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OPTICAL ANISOTROPY OF NEMATIC LIQUID CRYSTALS

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Temperature dependence of the principal refractive indices $(n_0, \text{ and } n_e)$ of three nematic liquid crystals were measured using an Abbé refractometer with a large refractive index prism. The variation of the refractive index anisotropy in the nematic phase which reflects the variation of the orientational order parameter have been evaluated. The validity of the Lorenz-Lorentz equation for the relation between polarizability of the molecules and the refractive index has been tested for the mesogenic molecules.

Keywords: Nematic liquid crystals; ordinary and extraordinary refractive indices; optical anisotropy

1. INTRODUCTION

The mesogenic phase **of a** uniaxial nematic liquid crystal is optically anisotropic. It has two principal refractive indices, n_o and n_e . The first one, n_o , is observed for an "ordinary" ray associated with the light wave where the electric vector vibrates perpendicular to the optical axis. The "extraordinary" index, n_e , is observed for linearly polarized light wavc where the electric vector is parallel to the optical axis. The optical anisotropy of the liquid crystal, $\Delta n = n_e - n_o$ is large and controllable by an external field. Many electro-optical devices employing liquid crystals take advantage of the fact that a significant phase change can be accomplished by a reasonable low voltage. Examples are liquid crystal based tunable phase retardation plate [1], a liquid crystal light switch [2], a large screen high-definition color liquid

crystal display [3], etc.. For display applications employing liquid crystals, knowledge of its optical anisotropy is particularly important.

The optical anisotropy of liquid crystals are governed by the liquid crystal constituents, wavelength and temperature considered. In the mesogenic phase of a liquid crystal, n_o is found to increase slightly as temperature increases, however, a more pronounced change occurs near the phase transition. Contrary to n_o , n_e declines as temperature rises $[4-7]$.

Measurement of the refractive indices of a liquid crystal can conveniently be carried out using Abbe's double-prism method. In this method the liquid crystal is used as a thin film between the hypotenuse areas of the two prisms. If the refractive index of the prism is greater than the indices of the liquid crystal, the boundary angles corresponding to total reflection of ordinary as well as extraordinary ray can be measured. In practice it suffices to use a commercial refractometer, which provides direct reading of n_o and n_e .

In this paper we report the temperature dependence of principal refractive indices anisotropy of three liquid crystals E_7 , E_8 and K_{24} measured using an Abbé refractometer.

2. EXPERIMENTAL DETAILS

The refractive indices, n_o and n_e , for the mesogenic, and n_i that is for the isotropic phase of the liquid crystal was measured using an Abbé refractometer (Bellingham and Stanley Ltd., model 60/ED) with a large refractive index prism (prism index: 1.76142 for 589.6 nm sodium *D*). The value of the refractive indices measured by Abbé refractometer were calibrated by the scale of the sodium *D-* line and refractive indices could be measured from with an accuracy of ± 0.0001 . To obtain homeotropic molecular orientation at the interface, the heated liquid crystal in the isotropic state were allowed to fall as drops on the lecithin coated surface of the fixed prism, gradually cooled, and kept for several tens of minutes. A polarizer was attached to the eye lens of the refractometer, the ordinary or the extraordinary ray was selected by adjusting its polarization direction, and then each refractive index, n_o and n_c was measured. The temperature of the liquid

crystal was controlled by circulating water from *a* bath whose temperature was controlled to ± 0.1 °C.

Three liquid crystals used for the study, E_7 , E_8 and K_{24} (BDH Chemicals, U. **K.),** are cyanobiphenyl based compounds. *E7* and *Ex* are nematic liquid crystals while K_{24} is polymorphic with nematic and smectic A phases. The nematic-isotropic (T_{NI}) and the smectic A nematic (T_{AN}) transition temperatures were determined using a polarizing microscope equipped with a heating stage. The following transition temperatures were obtained: E_7 : $T_{NI} = 60.0^{\circ}\text{C}$; E_8 : T_{NI} = 70.5°C; K_{24} : T_{AN} = 33.5°C, T_{NI} = 40.5°C. These values are in agreement with the transition temperatures reported earlier for these liquid crystals [8,9]. During the measurement the liquid crystal which is in contact with air is subject to chemical degradation. The transition temperature was therefore checked for each of these liquid crystals at the end of the measurement. However, no significant changes were observed.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Temperature dependence of refractive indices, n_o for the ordinary ray and n_e for the extraordinary ray measured at the sodium *D* line in the nematic phase for the liquid crystals E_7 , E_8 and K_{24} are shown in Figures I(a). (b) and (c), respectively. The data are presented in terms *of the reduced temperature* $\Gamma = (T - T_{NI})/T_{NI}$, with $\Gamma = 0$ corresponds to the transition temperature $T_{ML} \Gamma \le 0$ the nematic phase and $\Gamma \ge 0$ the isotropic phase. In the temperature range measured in this work, n_e tends to decrease monotonically as the temperature rises in all liquid crystals. On the other hand, n_o is found to increase monotonically as the temperature increases. In both cases the change is more pronounced as temperature approaches T_{M} . For $\Gamma > 0$, the liquid crystal turns into an isotropic liquid and the anisotropy in the refractive index disappears.

Note that the data for the smectic phase for the liquid crystal K_{24} is not presented here. The liquid crystal becomes *so* thick in the smectic phase so that **too** much of light is being absorbed in the sample **film** or being so scattered that the detinition is lost. The boarder line as seen in

FIGURE 1 Refractive indices of liquid crystals E_7 , E_8 and K_{24} versus reduced temperature $\Gamma = (T - T_{NI}) \cdot T_{NP}$

the field telescope will not have good contrast and the accuracy of the measurement will be considerably reduced. We could not, therefore, get reproducible result in the smectic A phase.

The decrease of n_e and the increase of n_o in the nematic phase as the temperature approaches the transition has resulted in a decrease in the optical anisotropy. It is known that the optical anisotropy is related to the orientational order parameter **S** as [IO].

$$
\Delta n \sim \rho^{1/2} S \tag{1}
$$

where ρ is the density. As the variation of ρ over the temperature range of the nematic phase is very small, this means that relatively easy measurement of the temperature dependence of Δn gives a good indication of the variation of **S** with temperature. The variation of the refractive index anisotropy reflecting the orientational order parameter in the nematic phase for the three liquid crystals is given in Figure *2.*

The validity **of** the Lorenz - Lorentz equation for the relation between the polarizubility **of** the molecule and the refractive index (or dielectric constant in the high frequency limit) of dense liquids has been the subject of many experimental and theoretical investigations. Several models have been developed for correlating the refractive

FIGURE 2 Optical anisotropy, Δn versus reduced temperature $\Gamma = (T/T_{NP})T_{M}$ for liquid crystals E_7 , E_8 and K_{24} .

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indices of liquid crystals to its microscopic molecular parameters $[11 -$ 131. A semi-emperical formula correlating molecular polarizabilities of a liquid crystal with macroscopic refractive indices has been obtained by Vuks [14]:

$$
(\overline{n^2} - 1)/(\overline{n^2} + 2) = \left(\frac{4}{3}\pi\right)N\bar{\alpha}
$$
 (2)

where $\bar{\alpha}$ is the mean polarizability, *N* is the number of molecules per unit volume, and in the nematic phase

$$
\overline{n^2} = (n_e^2 + 2n_o^2)/3\tag{3}
$$

is the averaged value of the two refractive indices. In the isotropic phase $n=n_i$, the measured refractive index. In Vuks' equation the local-field effect has been assumed to be isotropic. Although Vuks' equation was not derived rigorously, it provides some important physical insight for understanding the refractive indices of an anisotropic liquid crystal.

Since the mean polarizability is independent of temperature and the state of matter, a plot of the left-hand side of equation (2) as a function of temperature, if the formula is applicable, reflect the temperature variation of density only. In Figure 3 we have plotted the left-hand side of equation (3) against the reduced temperature, Γ , for the liquid crystal *E,.* As seen in the figure, the trend of variation is very similar to that of the density data available from a previous work [15]. With increase in temperature the data tends to decrease slowly in the nematic phase away from the transition. However, significant variation has been observed on approaching the transition temperature. This is also very similar to the observed drop in density as the transition temperature is approached [15].

Active researches are being carried out that aim at applications of liquid crystals to various sensors and optical devices, mainly to display devices. It is becoming increasingly important that the accurate values of refractive indices and birefringence should be measured for an optimum design of these various devices. Another subject of interest, as far as applications are concerned, is the dispersion properties of liquid crystals. Both these measurements require the use of a more

FIGURE 3 Temperature dependence of $(\overline{n^2} - 1)/(\overline{n^2} + 2)$ for liquid crystal E_7 .

accurate temperature control device to look more close to the phase transition. Experiments in this direction are under way.

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