Dielectric relaxation of a short molecule in a liquid-crystalline solvent

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Dielectric relaxation of a short molecule in a liquid-crystalline solvent

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Dielectric relaxation measurements of 5 mole % 4-n-hexyloxycyanobenzene (I) dissolved in 4-n-pentyloxyphenyl-trans-4-n-octylcyclohexylcarboxylate (II) were carried out from 1 kHz to 10 MHz in the nematic, smectic A and smectic B phases. The relaxation frequency of I parallel to the director is about 0·5 MHz in the S_B phase and increases rapidly at the transition from S_B to S_A.

Dielectric relaxation measurements are a powerful tool for the investigation of dynamics in liquid crystals because of the possibility to align the samples [1]. The relations between the structure of the phase and its dynamics with respect to reorientation around the short axis of the rod-like molecules have been intensively investigated [2–6]. Dielectric relaxation times were measured in suitable binary systems as a function of the concentration, temperature and the chemical structure [7–10]. In the past nematic mixtures which contain cyano substituted molecules with different molecular geometries were studied systematically in order to find a good mixture for a dual frequency addressing display [11–14] or to carry out basic research [15]. Here the variation of the relaxation frequency for the reorientation around the short molecular axis of a short molecule dissolved in a liquid-crystalline solvent was investigated at the transition from the more liquid-like smectic A into the solid-like smectic B.

5 mole % of the non-liquid-crystalline 4-n-hexyloxycyanobenzene

I
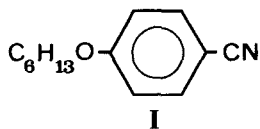
was dissolved in 4-n-pentyloxyphenyl-trans-4-n-octylcyclohexylcarboxylate

II
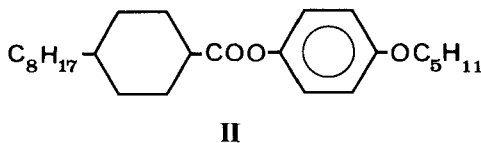
C 324 K S_B 331·5 K S_A 338 K N 346·5 K I.

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A derivative of sample **II** in which the $-OC_5H_{11}$ group is replaced by $-OC_6H_{13}$ has already been investigated using dielectric relaxation [16]. The main results were

(i) within the experimental error of $\varepsilon_{\parallel}'' < 0.005$ (1 kHz–100 kHz) and $\varepsilon_{\parallel}'' < 0.05$ (100 kHz–10 MHz) no dielectric absorption could be detected;

(ii) the static dielectric constants at 336 K (S_A phase) are $\varepsilon_{0\parallel} = 3.09$ and $\varepsilon_{0\perp} = 3.06$ whereas in the S_B phase at 307.4 K $\varepsilon_{0\parallel} = 3.14$ and $\varepsilon_{0\perp} = 3.94$.

The small chemical variation should not cause a major change in the dielectric data. Therefore, all dielectric absorptions which can be detected in the parallel direction of a mixture of **I** and **II** are only related to the polar solute **I**. The mixture of 5 mole % **I** and 95 per cent **II** (S_B 323–326 K S_A 336–337 K N 344–345 K I) could be supercooled to 303 K. Dielectric relaxation measurements were performed in a double plate capacitor ($A \sim 2\,\mathrm{cm}^2$, $d = 0.02\,\mathrm{cm}$) using a Hewlett Packard impedance analyser HP 4192 A [11]. The temperature stabilization was better than ± 0.1 K. The sample was oriented magnetically ($B \sim 1$ T), with the director perpendicular to the surface of the capacitor plates.

The experimental absorption curves, calculated from

$$\varepsilon_{\parallel}'' = (R_{\parallel}\, 2\pi f\, C_{\mathrm{g}})^{-1},$$

where f is the frequency, $R_{\parallel}$ is the resistance and C_{g} is the geometrical capacitance of the cell, are shown in figure 1. Whereas at lower frequencies a dielectric absorption can be separated, $\varepsilon_{\parallel}''$ increases continuously at higher frequencies.

The low frequency absorption can be described at $f < 2$ MHz by a simple Debye mechanism [17] as shown by the Cole–Cole plot in figure 2. At higher frequencies the

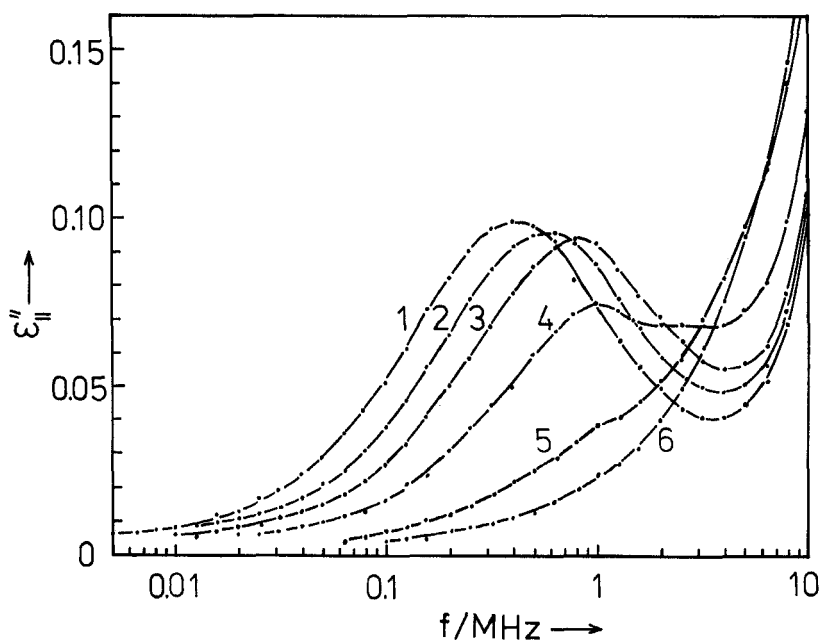Figure 1. Dielectric absorption curves of the mixtures. Smectic B phase: $T(1) = 307.4$ K, $T(2) = 312.2$ K, $T(3) = 317.3$ K; two phase region S_A/S_B: $T(4) = 322.2$ K, $T(5) = 326.2$ K; smectic A phase: $T(6) = 328.0$ K.
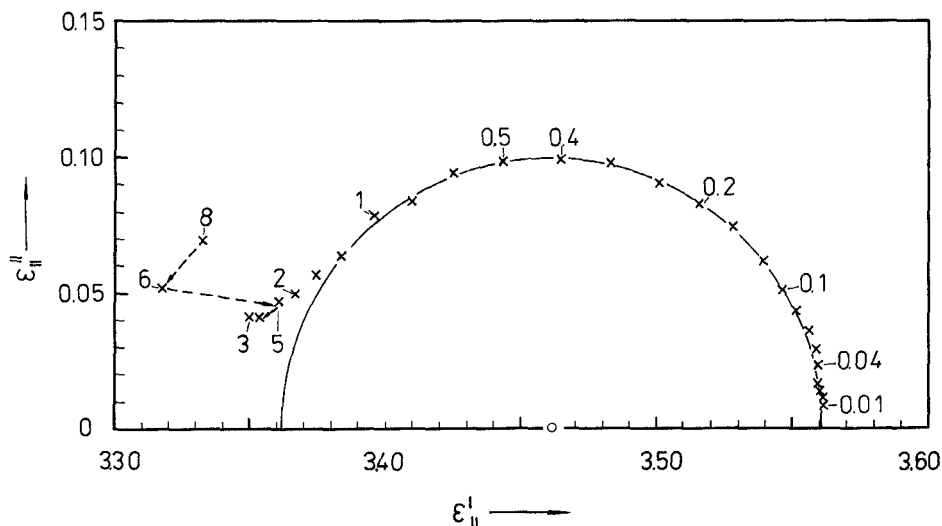
Figure 2. Cole–Cole plot at 307·4 K. The numbers are the frequencies in MHz.

values of the dielectric constant $\varepsilon'_\parallel$ are uncertain indicating irregularities of the measurements. The high frequency limit for $\varepsilon_{\infty\parallel}$ of 3·36 is higher than $\varepsilon_{0\parallel}$ which is 3·14 for the homologous hexyloxy derivative in the S_B phase at the same temperature. At 322·2 K a tendency for the formation of a second absorption maximum at $f > 3$ MHz can be detected, and at 326·2 K (see curve 5) only small deviations from the continuous increase of $\varepsilon''_\parallel$ with frequency can be seen at about 1·1 MHz. These curves (see curves 4 and 5) which were measured in the two phase range S_A/S_B exhibit a strong increase in $\varepsilon''_\parallel$ at $f > 4$ MHz in comparison with curves 1–3. Furthermore, we can detect that the high frequency absorption increases in the same way in which the low frequency maximum at $f \sim 1$ MHz decreases. From this we conclude that the relaxation frequency changes rapidly at the phase transition S_A/S_B. For the separation of the dielectric relaxation effects from the experimental artifact at higher frequencies a detailed analysis in terms of an equivalent circuit is necessary. However we do not have enough data at high frequencies for this and so quantitative considerations are limited to $f < 2$ MHz.

The following results are important.

(i)   In the S_B phase the solute molecules I have a relatively high relaxation frequency. The low value of the activation energy of about 50 kJ mol^{-1} corresponds to data on a nematic mixture with weak interactions between solute and solvent [15].

(ii)   In the S_A phase we expect a relaxation frequency $f_R > 10$ MHz. This is mainly the result of the low degree of order of I in the solvent II. Therefore, the orientational interaction of I with the liquid-crystalline solvent is weak.

(iii)   At the transition from S_B to S_A the relaxation frequency increases rapidly. This effect, which is connected with a jump in the degree of order, is known from pure liquid crystals [2]. In the two phase region two absorption ranges should exist from which only the low frequency one could be clearly detected. The intensity of the low frequency mechanism decreases with increasing temperature indicating the coexistence of the S_A and S_B phases at this first order transition.

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