



Determination of order parameter and birefringence depending on temperature of nematic calamitic mesophase formed by TTAB + water binary system using polarized microscopy

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Abstract

In the present study, the temperature-dependent optical transmittances of lyotropic nematic calamitic mesophase formed by TTAB-water binary system were measured for certain wavelengths under polarized microscopy to obtain macroscopic order parameter with birefringence. Because birefringence in lyotropics is quite small (order of 10^{-3}), it is very difficult to make sensitive measurements of birefringence and to obtain order parameter. The study easily achieved the order parameter depending on temperature for different wavelengths only using polarized microscopy. Therefore, the parameter could be more easily determined in liquid crystal application and the physical properties of liquid crystals, especially for lyotropics, can be better understood.

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1. Introduction

Liquid crystals are specific mesophases of matter which are between liquid and solid phases and they can simultaneously exhibit anisotropic properties of solids and fluidity ones of liquids [1]. Such mesophases are currently of great importance in terms of technology and they have recently been prominent in optical studies [2,3]. They are generally found in biological systems as lyotropics which are one of their types and thus, lyotropics are taken attention in liquid crystals. These systems are generally formed by the solution of surfactant molecules in water [4]. Basic structural units are micelles, which are spontaneously constituted by the aggregation of surfactant molecules in water. There are different lyotropic mesophases based on micellar structures [5]. Besides, the addition of cosurfactants such as alcohol to the solution enables the formation of a variety of micelles and it can be increased the diversity of lyotropic mesophases [6]. Among the lyotropic mesophases, the most common ones are nematics. There are three different nematic phases as being uniaxial calamitic (N_C), discotic (N_D) and biaxial (N_{BX}) ones. The N_C and N_D phases consist of rod-like and discotic-like micelles, respectively. Because they have anisotropy, it is quite important to study the optical properties of lyotropic nematics in particular [7]. On the other hand, the fact that lyotropics are present in biological materials such as

blood, cellular plasmas and membranes are promising materials in terms of biotechnological studies. Today, they have application fields as in the production of biosensors [8,9]. In order to develop their fields of use, the optical study of their physical properties is necessary. These properties are governed by the order parameter [10]. Thus, the study of the order parameter of lyotropics has accelerated in recent years [11-13]. As the most popular method to measure the parameter, optical anisotropy measurements are preferred due to obtaining better results [14,15]. The optical anisotropy of the nematic phases is given by birefringence (δn). Because the uniaxial nematic phases are described by two refractive indices, the birefringence is found as the difference between these two refractive indices, $\delta n = n_e - n_o$, where n_e and n_o are the refractive indices for extraordinary and ordinary rays, respectively. The polarization direction of n_e (n_o) is parallel (perpendicular) to the nematic phase director, also called optical axis [16,17]. In general, $\delta n < 0$ for N_C and $\delta n > 0$ for N_D mesophases. In the case of the biaxial nematic phase, there exist three principal refractive indices of the medium (n_1 , n_2 and n_3) along three orthogonal laboratory frame axes, and two optical birefringences, $\delta n = n_2 - n_1$ and $\delta n = n_3 - n_2$ [18].

The birefringence of lyotropics is much lower than other liquid crystal mesophases and for this reason, it is quite difficult to determine order parameter in the birefringence measurements. In general, laser

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conoscopy may be preferred, but this method has a very time-consuming and complex setup in the measurements [19,20]. Berek compensator measurements in a polarizing microscope and refractometry ones are not as sensitive as desired. This study suggests a simpler method to obtain the optical birefringence and order parameter. They were easily calculated from the optical transmittance of given wavelengths in N_C mesophase formed by binary lyotropic system using only polarized microscopy. The optical birefringence and order parameter were found based on wavelength and temperature. In addition, the literature has relatively insufficient for the birefringence and order parameter studies for the lyotropic N_C system at different wavelengths and therefore, the present study aims to eliminate this gap.

2. Materials and Methods

The lyotropic sample was obtained from Tetradecyltrimethylammonium bromide (TTAB) and deionized water. TTAB with purity of not less than 99% was purchased from Sigma (cat. no. T-4762). The concentration of the sample was TTAB: 38.6 and water: 61.4 in weight percent. Per each g of the solution, 1 μ L ferrofluid was used for a better orientation under a magnetic field. Water-based ferrofluid was acquired from Ferrotec Corp. (cat. no. EMG 605). The sample constituents were weighed in a glass tube by an And HR-120 balance with a precision of 10^{-4} g. Then, the sample was kept in Memmert 400 oven at 323 K for two weeks and mixed with a vortex (Nüve NM110) occasionally. The formed sample was placed in sandwich cells of 20 mm in width and 360 μ m in thickness and studied under Olympus BX50 polarizing microscope. The textural properties of the sample were analyzed by the microscope to find out that it was N_C mesophase. Later, the sample was exposed to a 3.7 kG magnetic field parallel to sandwich cell surfaces for 5 hours and it was obtained planar orientation. The temperature of the sample was changed by 0.10 K/min on the Linkam PE120-BX thermoelectric heating table attached to the polarizing microscope. In the process, light intensities of the sandwich cells with and without the sample (I and I_0 , respectively) were measured by Adafruit TSL2561 sensor Arduino system which is sensitive to light transmittance under the polarizing microscope. Optical transmittance (I/I_0) was obtained by a magnification of $\times 100$ by means of optical filters of 440 nm, 550 nm and 694.3 nm placed on the optical way of the microscope.

3. Results and Discussion

The optical transmittances of planar-oriented N_C sample (I/I_0) as a function of temperature were measured for different wavelengths under polarizing microscopy and presented in **Figure 1**. The measurements of the optical transmittance in wavelengths were found to be very different from each other. At 440 nm blue and 550 nm green wavelengths, the transmittances were changed a lot in the N_C mesophase region. However, the differences in the optical transmittance of 694.3 nm red wavelength with temperature were less than the blue and green ones and the wavelength was exhibited a quite high transmittance in the mesophase region.

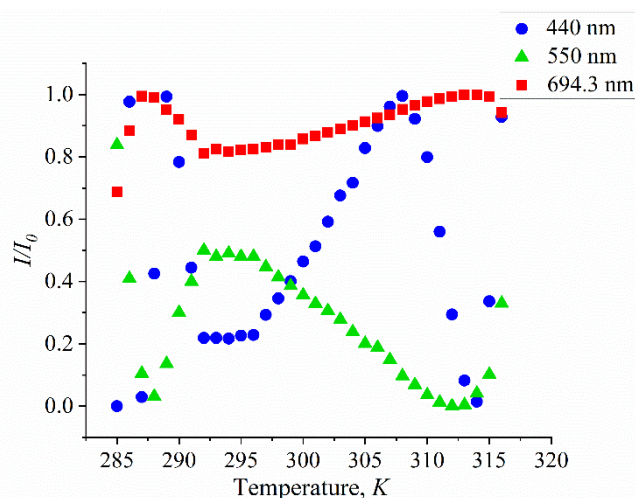


Figure 1. The optical transmittances as a function of temperature for 440 nm, 550 nm and 694.3 nm wavelengths in the lyotropic sample.

The relationship between the optical transmittances and birefringence can be explained by a phase difference. Under the microscope, the polarized light is separated into two rays, which are extraordinary and ordinary ones whose electric field vectors vibrating in parallel and perpendicular to the director, respectively. Therefore, the phase difference ($\Delta\phi$) occurs between the rays after passed passing through the sample. The refractive indices corresponding to these rays are n_e and n_o , and the difference can be explained by the birefringence (δn) as follows:

$$\Delta\phi = \frac{2\pi t}{\lambda} \delta n \quad (1)$$

where λ and t is the wavelength and thickness of the sample, respectively. Thus, the optical transmittance in terms of the phase difference can be as follows [15]:

$$\frac{I}{I_0} = \sin^2 2\theta \sin^2 \frac{\Delta\phi}{2} \quad (2)$$

where \square is the angle between the light polarization direction and director and it was set up as 45° under the microscope. The phase difference in Equation 1 and the optical transmittance in Equation 2 were used to obtain the birefringence of each wavelength (Figure 2). Accordingly, the phase transition from reentrant-isotropic to N_C mesophase occurred at 284 K and N_C mesophase to isotropic phase transition was achieved at 317 K. The birefringence of the 440 nm blue wavelength was highest in value whereas the 694.3 nm red wavelength had the lowest value.

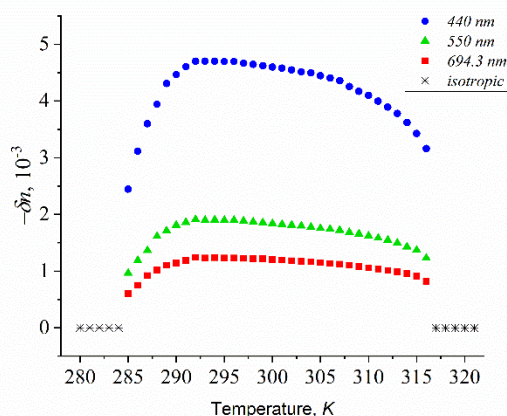


Figure 2. The birefringence as a function of temperature for 440 nm, 550 nm ve 694.3 nm wavelengths.

Macroscopic order parameter (Q) can be obtained from Figure 2 using Haller method [19]. The order parameter can be written in terms of birefringence as follows:

$$Q = \frac{\delta n}{\Delta n} \quad (3)$$

where Dn is birefringence at $T=0$ K which is absolute temperature where liquid crystals are assumed to be completely oriented as in solids and therefore, $Q=1$. The order parameter is very important because it governs all physical properties of liquid crystals. To obtain this parameter, a line was drawn at $\log(dn)$ versus $\log(1-T/T_c)$ in dn -temperature graph. At the point where the line intercepts at $T=0$ K, $\log(Dn)$ is obtained. Dn values for 440 nm, 550 nm and 694.3 nm are 6.851×10^{-3} , 2.794×10^{-3} and 1.777×10^{-3} , respectively. Figure 3 shows the order parameter based on temperature. The parameters were found to be similar for each wavelength and in the sensitivity of 10^{-2} according to each other. However, the maximum order parameter was found as 0.697 at 292 K.

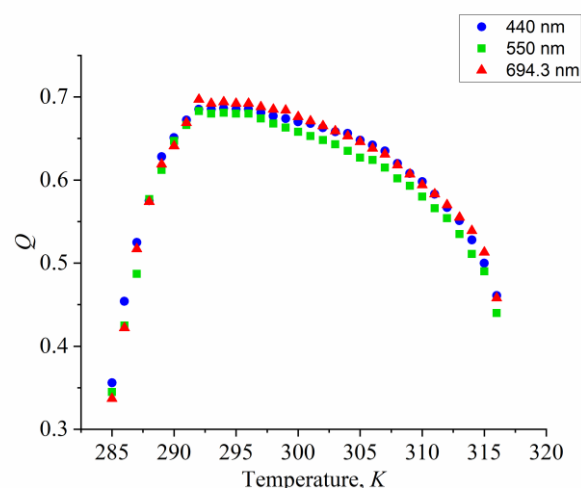


Figure 3. The temperature-dependent order parameter for 440 nm, 550 nm and 694.3 nm wavelengths.

4. Conclusion

In the present study, both the birefringence and order parameter of a lyotropic N_C mesophase were found from the optical transmittances for different wavelengths under the microscope. A variety of methods, especially laser conoscopy, are used to obtain order parameter [19,20]. On the other hand, this study shows obtaining the birefringence and order parameter more sensitively by measuring the optical transmittances only using polarizing microscopy. By evaluating the parameter more easily, the analysis of the physical properties of liquid crystals could be made simpler, especially in applications.

Conflicts of interest

The authors state that did not have conflict of interests.

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