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The Method of the Order Parameter "S" Calculations for Cholesteric Liquid Crystals

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On the basis of experimentally determined polarisability anisotropy the order parameter S for cholesteryl propionate, nonanoate and decanoate was calculated. In this work to avoid difficulties in the determination of S for other esters of the investigated homologous series a method of calculation S is proposed. The S_0 and η coefficients were obtained from the equation

$$S = S_0\left[1 - \frac{T}{T_c}\right]^{\eta}$$

It makes the calculation of the temperature dependence of S for any compound of the series of cholesteryl esters of homologous fatty acids possible. The method was verified for cholesteryl myristate.

The degree of order of molecules in mesomorphic materials is a very important parameter for knowledge of their structure and properties. Its value is a component of the equation for calculations of free energy. Much attention was paid recently to the question of the determination of the order parameter. The purpose of this work is the application to cholesteric esters of homologous fatty acids of formula enabling calculations of order parameter in nematic compounds.[1,2] Literature dealing with nematic compounds is relatively comprehensive. Methods used for nematic crystals are, however, not always suitable for cholesteric liquid crystals. Among experimental methods being used NMR spectroscopy, investigations of X-ray diffraction on liquid crystal layers, dichroism and optical methods should be mentioned. Papers on order parameter "S" determination in a cholesteric phase are not numerous.[3–6] Optical methods being the most frequently used.

The authors applied in this work the optical method based on measurements of refractive indices with an Abbe refractometer and determined in this way the order parameter. The refractive indices were measured as a function of temperature; density, however, necessary for polarizability determination were taken from literature.[7,8] No literature data on cholesteryl decanoate were available. Since its molecule differs from that of cholesteryl nonanoate by a CH_2 group, the only difference in their density values are slight. The density values calculated for cholesteryl nonanoate were applied as well for cholesteryl decanoate. The knowledge of experimental data i.e. values of refractive indices and density[6-8] in mesophases as well as in the solid state made it possible to determine the degree of order for the investigated liquid crystals.

Calculations of the order parameter S from refractive indices data require their values not only in individual mesophases but also in the solid state. The difficulty lies in obtaining the solid state which is necessary for the determination of polarizability anisotropy. Measurements of refractive indices of cholesteric liquid crystals in the solid phase by the refractometric method are possible only if a growing spherulite appears in the field of vision of the instrument and is considerably greater than the observed field. It becomes essential to grow a spherulite with uniformly oriented part located in the refractometer's field of vision. To obtain such spherulites the proper thermal treatment is required. The thermal treatment consisted of a selection of the isothermal crystallization temperature which for the compounds investigated was in the range 35–40°C. From the isothermal crystallization temperature dependence of growth rate and nucleation rate it appears that the rise of temperature causes the increase of spherulite growth rate as well as the decrease of nucleation rate.[9] Practically, for each liquid crystalline compound the selection of a proper temperature of isothermal crystallization is necessary. Data[9,10] were utilized for the growth of spherulites in cholesteryl propionate, nonanoate and decanoate. The impossibility of the observation of a single spherulite during each measurement is responsible for a considerably greater dispersion of refractometrically determined refractive indices in the solid state when compared to those in the mesophases. Of the investigated cholesteryl esters, only cholesteryl propionate, nonanoate and decanoate possess sufficiently slow crystallization processes in the form of spherulites, to obtain satisfactory spherulites for other cholesteric compounds is very difficult.

The relation between the order parameter S and the polarizability anisotropy $\Delta\alpha$ is mesophases and $\Delta\gamma$ in the solid state is expressed:

$$S = \frac{\Delta\alpha}{\Delta\gamma} \tag{1}$$

It is accepted[1,2] that the dependence of the order parameter on reduced temperature is of exponential character:

$$S = S_0\left[1 - \frac{T}{T_c}\right]^{\eta} \tag{2}$$

For nematic compounds such an approximation results in values being in agreement with those obtained experimentally. Finding S_0 and η coefficients would make therefore calculations of temperature dependence of the order parameter for each compound of the homologue series possible.

The purpose of our work is to find S_0 and η values and next the verification of Eq. (2) for cholesteric esters of the homologous fatty acids. In this work experimental valus of refractive indices for cholesteryl propionate,[11] nonanoate,[6] and decanoate (Figure 1) were applied to determine the polarizability anisotropy of the compounds in the solid state.

The polarizability anisotropy was calculated according to the Vuks model,[12] V, and from the Lorentz-Lorenz equation, LL, given in the form found in Ref. 6. Temperature dependence of the order parameter was then

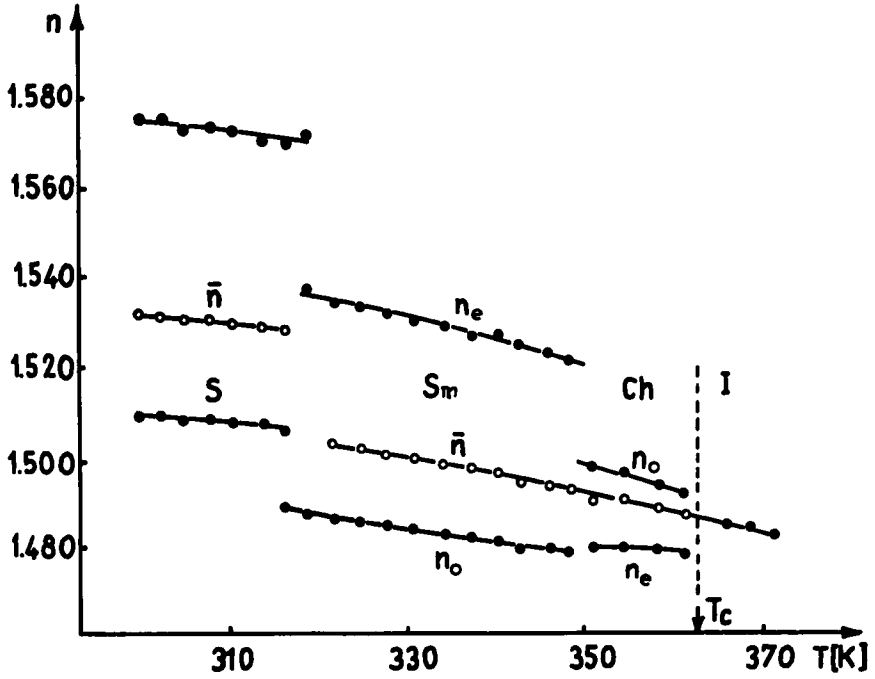

FIGURE 1 Relationship between light refractive indices and temperature for cholesteryl decanoate.

TABLE I

	cholesteric mesophase			smectic mesophase		
	S_o	η	$\bar{\eta}$	S_o	η	$\bar{\eta}$
model LL	0.55	0.15–0.2	0.17	0.98	0.08–0.11	0.09
model V	0.53	0.15–0.2	0.17	0.99	0.08–0.12	0.10

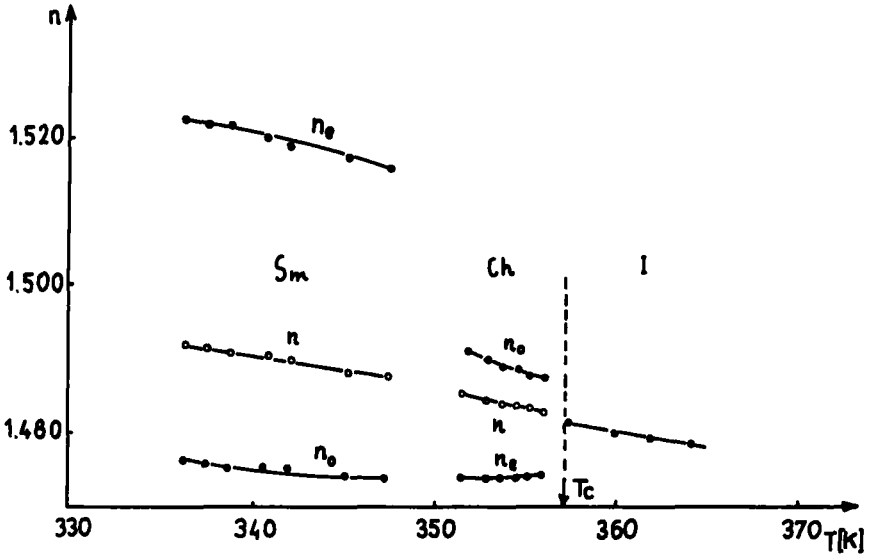

FIGURE 2 Refractive indices, n, vs. temperature T for cholesteryl myristate.

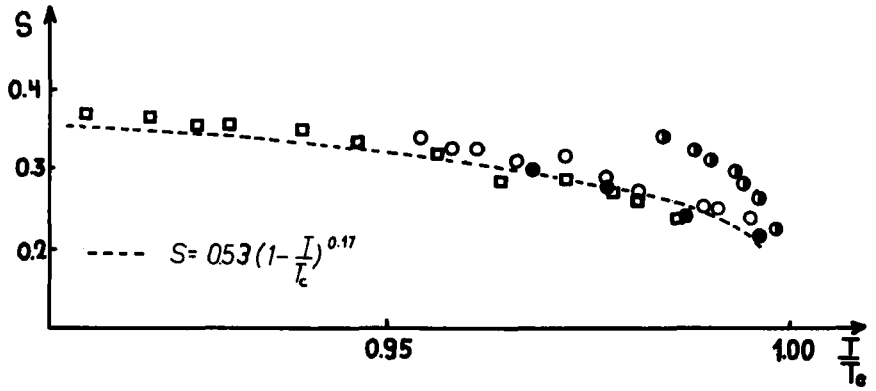

FIGURE 3 Order parameter S as a function of temperature for cholesteric mesophase (model V), (□—cholesteryl propionate, ○—cholesteryl nonanoate, ●—cholesteryl decanoate, ◑—cholesteryl myristate).

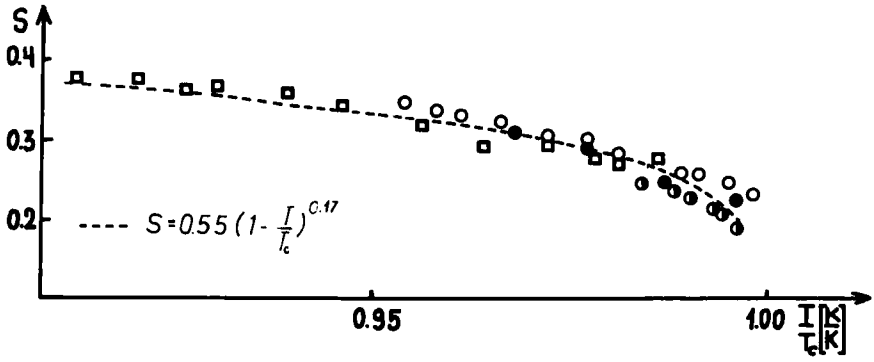

FIGURE 4 Order parameter S vs. temperature for cholesteric mesophase (model LL), (□—cholesteryl propionate, ○—cholesteryl nonanoate, ●—cholesteryl decanoate, ◑—cholesteryl myristate).

found from the Eq. (1). It enabled finding S_0 and η from Eq. (2) for all three investigated compounds (Table I).

The above data may suggest that all the compounds from the homologous series will have identical values of their coefficients. It would allow the calculation of the order parameter S dependence on temperature for any compound from Eq. (2) in relation to melting points and mesophase ranges. As an example, the obtained values of S_0 and η were applied for calculations of S temperature dependence for cholesteryl myristate. Obtained temperature dependence of refractive indices for cholesteryl myristate are presented on Figure 2. To

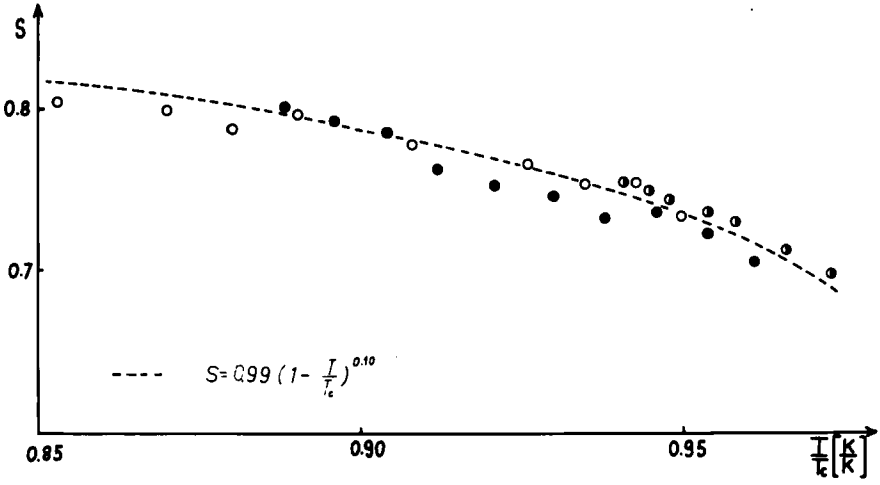

FIGURE 5 Order parameter S vs. temperature for smectic mesophase (model V), (○—cholesteryl nonanoate, ●—cholesteryl decanoate, ◑—cholesteryl myristate).

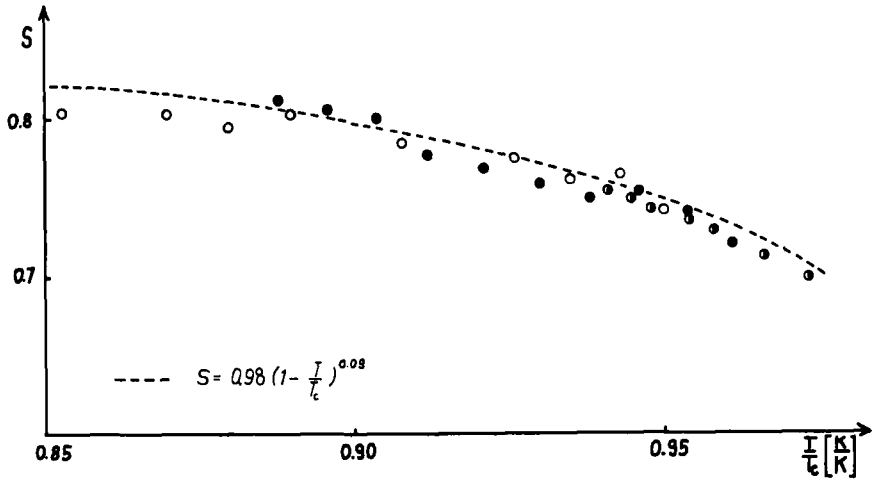

FIGURE 6 Order parameter S vs. temperature for smectic mesophase (model LL), (○—cholesteryl nonanoate, ●—cholesteryl decanoate, ◑—cholesteryl myristate).

calculate the order parameter S temperature dependence S_0 and η values were obtained from the Vuks and Lorentz-Lorenz model were applied.

The calculated results are presented in Figures 3–6 for smectic and cholesteric mesophases and coefficients S_0 and η obtained from the models of Vuks and Lorentz-Lorenz respectively. For both models good, agreement of Eq. (2) originated curve with the experimental curve was achieved. In our opinion the proposed method should yield satisfactory results for other compounds from the investigated homologous series.

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