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MICROWAVE DIELECTRIC RELAXATION OF 4-*n*-OCTYLOXYPHENYL 4-*n*-PENTYLOXYBENZOATE (C_5O/OC_8)

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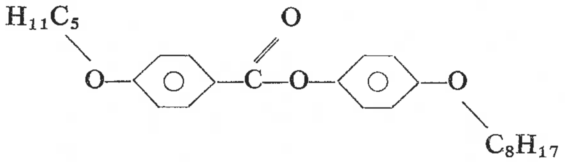
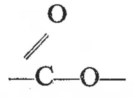
The complex dielectric permittivity $\varepsilon^* = \varepsilon' - j\varepsilon''$ was measured in the nematic and isotropic phases of C_5O/OC_8. The existence of a relaxation phenomenon with relaxation time of the order of 10^{-10} s in both phases has been established.

The substance investigated, C_5O/OC_8, is a nematogen liquid-crystalline compound with transition temperatures as follows:

solid — 323.2 K — nematic — 357.0 K — isotropic

The structure of the C_5O/OC_8 molecule



implies the existence of a permanent molecular dipole moment, mainly due to the alkyloxy terminal groups and central  $-\overset{\overset{\displaystyle O}{/\!/}}{C}-O-$ group. The result of simple vector analysis (assuming parallelism of para-axes, independent rotation of the perpendicular components of particular dipole moments and neglecting the electronic-donator (acceptor) function

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of the R—O (=CO) groups at the first benzene ring [1]) leads to the total permanent dipole moment

$$\mu_{\text{th}} = 8.6\times 10^{-30}\ \text{C.m}$$

with components

$$\mu_1 = 3.0\times 10^{-30}\ \text{C.m} \quad \text{and} \quad \mu_2 = 8.1\times 10^{-30}\ \text{C.m}$$

parallel and perpendicular to the para-axes respectively. The μ_{th} value is in good agreement with our experimental value

$$\mu_{\text{exp}} = 8.7\times 10^{-30}\ \text{C.m [1]}$$

and suggests a negative dielectric anisotropy.

The existence of dipolar relaxation due to rotation of the molecules in the nematic and isotropic phases of liquid crystals is well documented [2]. From numerous dielectric measurements [2] it is clear that in the nematic phase the relaxation regions associated with the rotation of molecules about their short and long axes are distinctly separated. As a consequence of this fact the rotation about the long axis (microwave frequency range) can be carried out on unoriented samples of the nematic phase.

The complex dielectric permittivity measurements of relaxation connected with molecular reorientations about short molecular axes (MHz frequency range) were performed for C_5O/OC_8 earlier [3]. The aim of the present investigation is to study the fast molecular relaxation in both liquid phases of C_5O/OC_8.

The measurements of the complex permittivity $\varepsilon^* = \varepsilon' - j\cdot\varepsilon''$ were performed on non-oriented samples by the short circuit waveguide technique [4] at the following frequencies ν (wavelength in cm): 1.0 GHz (29.88), 1.8 GHz (16.57), 6.0 GHz (4.99), 9.6 GHz

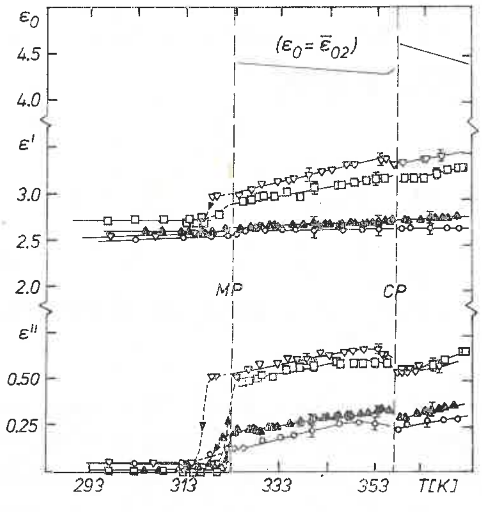

Fig. 1. Temperature dependence of the ε' and ε'' in the GHz range: ▽ — 1.0 GHz, □ — 1.8 GHz, ▲ — 6.0 GHz, ○ — 9.6 GHz. The ε_0 data from [3] are also plotted

(3.14). The experimental errors for ε' and ε'' were less than 0.1 and 0.05 respectively. The temperature was stabilized to within an accuracy of ± 0.3 K by means of a water thermostat and was measured by a platinum thermometer located right in the sample. The construction of the cryostat and the sample vessels have been described elsewhere [4].

For each frequency a few independent measurements were made, each of them on a new sample. The measurements vessel was filled with the sample at a temperature of about 365 K (isotropic phase). The measurements were performed while the sample was both slowly heated and slowly cooled. The temperature was stabilized every 2–4 K.

Reproduction of both the ε' and ε'' values obtained during the various experimental runs was very good. Subsequent analysis employed the $\varepsilon'(T)$ and $\varepsilon''(T)$ curves which were closest to the average ones.

Figure 1 contains the results of the present measurements of ε^* together with static permittivity data $\varepsilon_0 = \varepsilon'$ (0.1 MHz) [3] as a function of temperature. The existence of pronounced dielectric dispersion is evident.

To analyse the observed dielectric relaxation the Cole–Cole equation [5] was used

$$\varepsilon_t^*(\nu) = \varepsilon_{\infty t}+(\varepsilon_{0t}-\varepsilon_{\infty t})/(1+(j\cdot 2\pi\nu\tau)^{1-h}), \tag{1}$$

where ν is a frequency at which ε^* was measured; ε_{0t} and $\varepsilon_{\infty t}$ — parameters which limit the values of permittivity at the low and high frequencies, respectively; τ — an effective dielectric relaxation time, and h is a phenomenological parameter associated with the symmetric distribution of relaxation times.

For selected temperatures of nematic and isotropic phases formula (1) is fitted to the experimental data by means of the least-squares method viz. minimizing the sum:

$$S = \sum_i [\varepsilon^*(\nu_i)-\varepsilon_t^*(\nu_i)]^2. \tag{2}$$

The adjustable parameters are: ε_{0t}, $\varepsilon_{\infty t}$, τ, h. For the isotropic phase the ε_0 experimental values have been taken from earlier studies [3] directly — also see Fig. 1, for an unoriented sample of the nematic phase the static permittivity for the microwave frequency has been adopted from [3] in the following way:

$$\varepsilon_0 = \bar{\varepsilon}_{02}(\mathrm{GHz}) = \frac{2\varepsilon_{0\perp}(\mathrm{MHz})+\varepsilon_{\infty\parallel}(\mathrm{MHz})}{3}, \tag{3}$$

where $\varepsilon_{0\perp}$ is the static permittivity value for the sample oriented perpendicular to the measuring field (this value remains constant in the kHz and MHz frequency range), $\varepsilon_{\infty\parallel}$ is the permittivity value in the high frequency limit for the sample oriented parallel to the MHz-frequency measuring field.

To make sure of a symmetric distribution of relaxation times two fits are performed: with and without ε_0 data (a distribution is really symmetric if both fits give the same values of all parameters). In Fig. 2 the experimental results with fitted arcs are presented on the $(\varepsilon', \varepsilon'')$ plane for one representative temperature of each phase. In the nematic phase we have got the same set of ε_{0t}, $\varepsilon_{\infty t}$, τ and h no matter whether we have taken $\varepsilon_0 = \bar{\varepsilon}_{02}$ or not into account. The Cole–Cole arcs yielded approximately the same value of $\varepsilon_{\infty t} = 2.53$

± 0.01 and $h = 0.21$ with $\varepsilon_0 = \bar{\varepsilon}_{02}$ for all temperatures. The temperature dependence of the effective relaxation time τ is shown on Fig. 3 — it is a typical activational behaviour with activation energy 33 kJ/mole.

A more complicated situation is in the isotropic phase. There is no coincidence between the results of both fits. Although the values of $\varepsilon_{\infty t} = 2.50 \pm 0.02$ are approximately the same, the values of ε_{0t} as well as relaxation times are distinctly different. In the case where we have taken ε_0 into account, the arcs pass through these values i.e. $\varepsilon_{0t}(T) = \varepsilon_0(T)$ — see full arc on Fig. 2a. The temperature dependence of the calculated relaxation time is not simply activational, average activation energy is of the order of 20 kJ/mole.

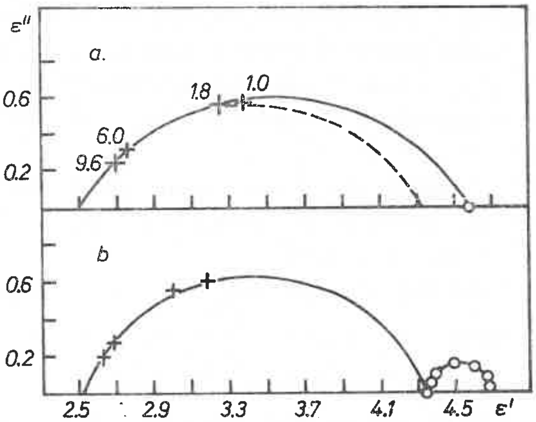

Fig. 2. Representative Cole–Cole plots for isotropic — (a) and nematic — (b) phases. Crosses denote results from GHz (frequencies in GHz), circles — results from MHz region [3]

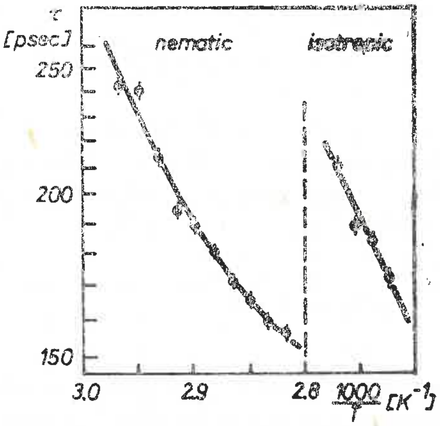

Fig. 3. Temperature dependence of the relaxation time τ

The fits without ε_0 have led to lower values of ε_{0t} — see dashed arc on Fig. 2a, and the relaxation times lowered by a factor of 0.77 in the whole temperature range. These results seem to indicate a distorted Cole–Cole plot for dielectric dispersion in the isotropic phase of C_5O/OC_8.

It must be pointed out, however, that the present measurements on C_5O/OC_8 have demonstrated, in nematic and isotropic phases, the existence of high frequency dielectric relaxation, created mainly by rotational movements of molecules around their long axes, the mechanism of observed relaxation in the isotropic phase is more complicated.

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