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Colloidal State of the System 4-Octylphenol–NaOH–Water and Its Catalytic Activity in Nucleophilic Substitution in Phosphorus Acid Esters

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Abstract—The kinetics of decomposition of 4-nitrophenyl ethyl ethylphosphonate in the system 4-octylphenol–NaOH–water was studied spectrophotometrically. Electrophoretic, tensimetric, and kinetic studies proved formation of cationic associates in which phenolysis or base hydrolysis occurs, depending on the concentration ratio of 4-octylphenol and NaOH.

Interest in phenol and its alkyl derivatives is due to their significance as raw materials for preparing surfactants, stabilizers, additives, and extraction systems with ion-exchange and micellar action [1]. In addition, phenolic compounds widely occur in animals and plants; they are secondary metabolites [2]. Therefore, simulation of the action of biostructures based on associated phenols is an urgent problem.

Phenol and its derivatives have several reactive sites. Chemical bonds can form both by reaction with the hydroxy group and by electrophilic substitution at the *o*- and *p*-positions of the benzene ring. Also, phenol can form hydrogen bonds via hydroxy group and π complexes by interaction of the benzene π system with cations; long-chain alkyl substituents enhance hydrophobic interactions with phenols. All these features results in diverse types of association [3, 4].

It seemed interesting to find how association phenomena in systems containing long-chain alkylphenols affect their reactivity in processes used for detoxification of phosphorus acid esters [5].

Unsubstituted phenol, being a weak acid (pK_a 10), readily dissolves in alkalis to form water-soluble phenolates, which are strong nucleophiles. Data on the colloidal properties and catalytic behavior of long-chain alkylphenols in aqueous alkalis are virtually lacking [6].

We studied the capability of the system 4-octylphenol (4-C_8H_{17}PhOH, pOP)–NaOH–water to control the rate and direction of nucleophilic substitution using decomposition of 4-nitrophenyl ethyl ethylphosphonate **I** as example. In this system, formation of the 4-octylphenolate ion (4-C_8H_{17}PhONa) by the reaction of 4-C_8H_{17}PhOH with NaOH should be expected [scheme (1), first stage].

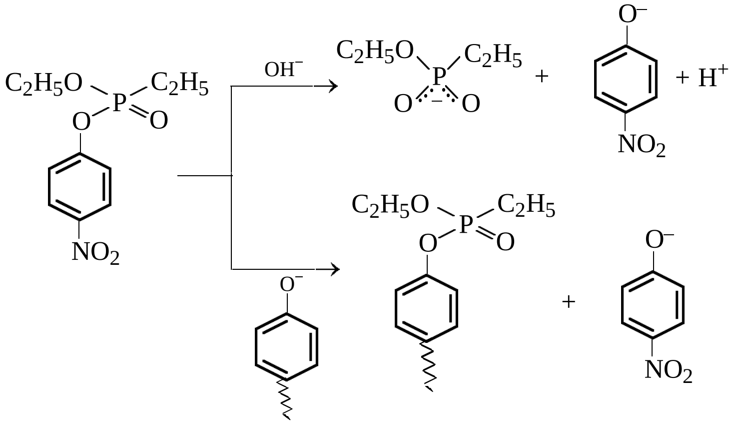
Introduction of alkyl groups into the phenol molecule increases the electron density on the hydroxyl oxygen atom; associative processes in this case can give rise to micellar catalytic effects. However, in aqueous solution the oxygen center of phenolate ions is involved in hydrogen bonding with the solvent. The oxygen center can also be blocked in ion pairs of alkali metal phenolates.

In the system 4-C_8H_{17}PhOH–NaOH–water, substrate **I** can undergo phenolysis and base hydrolysis [scheme (2)].

It is known that, in molecular solutions, reactions of four-coordinate phosphorus acid 4-nitrophenolates with phenolates and hydroxide ion follow the pattern of bimolecular nucleophilic substitution at the P atom (S_N2P), with the release of 4-nitrophenolate ion. The observed rate constants are linear functions of the reactant concentrations [6]. In our case, the second product of phenolysis is 4-octylphenyl ethyl ethylphosphonate **II**, and the second product of hydrolysis, ethyl hydrogen ethylphosphonate **III** [scheme (2)].

The presence of a long-chain alkyl radical makes 4-C_8H_{17}PhOH virtually insoluble in water, and the system 4-C_8H_{17}PhOH–water undergoes phase separation (4-C_8H_{17}PhOH is not dispersed in water). On

$$C_8H_{17}C_6H_4OH \xrightleftharpoons{NaOH} C_8H_{17}C_6H_4ONa \xrightleftharpoons{NaOH} C_8H_{17}C_6H_4ONa_2^+, \qquad (1)$$



(2)

adding an alkali, the solubility of 4-C_8H_{17}PhOH increases, and a colloidal solution stable for 2 months is formed. Using tensimetric, potentiometric, and conductometric methods, we proved formation of associates in the system 4-C_8H_{17}PhOH–NaOH–water and determined the critical association concentrations. Figure 1 illustrates determination of the critical association concentrations at $n = C_{NaOH}/C_{pOP} = 3$ by these methods. The results obtained by different methods are in good agreement. Figure 2 shows that, in going from $n = 1$ to $n = 2$, the critical association concentration sharply decreases, after which it weakly grows and then flattens out.

The direction and rate of the reaction in the system 4-C_8H_{17}PhOH–NaOH–water depends on the ratio *n*. The ^{31}P NMR chemical shifts in the spectra of the reaction products obtained in aqueous and aqueous-alkaline solutions and in the system 4-C_8H_{17}PhOH–NaOH–water at various *n* are listed in Table 1. These data show that, at a constant 4-C_8H_{17}PhOH concentration of 0.005 M, at $n = 1$ or 2, the reaction occurs as phenolysis, yielding ester interchange product **II**. The occurrence of phenolysis is confirmed by existence of 4-C_8H_{17}PhONa at low *n*. Starting from $n = 3$, the reaction occurs as base hydrolysis, and acid **III** becomes the only reaction product. With increasing alkali concentration, i.e., with accumulation of reactive counterions, decomposition of **I** follows the hydrolysis pathway.

The dependence of the observed rate constant of decomposition of **I** (k_{obs}, s^{-1}) in the system 4-C_8H_{17}·PhOH–NaOH–water on the 4-C_8H_{17}PhOH concentration at various *n* is nonlinear, which is typical of micellar catalysis (Fig. 3). The rate constants in the colloidal system first vary only slightly and then increase, reaching a limiting value at C_{pOP} ~0.005 M.

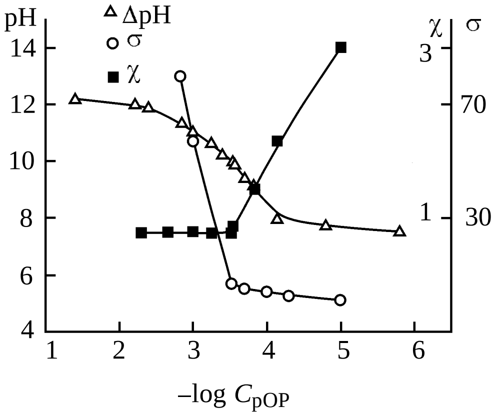


Fig. 1. pH, specific electrical conductivity (χ, Ω^{-1} cm^{-1}), and surface tension (σ, dyne cm^{-1}) as functions of the 4-C_8H_{17}PhOH concentration at $n = 3$ (40°C).

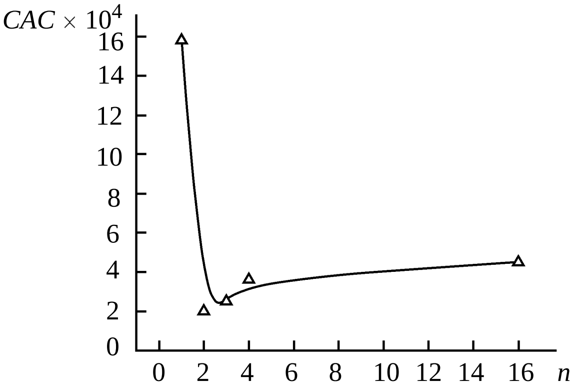


Fig. 2. Critical association concentration (*CAC*, M) as a function of the ratio *n* (C_{pOP} 0.005 M, 40°C).

Table 1. ^{31}P NMR chemical shifts (δ_P, ppm) of 4-nitrophenyl ethyl ethylphosphonate and products of its decomposition in various media (40°C)

Medium	*n*	δ_P, ppm	Reaction product
H_2O		34.65	$EtOEtP(O)OC_6H_4NO_2$-*p* (**I**)
$NaOH–H_2O$		29.81	EtOEtP(O)OH (**III**)
$4-C_8H_{17}PhOH–NaOH–H_2O$	1	35.77	$EtOEtP(O)OC_8H_{17}$ (**II**)
$4-C_8H_{17}PhOH–NaOH–H_2O$	2	35.53	$EtOEtP(O)OC_8H_{17}$ (**II**)
$4-C_8H_{17}PhOH–NaOH–H_2O$	3	30.09	EtOEtP(O)OH (**III**)
$4-C_8H_{17}PhOH–NaOH–H_2O$	8	30.98	EtOEtP(O)OH (**III**)
$4-C_8H_{17}PhOH–NaOH–H_2O$	30	30.90	EtOEtP(O)OH (**III**)

Assuming that the reaction occurs in an aggregate and in the bulk of solution, we can use the equation for micelle-catalyzed reactions [7]:

$$k_{\text{obs}} = (k_0 + k_{\text{as}}K_SC)/(1 + K_SC),$$

where k_0 is the rate constant of the reaction in the bulk; k_{as}, rate constant of the reaction in the aggregate; K_S, constant of substrate binding with the associate; and *C*, concentration of $4-C_8H_{17}PhOH$ minus critical association concentration.

The kinetic parameters of associate-catalyzed decomposition of **I** in the system $4-C_8H_{17}PhOH–NaOH–$water at various *n*, calculated with this equation, are listed in Table 2. It should be noted that, in the associate, the rate of hydrolysis of **I** ($n > 3$) is higher than the rate of its phenolysis ($n = 1$ or 2).

Acceleration of hydrolysis of **I** in the associate with increasing *n* (C_{pOP} 0.005 M, Fig. 2, Table 2) is difficult to explain assuming formation of aggregates of the anionic surfactant from $4-C_8H_{17}PhONa$ monomers. It is known that anionic micelles drastically decrease the rate of nucleophilic substitution in four-coordinate phosphorus acid esters owing to electrostatic repulsion of hydroxide ions, decreasing the effect of their concentrating [8].

Electrophoretic studies showed that the dispersed phase is positively charged at any *n* (Table 3), which suggests incorporation into the surface layer of mixed aggregates consisting, along with $4-C_8H_{17}PhONa$ and $4-C_8H_{17}PhOH$, of monomers containing excess sodium ions, $4-C_8H_{17}PhONa_n^+$.

Figure 4 shows the optical density *D* as a function of wavelength λ (nm) for the systems with different *n* at a constant concentration C_{pOP} 0.005 M. From these data, using the Rayleigh–Debye approximation for the condition of optically soft particles, we calculated the characteristic size *R* of dispersed phase particles [9, 10] (Table 3). It is seen that the characteristic size of colloidal particles in this system considerably exceeds the length of the hydrocarbon radical $4-C_8H_{17}PhOH$. The dependence $R = f(n)$ passes through a minimum at a 30-fold excess of alkali (Table 3). The experimental data suggest the presence of several ranges of alkali concentration in which the dependences of the

Table 2. Kinetic parameters of micelle-catalyzed decomposition of 4-nitrophenyl ethyl ethylphosphonate in the system $4-C_8H_{17}PhOH–NaOH–$water at various *n*, 40°C

$C_{\text{pOP}} : C_{\text{NaOH}}$, *n*	$CAC \times 10^4$,[a] M	$k_{\text{as}} \times 10^3$, s^{-1}	K_S, $l\ mol^{-1}$
1 : 1	17.20	4.06	104.23
1 : 2	1.39	4.59	127.70
1 : 3	4.68	7.81	287.90
1 : 4	7.58	11.90	219.14
1 : 8	2.62	22.81	268.72
1 : 16	1.00	27.20	259.45

[a] (*CAC*) Critical association concentration.

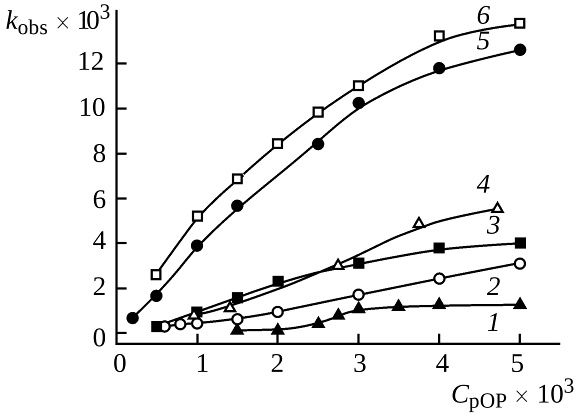


Fig. 3. Observed rate constant ($k_{\text{obs}} \times 10^3$, s^{-1}) as a function of the $4-C_8H_{17}PhOH$ concentration ($C_{\text{pOP}} \times 10^3$, M) at various *n* (40°C). *n*: (*1*) 1, (*2*) 2, (*3*) 3, (*4*) 4, (*5*) 8, and (*6*) 16.

Table 3. Colloidal properties of aggregates in the system 4-C_8H_{17}PhOH–NaOH–water as influenced by the ratio $n = C_{NaOH}/C_{pOP}$ (40°C)

Parameter	Phenolysis		Hydrolysis										
n	1	2	3	4	5	6	7	8	16	30	40	50	60
$B \times 10^4$, $cm^2\ V^{-1}\ s^{-1}$	+3.7	+3.2	+1.8	+1.5	+1.2		+1.3	+1.4	+2.5	+3.59			
R, nm	640	680	768	680	704	696	560	560	200	80	102	133	248

electrophoretic mobility *B*, characteristic radius *R* (Table 3), and electrical conductivity χ on *n* (Fig. 4) noticeably differ. This fact suggests that the formed colloidal structures are different. At $n < 3$, mixed ion–molecule aggregates consisting of the monomers $Q(4\text{-}C_8H_{17}PhO)Na_n^+$, 4-$C_8H_{17}$PhONa, and 4-$C_8H_{17}$·PhOH are formed. According to the kinetic studies at $n = 1$ and 2, the head groups of 4-C_8H_{17}PhONa exhibit nucleophilic properties and participate in phenolysis (Table 1). Starting from $n = 3$, the head groups of the 4-C_8H_{17}PhONa monomers become inacccessible. At $n = 3$ and 4, the radius *R* and electrophoretic mobility decrease. At $4 < n < 8$, the electrical conductivity grows (Fig. 5), with the electrophoretic mobility remaining constant (Table 3).

At $8 < n < 20$, addition of alkali does not cause a noticeable increase in the electrical conductivity (Fig. 5), suggesting intense binding of charge carriers. The relative content of cationic monomers in the associate grows, causing a decrease in the aggregation number and aggregate size and an increase in the electrophoretic mobility. In the process, the counterion layer of the aggregate becomes much denser, since there is a considerable gradient in the distribution of the hydroxy groups and Na^+ ions between the dispersed phase and dispersion medium. The conditions become unfavorable for phenolysis, and substrate **I** undergoes hydrolysis.

At *n* ~20, formation of a uniform cationic associate consisting of $Q(4\text{-}C_8H_{17}PhO)Na_n^+$ is apparently complete, and at $n > 20$ the degree of ionization of the associates decreases, which results in their certain coarsening (Table 3). This is favored by the fact that the fraction of counterions (OH^- ions) bound to the micelle surface increases, and the micelle charge and electrostatic repulsion forces between the head groups of the amphiphilic substance on the micelle surface decrease [11–13].

Thus, the role of alkali in our system consists in that initially it acts as a component forming an ionic surfactant, $[Q(4\text{-}C_8H_{17}PhO)Na_n^+OH^-]$, and then, as an electrolyte.

The possibility of such a mechanism of structural rearrangements is confirmed by the following reasonings. If aggregates were built exclusively of 4-C_8H_{17}·PhONa molecules, then the charge of the dispersed phase would be either negative or neutral owing to blocking of the negative charge of the phenoxyl oxygen by the sodium ion in the ion-pair associate. If ag-

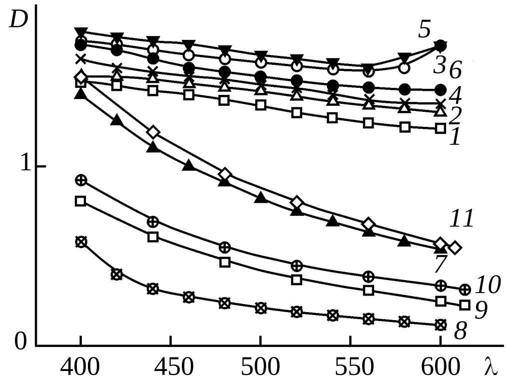


Fig. 4. Optical density *D* of the system 4-C_8H_{17}PhOH–NaOH–H_2O as a function of the wavelength λ (nm). *n*: (*1*) 1, (*2*) 2, (*3*) 3, (*4*) 4, (*5*) 5, (*6*) 6, (*7*) 16, (*8*) 30, (*9*) 40, (*10*) 50, and (*11*) 60.

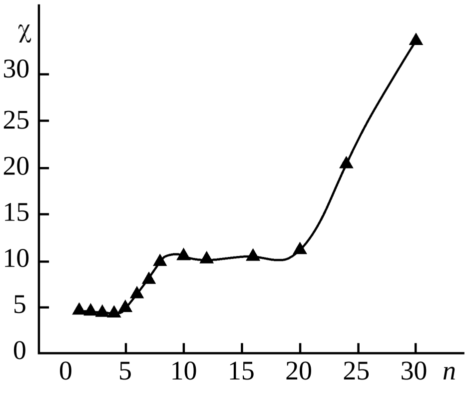


Fig. 5. Specific electrical conductivity χ (Ω^{-1} cm^{-1}) as a function of *n* at C_{pOP} 0.005 M (40°C).

gregates were built exclusively of $Q(4\text{-}C_8H_{17}PhO)Na_2^+$ cations, with a counterion layer of hydroxide ions, then it would be difficult to explain the decrease in the size *R* and increase in the electrophoretic mobility of the agregates with increasing concentration of alkali in the range $8 < n < 20$.

Thus, our study revealed formation in the system $4\text{-}C_8H_{17}PhOH$–NaOH–water of mixed associates and of cationic aggregates enriched in sodium ions in the associated state. We also found that the substrate decomposes by the pathway of ester interchange or base hydrolysis, depending on the ratio *n* in the system $4\text{-}C_8H_{17}PhOH$–NaOH–water. Associates exhibit different catalytic activities in decomposition of 4-nitrophenyl ethyl ethylphosphonate **I**.

EXPERIMENTAL

The UV spectra were recorded on a Specord UV-Vis spectrophotometer.

The ^{31}P NMR spectra were taken on a Bruker CXP-100 spectrometer at 36.47 MHz.

The substrate, 4-nitrophenyl ethyl ethylphosphonate **I**, was prepared as described in [14]. 4-Octylphenol (pure grade, Reakhim) was double-distilled in a vacuum, bp 92–93°C (4×10^{-2} mm), mp 44 – 45°C (in agreement with published data). To prepare solutions, an appropriate amount of 4-octylphenol was weighed in a volumetric flask, and a titrated NaOH solution in the amount corresponding to the required ratio NaOH : phenol was added. The mixture was brought to the mark with double-distilled deionized water. The solutions were thoroughly stirred and kept at 40°C for 30 days. The surface tension was determined with a Du Nouy tensimeter by the ring detachment method. Electrophoretic studies of the system $4\text{-}C_8H_{17}PhOH$–NaOH–water were performed by the microelectrophoretic method on a Parmoquant-2 automatic measuring microscope for adequate measurement of the electrophoretic mobility of microparticles. The electric field intensity in the cell was varied in the range $(2.93–3.11) \times 10^{-3}$ V m^{-1}. The phoresis current was 1 mA, and the temperature, 298 ± 0.15 K. The measurement error was 1.5%.

The characteristic particle size was calculated in the Rayleigh–Debye approximation [10]. Its advantage is that it is applicable to particles of any shape with the size comparable with the radiation wavelength.

The kinetics of nucleophilic substitution in **I** was monitored spectrophotometrically, by the growth of the absorption band of the reaction product, 4-nitrophenolate anion, at λ 400 nm.

The reaction rate constants were determined under pseudomonomolecular conditions at a large (no less than tenfold) excess of the nucleophile from the first-order relationship

$$-\log (D_t - D_1) = 0.434k_{\text{obs}} + \text{const},$$

where D_t an D_1 are the optical densities at time *t* and after reaction completion, respectively.

The pseudophase model equation was solved by the least-squares method. Only the constants for which the correlation coefficient was 0.99 were included.

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