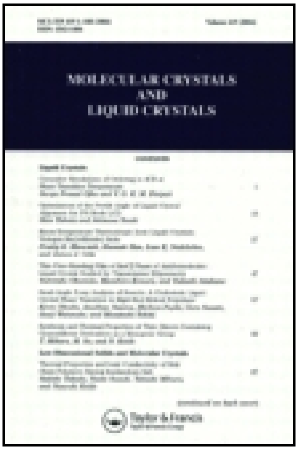

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Dielectric Relaxation in Nematic Liquid Crystals

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Abstract—In homogeneously ordered liquid crystals of the nematic type, two principal dielectric constants can be measured: ϵ_1 parallel and ϵ_2 perpendicular to the symmetry axis of the liquid crystal. The two dielectric constants may show a very different relaxation behaviour. With alkoxy derivatives of azobenzene, only the normal Debye dispersion region at microwave frequencies has been observed. With alkoxy derivatives of azoxybenzene, ϵ_2 shows again only the normal Debye dispersion region at microwave frequencies, but ϵ_1 has an additional dispersion at very unusually low frequencies in the radio region. This dispersion is due to the permanent electric dipole moment of the azoxy group, more exactly to its component parallel to the long molecular axis. The reorientation of this component in direction 1 is hindered by a potential barrier due to intermolecular forces. The corresponding relaxation time is increased by a factor g. Starting from a modification of the Debye theory of dielectric relaxation, this retardation factor may be used to calculate the height of the potential barrier. Numerical values are in satisfactory agreement with other values, calculated from the observed long range order.

In this paper we will give a review of our investigations on the dielectric properties of liquid crystals of the nematic type. The molecular structure of a nematic liquid crystal is fixed by only one principle of order: the long axes of the molecules are in the average parallel to a distinct direction. Because of the thermal motion, the long axes of the molecules oscillate around the preferred direction. From this principle of order there follows an anisotropy of all physical properties and this anisotropy is that of a uniaxial crystal. The preferred direction is equal to the optical axis of the liquid crystal. We denominate the preferred direction by the subscript 1 and any transverse direction by the subscript 2. The angle between the molecular axis and the preferred direction is denominated by θ. In a macroscopic sample the preferred direction may vary from one domain to another. A uniform alignment can be established very easily by a magnetic field of 1000–2000 G. With such magnetically orientated layers two principal dielectric constants can be measured. In the absence of a magnetic field, we observe values, that lie between the two principal dielectric constants. They are not well defined because they depend on the previous history of the sample. With an increasing magnetic field the measured values become more and more stable and constant. In the region of 1000 to 2000 G there occurs a saturation and a further increase of the magnetic field does not change the values. We must emphasize that the only effect of the magnetic field is to give a distinguished direction to the molecular order. The principal dielectric constants are constants of material and do not depend on the magnetic field. The preferred

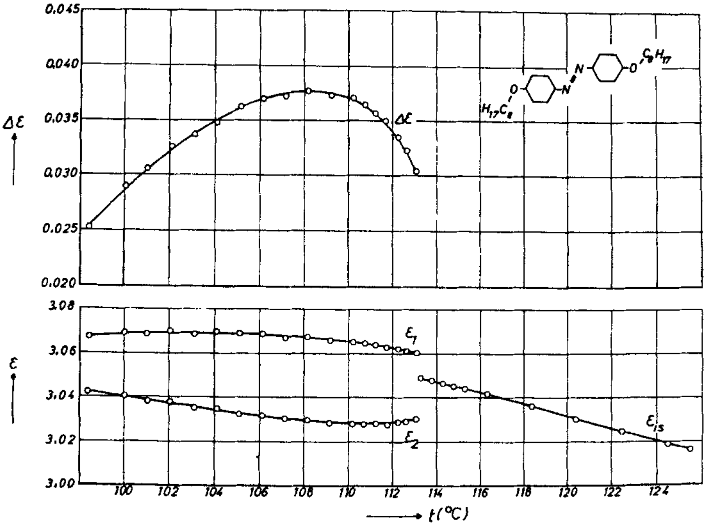

Figure 1. 4,4′-di-n-octyloxy-azobenzene: dielectric constants and their difference.

direction of the molecular order is equal to the direction of the magnetic field, and therefore ϵ_1 is measured, if E is parallel to H, whereas ϵ_2 is measured, if E is perpendicular to H.

As an example we show the results of measurement with 4,4′-di-n-octyloxy-azobenzene, as measured by Maier and Meier.[1] In Fig. 1, the principal dielectric constants and their difference are plotted *vs.* the temperature. ϵ_1 is larger than ϵ_2. The difference is small and amounts to only 1%. At the transition point from the liquid crystalline to the normally liquid state the anisotropy vanishes discontinuously.

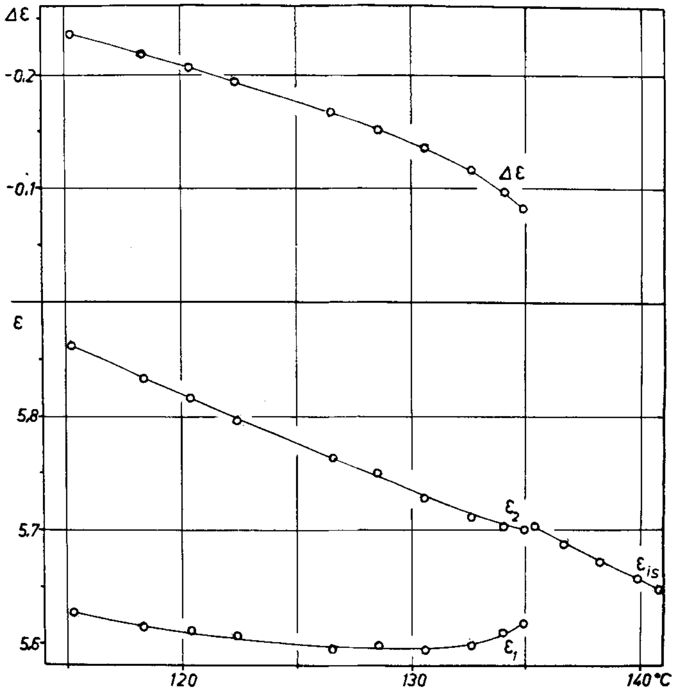

Figure 2. 4,4′-di-n-methyloxy-azoxybenzene (*p*-azoxyanisole): dielectric constants and their difference.

As another example we show the results with *p*-azoxyanisole in Fig. 2 after measurements of Maier and Meier.[2] Here ϵ_2 is larger than ϵ_1. The difference amounts to a few per cent. The frequency of the electric field was 100 kc to 1 Mc.

The question, which of the two principal dielectric constants will be larger than the other, depends on the amount and the direction of the molecular permanent dipole moment. In the case of *p*-azoxyanisole, there is a strong dipole moment that makes a large angle with the molecular long axis. Therefore ϵ_2 is greater than ϵ_1.

Starting from a modification of the Onsager theory of dielectric polarization, Maier and Meier[3] succeeded in explaining these values. The principal dielectric constants depend on the principal polarizabilities of the molecule, the permanent dipole moment and its direction with respect to the long molecular axis, and the degree of order of the liquid crystal. These calculations have shown that the principal dielectric constants are defined only by these molecular properties and the nematic ordering. At low frequencies the dipoles must be regarded as reorientating freely as in the isotropic phase. The average dipole or orientation polarization is essentially as large as in the isotropic phase. Therefore we must assume that there is no unusually strong dipole association.

Now we have to make some remarks to the effect of the electric field on the molecular order. In their early investigations, Ornstein and Kast[4] observed a relaxation range at frequencies of some 100 kc, that they tried to explain by a reorientation of swarms. But we think, that this is not an actual relaxation process but perhaps a phenomenon which is connected with the existence of liquid flows that are easily observed at low frequencies. These flows also may be the cause for the abnormal behaviour of macroscopic alignment at direct current or very low frequencies. At higher frequencies these flows break off, and the liquids show a normal behaviour of alignment, at least in all cases, that have been investigated hitherto. That means that the liquid orientates macroscopically in such a manner that the axis of largest dielectric constant shows in the direction of the electric field.

We give two examples: the above-mentioned azo compound has a principal dielectric constant ϵ_1 that is larger than ϵ_2. At higher frequencies and sufficiently strong electric fields, the preferred molecular orientation is in the direction of the field, if there are no other orienting forces. With *p*-azoxyanisole, ϵ_1 is smaller than ϵ_2. Here the preferred direction is perpendicular to the electric field. With the above referred dielectric measurements this orientation was of no importance, since Maier and Meier employed very weak electric fields and oriented by comparatively strong magnetic fields.

Now we must turn up to the question of the mechanism of the dipole orientation. Regarding the molecular order of a nematic liquid crystal, we can easily see, that a rotation of a molecule around a transverse axis must be very much more hindered than the other motions of rotation, par example a rotation around the long molecular axis is essentially not hindered. Therefore a dipole orientation, that can only be realized by a changement of the angle θ, must show a higher relaxation time.

We have to discuss this fact more exactly. Let us consider a molecule like *p*-azoxyanisole. The permanent dipole moment may be composed of two parts: one part μ_E that belongs to the end groups of the molecule and can rotate in a more or less free manner, and another part, that belongs to the central group of the molecule and is fixed in the molecule. We denominate it by μ_F. It is only μ_F that is touched by the restriction of the θ orientation, since μ_E can reorientate by the inner degree of freedom, even if the angle θ is fixed. Now we divide μ_F into a longitudinal component μ_{FL} in the direction of the long molecular axis and a component μ_{FT} in a transverse direction. The reorientation of the component μ_{FL} into the direction 1 is hindered because it is connected with a rotation of the molecule about a transverse axis. The transverse component can reorientate freely by rotation around the long axis, and there is no hindrance at all for the dipole reorientation into the direction 2.

Therefore we have to expect the principal dielectric constant ϵ_2 to have an ordinary dependence of frequency, whereas ϵ_1 will have an additional region of dispersion. In Fig. 3 we see the expected values for *p*-azoxyanisole. ϵ_2 is constant up to the microwave region. There we have the normal Debye relaxation, and ϵ_2 drops down to the optical value. On the other hand, ϵ_1 must have an additional and very unusual dispersion below the Debye region. This dispersion is due to the intermolecular forces that cause also the long range order of the nematic liquid crystal. Maier and Meier[5] succeeded in finding the range, where the relaxation occurs. In Fig. 4 we see the results of measurements with *p*-hexyloxy-azoxybenzene. The frequency range is from 100 kc to 4 Mc. In this range ϵ_2 is not dependent on the frequency but ϵ_1 shows a pronounced dispersion. The dispersion vanishes at the transition point. In Fig. 5. we see the dielectric loss plotted against the temperature. The frequency at maximum loss is extremely dependent on the temperature.

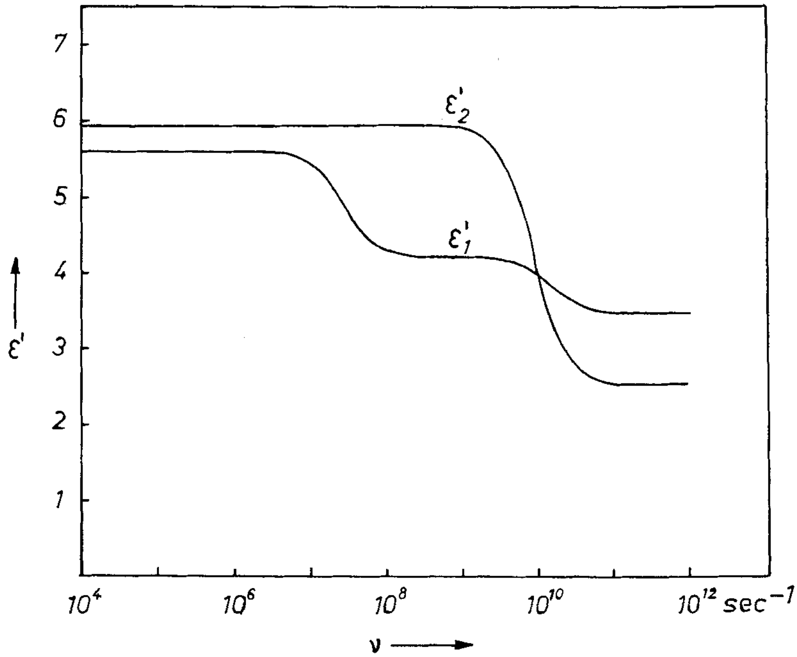

Figure. 3 Expected dispersion of the dielectric constants of *p*-azoxyanisole.

We will characterize the relaxation process by a relaxation time τ_1. We denominate the corresponding relaxation time of the ordinary Debye relaxation by τ_0. τ_0 may for instance be experimentally determined by extrapolation from measurements in the isotropic phase. Now we define the retardation factor g by the ratio $g = \tau_1/\tau_0$. This retardation factor is very strongly dependent on the

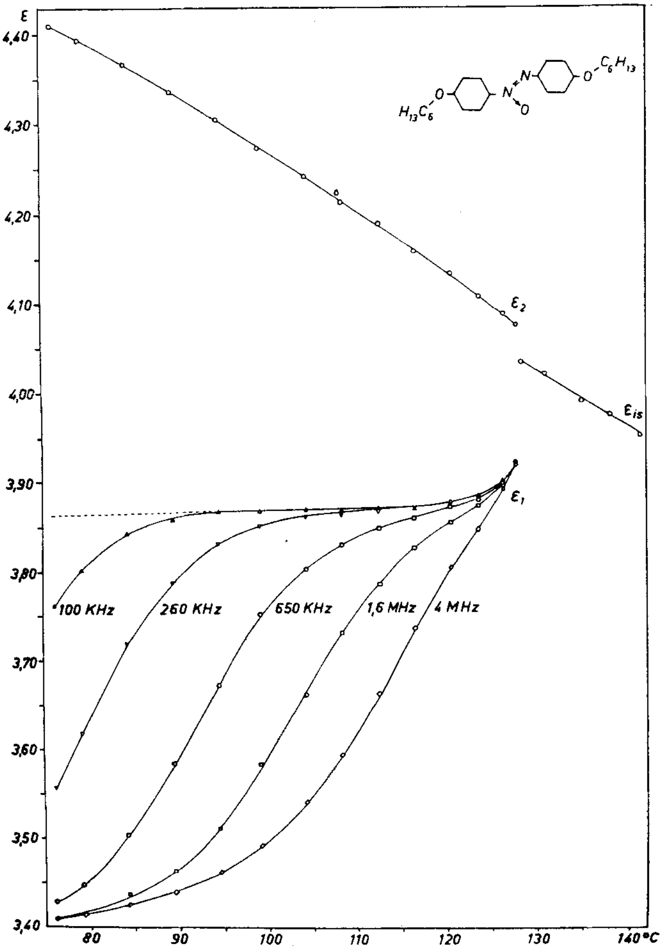

Figure 4. 4,4′-di-n-hexyloxy-azoxybenzene: dielectric constants.

temperature. Its order is 100 to 1000. We have to emphasize that these values are extremely high and that it is very unusual that a radio frequency dispersion occurs with liquids. At first sight this is very surprising since the viscosities of the regarded liquid crystals have normal values. Therefore we have the problem to make understandable this great retardation factor, that is we must find a connection between τ_1 and the intermolecular forces.

We start from the Debye differential equation

$$\frac{\partial f}{\partial t} = \frac{1}{2\tau_0 \sin\theta}\frac{\partial}{\partial\theta}\left\{\sin\theta\left(\frac{\partial f}{\partial t} - \frac{M}{kT}f\right)\right\} \tag{1}$$

f is the distribution function and is dependent on θ and the time t:

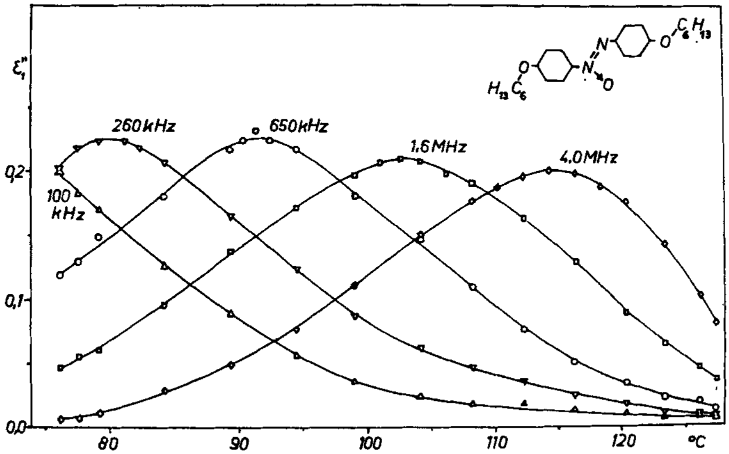

Figure 5. 4,4′-di-n-hexyloxy-azoxybenzene: dielectric loss.

$f = f(\theta, t)$. f describes at any time the distribution of the dipoles among the various directions in space. We assume that there is a permanent dipole moment, that is parallel to the long molecular axis. The angle $\theta = 0$ gives the direction of the applied electric field (measurement of ϵ_1). The meaning of f will be obvious if we consider the expression

$$dN = N_0 f \sin\theta \, d\theta$$

dN is the number of dipoles per cubic centimetre whose directions are included between θ and $\theta + d\theta$. N_0 is the number of dipoles per cubic centimetre. The function f is normalized such that

$$\int_0^\pi f \sin\theta \, d\theta = 1$$

τ_0 is the ordinary Debye relaxation time and M is the torque acting on a dipole. The electric polarization P is given by

$$P = N_0\bar{\mu} = N_0\mu\int_0^{\pi} f\cos\theta\sin\theta\, d\theta$$

Let us now suppose that there is an electric field E_0 acting on the dipoles and that this field is turned off at a time t_0. In order to simplify the calculations we assume that the distribution function f always will have the form

$$f(\theta,t) = f_0\left(1+\frac{a(E_0,t)}{kT}\cos\theta\right)$$

where f_0 is the undisturbed distribution of the nematic order. With this assumption we obtain from (1) the following differential equation

$$\frac{\partial P}{\partial t} = -\frac{1}{\tau_0}\frac{f_0(\pi/2)}{\langle|\cos\theta|\rangle}P \tag{2}$$

Here $\langle|\cos\theta|\rangle$ is the expectation value of the absolute value of $\cos\theta$ in the undisturbed distribution f_0. The solution is

$$P = P_0 e^{-t/\tau_1} \tag{3}$$

The polarization P falls off with a decay rate that is given by the relaxation time $\tau_1 = g\tau_0$, where

$$g = \frac{\langle|\cos\theta|\rangle}{f_0(\pi/2)} \tag{4}$$

We started from the assumption that the perturbation of the distribution function f_0 always will have a form like the cosine function. Now we have to discuss the significance of this assumption. For this purpose we divide the dipoles contained in 1 cm^3 into two ranges:

N_1 is the number of dipoles with direction from 0° to 90°
N_2 is the number of dipoles with direction from 90° to 180°

Our assumption means firstly that we neglect the influence of the reorientation within the two ranges on

$$\frac{\partial}{\partial t}(N_1-N_2)$$

More detailed considerations show that this neglection is not serious with respect to the value of the retardation factor. We estimate that the error in g does not exceed 20%. Secondly, our assumption means, that we put

$$\frac{\partial P}{\partial t} \sim \frac{\partial}{\partial t}(N_1 - N_2)$$

This is not exactly true. We take into account only such variations, that arise from the transition of a dipole from one range to another. We neglect all variations of the polarization that are caused by reorientations of the dipoles within the two ranges. However we could show that this process involves only a small part of the whole polarization. Therefore we think that our assumption in this point is justified.

Now let us discuss the formula (4) for the retardation factor. In the normal liquid phase, the distribution function f_0 is a constant. Its value is $\frac{1}{2}$ because of our normalization. The expectation value of $|\cos\theta|$ is $\frac{1}{2}$. In a perfectly ordered liquid crystal, $\langle|\cos\theta|\rangle$ amounts to 1 and in a real liquid crystal we can assume a typical value of 0.8. Therefore we are able to calculate $f_0(\pi/2)$ without any further assumption. We obtain $f_0\ (\pi/2) = 0.8/g$. Since g has values of 100 or 1000, we see that the density of population about an angle of 90° is reduced to a very little fraction of the correspondent value in the isotropic phase.

Now we turn to the problem to correlate the retardation factor to the potential given by the intermolecular forces. For this purpose we assume the distribution function to have the following form

$$f_0(\theta) = C\,e^{-(q/kT)\sin^2\theta}$$

q is a parameter that must be adapted to give the right value of g. This function is one of the most simple possibilities to describe the molecular ordering and is commonly used in the long range order theories.[6–8] With this function we can also evaluate the expectation value of $|\cos\theta|$. We obtain the following relation between the retardation factor and the parameter q

$$g = \frac{kT}{q}(e^{q/kT}-1) \approx \frac{kT}{q}e^{q/kT}$$

With *p*-azoxyanisole the experimental value is $g = 100$ at 121° C. From this it follows $q = 0.22$ eV.

Now there is another way of calculating the value of q. The intermolecular forces are the cause for the long range order, and therefore there must be a relationship between q and the degree of order. This degree of order S is defined by

$$S = \tfrac{1}{2}\langle 3\cos^2\theta - 1\rangle$$

The degree of order S can be evaluated experimentally, par example by measurements of the diamagnetic susceptibility. With azoxyanisole $S = 0.56$ at 121°C. If we assume again the same distribution function as before, we can calculate the value of q. The result is $q = 0.14$ eV.

In this evaluation we have taken into account the long range order. But with respect to the dielectric relaxation the important quantity is the short range order. It is evident that the long range order must be smaller than the short range one. Therefore it is understandable that we obtain a smaller value of q if we start from the long range order. We have to emphasize that it was our aim to understand the existence of a low frequency dispersion region. In this sense we think that the agreement between the two values may be regarded as satisfactory.

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