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Dielectric Properties of Multi-Component Systems

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Dielectric Properties of Multi-Component Systems

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(*Received April 21, 1977*)

The phase diagram of 4-n-octyloxyphenyl 4-n-pentyloxybenzoate (nematic) and 2-methylphenylbenzoate (not liqu. cr.) was investigated. In the nematic part of the diagram the complex dielectric constants and the relaxation were evaluated as functions of the temperature and the concentration. In the isotropic state the viscosities were measured as functions of the temperature and the concentration. The results allowed the calculation of the nematic retardation factor, the nematic interaction energy E and the activation energy of the rotation of the longitudinal dipole component. E is only slightly influenced by addition of the not liquid crystalline component. The temperature and concentration dependence of the dielectric anisotropy allows the conclusion, that at a constant temperature difference from the initial clearing in the binary system there are constant values of the retardation factor and the degree of order.

1 INTRODUCTION

The thermal desorientation of the single molecular long axes in the nematic state can be described by the degree of order

$$S = 1 - \tfrac{3}{2}\overline{\sin^2\theta} \tag{1}$$

θ = angle between the single molecular long axes and the nematic director, $\overline{\sin^2\theta}$ = mean value averaged over all molecules. The value of the degree of order is depending on the competition of the thermal energy of the molecules and the energy gain by the parallel orientation. At temperatures above the clearing point the thermal energy is dominant, therefore the molecules possess rotational freedom. Besides by temperature increase the rotational freedom can be reached by addition of respective amounts of isotropic liquids. It is of theoretical and practical interest, to investigate the influence of the addition of isotropic liquids on the degree of order of nematic liquid crystals.

We have explored the nematic state in the binary system of 4-n-octyloxyphenyl 4-n-pentyloxybenzoate (as pure component nematic) and 2-methylphenyl benzoate (as pure component isotropic liquid). We have measured the dielectric anisotropy, which may be considered as a measure for the degree of order, and the dielectric relaxation time, which is a measure for the mobility of the molecules.

2 SUBSTANCES

The 4-n-octyloxyphenyl 4-n-pentyloxybenzoate has been synthesized according to Ref. 1, distilled in the vacuum (boiling point 250°C at 0.25 Torr) and several times recrystallized. Its m.p. 50.0°C resp. its clearing point 83.8°C differ slightly from other dates (m.p. 50.2°C resp. cl. 84.5 in Ref. 2, see also Ref. 3). It is to be supposed, that by distillation some impurities have been separated.

Also the 2-methylphenyl benzoate has been distilled in the vacuum. By gas chromatographic analysis we found an impurity concentration of less than 0.5%.

3 RESULTS

We have investigated the diagram of state of the binary system by a heating stage microscope. Figure 1 shows the part of the diagram, which is important for the present problem. Table I comprehends the different samples, at which the measurements have been done.

The experimental details for the dielectric measurements we have published in a former work.[2]

Initially we have measured the dependence of the dielectric anisotropy† $\Delta\varepsilon' = \varepsilon'_{\parallel} - \varepsilon'_{\perp}$ on the magnetic induction. As the limiting values of $\Delta\varepsilon'$ indicate, all samples have been fully oriented above 2 k Gauss. We could not detect a noticeable influence of the isotropic component on the limiting magnetic induction, which has been necessary for full orientation. At the following measurements we have used a magnetic induction of 5.15 k Gauss.

Curve A in Figure 2 shows the dielectric behavior of the highly purified 4-n-octyloxyphenyl 4-n-pentyloxybenzoate. The values are about 2%

† In accordance with the international usual designation $\varepsilon'_{\parallel}$ resp. $\varepsilon'_{\perp}$ means the dielectric constant parallel resp. perpendicular to the nematic director (electric field parallel resp. perpendicular to the orienting magnetic field). $\varepsilon''_{\parallel}$ denotes the dielectric loss parallel to the nematic director in the MHz region.

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TABLE I

Sample	Mole Fraction of the Methylphenyl benzoate
A	0.0000
B	0.0567
C	0.0928
D	0.1446
E	0.1937

smaller than those of the less purified substance.[2] The results after addition of 14.46 mol% 2-methylphenyl benzoate are given in curve D and the detailed dielectric behavior in the two-phase-region is shown in Figure 3. The nematic portions, which appear bright in the polarizing microscope (Fig. 4), are obviously oriented by the influence of the magnetic field and cause a small dielectric anisotropy. Figure 5 gives a survey on the dielectric anisotropy at different concentrations and temperatures.

Further information can be obtained from the dispersion step in the MHz region, which is characteristic for numerous nematic liquids.[4] As well in the pure nematic ester as in all mixtures we found relaxation behaviour which can be described by a single relaxation time. Representative for all mixtures,

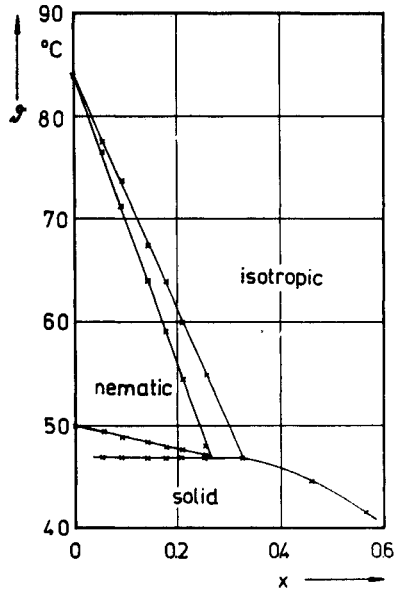

FIGURE 1 Diagram of state of the binary system 4-n-octyloxyphenyl 4-n-pentyloxybenzoate and 2-methylphenyl benzoate. x = mole fraction of the 2-methylphenyl benzoate.

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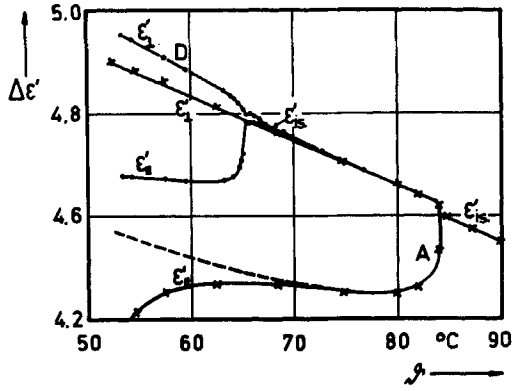

FIGURE 2 Temperature dependence of the dielectric constants of the samples A and D.

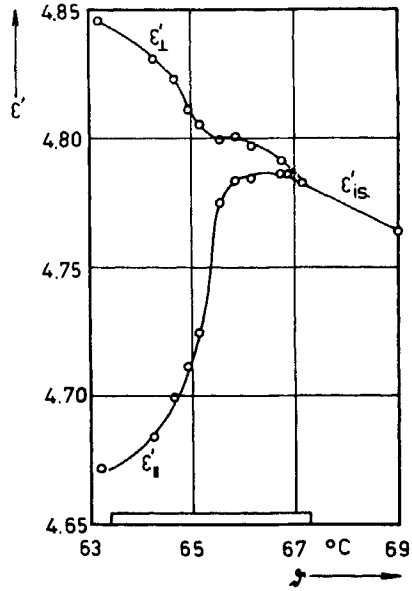

FIGURE 3 Temperature dependence of the dielectric constant in the two phase region, which is indicated by the rectangle above the temperature axis (sample D).

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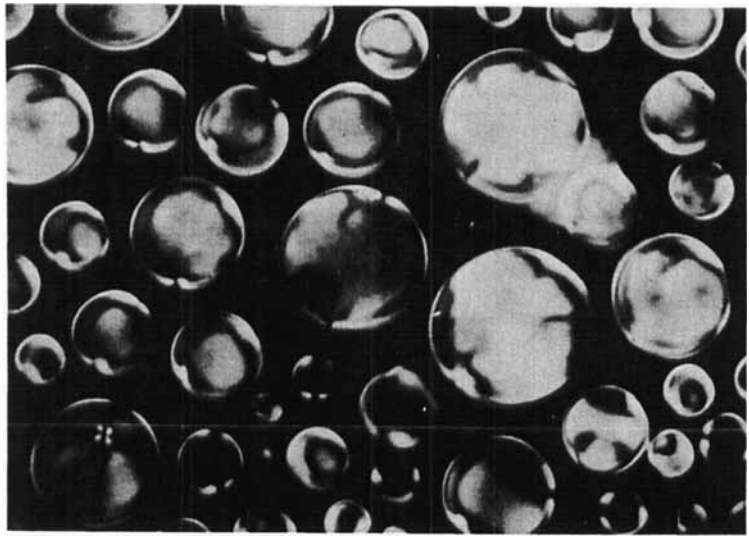

FIGURE 4 Microphoto of the sample D in the two phase region. With crossed polarizers in the bright nematic droplets appears the typical cross characteristic for uniaxial crystals.

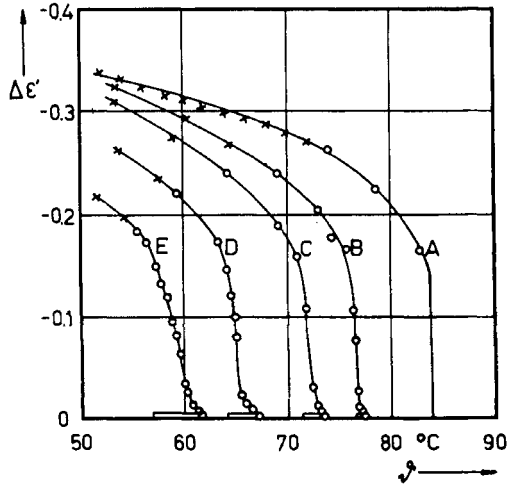

FIGURE 5 Dielectric anisotropy of the samples A–E as a function of the temperature. ⊙ experimental values; x experimental values which are corrected by aid of Cole-Cole plots. The two phase regions are indicated by rectangles above the temperature axis.

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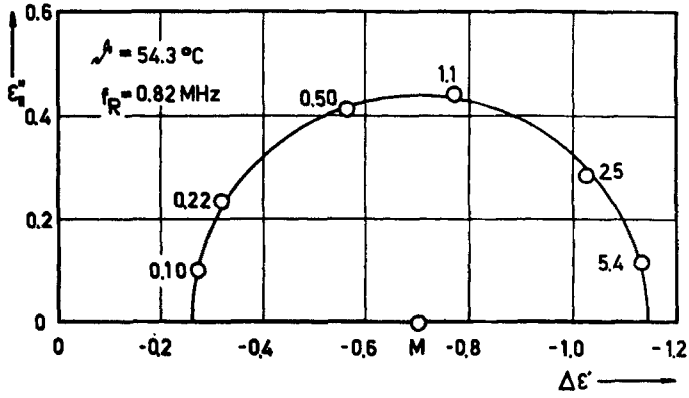

FIGURE 6 Cole-Cole circles for sample D.

in Figure 6 the Cole-Cole-plots[5] of the sample D are given at four different temperatures.

From the frequency dependence of the dielectric loss parallel to the magnetic field we obtained the relaxation time τ as function of the concentration and the temperature. Figure 7 shows the logarithmic plot of the relaxation time versus the reciprocal absolute temperature.

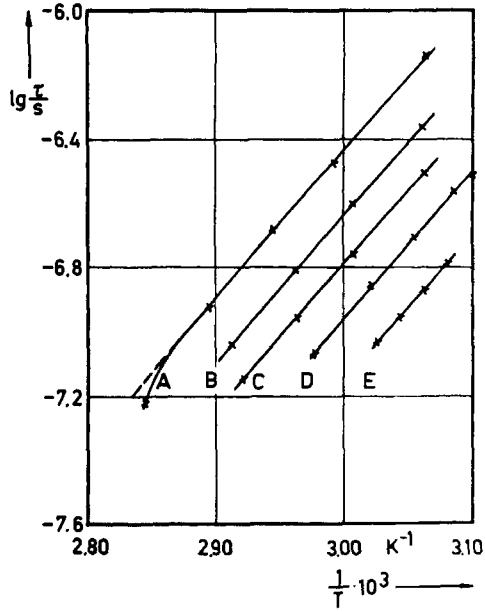

FIGURE 7 Logarithmic plot of the relaxation time in dependence on the reciprocal absolute temperature for the samples A–E; τ in seconds.

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We have measured the kinematic viscosity of the isotropic phase with the aid of an Ubbelohde viscosimeter. Figure 10 gives a survey on the temperature dependence of the viscosity of the different samples.

3 DISCUSSION

3.1 Dielectric Anisotropy

The dielectric anisotropy of a pure nematic liquid can be calculated from molecular parameters:[6]

$$\Delta\varepsilon = 4\pi \frac{N_A \rho}{M} hFS\left[\Delta\alpha - F\frac{\mu^2}{2kT}(1 - 3\cos^2\beta)\right] \tag{2}$$

N_A = Loschmidt's number
ρ = density
M = molecular mass
h, F = factors of the Onsager theory
$\Delta\alpha$ = anisotropy of molecular polarizability
μ = dipole moment of the nematic compound
β = angle between dipole moment and the molecular axis
k = Boltzmann's constant
T = absolute temperature

Both of the components of our system are chemically similar substances. Therefore it is to be assumed that the factors h and F are only slightly dependent on the concentration. Further we suppose that the molecular parameters $\Delta\alpha$, μ and β do not change by addition of the isotropic component. For the dependence of the dielectric anisotropy of the binary system ($\Delta\varepsilon'_x$) on the mole fraction x of the isotropic component we assume in first approximation the validity of the simple mixture rule:

$$\Delta\varepsilon'_x = (1 - x)\,\Delta\varepsilon' + x\,\Delta\varepsilon'_B \tag{3}$$

The 4-n-alkylphenyl 4-n-alkylbenzoates possess only a very small (positive) dielectric anisotropy.[7] Therefore we suppose that the chemically very similar isotropic component of our two component system, which in analogy to the guest-host-effect[8] can be oriented by the nematic matrix, does not cause a remarkable contribution to the dielectric anisotropy $\Delta\varepsilon'_x$. In the case of rotational freedom the isotropic component does not influence the anisotropy of the physical properties. Therefore approximately we write

$$\Delta\varepsilon'_B = 0$$

and consequently

$$\Delta\varepsilon'_x = (1 - x)\Delta\varepsilon' \tag{4}$$

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By combination of Eqs. (2) and (4) we obtain under consideration of the above discussed facts:

$$\Delta\varepsilon'_x = (1 - x)4\pi \frac{N_A \rho}{M} hFS(T, x)\left[\Delta\alpha - \frac{\mu^2}{2kT}(1 - 3\cos^2\beta)\right] \qquad (5)$$

Eq. (5) gives in first approximation the dielectric anisotropy as a function of the mole fraction. Mixture effects as for instance the influence of the partial mole volumina or the different molecular masses of the components are not in consideration. Further we suppose the density of the nematic mixtures approximately to be independent on the temperature.† Only the degree of the order S shall be considered as a function of temperature and concentration. It is known in the literature, that the degree of order of different substances plotted as a function of the reduced temperature yields in first approximation equal curves.[10,11] Also substances of different purity give nearly equal curves, if the difference between the temperature of the initial clearing T_{cli} and the measuring temperature is used as a measure for the reduced temperature.[12,13]

Considering the above suppositions, from Eq. (5) follows, that the temperature dependence of the dielectric anisotropy for all probes should be similar. Figure 8 shows the dielectric anisotropy as a function of the reduced temperature. The above explained suppositions are justified by the relatively good agreement between all curves. After Eq. (5) a decrease of the dielectric anisotropy with increasing mole fraction is to be expected. Obviously this effect is partly compensated by the lower temperature of the existence region of the mixtures (influence of the second term in the brackets in Eq. (5)) and by mixture effects.

Considering Eq. 5, at isothermic conditions $\Delta\varepsilon'_x$ is a linear function of the mole fraction, and the above suppositions being valid it depends only on $S(T, x)$. Therefore it is possible to gain some information about the degree of order as a function of the concentration. In Figure 9 the dielectric anisotropy at different temperatures is plotted as a function of the concentration of the isotropic component. The curves are linear similar to the curves of dielectric anisotropy versus temperature (Figure 5, D). $\Delta\varepsilon'$ decreases more rapidly and falls after crossing the two phase region to zero. From the far

† After Sonntag[9] the density of the pure 4-n-octyloxyphenyl 4-n-pentyloxybenzoate is at 65°C:

$$\rho = 1.007 \text{ g cm}^{-3}, \frac{d\rho}{dt} = 9 \cdot 10^{-4} \text{ g cm}^{-3} \text{ K}^{-1}$$

The failure which is caused by the neglection of the temperature dependence of ρ is in the existence interval of the nematic phase of 34°C about 3%.

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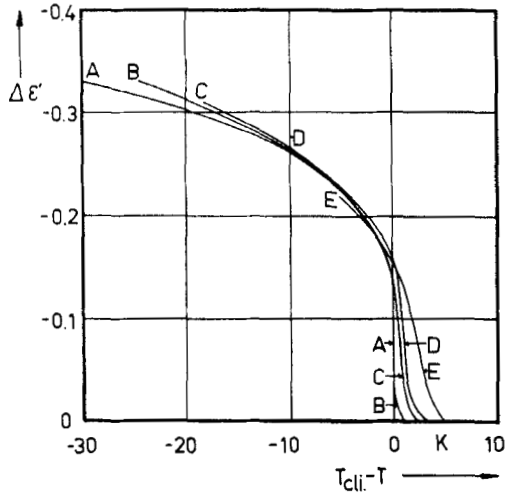

FIGURE 8 The dielectric anisotropy as a function of the difference between the temperature of initial clearing and the measuring temperature. The values with $(T_{cli} - T) > 0$ belong to the two phase region.

extended parallel slope of the curves follows, that the degree of order at isothermic conditions is approximately an universal function of the concentration.

3.2 The dielectric relaxation

For the interpretation of the measurements we can use a solid state model[14] as well as models on the base of the rotational diffusion.[15,16] The solid state models of Arrhenius and Eyring[14] allow the determination of a potential barrier E for the respective relaxation process. Our experimental results given in Figure 7 are well reproduced by the Arrhenius equation:

$$\ln \tau = A + \frac{E_{A,\tau}}{RT} \tag{6}$$

$E_{A,\tau}$ = activation energy of the relaxation process in the MHz region.

As we know from experience, the Arrhenius equation is also valid for the relaxation process in the G Hz region (relaxation time τ_0):

$$\ln \tau_0 = B + \frac{E_{A,\tau_0}}{RT} \tag{7}$$

E_{A,τ_0} = activation energy of the relaxation process in the G Hz region.

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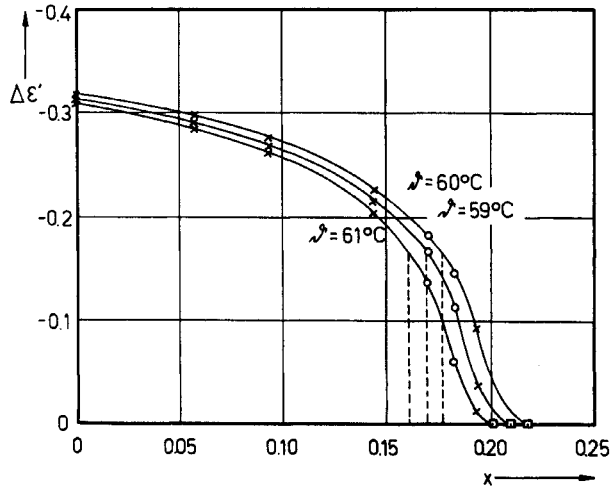

FIGURE 9 The isothermic dielectric anisotropy as a function of the mole fraction x of the 2-methylphenyl benzoate. The measured points on the abzissa are the concentrations of the clearing end. The broken line indicate the concentrations of the initial clearing.

There is only small experimental work concerning the relaxation times of nematic liquids in the G Hz region available. Therefore we assume according to Debye[17] a direct proportionality between τ_0 and the viscosity in the isotropic state (ν):

$$\tau_0 = k \cdot \nu \tag{8}$$

Instead of the dynamic viscosity η, which occurs in the original equation of Debye, we use the kinematic viscosity $\nu = \eta/\rho$. In good approximation then we can assume, that the activation energy E_{A,τ_0} in the isotropic phase is available from the temperature dependence of the viscosity.

$$\frac{\mathrm{d} \ln \tau_0}{\mathrm{d}(1/T)} = \frac{E_{A,\tau_0}}{RT} \approx \frac{\mathrm{d} \ln \nu}{\mathrm{d}(1/T)} = \frac{E_{A,\mathrm{visc}}}{RT} \tag{9}$$

$E_{A,\mathrm{visc}}$ = activation energy of the viscosity in the isotropic state.

As experimental investigations proved, the temperature dependence of τ_0 is not very different in the nematic and isotropic state. Especially for 4-n-octyloxyphenyl 4-n-pentyloxybenzoate is valid:

$$E_{A,\tau_0 \mathrm{is}} \approx E_{A,\tau_0 \mathrm{nem.}} \sim E_{A,\mathrm{visc}} = 6.0 \pm 1.5 \text{ kcal/mole [18].}$$

In pure single liquid crystals the relation

$$E_{A,\tau} > (E_{A,\tau_0,\mathrm{nem.}} \sim E_{A,\mathrm{visc}})\dagger$$

† Only in a mixture of 4 nematic substances Bata and Molnar[19] found $E_{A,\tau} \approx E_{A,\tau_0,\mathrm{nem}}$.

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TABLE II

Sample	$E_{A,\tau}$[Kcal/mole]	ΔE [Kcal/mole]
A	21.1 ± 0.4	13.9 ± 0.5
B	21.2 ± 0.4	14.0 ± 0.5
C	20.7 ± 0.5	13.5 ± 0.6
D	21.2 ± 0.7	14.0 ± 0.8
E	20.5 ± 1.0	13.3 ± 1.1

was found to be valid. In the sense of a potential model the difference

$$E_{A,\tau} - E_{A,\tau_{0,\text{nem}}} = \Delta E \tag{10}$$

could be interpreted by considering an additional potential barrier, which is caused by the nematic order.[7] However, the frame of the simple potential models is exceeded by identifying ΔE with the nematic interaction energy as it is used by Martin, Meier and Saupe[14,15] for the interpretation of the radio frequency absorption.

By the aid of the graphical plot of lg ν (Figure 10) resp. lg τ (Figure 7) *versus* the reciporcal temperature we have evaluated $E_{A,\text{visc}} = 7.2 \pm 0.1$ kcal/mole and the values for $E_{A,\tau}$, listed in Table II. The latter additionally contains the values of ΔE calculated with Eq (10).

The values listed in Table II show that the activation energies practically do not depend on the composition of the binary system. With increasing concentration of the 2-methylphenyl benzoate, however, at constant temperature the relaxation time in the MHz region is decreasing remarkably stronger than the viscosity in the isotropic phase (Figures 7 and 10).

With the model of Eyring it is possible to describe this fact formally by a decrease of the activation entropy:[20]

$$g_x = \frac{\tau_x}{\tau_{0x}} = \exp \frac{\Delta H_x}{RT} \cdot \exp - \frac{\Delta S_x}{R}$$

Values with the index x correspond to mixtures of the mole fraction x; Δ indicates the difference of the respective activation parameters in the MHz and the G Hz region. Within the experimental accuracy $\Delta H_x \sim \Delta E$ is independent from x (see Table II). Therefore supposing

$$\Delta S_x = \Delta S \cdot x (\Delta S = 14.5 \text{ cal} \cdot \text{mole}^{-1} K^{-1})$$

our experimental results can be well described by the equation (see also Eq. 15):

$$\ln g_x = \ln g - \frac{\Delta S \cdot x}{R}$$

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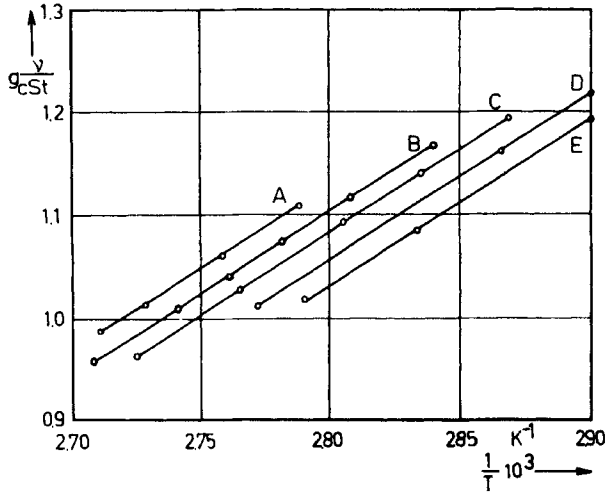

FIGURE 10 Logarithm of the kinematic viscosity plotted against the reciprocal absolute temperature for the samples A–E; ν measured in centistokes.

If we use the simple model of the rotational diffusion of Meier and Saupe[15] for the interpretation of the temperature dependence of the relaxation time τ and the viscosity (instead of τ_0), we yield similar conclusions as with the solid state model (see also Ref. [7]). There are contradictions, however, if the retardation factor g calculated after Eq. (11), using the interaction energies E in the sense of the solid state model, is compared with the experimentally evaluated g after Eq. (12).[18]

$$g = \frac{RT}{E}(e^{E/RT} - 1) \tag{11}$$

$$g = \frac{\tau}{\tau_0} \text{ (nematic phase)} \tag{12}$$

The evaluation on the base of the improved rotational diffusion model of Martin, Meier and Saupe[16] is only possible, if experimental values for τ as well as for τ_0 are available. For the pure 4-n-octyloxyphenyl 4-n-pentyloxybenzoate we have determined $g = 450$.[18] Considering this value, we can estimate $E = 6$ kcal mole^{-1}.

The change of g by addition of the isotropic component can be derived from empirical functions describing the experimental values. For constant temperature the following equations are valid within the range of the experi-

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mental accuracy:

$$\ln \tau_x = \ln \tau - 8.47x \tag{13}$$
$$\ln \nu_x = \ln \nu - 1.15x$$

This can be modified by use of Eq. (8):

$$\ln \tau_{0x} = \ln \tau_0 - 1.15x \tag{14}$$

For the binary mixture which is concerned in this paper therefore we have obtained:

$$\ln g_x = \ln g - 7.32x \tag{15}$$

At a mole fraction of the 2-methylphenyl benzoate $x = 0.2$ and the g value for the pure nematic compound, from Eq. (15) can be derived $g_{0.2} = 10.4$ and $E = 5$ kcal · mole^{-1}.

The model of Martin, Meier and Saupe,[16] which considering the above mentioned simplifications only with scruples can be applied to mixtures,

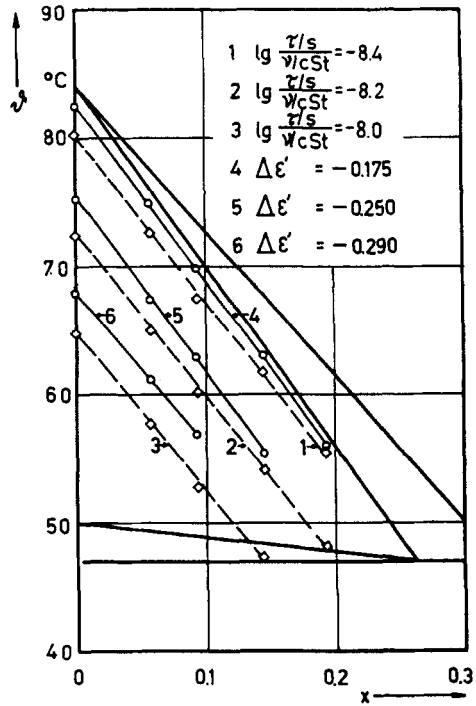

FIGURE 11 Curves of constant quotients from relaxation time and viscosity and dielectric anisotropy in the binary system; see also Figure 1.
x = mole fraction of the 2-methylphenyl benzoate.

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explains the influence of the isotropic component by the decrease of the nematic interaction energy. This seems to be better compatible with model conceptions than a formal description by an entropy effect.

Initially we have mentioned, that after Martin, Meier and Saupe[16] a connection between the degree of order and the change of the molecule mobility must be existing. In Figure 11 we have displayed in our binary system curves of constant $\Delta\varepsilon'$ respectively constant $\lg \tau_x/v_x$. According to the discussion of Eqs. (12) to (15) $\lg \tau_x/v_x$ is a measure for the g factor. As to be seen, at a constant temperature difference from the initial clearing there is resulting nearly a constant g. It seeems to be allowed, also to assume a constant degree of order along such a curve. With this assumption also the slope of the curves of constant $\Delta\varepsilon'$ is compatible, if we assume a compensation of the decrease of $\Delta\varepsilon'$ due to the addition of the isotropic component and an increase due to the lower temperatures, as we already have discussed in connection with Eq. (5) and Figure 8.

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