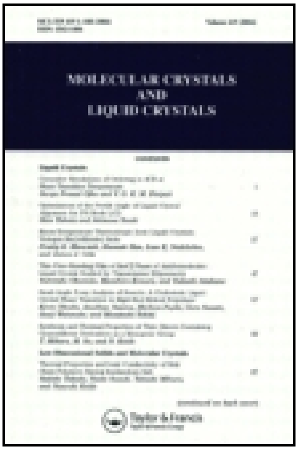

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Electrical Conductivity of Liquid Crystal Mixtures with Induced Smectic Phases†

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The electrical conductivity of the two liquid crystal mixtures *N*-(4-ethoxybenzylidene)-4′-amino benzonitrile (PEBAB)/4,4′-di-*n*-hexyloxy-azoxybenzene (HEXOAB) and 4-*n*-heptyloxy-4′-cyanobiphenyl ($\bar{7}$ CBP)/HEXOAB, which exhibit induced smectic A phases is investigated. In the smectic phases, the conductivity anisotropy of the PEBAB/HEXOAB mixtures is negative at the lowest PEBAB concentrations; this behaviour is usually expected for a smectic layer structure. With increasing PEBAB concentration the anisotropy increases and becomes positive. Possibly, this is an indication for a growing double layer structure, which was observed in polar smectic phases. In the nematic phases the conductivity anisotropy of the pure HEXOAB is considerably reduced by adding a relatively small amount of the polar component. An addition of 10 mole% $\bar{7}$ CBP reduces the anisotropy ratio of the electrical conductivity to $V = \kappa_{\parallel}/\kappa_{\perp} \approx 0.2$, which probably is the lowest value observed in a nematic phase so far. Besides the negative conductivity anisotropy, these mixtures also exhibit a positive anisotropy of the dielectric constant. They thus fulfil the conditions for inverse dynamic scattering.

Mixtures of nematic liquid crystals generally exhibit nematic phases whose thermal stability and other physical properties correspond to the average properties of the components. Recent measurements[1–4] have shown that mixtures of nematic liquid crystals with considerably different dielectric properties are an exception to this rule. They often produce smectic A phases which are stable over a wide range of temperatures and concentrations[2,4]. This tendency to form smectic phases is also expected to result in a change in the characteristics of the nematic phase.

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Measurements of the electrical conductivity in the homologous series of the 4,4′-di-*n*-alkoxy-azoxybenzenes[5,6] and the *N*-(4-*n*-alkoxybenzylidene)-4′-*n*-butylanilines[7] have shown that the increasing tendency to form smectic phases with increasing chain length results in a reduction of the conductivity anisotropy, $\Delta\kappa = \kappa_{\parallel} - \kappa_{\perp}$, which can even become negative throughout the entire nematic phase region. This behaviour can be explained by the formation of cybotactic groups with a smectic order.[8] Obviously the anisotropy of the electrical conductivity is very sensitive to the formation of such cybotactic groups. The results of investigations of the electrical conductivity of two liquid crystal mixtures, which exhibit induced smectic *A* phases are presented in the submitted paper.

The phase diagram (Figure 1) of the first mixture *N*-(4-ethoxybenzylidene)-4′-aminobenzonitrile(PEBAB)/4,4′-di-*n*-hexyloxy-azoxybenzene(HEXOAB) was obtained by differential scanning calorimetry (Perkin Elmer DSC Ib) and by measurements with a polarizing microscope. An induced smectic A phase appears whose maximum transition temperature to the nematic phase is displaced towards higher HEXOAB concentrations. The graph of

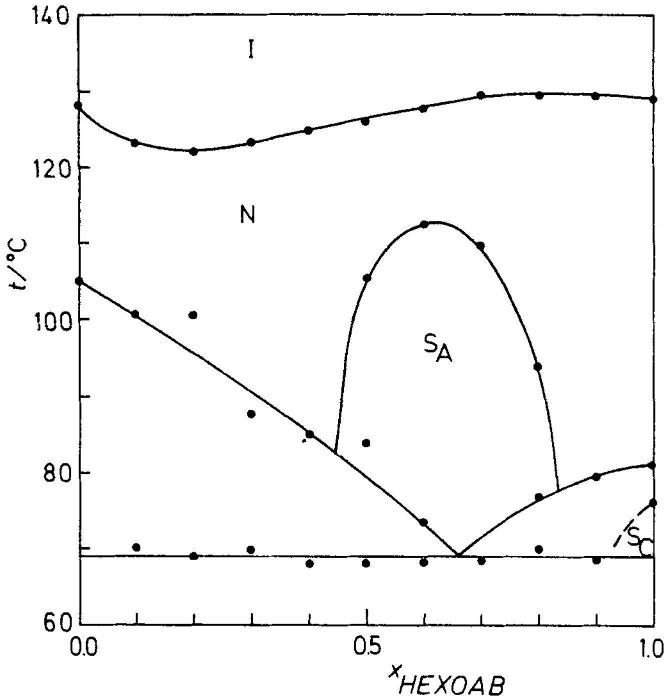

FIGURE 1 Phase diagram for the mixture *N*-(4-ethoxybenzylidene)-4′-aminobenzonitrile/4,4′-di-*n*-hexyloxy-azoxybenzene.

the clearing point temperature T_K of the nematic phase, which for these mixtures extends over the whole concentration range, also tends to peak at approximately the same concentration.

The electrical conductivity of the liquid crystal mixtures, to which 0.01 wt % tetrabutylammoniumpicrate had been added, was measured parallel ($\kappa_{\parallel}$) and perpendicular ($\kappa_{\perp}$) to the director in a conductivity cell with an electrode distance of 1 mm and an electrode area of 3 cm^2. The alignment of the liquid crystal was performed with a 12 kG magnetic field.[5,7] In Figure 2 the logarithm of the conductivity is plotted against the reciprocal of the temperature. In the isotropic phase the conductivity increases uniformly as the PEBAB concentration increases, which can probably be attributed to a reduced association in the more polar solutions.[9] In the nematic phase of PEBAB, the parallel conductivity is considerably larger than the perpendicular conductivity and their ratio, the anisotropy ratio $V = \kappa_{\parallel}/\kappa_{\perp}$, increases as the temperature decreases. This behaviour is to be expected from a nematic liquid crystal without cybotactic groups. It can be explained by an increase of the degree of order with decreasing temperature.[10] In the case of HEXOAB, however, the proximity of the monotropic smectic C phase results in the formation of cybotactic groups, which reduce the anisotropy ratio so much that it is considerably less than 1 at the melting point, i.e., the conductivity anisotropy, $\Delta\kappa$, becomes negative.

In the smectic phase the orientation of the liquid crystal cannot be altered by rotating the magnetic field. Therefore the alignment was performed in the nematic phase and the conductivity of the smectic phase was measured as a function of temperature keeping the orientation of the magnetic field constant.[5,7] The perpendicular conductivity curves, as shown in Figure 2, pass through the phase transition region without any significant change. However, both the value and the slope of the curves of the parallel conductivity change rapidly on passing through the phase transition. This results in an appreciable decrease of the conductivity value, which can be explained by the layer structure of the smectic phase.

The dependence of the anisotropy ratio on the composition of the mixture at various reduced temperatures T/T_K is shown in Figure 3. The anisotropy values were obtained by interpolation from the values for the corresponding neighbouring temperatures. For the highest reduced temperature, $T/T_K = 0.98$, the anisotropy curve is, as expected, almost linear throughout the entire range of concentrations. At lower temperatures, however, the effect of the induced smectic phase can be recognized by the pronounced minimum at the mole fraction $x_{\mathrm{HEXOAB}} = 0.7$. At lower temperatures one passes through the smectic phase at medium concentrations. The smallest anisotropy ratio is achieved in the smectic phase at the highest HEXOAB concentrations; but even there, with $V = 0.35$, it is considerably higher than the value for

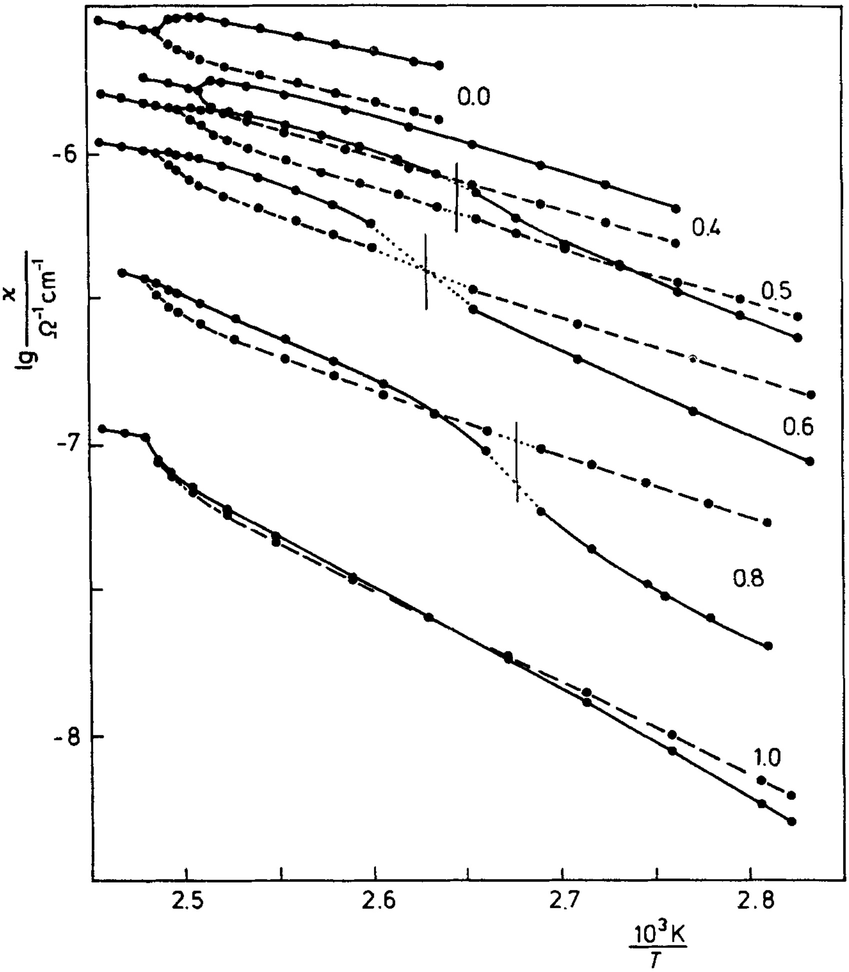

FIGURE 2 Logarithmic plot of the electrical conductivity parallel ($\kappa_{\parallel}$——) and perpendicular ($\kappa_{\perp}$----) to the director as a function of the reciprocal of the temperature for various PEBAB/HEXOAB mixtures. The mole fraction of HEXOAB is marked on the individual curves. The vertical lines indicate the temperatures of the phase transitions.

non-polar smectic liquid crystals, e.g. $V = 0.05$ for N-(4-n-hexyloxybenzylidene)-4′-n-butylaniline.[7] The anisotropy ratio increases with increasing PEBAB concentration. The 1 : 1 mixture has the relatively high value of $V = 1.25$ in the vicinity of the transition point to the nematic phase. This behaviour agrees with earlier measurements made on several single component polar smectic phases,[11] which, in contrast to non-polar compounds,[5,7,11,12] exhibit an anisotropy ratio greater than, or slightly less than

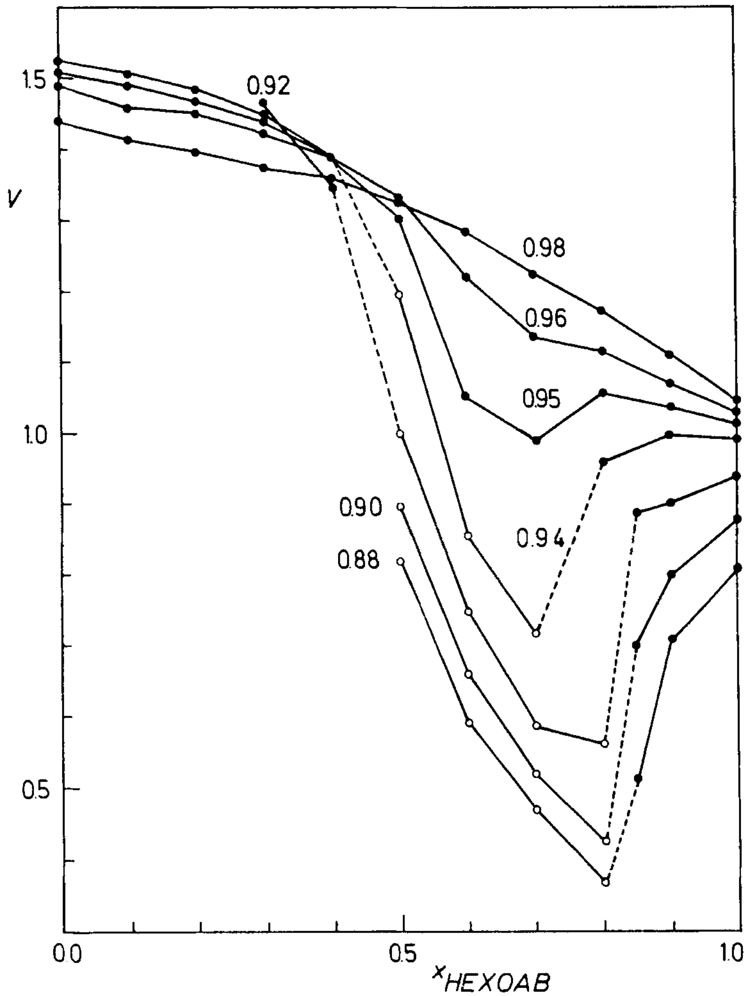

FIGURE 3 The anisotropy ratio $V = \kappa_{\parallel}/\kappa_{\perp}$ of the electrical conductivity as a function of the mole fraction of HEXOAB for PEBAB/HEXOAB mixtures in the nematic (●) and smectic (○) phase. The reduced temperature T/T_K is marked on the curves.

one. For example a value of $V = 1.18$ was found for 4-cyanobenzylidene-4′-*n*-octyloxyaniline,[13] whereas for 4,4′-di-*n*-octyloxy-azoxybenzene the value $V = 0.22$ was obtained.[5] So far no investigations have been reported concerning the impurity diffusion in polar smectic phases. If the relationship described above is also valid for the mobility of uncharged particles, this effect can possibly be attributed to the structure of the polar smectic phases, which are built up of double layers.[14]

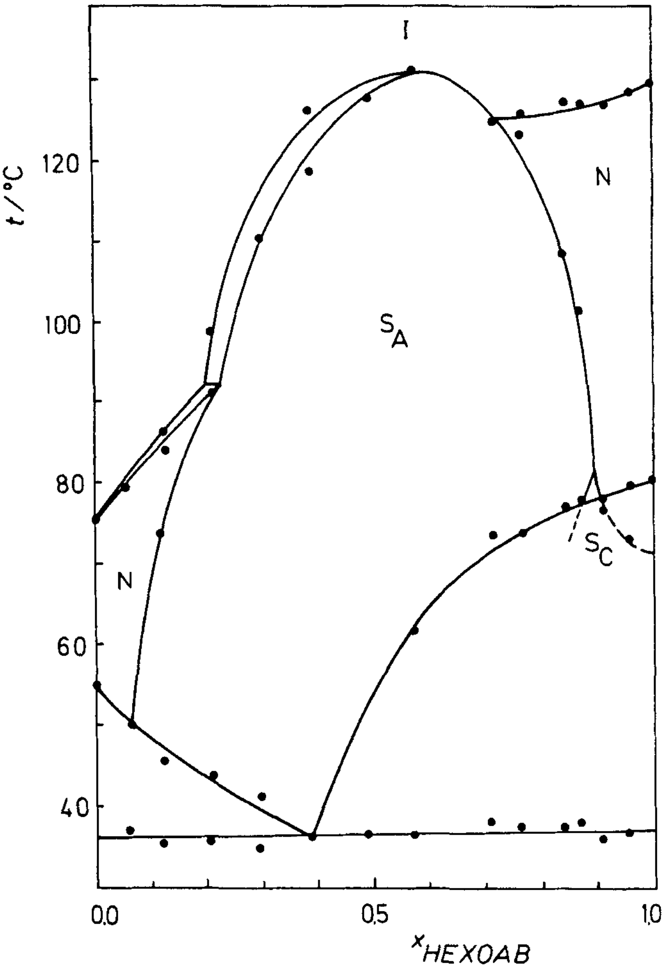

FIGURE 4 Phase diagram for the mixture 4-*n*-heptyloxy-4′-cyanobiphenyl/4,4′-di-*n*-hexyloxy-azoxybenzene.

The induction of the smectic phase results in a remarkable behaviour of the nematic phase conductivity anisotropy for the higher HEXOAB concentrations. Pure HEXOAB already exhibits a negative conductivity anisotropy $\Delta\kappa$ at low reduced temperatures. By adding a relatively small amount of PEBAB, which has a positive conductivity anisotropy, the anisotropy is further reduced, so that at concentrations in the vicinity of the smectic phase region, values of the anisotropy ratio of less than $V = 0.6$ are achieved.

4-*n*-Heptyloxy-4′-cyanobiphenyl ($\bar{7}$CBP)/HEXOAB was the second mix-

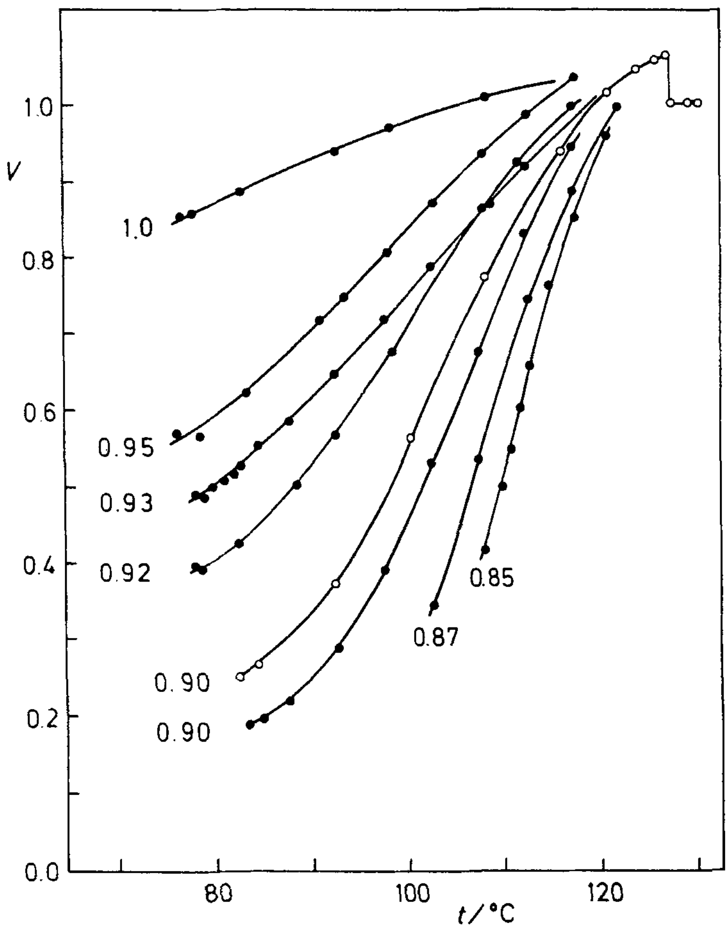

FIGURE 5 Anisotropy ratio $V = \kappa_{\parallel}/\kappa_{\perp}$ of the electrical conductivity as a function of temperature for several mixtures of $\bar{7}$ CBP and HEXOAB. The mole fraction of HEXOAB is given on the individual curves. The measured values, indicated by a circle (○), were determined in the way described above using a magnetic field. All other points (●) were obtained using an electric field for alignment,[15] whereby comparative measurements confirmed that both methods were substantially in agreement.

ture investigated. The induced smectic phase, existing over a range greater than 90 K, is so stable that a continuous nematic phase no longer exists (Figure 4). The monotropic smectic C phase of HEXOAB is stabilized by the addition of $\bar{7}$ CBP and, as shown by the contact method, is enantiotropic over a small range of concentration and temperature.

To investigate the electrical conductivity of these mixtures, dimethylditetradecylammonium tetraphenylborate was used as electrolyte with a concentration of 0.005% by weight, related to HEXOAB. The anisotropy ratio is found to be extremely dependent on the temperature as well as on the composition of the mixture (Figure 5). An addition of 10 mole% $\overline{7}$ CBP reduces the anisotropy ratio of the mixture at 80°C from $V = 0.85$ to $V = 0.23$, which probably is the lowest value observed in a nematic phase so far. With higher concentrations of $\overline{7}$ CBP the curves are even steeper. However the lowest anisotropy ratio does not become smaller since the formation of the smectic phase reduces the nematic phase region. The reduction of the anisotropy ratio compared with the first system PEBAB/HEXOAB may partly be caused by the absolute value of the conductivity, which is some 10 times lower because on the one hand the concentration of the electrolyte is lower and on the other the association is higher. As earlier measurements[5-7,16] concerning cybotactic nematic phases have shown, the anisotropy ratio increases considerably as the electrolyte concentration is increased. Contrary to the behaviour in normal nematic phases,[17] the type of the electrolyte appears to be of less importance. However, more detailed investigations have yet to be performed. Furthermore, the enthalpy of the transition from the nematic to the smectic phase should be smaller for the system $\overline{7}$ CBP/HEXOAB than for the system PEBAB/HEXOAB, due to the steeper phase boundaries. Consequently, the formation of cybotactic groups is favoured resulting in a lower anisotropy ratio.

In the nematic phase region, for polar component concentrations of a few mole per cent the mixtures investigated exhibit a negative conductivity anisotropy and a positive anisotropy of the dielectric constant. They thus fulfil the conditions for dynamical scattering corresponding to the Helfrich model,[18] provided the directions of the longitudinal and transverse axes are interchanged. The inverse dynamical scattering, which is to be expected was actually observed[19] for both of the mixtures investigated and will be described in a further paper.[20]

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15. The planar alignment is generated in a 125 μm sandwich cell by surface treatment, whereas the application of a high AC voltage (0, . . . , 100 V, 10 kHz) yields the homeotropic alignment ($\Delta\varepsilon > 0$). Thus both conductivity components ($\kappa_\perp$ and $\kappa_\parallel$) can be determined with a lock-in device (1 V, 135 Hz) similar to the one described elsewhere[5,7] (M. Bock and G. Heppke, to be published).
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