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Mahmut Acimisl[a]
[a] Ondokuz Mayis University, Faculty of Science, Department of Chemistry, Kurupelit-Samsun, Turkey

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PRELIMINARY COMMUNICATIONS

Micellar phases formed by a solution of *l*-serine hydrochloride decylester and orthophosphoric acid

by MAHMUT ACIMIŞ
Ondokuz Mayis University, Faculty of Science, Department of Chemistry, Kurupelit-Samsun, Turkey

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Polarizing microscope studies showed that the isotropic solution composed of *l*-serine hydrochloride decylester and orthophosphoric acid forms micellar cholesteric, nematic and lamellar phases, whereas the solution of the optically inactive ester gives micellar nematic and lamellar phases. The phase transitions were tentatively assigned as the result of two concurrent reactions at which orthophosphoserine hydrochloride decylester and orthophosphoric acid monodecylester are produced. Dilution of the optically active and the optically inactive lamellar phases with water gave a cholesteric and a nematic phase, respectively. The nematic director is aligned perpendicular to the glass plate, whereas that of the cholesteric phase is aligned parallel.

From the current work in our laboratory it is known that aqueous orthophosphoric acid, H_3PO_4, can be used as a solvent in forming micellar phases [1]. These studies were undertaken because some important biological molecules in living systems contain a phosphate group. Though the phosphate group is found in biological molecules, our immediate aim is to investigate the effect of the free H_3PO_4 in the aqueous layer of the micellar phases that are regarded as a crude model for biological membranes [2]. The effect of having H_3PO_4 in the aqueous layer on the phase structure will mainly be determined by the interaction of orthophosphoric acid molecules with the headgroups of the amphiphiles.

In this report our interest is focused on the interaction of H_3PO_4 molecules with the hydroxy group attached to the polar head of an amphiphile. To demonstrate clearly the effect provoked by H_3PO_4, the optically active amphiphile, *l*-serine hydrochloride decylester, *l*-SDE, and its racemic mixture, *dl*-SDE, have been chosen. These amphiphiles were synthesized and purified according to the procedure in [3]. The physical constants of these compounds were determined to be *dl*-SDE m.p. = 67–68°C; *l*-SDE m.p. = 88–89°C and $[\alpha]_{589}^{20} = -9{\cdot}7$ (ln HCl, $c = 4{\cdot}67$).

When a definite amount of *l*-SDE or *dl*-SDE was dissolved in an appropriate amount of 43 wt % H_3PO_4 (aqueous solution) in sealed tubes, a homogeneous optically isotropic solution was formed initially. After approximately 1 day, visual inspection through crossed polars showed that this solution had become birefringent. At the beginning, the birefringent phase was fluid, but with the passage of time (*c.* 1 day) the anisotropic and fluid phase became more viscous.

To understand the nature of this phenomenon, a solution of 56·67 wt % *l*-SDE in H_3PO_4 was studied under a polarizing microscope as soon as the isotropic solution was birefringent. The texture observed immediately after preparing the microscope slide changed continuously, and after about 15 min a cholesteric texture of low twist

appeared, as shown in figure 1. This cholesteric texture also changed continuously and grew into a micellar nematic (cf. figure 2). After about 30 hours from the beginning, the nematic texture shown in figure 2 changed to a lamellar phase of mosaic texture (cf. figure 3). This mosaic texture disappeared with time, i.e. almost a total extinction occurred when viewed through crossed polarizers. Using the polarizing microscope as a conoscope, isogyres appeared. Inserting a sensitive tint plate into the light path, two yellow-orange quadrants in the fast direction and blue-green quadrants in the perpendicular direction were observed. These results indicate that the optic axis or director of the final lamellar phase aligns perpendicular to the surface of the microscope slide [4, 5].

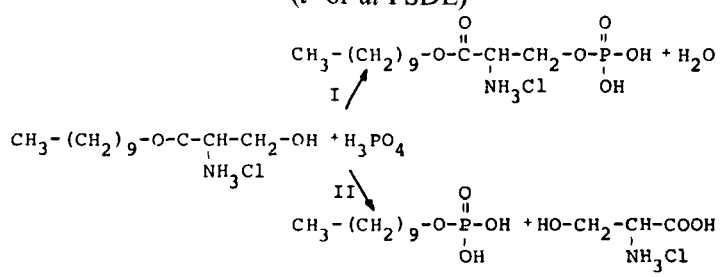
If the same experiment is repeated with a *dl*-SDE sample, about 10 min after preparing the microscope slide, a rod-like nematic texture is observed. As time proceeds, similar textures as in figures 2 and 3 are observed.

Samples of *l*-SDE and *dl*-SDE, contained in sealed test tubes, which reached the final lamellar phase were diluted with water. If the dilution was as much as half of the total weight of the phase, then for the *l*-SDE sample a micellar cholesteric phase was obtained, but for the *dl*-SDE sample a micellar nematic phase resulted. This nematic texture also disappeared in about 1 hour, and conoscopic observation gave the same results as determined for the aligned lamellar phase. Since the nematic director aligns perpendicular to the microscope slide surface, the helix axis of the derived cholesteric phase has to be aligned parallel to the glass plate [3, 6].

As the transitions from the micellar isotropic state to the liquid-crystalline state occur at constant composition, a reaction between SDE and H_3PO_4 must have taken place. In order to understand the nature of this reaction a paper chromatogram for amino acids was developed. Using the typical eluent, water-*n*-butanol-acetic acid (5 : 4 : 1), serine hydrochloride, SDE and the reaction product from the final lamellar phase were compared; the amino acids were located on the paper with ninhydrin solution. The reaction product from the final lamellar phase gave two equally coloured spots. The lowe one had an R_f value of 0·2 equal to that for serine hydrochloride. The higher one, however, had an R_f value of 0·8 and could not be matched with any R_f values observed on this chromatogram. The SDE also gave two spots. The lower one was very faint, indicating an unimportant impurity of non-reacted serine hydrochloride because it showed an R_f value of 0·2. The higher spot had an R_f value of 0·6, arising from SDE itself.

We have inferred tentatively from these chromatographic results that two reactions may be concurrent in the solution of SDE and H_3PO_4. Reaction (I), an esterification reaction between the hydroxy group in SDE and H_3PO_4, and the second (II), an acidolysis reaction, a replacement of an acid of an ester by a more nucleophilic one, may be formulated as:

Orthophosphoserine hydrochloride decylester
(*l*- or *dl*-PSDE)



Orthophosphoric acid decylester (PDE)

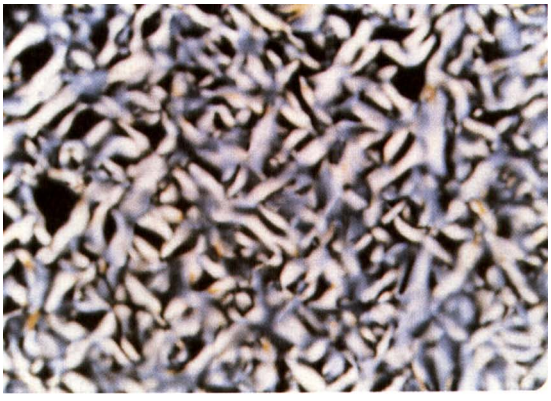


Figure 1.

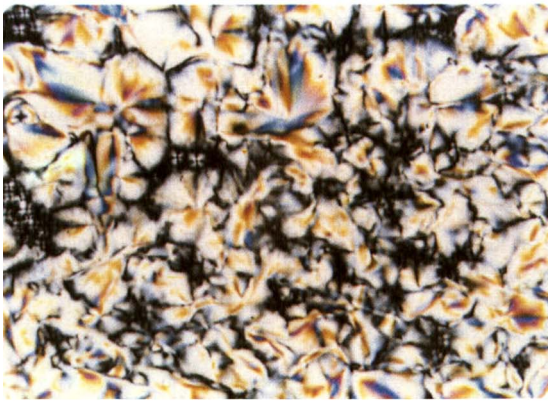


Figure 2.

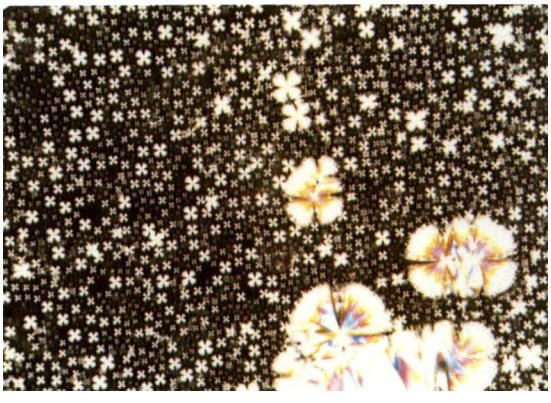


Figure 3.

Figure 1. The micellar cholesteric phase at 56·57 wt % in aqueous H_3PO_4 (43 wt %). The microscope slide was maintained at 32–35°C. Crossed polarizers, × 400.
Figure 2. The growth of the cholesteric into a nematic texture. Crossed polarizers, × 250.
Figure 3. The nearly complete change of the nematic into a lamellar mosaic texture. Crossed polarizers, × 250.

The products, PSDE, and PDE plus serine hydrochloride, formulated in reactions (I) and (II) would correspond to the paper chromatogram obtained for the reaction product of the final lamellar phase. The lower spot having resulted from serine hydrochloride would mean that reaction (II) occurs. Equivalently we could say that reaction (I) also occurs at the same time because the higher spot would match with the existence of PSDE.

It is then clear that as the products PSDE and PDE come to exist, a long-range orientational order, i.e. a liquid-crystalline state, is formed. This results probably because the motions of the bulky phosphate ions in water are now suppressed in general by the hydrophobic tails. In the starting isotropic solution of this given composition, however, the interactions of the head group, serine, with the bulky H_3PO_4–H_2O layer are obviously insufficient to create long-range orientational order, and so the solution is isotropic.

Some questions in respect to this communication obtain. These are: what is the exact effect of the content of H_3PO_4 on this reaction? What is the ratio of reaction (I) to reaction (II) in the final lamellar phase, and is it possible to obtain only reaction (I) by this method? These questions appear to us to be important for a thorough understanding of the system, SDE plus H_3PO_4, and are now under study.

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