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Relaxation of Light Scattering in Nematic Crystals and in Nematic–Cholesteric Mixtures†

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Abstract—The properties of the decay of dynamic scattering in a nematic substance after the suppression of the dc field as well as of the erasure by an ac voltage of the texture stored in a nematic–cholesteric mixture have been investigated. The variations of the times characterizing these relaxation processes with temperature, dc scattering and ac erasing voltage, cholesteric concentration and other parameters are presented.

1. Introduction

The possibility of application of liquid crystals in visualization and display systems has aroused a great interest in the study of the effects of electric fields on these substances. However, few results have been published up to now on the decay of dynamic scattering when the dc electric field that produced it in a pure nematic substance is suppressed or when an ac voltage is applied to a cholesteric–nematic mixture simultaneously with the dc field removal.

In nematic liquid crystals, Williams$^{(1)}$ has assumed that reorientation begins at the surface and propagates at a diffusion controlled rate; in these conditions the scattering light intensity I_s decreases as a function of time t following the relation

$$I_s = I_0\left(1 - \frac{2D^{1/2}t^{1/2}}{L}\right) \qquad (1)$$

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where I_0 is the initial intensity, D the diffusion coefficient and L the cell thickness. The decay time τ_D (defined as the time during which the scattered intensity falls from 90 to 10% of its initial value) is then

$$\tau_D = \frac{0.8L^2}{4D} \tag{2}$$

This model agrees with the experimental results obtained by Heilmeier *et al.*(1) on anisylidene para-aminophenyl-acetate films of 6 μm thickness. Creagh *et al.*(2) have studied the time dependent behaviour of some nematic liquid crystals including the variation of decay time, as well as of the delay and rise times with the cell thickness and temperature.

In point of fact in the decay of dynamic scattering, as reported by Jakeman and Raynes,(3) several relaxation times must be taken into account, the importance of which depends on the nematic substance conductivity: in high conductivity compounds having good dynamic scattering properties the dielectric relaxation time $\epsilon/4\pi\sigma$ where σ is the electrical conductivity and ϵ the dielectric constant is much shorter than the director relaxation time η/Kq^2 where η is the substance viscosity, q is the wave vector (function of the electric field) and K an elastic constant. In these conditions the director relaxation will dominate the decay process of the dynamic scattering.

In mixtures of cholesteric and nematic substances optical storage effects were described for the first time by Heilmeier and Goldmacher.(4,5) These authors have shown that in such a mixture (90% by weight of anisylidene-*p*-aminophenylacetate and 10% of cholesteryl nonanoate) the scattering of light produced by dc or low frequency (<50 Hz) ac field application persists after field removal. An erasure or clearing of the stored image can be obtained by application of an audio mid-range frequency (≥ 500 Hz) voltage. They have also found that the erasure time τ_E (defined as τ_D above) varies as a linear function of V^{-1}, V being the ac erasure voltage. Several authors(6,7) have shown that the application of high frequency fields results in the formation of the cholesteric Grandjean plane texture whereas low frequency fields produce a focal-conic texture which is scattering. It can be mentioned that optical storage effects are also observed by cooling cholesteric–nematic mixtures which have been heated above their isotropic point;⁽⁸⁾ the obtained structure can also be erased with an ac field.

In this paper we report:

—the variation of decay time and in particular its dependence on temperature, thickness and applied dc voltage, for a commercial product (LCI: nematic range 5–70 °C⁽⁹⁾ having a high conductivity; the results obtained have been compared to those found with a compound (Nematische Phase V⁽¹⁰⁾) of low conductivity;

—the characteristics of the erasure (by an ac voltage) of the texture stored by application of a dc field on mixtures of LCI and of cholesteryl nonanoate (CN) and specially the dependence of the erasure time on temperature, erasure voltage, CN concentration and dc applied field.

2. Experimental Set-up

The experimental arrangement used is the same in both series of measurements. The sample cells consist of a thin layer of the nematic substance or cholesteric–nematic mixture between two transparent electrodes (oxide coated glass) separated by mylar spacers of various thicknesses: 13 to 75 μm in the first case, 18 (or 36) μm in the second. The spacing of the electrodes is kept uniform by a constant pressure device. Homogeneous alignment of the liquid crystal is obtained by unidirectional rubbing on paper of the electrode surfaces, following the method suggested by Chatelain.⁽¹¹⁾

The cell being observed is placed in a box where the temperature kept constant (within ±0.1 °C) by circulating water, can vary between 10 and 50 °C approximately. It is illuminated with a white light source and the beam passing through the cell impinges on a photomultiplier, the anodic signal of which is photographed on an oscilloscope screen or registered on an X-Y recorder. The transmitted intensity I_t and the scattered intensity $I_s = I_0 - I_t$ where I_0 is the light intensity transmitted without electric field, can thus be determined at every instant when the electric fields (dc or ac) are applied or removed.

In the case of the pure nematic substance, we have studied the relaxation of dynamic scattering after suppression of the dc field either by an open circuit or by short-circuiting the electrodes. In our case both results were quite comparable, therefore we studied mainly the open circuit conditions. The shape of the curve that represents the variation of the scattered intensity as a function of time is shown in Fig. 1a.

In the case of the cholesteric–nematic mixtures, we have deduced from the decay curves an erasure time τ_E (defined as above) when simultaneously with the dc field removal an ac field is applied. We have chosen a frequency of 1 KHz, since preliminary experiments

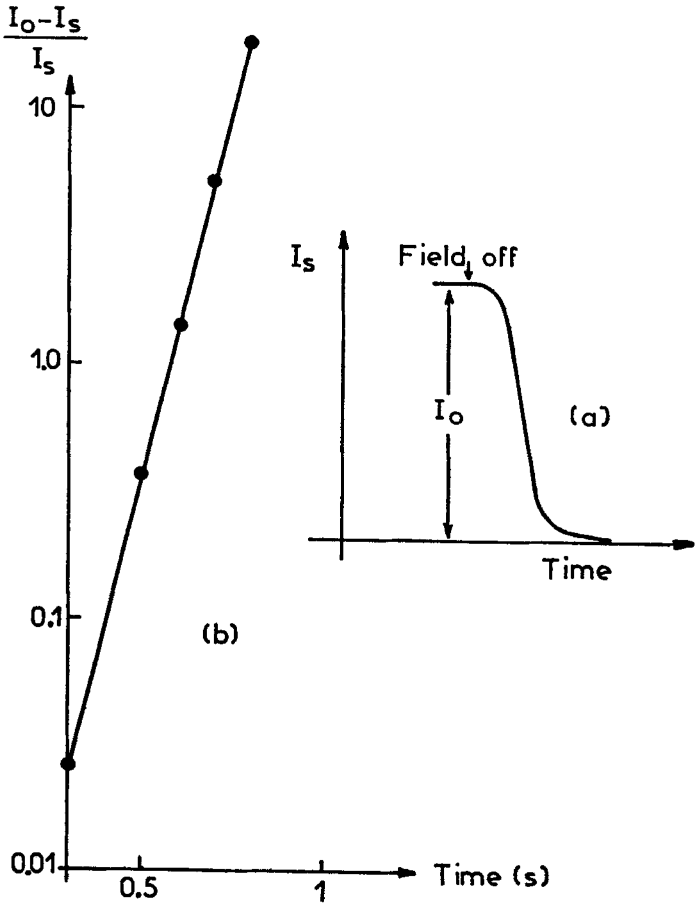

Figure 1. Time dependence of the decay of dynamic scattering after the suppression of the electric field.

had shown that the erasure time depends little on the frequency between 0.5 and 5 KHz.

In addition, for each cell the current versus voltage characteristics have been plotted for the various temperatures.

3. Results on the Pure Nematic Substance

1) It has been found for the different cells analyzed that the scattered intensity I_S varies as a function of time t, when the field is removed, according to the relation

$$\frac{I_0 - I_S}{I_S} = \exp\left(\frac{t - t_0}{\tau}\right) \tag{3}$$

or

$$I_S = \frac{I_0}{1 + \exp\left(\frac{t - t_0}{\tau}\right)} \tag{4}$$

where t_0 is a constant.

This relation which differs from that of Williams is well verified as shown in Fig. 1b even for variations of the ratio

$$\frac{I_0 - I_S}{I_S}$$

of above 1,000 times provided that the applied field is not too high. However we have not yet found a simple model to account for the law given by Eq. (4). In fact, as shown later, for voltages of 60 to 80 volts (or more) a slow component appears in the decay curve, which becomes more important for cells of thicknesses above 30 μm and at temperatures exceeding 40 °C.

In each case we have also determined the decay time τ_D defined above. From Eq. (4) it is easy to verify that

$$\tau_D \approx 4.4\tau$$

which is in good agreement with the experimental results.

We have studied the variation of τ (or τ_D) with the temperature T (°K), the thickness L of the liquid crystal film and the dc field $\mathscr{E}$ applied to the cell.

2) For a given thickness, when the temperature increases, the time constant τ decreases as shown in Fig. 2 for a dc applied voltage of 20 volts.

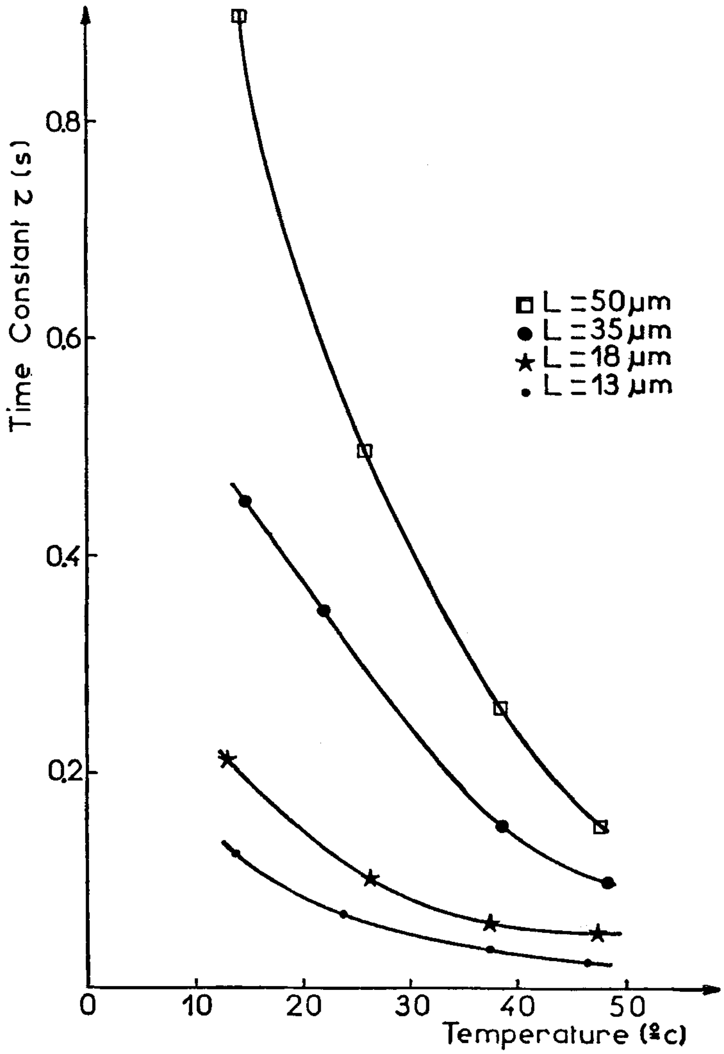

Figure 2. Temperature dependence of the time constant τ for various cell thicknesses (applied voltage: 20 volts).

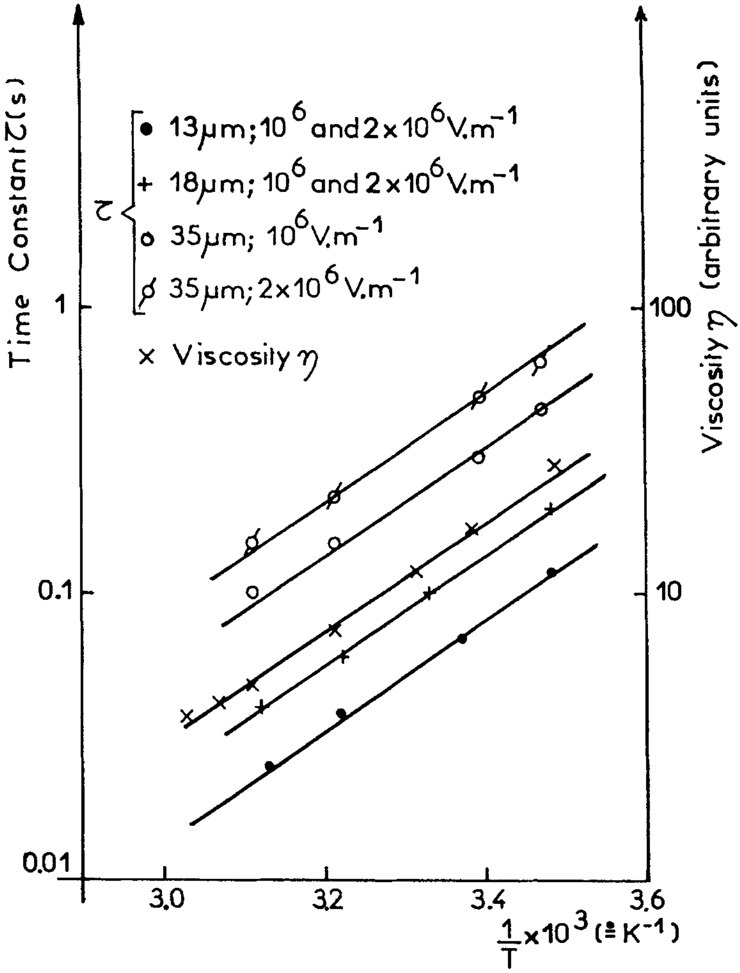

Figure 3. Variation with temperature of the LCI viscosity η and temperature dependence of the time constant τ for given electric fields (10^6 and 2×10^6 V m^{-1}) and three thicknesses (13, 18 and 35 μm).

On Fig. 3 we have plotted the variation of Log τ as a function of $1/T$ for cells of three different thicknesses and at constant electric fields of 10^6 and 2×10^6 V m^{-1} (the curves for both fields are identical for the cells of 13 and 18 μm). In the interval of measured temperatures which does not entirely cover the nematic range, this variation follows a law of the form

$$\tau = A \exp(\delta E/KT) \tag{5}$$

where K is Boltzmann's constant and A an arbitrary constant.

It can be seen that δE is practically independent of the thickness and of the electric field in the studied range; its value is approximately 0.4 eV. With the compound Merck V which has a considerably lower conductivity the variation of Log τ is similar and has an equal slope.

We assume that the variation of τ with the temperature is due exclusively to that of the nematic substance viscosity η. Indeed as reported by the Orsay Liquid Crystal Group,(12) whatever the conductivity may be, τ is proportional to η. Various authors(13,14) have investigated how the viscosity of nematic substances varies with temperature. We have also studied this variation for our products with a viscometer similar to that described by other authors.(15)

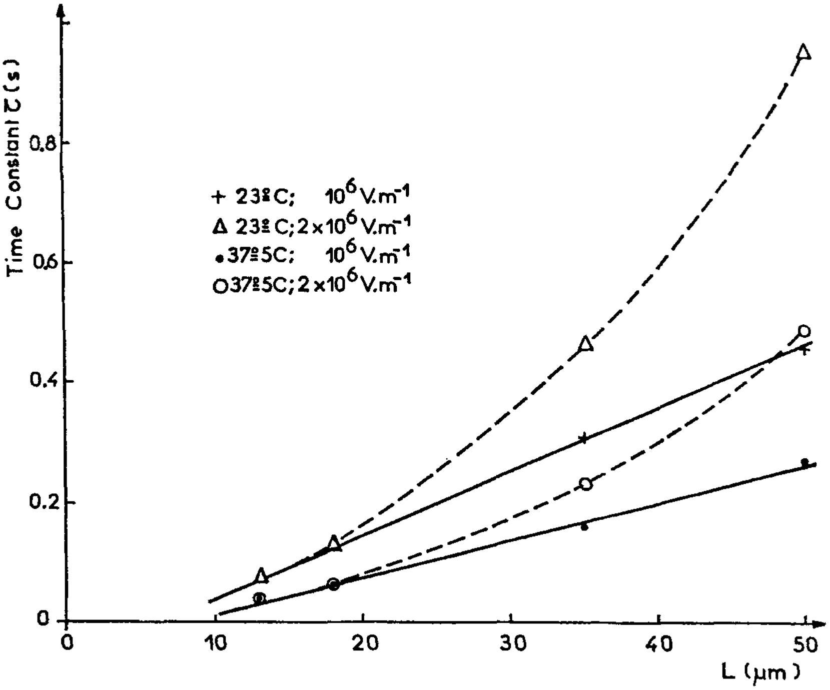

Figure 4. Thickness dependence of the time constant τ for various temperatures and for constant electric fields.

Our results plotted in Fig. 3 point out the relation between τ and the viscosity; they agree with those of Koelmans and van Boxtel(14) who have shown that in a mixture of Schiff bases the rise time t_r of dynamic scattering is proportional to η. They also found a variation of η (and t_r) with temperature similar to that of expression (5), with a practically equal slope.

3) For the high conductivity compound (LCI) the director relaxation should, as mentioned before, dominate the decay of the dynamic scattering. The correspondent time constant τ is a function of the thickness L and of the electric field $\mathscr{E}$.(3) We have examined experimentally the influence of these parameters.

a) In Fig. 4 the time constant τ has been plotted versus L for two temperatures and keeping the electric field constant. For fields up to 10^6 V m^{-1} the time τ is a linear function of L between 13 and 35 μm at least. It should be noted that τ depends little on the field for the low values of the thickness. If the field is raised, for example to 2×10^6 V m^{-1}, a logarithmic plot of τ versus L shows that τ varies approximately as L^2. This is in agreement with the results of other authors.(1,2)

b) In the cases where the slow component can be neglected, the time constant for the LCI compound is practically independent of the dc voltage applied provided that it is lower than approximately 50 volts. For higher voltages the time constant rises, as shown in Fig. 5 for a cell of 13 μm. This is in agreement with the observations of Nehring(16) and of Sussman.(17) The latter has observed that the speed of relaxation decreases with increasing voltage at turnoff for an originally homogeneous orientation as achieved by rubbing, which is the case in our experiments.

If the cell thickness is raised sufficiently the field effect should become more important compared to that of L and the time constant should decrease when the electric field increases. An experiment performed with a cell thickness of 75 μm shows such a decrease of the time constant.

On the contrary, for the Merck V compound, we have found that the influence of the electric field is low and can be even neglected, which indicates that the dielectric relaxation is the predominant process in the decay.

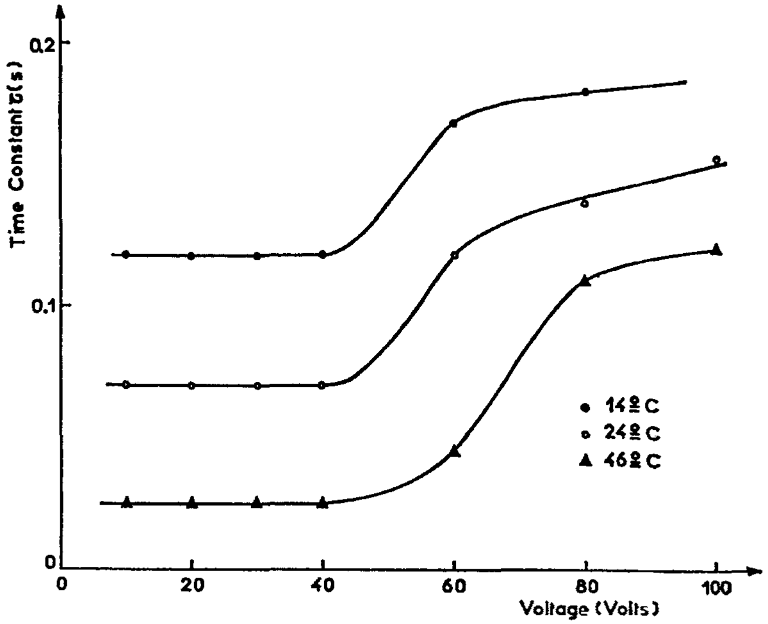

Figure 5. Voltage dependence of the time constant τ for various temperatures in a cell of 13 μm.

4. Results on Nematic–Cholesteric Mixtures

1) As observed by several authors(18) it must be mentioned at first that the addition of cholesterics to a nematic product, even in small percentages, induces cholesteric characteristics and particularly storage effects. In fact these effects appear only at a voltage V_m higher than the threshold V_n of dynamic scattering for the pure nematic substance. The voltage V_m corresponds approximately to the break point of the curve current vs voltage; it rises as previously observed(19) with the CN concentration and decreases for higher temperatures. For applied voltages between V_n and V_m the dynamic scattering disappears spontaneously after suppression of the dc field, according to a time constant whose value does not differ noticeably from that of the nematic product in the same conditions.

2) For a given thickness when the temperature increases in the range of 10 to 50 °C, the erasure time τ_E decreases following the same law (relation 5) as in the pure nematic product (Fig. 6). The quantity

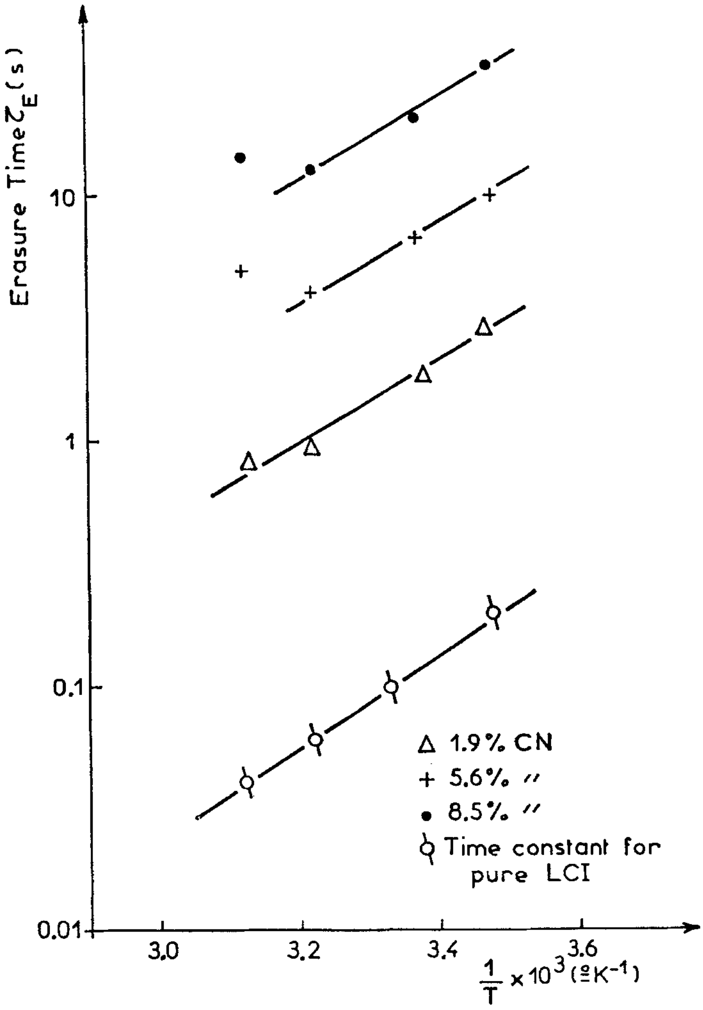

Figure 6. Temperature dependence of the erasure time τ_E for three CN concentrations in the following conditions: dc voltage 50 volts, erasing voltage 80 volts (rms).

δE varies little when the CN concentration increases from 1% to 9% (by weight) and its value is of the order of that found for the pure LCI (0.4 eV). However it must be noted that the values of τ_E obtained for temperatures of the order of 45 °C have some tendency

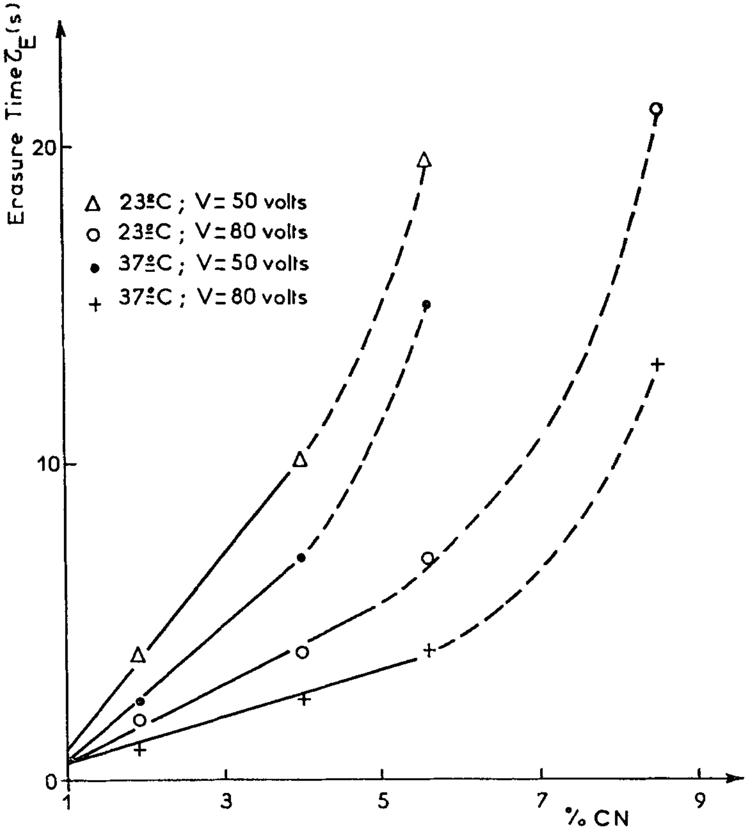

Figure 7. ac voltage dependence of the erasure time τ_E for various CN concentrations in the following conditions: temperature 24 °C, dc voltage 50 volts.

to deviate from this law; such a behaviour has been also observed by Berchet *et al.*⁽¹³⁾ in their viscosity measurements.

3) Our experimental results show that the time τ_E varies with the erasing ac voltage V following the relation

$$\tau_E = aV^{-n}$$

where a is a constant. Examples of this variation are given in Fig. 7 for various concentrations. In the studied range it may be verified that the exponent n is approximately independent of the temperature and of the dc field producing the diffusion of the light; it increases following a linear law with the cholesteryl nonanoate concentration:

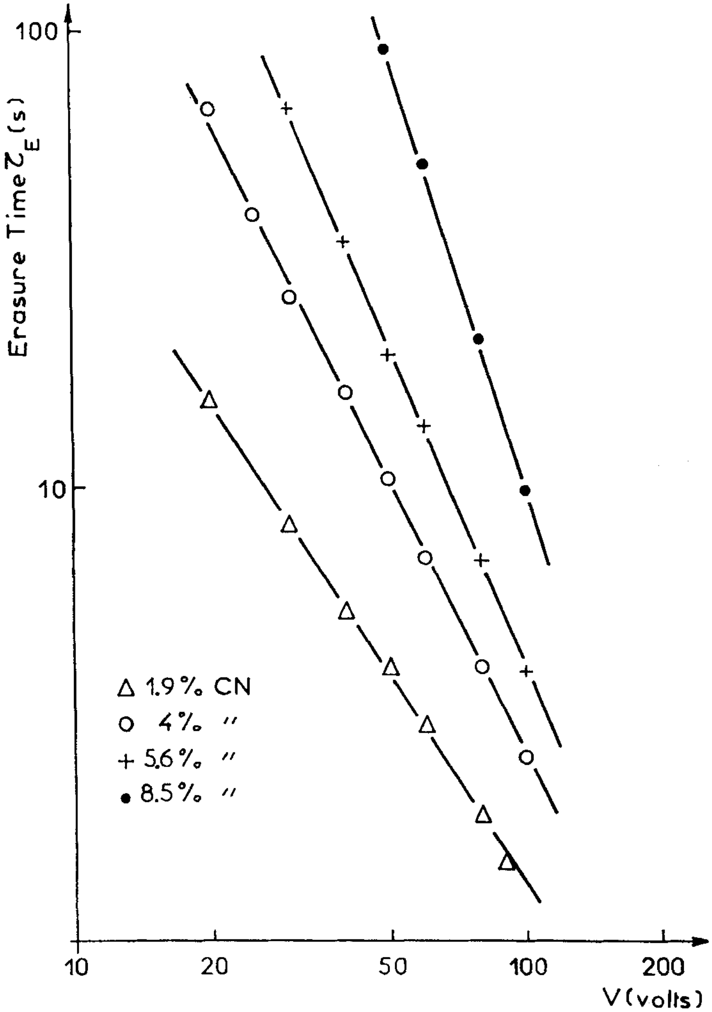

Figure 8. CN concentration dependence of the erasure time τ_E for a dc voltage of 50 volts.

for example $n = 1.5$ and 3.15 respectively for 1% and 8.5% of CN.

4) For a given temperature and for a constant erasure voltage, the time τ_E increases linearly with the CN concentration between 1% and 5 to 6% of CN. For higher concentrations the erasure time rises much more rapidly. This behaviour is shown in Fig. 8 for two temperatures and two erasure voltages V.

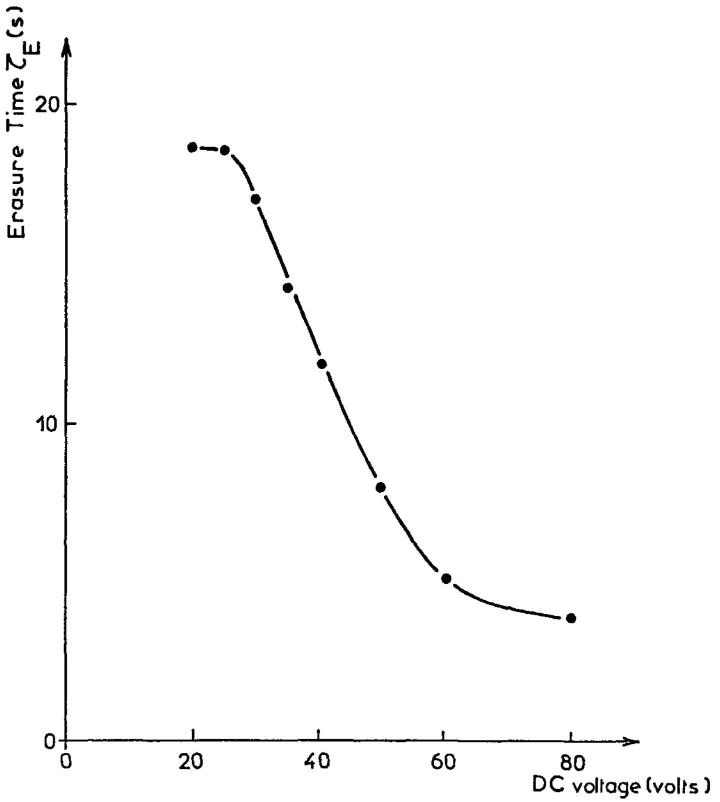

Figure 9. dc voltage dependence of the erasure time for a CN concentration of 9% for a temperature of 23 °C.

It should be noted that in the case of a CN concentration of 0.5% a spontaneous decay of the scattered light after removal of the dc field is observed. This decay is slowed-down quickly by the addition of more cholesteric product but it can be accelerated by application of an ac erasing voltage.

5) The influence on the erasure time τ_E of the dc field producing the diffusion of light has also been studied. For CN concentrations higher than 4% the time τ_E decreases markedly when the dc voltage is increased starting from 20 volts (for a cell thickness of 18 μm) and when the erasure voltage is applied simultaneously with the dc field removal. This variation is shown in Fig. 9. On the contrary for the

lower concentrations τ_E is practically independent of the dc voltage. We think that this effect is due to field-induced texture changes as those observed by several authors:(20,21) a transition of focal-conic into Grandjean texture which can be explained by energetic considerations would reduce the storage effect and the time τ_E.

We have also observed that if the erasing voltage is applied some time T_d after the dc field removal, τ_E is increased accordingly and for a sufficient time T_d (two minutes approximately) it tends towards the order of value corresponding to low voltages (20 volts for a cell of 18 μm). This effect could be due to a texture transformation passing through a more stable condition of which the mechanism is not yet well known.

5. Conclusions

The addition of small amounts of cholesterics into a nematic product introduces an effect of memory but the dependence on the temperature of the decay time τ_D for the nematic substance and that on the erasure time τ_E for the mixtures are very nearly the same and related to the viscosity. However the effect of the dc voltage V is different for both cases since τ_D is not affected noticeably except for values higher than 50 volts whereas τ_E diminishes considerably with the augmentation of V. As for the mixtures, the erasure time increases with the concentration of cholesteric product but it can be strongly reduced by applying higher ac voltages; for example a voltage rise of 20 to 100 volts produces in τ_E a decrease of 30 times approximately.

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