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Structural and dielectric investigations of a binary system of a bi-swallow-tailed and a terminally-polar compound

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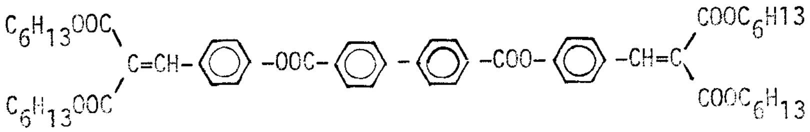
Induced smectic A phases in binary mixtures of a bi-swallow-tailed component and a second component are described as ‘filled smectic A phases’, since the second rod-like component is considered to occupy spaces between the terminal branches of the bi-swallow-tailed molecules. A new system of this kind is now described where the second rod-like component has a terminal dipole, thereby enabling dielectric studies of the mixtures. These measurements coupled with calorimetric and X-ray measurements give information about the packing and dynamics of the mixed phases.

1. Introduction

Different molecular reasons are considered to be responsible for the stabilization or induction of the smectic A phase in binary systems of nematogenic compounds: dipolar forces [1, 2], electron donor–acceptor (EDA) interactions [3, 4] or steric interactions [5–8]. Examples of the last case, which represents the influence of the repulsive forces, are binary mixtures of bi-swallow-tailed molecules with rod-like nematogenic molecules. The occurrence of the induced smectic A phases can be interpreted by a packing model whereby the gaps between the bulky terminal branches of the bi-swallow-tailed compound are filled with the rod-like molecules [6, 7]. Therefore, this new kind of induced S_A phase was called a ‘filled smectic A phase’ [6]. Here we present a filled S_A phase where the rod-like component posseses a terminal dipole. Because the rotation of the longitudinal dipole moment of the terminally-polar compound can be detected by dielectric measurements, we could study the dynamic behaviour of the molecules within these binary mixtures (see [9]). Calorimetric, X-ray and dielectric measurements should give information about the packing and the dynamic behaviour in this liquid crystalline mixed phase.

2. Materials

The bi-swallow-tailed compound of structure A exhibits a nematic phase and in addition, a metastable smectic C phase



A

C 354 K (S_C 341 K) N 398 K I [10]

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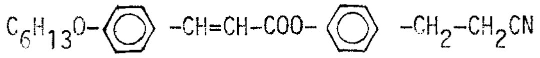
The terminally-polar compound of structure **B** (4-(2-cyanoethyl)phenyl 4-*n*-hexyloxycinnamate only forms a nematic phase



B

C 310·5 K N 346 K I [11]

3. Results

3.1. *The isobaric phase diagram and calorimetric data*

The phase diagram was studied by polarizing microscopy and the contact method [12], and by determination of the transition temperatures of selected mixtures of known concentration. For selected mixtures, the phase transition enthalpies also were measured by differential scanning calorimetry, DSC 7 Perkin–Elmer.

The phase diagram presented in figure 1 shows complete miscibility in the nematic phase. The smectic C phase of the bi-swallow-tailed compound exists over a wide concentration range up to about 55 mol% of B. The characteristic feature is the occurrence of an induced smectic A phase between 35 and 95 mol% of **B** with a pronounced maximum in the S_A–N transition curve at 75 mol% of **B**.

In figure 2, the nematic–isotropic and smectic A–nematic transition enthalpies are plotted against concentration. The clearing enthalpy changes continuously with concentration with only a small negative deviation from a linear dependence. On the contrary, the curve of the smectic A–nematic transition enthalpy shows a pronounced maximum. The concentration at the maximum agrees approximately with the maximum in the transition temperature curve.

3.2. *X-ray investigations*

X-ray investigations have been performed with a flat film camera. The samples were oriented in the nematic state using a magnetic field of about 1·5 Tesla. Figures 3 (*a*) and (*b*) shows the X-ray pattern of the nematic phase of both components of the mixture. In

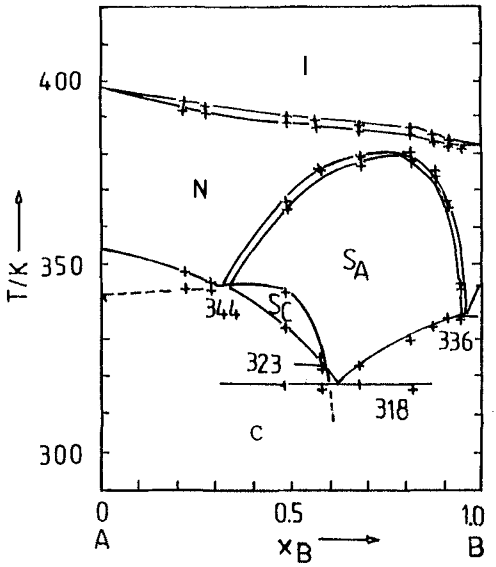


Figure 1. The isobaric phase diagram for the binary system of components A and **B** (*x*: molar fraction).

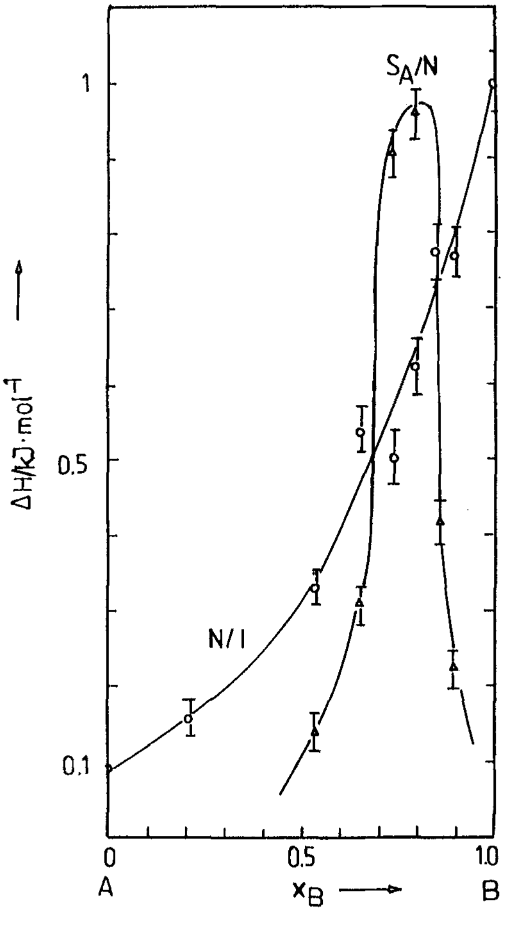


Figure 2. The molar transition enthalpies (kJ mol^{-1}) for the transitions smectic A–nematic (S_A/N) and nematic–isotropic (N/I) as a function of the molar fraction x.

both cases, the existence of smectic-like cybotactic groups is indicated by the strong diffuse scattering in the small angle region. From the pattern, it follows that the molecules of compound **B** are aligned parallel to the normal of the smectic-like layers, whereas for component **A**, the molecules are tilted (skewed cyobotactic groups [13]). For component **A**, the splitting of the inner scattering maxima allows an estimation of the tilt angle θ of about 30°. This is in good accordance with the value ($\theta = 29°$) obtained from

$$d = L \cos \theta,$$

where L is the molecular length. This means that the difference between d and L for the pure compound **A** can be explained by the tilt alone, and that it is not necessary to assume other influences such as interdigitation of the molecules.

However, in the mixtures the structural behaviour is more complex. Admixing the second component causes the splitting of the inner scattering to become more and more smeared out, indicating that the tilt angle decreases. Therefore, the period of the density fluctuations in the nematic phase increases (squares in figure 4). In the region of the S_A phase, an orthogonal alignment of the molecules within the layer exists. The d-values

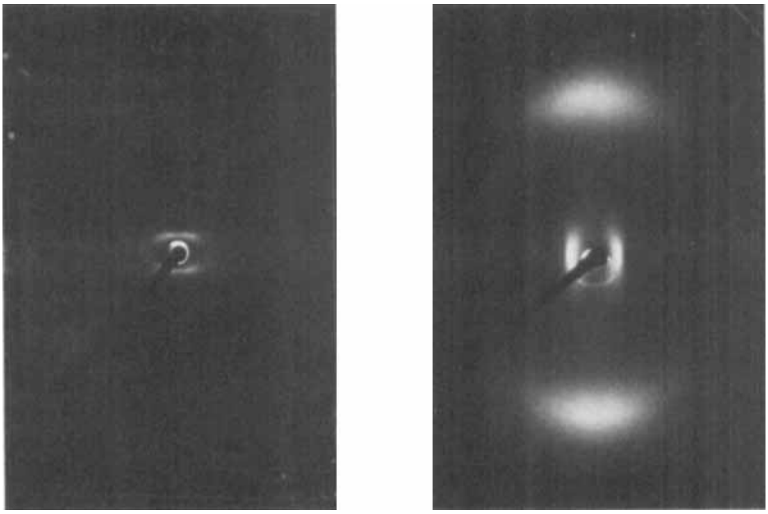

(*a*) (*b*)

Figure 3. X-ray diffraction patterns of oriented samples (*a*) nematic phase of component **A**, $T=373$ K, and (*b*) nematic phase of component **B**, $T=358$ K. The orienting field (1·5 Tesla) is vertical in (*a*) and horizontal in (*b*).

(crosses in figure 4), however, are significantly greater than the average molecular length $L=x_A L_A + x_B L_B$, where x_A, x_B are the molar fractions and L_A, L_B the molecular lengths of the components **A** and **B**, respectively. L is given by the connection line between L_A and L_B—see figure 4.

Such a $d/L>1$ relation is generally found when short rod-like molecules are mixed with bi-swallow-tailed molecules [6] and can be explained by the above mentioned model of a 'filled' S_A phase [6, 7].

3.3. *Dielectric investigations and discussion*

Dielectric measurements were carried out from 0·1 to 100 kHz using a silver capacitor for compound **B** and samples of mixtures with six concentrations. All samples studied (thickness of the cell 0·2 mm) were homogeneously oriented by a magnetic field of about 0·7 Tesla. The data for the dielectric loss parallel to the director $\varepsilon''_{\parallel}$ at $x_B=0{\cdot}76$ are presented in figure 5. The low frequency absorption can only arise from the reorientation of the longitudinal dipole of component **B**, because sample **A** has no longitudinal dipole moment due to its high symmetry. The observed absorption curves are of the Debye relaxation type, indicating only a single relaxation process [14].

In order to study the dipole–dipole interaction in the direction of the molecular long axes, dielectric measurements at low frequencies were performed. Figure 6 presents the static dielectric constants as a function of temperature for three selected concentrations ($x_B=1{\cdot}0$; 0·76; 0·55). Here $\varepsilon_{\parallel 0}$ and $\varepsilon_{\perp 0}$ are the static dielectric constants parallel and perpendicular to the director respectively. At lower temperatures, the static dielectric constant $\varepsilon_{\parallel 0}$ was calculated from the low frequency limit of the Cole–Cole semi-circle [14]. For the pure component **B**, the static dielectric constant parallel to the director ($\varepsilon_{\parallel 0}$) continuously increases with decreasing temperature, as proposed by the Maier–Meier model [15]. For a mixture $x_B=0{\cdot}76$, a stepwise decrease in $\varepsilon_{\parallel 0}$ is

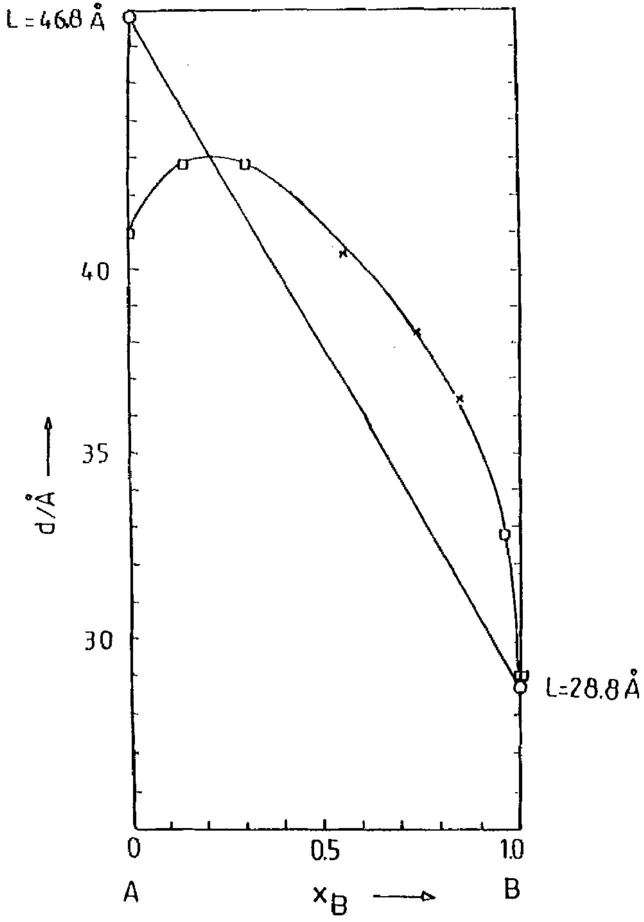


Figure 4. The dependence of the d-values upon the molar fraction. The crosses indicate the values in the smectic A phase and the squares correspond to the period of the density curve in the nematic phase. Open circles designate the molecular lengths of the single components.

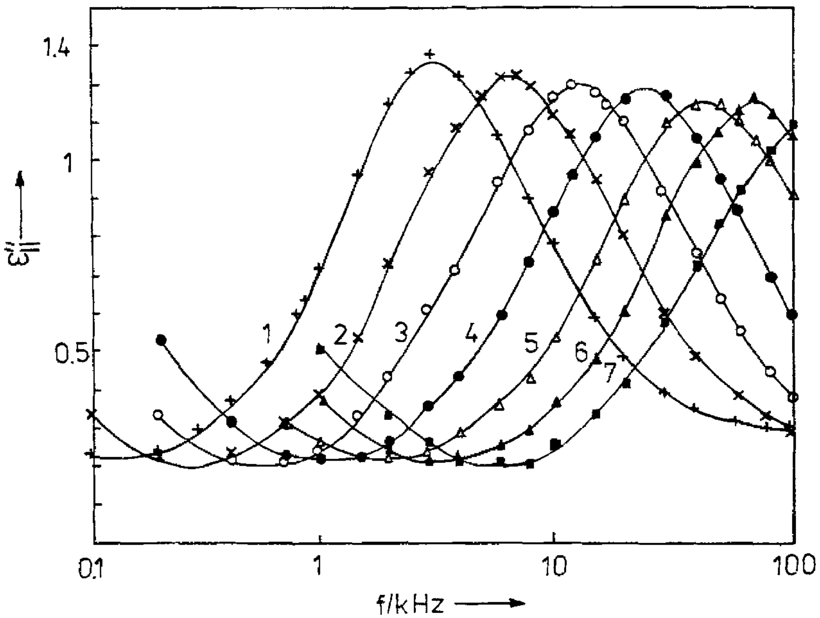


Figure 5. Dielectric absorption curves parallel to the director of the S_A phase when $x_B=0{\cdot}76$; (+) $T(1)=298{\cdot}5$ K, (×) $T(2)=305$ K, (○) $T(3)=310{\cdot}5$ K, (●) $T(4)=317{\cdot}2$ K, (△) $T(5)=323{\cdot}7$ K, (▲) $T(6)=330$ K, (■) $T(7)=336{\cdot}8$ K.

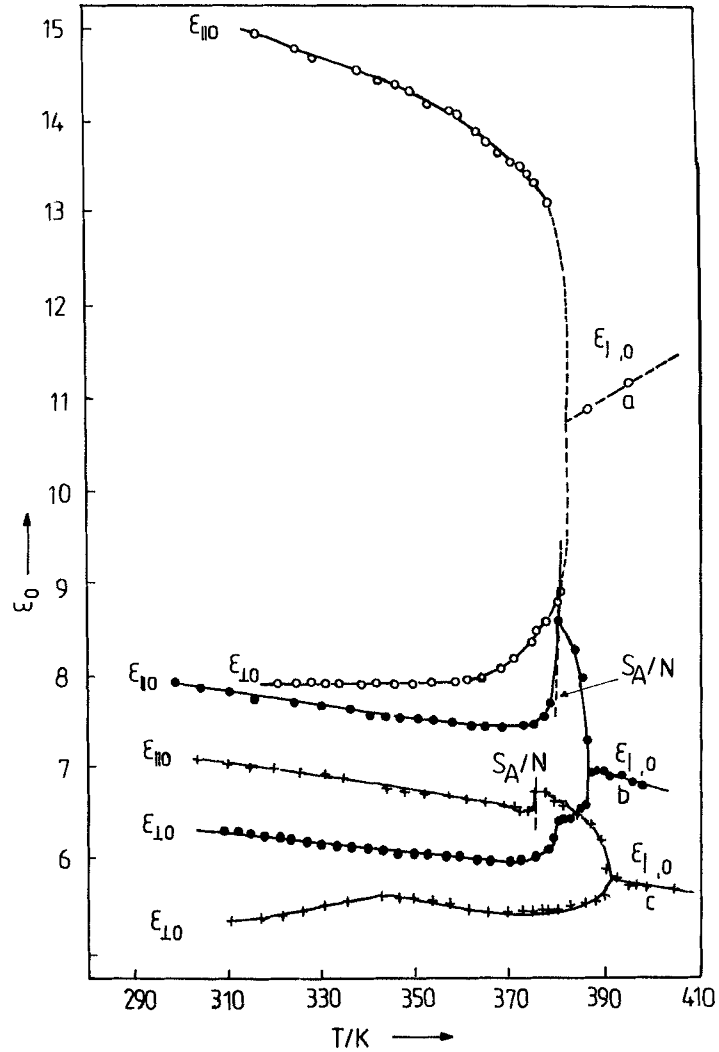


Figure 6. Dielectric constants as function of temperature. The experiments were performed using a magnetic field of 0·7 Tesla. The low frequency limit $\varepsilon_{\parallel 0}$ was calculated from Cole–Cole plots. (*a*) $x_B = 1{\cdot}0$, (*b*) $x_B = 0{\cdot}76$, (*c*) $x_B = 0{\cdot}55$. The phase transitions S_A/N for the last two concentrations are indicated by broken lines.

observed at the N/S_A transition. The decrease becomes weaker for the mixture $x_B = 0{\cdot}55$ and is no longer detectable for mixtures with further decreasing concentrations of **B**. The discontinuous change in $\varepsilon_{\parallel 0}$ is obviously the result of a stepwise increase of the antiparallel dipolar order in the direction of the molecular long axes connected with the formation of the layer structure at the phase transition $N \rightarrow S_A$.

Because the dielectric measurements could be carried out only up to 100 kHz, the study of the frequency dependence was only possible at lower temperatures. But in this case, comparison of the relaxation frequencies for different concentrations is difficult because, dependent upon the concentration, different liquid crystalline phases (N, S_A, S_C) exist. On the other hand, it is known from the literature [16] that there are only small steps in the relaxation frequency f_R at phase transitions, especially at the

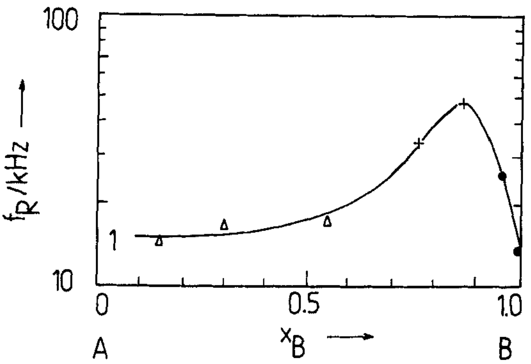


Figure 7. The relaxation frequency versus the concentration at $T = 317{\cdot}4$ K. At the given temperature the data were obtained for the (●) nematic, (+), S_A, and (△) S_C phases.

transition $N \rightarrow S_A$. For a qualitative interpretation, consideration of the concentration dependence of f_R at a constant temperature seems to be justified as a first approximation. Figure 7 shows the relaxation frequency as a function of concentration at 317·4 K.

It is obvious that, especially in the S_A region, f_R increases with increasing concentration of the bi-swallow-tailed compound **A**; this means that the dissolved molecules **A** give rise to an increase in the mobility of the molecules **B** by about a factor 5. It is improbable that this effect is due to a dramatic decrease in the order parameter, especially if one takes into consideration the curve of the $N \rightarrow I$ transition in this concentration range, as shown in figure 1. For this reason, the increasing mobility of the molecules **B** within the S_A mixed phase must be due to the special packing of the molecules in the short range order regions—as indicated also by the X-ray measurements. The pronounced maximum in the S_A–N transition curve, and also the high values of the transition enthalpies in the neighbourhood of the maximum are a strong indication of the stabilization of the S_A phase. In the S_A phase region, probably at relatively high concentrations of **B**, the molecules **B** involved within the gaps between the terminal branches of the swallow-tailed molecules possess a stronger tendency to antiparallel ordering of the terminal dipoles compared with that for the nematic phase of the pure compound **B**.

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