temperature drop over the heat meter thickness; $Q(s)$, $\Delta\theta(s)$, Laplace transforms of the heat flux $q(\tau)$ and the temperature drop $\Delta t(\tau)$; s, Laplace transform parameter; $Y_q(s)$ transfer function from the heat flux to the temperature drop.

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DISPERSION OF THE DIELECTRIC PERMITTIVITY IN MIXTURES
OF NEMATIC LIQUID CRYSTALS

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The spectrum of relaxation time for the low-frequency dispersion has been found to become wider in mixtures of nematic liquid crystals, which can be interpreted as a superposition of two Debye relaxation mechanisms.

The dielectric properties of uniformly oriented nematic liquid crystals are determined in terms of two principal values of the dielectric permittivity $\varepsilon_{\|}$ and $\varepsilon_{\perp}$, corresponding to measurements respectively along and across the axis of nematic order [1].

In single-component nematic liquid crystals at superhigh frequencies (hundreds of megahertz) $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ have a range of Debye dispersion with relaxation times ($\tau_{\|}$ and $\tau_{\perp}$ respectively) close to those in an isotropic liquid (τ_{is}) [2]. At low frequencies (hundreds of kilohertz) $\varepsilon_{\|}$ has an additional range of dispersion [3]. One associates the low-frequency range of dispersion with rotation of molecules about their short axes, this rotation being greatly inhibited by the nematic order, and the high-frequency range of dispersion with rotation of molecules about their long axes. The latter rotation differs insignificantly little from analogous rotation in the isotropic phase.

In a multicomponent system of nematic liquid crystals the pattern of dipole relaxation can be much more complex.

The object of this study was to experimentally analyze the dispersion of the dielectric permittivity in mixtures of nematic liquid crystals.

The compounds dealt with in this study are listed in Table 1.

Experimental. The dielectric characteristics were measured over the 0.1-10 MHz frequency range by the resonance method with a set of "Tangens-2M" instruments. The test cell consisted of a capacitor with plane-parallel silver plates with the gap between them not exceeding 2.5 mm. The capacitance with air between the plates was 3.2 pF. The measurement error did not exceed 0.6 and 7% for ε' and ε'' respectively. A uniform orientation of the nematic liquid crystals was achieved by means of a constant magnetic field of 6 kG strength. The temperature was maintained accurately within ±0.1°C. More details about the experimental apparatus and procedure can be found in the earlier reports [4,5].

Results. The frequency dependence of the dielectric characteristics ($\varepsilon_{\|}$ and $\varepsilon_{\perp}$) was determined from measurements at discrete frequencies 0.1, 0.2, 0.5, 1.1, 2, 5, 10 MHz. Their temperature dependence was studied in the mesophase and in the isotropic-liquid phase.

TABLE 1. Mixtures Studied

Mixture	Composition	Temp. of transition from nematic liquid crystal to isotropic liquid, T_c, °K
A	Eutectic mixture of isomers CH_3O—◯—$NO=N$—◯—C_4H_9+ +CH_3O—◯—$N=NO$—◯—C_4H_9	348
B	Eutectic mixture of isomers $C_6H_{13}OCO$—◯—$NO=N$—◯—C_4H_9+ +$C_6H_{13}OCO$—◯—$N=NO$—◯—C_4H_9	353,5
C	67% mixture A + 33% mixture B	346,3
D	88% mixture C + 12% B	343,5
E	C_7H_{15}—◯—COO—◯—CN	

Fig. 1   Fig. 2

Fig. 1. Temperature and frequency dependence of the di-
electric characteristics of A: 1) 0.1-10 MHz; 2) 0.1; 3)
0.5; 4) 1.1; 5) 2.0; 6) 10.0; 7) 0.1; 8) 10.0; (a) Coule—
Coule diagram for T = 34.7°C.
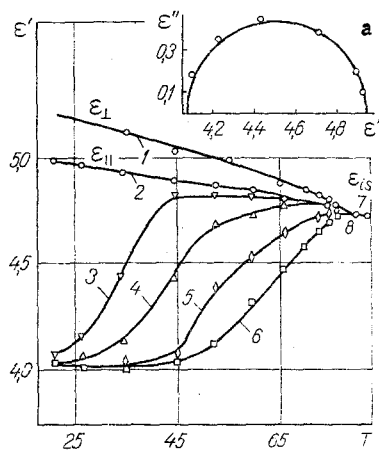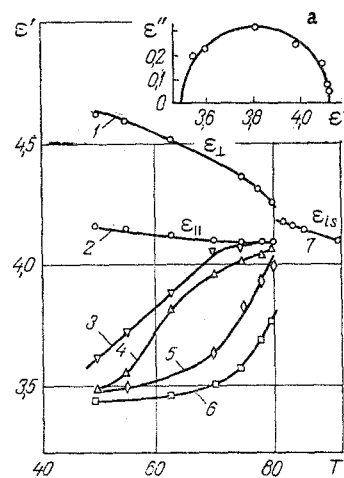
Fig. 2. Temperature and frequency dependence of the di-
electric characteristics of B: 1) 0.1-10 MHz; 2) 0.1; 3)
0.5; 4) 1.1; 5) 2.0; 6) 10.0; 7) 0.1-5.0; (a) Coule—Coule
diagram for T = 54.9°C.

Typical results obtained in the study of the said compounds are presented in Figs. 1-4.
All these substances are characterized by a dispersion of $\varepsilon_{\parallel}$ within the rf range. A disper-
sion of $\varepsilon_{\perp}$ within this frequency range is found only in the case of mixture C. Typical Coule—
Coule diagrams depicting the frequency dependence $\varepsilon_{\parallel}'(\omega)$ at several different temperatures
are shown in Figs. 1-3.

The dependence of $\varepsilon_{\parallel}''$ on $\varepsilon_{\perp}'$ for the eutectic mixture A and B is described by the Coule—
Coule equation, with the center of the semicircle diameter on the real ε'-axis. It therefore
would be logical to hypothesize that only one relaxation mechanism operates within this dis-
persion range. The activation energy for this relaxation process in mixtures A and B, ac-
cording to the equation

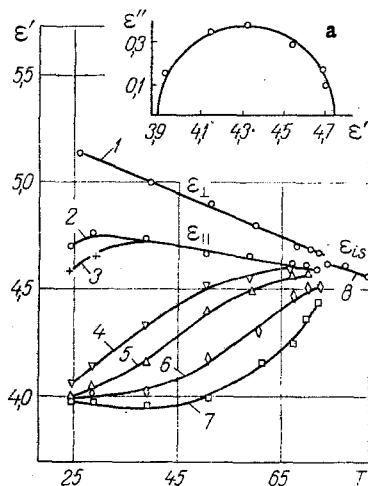$$\tau = \tau_0 \exp \frac{U}{kT},$$

(1)

829

Fig. 3

Fig. 4

Fig. 3. Temperature and frequency dependence of the dielectric characteristics of C: 1) 0.1-10 MHz; 2) 0.1; 3) 0.2; 4) 0.5; 5) 1.1; 6) 2.0; 7) 10.0; 8) 0.1-5.0; (a) Coule—Coule diagram for T = 38.8°C.
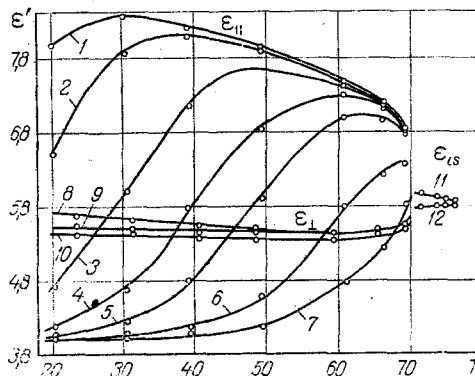
Fig. 4. Temperature and frequency dependence of the dielectric characteristics of D: 1) 0.1; MHz; 2) 0.2; 3) 0.5; 4) 1.1; 5); 2.0; 6) 5.0; 7) 10.0; 8) 0.1; 9) 5.0; 10) 10.0; 11) 0.1; 12) 5.0.

is respectively $U_1 = (0.60 \pm 0.02)$ eV and $U_2 = (0.72 \pm 0.02)$ eV.

In the case of mixture C the center of the semicircle diameter on the Coule—Coule diagram lies below the real axis. This indicates a broadening of the relaxation times. The simplest hypothesis acceptable for describing the dipole relaxation in such a system is that two independent relaxation processes operate here which are associated with the presence of two kinds of polar molecules in the mixture. An analysis of experimental data, based on assuming a relaxation process which satisfies the Berman equations [6] and modified by Bkhatachar [7, 8] for simplifying the calculations, indicates that the detected dispersion $\varepsilon_{\parallel}(\omega)$ can be regarded as a result of a superposition of two independent dipole relaxation mechanisms with times τ_1 and τ_2 respectively which are associated with the presence of two kinds of substantially different molecules. The temperature dependence of the relaxation times τ_1 and τ_2 (Table 2) can, with an error not larger than 5-7%, be described by Eq. (1) with the activation energy $U_1 = (0.32 + 0.02)$ eV or $U_2 = (0.59 + 0.02)$ eV respectively. The part of the relation process with time τ_2, moreover, decreases in intensity with rising temperature (Table 2).

No widening of the relaxation time spectrum was detected in the case of mixture D. The relaxation process can be described by the Debye equation. The activation energy for this process is $U = (0.68 \pm 0.02)$ eV.

We note that the behavior of mixture D differs substantially from that of mixture C. This is, apparently, because mixture D contains polar molecules of n-cyanophenyl ether of n-alkylobenzoinic acid E, the dielectric characteristics of which are given in an earlier report [9]. Compound E is characterized, moreover, by a strong positive anisotropy. This is why the dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{\parallel}' - \varepsilon_{\perp}'$) changes sign upon transition from mixture C to mixture D and also why $\Delta\varepsilon$ changes sign, as has been noted, along the 0.1-10 MHz frequency range.

Discussion of Results. The study has revealed a low-frequency dispersion of $\varepsilon_{\parallel}$ in mixtures of nematic liquid crystals, as should be expected because of the presence of polar molecules in these mixtures.

Noteworthy is the detected widening of the relaxation time spectrum for some mixtures, which can be regarded as a result of superposition of two relaxation processes. Two ranges of low-frequency dispersion of $\varepsilon_{\parallel}$ were first discovered by Bata and Molnar [10]. No such widening of the time spectrum of low-frequency relaxation was observed by others [11,12], who found it possible to describe the low-frequency dispersion by introducing one relaxation time.

TABLE 2. Temperature Dependence of Theoretical Relaxation Times within Two Dispersion Ranges for Compound C, and Relative Contribution of the Second Dispersion Range S to the Relaxation Process.

T, °C	$\tau_1 \cdot 10^6$, sec	$\tau_2 \cdot 10^6$, sec	S
24,8	0,0082	0,419	0,897
28,4	0,0103	0,287	0,850
38,8	0,0062	0,153	0,775
50,2	0,0036	0,061	0,620
61,4	0,0032	0,033	0,499

The relaxation occurring in mixtures of nematic liquid crystals can be explained on the premise that the relaxation time for molecules of the i-th kind in a mixture is determined by the time within which a free volume will form sufficiently large to allow for their rotation. This relaxation time depends on the mean relaxation time for the surrounding molecules as well as on the ratio between the volume of molecules of a given component and that of the surrounding molecules.

Therefore, the Debye mode of relaxation observed in eutectics A and B can be attributed to the structural similarity between molecules of isomers with similar relaxation times. Consequently, one cannot resolve by measurement the two possible ranges of dispersion due to rotation of each kind of molecules about their short axes. One can assume that relaxation in mixture C has to do with the motion of two entirely different kinds of molecules. It would be logical to conclude that shorter relaxation times correspond to molecules with a smaller characteristic dimension. According to calculations, the relaxation times for the eutectic mixtures A and B ($\tau_A = 0.052 \cdot 10^{-6}$ sec and $\tau_B = 0.14 \cdot 10^{-6}$ sec) at the referred temperature $0.93T_C$ (corresponding to one and the same degree of ordering in the Meier—Saupe theory) are comparable respectively with $\tau_1 = 0.0048 \cdot 10^{-6}$ sec and $\tau_2 = 0.086 \cdot 10^{-6}$ sec, these values being based on the assumption of two independent dispersion ranges and corresponding to a system of molecules with different characteristic dimensions.

The much shorter relaxation time τ_1, as compared with τ_A, and the lower activation energy for the dipole relaxation process characterizing this kind of molecule can be explained by the more free rotation of smaller molecules about their short axes in a mixture containing also larger molecules.

Meanwhile, the mode of rotation of large molecules does not have to and, indeed, does not undergo such appreciable changes.

The presence of component E in mixture D causes an appreciable change of the relaxation mode, namely to one of the Debye kind. At the temperature $0.93T_C$ the relaxation time in mixture D is $0.088 \cdot 10^{-6}$ sec.

This result can be explained by the addition of E molecules to the original mixture C, the characteristic dimensions of E molecules being close to those of A molecules but their relaxation time being long and thus impeding the rotation of A molecules. In turn, according to what has been said here before, the presence of B molecules can somewhat shorten the rotation time of E molecules and lower the activation energy for this process. This is, indeed, happening: at $T = 0.93T_C$ the relaxation time in substance E is $\tau = 0.242 \cdot 10^{-6}$ sec and the activation energy is $U = (0.58 \pm 0.03)$ eV [9].

The dispersion of $\varepsilon_\perp$ in mixture D is, apparently, associated with the dispersion of $\varepsilon_\perp$ in substance E.

The values of static dielectric permittivity referring to the same referred temperature $t = (T_C - T)/T_C$ and calculated according to the Coule—Coule equation for mixtures C and D of nematic liquid crystals differ, within the mesophase range, by 6-7% from those calculated on the basis of additive relations from the static dielectric characteristics and the volume fractions of components A, B, and E.

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