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THICKNESS DEPENDENCE OF REFRACTIVITY IN WALL-ADJACENT EPITROPIC LIQUID CRYSTAL

UDC 535.34

Peculiarities of the behavior of some optical characteristics of orientationally ordered wall-adjacent layers of nonmesogenic liquids – epitropic liquid crystals (ELC) – are analyzed. A suggested model develops the well-known Maier–Saupe–Neugebauer theory and takes a two-component structure of ELC (dynamic equilibrium between monomers and dimers) into account. The experimentally measured thickness and temperature dependences of the refractive index and the value of birefringence are in good agreement with theoretical calculations.

Keywords: orientationally ordered wall-adjacent layer; dimer, monomer, refractive index, birefringence.

1. Introduction

Under certain conditions, a solid substrate may induce an orientational ordering in wall-adjacent layers of some nonmesogenic organic liquids, which were called epitropic liquid crystals (ELC) because of a similarity of their physical properties to those of nematic liquid crystals. The effect of orientational ordering with the value of order parameter S of about 0.2–0.4 was found in ELC layers. It was shown that two types of molecular particles in the studied system exist, namely, dimers (D) and monomers (M). The D-concentration decreases, the M-concentration increases, and the S value sharply decreases to zero the in isotropic bulk phase, as the distance to the solid substrate increases [1–3, 5]. Earlier, in various works [1–5], such properties were investigated experimentally, and some models were suggested in order to explain this phenomenon. In particular, the interfacial structure of liquid layers at solid interfaces has been a subject of numerous molecular dynamics simulations [6, 7], and various semiphenomenological models [8–10] were suggested. Thermodynamic and dielectric peculiarities of these layers were discussed in [2], but the complete explanation of some of their optical properties is still needed.

The aim of this paper is to propose a theoretical model that describes some peculiarities of ELC optical properties.

2. Theoretical Model

It is well known [11–13] that the following relations are satisfied with high accuracy for the crystal, liquid crystal, and isotropic phases of mesogenic liquids:

$$\left(\frac{1}{\rho} \times \frac{\bar{\varepsilon} - 1}{\bar{\varepsilon} + 2}\right)_{\mathrm{C}} = \left(\frac{1}{\rho} \times \frac{\bar{\varepsilon} - 1}{\bar{\varepsilon} + 2}\right)_{\mathrm{LC}} = \ldots$$

$$\ldots = \left(\frac{1}{\rho} \times \frac{\bar{\varepsilon} - 1}{\bar{\varepsilon} + 2}\right)_{\mathrm{ISO}} = \mathrm{const}, \qquad (1)$$

where $\bar{\varepsilon}_{\mathrm{C}}$ and $\bar{\varepsilon}_{\mathrm{LC}}$ are the dielectric permittivities of the crystal and uniaxial liquid crystal phases, respectively.

$$\bar{\varepsilon}_{\mathrm{C}} = \frac{1}{3}\left(n_1^2 + n_2^2 + n_3^2\right), \quad \bar{\varepsilon}_{\mathrm{LC}} = \frac{1}{3}\left(n_\parallel^2 + 2n_\perp^2\right), \quad (2)$$

where $n_{1,2,3}$ are the main refractive indices of a crystal, $n_{\parallel,\perp}$ are the refractive indices of a liquid crystal, and ρ is the density of the system under study.

In order to calculate the refractive indices of the above-mentioned thermodynamic phases, the Maier–Saupe–Neugebauer model based on Eq. (1) was suggested [14, 15]. It allows one to establish a relation between the tensor components of the dielectric permittivity and the effective molecular polarizability in the main coordinate system of crystals with one molecule in the unit cell. Maier and Saupe used this lattice model for a uniaxial liquid crystal and assumed that the main value of polarizability $\bar{\gamma}$ does not depend on the phase state and on the degree of molecular ordering of the mesophase. The Maier–Saupe
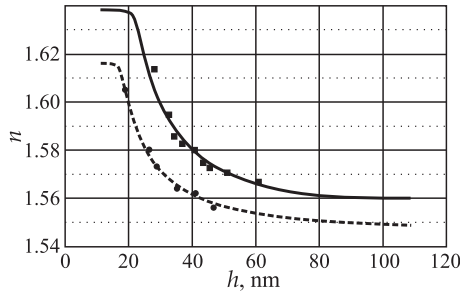
Fig. 1. Thickness dependence of the refractive index of a nitrobenzene wetting film formed on the quartz substrate at various temperatures. Experimental results (■ – $t = 20$ °C, ● – $t = 50$ °C) and the results of calculations (solid and dotted curves)
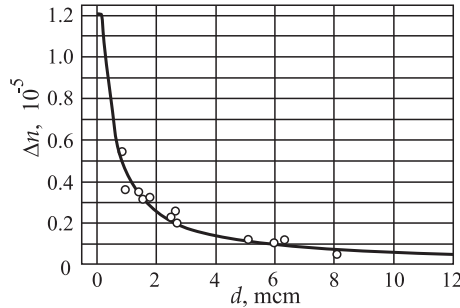

Fig. 2. Thickness dependence of the birefringence of a nitrobenzene interlayer $\Delta n(d) = a \times S$, $a = 3.02 \times 10^{-5}$ bounded by quartz substrates. Experimental results and the results of calculations
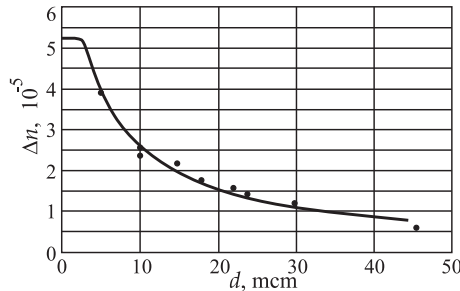

Fig. 3. Thickness dependence of the birefringence of a nitrobenzene interlayer $\Delta n(d) = a \times S$, $a = 4.22 \times 10^{-5}$ bounded by conductive substrates. Experimental results and the results of calculations

model is based on the Lorenz–Lorentz equation for the isotropic phase:

$$\frac{\varepsilon_i - 1}{\varepsilon_i + 2} = \frac{4\pi \times N_i}{3}\bar{\gamma}_i, \qquad (3)$$

which allows one to overcome the difficulties connected with the choice of the uniaxial unit cell type and with the uncertainty of cell parameters. Here, N_i is the number of molecules per unit volume. For uniaxial liquid crystals, an analog of Eq. (3) can be written as

$$\bar{\varepsilon} - 1 = 4\pi \cdot N \left[\bar{\gamma}\bar{f} + \frac{2}{9}S\Delta\gamma \times \Delta f\right],$$

and rewritten in the form proposed in [15, 16]:

$$\frac{1}{\rho} \times \frac{\bar{\varepsilon} - 1}{\bar{\varepsilon} + 2} = \frac{4\pi \times N_A}{3M}\bar{\gamma} \times ...$$

$$... \times \left[1 + \frac{2\Delta\varepsilon \times \tau}{\bar{\varepsilon} + 2} + \frac{2S\Delta\gamma \times \Delta f}{3\bar{\gamma} \times (\bar{\varepsilon} + 2)}\right]. \qquad (4)$$

All parameters in Eq. (4) are given in [15]. Taking into account that $\bar{n}^2 = \bar{\varepsilon}$, we obtain the expression for the dependence $\bar{n}(S)$ in ELC layers:

$$\bar{n}(h, T) = \sqrt{a + b \times S(h, T)}. \qquad (5)$$

Here, a and b are the constants determined by the comparison of Eqs. (4) and (5). The constants a and b in (5) are functions of the temperature because of the temperature dependence of the factor in square brackets in Eq. (4). Their values were determined by the comparison with experimental results with regard for the temperature and thickness dependences of the order parameter $S(T, h)$ of an ELC layer. The two-component model of ELC proposed in [2, 5] was used to determine this dependence. The experimental data on the order parameter S characterize the state of orientational ordering throughout the interlayer. That is why the values, which were substituted in formula (5), were averaged over the thickness as

$$S = \frac{1}{h}\int_0^h \{[p(x)S_1(x) + [(1 - p(x))]S_2(x)]\}\,dx,$$

where S_1 and S_2 are the order parameters of monomers and dimers, respectively. Finally, the values of a and b parameters were calculated by the least square method.

At the same time, the degree of anisotropy of various physical characteristics may be used to characterize the state of ordering of the studied sample. The degree of surface-induced optical birefringence

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$\Delta n = n_{\parallel} - n_{\perp}$ is a convenient parameter, which is closely correlated with the value of order parameter S [17–20]. It was shown [18–21] that the proportionality $\Delta n \sim S$ holds within several percent.

3. Results and Discussion

The ellipsometric study of a wetting film [22] disposed on the quartz substrate allowed one to calculate the thickness h of the film and its refractive index n by the Drude model [23]. It was assumed in [22] that the value of refractive index is almost constant within the film. However, the correct recalculation of experimental results shows that $\overline{n}$ value increases near the solid substrate, i.e., with the film thinning. The retreatment of experimental results according to Eq. (5) by the least square method yielded the following values of a and b constants: $a = 2.3601$, $b = 0.7326$ at $t = 20\,°C$ and $a = 2.3786$, $b = 0.5649$ at $t = 50\,°C$. Experimental results and the theoretically calculated curve are shown in Fig. 1.

Analyzing the results presented in Fig. 1, it is possible to conclude that

1. Within an orientationally ordered ELC layer, the refractive index is almost constant, and its value decreases with the temperature.

2. The ELC equilibrium thickness decreases with the temperature because of the layer-by-layer melting.

3. Increasing the distance to the solid substrate leads to a monotonic decrease of the refractive index. The refractive index approaches asymptotically the bulk values (isotropic liquid phase) $n = 1.56$ ($t = 20\,°C$) and $n = 1.55$ ($t = 50\,°C$).

The value of surface induced birefringence was measured earlier [1, 24] by the micropolarimetry of a plane light-guide with variable thickness, by using the Senarmon compensator. The experimentally determined value of phase shift $\Delta\varphi$ allowed us to calculate the value of birefringence using the obvious relation $\Delta\phi = \frac{2\pi}{\lambda}\Delta n \times L$, where λ is the wave length ($\lambda = 0.543$ mcm), and L is the optical path ($L \sim 1$ mm). The liquid interlayers were bounded both with conductive (metallic) and dielectric substrates. Note that the substrate material determines essentially various properties of the wall-adjacent layers.

The approximation of the results by the relation $\Delta n \sim S$ shows a good agreement with the experimental data (see Figs. 2 and 3).

4. Conclusions

A two-component model of ELC that has been proposed above gives a good explanation of the measured optical peculiarities such as the thickness and temperature dependences of the refractive index and the order of birefringence in a two-phase liquid interlayer.

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ТОВЩИННА ЗАЛЕЖНІСТЬ
КОЕФІЦІЄНТА СВІТЛОЗАЛОМЛЕННЯ
ЕПІТРОПНИХ РІДКИХ КРИСТАЛІВ

Р е з ю м е

Проаналізовано особливості поведінки деяких оптичних
властивостей орієнтаційно впорядкованих приповерхневих
шарів немезогенних рідин – епітропних рідких криста-
лів (ЕРК). Запропоновано модель, яка є розвитком тео-
рії Майера–Заупе–Нойгебауера і враховує двокомпонентну
структуру ЕРК (динамічна рівновага між димерами та мо-
номерами). Експериментальні результати по товщинним і
температурним залежностям коефіцієнта рефракції та ве-
личини двопроменезаломлення досить добре узгоджуються
з теоретичними розрахунками.

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ТОЛЩИННАЯ ЗАВИСИМОСТЬ
КОЭФФИЦИЕНТА ПРЕЛОМЛЕНИЯ
ЭПИТРОПНЫХ ЖИДКИХ КРИСТАЛЛОВ

Р е з ю м е

Анализируются особенности поведения некоторых оптиче-
ских свойств ориентационно упорядоченных приповерхно-
стных слоев немезогенных жидкостей – эпитропных жид-
ких кристаллов (ЭЖК). Предлагается модель, которая
является развитием теории Майера–Заупе–Нойгебауэра и
учитывает двухкомпонентную структуру ЭЖК (динамиче-
ское равновесие между димерами и мономерами). Экспе-
риментальные результаты по толщинной и температурной
зависимостям коэффициента преломления и величины дву-
лучепреломления достаточно хорошо согласуются с теоре-
тическими расчетами.