Vol. A56 (1979) *ACTA PHYSICA POLONICA* No 6

MOLECULAR MECHANISMS OF DIELECTRIC POLARIZATION AND ITS RELAXATION IN NEMATIC LIQUID CRYSTALS*

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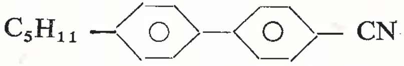
(Received November 7, 1978)

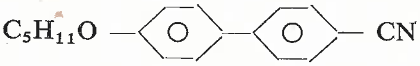
Dielectric properties of a nematic liquid crystal mixture forming the mesophase in the temperature range from $-60°C$ to $+51°C$ have been investigated at frequencies 10^2 Hz — 3×10^7 Hz. Analysis of the experimental data shows that two molecular mechanisms of dipole polarisation are responsible for each of the main components of dielectric permittivity $\varepsilon_{||}$ and $\varepsilon_{\perp}$.

The theory of dielectric anisotropy of nematic liquid crystals (NLC) [1] considers the main mechanisms of dipole polarization of the mesophase related to the rotation of polar molecules about the long and the short geometrical axes. Some of them have been experimentally found and studied [2–8] in investigations of static and relaxational properties of NLC with both negative and positive dielectric anisotropy. However, the comparatively narrow temperature range in which the anisotropic-liquid state exists in the investigated substances and the finite character of the frequency range of the electric field used in each work prevented the possibility of a direct experimental determination and study of all predicted [1] molecular mechanisms using only one liquid-crystalline sample. This possibility was provided by using NLC mixtures that form the mesomorphic state over a wide temperature range and exhibit high dielectric anisotropy owing to the strong polarity of their molecules.

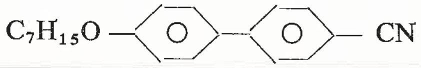
This paper presents and discusses the results of the investigations of the dielectric properties of a three-component mixture with the following composition:

4-n-amyl-4′-cyanobiphenyl 

58.6%

4-n-amyl-oxy-4′-cyanobiphenyl 

21.6%

4-n-heptyloxy-4′-cyanobiphenyl 

19.8%

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* Presented at the Second Liquid Crystal Conference of Socialist Countries, Sunny Beach, Bulgaria, September 27–30, 1977.

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This mixture forms the nematic phase in the temperature range from +51°C to −60°C. The components are similar in their molecular structure and show little difference in the geometrical dimensions of the molecules and in the value of the dipole moment μ and its direction (angle β between the direction of μ and the axis of the highest polarizability of the molecule). According to our measurements the values of μ of the components in solutions are 5.1, 5.2 and 5.2 D, respectively, and β is 10°. This is very important in discussing the experimental results of our investigations.

Experimental

Real (ε') and imaginary (ε'') parts of the main dielectric permittivities, $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ in the directions parallel and normal to the optical axis of the liquid crystal and also in the isotropic phase ε_{is} were measured in the frequency band $f = 10^2 - 3 \times 10^7$ Hz with the R — 551 ($f = 10^2 - 10^4$ Hz), E 7 — 5 A (10^5—10^6 Hz) and E 10 — 2($4 \times 10^5 - 3 \times 10^7$ Hz) apparatus. The experimental procedure and the calibration of the apparatus have been described

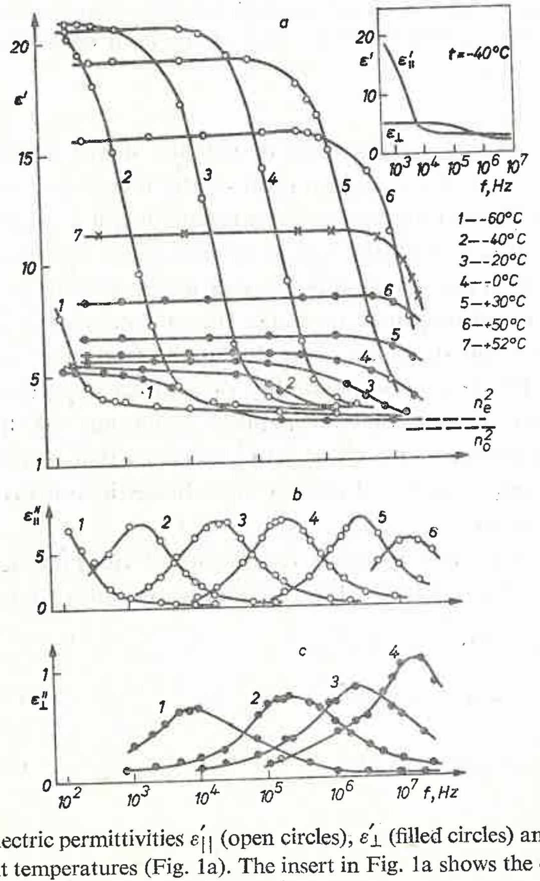

Fig. 1. Main values of dielectric permittivities $\varepsilon'_{\parallel}$ (open circles), $\varepsilon'_{\perp}$ (filled circles) and ε'_{is} (crosses) vs electric field frequency f at different temperatures (Fig. 1a). The insert in Fig. 1a shows the dependence of $\varepsilon'_{\parallel}$ and $\varepsilon'_{\perp}$ on f at $t = -40$°C. Dielectric losses $\varepsilon''_{\parallel}$ (Fig. 1b) and $\varepsilon''_{\perp}$ (Fig. 1c) vs frequency f at different temperatures

in [6, 9, 10]. A flat titanium condenser with intrinsic capacitance $C_0 = (11.0 \pm 0.1)$ pF was used as the measuring cell. The uniform macroscopic orientation of the sample in the condenser was ensured by applying a magnetic field of 6 KOe. The direction of the magnetic field could be either parallel or normal to the plane of the condenser plates (for measuring $\varepsilon_\perp$ and $\varepsilon_{||}$, respectively). The temperature was maintained to within 0.2°C by using liquid nitrogen and ethyl alcohol as the cooling medium and the thermostating liquid, respectively.

The experimental results are shown in Fig. 1 which gives the frequency dependences of $\varepsilon_{||}$, $\varepsilon_\perp$ and ε_{is} at different temperatures. A marked dispersion of all the main values of the dielectric permittivities was found in the investigated range of frequencies and temperatures (Fig. 1a). The study of the frequency dependence of dielectric losses ε'' showed that in the dispersion range of $\varepsilon'_{||}$ and $\varepsilon'_\perp$ distinct maxima are observed, $\varepsilon''_{||}$ and $\varepsilon''_\perp$. The corresponding experimental data are shown in Figs. 1b and 1c. Fig. 2 shows the Cole–Cole diagrams constructed by using the experimental values of $\varepsilon'_{||}$, $\varepsilon'_\perp$, $\varepsilon''_{||}$ and $\varepsilon''_\perp$ for several temperatures.

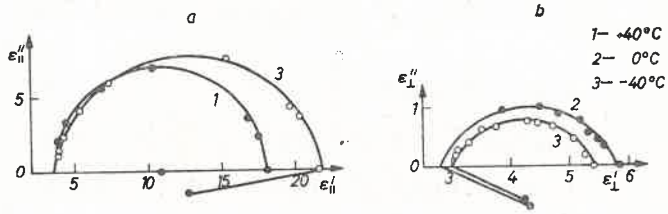

Fig. 2. The Cole–Cole diagrams plotted from experimental values of $\varepsilon'_{||}$ and $\varepsilon''_{||}$ (Fig. 2a) and $\varepsilon'_\perp$ and $\varepsilon''_\perp$ (Fig. 2b) at different temperatures

These diagrams show directly that the relaxation of $\varepsilon_{||}$ (Fig. 2a) can be described by the dispersion curve with one time of dielectric relaxation τ only at relatively high temperatures. In contrast, at low negative temperatures a spectrum of relaxation times corresponds to each dispersion curve of $\varepsilon_{||}$. It should be noted that the spectrum of τ is also characteristic of the relaxation of $\varepsilon_\perp$ (Fig. 2b).

Discussion of results

Experimental results shown in Fig. 1a suggest that at the static dielectric polarization the liquid-crystal sample investigated is characterized by high positive dielectric anisotropy, $\Delta\varepsilon = \varepsilon'_{||} - \varepsilon'_\perp$. This circumstance [11, 12] is a sequence of a large dipole moment of the molecules $\mu = 5.2$ D directed at an angle $\beta = 10°$. At the same time data in Fig. 1a show that the great dispersion of $\varepsilon'_{||}$ and $\varepsilon'_\perp$ profoundly affects not only the value but also the sign of dielectric anisotropy. At each temperature the relaxation of $\varepsilon'_{||}$ and $\varepsilon'_\perp$ becomes apparent at quite different frequencies. The dispersion of $\varepsilon'_{||}$ responsible for the decrease in the positive dielectric anisotropy and the change in the sign of $\Delta\varepsilon$ from positive to negative is most pronounced and appears at lowest frequencies. In contrast, when the frequency increases, a strong dispersion of $\varepsilon'_\perp$ occurs causing the secondary change in the sign of $\Delta\varepsilon$ from negative ($\varepsilon'_{||} < \varepsilon'_\perp$) to positive ($\varepsilon'_{||} > \varepsilon'_\perp$). This is shown in Fig. 1a. Thus, in the temperature–frequency range investigated the dielectric anisotropy of the sample changes its sign twice. Moreover, the sign of the high-frequency positive $\Delta\varepsilon$ coincides with that of the optical anisotropy of the mesophase $\Delta n = n_e - n_o$ and at the maximum frequencies (used in this work) and lowest temperatures the absolute values of $\varepsilon'_\parallel$ and $\varepsilon'_\perp$ are close to the corresponding squares of the extraordinary ($n_e^2 = 3.025$) and ordinary ($n_o^2 = 2.310$) refractive indices of the mixture extrapolated to an infinitely great wavelength (Fig. 1a). This means that as a result of the dispersion of $\varepsilon'_\parallel$ and $\varepsilon'_\perp$ the dipole part of the dielectric polarization is virtually completely excluded from it.

The theory of dielectric anisotropy of NLC put forward in Ref. [1] can be used to establish the molecular mechanism responsible for the dielectric polarization and the relaxation of the main dielectric permittivities of the liquid-crystalline sample investigated. According to this theory, the expressions for the main molar dielectric susceptibilities in the directions parallel ($\sigma_\parallel$) and normal ($\sigma_\perp$) to the optical axis of the liquid crystal

$$\sigma_\parallel \equiv \frac{(\varepsilon'_\parallel - 1)M}{4\pi\varrho} = (\sigma_\parallel)_{\text{def}} + (\sigma_\parallel)_{\text{or}}^{\parallel} + (\sigma_\parallel)_{\text{or}}^{\perp}, \tag{1}$$

$$(\sigma_\parallel)_{\text{def}} = PQN_A(\bar{\alpha} + \tfrac{2}{3}\,\Delta\alpha S), \tag{1a}$$

$$(\sigma_\parallel)_{\text{or}}^{\parallel} = [PQ^2N_A\mu^2 \cos^2\beta(1+2S)/3kT]\,(1+x_1), \tag{1b}$$

$$(\sigma_\parallel)_{\text{or}}^{\perp} = [PQ^2N_A\mu^2 \sin^2\beta(1-S)/3kT]\,(1+x_2), \tag{1c}$$

$$\sigma_\perp \equiv \frac{(\varepsilon'_\perp - 1)M}{4\pi\varrho} = (\sigma_\perp)_{\text{def}} + (\sigma_\perp)_{\text{or}}^{\parallel} + (\sigma_\perp)_{\text{or}}^{\perp}, \tag{2}$$

$$(\sigma_\perp)_{\text{def}} = PQN_A(\bar{\alpha} - \tfrac{1}{3}\,\Delta\alpha S), \tag{2a}$$

$$(\sigma_\perp)_{\text{or}}^{\parallel} = PQ^2N_A\mu^2 \cos^2\beta(1-S)/3kT, \tag{2b}$$

$$(\sigma_\perp)_{\text{or}}^{\perp} = [PQ^2N_A\mu^2 \sin^2\beta(S+2)/6kT]\,(1+x_2), \tag{2c}$$

(where P and Q are factors of the internal field according to Onsager [13], M and ϱ are the molecular weight and the density of the substance and N_A is Avogadro's number) include as items the terms that take into account the anisotropy of the deformational polarizability of molecules $\Delta\alpha - (\sigma_\parallel)_{\text{def}}$ and $(\sigma_\perp)_{\text{def}}$, the mechanisms of rotation of the longitudinal axis of the polar molecule about its short axis $(\sigma_\parallel)_{\text{or}}^{\parallel}$(1b) and the rotation of its transverse axis about its longitudinal axis $(\sigma_\parallel)_{\text{or}}^{\perp}$(1c) and $(\sigma_\perp)_{\text{or}}^{\perp}$(2c). The contribution to $\sigma_\parallel$ of items (1b) and (1c) is determined by the multipliers $(1+x_1)$ and $(1+x_2)$ where x_1 and x_2 are parameters characterizing the limitations and hindrances of the freedom of these two types of dipole rotation. The absolute values and the sign of parameters x_1 and x_2 are determined by potential barriers (intermolecular interactions) and relaxation phenomena [1, 6–10] limiting and hindering the rotation of molecules in the mesophase.

Eq. (2) shows that the dipole part of the susceptibility $\sigma_\perp$ also includes two items $(\sigma_\perp)_{\text{or}}^{\parallel}$ and $(\sigma_\perp)_{\text{or}}^{\perp}$ the first of which (2b) determines the polarization caused by the rotation of the longitudinal axis of the polar molecule in the range of the solid angle ϑ allowed by the value of the degree of ordering of NLC $S = \frac{1}{2}\,(3\,\overline{\cos^2\vartheta} - 1) < 1$. This type of molecular rotation corresponds to dipole polarization in an isotropic liquid since it does not need to surmount the potential barriers supporting the long range order in the mesomorphic substance. Item (2c) in Eq. (2) reflects the rotation of the transverse axis of the molecule about its longitudinal axis and, hence, depends on the x_2 parameter. Consequently, in accordance with Eqs (1) and (2), two mechanisms of rotation of polar molecules can be responsible for each of the main values of $\sigma_{||}$ and $\sigma_{\perp}$. The significance of each of these mechanisms can be established directly by examining the experimental data in this work. For this purpose it is necessary to analyse the results of investigations of the frequency dependences of $\varepsilon_{||}$ and $\varepsilon_{\perp}$. It is convenient to use the plots of dependences of $\varepsilon'_{||}$ and $\varepsilon'_{\perp}$ as functions of $\varepsilon''_{||} \times 2\pi f$ and $\varepsilon''_{\perp} \times 2\pi f$. According to the method suggested by Cole [14], in these coordinates in accordance with the equation

$$\varepsilon' = \varepsilon'_0 + \tau(2\pi f \times \varepsilon'') \tag{3}$$

(where ε'_0 in the static dielectric permittivity) the slope of experimental curves permits the determination of times of dielectric relaxation, τ. These plots based on experimental data are shown in Figs 3a and 3b. Fig 3a shows experimental results concerning the dispersion of $\varepsilon_{||}$. They illustrate directly the above mentioned fact that at relatively high temperatures the relaxation of $\varepsilon_{||}$ can be described by a dispersion curve with single τ (curve 1). This means that under these conditions the relaxation of only one molecular mechanism of the dipole polarization is responsible for the frequency dependence of $\varepsilon_{||}$. This mechanism is fairly well investigated [2–6, 15–17] and is the relaxation of the rotation of longitudinal axes of the polar molecules about their transverse axes (Eq. (1b)).

When the temperature decreases and the viscosity of the substance sharply increases over the frequency band used in this work the second mechanism of dispersion of $\varepsilon_{||}$ becomes noticeable (Fig. 3a, curve 3) and can be reliably determined experimentally (Fig. 3a, curve 4). It should be noted that this high-frequency mechanism of relaxation of $\varepsilon'_{||}$ becomes apparent only in the temperature–frequency range of the dispersion of $\varepsilon'_{\perp}$. The analysis of Eqs. (1) and (2) shows that the rotation of short transverse axes of the molecules of NLC about the longitudinal axes (Eq. (1c) can constitute the second mechanism of dipole polarization in the direction of the optical axis of the mesomorphic sample. When static polariza-

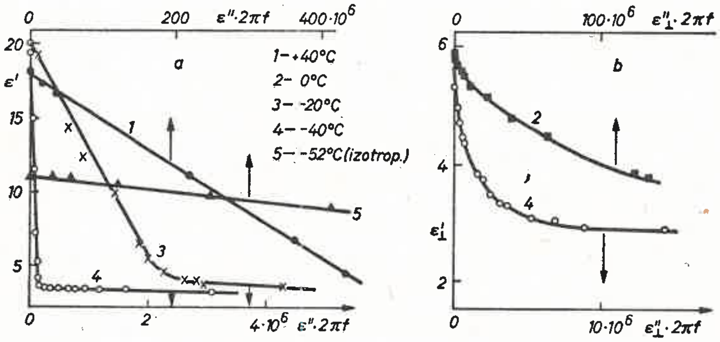

Fig. 3. Values of $\varepsilon'_{||}$ vs $\varepsilon''_{||} \times 2\pi f$ (Fig. 3a) and $\varepsilon'_{\perp}$ vs $\varepsilon''_{\perp} \times 2\pi f$ (Fig. 3b) at different temperatures

tion exists, this rotation contributes not only to the value of $\sigma_{\parallel}$ but also to that of $\sigma_{\perp}$ (Eq. (2c)). As a result the relaxation of $\varepsilon'_{\perp}$ and $\varepsilon'_{\parallel}$ related to the exclusion of this molecular mechanism from the dipole polarization of NLC should naturally become apparent at the same temperatures and frequencies. Hence, it seems evident that the second mechanism of dispersion of $\varepsilon_{\parallel}$ is the relaxation of rotation of the transverse molecular axes about the longitudinal axes. This means that these results are the experimental manifestation of two molecular mechanisms of dipole polarization and, hence, of its relaxation in the direction of the optical axis of NLC. Probably, the possibility of a direct experimental separation of these two mechanisms of dipole polarization of $\sigma_{\parallel}$ is a result of the considerable difference in the temperature-frequency ranges of the dispersion $(\sigma_{\parallel})^{\parallel}_{\text{or}}$ and $(\sigma_{\parallel})^{\perp}_{\text{or}}$.

Corresponding relaxation times $(\tau_{\parallel})^{\parallel}$ and $(\tau_{\parallel})^{\perp}$ found by using Eq. (3) and experimental data in Fig. 3a are shown at different temperatures (Table I). It is clear that at each temperature the values of $(\tau_{\parallel})^{\parallel}$ and $(\tau_{\parallel})^{\perp}$ differ by virtually three orders of magnitude.

TABLE I

Relaxation times of dielectric polarization in the liquid-crystalline and amorphous phases

Nematic phase

t °C	−60	−50	−40	−20	0	+30	+50
$(\tau_{\parallel})^{\parallel}\times 10^6$ sec	2530	531	106	7.24	0.80	0.06	0.012
$(\tau_{\parallel})^{\perp}\times 10^6$ sec	0.9	0.2	0.07				
$\bar{\tau}_{\perp}\times 10^6$ sec	17.7	2.30	0.79	0.06	0.011		

Isotropic phase

t °C	52	56	60	70	80
$\tau_{\text{is}}\times 10^8$ sec	0.54	0.42	0.40	0.29	0.20

Eq. (2) shows that two mechanisms of rotation of rod-like polar molecules can also be responsible for the dipole polarization of NLC in the direction normal to its optical axis. It can easily be seen that the part played by each of them depends strongly on the dipole structure of the molecules of the substance on the values of μ and β. Actually, as has been shown previously [7], in the case of liquid crystals with negative dielectric anisotropy $\Delta\varepsilon < 0$, (β is close to 90°), the value of $(\sigma_{\perp})^{\parallel}_{\text{or}}$ is negligible (hundredfold lower) than $(\sigma_{\perp})^{\perp}_{\text{or}}$. In this case the experimental dispersion of $\varepsilon'_{\perp}$ is determined only by the frequency dependence of $(\sigma_{\perp})^{\perp}_{\text{or}}$, i.e. by the relaxation of rotation of the longitudinal axis of the molecule about its transverse axis. In contrast, for nematic liquids with $\Delta\varepsilon > 0$ both molecular mechanisms of dipole polarization described by Eqs. (2b) and (2c) can be significant. The use of the static (independent of f) values of $\varepsilon'_{\perp}$ (Fig. 1a), of Eq. (2) and the molecular characteristics $\mu = 5.2$ D, $\beta = 10°$, $\bar{\alpha} = 400\times 10^{-25}$ cm^3, $\Delta\alpha = 160\times 10^{-25}$ cm^3, S and ϱ found for cyanobiphenyls [18] leads to the values of $(\sigma_{\perp})^{\parallel}_{\text{or}} = 49$ and $(\sigma_{\perp})^{\perp}_{\text{or}} = 11$. These values are of the same order of magnitude. This means that in contrast to negatively anisotropic substances not only the (2c) ratio but also the (2b) item (the mechanism of rotation of polar molecules taking place in the isotropic-liquid state) plays an important part in the dipole polarization of the liquid-crystalline mixture of cyanobiphenyls ($\Delta\varepsilon > 0$). This conclusion is very important when we consider the relaxation of $\varepsilon_\perp$ established in this work. Experimental data in Fig. 1a show that as a result of dispersion of $\varepsilon'_\perp$ the dipole component of dielectric polarization determined by the values of $(\sigma_\perp)^{||}_{\text{or}}$ and $(\sigma_\perp)^{\perp}_{\text{or}}$ is almost completely excluded. At the same time in the range of frequencies (5–30)M Hz the dispersion of ε'_{is} is experimentally observed (Fig. 1a, curve 7). Eq. (2) shows that the "isotropic" mechanism of relaxation of dielectric permittivity $\varepsilon'_\perp$ (item (2b)) can also appear at the temperatures below that of the phase transition: amorphous liquid-liquid crystal. Under these conditions the viscosity of the sample is much higher than in the isotropic phase ($\eta = 200$ cp. at $t = 0°\text{C}$, $\eta = 40$ cp. at $t = 53°\text{C}$). Hence, it is natural to expect the dispersion of $\varepsilon'_\perp$ related to this mechanism at a frequency below 5 MHz. This means that in positive anisotropic NLC the frequency dependence of $\varepsilon_\perp$ is governed by the relaxation of both mechanisms of molecular rotation responsible for the dispersion $(\sigma_\perp)^{||}_{\text{or}}$ and $(\sigma_\perp)^{\perp}_{\text{or}}$. The Cole–Cole diagrams (Fig. 2b) and the plots of $\varepsilon'_\perp$ vs. $\varepsilon''_\perp \times 2\pi f$ (Fig. 3b) confirm this conclusion. At all temperatures at which of the anisotropic-liquid phase of the sample exists, the spectrum of relaxation times τ corresponds to the curves of dispersion of $\varepsilon_\perp$. Moreover, in this case it is impossible to separate the mechanisms of dispersion of $\varepsilon_\perp$ related to the "isotropic" relaxation and to the relaxation of the rotation of transverse axes of the molecules about their longitudinal axes since these mechanisms, in contrast to the dispersion of $\varepsilon_{||}$, probably appear at relatively similar or even overlapping frequencies. As a result, the dependences of $\varepsilon'_\perp$ on $\varepsilon''_\perp \times 2\pi f$ are smooth curves with a changing slope (Fig. 3b). For this reason Table I gives average values of relaxation times $\bar{\tau}_\perp$ found by using the frequencies $f_{\max}$ corresponding to maxima of dielectric losses $\varepsilon^{||}_\perp$ (Fig. 1b). At the same time in the investigated frequency range the relaxation of dielectric permittivity in the isotropic-liquid phase can be adequately approximated by a linear dependence of ε'_{is} on $\varepsilon''_{\text{is}} \times 2\pi f$ (Fig. 3a, curve 5). These dependences were used to determine the values of τ_{is} at different temperatures (Table I). This also directly confirms the viewpoint in Ref. [1] according to which two mechanisms of dielectric polarization and its relaxation are responsible for the dielectric permittivity of positively anisotropic liquid crystals in the direction normal to their optical axis.

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