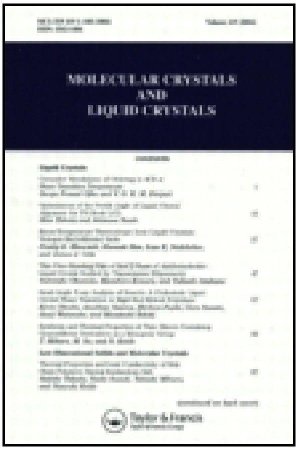

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Colloidal Associates in the P-Octylphenol/NaOH / Water System and their Catalytic Properties at the Phosphorus Acid Decomposition

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Colloidal Associates in the P-Octylphenol / NaOH / Water System and their Catalytic Properties at the Phosphorus Acid Decomposition

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Using the tensiometric, potentiometric and conductivity methods we studied the association processes in the p-Octylphenol-NaOH-water system. We have used the spectrophotometric method and investigated the kinetic of decomposition of phosphorus acid esters in this system. We observed nonlinear reaction rate acceleration at the addition alkali. It may be explained in terms of increasing the positive charge of associates. This fact was confirmed by electroforetical experiments.

Keywords: supramolecular associates; p-octylphenol; phosphorus acid esters; kinetic

INTRODUCTION

It is known, that simple phenols, polyphenols, and their derivatives, including the long chain phenols very spread in plant and animal worlds and is secondary metabolites [1]. The long chain phenols also applied as extracting agents for alkali metals. The mechanism of extraction may have ion exchange and micellar nature [2].

The using the associative phenomena for regulation the rate and path of chemical reaction gave the nice results in the nucleophilic substitution reactions at tetracoordinated phosphorus atom [3]. The mixed micelles, formed by longchain amines and longchain ammonium salt are very effective in the catalysis of phosphorus acid esters (PAE) decomposition, because they have the reactionary nucleophile (NH_2-group). This lead to growth rate of the reaction so far as the center of the reaction transforms from water to micelle and reagents concentrate in micellar phase [4].

We believe that it is very interesting to investigate the selfassociation of p-octylphenol in p-octylphenol-NaOH-water system (**I**) and its influence on the decomposition PAE, for example O-p-nitrophenol-O-ethylethylphosphonate (**S**).

EXPERIMENTAL

O-p-Nitrophenyl-O-ethylethylphosphonate (**S**) was synthesized according to the method given in [5]. P-Octylphenol (POP) was twice distilled in the vacuum (bp=92-93 ^{0}C 0.04 mm, mp 44-45 ^{0}C). Aqueous solutions of POP and NaOH were prepared by weighing of needing amount of this components, so as the ratio $1/n = C_{POP}/C_{NaOH}$ 1:1, 1:2, 1:3, 1:4, 1:8, 1:16, 1:40, 1:50, 1:60 was kept. The phase equilibrium in these systems was achieved for two weeks.

The reactions was initiated by adding of solution **S** in CH_3CN in quartz cuvettes, with appropriate solution of **I** system. The end concentration was $4{\cdot}10^{-4}$M. The kinetic experiments involved the tracing of changes in the intensity of the reaction product (p-nitrophenolate anion) absorption at 25000 cm^{-1} with time on the spectrophotometer «Specol» at the 40^{0}C. The quartz cuvette were equipped with temperature control to 0.5 ^{0}C. The rate constant (k_{obs}, c^{-1}) we calculated from the kinetic equation for the first order reaction: $\log(D_t\text{-}D_\infty)=0.434k_{obs}\cdot t$ + const, because the reaction was under pseudo molecular conditions.

The values of surface tension was defined by the tensiometer Du Nouy, a conduction was defined by the «Conductivity meter», type CDM 2d. Electrophoretic studies of the POP/NaOH/water system carried out with the PARMOQUNT-2 automatic measuring microscope for objective measuring the electrophoretic mobility of microparticles.

The intensity of the electric field within a cell was varied in the range from $2.93 \cdot 10^{-3}$ to $3.11 \cdot 10^{-3}$ V/M. Electrophoresis current was 1 mA. Temperature was kept at 25.0 ± 0.1 ^{0}C. The measurement error was within 1.5 %.

RESULTS AND DISCUSSION

The reactions of PAE with strong, but weakly based nucleophile phenolate anions easy run in water media under low values of pH [6]. But we don't know anything about the processes with long chain phenols in alkali media. Originality of this compounds behavior consist in there ability for forming a multiple type of associates with several centers and different types of bond (H-bond, cation-π) [7].

The macrophase separation is observed in the POP/water system. POP cannot be dispersed in water (HLB for POP approaches zero on the Griffin-Davies scale). The alkali adding results in the POP solubility rise. The microphase separation is observed at an equivalent components ratio and alkali excess in the POP/NaOH/water system (a turbid solutions are formed). Rayleigh light scattering is well exhibited in the wavelength range from 400 to 600 nm (Figure 1).

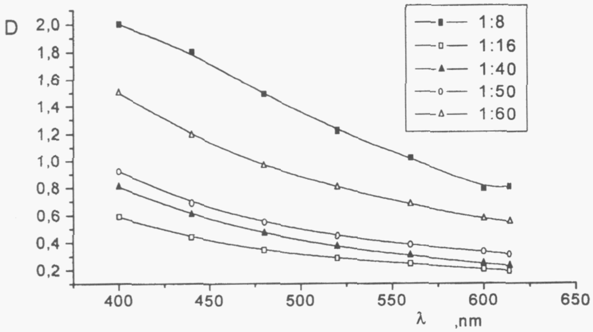


FIGURE. 1. The optical density (D) versus λ for the systems POP/NaOH/water with different *n*, $C_{POP}=5 \cdot 10^{-3}$, $t=40^0$C, l=1cm.

We have shown the formation of micelles in the **I** system by some independent methods. We studied the alteration of surface tension with the increasing POP concentration and constant *n*. Also we defined the dependence of the conductivity and pH on C_{POP} ($\chi = f\,(C_{POP})$ pH $= f\,(C_{POP})$).

Figure 2 shows the dependence of volume and surface properties of the system on POP concentration at the molar ratio n=3. The values of critical micelle formation concentration (CMC) were defined as the points of break on the curves.

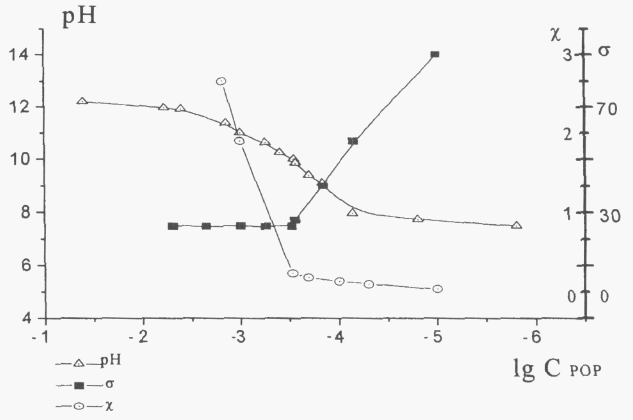


FIGURE 2. The alteration of surface tension (σ, din/cm), conductivity (χ, om^{-1}) and pH with the concentration of POP, n=3

TABLE 1. The CMC values defined by different methods in the POP/NaOH/water system, 40^0C.

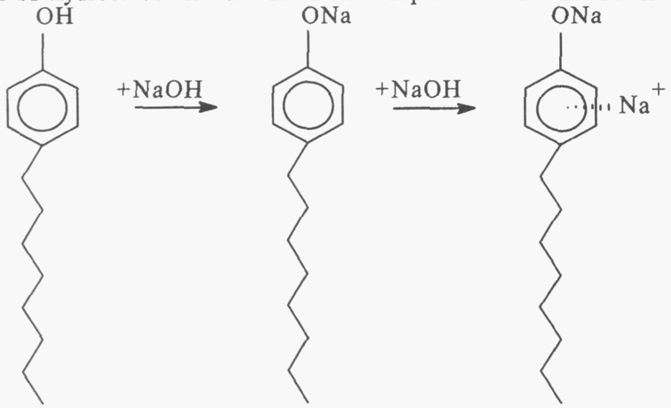
1/*n*	CMC, M		1/*n*	CMC, M	
	σ=f(lgC_{POP})	pH=f(lgC_{POP})		σ=f(lgC_{POP})	pH=f(lgC_{POP})
1:1	1.82 10^{-3}	1.25 10^{-3}	1:4	3.46 10^{-4}	
1:2	2.48 10^{-4}	3.19 10^{-4}	1:8		
1:3	3.16 10^{-4}	3.16 10^{-4}	1:16	3.98 10^{-4}	1.0 10^{-4}

They are represented in the Table 1. Values of CMC determined by independent methods are close. It is interesting to note that CMC for system with n=1 the most high. This may be explained by the mixed associates formation. These micelles consist of p-octylphenol (POP) and sodium p-octylphenolate .

Below are given the characteristic sizes (radius, *R*, nm) of the disperse phase particles calculated from spectrophotometric data (Figure 1) within the Rayleigh-Debye approximation (the condition of «optically soft» particles) [8,9]:

n	8	16	40	50	60
R, nm	266.3	126.5	102.2	133.2	247.8

It is evident that particles are relatively large in size. The characteristic size of the particles is as great as 100-fold length of the POP hydrocarbon radical. The *R* vs. *n* dependence has an extremum.



POP **POPNa** **QPOPNa$^+$**

The particle dimensions pass minimum at 40-fold alkali excess. Besides, electrophoretic studies have shown that the colloid particles are positively charged. The particle charge rises when the *n* ratio is increased from 8 to 16. Obviously, the formation of the colloid system as the NaOH concentration increases is due to the formation of micelle-like aggregates. The last process would be possible if POP HLB increases.

It is known that the increasing alkali (e.g. NaOH) concentration in the POP/H_2O system is followed by the formation of common sodium p-octylphenolate (POPNa) as the result of exchange reaction. At the same time the surfactant cation POPNa$^+$ formed due to the cation-π interaction [7]. We suggest that such a quasi-sodium p-octylphenolate

($QPOPNa^+$) can be stable in water predominantly in an associated micelle-like state. If only POPNa molecules served as a structural material for the micelle-like aggregates, the formation of positively charged particles would be difficult to explain. If the aggregates were made up of only $QPOPNa^+$ cations and a layer of hydroxyl counterions, it would be difficult to understand the increase in the aggregate size and surface charge as NaOH concentration rises in the n range from 8 to 40. It is known that electrolyte added decreases the ionization degree of the surfactant electrolyte in true solution as well as in a micellar state. The fraction of counterions bound to the surface of micelles rises and the micelle charge falls.

The forces of electrostatic repulsion between surfactant head groups on the micelle surface weaken and this results in the micelle enlargement [10,11].

It is also known that the aggregation numbers and the dimensions are greater for the mixed ionic-nonionic micelles than those for unmixed ionic micelles. For the sake of simplicity it is a reasonable assumption that in the system under study real micelle-like aggregates differ little in properties from classic micelles. Relying on the data above it may be suggested that under the excess of NaOH ($n>>1$) in the POP/NaOH/H_2O system firstly large slightly charged mixed cationic-nonionic micelles are formed consisting of POPNa and $QPOPNa^+$. OH^- groups play a role of counterions (Figure 3a). As NaOH concentration rises (n increases from 6 to 40) all the POPNa in the micelles is gradually converted into $QPOPNa^+$, and micelles become unmixed and more cation-active (Figure 3, b). Since for mixed ionic-nonionic micelles the higher aggregation numbers than those for unmixed ionic micelles are typical, the particle dimensions must decrease and the surface charge must rise with increased alkali concentration.

This is in agreement with the experimental data: as NaOH is added, in the n range from 6 to 40 the characteristic size falls whereas the electrophoretic mobility and, accordingly, the particle surface charge rises. Thus, with $1<n<40$ the micelle solubilizes metal ions on the surface. The effect of further alkali concentration increase ($n>40$) is similar to the influence of rising ionic strength in the micellar solution of an ionogenic surfactant. NaOH introduction leads to the increase in the particle characteristic size just as the electrolyte introduction results in micelle enlargement (Figure 3, c).

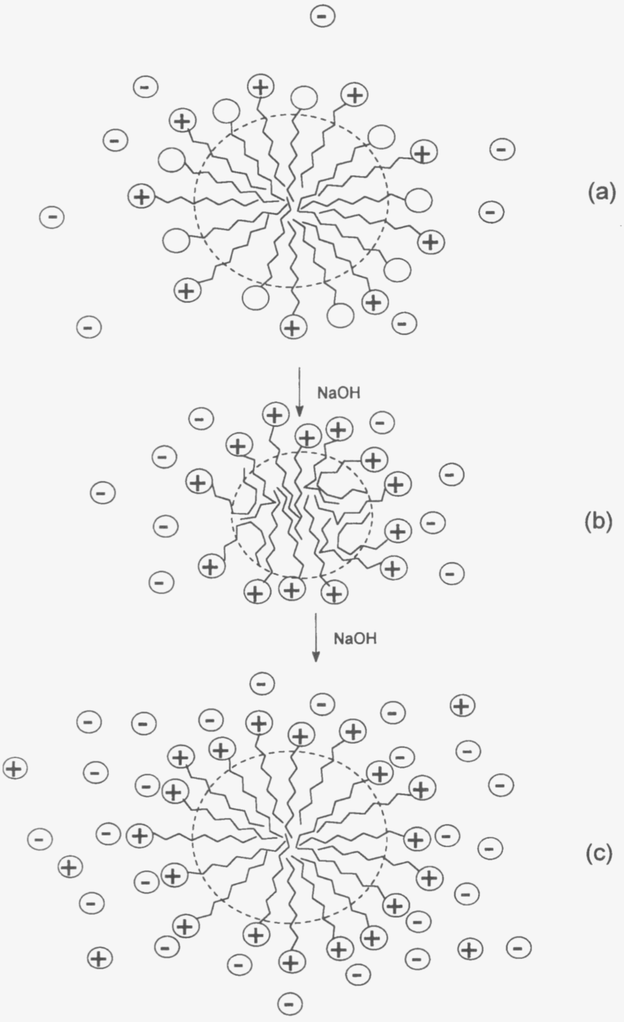
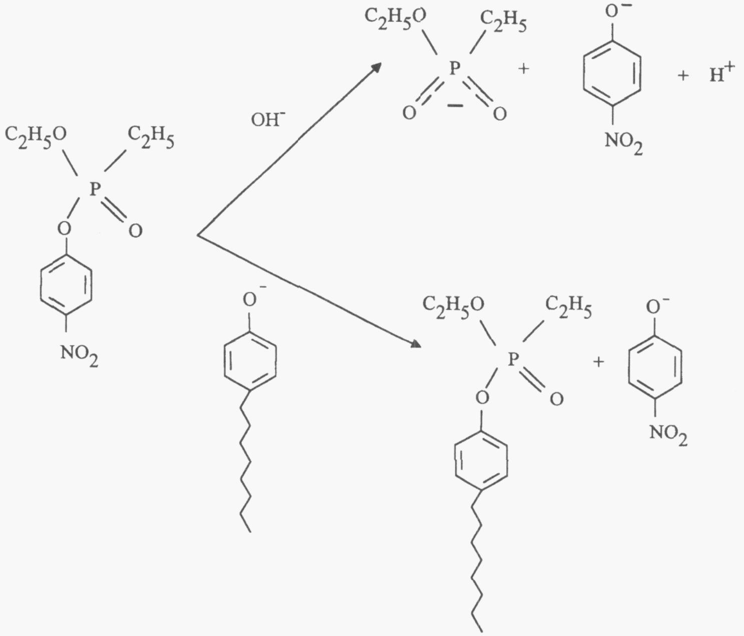


FIGURE 3. Schematic presentation of micellar transitions: a – ionic-nonionic micelle; b-ionic micelle at low ionic strength; c-ionic micelle at high ionic strength

These conclusions were confirmed by the kinetics experiments. We studied the decomposition of O-p-nitrophenyl-O-ethylethylphosphonate in the system POP/NaOH/water. There may be two processes (hydrolysis and phenolysis):



SCHEME 1. The paths of the substrate's decomposition in I system.

It is known that the reaction of PAE with nucleophiles (POP, OH^-) proceeds as bimolecular nucleophilic substitution. There are the linear dependencies between of the observed rate constants (k_{obs}) and concentration of nucleophiles. The catalytic constants linear dependent from pK_a of phenols too. The control process is the isolation of n-nitrophenolate anion (PNPA). We studied the kinetic of loss PNPA for **S** in the **I** system at different *n*.

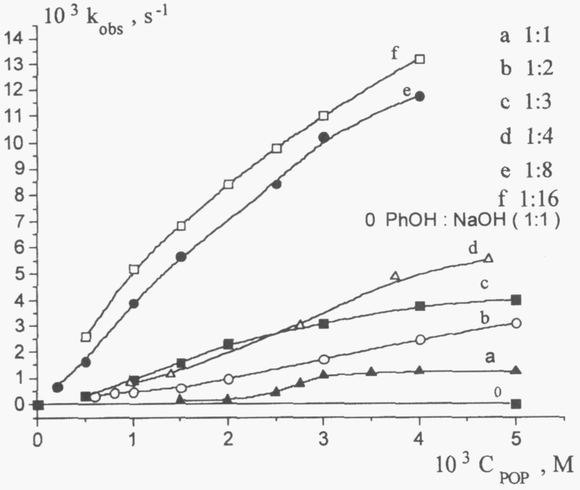


FIGURE 4. The alteration of observed rate constants with concentration of POP at different *n*.

On the Figure 4 it is shown the dependencies of k_{obs} from C_{POP}. One can see, that this dependencies are nonlinear and the velocity of the decomposition give rise with *n* increasing. Reactions are both in volume and in associate. In this case we can use the pseudophase model for micellar catalysis and the equation, proposed by authors [12].

$$k_{obs} = \frac{k_i + k_m K_S C}{1 + K_S C}$$

We calculated the k_m and K_S values and represented there in the Table 2.

The alteration of rate of the reaction in the associate with POP concentration is nonlinear too (see Table 2). At the beginning the rate of the decomposition of **S** is increasing, and then it achieves the limiting value.

TABLE 2. The kinetic parameters of micelle catalyzed reactions decomposition of O-p-nitrophenyl-O-ethylethylphosphonate in POP/NaOH/water system at different *n*. 40 ^{0}C.

C_{POP}/C_{NaOH}	10^4CMC M	$10^3 k_m$, s^{-1}	K_S, M^{-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

In the Figure 6 we may see the alteration of the conductivity (χ) and observed rate constants for systems with different *n* and C_{POP} = 0.005 M. There are two plateaus on the first dependents (*n*=2÷6 and *n*=8÷20).

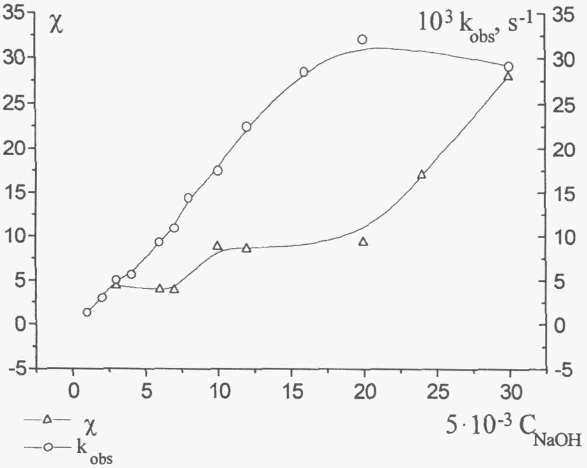


FIGURE 6. The dependencies of χ and k_{obs} from *n* at the C_{POP}=0.005M

This confirms the assumption that there exist different kinds of associates. As it was shown above these associates are positively charged and have the quasi phenolate group as head group. In this case the associates became the cationactive and there arise the opportunity of acceleration of **S** alkali hydrolysis [3]. It is known that the surfactant anions are an inhibitors of alkali hydrolysis in consequence of electrostatic repulsion of hydroxide ion and surfactant - anion. It may be so if in system **I** would be form only the p-octylphenolate-anions. But the acceleration of rate of **S** decomposition is in agreement with the conception of $QPOPNa^+$-ion. The $QPOPNa^+$-ion has the OH^- reactionary counterion. The increasing concentration of NaOH leads to the increasing of the concentration of the activated complex and the acceleration of **S** hydrolysis.

Thus the conductivity, electroforetical and kinetic data give evidence of formation of quasi sodium p-octylphenolate ion ($QPOPNa^+$) in POP/NaOH/water system. This is the explanation of acceleration rate of the **S** decomposition there.

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