Dielectric Relaxation of Long Molecules in Nematic Host Matrices

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The relaxation times τ of the slowest processes in the parallel dielectric permittivity of various nematic guest-host systems have been measured as a function of temperature. A correlation between τ and its temperature dependence is found, indicating increasing temperature dependence for increasing τ, independent of structural details of the guest molecules or properties of the host matrices which, however, had similar clearing temperatures. Alternations in τ for a homologous series of guest molecules are observed. Increasing host permittivity leads to increased values of τ while the viscous properties of the host show little influence on τ.

1. Introduction

Relaxation at radio frequencies in the dielectric permittivities of nematic substances has been studied by many authors [1]. In isotropic liquids of molecules of a size similar to nematogenics the rotational motion of polar molecules leads to relaxation phenomena in the 100 MHz region. In nematics, similar processes occur which are, however, complicated by the anisotropic nature of the fluid. For the longitudinal permittivity a much slower process in the 1 MHz region is also observed. It can be attributed to the "180°-jumps" by which, roughly speaking, the molecules switch from parallel to antiparallel alignment (up or down) with respect to the director.

This jump process is expected to be a very slow isolated mode, well distinct from the fast modes of orientational realignment preserving the up- or down property. For this reason one expects that this jumping process is well described by a single-relaxation time formalism which leads to the classical Debye formula for the dispersion of the parallel dielectric permittivity in accordance with many observations [2]. In systems with more than one component several slow relaxation processes for the individual species have been separated when they differed sufficiently in their relaxation times [3]. In simple theories of rotational diffusion in isotropic liquids the viscosity determines the rotational diffusion coefficient and hence the relaxation time for reorientation [4]. By analogy it has been suspected that the slow relaxation in nematics is correlated with viscous properties of the nematic. In the present investigation we consider a series of relatively long molecules dissolved in nematic host. By varying the structure of the solutes and of the solvents we obtain some insight in the factors determining the relaxation time of the solutes and its dependence on temperature. For applications these relaxation processes are interesting with respect to two-frequency addressing schemes for twisted nematic displays. These methods utilize the change in sign of the dielectric anisotropy wich may occur upon changing the frequency, due to the above-mentioned relaxation processes [5]. For these applications large relaxation times with weak temperature dependence are desirable.

2. Experimental, Substances and Parametrization of Measurements

The measurements have been made in a capacitor with an area of $\pi\,\mathrm{cm}^2$ and a plate spacing of 1 mm provided by a teflon ring. To eliminate the influence of stray capacitances a guard ring construction was used. The measurements were made with a Wayne-Kerr B 642-bridge in the low-frequency range up to 20 kHz and with a Wayne-Kerr B 602-bridge between 100 kHz and 10 MHz. In the range between 20 kHz and 100 kHz a labor-made bridge was used. The connecting cables were kept short for low inductance. When evaluating the measurements we took into account their inductance which, however, led to sizable corrections only for frequencies above 3 MHz. The nematic liquid crystal was oriented by a magnetic field of about 7 kOe in which the surface orientation of the director pene-

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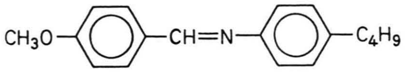
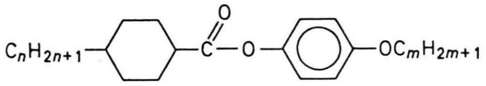
Table 1. Composition, clearing temperature T_c, dielectric permittivities $\varepsilon_\parallel$ and $\varepsilon_\perp$, flow aligned shear viscosity η_s, average Debye relaxation time τ_h, amplitude of relaxation $\delta\varepsilon_h$ and estimated ratio for the rotational viscosity γ_1 over η_s for the pure host mixtures.

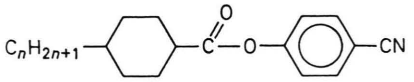
Host mixture	H1	H2	H3
Components (mole%)	MBBA (54), 4ECH2 (24), 5ECH1 (22)	PCH5 (55), PCHE3 (23), PCHE5 (22)	E6 (18), E7 (19), E8 (12), M18 (16), M21 (17), M24 (18)
T_c [°C]	58.8	62.7	62.5
$\varepsilon_\parallel$ (25 °C)	4.01	16.30	24.10
$\varepsilon_\perp$ (25 °C)	5.01	5.45	6.80
η_s (25 °C) [cP]	25	24	77
τ_h (25 °C) [μs]	0.204	0.172	0.456
$\delta\varepsilon_h$ (25 °C)	0.38	13.2	20.3
(γ_1/η_s) est.	4.5	6.0	4.6

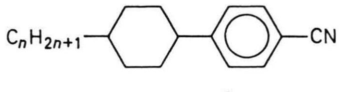
trates by less than 5 μm into the bulk. The temperature was kept constant within 0.1 K by a circulating water thermostat (Haake F3K).

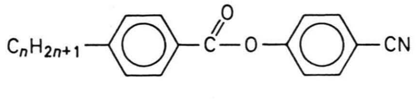
Three nematic host matrices have been used which are characterized in Table 1. They where chosen as representatives having various polarity- (dielectric permittivities $\varepsilon_\parallel$ and $\varepsilon_\perp$) and viscous (flow aligned shear viscosity η_s) properties. In order to yield large mesophase ranges each of them contains several of the following components:

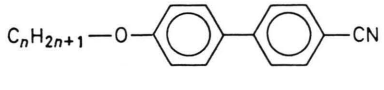

MBBA


*n*ECH*m*


PCHE*n*

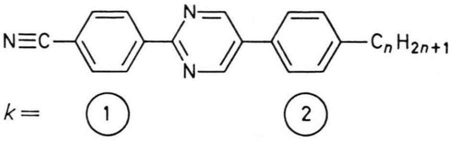

PCH*n*


E*n*

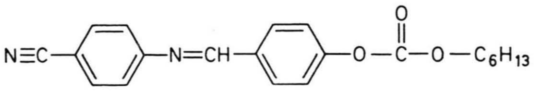

M3*n*

The numbers before and after the short names indicate the number of C-atoms in the alcyl substituents except for the biphenyl component *M* where it has become a custom to indicate three times the number of C-atoms.

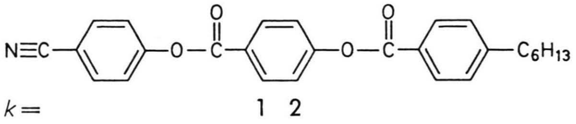
As guest molecules we have used several pyrimidine derivatives of the general structure [6]



which we denominate by TP*n*. A subscript $TP_k n$ indicates that the benzene ring number *k* was hydrated. The only two-ring system investigated was the Schiff base S [7]



The longest molecules investigated were the diesters DEk of the structure [8]



This index *k* indicates that in position number *k* the hydrogen was substituted by a methyl group. Because of the length of these guest molecules they are expected to show dielectric relaxation processes well separated from those of the shorter host molecules.

Solutions of roughly 10 mole.% of all the guest molecules with the host mixture H1 have been investigated. The hosts H2 and H3 were only used with the molecule DE2.

The complex parallel permittivity $\varepsilon_\parallel$ was determined as a function of the frequency *f* of the electric field and of the temperature. The frequency was varied in steps of a factor ~ 1.5 in the range where $\varepsilon_\parallel$ changed appreciably. The measurements were fitted by a Debye-type relaxation formula of the form

$$\varepsilon_\parallel(\omega) = \varepsilon_{\parallel,0} + \sum_{l=1}^{L} \frac{\delta\varepsilon_l}{1 - i\,\omega\,\tau_l}\,, \tag{2.1}$$

where $\omega = 2\pi f$.

Table 1 contains the values of the relaxation times τ_h and of the amplitudes $\delta\varepsilon_h$ of the pure host mixtures which were obtained from a single-relaxa-

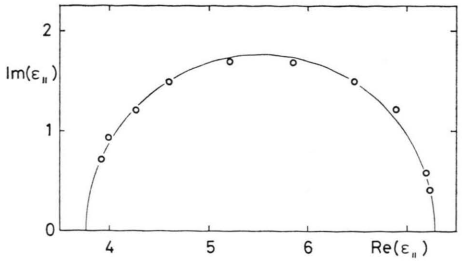


Fig. 1. Cole-Cole plot of the longitudinal dielectric permittivity $\varepsilon_{\|}$ in the frequency range 50 kHz $< f <$ 3.5 MHz for the solution of TP_17 in H1 at a temperature of 39 °C. The solid circle corresponds to $L = 1$, $\delta\varepsilon = 3.525$ and $\tau = 0.278$ µs in (2.1). The points are measured.

tion time fit ($L = 1$ in (2.1)). A characterization of the relaxation of the pure host by a single relaxation process is often a good approximation in these multicomponent mixtures of molecules of similar size [9]. Furthermore, in our case the interest was focussed on the relaxation behaviour of the added guest molecules which occurred at considerably longer time scales. To extract the guest relaxation times τ from the measurements the characterization of the host relaxation by a single relaxation time τ_h proved to be sufficient for the hosts H2 and H3, in which cases τ and τ_h differed by a factor of more than 30. In the case of H1 it was not even necessary to take into account the host relaxation in the fitting procedure (τ_h smaller by a factor of 3 to 15) because in addition the amplitude of the host relaxation process $\delta\varepsilon_h$ was by a factor of 10 smaller than the one for the guest molecules. In these cases a two term expression ($L = 2$ in (2.1)) would have been inadequate, owing to the limited measuring accuracy at the high frequency ranges where the host relaxations become effective. The Cole-Cole-plot of Fig. 1 gives an indication of the quality of the agreement between experimental points and fitting curve.

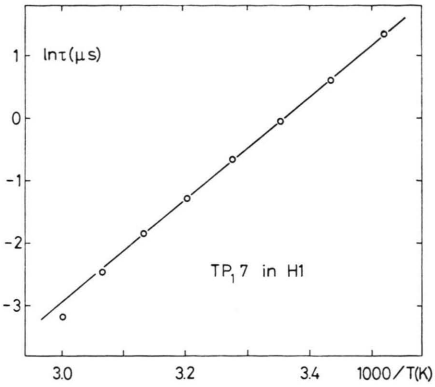


Fig. 2. Logarithm of the guest relaxation time τ versus reciprocal temperature for TP_17 dissolved in H1. The measured points are well fitted by the Arrhenius line (3.1) except at temperatures near the clearing point.

3. Results and Discussion

A typical graph of the logarithm of the Debye relaxation time τ of the guest molecule versus the reciprocal absolute temperature is shown in Figure 2. The curve is acceptably well linear although one observes near the clearing temperature an enhanced reduction in τ while at low temperatures there seems to be an indication of an enhanced rise. Table 2 contains a compilation of the experimental results obtained for the various solutions. The temperature dependence of $\tau(T)$ is characterized by a temperature T_a which was obtained from adapting an expression of the form

$$\tau(T) = \tau_\infty \cdot \exp\{T_a/T\} \qquad (3.1)$$

to the linear portion of the measured ln τ-versus-T^{-1} graphs. In an Arrhenius type interpretation T_a multiplied by Boltzmanns constant is an activation energy. A further quantity of interest is the amplitude $\delta\varepsilon$ ((2.1) for $L = 1$) divided by the molarity of the solute per unit volume. This quantity depends on the order parameter and magnitude

Table 2. Guest concentration c, lowest relaxation (guest relaxation) time τ and corresponding amplitude $\delta\varepsilon$ (2.1) at 25 °C and activation temperature T_a (3.1) for several solutions. Also given are the clearing temperatures T_c (guest) of the pure guest material.

Guest molecule	host	c [mole/kg]	τ [µs]	$\delta\varepsilon/c$ [kg/mole]	T_a [k K]	T_c (guest) [°C]
TP_13	H1	0.348	0.563	11.64	7.77	194.5
TP_14	H1	0.347	0.583	11.58	7.79	179.6
TP_15	H1	0.346	0.771	11.44	7.91	175.5
TP_16	H1	0.343	0.779	11.23	8.00	163.0
TP_17	H1	0.340	0.942	11.21	8.21	159.8
TP_18	H1	0.339	1.020	11.57	8.31	152.3
TP 5	H1	0.278	1.246	14.05	8.26	241.0
TP_25	H1	0.277	1.323	13.25	8.30	231.0
$TP_{1,2}5$	H1	0.277	0.650	11.29	7.89	175.0
S	H1	0.410	0.705	9.09	7.81	96.4
DE1	H1	0.219	3.004	17.38	9.37	159.7
DE2	H1	0.218	3.254	17.82	9.44	174.7
DE2	H2	0.194	11.27	10.06	11.60	174.7
DE2	H3	0.203	14.15	11.52	11.67	174.7

of the molecular dipole and is also influenced by solvent properties as expressed for instance by reaction field and cavity factors [10]. Since we have no density data available, Table 2 instead contains the $\delta\varepsilon$-values divided by c, the molality of solute, taken per unit mass of solution. For comparison purposes this quantity is equally useful because we expect in our systems only small variations in density.

The values of τ measured at constant temperature $T_R = 298.2$ K show a clear correlation with the values of T_a as can be seen in Figure 3. The larger the guest relaxation time $\tau_x(T_R)$ of a guest-host system x, the larger is its activation temperature $T_{a,x}$. A linear relaxation of the form

$$T_{a,x} = T_{0,R} \ln[\tau_x(T_R)/\tau_0] \qquad (3.2)$$

described the general trend of the measurements rather satisfactorily although it neglects some more detailed features. The particular choice of the reference temperature T_R is of no significance for the validity of a relaxation of the form (3.2) as can be seen by writing

$$T_{0,R}^{-1} = T_R^{-1} - T_0^{-1}. \qquad (3.3)$$

A reference temperature independent characterization of (3.2) is hence given by the two parameters τ_0 ant T_0. Our measurments yield the following values

$$\tau_0 = 1.33\ \text{ns}, \quad T_0 = 392\ \text{K}. \qquad (3.4)$$

Pictorially the relation (3.2) implies that the straight lines (3.1) in the $\ln\tau$ versus T^{-1} plots (Fig. 2) have a common intersection occurring at the point ($\ln\tau_0$, T_0^{-1}). However, T_0 lies far above the clearing temperature of the hosts whence τ_0 is a fictive relaxation time. In addition one must perhaps remember here that the three host materials have very similar claearing temperatures, some 60 K below T_0. If the relation (3.2) applies to further systems at all, we suspect that they must probably have similar host clearing temperatures.

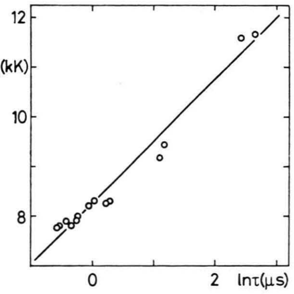


Fig. 3. Activation temperature T_a of the relaxation time of various large molecules in nematic matrices versus logarithm of the relaxation time at 25 °C. The measured points fall reasonably well on the line (3.2) with the parameters of (3.4), which is also plotted.

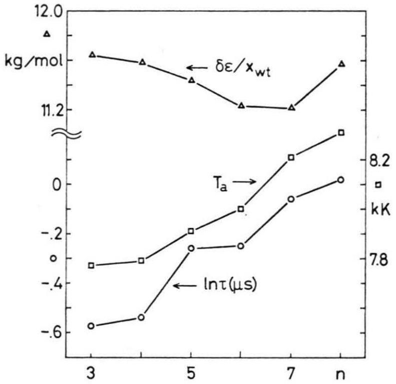


Fig. 4. Logarithm of the relaxation times and amplitudes of the relaxation process at 25 °C for a homologous series of TP_1n dissolved in the host matrix H 1. Also shown are the activation temperatures T_a which, similar to $\ln\tau$, show an alternation.

The homologous sequence of the TP_1n shows distinct alternations in $\ln\tau$ (25 °C) as well as in T_a which are superimposed onto the considerable increase in these quantities with increasing alkyl chain length (Figure 4). The molecules with an odd number of carbon atoms in the alkyl chain show enhanced values compared with the even ones. This alternation parallels the behaviour of the clearing temperatures of the pure guest molecules as shown in the last column of Table 2. The property of odd-chain homologues to show enhanced nematogenic tendencies, thus, seems to correlate with a reduced probability of undergoing 180° reorientational jumps.

Also shown on Fig. 4 are the amplitudes $\delta\varepsilon$ ((2.1) with $L = 1$) divided by the molarity of the solute. Surprisingly these values show a minimum around the hexyl compound. From the similarity of the surrounding we expect that reaction field and cavity contributions [10] vary little while the magnitude of the molecular dipole moment is expected to be the same for the whole series. The chain length thus seems to influence the dipolar order possibly via average conformation properties and geometrical compatibility with the host molecular arrangement.

Of interest is furthermore a comparison of the influence of the different molecular core structures on the dielectric relaxation properties. Comparing the TP_k5 compounds, a striking feature is the influence of hydrating the first benzene ring, which reduces the relaxation times by about a factor of two. On the other hand hydration of ring ② has little effect on the value of the relaxation time. However, as expected, the length of the rigid core of the molecule has the dominant influence on the values of τ [11].

The amplitude $\delta\varepsilon/x_{\omega t}$ of the terpyrimidines TP5 decreases considerably upon hydration of the benzene ring ① possibly due to reduction and misalignment of the molecular dipole. Hydration of ring ② in turn has again little influence.

Interesting differences are seen for the molecule DE2 in the three host mixtures. Most obvious is the strong increase of τ with increasing average dielectric constant $\bar{\varepsilon}$ of the host (Table 1). On the other hand, if $\bar{\varepsilon}$ is taken as a parameter which influences τ it seems that the viscosity is unnecessary as an additional parameter. Almost no change of η_s is seen in going from H1 to H2 where τ increases by more than a factor of three, while between H2 and H3 a big change in η_s and little change in τ is observed. This surprising [11, 12] finding is hardly modified if instead of η_s the rotational viscosity is considered. From viscosity measurements on class specific binary mixtures [13] one would deduce for the ratios γ_1/η_s the estimates quoted in Table 1, which vary only by 30%. A further interesting result is the value of $\delta\varepsilon/c$ observed in the three different host materials. Although low values of $\delta\varepsilon/c$ seem to correlate to some extent with high $\bar{\varepsilon}$-values of the host, the difference between H2 and H3 indicates that other parameters must be of importance.

4. Conclusion

For the slow dielectric relaxation processes of large molecules in nematic solvent it appears to be a rule that the slower the relaxation, the stronger is its temperature dependence. Quantitatively this is expressed in (3.2) to (3.4). Secondly, for structurally similar molecules the relaxation time is higher in cases of increasing nematogenic tendencies of the pure solutes. In homologous series alternations in the relaxation times are observed. With regard to the host properties it appears that its dielectric properties strongly influence the relaxation times of the guest molecules while the viscous properties of the host are of minor importance. This last indication is rather unexpected [11, 12] since in the simplest theories for isotropic liquids a direct correlation occurs.

From the point of view of applications the connection between τ and its temperature dependence is against the need for large τ and low temperature dependence. On the other hand the lack of influence of the host viscosity on τ may give hope to find systems suitable for two frequency addressing with fairly low viscosity.

Acknowledgement

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