the presence and in the absence of 4-isononylphenol. For this purpose, we used the Stokes–Einstein equation

$$D = kT/6\pi\eta R,$$

where k is the Boltzmann constant, T is temperature, and η is the viscosity of the medium. The viscosity of a pure solvent (1.033 cP for deuterated water at 30°C) was used as the value of η. An analysis of the hydrodynamic radii of micelles (Table 3) demonstrated that, on the addition of 4-isononylphenol, R increased by ~20%, as compared with that in the initial micellar solution of CTAB; this resulted from the incorporation of 4-isononylphenol in CTAB micelles.

Thus, we experimentally found the formation of CTAB/4-isononylphenol mixed micelles and determined structural characteristics of these micelles. The micellar catalytic effect observed in the transesterification of PNPA in these systems can accelerate the reaction by a factor of about 70. We found the values of pK_a of phenol and 4-isononylphenol and evaluated the effect of surfactants on their acid–base properties. This is of importance for considering the behavior of these compounds in nucleophilic substitution reactions in micellar solutions.

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