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Classical behaviour of the non-linear dielectric effect in the isotropic phase of nematogens

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Results are presented of temperature and pressure studies of the non-linear dielectric effect (NDE) in the isotropic phase of MBBA (*N*-4-methyoxybenzylidene-4′-*n*-butylaniline) and EBBA (*N*-4-ethoxybenzylidene-4′-*n*-butylaniline). In both nematogens the pretransitional increase of the NDE is described by the classical relation obtained on the basis of the Landau–de Gennes model. The value of the ratio of amplitudes describing the pretransitional effect of MBBA and EBBA shows a dependence on the measurement frequency of the NDE (a few MHz). In nematogens with a large positive anisotropy of the electric permittivity, change in the measurement frequency even leads to a change in sign of the NDE on approaching the clearing temperature.

1. Introduction

Studies of the Kerr effect (KE), the Cotton–Mouton effect (CME) and the intensity of scattered light (I) are standard procedures for investigating the properties of the isotropic–nematic transition [1–3]. They also enable determination of certain molecular characteristics of the nematic phase in the isotropic phase. This is possible because the behaviour of these quantities may be described by the Landau–de Gennes model [3], which predicts the same, classical (mean field) type of temperature behaviour for all the properties mentioned [1–3]

$$\text{KE, CME}, I \simeq \frac{1}{T-T^*}, \quad T^* = T_c - \Delta T, \quad T > T_c, \tag{1}$$

where T_c is the clearing temperature, ΔT is the value of the discontinuity of the phase transition, and T^* denotes the extrapolated temperature of the hypothetical, continuous phase transition.

In this group of effects may be classed the non-linear dielectric effect (NDE), which is the measure of changes in electric permittivity ($\Delta\varepsilon^E = \varepsilon^E - \varepsilon$) due to the application of a strong electric field (E). To a large extent the NDE is an analogue of the Kerr effect for radio frequencies [4].

In this paper the behaviour of the NDE in the isotropic phase of nematogens is discussed.

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2. Experimental

The measurements described were made by means of an apparatus based on an idea proposed by Małecki [5]. Changes in electric permittivity for a measurement frequency of about 5 MHz were induced using rectangular, 1 ms pulses from a strong (DC) electric field. The sample was placed in a flat, parallel capacitor of 0·3 mm gap and applied voltage of 300–1000 V.

In NDE studies, it is important to prepare samples with a relatively low conductivity [4, 5]. For this reason samples of all liquid crystal materials studied were degassed immediately prior to the measurement.

Studies have been conducted using the isotropic phase of two nematogens, belonging to the same homologous series, namely MBBA (*N*-4-methyoxybenzylidene-4′-*n*-butylaniline) and EBBA (*N*-4-ethoxybenzylidene-4′-*n*-butylaniline). Their clearing temperatures are 44·9 and 76°C, respectively.

3. The Landau–de Gennes model

de Gennes applied Landau's description of the weakly discontinuous phase transition to the case of the isotropic–nematic transition [1, 3]

$$f = f_i + \tfrac{1}{2}Q_{\alpha\beta}Q_{\alpha\beta} - \tfrac{1}{3}Q_{\alpha\beta}Q_{\alpha\gamma}Q_{\gamma\alpha} + \tfrac{1}{4}C(Q_{\alpha\beta}Q_{\beta\alpha})^2 + \dots, \tag{2}$$

where f_i is the part of the Gibbs free energy f density describing the isotropic liquid. The other terms of the above series are associated with nematic fluctuations on approaching the clearing temperature. The tensor order parameter may be written as

$$Q_{\alpha\beta} = S(3n_\alpha n_\beta - \delta_{\alpha\beta}), \tag{3}$$

where S is the scalar order parameter, n_α and n_β are components of the unit vector describing the orientation of the rod-like molecule. This gives

$$Q_{\alpha\beta}Q_{\beta\gamma} = \tfrac{2}{3}S^2, \quad Q_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha} = \tfrac{2}{9}S^2, \tag{4}$$

and

$$f = f_i - AS^2 - \tfrac{2}{27}BS^3 + \tfrac{1}{9}CS^4 + \dots. \tag{5}$$

For a weakly discontinuous transition, fluctuations are small and in relation (2) only the first terms need to be taken into account. Hence, for the NDE measurements

$$f_n = f_i + \tfrac{1}{2}a(T - T^*)S^2 - \tfrac{1}{3}\varepsilon_0\Delta\varepsilon^0 SE^2, \tag{6}$$

where ε_0 is the dielectric constant, $\Delta\varepsilon^0$ denoted the anisotropy of the electric permittivity of a molecule of the nematogen for the zero-frequency limit, and a is the amplitude. This relation has a minimum for

$$S = \frac{\varepsilon_0\Delta\varepsilon^0 E^2}{3a(T - T^*)}. \tag{7}$$

The electric permittivity for the measurement frequency of NDE (lying typically in the range of a few MHz) may also be used as an order parameter. Using relation (3), it follows that

$$\Delta\varepsilon^E = \varepsilon^E - \varepsilon = \tfrac{2}{3}\Delta\varepsilon^f S, \tag{8}$$

where $\Delta\varepsilon^f$ is the anisotropy of the electric permittivity of the molecule for the measurement frequency f.

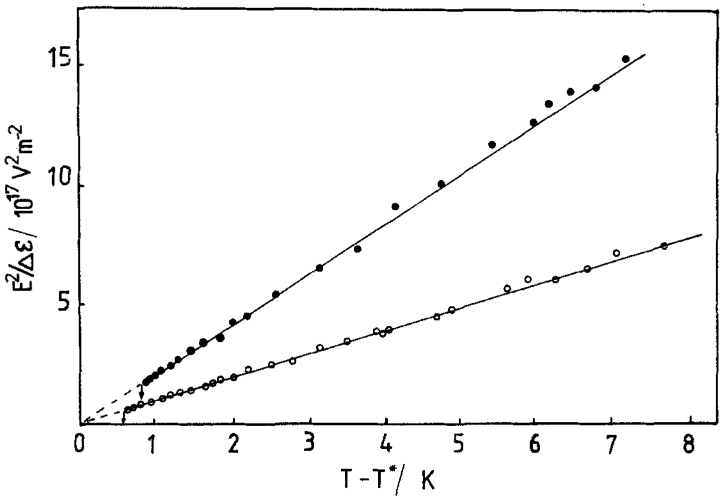

Figure 1. Inverse of the NDE versus temperature for MBBA (open circles) and EBBA (full circles). Arrows indicate the clearing point.

A combination of the last two relations gives

$$\frac{\Delta\varepsilon^E}{E^2} = \varepsilon_0 \frac{2}{9a} \frac{\Delta\varepsilon^0 \Delta\varepsilon^f}{(T - T^*)}, \quad \text{for} \quad T > T_c, \quad T^* = T_c - \Delta T. \tag{9}$$

4. Experimental results

The results of measurements of the NDE in the isotropic phase of MBBA are presented in figure 1 and show that the pretransitional increase in NDE on approaching the clearing temperature is described by the relation

$$\frac{\Delta\varepsilon^E}{E^2} \simeq \frac{11}{(T - T^*)} (10^{-18} \, m^2 \, V^{-2}), \tag{10}$$

i.e. with the classical exponent $\psi = 1$.

The determined value of $\Delta T = 0{\cdot}68 \pm 0{\cdot}05$ is, within the limits of experimental error, the same as in the earlier, preliminary studies of the NDE [6] and the investigations by means of other methods mentioned in the introduction [1–3, 7–9].

The same type of temperature behaviour has also been obtained using EBBA (see figure 1)

$$\frac{\Delta\varepsilon^E}{E^2} \simeq \frac{5{\cdot}5}{(T - T^*)} (10^{-18} \, m^2 \, V^{-2}). \tag{11}$$

The value of $\Delta T = 1{\cdot}1 \pm 0{\cdot}05°C$ is also in agreement with that obtained earlier in the Kerr effect studies [10]. In the analysis, for both samples tested, a small non-critical background effect has been taken into account.

The amplitude of the NDE for EBBA is much less than that for MBBA. This further supports relation (9), because $\Delta\varepsilon^0 \simeq 0{\cdot}6$ for MBBA and $\Delta\varepsilon^0 \simeq 0{\cdot}3$ for EBBA [10]. It is worth mentioning that for cholesteryl oleate and cholesteryl oleyl carbonate, on approaching the blue phase, both the anisotropies of the electric permittivities and the amplitudes of the NDE are about one-tenth of those obtained in the present studies [11].

Comparison of absolute values of amplitudes calculated from theory with experimental values may be ambiguous due to experimental errors. This may be

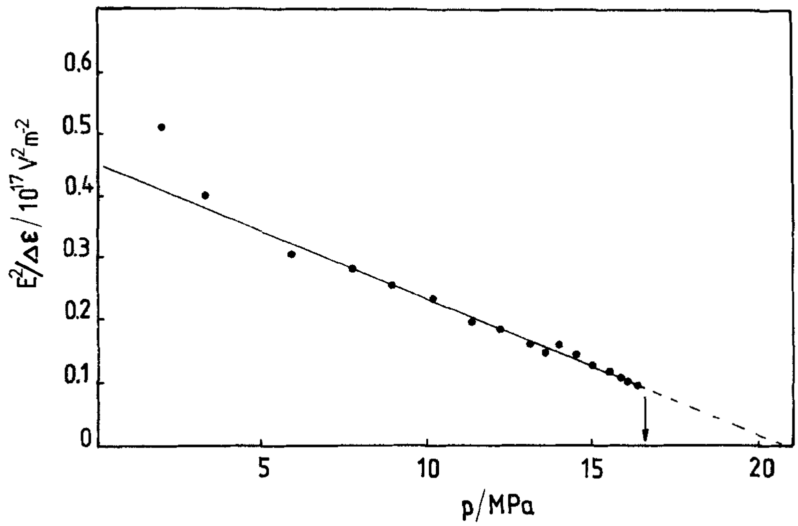

Figure 2. Isothermal dependence of the $(NDE)^{-1}$ versus hydrostatic pressure on approaching the clearing point for MBBA. The arrow indicates the clearing point. Parameters: $T = \text{const.} = 52°C$, $p_c \simeq 16{\cdot}5$ MPa, $\Delta p \simeq 5$ MPa.

minimized by analysing the ratio of the amplitudes for MBBA and EBBA, obtained using the same measurement apparatus. Based on relation (9)

$$\frac{A_{MBBA}}{A_{EBBA}} = \frac{a_{EBBA}}{a_{MBBA}} \frac{(\Delta\varepsilon^f \Delta\varepsilon^0)_{MBBA}}{(\Delta\varepsilon^f \Delta\varepsilon^0)_{EBBA}}. \tag{12}$$

Substituting—see [10]

$$\frac{a_{EBBA}}{a_{MBBA}} \simeq 1{\cdot}7, \quad (\Delta\varepsilon^0)_{MBBA} \simeq -0{\cdot}6, \quad (\Delta\varepsilon^0)_{EBBA} \simeq -0{\cdot}3,$$

and assuming that instead of the unknown value of $\Delta\varepsilon^f$, the anisotropy of the polarizability may be introduced [12]

$$(\alpha)_{MBBA} \simeq 3{\cdot}8 \times 10^{-24}\,\text{cm}^3, \quad (\alpha)_{EBBA} \simeq 5{\cdot}3 \times 10^{-24}\,\text{cm}^3,$$

the value of 2·4 is obtained. The agreement with the experimental ratio of the amplitudes $(A_{MBBA}/A_{EBBA}) \simeq 2{\cdot}2$, is, in the opinion of the authors, surprisingly good.

Generally the parameters of the expansion (2) are functions of temperature and pressure. In all the mentioned cases, the pressure has a constant, atmospheric value.

The Landau–de Gennes model may also be considered for the isothermal pressure case. For the NDE this leads to a relation analogous to (9)

$$\left.\begin{aligned} \frac{\Delta\varepsilon^E}{E^2} &= \frac{A'}{(p-p^*)}, \\ p > p_c, \quad p_c &= p^* + \Delta p, \quad T = \text{const.}, \end{aligned}\right\} \tag{13}$$

where p denotes pressure, the indices, * and c are for the hypothetical point of continuous phase transitions and the clearing point, respectively, and A' denotes the amplitude.

The results of isothermic, pressure measurements on MBBA are presented in figure 2 and confirmed the application here of the above, mean-field formula.

5. Conclusions

Results presented show that the pretransitional behaviour of the NDE in the isotropic phase of nematogens is described within the classical, mean field theory by the Landau–de Gennes model. The quantitative analysis of the ratio of amplitudes indicates an eventual influence of the frequency of the weak, electric field used in the measurements (a few MHz).

It is noteworthy that for nematogens with a large positive dielectric anisotropy (for instance in HCPP, HCPB [13], 5CB [14]), this influence on the NDE appears much stronger. For a frequency of about 1·5 MHz, a strong positive increase, as in the measurements presented here, takes place. For a frequency of 5–6 MHz, the pretransitional increase on approaching T_c changes this to a negative one.

In the opinion of the authors, all this indicates that on the pretransitional behaviour of the NDE in the isotropic phase of nematogens, an important influence may also be the angle between the permanent dipole moment and the main axis of the molecule. In the case of MBBA and EBBA they are almost perpendicular [10] and for CB5, HCPP, HCPB, parallel. The influence of this factor has been observed previously for the electro-optic Kerr effect [2]. Results obtained show that the NDE may be a useful tool for studying the isotropic–nematic or isotropic–blue phase transitions. As a research method, it is similar to those mentioned in the introduction, and particularly to the Kerr effect. The new feature of the NDE, which needs further study, is the influence of the amplitude measurement frequency on the pretransitional increase of the non-linear dielectric effect.

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