HIGHLY ORGANIZED
CATALYTIC SYSTEMS

Catalysis of O-(para-Nitrophenyl) O,O-Dimethyl Thiophosphate Decomposition by Chromonic Mesophases Based on Polymerized Ionic Amphiphiles

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Abstract—The formation of a nematic chromonic mesophase in aqueous solutions of quaternized poly(ethylene imine) has been found using polythermal polarization microscopy. The reaction kinetics of O-(para-nitrophenyl) O,O-dimethyl thiophosphate hydrolysis has been studied by spectrophotometry, and a comparative analysis of the effects of lyotropic liquid crystals constructed as hexagonal and chromonic mesophases on this kinetics has been performed. It has been found that the hydrolysis of the substrate in a nematic chromonic mesophase is accelerated due to the concentration of the reactants.

It is well known that micellar effects on the rates and directions of various chemical processes are due to a decrease in permittivity and an increase in reactant concentrations in micelles (as compared to those of a bulk phase), as well as the stabilization or destabilization of the transition state [1–3]. Analogous effects can also be observed in a lyotropic liquid-crystal matrix because the surface structures of lyotropic liquid-crystal matrices and micelles are similar [4, 5]. Lyotropic liquid-crystal matrices are ordered structures; for this reason, the following factors should be taken into account: the correspondence between the structure of a liquid-crystal environment and the size and geometry of substrate molecules; the anisotropic character of molecular mobility, diffusion, and intermolecular interactions; selective solvation in structurally different microregions of a liquid-crystal system [6, 7]. It is well known that lyotropic liquid-crystal matrices are more adequate biomimetic models than micelles because vitally important biological structures are constructed similarly to lyotropic liquid-crystal matrices [8].

A lyotropic liquid-crystal matrix is a medium that can either catalyze or inhibit the hydrolysis of tetracoordinated-phosphor acid esters, depending on the mode of supramolecular organization (lamellar, hexagonal, nematic, etc.) and the presence or absence of nucleophilic components [6, 9, 10].
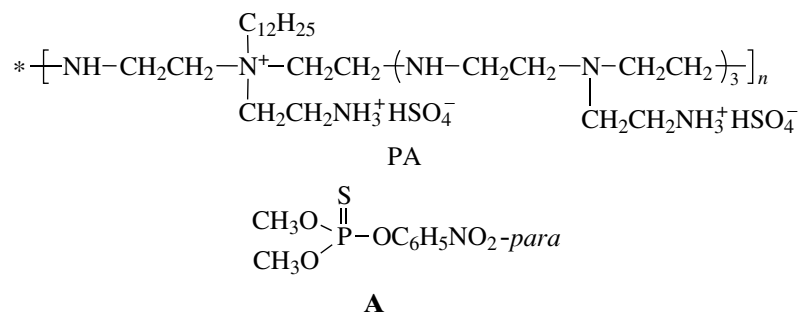
Previously [9–11], it was found that, in the cetyldimethylethylammonium bromide (CDEAB)–sodium hydroxide–water system (**I**), micelles were formed when a CDEAB concentration of 5.2×10^{-4} mol/l

was reached, a monotropic hexagonal mesophase was formed at $C_{\mathrm{CDEAB}} = 0.1$ mol/l, and a hexagonal mesophase (E phase) was formed at $C_{\mathrm{CDEAB}} = 0.4$ mol/l (to 45°C). This hexagonal mesophase was composed of the hexagonally packed cylinders of amphiphilic CDEAB molecules arranged at a distance of 135 Å. This follows from the appearance of an angular texture in the polarization micrograph and a maximum in the curve of the intensity of the neutron scattering vector plotted against the value of the scattering vector [9, 10]. The rate of hydrolysis of O-(para-nitrophenyl) O,O-dimethyl thiophosphate (**A**) on the formation of micelles in system **I** increased by a factor of 6, as compared with alkaline hydrolysis, whereas it decreased by a factor of 3 in a hexagonal mesophase [9]. Thus, the kinetics of alkaline hydrolysis of this substrate is sensitive to order changes in the system in the course of the micelle $\longrightarrow$ E phase transition.

Here, we report the results of a study of the structural effect of a system composed of a polymerized amphiphile (PA), sodium hydroxide, and water (**II**) on the rate of hydrolysis of compound **A**.

EXPERIMENTAL

Materials. The polymerized amphiphile was synthesized in accordance with a published procedure [12].

$$* \!-\!\!\left[\!\!-\!\mathrm{NH\!-\!CH_2CH_2\!-\!N^+\!-\!CH_2CH_2\!-\!\!\left(\!NH\!-\!CH_2CH_2\!-\!N\!-\!CH_2CH_2\!\right)_{\!\overline{3}}\!\right]_n}$$

with side groups:
$\mathrm{C_{12}H_{25}}$ on the $\mathrm{N^+}$
$\mathrm{CH_2CH_2NH_3^+\,HSO_4^-}$ on the $\mathrm{N^+}$
$\mathrm{CH_2CH_2NH_3^+\,HSO_4^-}$ on the N

PA

$$\begin{array}{c}\mathrm{CH_3O}\\\\\mathrm{CH_3O}\end{array}\!\!\!\underset{}{\overset{\displaystyle S}{\underset{\displaystyle \|}{P}}}\!\!\!-\mathrm{OC_6H_5NO_2}\text{-}\textit{para}$$

A

O-(*para*-Nitrophenyl) *O,O*-dimethyl thiophosphate from Aldrich (USA, Germany) was used in this study. Deionized water was used for preparing solutions.

Methods. Nematic mesophase samples were prepared by sonicating aqueous PA solutions in a Sonorex RX 52 H ultrasonic bath (Bandelin) at 30°C until complete dissolution followed by the addition of NaOH.

To determine the type of a mesophase, the solution was placed between two mica plates, which were glued to prevent water evaporation, and analyzed under a Laborlux 12 POLS polarization microscope with a Mettler FP 82 HT hot stage. The identification of mesophase textures was performed in accordance with a published procedure [13].

The rate of hydrolysis was determined by spectrophotometry on a Perkin-Elmer Lambda UV–VIS spectrophotometer in thermostated quartz cells with an optical path length of 0.5 cm at 30°C. The reaction was monitored by measuring the increasing intensity of the absorption band due to the hydrolysis product (*para*-nitrophenolate anion) at 400 nm.

The reaction was initiated by the addition of a substrate solution in acetonitrile with an initial concentration of 2×10^{-4} mol/l to a nematic solution. The reaction was conducted under pseudo-unimolecular conditions with a considerable excess of PA at pH 12.

The pseudo-first-order reaction rate constant was calculated using the equation

$$\ln(A_1 - A_t) = -k_{\mathrm{obs}} + \mathrm{const},$$

where A_1 and A_t are the absorbances at the end of reaction and at a time point t, respectively.

RESULTS AND DISCUSSION

At low concentrations, the dodecylammonium compounds form micelles in aqueous solutions, whereas the poly(ethylene imines) form globules. Mixed systems containing poly(ethylene imines) and cetylthrimethylammonium bromide (CTAB) form polymer–colloid complexes. Both of these systems facilitate the catalytic hydrolysis of **A** [14]. It was of interest to monitor changes in mesogenic and catalytic properties in the presence of hydrocarbon and poly(ethylene imine) fragments in a single compound. For this purpose, we synthesized a PA sample.

The micrograph of the starting PA powder in polarized light was a dark field, which suggested the absence of optical anisotropy and crystal structure. The latter
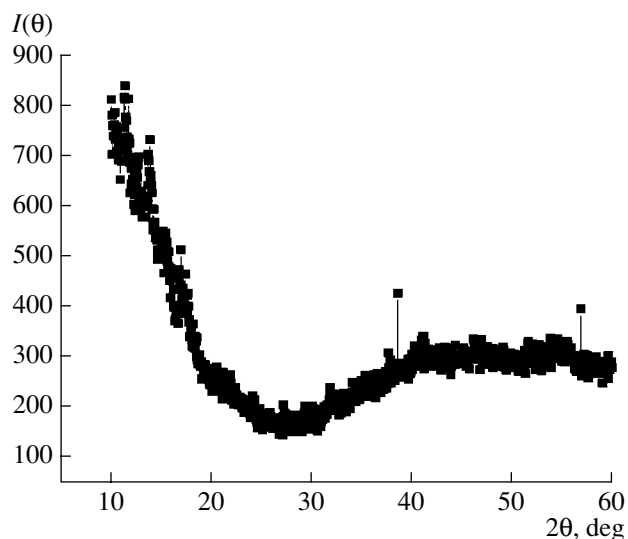

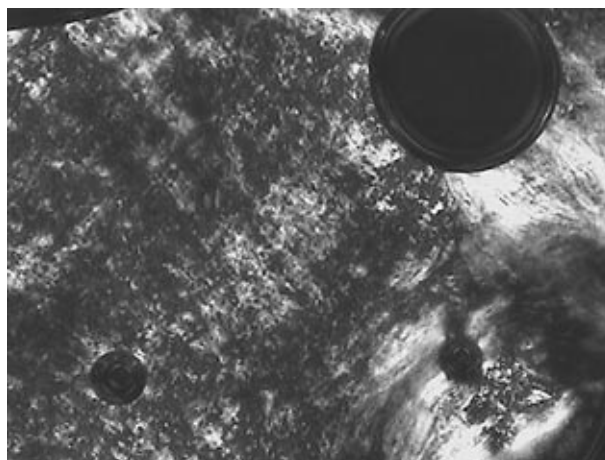**Fig. 1.** Diffraction patterns of PA powder.

Fig. 2. Micrograph of the grainy texture of the M phase in the PA–H$_2$O system after keeping between glued mica plates for three days. Crossed nicols.
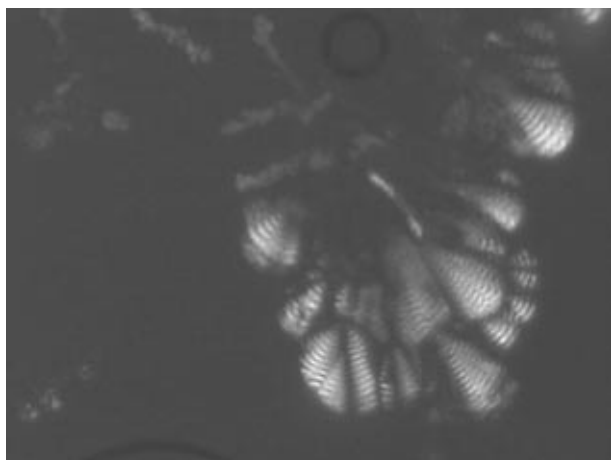
Fig. 3. Micrograph of the PA–NaOH–H$_2$O system (C_{PA} = 0.0332 g/10 ml). Crossed nicols.

Fig. 4. Changes in the pseudo-unimolecular constant with increasing PA concentration.

was supported by the absence of significant reflections from the diffraction pattern, which is shown in Fig. 1.

The addition of a small amount of water resulted in the appearance of a grainy texture in the polarization micrograph (Fig. 2). This grainy texture was analogous to that reported previously [13]; this fact suggests the formation of a chromonic mesophase (M phase), which remained unchanged on heating to 90°C followed by cooling. It is well known that the M phase results from the stacking interaction of molecules with each other
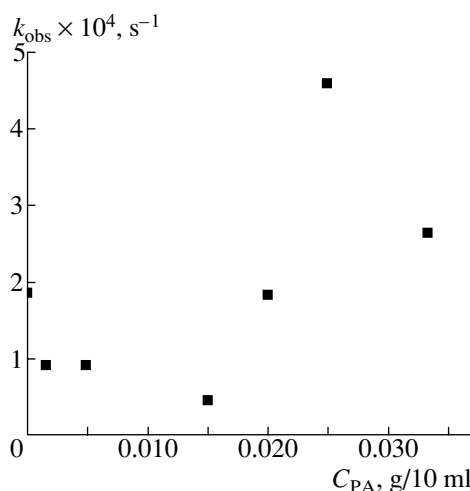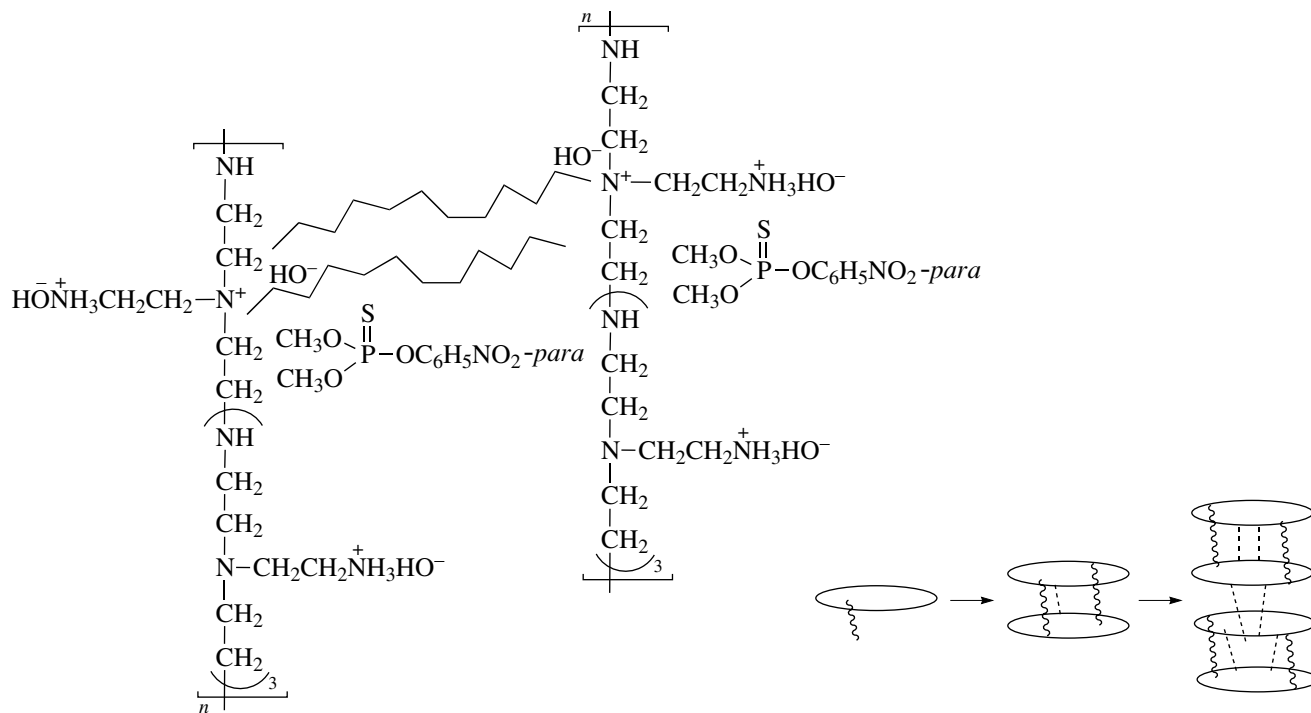
and the formation of columns because of this. In our case, the association of PA molecules is possible because of the hydrophobic interactions of dodecyl chains and the formation of hydrogen bonds. The scheme illustrates the possible stacking of PA molecules in an alkaline medium.

The critical micelle concentration (CMC) cannot be determined in these systems because an optimum column length in terms of thermodynamics does not exist in the course of column formation [13]. In dilute solu-
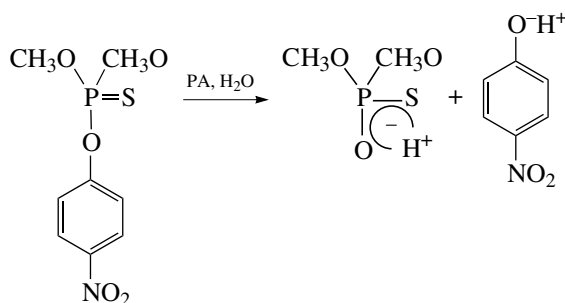

Scheme.

tions, a chromonic nematic mesophase and an isotropic phase coexist. Figure 3 shows the M-ribbons textures for the PA–NaOH–H$_2$O system (**II**) at $C_{PA} = 0.0332$ g/10 ml, which were obtained after keeping between glued mica plates for 10 days.

Thus, system **II**, which was used as a reaction medium, was structured as the M phase.

We chose O-(*para*-nitrophenyl) O,O-dimethyl thiophosphate as a model substrate because of its interesting structure with two ambident reaction sites: the phosphorus and oxygen atoms. It is also a readily polarizable substrate; therefore, its conformation essentially depends on the microenvironment in a lyotropic liquid-crystal matrix, that is, on the site of localization.

In aqueous alkaline solutions and alkaline micellar solutions (for example, the CTAB–NaOH–H$_2$O system), the phosphorus atom was attacked with 100% probability. In the systems containing components with unprotonated nitrogen atoms, for example, decylammonium chloride–decylamine–water, the carbon atom was attacked with 100% probability in micellar and lamellar mesophases (**A** dealkylation) [15]. In system **II**, the release of *para*-nitrophenol in an amount equivalent to that of the substrate was observed and the liberation of the *para*-nitrophenyl methyl thiophosphate anion was not observed; this is indicative of the hydrolysis reaction

The bimolecular rate constant of hydrolysis of substrate **A** is $k_2 = 3.35 \times 10^{-3}$ mol^{-1} s^{-1}, and $k_{obs} = 1.87 \times 10^{-4}$ s^{-1} ($k_{obs} = k_2 C_{OH}$) at pH 12.75. In system **II**, the apparent pseudo-unimolecular reaction rate constant as a function of PA concentration nonlinearly increased analogously to that in micelle-catalyzed reactions and its maximum value was higher than the rate constant of the alkaline hydrolysis of compound **A** by a factor of 2 (Fig. 4).

Note that the addition of an alkali to the PA–H$_2$O system resulted in the exchange of the HSO_4^- acid residue for hydroxide ions, which are a reactant concentrated at the ammonium group. Substrate **A** is sparingly soluble in water, readily soluble in methanol, and limitedly soluble in heptane. It exhibits an absorption band at 267, 272, or 276 nm in the UV spectrum in heptane, methanol, or M mesophase, respectively. This allowed

us to assume that substrate **A** primarily penetrated into the polar region of the associate, where the hydroxide ion also occurred. That is, the concentration of reactants in the associate can be responsible for the acceleration of the hydrolysis of compound **A**.

As mentioned above, the rate of hydrolysis of compound **A** in a hexagonal mesophase of the CDEAB–NaOH–H$_2$O system decreased by a factor of 3 [9], whereas this rate increased by a factor of 2 in a chromonic mesophase. That is, the column organization mode has a considerable effect on the rate of hydrolysis of compound **A**.

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