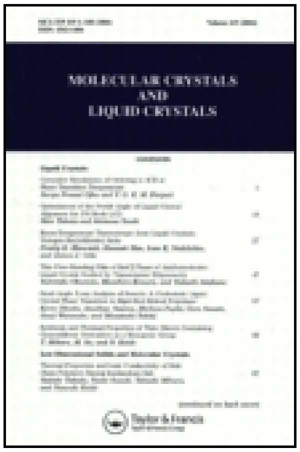

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Dielectric Dispersion in the Commensurate and Incommensurate Smectic Phases

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Dielectric Dispersion in the Commensurate and Incommensurate Smectic Phases

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The low frequency dielectric dispersion was measured and data compared in N, S_A, S_B and S_E phases of 7BEF5 and in the same induced phases of the 80CB/EBBA binary mixture. Critical frequencies, activation energies were determined. Dielectric dispersion method proved to be useful to modify the phase diagram obtained by contact method.

INTRODUCTION

Some smectic liquid crystals with a strong terminal dipole moment exhibit unusual properties such as commensurate bilayer structure—S_{A2}, incommensurate partially bilayer structure S_{Ad} and phase transitions of S_A–S_A type.[1] The static dielectric permittivity behaviour was expected to be different for a monolayered S_A phase† and the S_{A2} structure, the latter being the result of long-range antiferroelectric ordering,[2] but no significant difference could be observed. The static dielectric permittivity of S_A and S_{Ad} has also been compared.[3] The behaviour of the permittivity $\epsilon_{\parallel}(0)$ around the N–S_A and N–S_{Ad} phase transitions was analysed. The decrease of $\epsilon_{\parallel}(0)$ proved to be proportional to the T_{NA}/T_{NI} temperature ratio indicating that the effect was governed not only by the nearest neighbour dipole-dipole interaction

†S_A has a single-layer periodicity, $d/l \approx 1$ and used to be labelled as S_{A1} in works.[2,12,13]

as was suggested earlier,[4] but by macroscopic, thermodynamic effects as well.

The purpose of the present work was to extend the static permittivity investigation of a liquid crystal mixture exhibiting different smectic phases to the dynamic behaviour and to compare induced smectics with similar structures of one-component liquid crystalline systems.

EXPERIMENTAL

The mixture of 80CB and EBBA was chosen for the dielectric investigation. The system exhibits nematic, induced S_A, S_B, S_E and incommensurate S_{Ad} phases. The state diagram of the mixture shown in Figure 1 was taken from the work of Schneider and Sharma[5] the phase boundaries were controlled.

The low frequency dielectric dispersion of 80CB/EBBA was investigated versus temperature and concentration. For comparison data

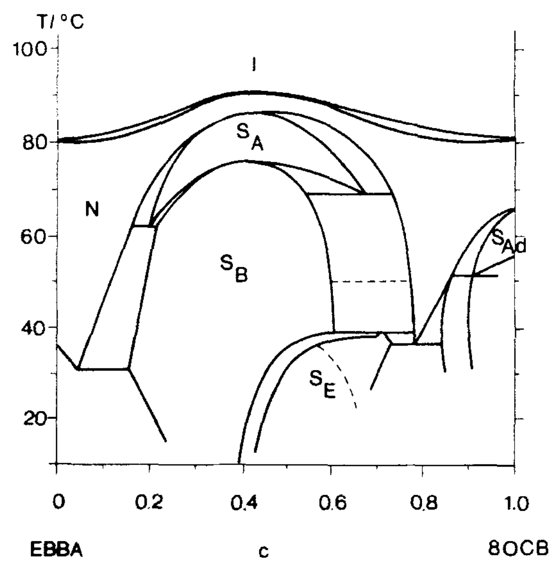
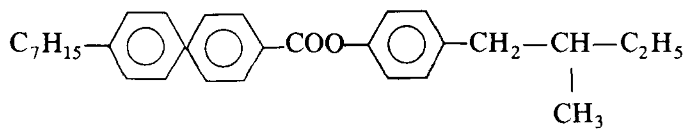


FIGURE 1 Phase diagram of 80CB/EBBA taken from.[5]—modification by present work.

of 7BEF5, that is,



are presented, the phase sequence of this compound is as follows:[10]

$$\mathrm{Cr{-}40\,{}^\circ C{-}S_E\dagger{-}57\,{}^\circ C{-}S_B{-}68\,{}^\circ C{-}S_A{-}138.5\,{}^\circ C{-}N{-}148\,{}^\circ C{-}I}$$

RESULTS AND DISCUSSION

In Figures 2, 3a and 3b Arrhenius plots are given of the low frequency parallel dispersion for 7BEF5 and for the 80CB/EBBA system. The relaxation is connected with a rotation around the molecular short axis and was extensively studied for other one-component liquid crystals.[6]

The most striking effect was found at order-disorder phase transitions occuring inside the smectic layers such as S_A–S_B or S_C–S_I transitions. The change of the critical frequency was more than one decade.[7,8] The motion is not frozen even in the S_E phase (see Figure 2), which represents a herring-bone structured two-dimensional crystal. In Figure 3a Arrhenius plots are given for the compounds 80CB ($c = 1$) and EBBA ($c = 0$), and for their mixtures in the concentration region $c = 0.9$ to 1.0 where the incommensurate partially bilayer S_{Ad} phase exists. For one-component systems a change was observed[6] in the slope of the Arrhenius plot at the N–S_A phase transition: the activation energy decreased towards the more ordered, "colder" phase. 7BEF5 and 80CB follow this rule, $\Delta H(\mathrm{N}) > \Delta H(\mathrm{S_A})$. Activation energy data are given in Table I.

The addition of a small amount of EBBA to 80CB (see $c = 0.96$ and 0.92 in Figure 3a) does not affect the Arrhenius plot in the nematic phase, but there is a definite increase of ΔH with increasing EBBA content in the S_A phase. This leads to $\Delta H(\mathrm{N}) < \Delta H(\mathrm{S_A})$ for the $c = 0.96$ and 0.92 mixtures; such a relation has not previously been observed for one-component systems.

In Figure 3b, results are shown for the $c = 0.65$ to 0.25 concentration region, where the induced S_A, S_B and S_E phases are present. The

†There is an indication based on X-ray diffraction measurements that below 55 °C 7BEF5 exhibits S_G phase.[11]

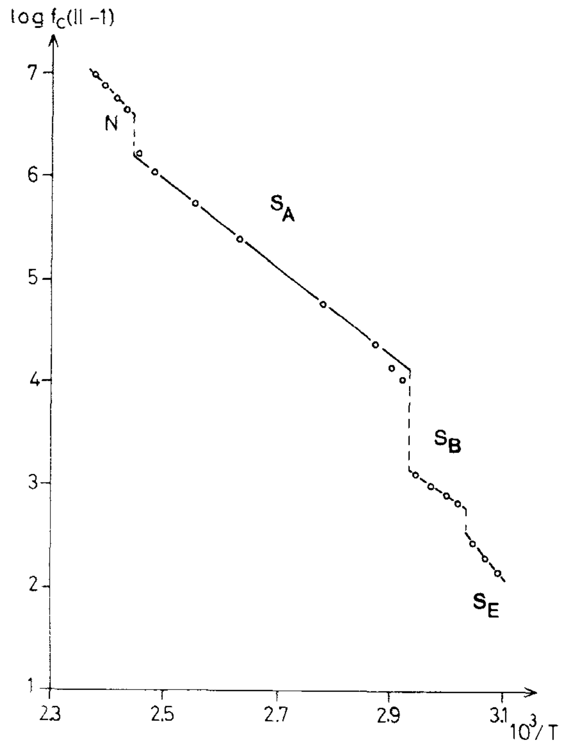


FIGURE 2 Arrhenius plot of the low frequency parallel dispersion of 7BEF5.

TABLE I

Activation parameters of 7BEF5 and 80CB/EBBA. ΔH is given in kJ/mole

Substance	C[a]	$\Delta H(\mathrm{N})$	$f_c^{\mathrm{N}}/f_c^{\mathrm{S_A}}$ at $T = T_{\mathrm{NA}}$	$\Delta H(\mathrm{S_A})$	$f_c^{\mathrm{S_A}}/f_c^{\mathrm{S_B}}$ at $T = T_{\mathrm{AB}}$	$\Delta H(\mathrm{S_B})$	$f_c^{\mathrm{S_B}}/f_c^{\mathrm{S_E}}$ at $T = T_{\mathrm{BE}}$	$\Delta H(\mathrm{S_E})$
80CB/EBBA	1	29		19				—
	0.96	29		49		—		—
	0.92	29		57		—		—
	0.65	26		40	9	81		—
	0.52	167	3	118	10	89	2	86
	0.40	190	1.7	129	11	96		—
	0.25	119	1.6	174	24	102		—
	0	53		—		—		—
7BEF5		127	2.5	94	9	108	1.5	142

[a] C is the mole fraction of 80CB

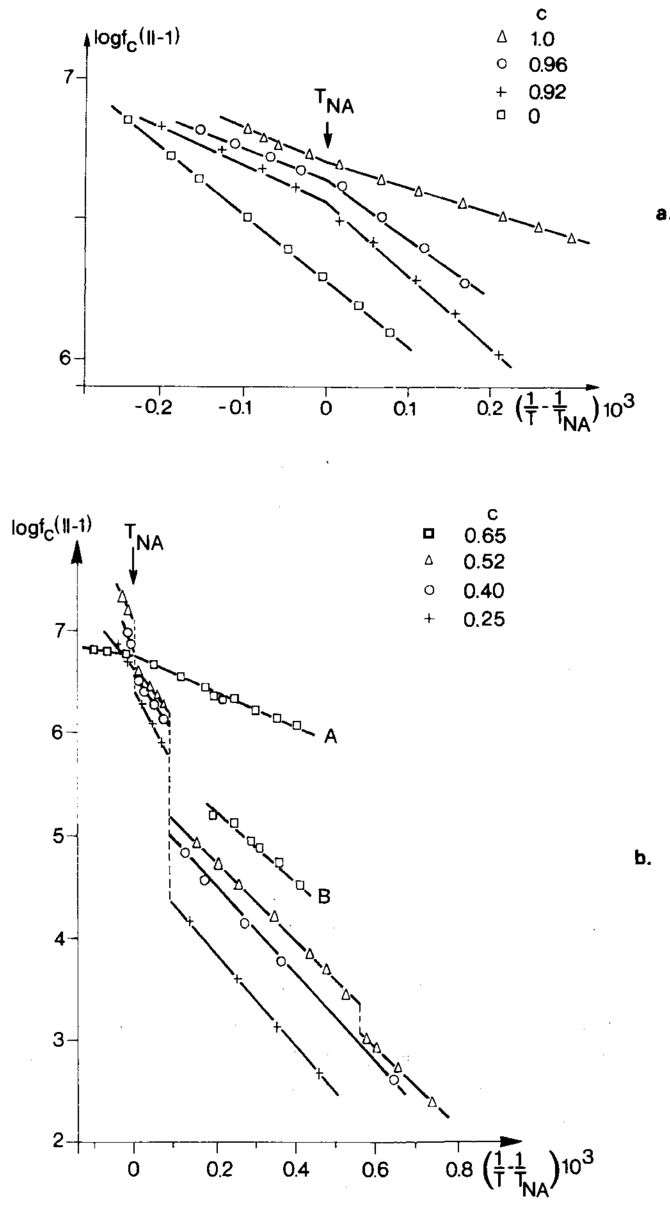


FIGURE 3 Arrhenius plot of the low frequency parallel dispersion of 8OCB/EBBA binary mixture. (a) c = 0; 0.92; 0.96; 1.0. (b) c = 0.25; 0.40; 0.52; 0.65.

main characteristics of the dielectric dispersion in the induced smectic phases are similar to those of the one component systems, see 7BEF5 in Figure 2. Activation energy data were found within the same limits and the behaviour of the critical frequency was similar around the phase transitions. This provides the possibility to identify smectic structures (induced or not), on the basis of the dielectric dispersion data.

Table I presents activation energy data for 7BEF5 and all phases of the 80CB/EBBA. In the N phase of the mixture there is an increase of ΔH with decreasing 80CB content; the value reaches its maximum at $c = 0.4$ the concentration at which the smectic induction is maximum, after which it decreases again. A similar effect was found by Yano *et al.*[9] in the N phase of a three-component mixture. The maximum of ΔH(N) versus concentration was observed at the eutectic points.

In the S_A and S_B phases of 80CB/EBBA we observed a monotonic increase of ΔH with decreasing concentration.

Somewhat unusual behaviour of 80CB/EBBA was found at $c = 0.65$. At this concentration the system exhibits mixed states in wide temperature regions, i.e. two different phases are present simultaneously in thermal equilibrium. In the Arrhenius plot (Figure 3b) a change was found of the slope at about 70 °C indicating a phase transition. Between 70 °C and 50 °C, N and S_A phases coexist, but we found only a single Debye relaxation process, demonstrated in Figure 4 at 50 °C by the frequency dependence of the dielectric loss. The relaxation parameters in N and S_A are close to each other (see Figure 3), which is why the $\epsilon''(\omega)$ curves of the two phases coincide.

Below 50 °C, double peaks were measured. This was interpreted as the result of the rotation around the molecules' short axis but in two different phases: N and S_B, consequently one can separate the $\epsilon''(\omega)$ plot into two Debye curves. This results in a splitting of the Arrhenius plot into two branches, labelled A and B in Figure 3b. The temperature dependence of the critical frequencies was different, the B branch had a higher activation energy. The $\epsilon''(\omega)$ intensity changed with temperature in opposite ways in the two branches. The high frequency peak decreased whereas the low frequency one increased on cooling—as shown in Figure 4. This corresponds to the temperature dependence of the proportion of the two coexisting phases in the mixture. The amount of the more ordered S_B increases by cooling, the N disappears.

These results can be used to identify liquid crystalline phases and to compare them with polarization microscope data. In our case we were able to modify the phase diagram obtained by contact method, see

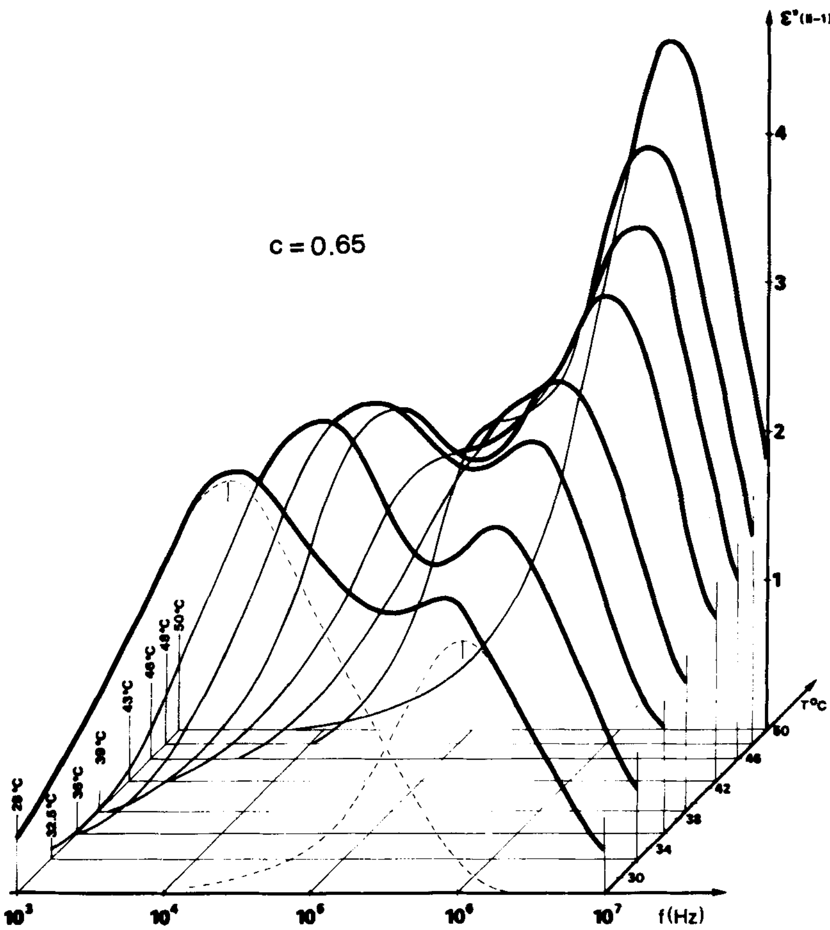


FIGURE 4 Dielectric loss versus frequency for different temperatures of 80CB/EBBA at $c = 0.65$.

dotted lines in Figure 1. At $c = 0.65$ we were not able to get a S_B–S_E phase transition down to 28 °C. This modification gives a phase boundary shape of S_E similar to that of the other induced phases, i.e. a nearly symmetric curve with a maximum versus concentration.

CONCLUSION

The low frequency dielectric dispersion data of induced smectic phases in 80CB/EBBA binary mixture proved to be similar to those of the same phases in 7BEF5 i.e. jumps of f_c were found at phase transitions.

Activation parameters and their behaviour around phase transitions were found similar in all phases of the one-component system and the respective induced phases.

At $c = 0.65$ of 80CB/EBBA, somewhat unusual behaviour was found, viz. the coexisting N and S_B phases could be separated by dielectric dispersion.

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