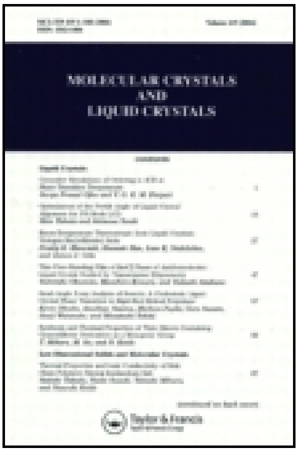

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MESOPHASES IN LONG CHAIN ALKOXY ALCOHOL/ORTHO-PHOSPHORIC ACID SYSTEMS

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Abstract Optical, DSC and X-ray studies show that $C_n H_{2n+1} O C_m H_{2m} OH$ (n=16; m=4; n =18 and 20, m= 2 and 3; n = 22, m=3) / aqueous $H_3 PO_4$ systems exhibit mesophases in the order middle - viscous isotropic - lamellar - gel. The low temperature gel displays characteristically the chevron pattern due to an undulation instability of bilayers; it is possibly caused by hydrocarbon chain elongation and stiffening.

INTRODUCTION

Aqueous orthophosphoric acid was first demonstrated by Acimis[1] as a possible solvent for generation of micellar cholesteric, nematic and lamellar phases in a chiral amphiphile. Subsequently, Marthandappa et al[2,3] reported thermotropic smectic phases S_A, S_D, S_B and S_E, in cetyl and stearyl alcohols, dissolved in nonaqueous H_3PO_4. Present studies on title systems involving some of the surfactants known for their water evaporation retardation property as monolayers,[4] reveal lyotropic structures derived by thermal rather than concentration changes. All the systems showed, over a wide composition range (10-50 wt %), a similar optical behaviour which we discuss in this paper with reference to the system eicosanoxy propanol, EP/ H_3PO_4.

EXPERIMENTAL

Purity of the amphiphiles, as determined by GLC, was better than 99%. AR grade H_3PO_4 of 88% concentration was used. The mixtures were usually homogenised by keeping at ~ 100 °C for a few hours prior to use. For optical studies, a Carl Zeiss microscope was used. The samples examined were thin layers between a slide and cover slip, with the cell edges open. Concentration gradients over the sample area resulted in transition temperature variations between the peripheral and central zones. The temperatures given generally correspond to the textures formed near the edges. For thermograms, a Perkin-Elmer instrument (DSC-7) was used. Low angle patterns were determined employing the image plate (Maresearch) detector and Cu K_α radiation.

RESULTS AND DISCUSSION

Optical Textures

A thin layer of EP dissolved in H_3PO_4, on cooling from the isotropic liquid phase at ~ 200 °C, develops, at ~ 180 °C, batonnets that gradually grow into fan-shaped objects (Figures 1a-c). The fans, usually with radial discontinuities (Figure 1c), melt at about 130 °C to result in an optically isotropic phase. No regular shape is displayed by the molten zones during the transition. The backs of the fans are marked by transition bars during melting (Figures 1d,e). Below 110 °C, spherulitic domains, homeotropic plates with birefringent borders, oily streaks and a variety of myelinic figures are observed (Figures 1f-i). Finally, at 65 °C a sharp transition ocuurs to a state showing the chevron or striped texture in the originally homeotropic areas (Figures 2a-c). The stripes are very common around air bubbles and always involve a large number of edge dislocations (Figure 2b). Additionally, the chevron pattern is initially very feeble, but the contrast improves steadily over hours and days with growing maximum birefringence. The stripes are best visualised between crossed polarizers in the diagonal position or with a single polarizer set perpendicular to them; when a single polarizer is parallel to the stripes, the contrast deteriorates considerably. A tilting calcite compensator with its axis along the stripes decreases the birefringence, showing that the stripes run normal to the principal plane. The two sets of alternate lines of this pattern come to focus in two different planes on either side of the sample midplane. Other textures of the low temperature phase include those of the precursor (spherulites, myelin rods and oily streaks), but these develop angular features and facetedness with passage of time, over several hours (Figures 2d-i).

Now we turn to an interpretation of the textures observed during cooling. The striated appearance and facetedness of the fan shaped figures (Figures 1c-e) indicate an ordered layer arrangement for the high temperature phase. The smectic B structue is ruled out as it is expected to form from the isotropic mesophase (when both the phases are present), rather than melt into it. It appears that we are having here the lyotropic middle phase M_1.[5] It gives way to the viscous isotropic phase V_1 , which in turn changes over to the lamellar G modification on cooling. Interestingly, a similar polymesomorphism, but with the phase sequence in reverse, is observed in dipotassium hexadecanedioate / H_2O system.[6]

The striped texture of the type presented in Figures 2a-c could arise for various reasons: In thermotropic liquid crystals undergoing a weakly first order transformation

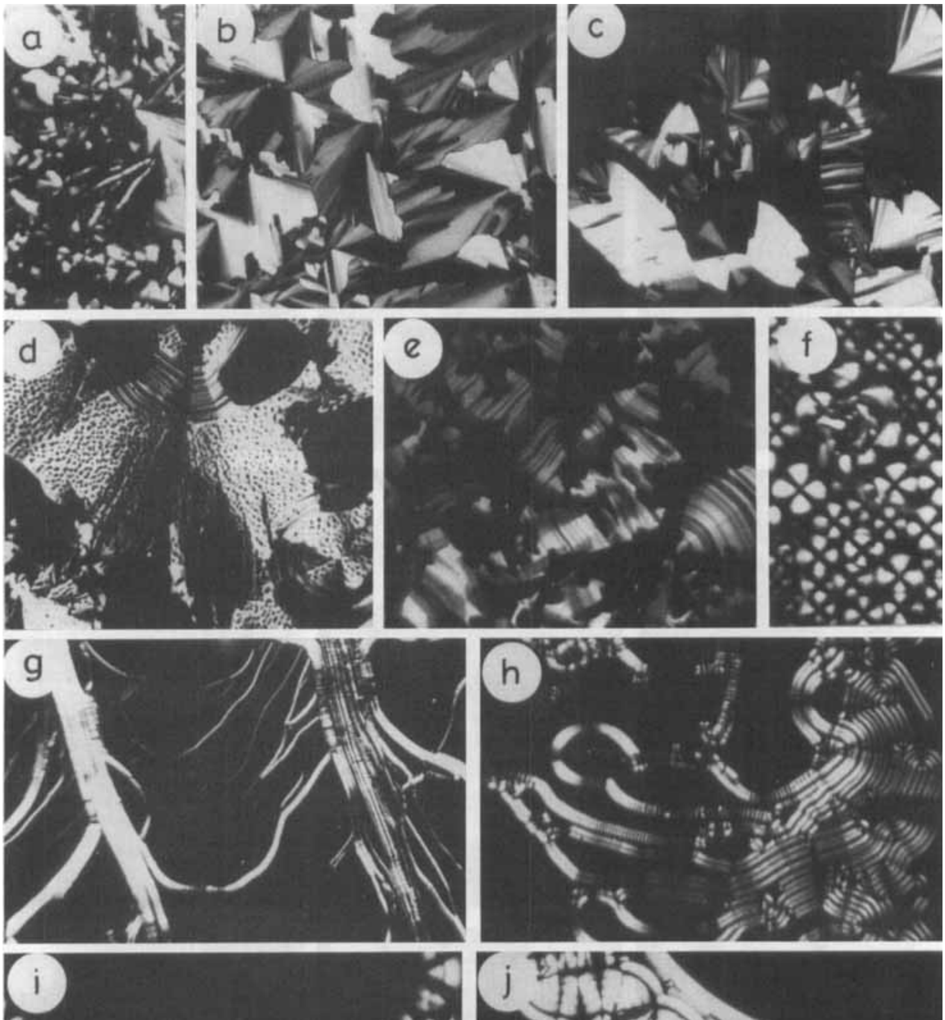


FIGURE 1 Textures of mesophases in EP/H_3PO_4 system observed while cooling; crossed polarizers; 12-25 wt % EP. High temperature phase (180-130 °C): Batonnets (a), focal conics (b), and striated tapes and fans (c). (d,e) Isotropic phase (130-110 °C) at its onset. Lamellar phase (110-65 °C): Homeotropic plates with birefringent borders and oily streaks (f); folded and striated long myelin tubes (g); spherulitic domains (h); characteristic extinctions between crossed polarizers in the diagonal position, due to a transverse undulatory structure, in oily streaks (i) and myelin tubes (j).

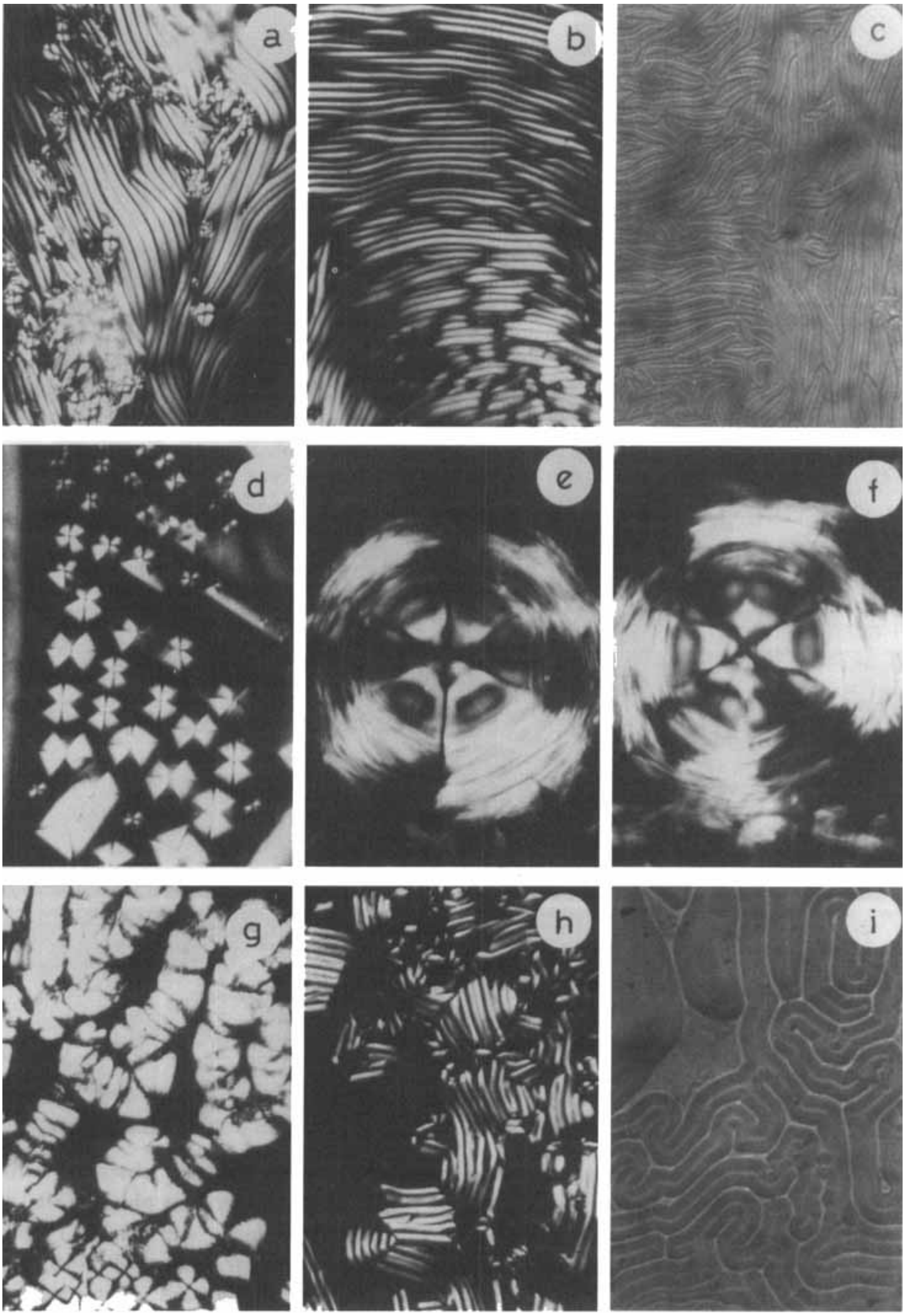


FIGURE 2 Textures in EP/H_3PO_4 system (12-25 wt % EP) at room temperature.

Stripes (chevrons); crossed polarizers (a,b); single polarizer parallel to the longer edge (c). A colony of faceted drops; crossed polarizers parallel to the figure edges (d). A drop showing hexgonally symmetric well developed faces in the central zone and circularly bent birefringent bands in the outer zone; crossed polarizers, parallel to the figure edges (e), diagonally set (f). Pseudomorphic fans (g) and myelin figures (h) with slowly developed crystal-like features. Focusing of light by pseudomorphic myelinic tubes, single polarizer (i).

from the nematic to S_A state, stripes appear[7,8] due to the Shubnikov-like intermediate phase. It is characterized by an array of edge dislocations that develop to minimise the bend elastic energy. The well known TGB_A phase also shows the striped pattern. Some of the striped textures in alkyl cholestanyl ethers,[9] tentatively attributed to the TGB_A phase, closely resemble the pattern in Figure 2a, but as we are dealing with an achiral system this similarity appears coincidental. Stripes also arise from an undulatory instability in smectic lamellae under a dilatory mechanical stress.[10] The optical characteristics of this pattern are the same as observed here. It appears that the low temperature phase in the title systems is a gel composed of corrugated bilayers. The ripples may be ascribed to the extension and stiffening of the hydrocarbon chains. The presence of internal order for the phase is also indicated by the optical aspects of the drops and rods in Figures 2d-i.

DSC and X- ray Measurements

The DSC thermograms generally agree with the optical observations as indicated in Figure 3a.

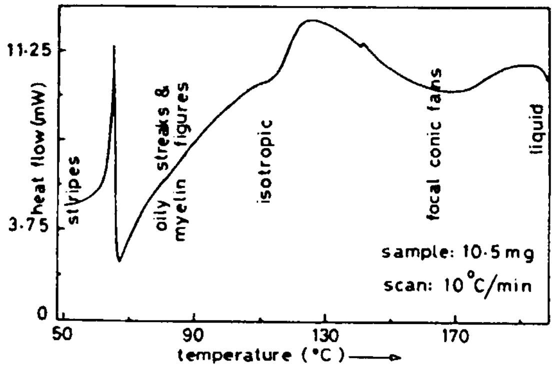


FIGURE 3 DSC thermogram of EP/H_3PO_4 (1:7.5 wt)

The low angle X-ray diffraction patterns recorded at various temperatures in the range 30-155 °C may be divided into four categories (Figure 4). The high temperature

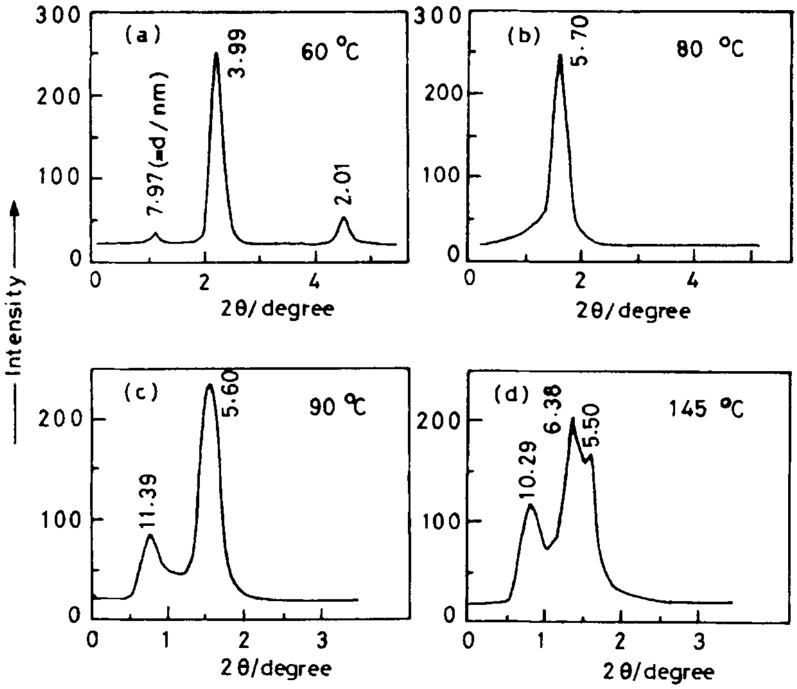
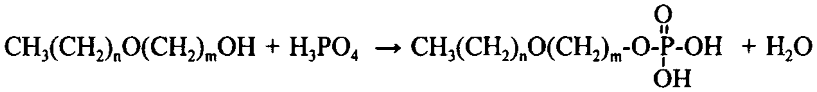


FIGURE 4 Low-angle X-ray patterns for 25 wt % EP in H_3PO_4.

mesophase shows three reflections with the d-spacings nearly in the ratio $1:1/\sqrt{3}:1/\sqrt{4}$ (Figure 4d). This is characteristic of the hexagonal middle phase M_1. The 90 °C pattern in Figure 4c, showing only two peaks at spacings in the ratio 1:1/2 is typical of the phase derived from M_1 and identified as V_1. The M_1-V_1 transition is accompanied by a slight increase in the size of micellar aggregates. The lameller G phase (Figure 4b) shows only a single reflection as often occurs in aqueous systems. The bilayer thickness here is much reduced compared to the size of micellar aggregates in the precursors. The pattern at the low temperature end showing three sharp reflections in the ratio 1:2:4 (Figure 4a), is tentatively assigned to the gel phase. The bilayer thickness for the gel is considerably enhanced over its value for the G phase, indicating a possible elongation of the hydrocarbon chains.

CONCLUDING REMARKS

The mesophases in title systems occurred in the same sequence with no significant variation. However, for a given system, the transition temperatures varied considerably in the successive thermal cycles. This may be due to interactions between the components, particularly at elevated temperatures. In fact, Acimis[1] attributed the mesogenic behaviour to some of the reaction products. For long chain alcohols, however, earlier studies indicated no evidence of interaction.[2,3] In the present case a strong possibility to consider is the esterification:



$$CH_3(CH_2)_nO(CH_2)_mOH + H_3PO_4 \rightarrow CH_3(CH_2)_nO(CH_2)_m\text{-O-}\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}\text{-OH} + H_2O$$

Comparison of the room temperature IR spectra of neat EP and its mixture with H_3PO_4 shows a strong enhancement of the absorption due to the polar groups (1000-1200 cm^{-1}). Besides the COH and COC asymmetric stretching, POC asymmetric stretching may also contribute to this absorption. Detailed chemical analysis of the mixtures at various stages of heating is required for a better understanding of their phase behaviour during repeated thermal cycling.

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