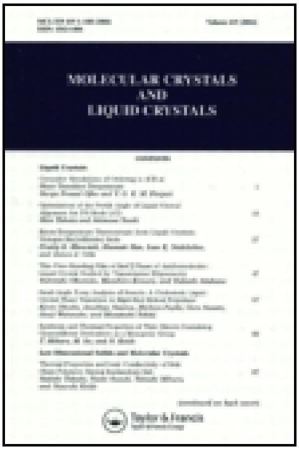

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# Dielectric Relaxation and Molecular Geometry in Nematic Mixtures

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# Dielectric Relaxation and Molecular Geometry in Nematic Mixtures

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Four cyano-substituted liquid crystals of different length to width ratio have been added to a nematic basic mixture. Their influence on the dielectric relaxation process observed parallel to the nematic director was investigated in the frequency range from 0.1 to 100 kHz. The decrease of the relaxation frequency by increasing molecular length has been correlated to the molecular geometry as well as to the increasing activation energy.

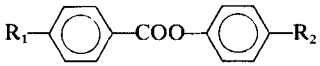
*Keywords: dielectric relaxation, liquid crystals, mixtures, molecular geometry, activation energy, length-to-width ratio*

## 1. INTRODUCTION

Most of the thermotropic liquid crystals are composed of rodlike molecules. This geometrical model is a simplification of the structure and molecular dynamics because of the fast reorientation of the molecules around their long ($\perp$) and the slower reorientation around the short ($\parallel$) molecular axis.[1] The collective reorientation around the short molecular axis can be easily observed by dielectric relaxation measurements in the frequency range between some kHz[2] and a few MHz.[3] The strong decrease of this relaxation frequency $f_{R\parallel}$ in relation to critical frequencies connected with other molecular motions can be explained by the formation of the liquid crystalline order as well as by the increase of the viscosity.[4] In previous experiments[2] it was demonstrated that $f_{R\parallel}$ as well as $f_{R\perp}$ (relaxation frequency for the reorientation around the long molecular axis) decrease if the viscosity increases. Therefore, we have investigated molecules with different geometrical shape in a nematic mixture in order to have only a small change in the bulk viscosity. The same technique has been used for

TABLE I

The basic mixture BM



| $R_1$ | $R_2$ | mol% |
|---|---|---|
| $C_5H_{11}O$— | —$OC_8H_{17}$ | 27 |
| $CH_3O$— | —$OC_6H_{13}$ | 24 |
| $C_6H_{13}O$— | —$OC_7H_{15}$ | 12 |
| $C_6H_{13}$— | —$OC_4H_9$ | 37 |

the characterization of substances for two-frequency addressing displays.[5,6]

## 2. SUBSTANCES

The basic mixture (BM) consists of four derivatives of the phenyl benzoate given in Table I. The BM shows a nematic (N) phase between 283 K and 344 K.

At $T = 285.5$ K a Cole–Cole absorption mechanism[7] parallel to the nematic director with a dielectric increment $\Delta_{\|} = 1.5$ could be detected (Cole–Cole distribution parameter $\alpha = 0.15$; relaxation frequency $f_{R\|} = 28$ kHz). The data on BM are presented in Figures 1 and 5, respectively.

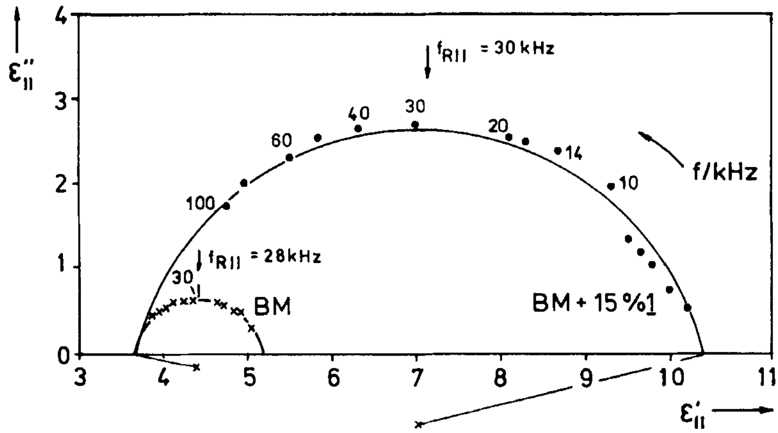


FIGURE 1 Cole–Cole diagram for the orientation electric field parallel to the nematic director for the basic mixture BM: $T = 285.5$ K, $f_{R\|} = 28$ kHz, dielectric increment $\Delta = 1.50$ and for the mixture BM + 15 mol% *1*: $T = 288.5$ K, $f_{R\|} = 30$ kHz, $\Delta = 6.7$. f = frequency in kHz.

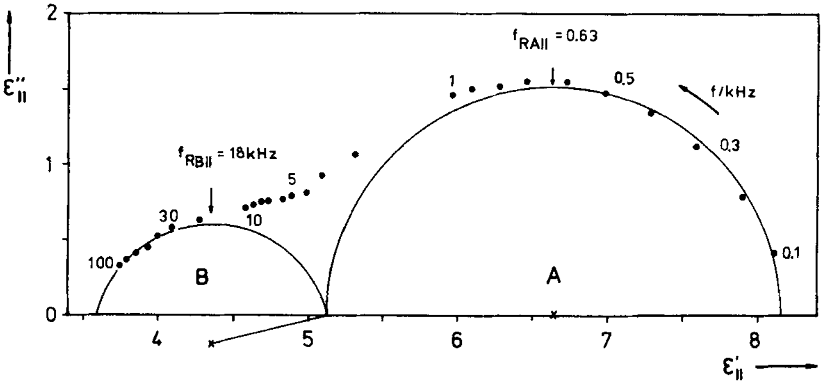


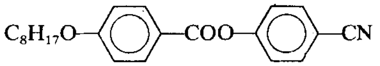
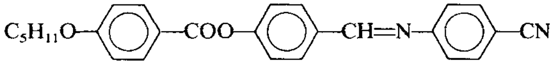
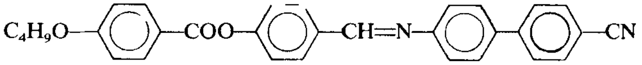
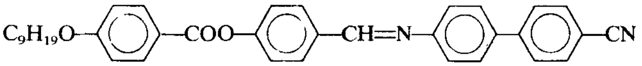
FIGURE 2 Cole–Cole representation of BM + 5 mol% *2* at $T = 286.0$ K, mechanism A: $f_{R\parallel} = 0.63$ kHz; $\Delta = 3.02$; mechanism B $f_{R\parallel} = 18$ kHz, $\Delta = 1.53$.

The following compounds with a strong dipole moment in the direction of the long molecular axis were added to BM.

For the characterization of the molecular geometry the ratios of molecular length to width estimated from Stuart-Briegleb calott models have been used. In Table II, S and C, respectively denote the ratio without taking into account the alkyl groups (S) and the same ratio under consideration of an overall trans-conformation of the alkyl chains (C). It is worth pointing out that the formation of bilayer-structures, which often can be observed in cyano-substituted molecules, can be excluded at these concentrations.[8]

TABLE II

The cyanosubstituted compounds added to the basic mixture

| no | Compound<br>transition temperatures/K | $x$/mol% | S | C |
|---|---|---|---|---|
| *1* |  <br>Cr 347 N 357 is | 15 | 2.0 | 3.3 |
| *2* |  <br>Cr 395 ($S_E$ 347) N 553 is | 5 | 3.0 | 4.0 |
| *3* |  <br>Cr 406 $S_B$ 417 $S_A$ 519 N 630 is | 5 | 3.7 | 4.5 |
| *4* |  <br>Cr 366 $S_B$ 436 $S_A$ 611 N 630 is | 5;10 | 3.7 | 5.0 |

## 3. RESULTS

Dielectric investigations in the frequency range from 10 Hz to 100 kHz have been carried out in a microcapacitor ($A \approx 2$ cm$^2$, $d = 0.02$ cm). From such experimental quantities as resistivity, capacity and the respective calibration factors the dielectric constant $\epsilon'$ and the dielectric loss factors $\epsilon''$ have been calculated. The low frequency conductivity due to the ionic transport has been used for the separation of the ionic part of $\epsilon''$ and the part which arises from the dielectric loss. All measurements have been done in magnetically oriented samples for the case **E** ∥ **H**, that means the nematic director was in direction of the measuring field and the qualities $\epsilon''_\parallel$ and $\epsilon'_\parallel$ have been measured.

The data in the form of the Cole–Cole representation for BM and BM+ 15 mol% of *1* are given in Figure 1. Due to the good solubility of substance 1 in the BM a greater concentration has been used. A separation of the dielectric absorption ranges of BM and 1 was not possible but the quite higher absorption intensity of sample B in Figure 1 indicates that the dielectric increment of substance 1 is very high in comparison with $\Delta\epsilon$ for the starting mixture BM.

This again means that the observed relaxation frequency $f_{R\parallel} = 30$ kHz should be close to the relaxation frequency of BM. Substance 2 shows a tendency to form a separate low frequency absorption A (Figure 2). The separation into a Debye-mechanism[7] A and a high frequency Cole–Cole mechanism B has been done by means of the computer. As it is seen for the compounds *3* and *4* nearly separate relaxation ranges for the reorientation of the longitudinal dipole mo-

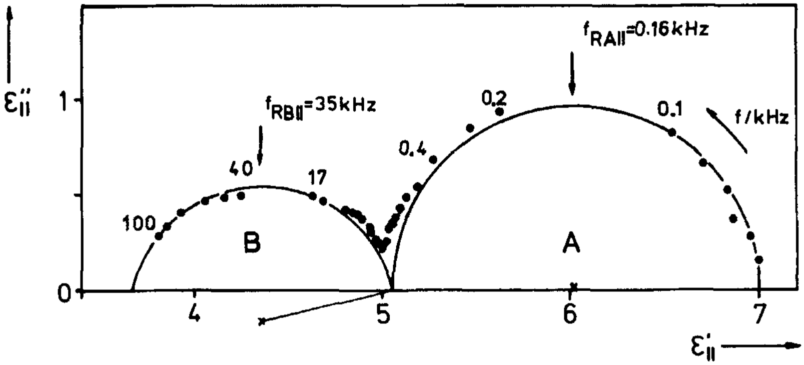


FIGURE 3 Cole–Cole plot of BM + 5 mol% *3* at $T = 298$ K. Mechanism A: $f_{R\parallel} = 0.16$ kHz, $\Delta = 1.92$; mechanism B: $f_{R\parallel} = 35$ kHz, $\Delta = 1.40$.

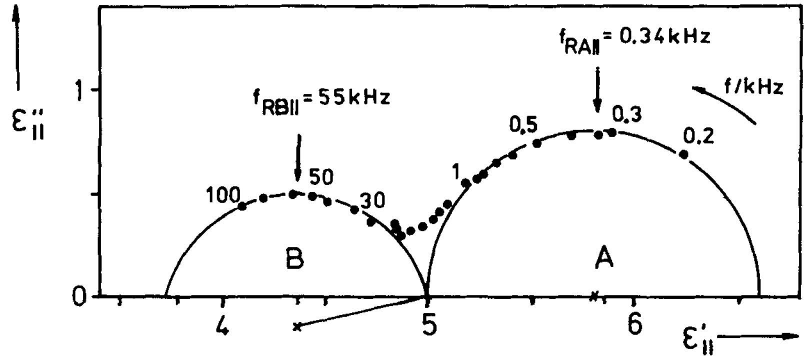


FIGURE 4 Cole–Cole representation of BM + 5 mol% *4* at $T$ = 298 K. Mechanism A: $f_{R\parallel}$ = 0.34 kHz, $\Delta$ = 1.60; mechanism B $f_{R\parallel}$ = 55 kHz, $\Delta$ = 1.25.

ment around the short molecular axis have been detected (see Figures 3 and 4, respectively).

From measurements at different temperatures the activation energies $E_A$ according to the Arrhenius equation could be calculated.

A survey of the results is presented in Figure 5 and Table III, respectively. The experimental data in Table III can be fitted to the equation

$$\ln f_R/\text{kHz} = \text{A} + \text{B} * E_A \tag{1}$$

by means of linear regression.

For A = 115.4 and B = −9.09 mol kJ$^{-1}$ a correlation of 0.997 has been found.

TABLE III

Relaxation frequencies and activation energies of the mixtures in Table II

| Mixture | Relaxation process | $f_R$/kHz $T$ = 313 K | $E_A$/kJ mol$^{-1}$ |
|---|---|---|---|
| BM | B | 300 | 64 |
| BM + *1* | A+B | 150 | — |
| BM + *2* | A;B | 15 | 89 |
| BM + *3* | A;B | 1.4 | 113 |
| BM + *4* (5%) | A;B | 2.5 | 106 |
| BM + *4* (10%) | A | 6 | 101[a] |

[a] Two points only due to restrictions in the solubility
A + B: Separation of the relaxation processes impossible
A;B: Separation by computer

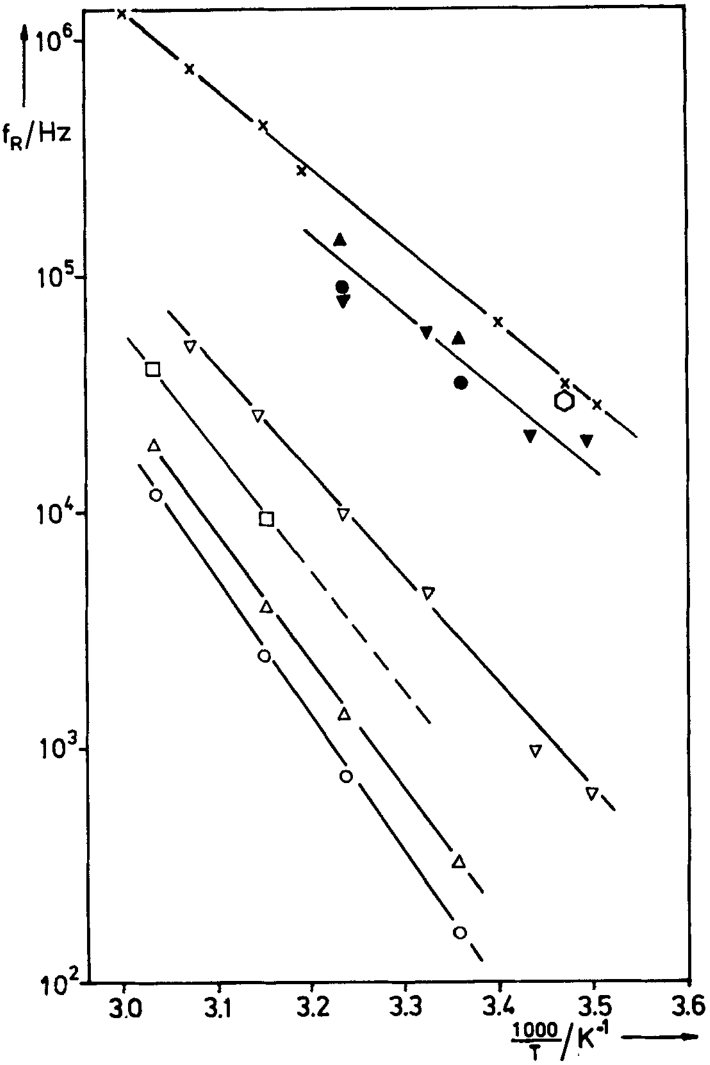


FIGURE 5 Arrhenius plot of the relaxation frequencies for BM (X) for the mechanism B(▼, ●, ▲) found for the respective mixtures and mechanism A (▽: BM + *2*, ○: BM + *3*, △: BM + 5% *4*, □: BM + 10% *4*). ⬡: BM + *1* (mixture of mechanism A + B).

## 4. DISCUSSION

Two aspects should be discussed here:

1. the correlation (1) which contains no any information about the geometry of the respective molecules, and
2. the connection between $f_R$ and the molecular parameters.

Equation (1) clearly demonstrates that the activation energy $E_A$ increases if the relaxation frequency decreases. This general behaviour was also found by Heppke et al.[5] in another basic mixture and by Kresse, Stettin, and Tennstedt[9] in a binary system. If we take into account these experimental results we have to explain correlation (1) from basical relations of the liquid crystalline state. Due to the presence of the so called "nematic potential," which arises from the molecular anisotropy, the dielectric reorientation is more or less hindered. An increase of this potential on one hand reduces the probability

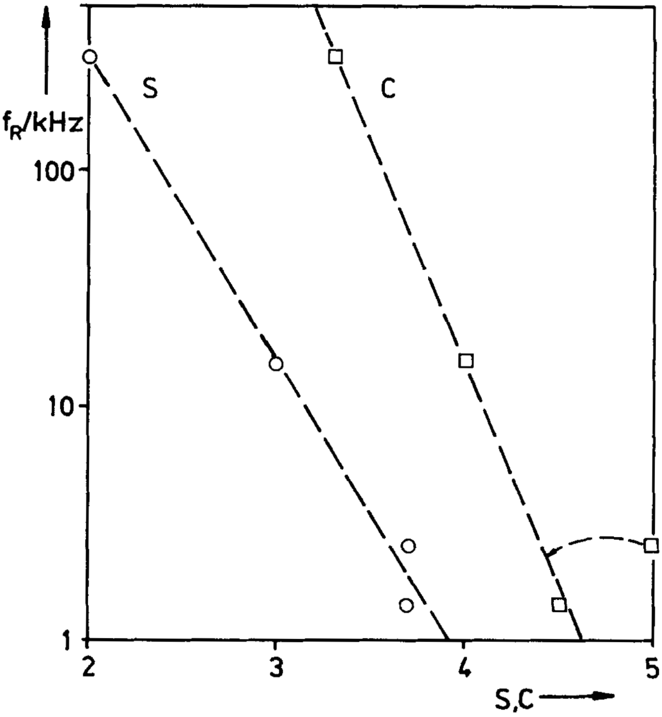


FIGURE 6 Correlation between the relaxation frequencies at $T = 313$ K and the geometrical quantities S and C shown in Table II.

for the reorientation around the short molecular axis (decrease of $f_R$), and on the other hand the potential barrier $E_A$ increases itself.

The nature of the "nematic potential" is complex. The attractive forces as well as geometrical reasons can explain the formation of nematic liquid crystals.[10]

Therefore, the relaxation frequencies are plotted as function of the length to width ratios in Figure 6. The correlation is quite good, if we neglect the alkyl group (S). If we take into consideration the alkyl in a trans-conformation, the points for the butyl and nonyl derivates (substances 3 and 4 respectively in Table II) show strong deviations from each other. A formal correction is possible by changing of the C value of nonyl derivative from 5 to about 4.4. This only means that due to the conformational changes in the elongated alkyl chain the effective length-to-width ratio is decreased. Generally we can say: the elongation of the molecules by one benzene unit decreases the relaxation frequency by about one decade. It should be noted here that an increase of the concentration of the elongated molecule must not necessarily cause a decrease of the relaxation frequency as it is demonstrated for BM + 5% and 10% of substance 4 in Figure 5.

From all the experimental data one can conclude that the geometry of the solute molecules, especially the length of the rigid part, has a strong influence upon the dielectric relaxation behaviour.

## References

1. H. Kresse, *Advances in Liquid Crystals*, **6**, 109 (1983).
2. H. Kresse, K. Worm, W. Schäfer, H. Stettin, D. Demus and W. Otowski, *Cryst. Res. Technol.*, **21**, 293 (1986).
3. A. Axmann, *Z. Naturforsch.*, **21A**, 290 (1965).
4. A. J. Martin, G. Meier and A. Saupe, *Symp. Faraday Soc.*, **5**, 119 (1971).
5. G. Heppke, J. Kayed and U. Müller, *Mol. Cryst. Liq. Cryst.*, **98**, 309 (1983).
6. M. Schadt, *Mol. Cryst. Liq. Cryst.*, **66**, 319 (1981).
7. N. E. Hill, Vaughan, A. H. Price and M. Davis, *Dielectric Properties and Molecular Behaviour* (Princeton, New Jersey, 1969).
8. J. Szabon and S. Diele, *Cryst. Res. Technol.*, **17**, 1315 (1982).
9. H. Kresse, H. Stettin and E. Tennstedt, *Cryst. Res. Technol.*, **21**, 1109 (1986).
10. M. A. Cotter, *Phil. Trans. R. Soc. Lond.*, **A309**, 127 (1983).