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Specific Features of the Approximation of the Dielectric Spectra of Alkylcyanobiphenyl Liquid Crystals

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Abstract—The frequency dependences of the longitudinal and transverse permittivities of oriented nematic liquid crystals belonging to the alkylcyanobiphenyl group nCB ($n = 5$–8) are measured in the relaxation region in the meter and decimeter wavelength ranges. It is established that the dispersion of the longitudinal permittivity is well approximated by the sum of two Debye processes with different relaxation times. The frequency dependence of the transverse permittivity is represented by the dispersion relation with a continuous distribution of relaxation times in a specified time range. It is demonstrated that, in the high-frequency range ($f > 200$ MHz), in which the dielectric spectra exhibit a number of weakly pronounced dispersion features, the total dispersion of the permittivity is adequately described by the sum of relaxation and resonance processes. © *2003 MAIK "Nauka/Interperiodica".*

1. INTRODUCTION

As a rule, the observed dependence of the permittivity of liquid crystals on the frequency f has been analyzed in terms of the orientational (dipole) mechanisms of dielectric polarization of rigid anisotropic molecules [1–3]. Within this approach, the dispersion of the longitudinal (parallel) $\varepsilon_{\parallel}(f)$ and transverse (perpendicular) $\varepsilon_{\perp}(f)$ permittivities of an oriented liquid crystal is associated with rotations of molecules about the long and short molecular axes. It is well known that, for liquid crystals with a large positive anisotropy (for example, liquid crystals belonging to the alkylcyanobiphenyl group nCB), the low-frequency ($f = 0.1$–10 MHz) part of the dispersion of the longitudinal permittivity $\varepsilon_{\parallel}(f)$ is well approximated by a simple Debye equation with one relaxation time [4–6]. The frequency dependences of the transverse permittivity $\varepsilon_{\perp}(f)$ are characterized by noticeable deviations from the Debye behavior in the low-frequency and microwave ranges. A more correct approximation of the dependence $\varepsilon_{\perp}(f)$ can be obtained using the Cole–Davidson or Havriliak–Negami relations [7, 8]. However, the assessment of the accuracy of the above approximations is complicated by the lack of experimental information. Traditionally, the permittivity in the microwave frequency range has been measured at several fixed frequencies with the use of measuring cells of different designs. The errors in these dielectric measurements differ significantly. In the majority of works dealing with the permittivity, the dielectric dispersion was determined only up to frequencies $f \sim 10$–15 MHz.

In our recent work [9], we carefully measured the dielectric spectra of liquid crystals of the nCB group in the decimeter wavelength range. It was found that, for

all the liquid crystals studied, an increase in the frequency is accompanied by the appearance of several low-intensity narrow-band dispersion regions of the resonance nature, which are clearly distinguished against the background of the slowly descending orientational part of the dispersion of the real permittivities $\varepsilon_{\perp}'(f)$ and $\varepsilon_{\parallel}'(f)$. It should be noted that similar dispersion regions were revealed earlier for a 5CB crystal [10]. The resonances were observed in the frequency range 200 MHz $< f <$ 1000 MHz. As was shown in our previous work [11], the real part of the dielectric spectra $\varepsilon'(f)$ can be approximated by the sum of two processes described in terms of the Debye equation for dipole relaxation and the appropriate equations for dielectric resonances. However, such a simple approximation leads not only to disagreement between theory and experiment in certain spectral ranges but also to a considerable difference between the longitudinal ($\tau_{\parallel}$) and transverse ($\tau_{\perp}$) relaxation times calculated in our earlier work [11] and determined by other authors [4–8].

In this work, we measured the dielectric spectra of liquid crystals of the alkylcyanobiphenyl group nCB ($n = 5$–8) over a wide range of frequencies (from 1 to 1000 MHz) and analyzed the possible numerical approximations of these spectra in a more correct form.

2. EXPERIMENTAL TECHNIQUE

Since the dispersion dependences $\varepsilon(f)$ of alkylcyanobiphenyl liquid crystals in the frequency range 1–10 MHz were well known, the low-frequency data on the dielectric spectra were taken from [4–6]. These data were complemented by the results of check measurements performed by the resonance method at several frequencies with the use of a Tesla BM560 stan-

dard Q-meter and a measuring cell in the form of a parallel-plate capacitor.

As is known, dielectric measurements of materials with the use of resonance methods in the decimeter wavelength range 100–1000 MHz involve considerable difficulties. In our measurements of liquid crystals, this problem was solved using specially devised sensors based on microstrip resonators. The sensor design and the technique used in resonance measurements [11] made it possible to determine the dielectric characteristics of liquid crystals in the aforementioned frequency range with absolute errors no larger than $\delta\varepsilon' \sim 0.05$ and $\delta\varepsilon'' \sim 0.01$.

The longitudinal and transverse permittivities of liquid-crystal samples were measured in the nematic phase in the orienting magnetic field $H = 2.5$ kOe. During measurements of the high-frequency dielectric spectra, the temperature T in a thermostat was maintained accurate to within ± 0.1 K. For each sample, the temperature of high-frequency dielectric measurements was chosen equal to the temperature for which the most comprehensive data on the dielectric dispersion in the low-frequency range were available in the literature. As a rule, these temperatures fall in the range $(T_{ni} - 5$ K$) < T < (T_{ni} - 3$ K$)$, where T_{ni} is the temperature of transition from the nematic state to the isotropic state.

3. RESULTS AND DISCUSSION

Figure 1 shows the frequency dependences of the real permittivities $\varepsilon'_{\perp}(f)$ and $\varepsilon'_{\parallel}(f)$ of the 5CB liquid crystal in the frequency range 1–1000 MHz at the temperature $T = 35°$C. The data on the permittivity in the low-frequency spectral range 1–10 MHz were taken from [4, 5]. The frequency dependences of the permittivities $\varepsilon'_{\parallel}(f)$ and $\varepsilon'_{\perp}(f)$ in the Debye approximation with relaxation times $\tau_{\parallel} = 28$ ns and $\tau_{\perp} = 3$ ns are depicted by solid and dashed lines, respectively. The approximated dependences correspond to the best agreement between the Debye theory and the experiment in the frequency range 1–10 MHz; however, they cannot be considered a satisfactory approximation over the entire range of measurements. Actually, the experimental points substantially deviate from the curve $\varepsilon'_{\parallel}(f)$ in the range 15 MHz $< f <$ 500 MHz and from the curve $\varepsilon'_{\perp}(f)$ at $f >$ 80 MHz.

The frequency dependence of the longitudinal permittivity $\varepsilon''_{\parallel}(f)$ can be more accurately approximated using the sum of two Debye relaxation processes [12]; that is,

$$\varepsilon'_{\parallel}(f) - n_e^2 = \frac{(\varepsilon'_{\parallel 0} - n_e^2)g_1}{1 + (2\pi f)^2 \tau_{\parallel 1}^2} + \frac{(\varepsilon'_{\parallel 0} - n_e^2)g_2}{1 + (2\pi f)^2 \tau_{\parallel 2}^2}, \quad (1)$$

where n_e is the extraordinary refractive index, $\varepsilon'_{\parallel 0}$ is the static permittivity, g_1 and g_2 are the weighting factors of
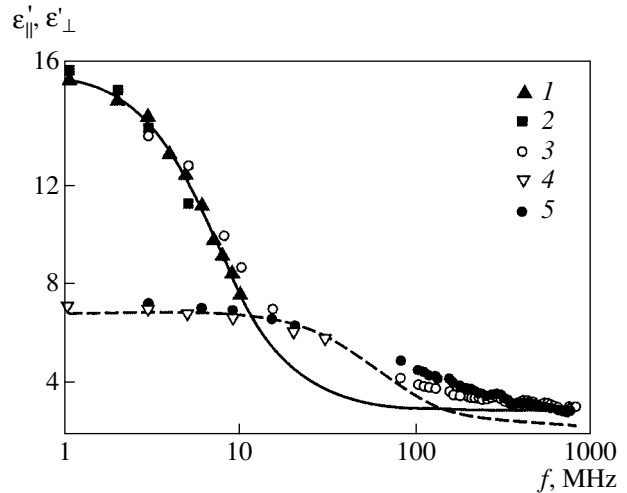

Fig. 1. Frequency dependences of the longitudinal and transverse permittivities of the 5CB liquid crystal and their approximation according to the Debye formulas with (*1, 2, 4*) data taken from [4, 5, 7] and (*3, 5*) data obtained in this work.

two processes ($g_1 + g_2 = 1$), and $\tau_{\parallel 1}$ and $\tau_{\parallel 2}$ are the relaxation times corresponding to these processes. This approximation is based on the results obtained by Buka *et al.* [13], who demonstrated that the frequency dependence of the imaginary part of the permittivity $\varepsilon''_{\parallel}(f)$ for 7CB and 7OCB liquid crystals can exhibit two absorption maxima.

The dispersion curve obtained by approximating the experimental data on $\varepsilon'_{\parallel}(f)$ for the 5CB liquid crystal with the use of formula (1) is represented by the solid line in Fig. 2. This curve was constructed for the following parameters of the liquid crystal: $\varepsilon'_{\parallel 0} = 16.4$, $\tau_{\parallel 1} = 24 \times 10^{-9}$ s, $\tau_{\parallel 2} = 7.0 \times 10^{-10}$ s, $n_e = 1.72$, $g_1 = 0.92$, and $g_2 = 0.08$. As can be seen from Fig. 2, the frequency dependence of the longitudinal permittivity, which is calculated within the proposed approximation based on the sum of two relaxation processes, almost completely coincides with the experimental curve over the entire frequency range covered. Dashed line *1* in Fig. 2 corresponds to the frequency dependence calculated at weighting factors $g_1 = 1$ and $g_2 = 0$ and fits the experimental data well only in the low-frequency dispersion region. Dashed line *2* represents the dispersion dependence obtained at $g_1 = 0.92$ and $g_2 = 0.08$, which, by contrast, agrees reasonably with the experimental data only in the high-frequency dispersion region. Dot-dashed line *3* shows the refractive index n_e^2. As in the case of 5CB liquid crystals, close agreement between the calculated and experimental frequency dependences of the longitudinal permittivity $\varepsilon'_{\parallel}(f)$ is observed for all the alkylcyanobiphenyl liquid crystals under investigation. The parameters of the Debye approximation for these compounds are listed in Table 1.
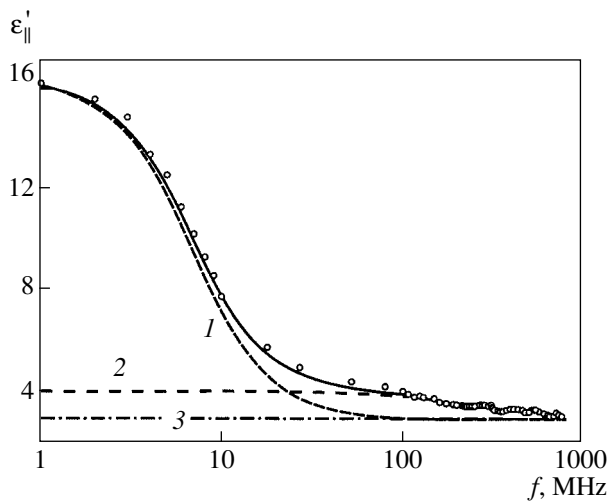
Fig. 2. Frequency dependence of the longitudinal permittivity of the 5CB liquid crystal (points), the approximation by the sum of two Debye processes with different relaxation times (solid line), and the approximations according to the Debye formulas with (*1*) the longest relaxation time and (*2*) the shortest relaxation time. Line *3* indicates the n_e^2 level.

According to the universally accepted concepts regarding the possible mechanisms of dielectric polarization in liquid crystals, the occurrence of two relaxation processes can be explained, in particular, by the misalignment of the dipole moment μ and the long axis of the liquid-crystal molecule. In this case, the longitudinal permittivity contains a contribution from the transverse permittivity and vice versa. This contribution is governed by the transverse component of the dipole moment of molecules. In turn, the transverse component is determined by the deviation of the dipole moment from the long axis of the molecule. As a consequence, the computational formulas for the static permittivities $\varepsilon'_{\parallel 0}$ and $\varepsilon'_{\perp 0}$ include not only the magnitude of the dipole moment of the molecule μ but also the angle β between the dipole moment and the long axis of the molecule [1–3]. The angle β can be estimated from the following condition: the tangent β is equal to the ratio g_2/g_1. The angles β thus calculated are also given in Table 1. Note that, for the liquid crystals studied, these angles do not exceed 5°.

It is of interest that, according to the results obtained in [14, 15], the β angles for 6CB and 7CB liquid crystals are equal to zero. In our opinion, the disagreement

with the β angles presented in Table 1 stems from the fact that, in [14, 15], the permittivities were measured in the frequency range up to 10 MHz and the experimental data on $\varepsilon'_\perp(f)$ were approximated by the Debye dependence with one relaxation time. As is known, this approximation adequately describes experimental data in a narrow frequency range.

Analysis showed that the approximation of the transverse permittivity $\varepsilon'_\parallel(f)$ by the sum of two Debye processes with different relaxation times offers poor agreement with the experimental data. The best agreement between the calculated and experimental results for all the samples can be achieved using the equation with a continuous distribution of relaxation times [12]:

$$\varepsilon'_\perp(f) - n_0^2 = (\varepsilon'_{\perp 0} - n_0^2)\int_0^\infty \frac{G(\tau)}{1 + (2\pi f\tau)^2}d\tau, \qquad (2)$$

where n_0 is the ordinary refractive index and $G(\tau)$ is the distribution function of relaxation times. This approximation can be justified by the fact that the observed considerable deviation of the calculated spectrum $\varepsilon'_\perp(f)$ from the experimental points in the high-frequency range (Fig. 1) is most likely due to small-scale motions of mobile molecular fragments, for example, alkyl groups. Intramolecular motions can substantially affect the permittivity starting from the orientational dispersion region up to frequencies in the infrared region. Since intramolecular motions exhibit a wide variety of types, the dielectric relaxation times can be conveniently represented in the form of a continuous distribution in a specified time range. On this basis, the permittivity $\varepsilon'_\perp(f)$ can be approximated by the following asymmetric distribution function of relaxation times [12]:

$$G(\tau) = \frac{1}{A}\left(\frac{1}{\tau^{1-p}}\right) \quad \text{at} \quad \tau_{\perp 2} \leq \tau \leq \tau_{\perp 1},$$
$$G(\tau) = 0 \quad \text{at} \quad \tau_{\perp 2} > \tau > \tau_{\perp 1}, \qquad (3)$$

where *p* is a nonvanishing number (less than unity) and *A* is the weighting factor, which is defined by the expression

$$A = \frac{\tau_{\perp 1}^p - \tau_{\perp 2}^p}{p}. \qquad (4)$$

As a result, the frequency dependences thus numerically approximated for all the *n*CB liquid crystals under investigation agree well with the measured spectra

Table 1. Parameters of the Debye approximation for the longitudinal permittivity of *n*CB liquid crystals

n	$\varepsilon'_{\parallel 0}$	g_1	g_2	$\tau_{\parallel 1} \times 10^9$, s	$\tau_{\parallel 2} \times 10^{10}$, s	β, deg	n_e
5	16.4	0.92	0.08	24	7.0	5.0	1.72
6	16.1	0.95	0.05	38	7.6	3.0	1.68
7	15.2	0.94	0.06	25	8.0	3.7	1.74
8	13.8	0.94	0.06	30	3.9	3.7	1.65

$\varepsilon'_\perp(f)$ over the entire frequency range covered. The sufficiently high accuracy of the proposed approximation is illustrated in Fig. 3. In this figure, the solid line represents the results of calculations and points refer to experimental data on the real part of the transverse permittivity for the 7CB liquid crystal. Table 2 lists the static permittivities $\varepsilon'_{\perp 0}$, the refractive indices n_0, and the boundary relaxation times $\tau_{\perp 1}$ and $\tau_{\perp 2}$ determined for all the studied liquid crystals. This table also presents the relaxation times obtained by approximating the dielectric spectra with the use of the Debye equation with one relaxation time $\tau_\perp$ (as is shown for the 5CB sample in Fig. 1). These relaxation times characterize the rotation of molecules about the long axes and are close in magnitude to the relaxation times determined in [7, 8]. As can be seen, the relaxation times $\tau_\perp$ fall in the range between $\tau_{\perp 1}$ and $\tau_{\perp 2}$. It follows from Table 2 that, as the number of alkyl groups in the liquid-crystal molecule increases, the relaxation time $\tau_{\perp 1}$ decreases by approximately one order of magnitude, whereas the relaxation time $\tau_{\perp 2}$ decreases by more than two orders of magnitude. This indicates that the mobility of alkyl groups increases with increasing n and that their motion makes a considerable contribution to the high-frequency transverse permittivity.

It seems likely that the alkyl tails are also responsible for the resonance dispersion regions observed for all liquid crystals of the alkylcyanobiphenyl group at frequencies $f > 200$ MHz [9, 10]. Although these resonances are characterized by low intensities, they are clearly distinguished in the high-frequency range of the dielectric spectra $\varepsilon'_\parallel(f)$ and $\varepsilon'_\perp(f)$ (Figs. 1–3). The high-frequency portions of the dispersion curves of the longitudinal (open circles) and transverse (closed circles) permittivities for the 7CB liquid crystal are depicted on an enlarged scale in Fig. 4. The dashed line represents the result of the numerical approximation performed for the spectrum $\varepsilon'_\parallel(f)$ according to the above technique, and the dot-dashed line indicates the n_e^2 level to which the permittivity $\varepsilon'_\parallel$ tends when $f \longrightarrow \infty$. The origin of these resonances remains unclear. Most likely, they are associated with the excitation of collective vibrations of the molecular core and one or several nearest methylene fragments of the alkyl tail whose frequencies fall in the decimeter wavelength range.

As can be seen from Fig. 4, the experimental points in the region of the dielectric resonances substantially deviate from the Debye relaxation spectrum for both the longitudinal $\varepsilon'_\parallel(f)$ and transverse $\varepsilon'_\perp(f)$ permittivities. Therefore, in order to approximate more correctly the dielectric spectra of liquids crystals of the alkylcyanobiphenyl group in the microwave range, it is necessary to use equations that describe both relaxation and resonance processes. The frequency dependence of the
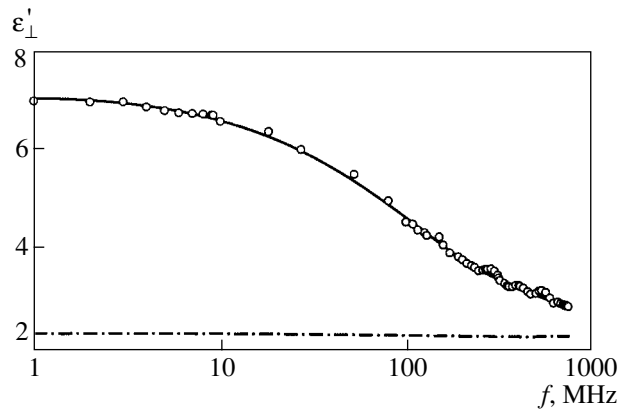

Fig. 3. Frequency dependence of the transverse permittivity of the 7CB liquid crystal (points) and the approximation in terms of according to the Debye relaxation processes with a continuous distribution of relaxation times (solid line). The dot-dashed line indicates the n_0^2 level.
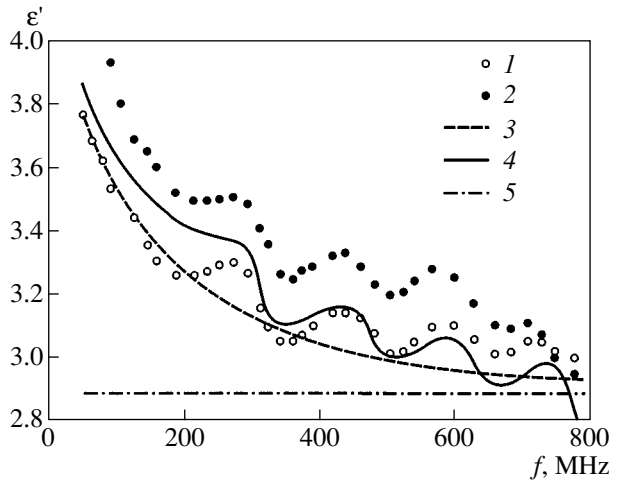

Fig. 4. Frequency dependences of the (*1*) longitudinal and (*2*) transverse permittivities of the 7CB liquid crystal and the approximations of the longitudinal permittivity $\varepsilon'_\parallel(f)$ according to (*3*) the Debye formulas and (*4*) the sum of the Debye and resonance processes. Line *5* indicates the n_e^2 level.

real part of the permittivity $\varepsilon'(\omega)$ in the portion involving m resonances can be written in the form [16]

$$\varepsilon'(\omega) - \varepsilon_\infty = \sum_{i=1}^{m} \Delta \varepsilon'_i \left[\frac{\omega_{0i}^2(\omega_{0i}^2 - \omega^2)}{(\omega_{0i}^2 - \omega^2)^2 + r_i^2 \omega^2} \right], \quad (5)$$

Table 2. Parameters of the approximation for the transverse permittivity of nCB liquid crystals

n	$\varepsilon'_{\perp 0}$	$\tau_{\perp 1} \times 10^8$, s	$\tau_{\perp 2} \times 10^{12}$, s	$\tau_\perp \times 10^9$, s	n_0
5	6.8	9	60	2.3	1.55
6	6.5	2	98	4.2	1.54
7	6.2	1.2	3	3.4	1.52
8	6.2	1.2	0.15	3.8	1.53

where $\omega_{0i} = 2\pi f_{0i}$ is the frequency of the ith resonance, $\Delta\varepsilon_i'$ is the amplitude of the ith resonance, and r_i is the relaxation frequency of the ith resonance. In Fig. 4, only the first four most intense resonances are clearly seen in the frequency dependences of the permittivities $\varepsilon_\parallel'$ and $\varepsilon_\perp'$ in the range up to 800 MHz. For this reason, the experimental dependence $\varepsilon_\parallel'(f)$ was approximated using the sum of Debye relaxation processes (1) and resonance processes (5) at $m = 4$. The approximating dependence is shown by the solid line in Fig. 4. In the course of the approximation, we determined all the resonance parameters: the natural frequencies $f_{01} = 310$ MHz, $f_{02} = 475$ MHz, $f_{03} = 630$ MHz, and $f_{04} = 780$ MHz; the resonance amplitudes $\Delta\varepsilon_1' = 1.77$, $\Delta\varepsilon_2' = 1.33$, $\Delta\varepsilon_3' = 1.51$, and $\Delta\varepsilon_4' = 1.97$; and the relaxation frequencies $r_1 = 400$ MHz, $r_2 = 550$ MHz, $r_3 = 700$ MHz, and $r_4 = 600$ MHz. It should be noted that the approximation of the transverse permittivity by the sum of Debye relaxation and resonance processes [expressions (2) and (5), respectively] also offers better agreement between the calculated and experimental data.

4. CONCLUSIONS

Thus, the main results obtained in the present work can be summarized as follows: the specific features in the dielectric spectra of liquid crystals of the alkylcyanobiphenyl group were revealed, and the methods of approximating these spectra were proposed and justified. It was demonstrated that the frequency dependence of the longitudinal permittivity $\varepsilon_\perp'(f)$ is well approximated by the sum of two Debye processes with different relaxation times. The transverse permittivity is characterized by a continuous distribution of relaxation times in a specified time range. This distribution is well represented by an asymmetric function. It was shown that the dielectric spectra in the high-frequency range can be adequately described by the sum of the relaxation and resonance processes. The basic parameters of the approximations of the dielectric spectra were determined for all the liquid crystals studied in the nCB series.

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