Russian Journal of General Chemistry, Vol. 72, No. 7, 2002, pp. 1017–1022. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 7, 2002, pp. 1088–1093.
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Micellization and Catalytic Properties of Polyethylene Glycol 600 Monolaurate in Toluene

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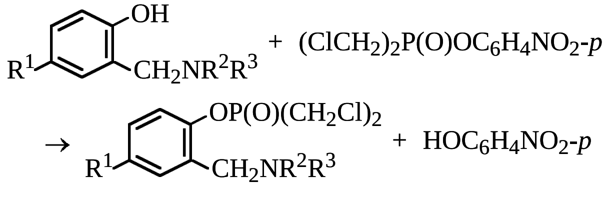
Received August 7, 2001

Abstract—The reaction of 4-nitrophenyl bis(chloromethyl)phosphinate with 2-dialkylaminomethylphenols in toluene solutions of polyethylene glycol 600 monolaurate was studied spectrophotometrically. The effect of structural features of the micellar system on the catalytic effect depends on the nucleophile hydrophobicity. Micellization of the nonionic surfactant was studied by dielectrometric titration and by the kinetic method. The aggregation numbers and the composition of detergent aggregates were determined.

It is known that inverted micelles of nonionic surfactants catalyze nucleophilic substitution in esters of four-coordinate phosphorus acids [1]. It was found with the examples of reactions involving amines [2, 3] and *p*-substituted 2-dimethylaminomethylphenols [4] that the catalytic activity of micelles depends on the structures and concentrations of a surfactant and a nucleophile, and also on structural features of micellar aggregates. For example, it was shown that, in reactions of 4-nitrophenyl bis(chloromethyl)phosphinate (**I**) with compounds **II**–**IV** [4], the catalytic activity of micelles increases at concentrations corresponding to structural rearrangement of micellar aggregates, and the strongest increase in the catalytic effect is characteristic for chlorine-substituted 2-aminomethylphenol. To consider in more detail the effect of structural features of the aggregates on the catalytic activity of micelles, we continued in this work a study of the reaction of phosphinate **I** with aminomethylphenols **V** and **VI** in toluene in the absence and in the presence of polyethylene glycol 600 monolaurate (**VII**).



II–**IV**, R^1 = Cl (**II**), H (**III**), *i*-C_9H_{19} (**IV**), $R^2 = R^3 = CH_3$; **V**, **VI**, R^1 = H, $R^2 = R^3 = C_nH_{2n+1}$, n = 7 (**V**), 12 (**VI**).

The observed rate constant (k) of the process involving **V** linearly depends on the aminomethylphenol concentration (C_{AMP}). At 40°C, it is described by the equation $k = k_{2,0}C_{AMP}$, where $k_{2,0}$ = 0.18 l mol s^{-1}. It is more than two times lower than the constant for aminomethylphenol **III** (0.39 l mol^{-1} s^{-1} [4]), which may be due to the steric effect of substituents. For more hydrophobic compound **VI**, the approach of nucleophile molecules to the substrate seems to be so hindered that the reaction becomes possible only when it is catalyzed by the second aminomethylphenol molecule. This results in the appearance of a quadratic term in Eq. (1) describing k as a function of C_{AMP} (40°C).

$$k = 0.15C_{AMP} + 10.1C_{AMP}^2. \qquad (1)$$

Higher k values for **VI** at high aminomethylphenol concentrations, as compared to **III** and **V** (Fig. 1),

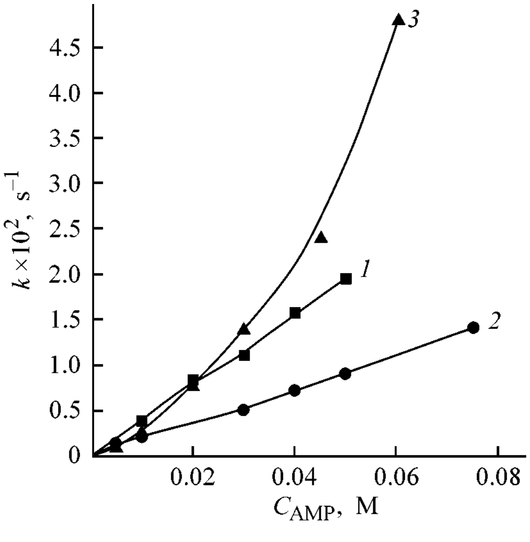


Fig. 1. Observed rate constants of reactions of aminomethylphenols (*1*) **III**, (*2*) **V**, and (*3*) **VI** with **I** in toluene as functions of aminomethylphenol concentration, 40°C.

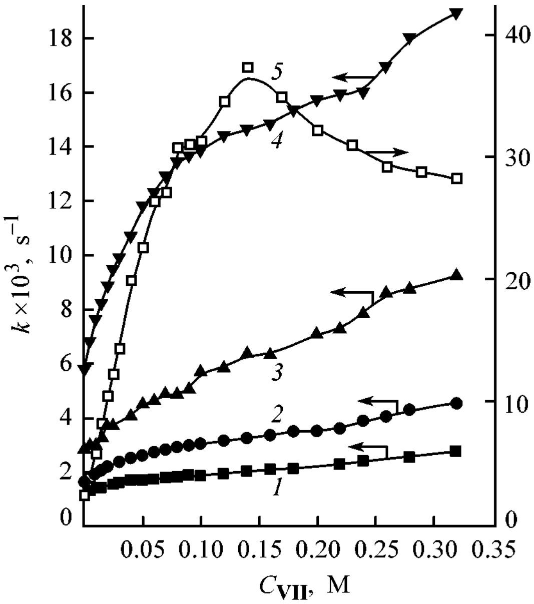


Fig. 2. Observed rate constants of reactions of **I** with aminomethylphenols (*1–4*) **V** and (*5*) **VI** in toluene as functions of the concentration of surfactant **VII**. Temperature, °C: (*1*) 25, (*2, 4, 5*) 40, and (*3*) 55; C_{AMP}, M: (*1–3, 5*) 0.01 and (*4*) 0.035.

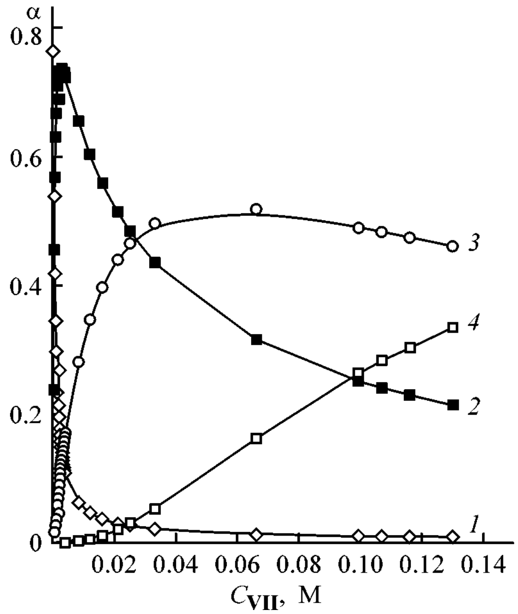


Fig. 3. Relative content of (*1*) monomers and (*2–4*) associates of **VII** with aggregation numbers (*2*) 4, (*3*) 8, and (*4*) 20 in toluene as a function of surfactant concentration at 20°C.

are attributable to a change in the form of the kinetic equation, and also to association, which becomes more probable with increasing aminomethylphenol hydrophobicity.

In the presence of surfactant **VII**, the rate constant *k* of the process increases (Fig. 2), which is due to the formation of inverted micelles. Micellization of **VII** was studied earlier by the method of solubilization of Eosin-BA dye and water, and also by viscometry [2, 3]. Characteristic curves obtained by these methods for the system under study have bends in the regions corresponding to the structural rearrangement of micelles: 0.07–0.1 M (CMC-2) and 0.21–0.24 M (CMC-3), where CMC is the critical micelle concentration. The range in which compound **VII** starts to aggregate, 1.6×10^{-4}–7.5×10^{-3} M (CMC-1) [2, 4, 5], was calculated from the kinetic data using equations of the pseudo-phase model of micellar catalysis [6]. In this work, to study micellization, we used dielectrometric titration along with the kinetic method. The thus obtained concentration dependences of permittivity (ε) and orientation polarization (P_{or}) of solutions of **VII** in the presence of aminomethylphenols were described on the basis of the mass action law [7] and analyzed by mathematical simulation with the CPESSP program. In this case, the theoretical value of ΔP_{or}^{theor} was calculated by the following formula:

$$\Delta P_{or}^{theor} = \Sigma \Delta P_{or,i} \alpha_{ij}.$$

Here $\Delta P_{or,i}$ is the change in the orientation polarization of solution upon the interaction of components in *i*th equilibrium, and α_{ij} is the fraction of the *i*th species solution relative to the *j*th component by which the experimental value of ΔP_{or} was calculated. In the absence of aminomethylphenol, the micellization can be described by the following simpler formula:

$$\Delta P_{or}^{theor} = \Sigma \Delta P_{or,i} \alpha_i.$$

Here α_i is the fraction of the surfactant transformed into a micelle at a given aggregation number *N*. Fisher's test determined from the functional *F* served as the index of convergence of the computed and experimental points.

$$F = \Sigma\left(\Delta P_{or}^{exp} - \Delta P_{or}^{theor}\right)^2 / \left(\Delta P_{or}^{exp}\right)^2 \sigma^2.$$

Here σ is the relative determination error.

The concentration dependences of the relative contents (α) of aggregates of **VII**, which consist, according to the calculations, of 4, 8, and 20 molecules of a surfactant, are shown in Fig. 3. The concentration range within which the fraction of aggregates with $N = 4$ increases (2.5×10^{-3}–6×10^{-3} M) coincides with the concentration range in which the micellization starts, as determined from the kinetic study (CMC-1, Table 1). The comparison of CMC-2 values (0.07–0.1 M) obtained by the methods of dye solubilization and viscometry [2, 3] shows that they virtually coincide with the concentrations of **VII** corresponding to maximal relative content of aggregates with $N = 8$. We can assume that the content of aggregates with $N = 20$ (Fig. 3) reaches a maximum at a concentration of **VII** equal to CMC-3. Thus, there is a correlation between the concentrations corresponding to the onset of micellization (CMC-1) and structural rearrangement of micelles (CMC-2), on the one hand, and concentrations of **VII** corresponding to the maximal relative content of aggregates with a certain aggregation number, on the other hand. The presence of solubilizing agents (aminomethylphenols and substrate **I**) strongly affects the composition of the forming aggregates. Using the above-stated approach, we calculated the concentration dependences of α in the systems toluene–surfactant **VII**–aminomethylphenol **II**, **III**, or **V** and toluene–surfactant **VII**–substrate **I**. Such dependences for solutions of **VII** containing aminomethylphenol **V** are shown in Figs. 4 and 5 as examples. In the presence of 5×10^{-3} M **V** at low concentrations of **VII**, aggregates with the composition **VII** : **V** = 1 : 4 are formed. As the concentration of compound **VII** is increased, they rapidly disappear to form aggregates with the compositions 4 : 3, 10 : 5, 20 : 2, and 20 : 4 (Fig. 4). Furthermore, aggregates of **VII** almost free from aminomethylphenol molecules and containing 4, 8, and 20 molecules of **VII** are also present in solution. In fact, the presence of **V** in solution does not affect the number of molecules of **VII** in aggregates binding aminomethylphenol molecules (4, 10, and 20), but appreciably shifts the range of concentrations of **VII** at which large aggregates containing 10 and 20 molecules of **VII** are formed. Namely, the maximal relative content of

Table 1. Parameters of micelle-catalyzed reactions of **I** with aminomethylphenols **II**, **III**, **V**, and **VI** (0.01 M) in toluene solutions of **VII**

Compound no.	T, °C	$k_0 \times 10^3$, s^{-1}	$k_m \times 10^3$, s^{-1}	K_b, M^{-1}	CMC-1 × 10^3, M	k_m/k_0
II[a]	40	0.54	2.7	11	7.5	5.0
III[a]	40	3.9	9.4	19	6.3	2.4
V	40	1.6	3.9	17	1.7	2.4
V[b]	40	5.8	14	41	2.4	2.4
V	25	1.3	2.2	18	1.2	1.7
	55	2.9	7.6	10	2.7	2.6
VI	40	2.5	60	12	5.6	24

[a] Data of [4]. [b] C_{AMP} 0.035 M.

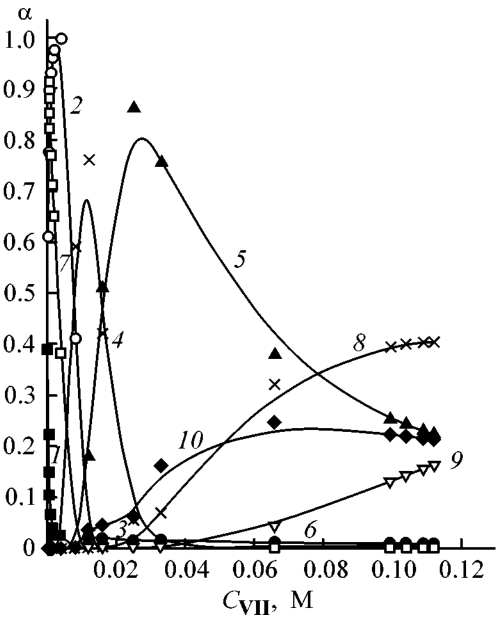


Fig. 4. Relative content in the system toluene–compound **VII**–aminomethylphenol **V** of associates of **VII** with the compositions (**VII** : **V**) of (*1*) 1 : 4, (*2*) 4 : 3, (*3*) 20 : 2, (*4*) 10 : 5, (*5*) 20 : 4, (*6*) 1 : 0, (*7*) 0 : 1, (*8*) 8 : 0, (*9*) 20 : 0, and (*10*) 4 : 0, as a function of the concentration of **VII**. C_{AMP} 5×10^{-3} M, 20°C.

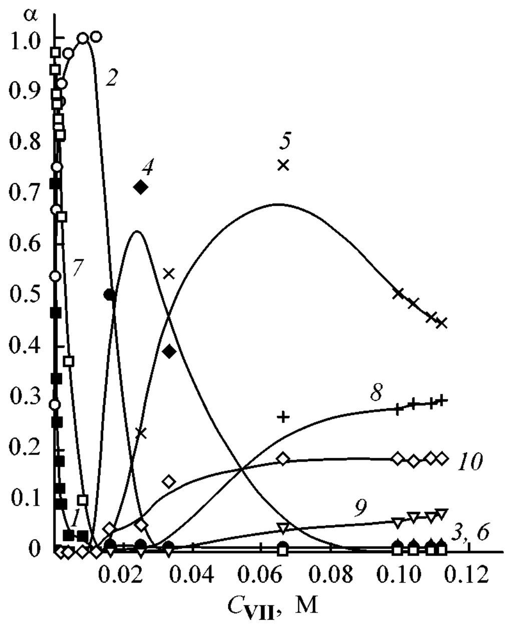


Fig. 5. Relative content in the system toluene–compound **VII**–aminomethylphenol **V** of associates of **VII** with the compositions (**VII** : **V**) of (*1*) 1 : 4, (*2*) 4 : 3, (*3*) 20 : 2, (*4*) 10 : 5, (*5*) 20 : 4, (*6*) 1 : 0, (*7*) 0 : 1, (*8*) 8 : 0, (*9*) 20 : 0, and (*10*) 4 : 0, as a function of the concentration of **VII**. C_{AMP} 0.01 M, 20°C.

10 : 5 aggregates corresponds to a concentration of 0.01 M, and that of 20 : 4 aggregates, to a concentration of 0.025 M, with the 20 : 4 aggregates dominating within a broad concentration range from 0.02 to 0.08 M. Thus, in the presence of hydrophobic aminomethylphenol, aggregates get consolidated already at low concentrations of a surfactant. A twofold increase in the concentraiton of **V** (to 0.01 M) results in a shift of the ranges of maximal relative content of aminomethylphenol-containing aggregates to higher concentrations of **VII** and in broadening of the ranges of their existence (Fig. 5).

The presence of less hydrophobic aminomethylphenol **III** in solution (5×10^{-3} M) has a weaker effect on the distribution of the above-described aggregates. For example, the concentrations of **VII** corresponding to the maximal content of the 4 : 3, 10 : 5, and 20 : 4 aggregates are, respectively, 0.01, 1.5×10^{-2}, and 0.03–0.05 M. For the most polar chlorine-substituted aminomethylphenol **II** (5×10^{-3} M), the 4 : 3 and 10 : 5 aggregates are formed at the same concentrations of **VII** as in presence of unsubstituted aminomethylphenol **III**, and the 20 : 4 aggregates, at 0.05–0.12 M and in a considerably smaller amount.

The dependence of the aggregation behavior of **VII** on the solubilizate polarity is observed also in the system toluene–compound **VII**–substrate. In the examined concentration range of **VII**, in the presence of 7.45×10^{-5} M of **I**, only one form of 10 : 5 aggregates is present.

Table 2. Rate constants of the reaction of aminomethylphenols (**III**–**VI**) with **I** in toluene solutions of **VII** at 40°C

Compound no.	C_{VII}, M	$k_{2,\mathrm{SA}}$, l mol^{-1} s^{-1}	C_{AMP} 0.01 M	
			W^a	W_1^b
III	0.025	0.5	1.3	0.65
	0.26^c	1.7	4.3	
IV	0.025	0.85	1.2	0.53
	0.26^c	1.7	2.4	
V	0.025	0.22	1.2	0.28
	0.08	0.3	1.7	
	0.26	0.42	2.3	
VI	0.025	1.4	5.6	–0.41
	0.08	3.4	13.6	
	0.26	3.3	13.2	

[a] $W = k_{\mathrm{VII}}/k_0$, where k_{VII} and k_0 are first-order rate constants of the reaction in the presence and in the absence of **VII**, respectively. [b] $W_1 = (k_i^{\mathrm{exp}} - k_i^{\mathrm{theor}})/(k_i^{\mathrm{exp}} - k_0)$, where k_i^{exp} and k_i^{theor} are experimental and calculated by Eq. (2) first-order rate constants for micellar solutions at 0.26 M concentration of **VII**. [c] Data of [4].

Thus, the aggregation numbers and composition of associates formed in solution of **VII** depend on the nature and concentration of the solubilized compounds. Vice versa, micelles also affect the properties, including chemical properties, of compounds being solubilized. According to [6], such an effect is due to the fact that the reagents are concentrated in the micellar pseudo-phase, and their microsurrounding changes. This follows from the change in the form of the kinetic equation for phosphorylation of **VI**. The dependence of k on C_{AMP} is linear for micellar solutions of **VII**. It is described by the equation $k = k_{2,\mathrm{SA}} C_{\mathrm{AMP}}$ ($k_{2,\mathrm{SA}}$ values are given in Table 2). The absence of a quadratic term in the equation, as is the case with aminolysis [2], results from the fact that, instead of the second aminomethylphenol molecule, polar groups of **VII** start to play a catalytic role in the process.

The dependences of the rate constants k for the reactions of aminomethylphenols **V** and **VI** with **I** on the surfactant concentration are shown in Fig. 2. At low concentrations of **VII**, they are described by Eq. (2) [6].

$$(k - k_0)/(k_m - k) = K_b C_{\mathrm{SA}}. \tag{2}$$

Here k_0 and k_m are the reaction rate constants in the bulk of the solvent and in the micellar phase, respectively; K_b, a constant of substrate binding with micelles; and C_{SA}, the concentration of **VII** corrected for CMC-1. The parameters k_m, K_b, and CMC-1 calculated by this equation are given in Table 1. The constant k_m for the reaction with **V** is lower than with **III**; however, it considerably grows in the case of the reaction involving aminomethylphenol **VI**. This results in that, with **VI**, passing of reactants into a micellar phase accelerates the reaction to a considerably greater extent (k_m/k_0) than with **V**. That is, with the most hydrophobic compound **VI**, the effect of the micellar microsurrounding and resolvation of reactants is the most favorable. The constant K_b decreases in the order **III** > **V** > **VI**. As the concentration of **V** grows, K_b and k_m increase, but k_m/k_0 ratio remains unchanged.

The dependence of k on the surfactant concentration for micellar-catalyzed processes usually tends to flatten out or passes through a maximum [6, 8]. However, Fig. 2 shows that, for **V**, as well as for **II**–**IV** [4], k increases in the regions of CMC-2 and CMC-3, whereas for **VI** it initially increases and then somewhat decreases. According to [4], the catalysis efficiency increases with rearrangement of micelles in

Table 3. Activation parameters of the reaction of **I** with **V** in toluene solutions of **VII**

$C_{\mathbf{VII}}$, M	$E_{a,ef}$, kJ mol^{-1}	$-\Delta S^{\neq}_{ef}$, J mol^{-1} K^{-1}	$C_{\mathbf{VII}}$, M	$E_{a,ef}$, kJ mol^{-1}	$-\Delta S^{\neq}_{ef}$, J mol^{-1} K^{-1}
0	22.3	234	0.1	28.3	211
0.015	23.2	230	0.16	28.3	210
0.04	23.8	227	0.22	31.2	200
0.06	26.4	218	0.28	31.3	199
0.08	26.6	217	0.32	33.1	192
0.09	27.1	215			

the order **IV** < **III** < **II**, i.e., in going to less hydrophobic nucleophiles.

The parameters W_1, which account for the variation in the catalysis efficiency in the series of aminomethylphenols **III**–**VI**, are given in Table 2. In the series **III**–**V**, W_1 decreases, and in going to **VI** it becomes negative. This fact shows that the unfavorable effect of the hydrophobicity of solubilized nucleophiles on the structural factor in the catalytic effect of micelles is manifested only up to a certain limit. As the length of hydrocarbon radicals of a reactant increases, this effect becomes less noticeable and even reverse. This may be due to the fact that the characteristics of a system (permittivity of aggregates, packing density of surfactant molecules in a micelle [9], solubilization of reactants [10, 11], etc.) and, therefore, its catalytic effect vary differently in the presence of aminomethylphenols differing in the hydrophobicity.

The effective activation parameters of the reaction between **I** and **V** are given in Table 3, which shows that an increase in the surfactant concentration results in increased activation energy of the process and in decreased absolute values of the activation entropy. A similar trend is typical for the nucleophilic substitution in inverted micelles of nonionic surfactants [4, 5, 12]; it reflects the fact that the reaction acceleration in solutions of **VII** is due to the entropy factor.

EXPERIMENTAL

Substrate **I** and aminomethylphenols **V** and **VI** were synthesized according to [13, 14]. A sample of polyethylene glycol 600 monolaurate (Ferak) was used without preliminary purification. Toluene was purified by a standard procedure. The reaction kinetics was studied with a Specord UV-Vis spectrophotometer under pseudo-monomolecular conditions by monitoring the increase in the optical density of the 4-nitrophenol absorption band at 322.6 nm. The substrate concentration in the kinetic experiments was $(5–7) \times 10^{-5}$ M. The observed rate constants were calculated by first-order equations. The dielectrometric titration was carried out as described in [15]. The permittivity of solutions was determined on an installation consisting of an E12-I device using the beat procedure and a temperature-controlled capacitor as a measuring cell [16]. The refractive index was measured on an IRF-23 refractometer.

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (project no. 00-03-32 119a).

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