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A Natural Dye in a Mesophase Region of Cetyltrimethylammonium Bromide/Octan-1-ol/Water System

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ABSTRAK

Satu pewarna semulajadi, kurkumin telah ditambahkan ke dalam satu siri struktur mesofasa hablur cecair lamela yang mengandungi setiltrimetilammonium bromida, oktan-1-ol dan air pada 30°C. Perubahan yang berlaku akibat dari penambahan pewarna tersebut telah diikuti dengan kaedah mikroskop berkutub dan pembelauan sinar X bersudut rendah. Jarak antara lapisan untuk hablur cecair lamela dengan pewarna didapati lebih rendah dari jarak antara lapisan tanpa pewarna pada nisbah isipadu air yang sama. Kesan air dan rantai hidrokarbon dari struktur hablur cecair lamela adalah minima dan penambahan pewarna seterusnya menghalang pembentukan mesofasa tersebut.

ABSTRACT

A naturally occurring dye, curcumin, was added to a series of lamellar liquid crystal mesophases consisting of cetyltrimethylammonium bromide (CTAB), octan-1-ol and water at 30°C. The changes brought about by the addition of the natural dye were followed by optical microscopy and small angle X-ray diffraction techniques. The interlayer spacings of the lamellar liquid crystal mesophases with the natural dye were observed to be lower than the corresponding structure without dye at the equivalent volume ratio of water. The effect of water and the hydrocarbon chain of the lamellar liquid crystal structure were found to be minimal and further inclusion of curcumin prevented the formation of the mesophase.

Keywords: curcumin, lamellar liquid crystal, small angle X-ray diffraction

INTRODUCTION

A characteristic feature of a particular dye, other than its spectrum in the UV range, is its solubility in various media. Dyes are colorants which are either partially or completely dissolved in the media of application (Zollinger 1987). In some applications, such as in inks for jet printing, waterfastness is desired in an ink which must be water-rich. One way of attaining this is by formulating inks which harden into a liquid crystal or crystal when applied.

The solubilization of dyes into a liquid crystalline structure has over the decades been focused on nonlyotropic or thermotropic liquid crystals due to their importance in colouring liquid crystal display, LCD. Lyotropic liquid crystal structure, however, has not received the corresponding attention it deserves. This amphiphilic structure has special appeal in biological systems such as biomembranes and a part of an integumentary system known as stratum corneum. It is well documented that the lipids of human stratum corneum form bilayers which are composed of sheets of fatty acids, cholesterol and ceramide layers separated by water layers (Elias 1983; Friberg and Osborne 1985). This molecular arrangement is similar to that of a lamellar liquid crystal mesophase often observed in the intermediate region of surfactant/co-surfactant/water systems (Ekwall 1975).

Work on the solubilization of dye in lamellar liquid crystals was initiated by Friberg and co-workers (Friberg *et al.* in press). This work, however, focused on the use of a synthetic dye, phenol red, as the guest constituent. The present work is concerned with the solubilization of a naturally occurring dye known as curcumin or 1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione (*Fig. 1*) in a lamellar liquid crystal mesophase. This investigation arises from the growing concern associated with many synthetic dyes and an awareness of environment-friendly materials. Curcumin is approved for use as a colorant in food processing (WHO 1975) and easily extracted from the rhizome of *Curcuma longa* L. (Zingiberaceae).

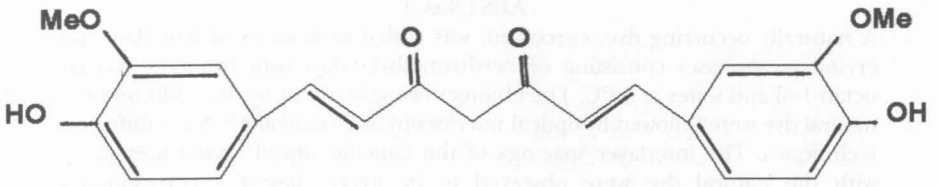

Fig. 1. Structure of curcumin

METHODS AND MATERIALS

Materials

The constituent materials of the liquid crystal chosen were octan-1-ol and cetyltrimethylammonium bromide (CTAB) at variable molar ratios in an aqueous system. The surfactant CTAB (MW 364.46 g/mol) (>99%) was obtained from Sigma Chemicals and the co-surfactant octan-1-ol (MW 130.23 g/mol) (>99%)

was from Aldrich. No further purification was done prior to usage. The curcumin (BDH) was purified through silica gel column using dichloromethane:methanol (98:2) as the eluent. It was then recrystallized from ethanol to give a bright orange-yellow crystal. Doubly distilled water was used to prepare the lamellar liquid crystal mesophase.

Preparation of Samples

The liquid crystal samples used as the host for the study of the solubilization employing a natural dye as the guest constituent were prepared as follows. First, the surfactant was combined with octan-1-ol at three different surfactant/octan-1-ol molar ratios of 0.66, 0.83 and 1.07 (line a, b and c respectively of *Fig. 2*). The samples were mixed by repeated centrifugation in a sealed 7-mm sample tube, vortexed and allowed to equilibrate at 30 ± 0.2°C. For each composition, a series of samples represented as points on lines a, b and c in *Fig. 2* was prepared with water content in the range of 30-40% by weight. For the solubilization of the natural dye into the lamellar structure, a point on line c of *Fig.* 2 at 33% by weight of water was selected and the dye is added to it directly. For the X-ray measurements, a fixed amount of 2% wt./(surfactant + co-surfactant) of curcumin was added to all the samples series and the water content was adjusted to maintain the initial values at 30-40% by weight. The resulting samples (host + dye) were then allowed to equilibrate overnight at 30 ± 0.2°C. The changes brought about by the above additions of the dye were followed by optical microscope and small angle X-ray diffraction techniques.

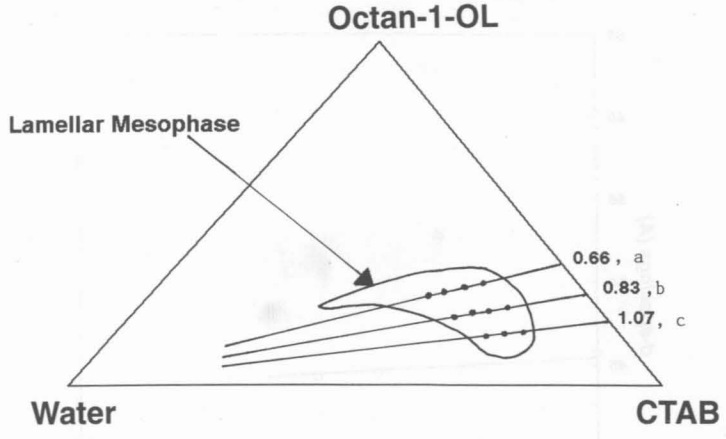

Fig. 2. Ternary diagram for the system of cetyltrimethylammonium bromide (CTAB), octan-1-ol and water, showing the location of the lamellar liquid crystalline region taken for the X-ray measurements

Small Angle X-ray Diffraction Measurements

The interlayer spacings of liquid crystalline phases were determined by small angle X-ray diffraction method at 30°C. A Kiessig small angle camera from

Richard Seifert with an Ni-filtered Cu source gradient at 40 kV, 30 mA was used. The reflection was detected by a Tennelec detector system (Model PSD1100). The exposure time for the samples was set to 1000 sec and the alignment of the instrument was checked by a lead stearate standard with an interlayer spacing of 48.2 Å.

RESULTS AND DISCUSSION

The solubility of curcumin to the lamellar liquid crystal over a water concentration of 30-40% is found to be relatively low, i.e. about 2.5% by weight at the higher CTAB/octan-1-ol molar ratio. An addition of a large excess of curcumin beyond the maximum solubility distorts the lamellar structure. The appearance of the sample under the polarized microscope is shown in *Plate 1.* Our results also showed a slight reduction or otherwise constant value of 45.0 Å in the interlayer spacing when curcumin is added directly to the liquid crystal samples (*Fig. 3*).

The interlayer spacings are calculated from the small angle X-ray diffractograms pattern and are plotted against the water ratio in the range of 30-40% by weight. The curcumin is then added to liquid crystalline samples across the points a, b and c of *Fig. 2.* The molar ratios of the surfactant/alcohol for a, b and c are 0.66, 0.83 and 1.07, respectively. A plot of the interlayer spacings for the compositions with a surfactant/alcohol molar ratio of 0.66 without curcumin is shown in *Fig. 4a.* The interlayer spacings observed in these compositions increased linearly with the water content in the interval used. Equivalent data for systems with surfactant/alcohol molar ratios of 0.83 and

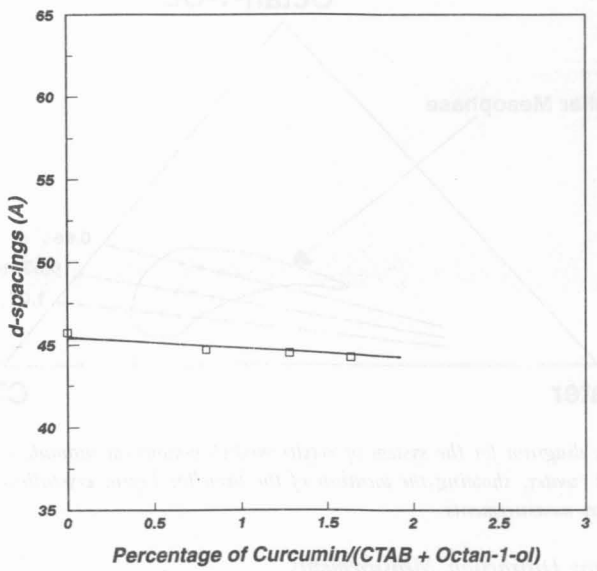

Fig. 3. Interlayer spacing versus curcumin percentage for a sample of initial composition: 50% CTAB, 17% octan-1-ol and 33% water. (% wt)

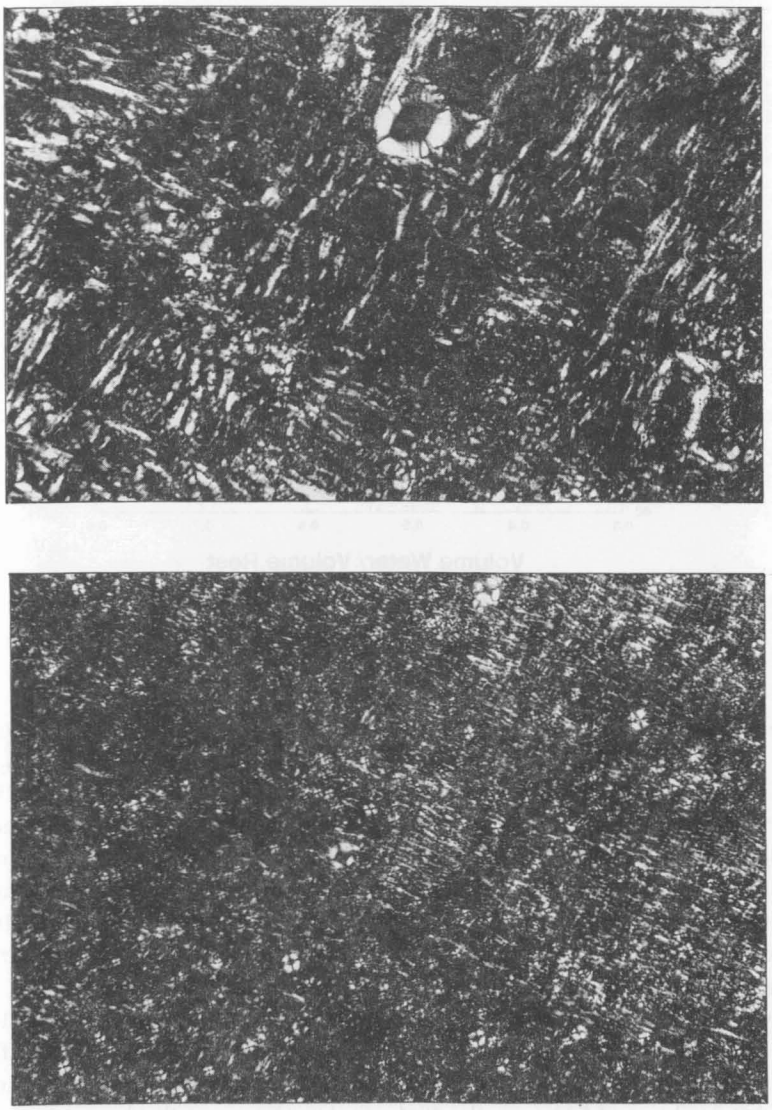

Plate 1. Optical pattern at a molar ratio of CTAB to octan-1-ol of 1.07: a) before, and b) after, addition of 1.5 wt. % of curcumin, indicating typical lamellar liquid crystalline structures of striated type. The water content for both samples was kept at 32 wt. %

1.07 are shown in *Fig. 4b, c,* respectively. Similar dependence on the water content is observed in these systems. Inclusion of curcumin also shows similar dependence on the water content. However, an interesting phenomenon is observed when graph for both systems are plotted together in *Figs. 5-7.* The interlayer spacings for the liquid crystals containing the curcumin is found to be lower than those without the curcumin with equivalent volume ratio of water.

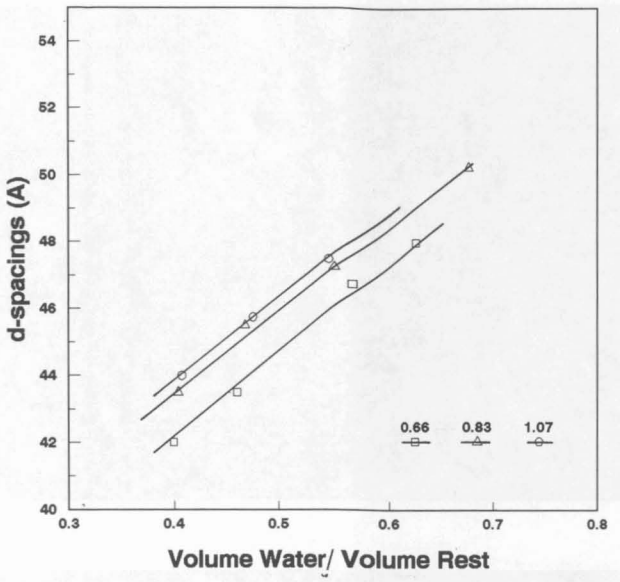

Fig. 4. Interlayer spacing as a function of water volume fraction for CTAB/octan-1-ol molar ratios of a) 0.66, b) 0.83 and c) 1.07, before the addition of curcumin

The above results only suggest the location of the curcumin in the liquid crystal structure (*Fig. 3*). Since the interlayer spacings and the slopes of the straight lines (*Figs. 5-7*) did not significantly increase as curcumin was added to the structure, it can be inferred that the curcumin is located between the methylene layer of the lamellar structure. The results, however, did not lend useful information on the dye-water, dye-hydrocarbon interaction nor the whole structure of the lamellar organization. In order to obtain such deduction, extrapolation of the curves in *Figs. 5-7* to zero water content and the calculation on the penetration factor become necessary. The values of the interlayer spacing at zero water (d_0) are given in Table 1. The almost identical values (d_0) showed that the presence of curcumin molecules have little influence on the hydrocarbon chains in the liquid crystal, suggesting again that curcumin molecules are located between the hydrocarbon layers of the liquid crystal. The dye-water interaction, on the other hand, is reflected by the extent to which the water penetrates the amphiphilic layer from the polar layer. This may be achieve to a satisfactory extent from the slopes (Table 1) of *Figs. 5-7*. However, a better understanding can be made possible by calculating the penetration of water which is characterized by the penetration factor α. The definition of the penetration factor α by Friberg and co-workers (Friberg *et al.* 1992) is adopted in this work and is described here to facilitate understanding and to make clear its vital role in this study.

For an added solvent (water in this case) that is localized entirely in the polar zone A or methyl zone C (*Fig. 8*) the penetration factor, $\alpha = 0$. If the

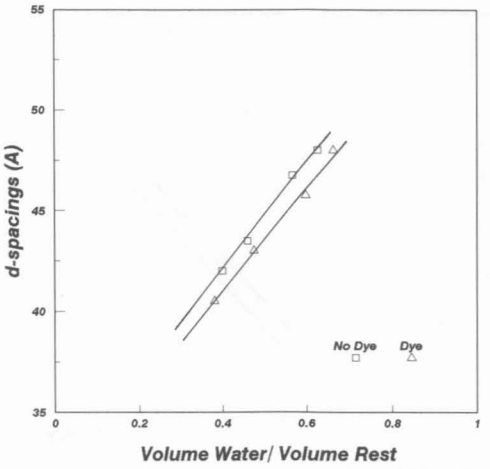

Fig. 5. Interlayer spacing as a function of water volume fraction for CTAB/octan-1-ol molar ratio of 0.66, i) before (() and ii) after (() addition of curcumin

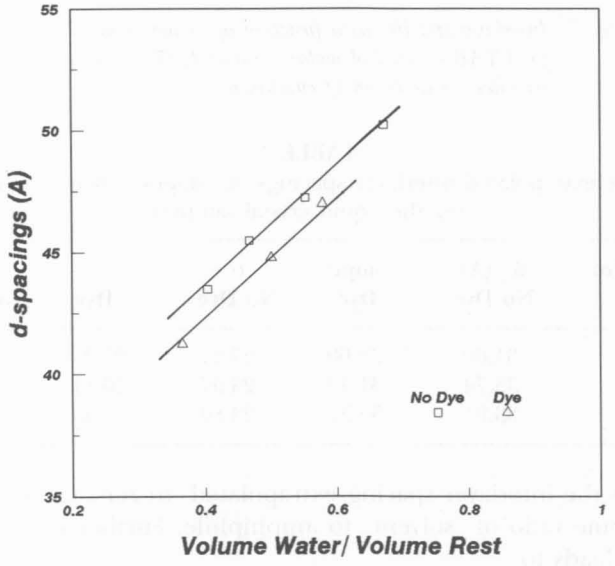

Fig. 6. Interlayer spacing as a function of water volume fraction for CTAB/octan-1-ol molar ratio of 0.83, i) before (() and ii) after (() addition of curcumin

solvent is partitioned equally into zones A, B, and C (*Fig. 8*) the penetration fraction, $\alpha = 1$. For partial penetration into zone B, the penetration factor is defined by

$$d = d_o\left[1 + (1 - \alpha)R\right] \quad (1)$$

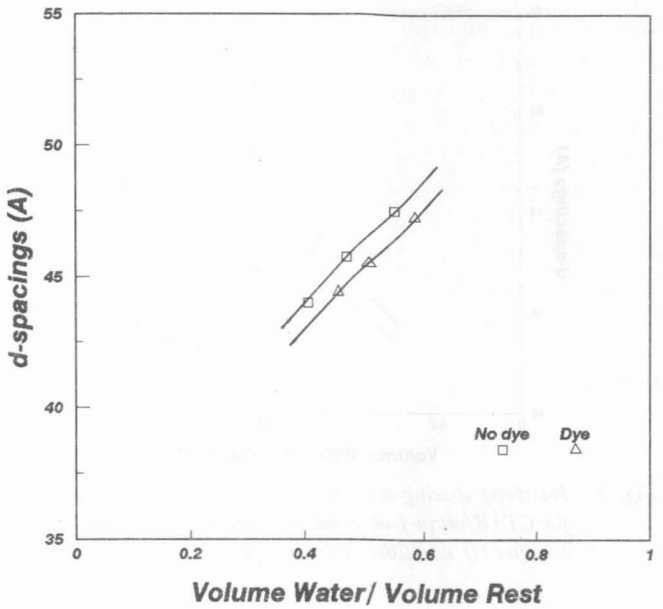

Fig. 7. Interlayer spacing as a function of water volume fraction for CTAB/octan-1-ol molar ratio of 1.07, i) before (() and ii) after (() addition of curcumin

TABLE 1
Values for the extrapolated interlayer spacings, d_o, slopes and penetration factor α, for the liquid crystal samples

CTAB/Octan-1ol Molar Ratio	d_o (A) No Dye	Dye	slope No Dye	Dye	α No Dye	Dye
0.66	31.09	30.60	27.21	25.89	0.13	0.15
0.83	33.74	31.42	24.57	26.81	0.27	0.15
1.07	33.91	33.53	24.80	23.53	0.27	0.29

in which d_o is the interlayer spacing extrapolated to zero solvent content and R is the volume ratio of solvent to amphiphile. Further rearrangements of equation (1) leads to,

$$d = d_o + (d_o - d_o\alpha)R \qquad (2)$$

where $(d_o - d_o\alpha)$ is the slope obtained from *Figs. 5-7.*
Therefore, the penetration factor for partial penetration into zone B (*Fig. 8*) is simplified into

$$\alpha = 1 - \text{slope}/d_o \qquad (3)$$

The penetration factors of water at various composition calculated from the interlayer spacings, before and after addition of curcumin are summarized in Table 1.

The α values of water in Table 1 exhibit two main features of interest. First, the presence of curcumin results in slight or no appreciable increase of water penetration into zone B (*Fig. 8*) and, second, the higher molar ratios of CTAB/ octan-1-ol lead to a higher penetration factor, α, for both systems (Table 1). The second feature is expected since a higher molar ratio of CTAB to octan-1-ol resulted in a greater electrostatic repulsion from the charged CTAB head groups. The first one, however, is surprising. Curcumin, being more hydrophobic than water should be expected to penetrate to a much higher degree. This phenomenon lies in the location of surfactant (CTAB) and co-surfactant (octan-1-ol) in the layered structure (*Fig. 8*) and the order parameter of their hydrocarbon chain. One explanation is that the presence of curcumin, being relatively bulky in nature (*Fig. 1*), induces a temporary disorder in the layered structure and causes the octan-1-ol originally located between zones B and C (*Fig. 8*) to penetrate into the layered structure and its polar group to be anchored at the polar interface (zone A, *Fig. 8*). Such an arrangement certainly does not permit further penetration of water or may to a certain extent reduce the penetration as observed in Table 1.

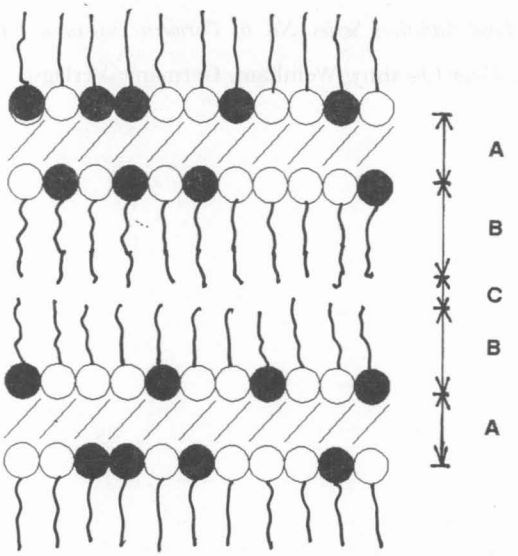

Fig. 8. A lamellar liquid crystal structure divided into three zones. A. water/ polar, B. hydrocarbon/ palisade, and C. methyl/nonpolar layer

In summary, it is found that the solubility of curcumin molecules in the lamellar liquid crystal mesophase of CTAB/octan-1-ol/water is quite modest. The solubility is also observed to be a function of the CTAB and octan-1-ol molar ratios. The inclusion of a large percentage of curcumin molecules in the lamellar liquid crystal structure may destabilize the structure. In addition, the location of the curcumin molecules is found between the hydrocarbon (methylene) layers of the lamellar liquid crystal structure.

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