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Analysis on the birefringence property of lyotropic liquid crystals below Krafft temperature

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ABSTRACT

The effect of lyotropic liquid crystalline material, below Krafft temperature, in changing the polarization of the optical beam has been demonstrated. It is found that the lamella structures formed in the material below Krafft temperature are birefringent and this birefringence can be controlled by flowing it in rectangular channel under a suitable flow rate.

1. Introduction

Liquid crystalline materials have attracted much interest in the past two decades due to their potential applications in displays, temperature and pressure sensors, etc. Rheological properties of surfactants, a lyotropic liquid crystalline material, are studied extensively [1–5]. The growth of these aggregates into various shapes depends mainly on concentration and temperature. It is also noted that the properties of aqueous solutions of surfactants above and below a particular temperature known as *Krafft temperature* is completely different. Above this temperature, surfactant is highly soluble and micelles start to form. Below Krafft temperature, aqueous surfactant solution is in two phase form, hydrated crystals and water. It is identified that the hydrated crystals are formed due to the crystallization of hydrophobic alkyl chains and the hydrophilic head group of the surfactant molecule [6,7]. The crystallization is favoured when the Van der Waals attraction energy exceeds thermal kinetic energy [6].

The properties of aqueous surfactant solution such as rheology, flow birefringence, etc. above the Krafft temperature was studied extensively [2–5]. However, the properties below Krafft temperature were inadequately investigated. Therefore, in this context we studied the birefringence property of a cationic surfactant, cetyltrimethylammonium bromide (CTAB) which is a lyotropic liquid crystalline material below Krafft temperature.

2. Experiment

The schematic set up is shown in Fig. 1. Diode laser with a wavelength of 641 nm was used for the experiment. Here the flow cell was kept between crossed polarizer to analyze the birefringence of CTAB solution. A linearly polarized laser beam was focused to the flow cell and the transmitted beam is again passed through a second polarizer (analyzer) with polarization axis perpendicular to the first polarizer. The output laser power was monitored using a power meter, connected to the computer for data analysis.

The surfactant cetyltrimethylammonium bromide was purchased from Sigma Aldrich Chem. Co. and used without further purification. All solutions were prepared in double distilled water.

A clear aqueous solution of CTAB was prepared initially and kept above Krafft temperature (25 °C) for few hours. Later, this solution was cooled to below 25 °C at which the hydrated crystals were formed by precipitation. This solution was kept for 2 days to attain equilibrium. Just before the experiment the turbid solution was stirred. The solution became glossy after stirring.

A rectangular channel with 1-mm width and 2-mm height was fabricated using glass slides with a refractive index of 1.52. Flow cell was connected to a syringe pump using silicone tubing with an outer diameter of 0.6 cm and an inner diameter of 0.3 cm. The channel was cleaned before introducing the surfactant. A magnetic stirrer was used to stir the solution in the syringe. Experiments were performed with and without stirring the solution in the syringe.

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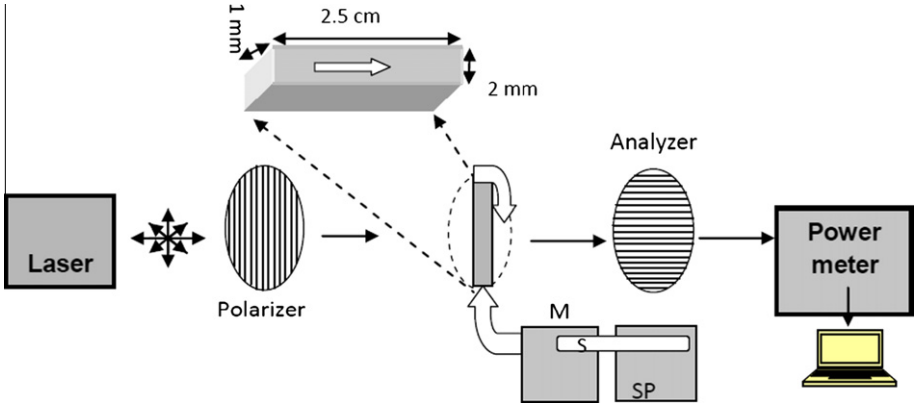

Fig. 1. Schematic diagram of the experimental set up. M-Magnetic stirrer, SP-Syringe pump and S-syringe.

The UV–VIS absorption spectrum and optical microscope image of the CTAB solution were also taken. Absorption spectrum was measured on a Shimadzu UV-1601 PC spectrophotometer and the baseline was corrected with water. Optical microscope images were taken on a microscope (ZEISS, Axiotech 181398). Sample for the optical microscopic image was prepared by drop-casting the aqueous solution on a glass slide.

3. Results and discussion

Fig. 2 shows the UV–VIS absorption spectrum of CTAB. The absorption spectra is characterised with a peak at 216 nm and a broad band centred around 275 nm. The spectrum clearly indicates that there is no absorption in the visible range. Fig. 3 shows the optical microscopic images of the hydrated crystals of CTAB. The metastable state (needle shaped) and stable state (plate like) of CTAB (Fig. 3A and B) are similar to those of cetylpiridinium chloride [6]. It was observed that the metastable–stable transition takes place in few hours.

In the experiment, the surfactant solution was introduced into the flow cell and the output laser power was monitored using a power meter. Fig. 4 shows the variation of the transmitted power with a constant flow rate of 80 ml/h. It was observed that the power increases to a maximum value and after few seconds it decreases exponentially. The initial increase in the power is attributed to the birefringence property of the hydrated crystals in the surfactant solution. Thus CTAB flow cell can be regarded as a birefringent medium with birefringence $\Delta n = n_e - n_0$, where n_e and n_0 are the refractive indices of extraordinary and ordinary rays that propagate with orthogonal polarizations. The change in the refractive indices will create a phase difference ϕ between the two rays when it is emerged from the birefringent medium of a length L.

$$\phi = \frac{2\pi\Delta nL}{\lambda} \tag{1}$$

When a particular flow rate was given, birefringence is varied which affects the light intensity. The transmitted light intensity can be written as

$$I = I_0 \mathrm{Sin}^2(2\theta)\mathrm{Sin}^2(\phi/2) \tag{2}$$

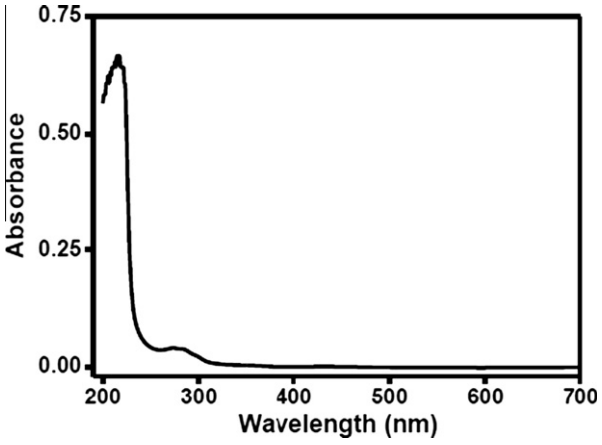

Fig. 2. UV–VIS absorption spectrum of aqueous solution of cetyltrimethylammonium bromide.

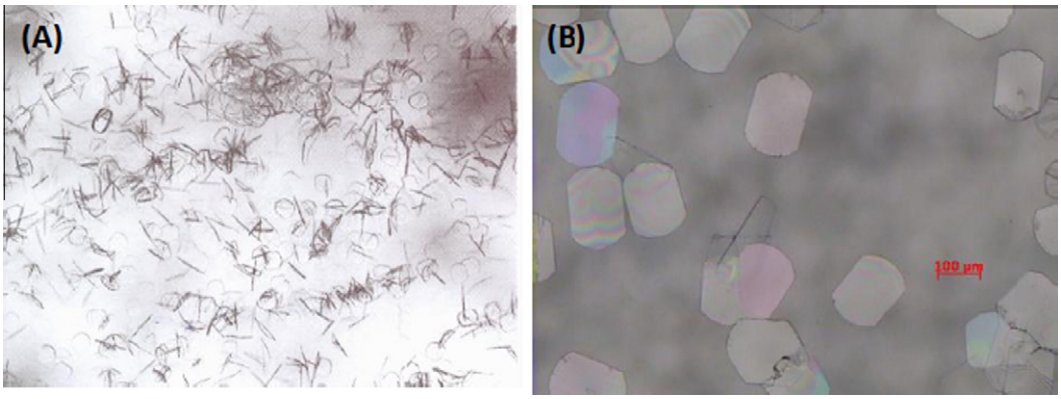

Fig. 3. Optical microscope image of the hydrated crystals formed in CTAB solution (A) metastable solid and (B) stable hydrated solid.