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DIELECTRIC RELAXATION IN MIXTURES OF LIQUID CRYSTALS OF DIFFERENT MOLECULAR LENGTH.

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Abstract It is experimentally investigated the dispersion of the dielectric permittivities in the frequency range of 1 kHz ÷100 MHz in both nematic and isotropic phases of binary mixtures of liquid crystals with different molecular lengths. Two low-frequency relaxation processes related to the dielectric relaxation of the mixture components are separated. The relaxation times and the nematic potentials of each components are determined and compared with molecular sizes.

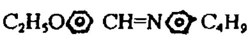
A radio-frequency dispersion of a permittivity anisotropy $\Delta\varepsilon=\varepsilon_{||}-\varepsilon_{\perp}$ in thermotropic liquid crystals (LC) is a phenomenon studied in detail in individual mesogens. The low frequency dependence of $\Delta\varepsilon$ is related to the dispersion of the dielectric permittivity $e_{||}$ parallel to the director for liquid crystal. Here $\varepsilon_{\perp}$ is the dielectric permittivity perpendicular to the director. The strong dispersion of $\varepsilon_{||}$ in the frequency range f=10^3 - 10^7 Hz is connected with a exclusion of the contribution from the orientational dipole polarization of LC of the rotation of the polar stick-like molecules around their short transverse axes. Such a rotation needs in overcoming of the potential barrier responsible for a long-range orientational order and hence, in the mesophase this process is significally slower than that in the isotropic phase.

The relaxation processes in the individual materials are quantitatively described by the Debye dispersion curves with single dipole relaxation time $\tau_{||}$. It is very difficult to study the effect of the chemical structure and the molecular shape asymmetry on the dielectric relaxation times $\tau_{||}$ related to the dispersion of $\varepsilon_{||}$ by comparing the experimental data obtained for different individual materials. The point is that variation of the chemical structure and the molecular shape asymmetry has a significant influence on the temperature interval of existance of mesophase, its viscosity, etc.

One of possible ways to solve this problem is to use the mixtures of liquid crystalline materials[1,2]. In this case the dielectric relaxation is being studied at the same absolute and relative (with respect to the phase transition temperature) temperatures and under condition of the same medium viscosity for the components of the mixture. Then the varying parameters are only the chemical structure and the molecular geometric shape.

Here the results of experimental study of the dielectric properties of some highly polar thermotropic LC and their mixtures, as well as the solution of highly polar LC in weakly polar nematic diluent are presented. We investigated the nematic and the isotropic phases of the materials (Table I) composed of molecules with various lengths. These molecules possess a large permanent dipole directed at a small angle β with respect to the longitudinal geometric axis.

TABLE I

Material	Structure	Transition Temp. (°C)		$\mu, 10^{-30}$ C·m	L,nm
		C · N · I			
LC-A		43.5	55.1	20.4	2.4
LC-B		76.6	158.2	25.1	3.0
LC-C	85% LC-A, 15% LC-B	14	67.5		
LC-D		111	229	21.7	2.6
LC-E		132	232		2.7
LC-F		36	77		2.3
LC-H	95% LC-F, 5% LC-D	20	84		
LC-I	95% LC-F, 5% LC-E	20	85		

*Molecular length was estimated from the ref.[2].

The dielectric permittivities were measured by "Tesla" BM-507 in the frequency range 5 Hz + 500 kHz and by "Tesla" BM-538 in the range 500 kHz ÷ 100 MHz. A plain titanium capacitor with capacity of 11 pF was used as a measuring cell. The homogeneous macroscopic liquid crystalline alignment was provided by the magnetic field of 0.6 T.

The circular diagrams plotted according to the experimental data on real ε' and imaginary ε'' part of complex permittivity ε for a number of the materials are shown in the Figures 1, 2, and 3.

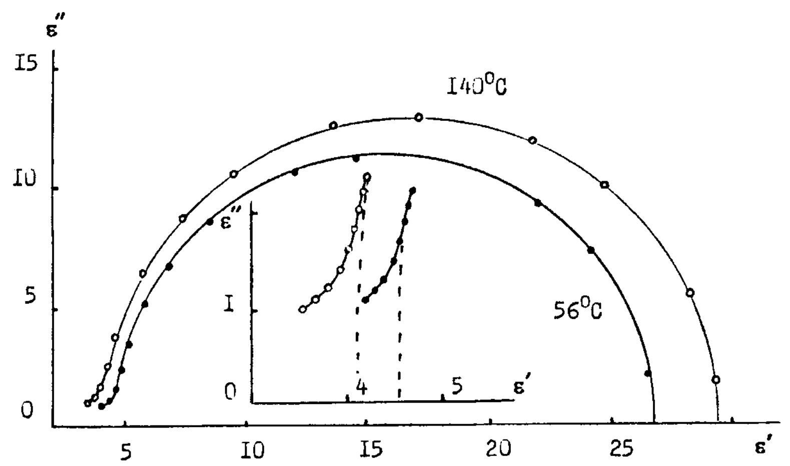


FIGURE 1 Dielectric loss $\varepsilon''_{\parallel}$ vs. $\varepsilon'_{\parallel}$ of LC-A (•) and of LC-B (o).

It is easily seen that the circular diagrams for individual LC ar e the semi-circumferences with centers situated on the absciss axis. A deviation of the diagrams from the Debye type are found only in the range of highest frequencies used in the measurements. The results obtained are sufficiently reasonable and evidence that aside from the main dispersion mechanism for $\varepsilon_{\parallel}$, related to the exclusion of the molecules rotation around their short axes from the dipole polarization, there is another high frequency mechanism for relaxation of $\varepsilon_{\parallel}$. The latter is due to the contribution of the normal dipole component to the polarization and, respectively, the rotation of the molecules around their longitudinal axes[3]. A strongly different result was obtained for the mixtures of liquid crystal materials. As seen from experimental data shown in

Figures 2 and 3 in the low frequency range the circular diagrams are significantly different from Debye ones.

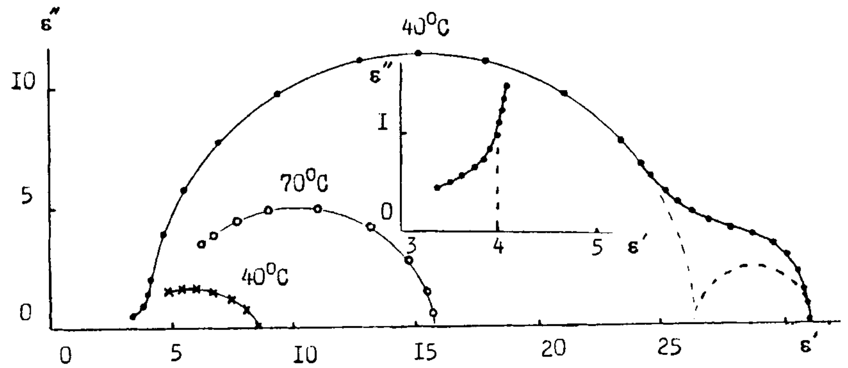


FIGURE 2 Dielectric loss ε'' vs. ε' of LC-C; $\varepsilon_{\parallel}$ - (•), $\varepsilon_{\perp}$ - (×), ε_{is} - (o).

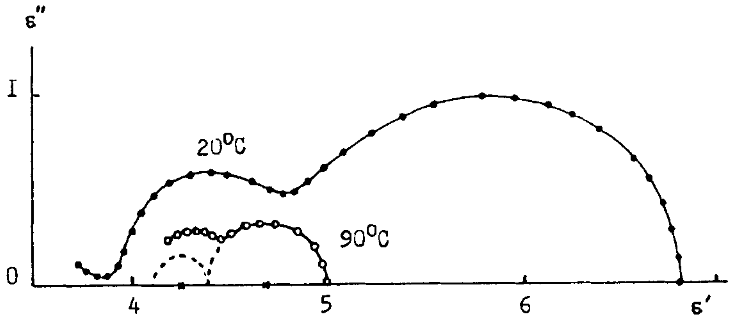


FIGURE 3 Dielectric loss ε'' vs. ε' of LC-I; $\varepsilon_{\parallel}$ - (•), ε_{is} - (o).

It means that in this case the dielectric dispersion of $\varepsilon_{\parallel}$ is related to several low frequency molecular mechanisms. Therefore, in further analysis of the results obtained it is convenient to plot the dependence of $\varepsilon'_{\parallel}$ on $\varepsilon''_{\parallel}\cdot 2\pi f$. According to the method proposed in[4], one can use the equation

$$\varepsilon' = \varepsilon_0 - \tau(\varepsilon''\cdot 2\pi f), \qquad (1)$$

where ε_0 is the static dielectric permittivity, and determine the dielectric relaxation time τ from the slope of experimental curve. Such a plot based on the experimental data (Figures 2 and 3) is shown in Figure 4. The present

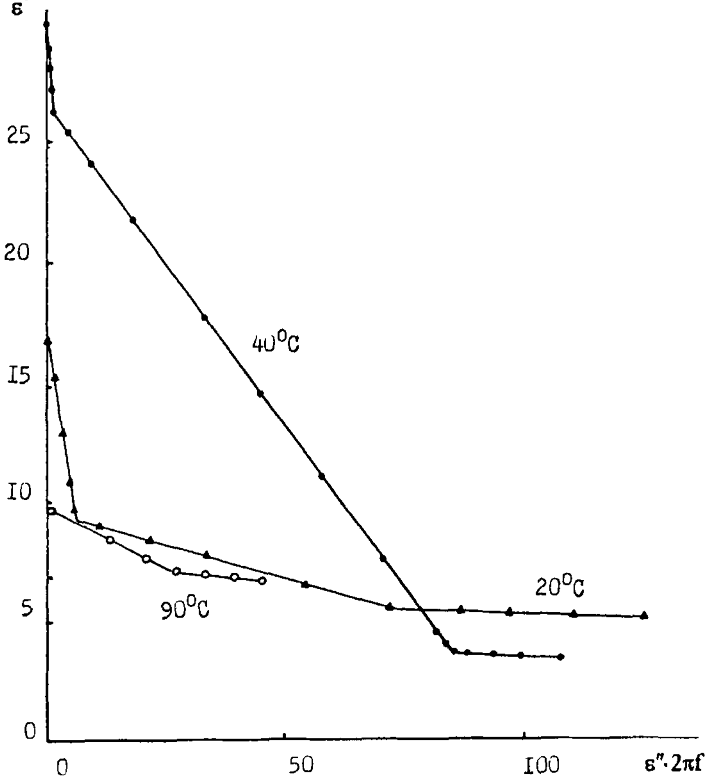


FIGURE 4 Variation of $\varepsilon'_{\|}$ vs. $\varepsilon''_{\|}\cdot 2\pi f$ of LC-C - (•) and LC-I - (×) ; ε'_{is} vs. $\varepsilon''_{is}\cdot 2\pi f$ LC-I - (o).

results illustrate directly that the $\varepsilon_{\|}$ dispersion in the liquid crystalline mixtures can be characterized by three dipole relaxation mechanisms with strongly distinguished (one order or more) relaxation times. The temperature dependences of the relaxation times $(\tau_{\|})_1$, $(\tau_{\|})_2$, and $(\tau_{\|})_3$, which correspond to different relaxation mechanisms, found in the nematic phase of LC-C, LC-H, and LC-I, are shown in Figure 5.

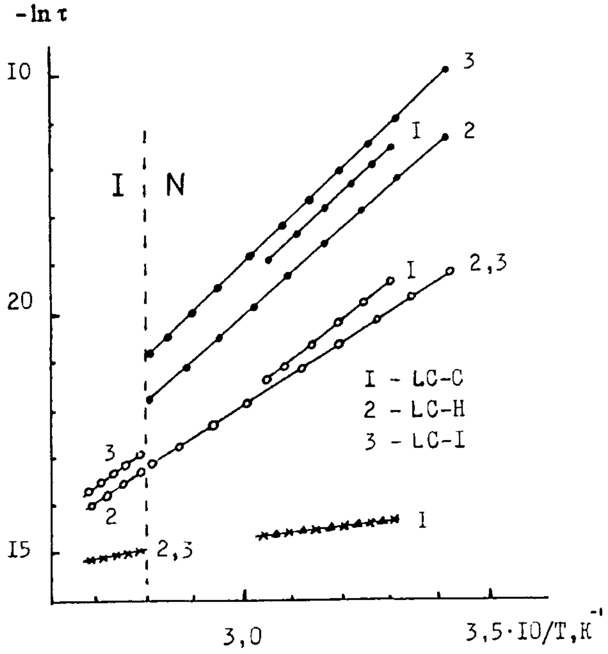


FIGURE 5 Temperature dependence of the relaxation times in nematic and isotropic phases τ_1 - (•), τ_2 - (o), τ_3 - (×), $\tau_\perp$ - (Δ) of the investigated samples.

As for a highest frequency mechanism of the $\varepsilon_{||}$ dispersion, it is evident that, as well as in individual materials, this mechanism is related to the rotation of the molecules around their longitudinal axes. The corresponding relaxation times $(\tau_{||})_3$ are sufficiently close to each other in all compounds investigated and similiar within an accuracy of measurement to the value $\tau_\perp = 1/2\pi f$ determined from the frequencies of maxima dielectric loss ε'' of the same samples (Figure 5).

Two low frequency relaxation processes which are characterized by the relaxation times $(\tau_{||})_1$ and $(\tau_{||})_2$, are related to the dipole contribution to the dielectric polarization of the rotation of the molecules of different lengths around their short axes. The possibility to separate experimentally the relaxation processes, responsible for $\varepsilon_{||}$ low frequency dispersion in the mixtures, allows to compare the relaxation times $(\tau_{||})_1$, and $(\tau_{||})_2$ for components of the samples investigated. This obvious, that the long relaxation times can be related to the corresponding components with large molecular size. Therefore, in the mixtures investigated the relaxation times $(\tau_{||})_1$ denoted as τ_B, τ_D, and τ_E characterize the dispersion of $\varepsilon_{||}$ related to the component LC-B, LC-D and LC-E, respectively, whereas the relaxation times $(\tau_{||})_2$, denoted as τ_A, τ_F are related to the components LC-A and LC-F.

The ratios of the relaxation times of the component of the mixtures, experimentally determined at the same temperatures, are presented in Table II (column 2).

TABLE II

	Nematic phase			Equation (2)	Isotropic phase	
T°C	20	49	84		84	97
τ_B/τ_A		15		2.5		
τ_E/τ_D	4.2	3.1	2.4	1.4	1.5	1.4
τ_D/τ_F	17.2	8.6	4.4	1.5	5.2	3.3
τ_E/τ_F	73	27	11	1.8	8	4.7

It is seen that the ratio τ_E/τ_F which is related to the liquid crystals with largest molecular size, has a largest value. On the other hand, it is well known that the relaxation time of the stick-like polar molecule, related to its free rotation around short axis in the medium with viscosity η, depends on the molecular length L and the molecular asymmetry P = L/d as follows[5,6]:

$$\tau = \pi\eta L^3 / [6kT(\ln 2p - 0.8)] \tag{2}$$

where d is the molecular thickness (diameter), k is the Boltzmann constant, and T is the absolute temperature. Using equation (2) and the values of L (Table I) and taking into account that the molecular relaxation of components is determined at the same temperature, one can easily obtain the ratios of the relaxation times for the same samples (Table II, column 3).

From the data presented in Table II one can conclude that the ratios of the relaxation times for the components of the mixtures, obtained from equation (2) are significantly different from those experimentally determined. The difference between theoretical and experimental values increases with difference between molecular size of the components and with decreasing temperature of the mesophase. This result can be understood if we take into account that in the mesophase the rotation of the molecules around their short axes is not free and needs in overcoming of potential barrier responsible for the orientational order in the substance. In this connection it should be interesting to consider the results obtained in the isotropic phase of the same samples. The circular diagram for isotropic phase of LC-C is shown in Figure 2 (curve 2). It is seen that this diagram is a semi-circumference with center lies below the axis of absciss. It means that the low frequency dispersion of $\varepsilon_{||}$ is characterized by the dielectric spectrum with at least two relaxation times. However, the significally smaller difference between the relaxation times of the components of the mixture LC-C in the isotropic phase, in comparison with that in the nematic phase, does not allow to separate the relaxation times corresponding to the individual components. Another picture is observed in solutions of the polar materials LC-D and LC-E in the weakly polar diluent LC-F (the samples LC-H and LC-I) (Figure 3). It is seen that the dependence of $\varepsilon''_{||}$ on $\varepsilon'_{||}$ can be divided into two semi-circumferences. The relaxation times $(\tau_{is})_i$, corresponding to the diluted components LC-D and LC-E and to the diluent LC-F, are determined from the dependence of ε'_{is} on $\varepsilon''_{is} 2\cdot\pi f$ (Figure 4) and shown in Figure 5. The ratios of the relaxation times of the components of solutions in the isotropic phase τ_E/τ_D, τ_D/τ_F, and τ_E/τ_F are presented in Table II (column 4). From the results obtained it follows that values of these ratios are much closer to the ratios, calculated for the free rotation than to those determined from the dispersion of $\varepsilon_{||}$ in the nematic phase. The possibility to determine experimentally the relaxation times, connected with the rotation of the moleculed around their short axes of the components of mixtures allows to calculate the retardation factors $g = \tau_{||}/\tau_{is}$ and to estimate the nematic potential.

The relation between the retardation factor g and potential of the nematic intermolecular interaction W is given by[7]:

$$g = kT/W \cdot [\exp(-W/kT) - 1] \approx kT/W \cdot \exp(-W/kT) \qquad (3)$$

The values of W for each component of the solutions are determined from the slope of the dependence of lng on 1/T. These values are:

$W_D = 0.16$ eV, $W_E = 0.21$ eV, $W_F = 0.38$ eV.

Thus, the investigation of the mixtures and solutions of liquid crystals with specially chosen composition allows to obtain a very important information concerning the relation between the molecular size and mobility and the value of the retardation factor. This information allows, in turn, to estimate the potential of the intermolecular interaction in the nematic phase of the components of the liquid crystalline mixtures.

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