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Non-linear dielectric studies of the isotropic-smectic phase transition in 6-DBT and 7-DBT

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Results are reported for measurements of $\Delta\epsilon/E^2$ for 6-DBT and 7-DBT (5-trans-*n*-alkyl-2(4'-isothiocyanianophenyl)-1,3-dioxane, $n = 6, 7$) in the isotropic phase, in the vicinity of $T_{S_{A1}}$, and for 6-DBT solutions in dioxane over a broad range of temperatures. In the immediate vicinity of $T_{S_{A1}}$ divergence from the Landau-de Gennes model was observed. From measurements made in solutions of 6-DBT in dioxane it was concluded that the antiparallel orientation of dipoles is preferred.

1. Introduction

In recent years non-linear methods have frequently been used to study critical properties both in liquids and in solids. In papers relating to the isotropic-liquid crystal transition, those dealing with the isotropic-nematic transition are found to dominate, while the isotropic-smectic phase transition has been relatively little studied. With regard to the research method presented here, i.e. the non-linear dielectric effect, it has already been applied to study the isotropic-nematic [1], the isotropic-blue phase [2] and also the isotropic-smectic A phase transition in DOBAMBC [3]. Results obtained in this latter case are entirely different qualitatively from the remainder and hence provided the immediate impulse for undertaking these investigations.

2. Non-linear dielectric effect

The non-linear dielectric effect belongs to the same class of research methods as the Kerr effect, the Cotton-Mouton effect or depolarized light scattering. The measure of the non-linear dielectric effect is $\Delta\epsilon/E^2$, where $\Delta\epsilon = \epsilon_E - \epsilon_0$ is the difference between the electric permittivities in a strong and weak electric field. This definition results from the fact that, in practice for liquids [4], $\Delta\epsilon \sim E^2$ and so the ratio $\Delta\epsilon/E^2$ is independent of the electric field strength. It is experimentally verified every time and for these studies with the results illustrated in figure 1. It must be admitted that the non-linear dielectric effect is a method exhibiting little selectivity. This means that it is influenced by a large number of mechanisms taking place both macroscopically and microscopically [4]. Nevertheless in the vicinity of a phase transition the contribution of critical fluctuations can be dominant.

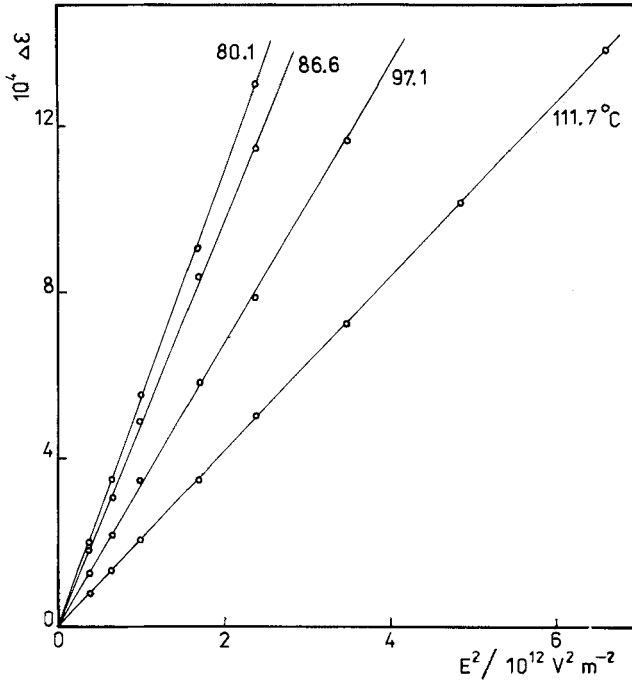


Figure 1. Experimental dependence of $\Delta\epsilon$ versus E^2 for 6-DBT at several temperatures.

For the purpose of applying this effect to investigate the pretransitional effects, it is assumed that the total value of $\Delta\epsilon/E^2$ is composed of two parts [5, 6], namely

$$\frac{\Delta\epsilon}{E^2} = \left(\frac{\Delta\epsilon}{E^2}\right)_B + \left(\frac{\Delta\epsilon}{E^2}\right)_C, \quad (1)$$

where $(\Delta\epsilon/E^2)_C$ is the part associated with the critical fluctuations. From both the theoretical model and the experimental data obtained it is clear that this part always has a positive value ($\Delta\epsilon > 0$) and its magnitude is roughly proportional to the permittivity anisotropy of the medium, induced by the critical fluctuations [5, 7]. The part $(\Delta\epsilon/E^2)_B$ is the background effect coming from other mechanisms associated with the electrical properties of the molecules and their short range interactions. Two basic mechanisms may be mentioned, the first is the orientational effect associated with the interaction between permanent dipole moments and a strong electric field; this effect is always negative [4]. The second mechanism is provided by the short range intermolecular interactions causing orientational correlations of the dipole moments. For the preferred antiparallel orientation of neighbouring dipoles the contribution to the total value of the effect is positive ($\Delta\epsilon/E^2 > 0$), while for the case of parallel orientation this contribution is negative ($\Delta\epsilon/E^2 < 0$) [4].

The temperature dependence of the critical part (cf. equation 1), in agreement with the Landau-de Gennes model and with experimental results obtained up to now (with the exception of DOBAMBC, in which the effect was negative), is described by [2, 8]:

$$\frac{\Delta\epsilon}{E^2} \sim \frac{1}{T - T^*}, \quad (2)$$

where $T^* = T_C - \Delta T$ and T_C is the clearing temperature.

3. Experimental and results

The non-linear dielectric measurements use was made of an apparatus developed by Malecki [9], in which a strong electric field is applied to a measurement capacitor in the form of rectangular impulses with a duration time of about 1 ms. Its intensity does not exceed $2.5 \times 10^6 \text{ V m}^{-2}$ and the frequency of the measuring field was about 1 MHz. Measurements of $\Delta\epsilon/E^2$ as a function of temperature were made for 6-DBT and 7-DBT 5-trans-*n*-alkyl-2(4'isothiocyanianophenyl)-1,3-dioxane, $n = 6, 7$) [10]. The feasibility of using this effect to determine the configuration of neighbouring dipoles, as already mentioned, was utilised for studying solutions of 6-DBT in dioxane.

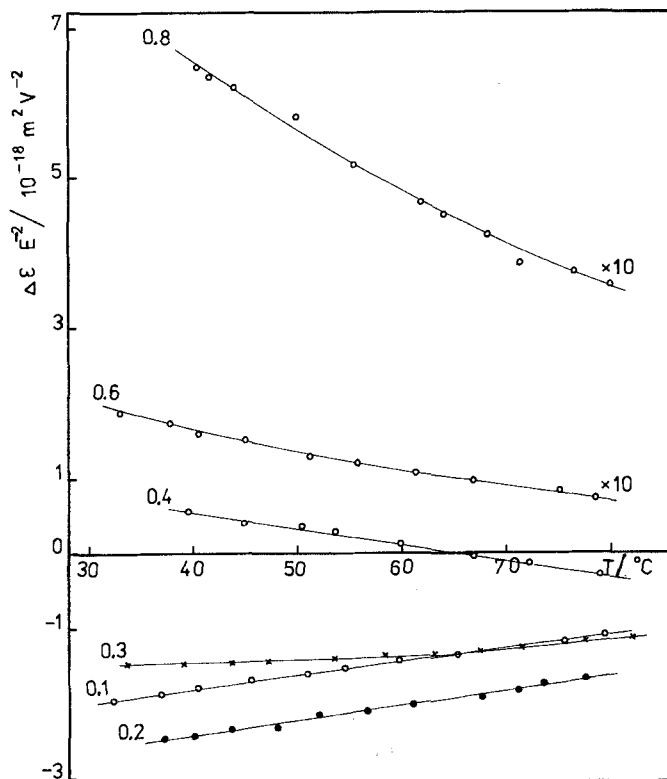


Figure 2. The temperature dependence of $\Delta\epsilon/E^2$ for several 6-DBT-dioxane solutions. Concentrations of 6-DBT (given on the figure) are in mass fraction.

Figure 2 shows the temperature dependence of $\Delta\epsilon/E^2$ for several 6-DBT solutions in dioxane with various concentrations of the liquid crystal component. Figure 3 shows the same data as a function of concentration for several isotherms. For small concentrations, when the interactions between the dipoles of neighbouring 6-DBT molecules are small, the domination of the orientational effect may be seen ($\Delta\epsilon/E^2 < 0$). With an increase in the concentration of the liquid crystal constituent the influence of the molecular interactions increases and the sign of the non-linear dielectric effect changes to positive, which indicates the preferred antiparallel orientation of neighbouring dipoles. For high concentrations the magnitude of $\Delta\epsilon/E^2$ rises sharply, which is associated both with an increase in the ordering of the 6-DBT molecules and also with the influence of the pretransitional fluctuation interactions with the electric field.

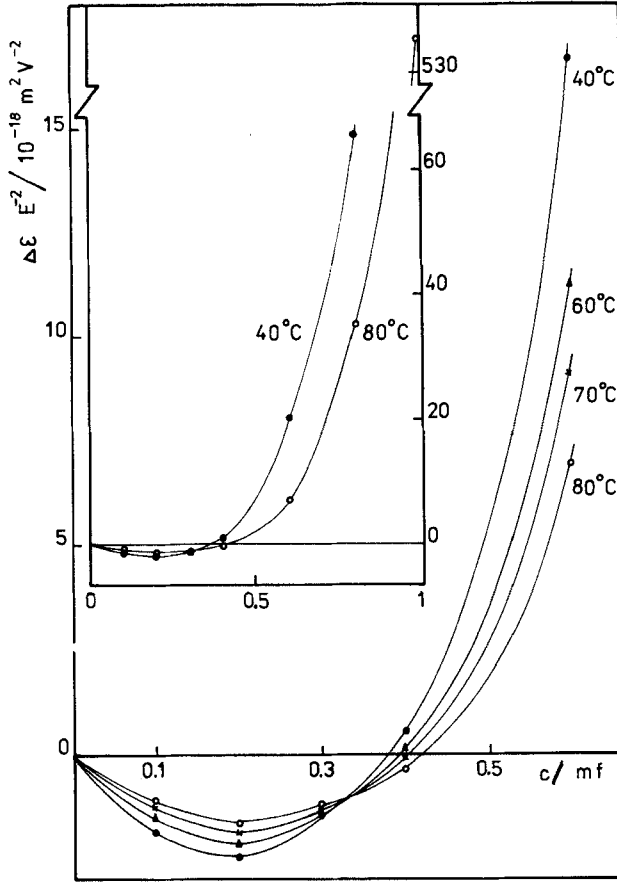


Figure 3. $\Delta\epsilon/E^2$ as a function of concentration of 6-DBT for several isotherms.

Figure 4 shows the temperature dependence of the reciprocal of $\Delta\epsilon/E^2$ for 6-DBT and 7-DBT. In both cases it may be seen that for temperatures above $T_{S_{A1}} + 4\text{ K}$, the Landau-de Gennes model holds good and the reciprocal of $\Delta\epsilon/E^2$ is a linear function $(T - T^*)$. The magnitude ΔT obtained in this way is about 17 K for 6-DBT and about 19 K for 7-DBT. In the immediate vicinity of $T_{S_{A1}}$ a deviation from mean field theory is found. Deviations of this kind were observed, among others, in measurements of the Kerr effect and light scattering for the isotropic-smectic transition [11, 12] and also the Kerr and Cotton-Mouton effect for the isotropic-nematic transition [13]. Elucidation of behaviour of this kind is not unequivocal. In [12] it was interpreted in terms of cross coupling between orientational and layer-like fluctuations resulting from a smectic A-like structure in the isotropic phase, while in [13] it is taken to be a cross-over phenomenon between classical mean field behaviour sufficiently far above T^* and critical behaviour. Yet another interpretation was recently formulated by Pyżuk [14]; he studied the isotropic-nematic phase transition in 5-*n*-heptyl-2-(4-cyanophenyl)-pyrimidine, which exhibits a marked permittivity anisotropy, and observed in the vicinity of $T_{S_{A1}}$ a very marked deviation from the Landau-de Gennes description. This was interpreted as due to the influence of a frequency dispersion.

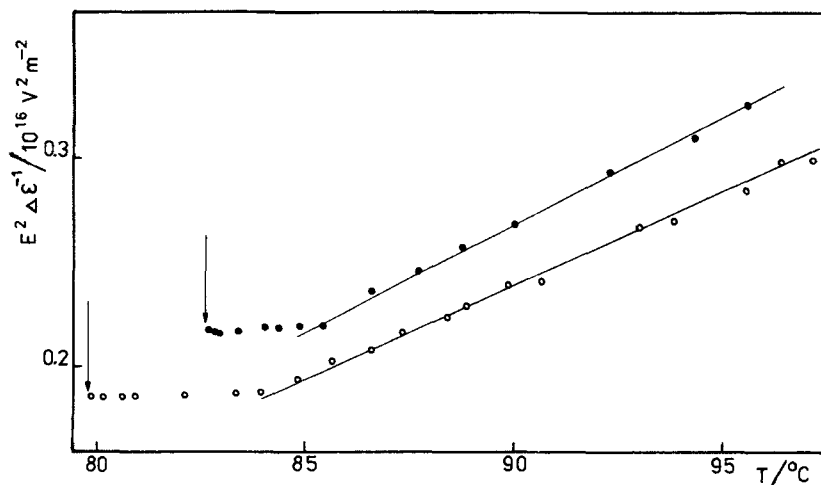


Figure 4. The temperature dependence of the reciprocal of $\Delta\epsilon/E^2$ for 6-DBT (open circles) and 7-DBT (full circles). Arrows indicate the clearing temperatures.

To achieve a precise interpretation of this non-classical behaviour of the non-linear dielectric effect temperature dependence in the vicinity of T_{SA1} for the isotropic-smectic transition would require further investigation. In our opinion the value of this paper lies in the fact that for the first time the NDE method has been used to achieve experimental results for the isotropic-smectic A transition, results which qualitatively confirm the results reported by other methods.

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