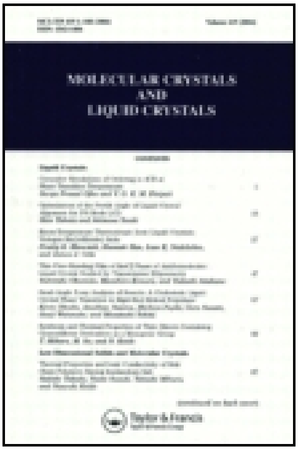

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Dielectric Relaxation and Viscosity in a Mixture of Liquid Crystalline Substances

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Dielectric Relaxation and Viscosity in a Mixture of Liquid Crystalline Substances

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Dielectric relaxation and viscosity measurements in a mixture consisting of one component with a high viscosity (A) and the basic mixture Mi 5 have been carried out. The dielectric relaxation times τ_A for the reorientation around the short molecular axis show a linear increase with the mole fraction of the high viscous compound x_A at constant temperature. τ_A has been extrapolated to $x_A \rightarrow 0$ and the relaxation time of A at infinite dilution $\tau_{A\infty}$ has been estimated. The difference between the relaxation times τ_{Mi5} and $\tau_{A\infty}$ is explained by geometrical factors.

Keywords: nematic liquid crystals, dielectric relaxation, viscosity, mixtures, molecular geometry, substituted benzoates

INTRODUCTION

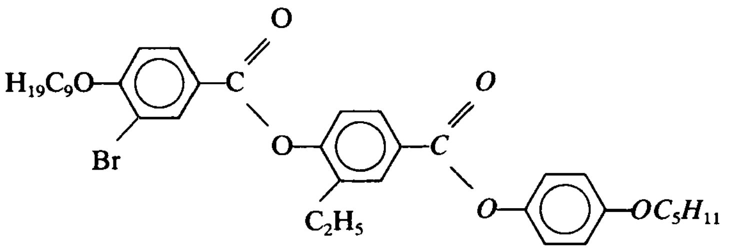
Considerable research effort has been expended in order to gain a better understanding of the dielectric relaxation in liquid crystals.[1–3] The low frequency absorption observed in the direction parallel to the nematic director is especially of interest because this dielectric relaxation process is connected with the viscosity and an additional potential barrier due to the parallel ordering of the molecules.[1] These borderline cases have been investigated in pure nematic substances[4] and in diluted solutions of molecules with different geometrical shapes.[5,6]

In this paper we will try to separate the influence of the bulk viscosity and of the molecular geometry on the relaxation behavior.

EXPERIMENTS

We have chosen as components

A:



Cr 342 N 351 is 4-*n*-pentyloxyphenyl 4-(3-bromo-4-*n*-nonyloxybenzoyloxy)-3-ethylbenzoate

and a mixture of

Mi 5:

27 mol% 4-*n*-octyloxyphenyl 4-*n*-pentyloxybenzoate

24 mol% 4-*n*-hexyloxyphenyl 4-methyloxybenzoate

12 mol% 4-*n*-heptyloxyphenyl 4-*n*-hexyloxybenzoate and

37 mol% 4-*n*-butyloxyphenyl 4-*n*-hexylbenzoate.

Cr 283 N 343 is (Cr, crystalline; N, nematic; is, isotropic phase).

Inside the experimental error the clearing temperature T_{NI} of the mixture is a linear function of the molar fraction x_A. The main reasons to choose these components were on one hand the strong difference in the viscosity and on the other hand the low conductivity and a sufficient dipole moment for measurements at smaller concentrations.

Dielectric measurements in a frequency range from 10 Hz to 100 kHz at different temperatures and concentrations have been carried out. Used was a modified Sawyer-Tower bridge in combination with a double-plate capacitor ($d \approx 0.2$ mm, $A = 2$ cm^2) made from silver. The sample was oriented magnetically ($H = 0.8$ T). The temperature was stabilized at >0.1 K by the aid of a temperature controller and measured by a thermocouple. The calibration of the cell was done with cyclohexane. From the measured capacities and resistivities at different frequencies the dielectric constants ϵ' and ϵ'' have been calculated.

The absorption curves of the molar fraction $x_A = 0.5$ are presented in Figure 1. Due to the superposition of the relaxation processes of A and Mi 5 the absorption

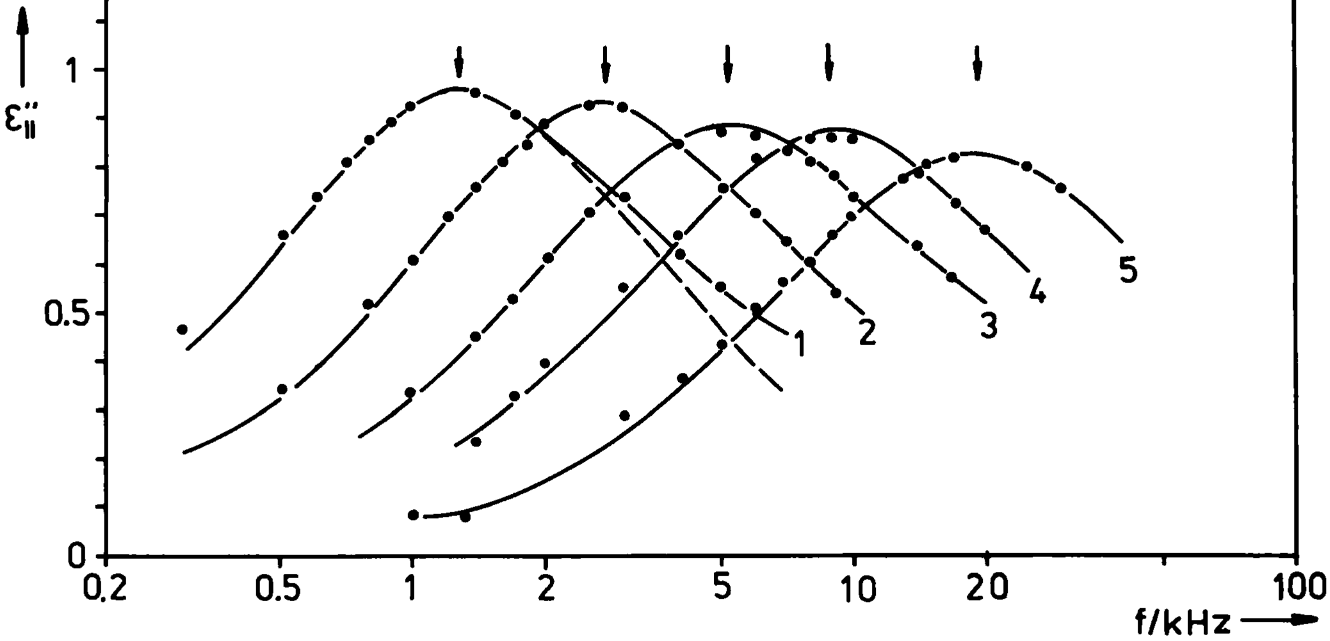


FIGURE 1 The dielectric absorption of the mixture with $x_A = 0.5$ parallel to the nematic director. Temperatures: 1:301.0 K, 2:305.2 K, 3:311.0 K, 4:315.2 K, 5:321.2 K. The relaxation frequencies f_R are indicated by arrows. The influence of the absorption of Mi 5 has been separated only for curve 1. -●-●-: Experimental results; – – –: after separation of the high frequency part connected with the absorption of Mi 5.

curves are not symmetrical, but at higher concentrations of A the influence of Mi 5 on the position of the maximum is relatively small (Figure 1, curve 1).

The absorption intensity of A decreases with decreasing x_A and the difference between the relaxation frequencies of A and Mi 5 becomes smaller. Therefore, we can observe at $x_A = 0.2$ two mechanisms of the same intensity which we have separated (Figure 2). The error of f_R and τ, respectively, is about 7% for $x_A \geq 0.7$ and 10% for $x_A = 0.2$–0.5. The experimental data of compound A have been fitted to the equation

$$\ln f_R/\text{kHz} = \ln f_o/\text{kHz} - \frac{E_A}{RT}. \tag{1}$$

The results are summarized in Table I. For E_A a maximal error of 5% could be calculated.

With the exception of the measurements on $x_A = 0.5$ we could observe an increase in f_o and E_A, respectively. The same tendency has been found in other systems.[5–7] The deviation at $x_A = 0.5$ is due to the experimental error of E_A. Furthermore, the viscosity has been measured by the aid of the rotational viscometer Rheotest. Under our experimental conditions the obtained viscosities in the nematic state are η_2-values.[8] Data of different concentrations are presented in Figure 3. The viscosities at T = 323.2 K and T = 350.2 K are listed in Table II.

The viscosities measured at different temperatures do not show an Arrhenius-like behavior. This is in contradiction to the dielectric data which show a good correlation to Equation (1).

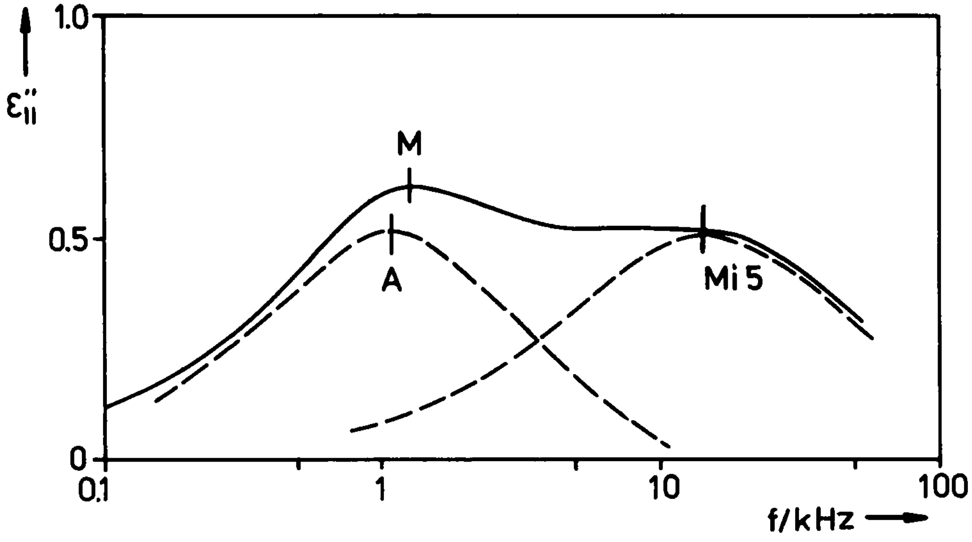


FIGURE 2 Dielectric absorption of the mixture M with $x_A = 0.2$ at T = 282.7 K (——) and the separation into a Debye curve A and a Cole–Cole mechanism of Mi 5.

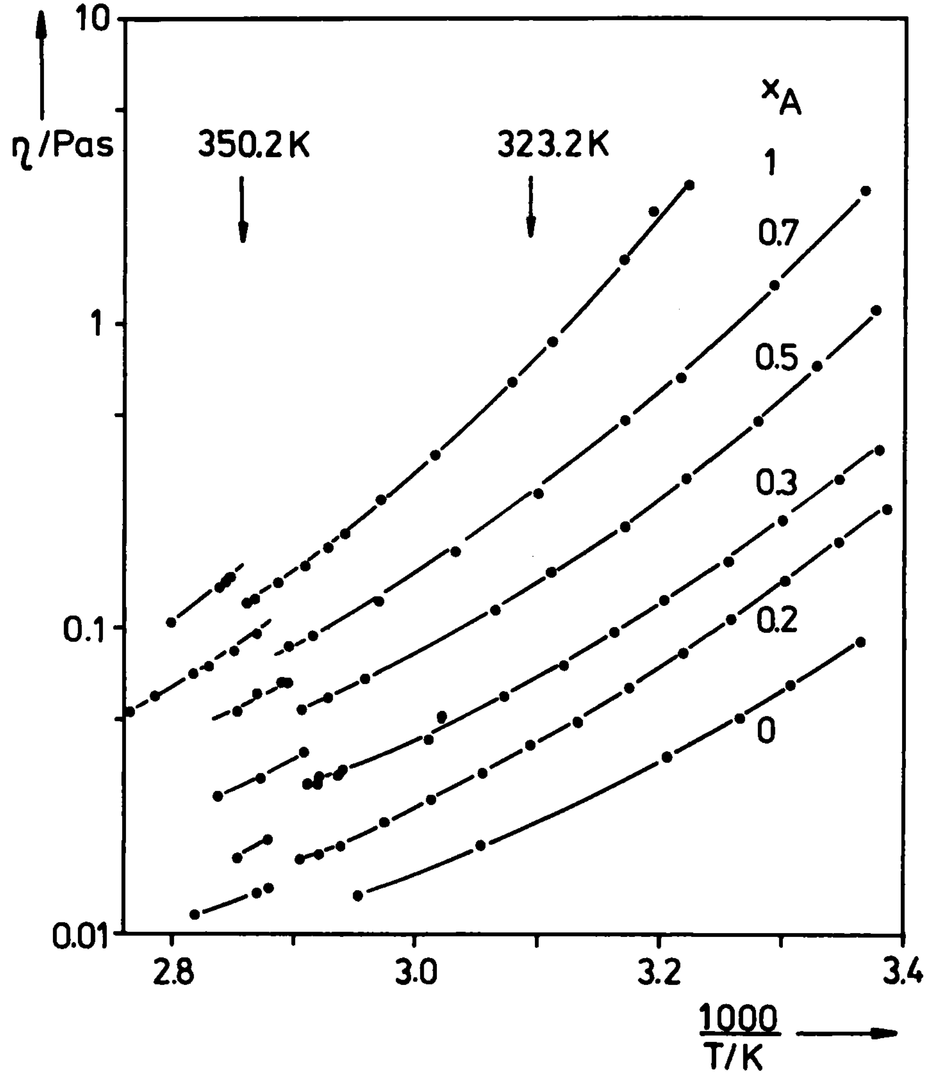


FIGURE 3 Arrhenius plot of the viscosity data in the isotropic (η) and nematic (η_2) phase for different x_A-values.

DISCUSSION

The dependence of the relaxation time τ_A on the molar fraction of A and the comparison with the respective behavior of the viscosity at constant temperature is the first interesting point. In order to avoid misunderstandings, the respective quantities have been designated τ_A (T) and η_2 (T).

It can be seen in Figure 4 that both curves are nearly parallel to one another. By changing x_A from 0 to 1 the viscosity increases by a factor of 33 and the relaxation

TABLE I

Fitting data of the binary system calculated from Equation (1)

x_A	n^a	f_o/kHz 10^{-18}	E_A/kJ mol^{-1}	K^b	$\tau_A(T)/\mu s^c$ (323.2 K)	$\tau_{Mi\ 5}(T)/\mu s$ (323.2 K)
0.0	8	1.607	94.17	–	–	0.163
0.2	6	1.973	102.20	−0.9940	2.66	0.300
0.3	5	5.660	105.64	−0.9983	3.30	0.400
0.5	4	1.176	103.35	−0.9989	6.85	–
0.7	7	8.293	110.12	−0.9980	12.03	–
1.0	5	10.220	113.38	−0.9987	32.82	–

[a] n, Number of f_R/T values used for the fit.
[b] K, Correlation factor.
[c] τ, Relaxation time for the reorientation around the short axis.

time by 24, respectively, at T = 323.2 K. This experimental result is important: The rotational viscosity of the reorientation around the short molecular axis [measured as τ_A (T)] and the viscosity η_2 (T) [measured in the volume phase] show in first approximation the same dependence on the concentration. It should be mentioned that the relaxation time of Mi 5 also increases with decreasing concentration.

From the theoretical point of view it is better to compare the viscosity in the isotropic phase with the relaxation times at constant temperature differences ΔT from the clearing point.[1,9] This can be deduced from the relation for the rotation of a spherical molecule of the radius a[10]

$$\tau'_{is} = \frac{4\pi a^3}{kT} \cdot \eta_r$$

where

k = Boltzmann constant

η_r = (micro)rotational viscosity.

The reorientation time for rodlike molecules around the short molecular axis in the isotropic state τ_{is} can be estimated from τ'_{is} if we take into consideration a cylindrical symmetry of the molecules.[11] Furthermore we must assume that the

TABLE II

Viscosities η_2 at T = 323.2 K (nematic) and T = 350.2 K (isotropic phase) estimated from Figure 3. The data for x_A = 1 at T = 350.2 K are extrapolated

x_A	0	0.2	0.3	0.5	0.7	1.0	T/K
1,000η_2	22.8	40.8	66	133	264	725	323.2
Pas	13.0	18.5	41	56	90	166	350.2

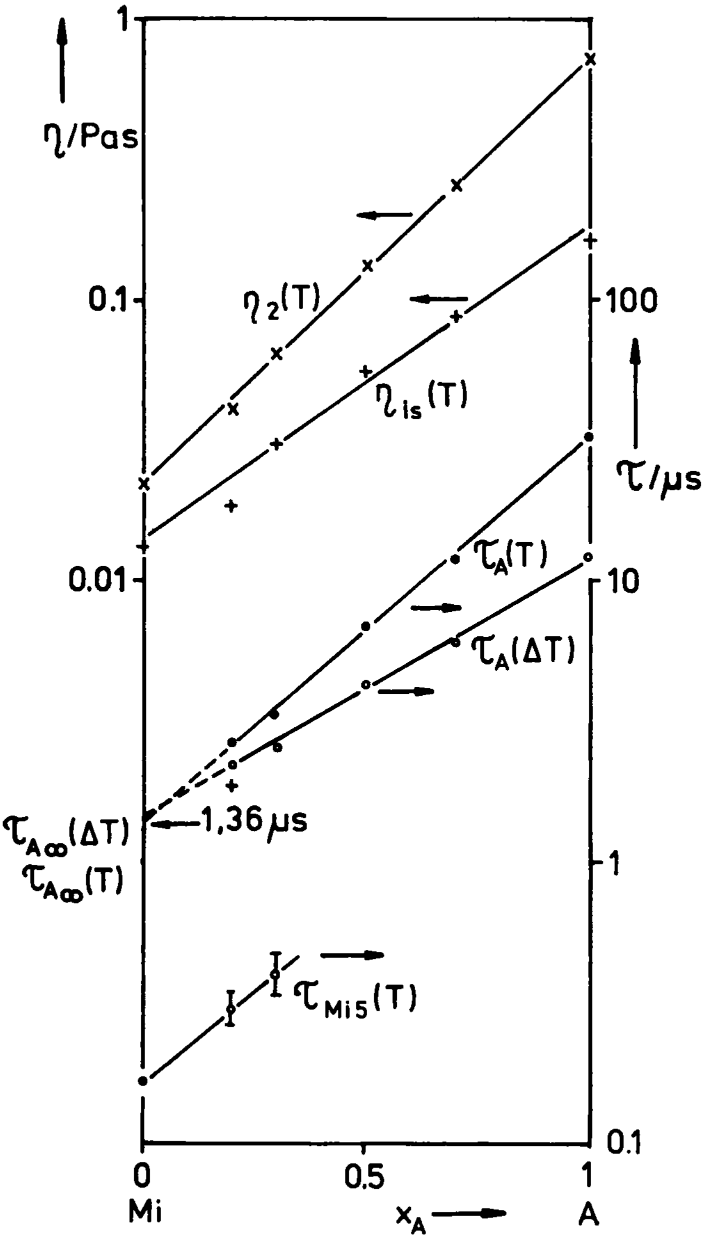


FIGURE 4 Comparison of the viscosity and relaxation time: x, ●: η_2 (T) and τ_A (T), respectively, at T = 323.2 K; +, η_{is} (T) at 350.2 K (isotropic phase); ○, τ_A (ΔT) for $T_{NI}-T$ = 20 K. The relaxation time of Mi 5 has been estimated only for three concentrations and T = 323.2 K.

retardation factor $g_{\|}$ depends only on the mean degree of order or on the temperature difference $T_{N/is}-T$[1]. Under these conditions we obtain

$$\tau = \tau_{is} \cdot g_{\|} \approx \eta_r \qquad (T = \text{const})$$

Assuming that η_r is proportional to the viscosity of the isotropic phase[10] the slope of the curves η_{is} (T) and $\tau_A(\Delta T)$ should be not so strongly different. The second point is the comparison of the relaxation times of the pure Mi 5 $\tau_{Mi\ 5}(T)$ and of the component A in the mixture τ_A (T) at infinite concentrations of A.

If we assume that τ_A (T) is a linear function of x_A we are able to extrapolate the relaxation time of A to $x_A \to 0$. Both $\tau_{A\infty}$ (T) and $\tau_{A\infty}$ (ΔT) are, here, about 1.4 μs because the temperature is T = 323.2 K in both cases. The interesting feature is that now the viscosity for the extrapolated concentration $x_A \to 0$ is the same as that of Mi 5. For the interpretation of the reorientation time $T_{A\infty}$ (T) we have to take into consideration the interactions between the different molecules. In the pure component A, τ_A (T) is reflecting the interaction between the molecules of A, whereas in the diluted solution of A ($x_A \to 0$) the interaction between A and Mi 5 is dominating. The obtained relation, $\tau_{A\infty}$ (T)/$\tau_{Mi\ 5}$ (T) = 8.6, indicates the influence of the molecular geometry on the microviscosity or on the retardation factor. The effects cannot be separated in our experiments.

References

1. A. J. Martin, G. Meier and A. Saupe, *Symp. Faraday Soc.*, **5**, 119 (1971).
2. P. L. Nordio, G. Rigatti and U. Segre, *Mol. Phys.*, **25**, 129 (1973).
3. H. Kresse, *Adv. Liq. Cryst.*, **6**, 109 (1983).
4. H. Kresse, K. Worm, W. Schäfer, H. Stettin, D. Demus and W. Otowski, *Cryst. Res. Technol.*, **21**, 293 (1986).
5. G. Heppke, J. Kayed and U. Müller, *Mol. Cryst. Liq. Cryst.*, **98**, 309 (1983).
6. H. Kresse, P. Rabenstein and D. Demus, *Mol. Cryst. Liq. Cryst.*, **154**, 1 (1988).
7. H. Kresse, H. Stettin and E. Tennstedt, *Cryst. Res. Technol.*, **21**, 1109 (1986).
8. W. Helfrich, *J. Chem. Phys.*, **50**, 100 (1969).
9. W. Maier and A. Saupe, *Z. Naturforsch.*, **14** A, 882 (1959).
10. P. Debye, "*Polare Molekeln*," S. Hirzel: Leipzig, 1929.
11. L. Bata, A. Buka and G. Molnar, *Mol. Cryst. Liq. Cryst.*, **38**, 155 (1977).