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Dielectric Permittivity at the Nematic-Smectic A Phase Transition

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The behaviour of the dielectric permittivity at the N – S_A phase transition has been studied. An empirical expression has been derived for a correction factor which accounts for the deviation of experimental data from the Maier-Meier equation. This expression enables orientational order parameters to be determined.

The model has been applied to two homologous series and to two binary mixtures with high positive dielectric anisotropy.

Keywords: dielectric permittivity, phase transition, Maier-Meier equation, dipole-dipole interaction

INTRODUCTION

The importance of the dipole-dipole interaction in dielectric permittivity and phase diagram measurements of liquid crystalline phases has been demonstrated.[1,2] The dipole correlation plays an important role in such phenomena as the occurrence of smectic phases, reentrancy and smectic induction.[3,4,5]

Considerable theoretical efforts have been made to calculate the dipole interaction energy.[6] The absence of any two-dimensional positional ordering in nematic and smectic A systems does not allow solid state physical methods (e.g. the Ising model calculation[7]) to be adopted. The liquid type approximation,[8] when only the nearest neighbour interaction is taken into account (by a correlation factor) has also proved to be unsuitable for the interpretation of the dielectric permittivity changes at T_{NA}. The long-range antiferroelectric dipole ordering must play an important role. The dielectric permittivity measurements[9] have also indicated that the dipole system behaves in a collective manner.

In this paper we shall discuss the effect of dipole-dipole interaction on the dielectric permittivity.

EXPERIMENTAL

For the interpretation of the static dielectric permittivity data of liquid crystals one usually starts with the well-known Maier-Meier (MM) equation[10] which was worked out for nematic systems:

$$\Delta\epsilon_{\parallel} = \epsilon_{\parallel} - \epsilon_{is} = 2\,\frac{\Delta\alpha NhF}{3}\,S - NhF^2\,\frac{S}{kT}\langle\mu^2\rangle = 2\,X\,S$$

$$\Delta\epsilon_{\perp} = \epsilon_{is} - \epsilon_{\perp} = \frac{\Delta\alpha NhF^2}{3}\,S - \frac{1}{2}\,NhF^2\,\frac{S}{kT}\langle\mu^2\rangle = X\,S$$

$$\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp} = 3\,X\,S \qquad (1)$$

where:

$$\epsilon_{is} = 1 + NhF\,\bar{\alpha} + F^2\,\frac{\mu^2}{3kT}\,Nh$$

$$\langle\mu^2\rangle = \frac{\mu^2}{3}\,(1 - 3\cos^2\beta)$$

$$X = \frac{1}{3}\,\Delta\alpha NhF - \frac{1}{2}\,NhF^2\,\frac{1}{kT}\langle\mu^2\rangle$$

From (1) it follows that both $\Delta\epsilon_{\parallel}$, $\Delta\epsilon_{\perp}$ as well as $\Delta\epsilon$ must be proportional to the order parameter S. This behaviour is qualitatively observed for systems which form nematic phases only. A typical example, a homologous series of nCB,[11] is shown in Figure 1.

For n = 5,6,7 (members of the series with only nematic phases) the formula (1) holds qualitatively and $\Delta\epsilon_{\parallel}$ and $\Delta\epsilon_{\perp}$ as well as $\Delta\epsilon$ follow a smooth, $S(T)$-like temperature dependence. Detailed analysis of the data for 5,6,7 CB-s shows that the ratios $\Delta\epsilon_{\parallel}/\Delta\epsilon = 2/3$ and $\Delta\epsilon_{\parallel}/\Delta\epsilon_{\perp} = 2$, expected from formula (1), differ slightly from the experimentally determined values.

For compounds with an S_A phase following the nematic at lower temperatures equation (1) implies proportionality of $\Delta\epsilon_{\parallel}$, $\Delta\epsilon_{\perp}$ and $\Delta\epsilon$ with S. By S we mean only the orientational part of the order pa-

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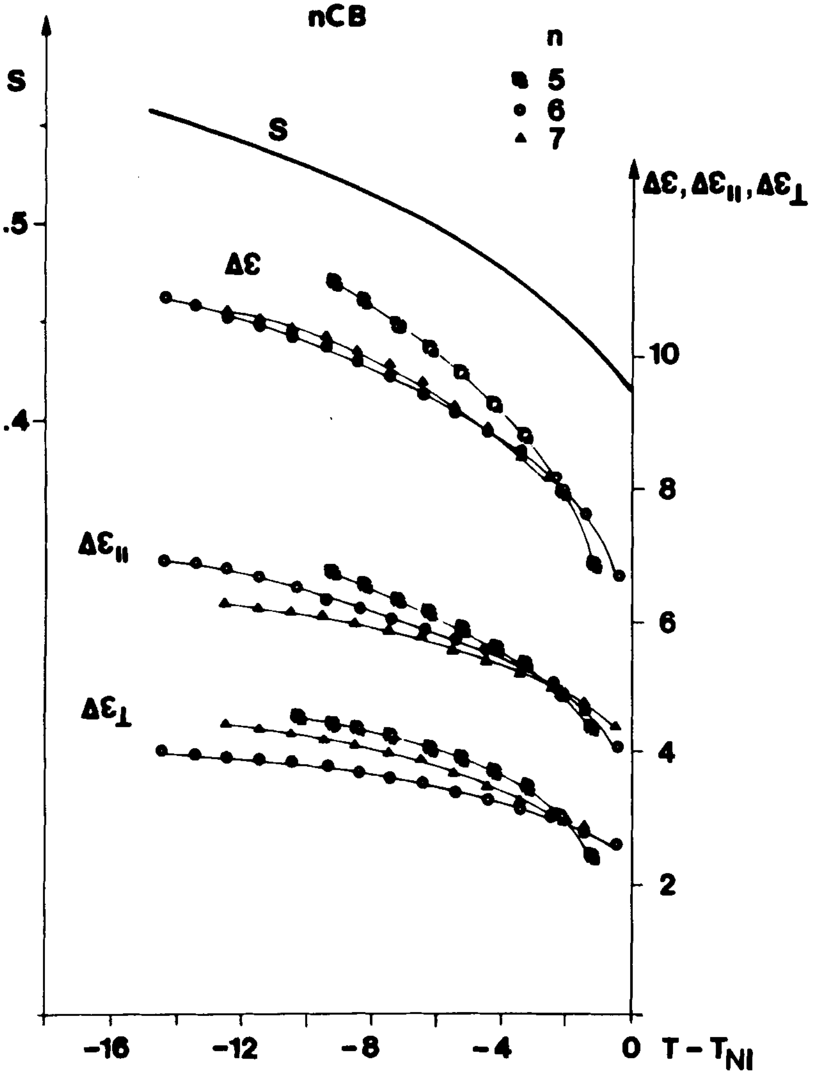

FIGURE 1 Temperature dependence of the dielectric permittivities for three nematics and that of the Meier-Saupe order parameter.

rameter, namely $S = \langle P_2(\cos\theta)\rangle$, even in the S_A phase. The orientational order will have a considerable effect on the dielectric permittivity by influencing the angle between the molecular dipole moments and the preferred direction. The presence of a density wave in the S_A, which causes a positional ordering, will have a weaker influence on the permittivity as far as it is affected by a transitional motion of

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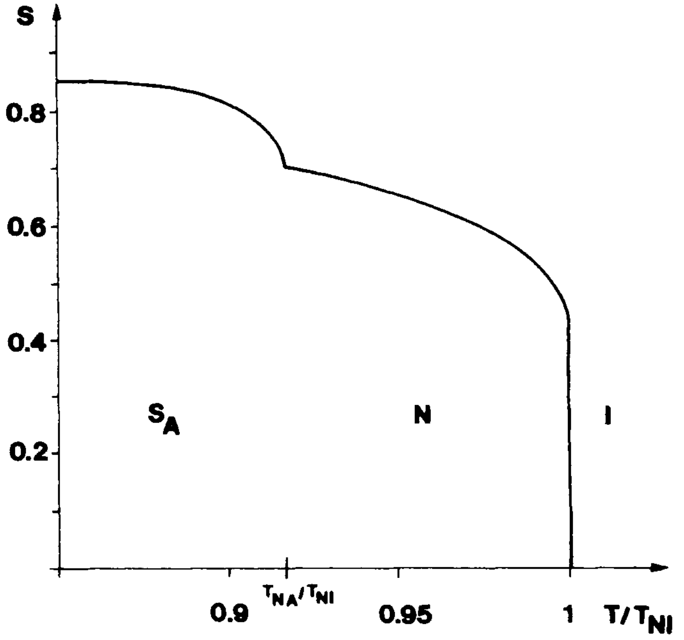

FIGURE 2 Orientational order parameter around a nematic-smectic A phase transition.

molecules parallel to the director. Theoretical predictions[12] of the temperature behaviour of the orientational order parameter have been verified experimentally.[13] S increases at T_{NA} with decreasing temperature. Figure 2 shows S versus T/T_{NI} taken from reference.[12]

On the basis of the above facts one would expect $\Delta\epsilon_{\parallel}$, $\Delta\epsilon_{\perp}$ and $\Delta\epsilon$ to behave similarly to $S(T)$ with temperature around the T_{NA}. However, in many cases one observes an opposite temperature dependence especially for $\Delta\epsilon_{\parallel}$ around T_{NA}.[3,11] The example of 8 and 9CB is shown in Figure 3. For comparison we show curves for the n = 6 member of the series which has only nematic phase.

The present work analyses the differences which occur in the dielectric permittivity when a smectic phase appears. The main features of these differences are:

1. $\Delta\epsilon_{\parallel}$ decreases with decreasing temperature at T_{NA}, *contrary* to the order parameter.
2. $\Delta\epsilon_{\parallel}$ values for 8 and 9CB are considerably lower than one would expect for the same compounds with nematic phase only. This dif-

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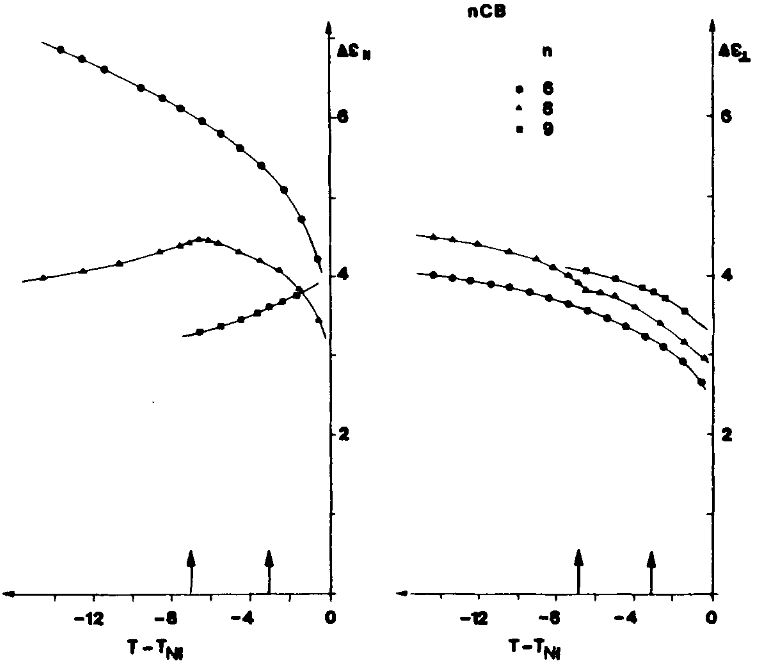

FIGURE 3 Dielectric permittivities around nematic-smectic A phase transitions. ↑ indicates T_{NA}.

ference is observed not only in the S_A phase but in the nematic phase also.

3. Although $\Delta\epsilon_\perp$ follows an *S*-like behaviour at T_{NA}, the increase of the $\Delta\epsilon_\perp$ values with increasing molecular weight contradicts the MM equation.

4. As a consequence of 2. and 3. the ratio $\Delta\epsilon_\parallel/\Delta\epsilon_\perp$ differs appreciably from the predicted value. It is much lower than 2, even in the nematic phase of 8 and 9CB, and it decreases further with decreasing temperature. Data are shown in Figure 4.

5. The deviation of the experimental data from the MM theory for substances with an S_A phase seems to be directly related to the width of the nematic range. The smaller $(T_{NI} - T_{NA})$, the greater is the deviation.

Similar conclusions could be drawn from the nOCB homologous series. Figure 5 shows $\Delta\epsilon_\parallel$ and $\Delta\epsilon_\perp$ for n = 6 with nematic phase only and n = 8 with $T_{NA} = T_{NI} - 12.5°C$.

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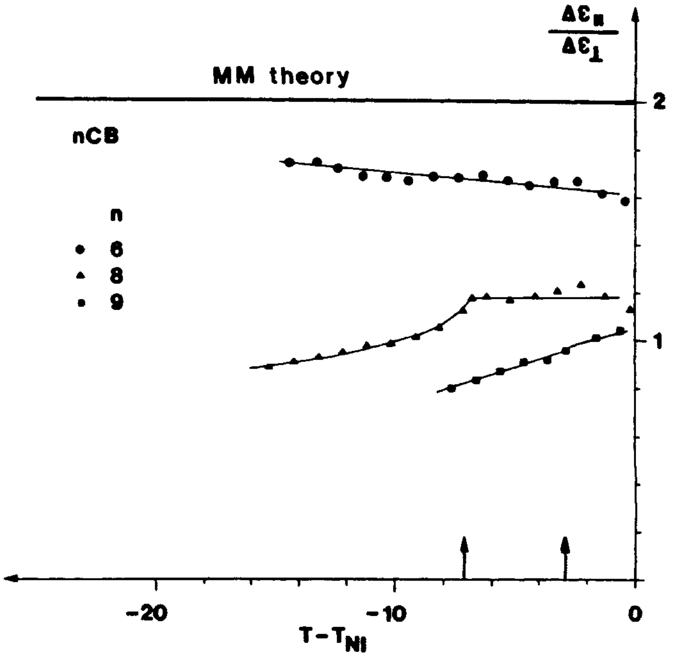

FIGURE 4 The ratio $\Delta\epsilon_\parallel/\Delta\epsilon_\perp$ versus temperature. ↑ indicates T_{NA}.

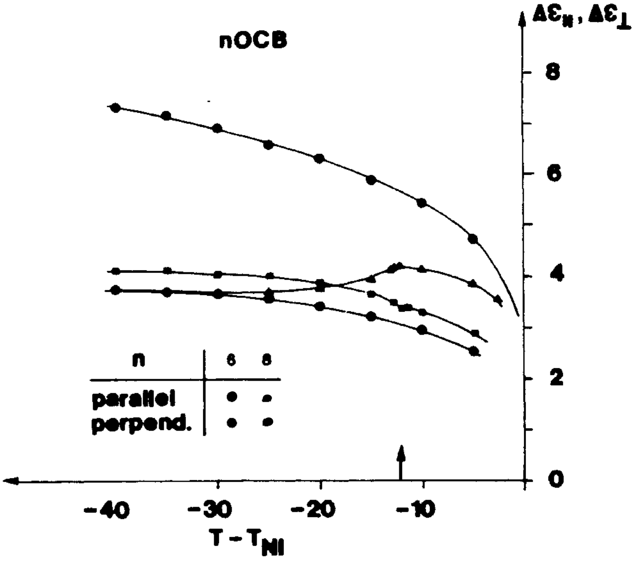

FIGURE 5 $\Delta\epsilon_\parallel$ and $\Delta\epsilon_\perp$ versus temperature for two members of the nOCB series. ↑ indicates T_{NA}.

THEORETICAL BACKGROUND

The refractive indicies show no anomaly similar to those for the permittivity at the N − S_A phase transition described above. Consequently, the deviations must be attributed to the dipole contribution of the permittivity. The term responsible for the dipole contribution in equations (1) is that containing $\langle\mu^2\rangle$. A more general form of that introduced by Bordewijk[14] is:

$$\left\langle\sum_i\sum_j \mu^i_\lambda\mu^j_\lambda\right\rangle \qquad \lambda = \parallel,\perp \tag{2}$$

where the summation extends over all n molecules. In the case where no dipole-dipole interaction is present the expression (2) reduces to $n\langle\mu^2_\lambda\rangle$. In our notation:

$$\langle\mu^2_\parallel\rangle = \frac{1}{3}\mu^2 - \langle\mu^2\rangle$$

$$\langle\mu^2_\perp\rangle = \frac{1}{3}\mu^2 + \frac{1}{2}\langle\mu^2\rangle \tag{3}$$

and one obtains the MM equation. In the case when one wishes to evaluate the effect of the dipole-dipole interaction, the averaging in (2) has to be carried out with a distribution function containing the dipole interaction energy term, V_{kl} in the total potential. After the procedure and approximations made by de Jeu, Goossens and Bordewijk[6] one obtains:

$$\left\langle\sum_i\sum_j \mu^i_\lambda\mu^j_\lambda\right\rangle_{\text{total}} = \left\langle\sum_i\sum_j \mu^i_\lambda\mu^j_\lambda(1 - f^\lambda(T))\right\rangle$$

$$f^\lambda(T) = \frac{1}{2kT}\sum_{k,l} V^\lambda_{kl}; \tag{4}$$

The averaging on the right hand side of equation (4) has to be performed with $\exp\{-W_i/kT\}$ only, $W_i(\theta)$, being the potential without the dipole interaction energy term. Many earlier theoretical efforts have been made to calculate $f^\lambda(T)$ (and the experimental results have not supported these calculations). This is the point where one has to take into account the collective behaviour of the dipole system and the liquid-like distribution of the centres of gravity.

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We try to solve this problem by interpreting the separated additional energy term, ΣV_{kl}^{λ} in a broader sense. Besides the short-range dipole-dipole interaction it includes long range interactions and could be approximated by an expression similar to the Maier-Saupe potential, i.e.:

$$\sum_{kl} V_{kl}^{\lambda} = c_{\lambda} S k \, \mathrm{T}_{\mathrm{NA}}$$

where $c_{\parallel} = 1$ and $c_{\perp} = -1$. It leads to

$$f^{\parallel}(T) = -f^{\perp}(T) = f(T) = \frac{S}{2} \frac{\mathrm{T}_{\mathrm{NA}}}{T} \tag{5}$$

The new feature of the correction factor $f(T)$ is that it does not depend on molecular parameters. The function $f(T)$ is determined by the macroscopic behaviour of the system as we expected on the basis of the experimental data.

Using (5),(4) and (3) we obtain the final expressions for the permittivities:

$$\Delta\epsilon_{\parallel} = 2\,X\,S\left(1 - \frac{S}{2}\frac{\mathrm{T}_{\mathrm{NA}}}{T}\right)$$

$$\Delta\epsilon_{\perp} = X\,S\left(1 + \frac{S}{2}\frac{\mathrm{T}_{\mathrm{NA}}}{T}\right)$$

$$\Delta\epsilon = X\,S\left(3 - \frac{S}{2}\frac{\mathrm{T}_{\mathrm{NA}}}{T}\right) \tag{6}$$

COMPARISON WITH EXPERIMENTAL DATA

One component systems

Correction factors $f(T)$ for the nCB series are shown in Figure 6. Data for 5,6,7CB-s, compounds with nematic phases only have a low, very slightly temperature dependent value. It does not contradict expression (5), though for these substances a real T_{NA} does not exist. The interactions between molecules with the short alkyl chains are too weak to give an $\mathrm{N} - \mathrm{S}_{\mathrm{A}}$ phase transition, but a latent $\mathrm{T}_{\mathrm{NA}}^{*}$ could

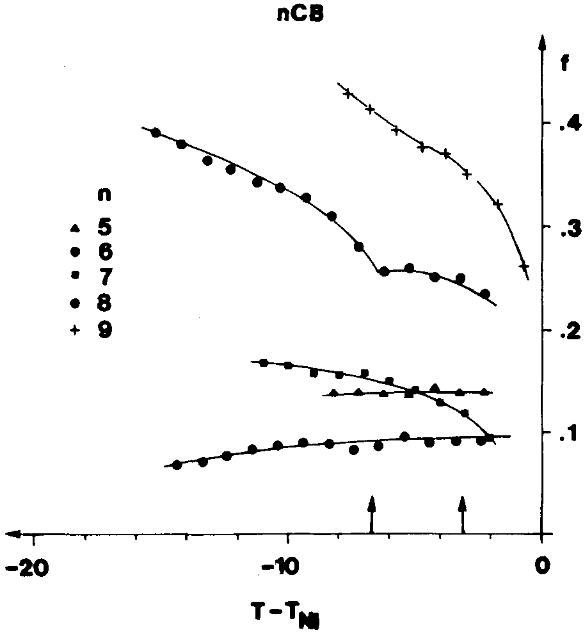

FIGURE 6 Correction factor versus temperature.

be given, which is lower than the crystallization temperature. A low T^*_{NA} results in a small $f(T)$.

For 8 and 9CB $f(T)$ is higher (even in the nematic phase) and there is a further definite increase in the S_A phase. The shorter the nematic range, the higher is the correction. In an ideal case, when the compound has an extended nematic phase and no smectic phase, the correction $f(T) = 0$ and the MM equations (1) hold.

We can use the correction factor $f(T)$, determined from the permittivity measurements, to obtain the orientational order parameter of the system in the case where T_{NA} is known. In Figure 7 we show $S(T)$ curves for 8 and 9CB. Both the actual values and the change with temperature are realistic.

Binary mixtures

The same treatment—suggested for one-component systems—has been used for the interpretation of the dielectric permittivity data of the two binary mixtures.

I.: EBBA/8OCB
II.: 8OCB/6OCB

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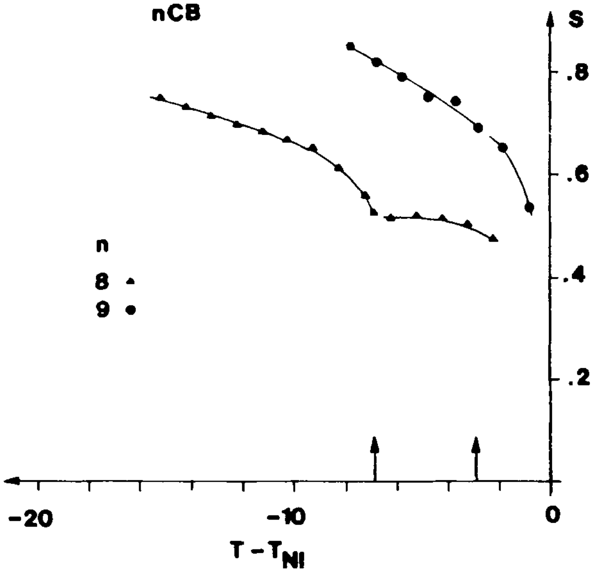

FIGURE 7 Order parameter versus temperature, calculated from (6) and (5).

These were chosen so that the dielectric correction factor introduced above could be compared. The considerable difference between the two systems I and II lies in the molecular dipole moments of the components. System I represents a strongly polar–weakly polar pair, whereas in II both components are strongly polar. Other parameters such as molecular weight, density and T_{NI} are similar in the two mixtures.

Detailed experimental results for I have been given elsewhere.[9] $\Delta\epsilon_{\parallel}$ and $\Delta\epsilon_{\perp}$ versus temperature for different concentrations for both systems are given in Figures 8 and 9.

Formulae (5) and (6) have been applied to systems I and II. The correction terms $f(T)$ versus $T - T_{NI}$ are given in Figures 10 and 11.

The correction has similar values for the two systems, though the relations of the molecular dipole moments are different for them. There is a systematic dependence on the $T_{NI} - T_{NA}$ range, supporting the idea that the correction must be determined principally by the long-range properties of the system rather than the molecular parameters.

The strong influence of the width of the nematic range on the permittivity is most obvious in the case of system I. The additivity rule alone[15] could not explain a higher value of $\Delta\epsilon_{\parallel}$ for the 96,92 and

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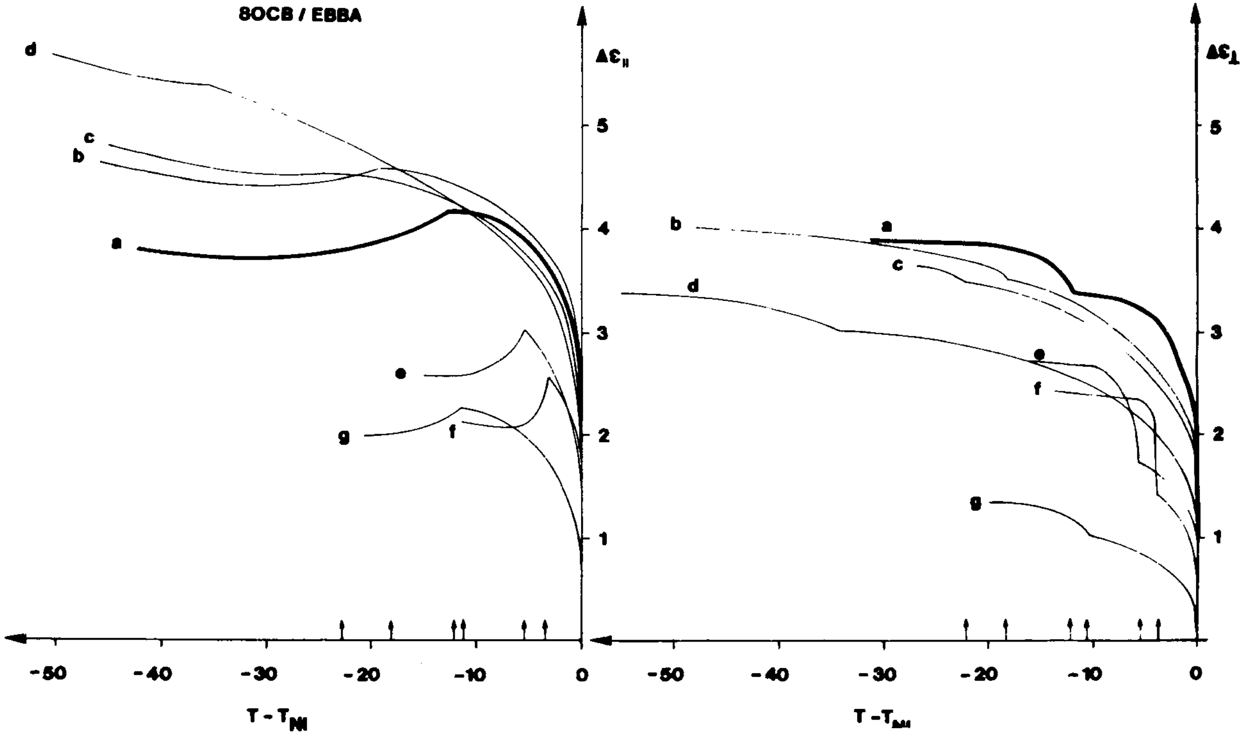

FIGURE 8 Temperature dependence of the dielectric permittivities of mixture I. Mole % of 8OCB is a: 100, b: 96, c: 92, d: 65, e: 52, f: 40, g: 25.

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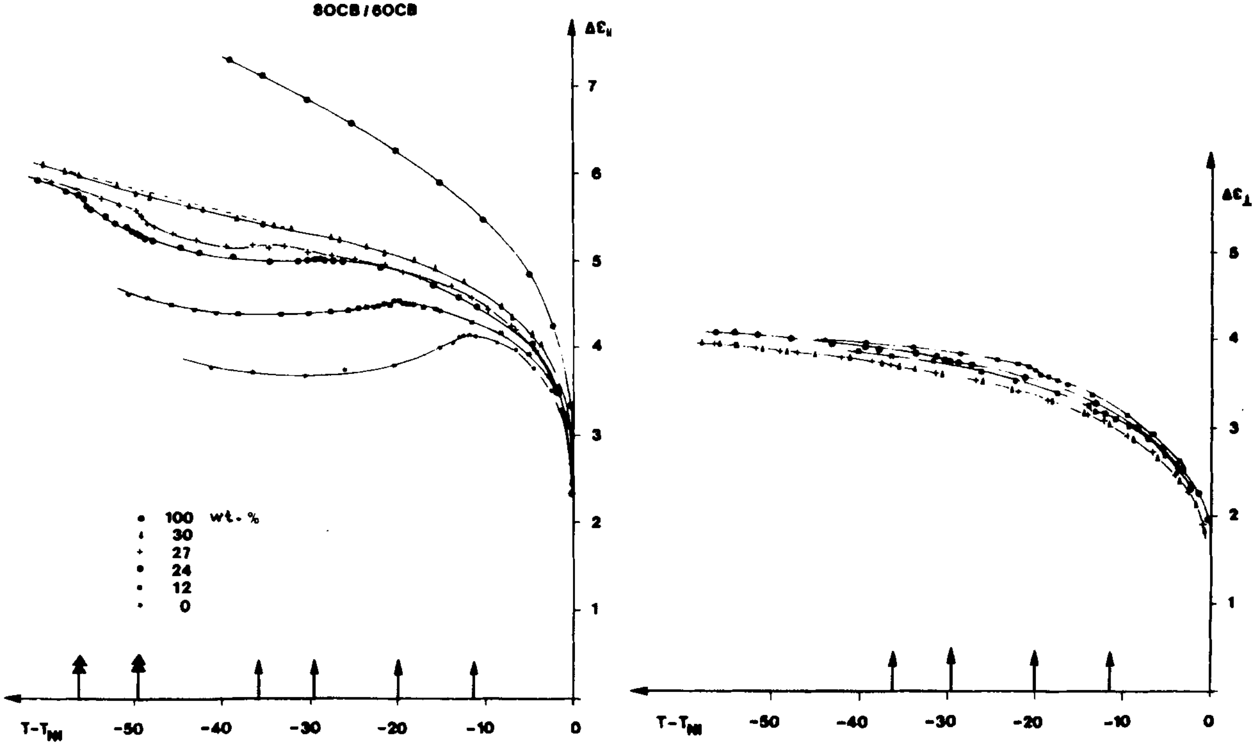

FIGURE 9 Temperature dependence of the dielectric permittivities of mixture II.

↑ indicates T_{NA}

↟ – ‖ – T_{ANre}

Weight % of 6OCB is indicated.

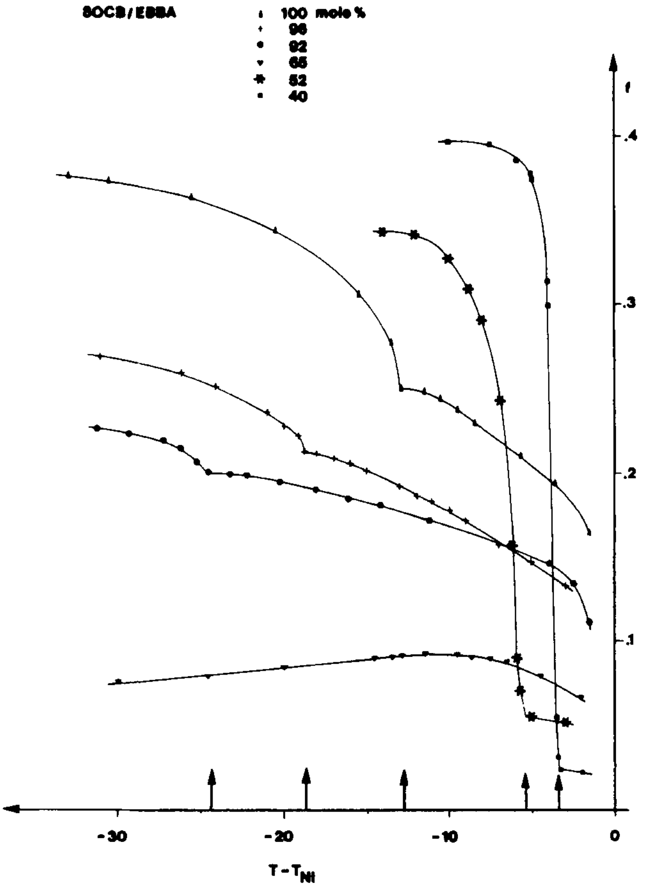

FIGURE 10 Correction factor vs. temperature for mixture I. Mole % of 8OCB is indicated.

even the 65% mixtures (which consist of 4,8 and 35% of the weakly polar component respectively) than that of the 100% strongly polar 8OCB (see Figure 8).

Order parameters calculated from $f(T)$ using relation (5) are given in Figures 12 and 13.

The low values of S in the nematic phase of the 52 and 40% mixture of 8OCB/EBBA are probably related to the very narrow nematic range. The $\epsilon(T)$ curves are too steep near T_{NI} and the recording accuracy is low.

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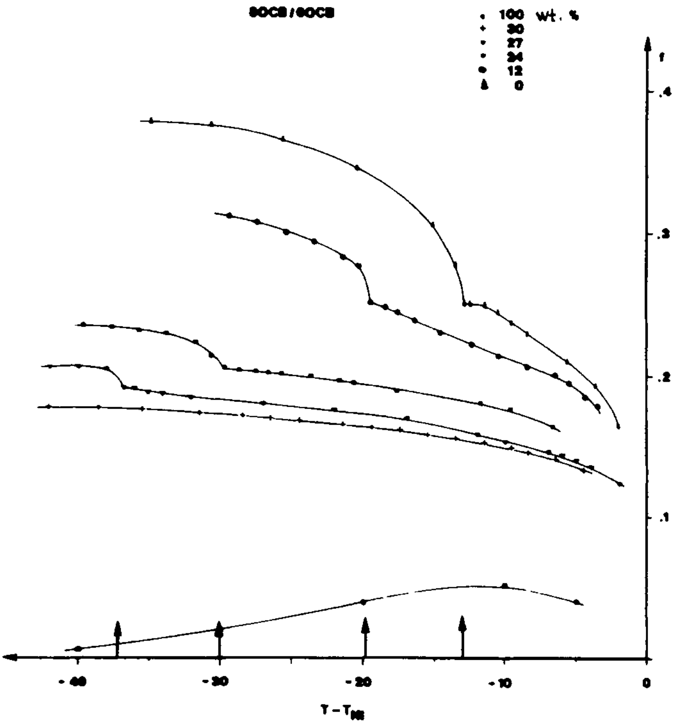

FIGURE 11 Correction factor vs. temperature for mixture II. Weight % of 6OCB is indicated.

WEAKLY POLAR SYSTEMS

The correction factor has been presented for two homologous series and two binary mixtures. All of the substances used except EBBA have a strong molecular dipole moment, more or less parallel to the long molecular axis. In all cases studied this gives a high permittivity value and a large anisotropy as well. These two facts made the application of the expressions (5) and (6) convenient to use by two reasons. First the temperature dependence of ϵ_{is} could be neglected and ϵ_{is} could be given a constant value which was measured at T_{NI}. Secondly, the polarisability anisotropy term containing $\Delta\alpha$ in equation (1) could be neglected with respect to the dipolar term.

The same approximations could not be used however for compounds with a low molecular dipole moment and low dielectric ani-

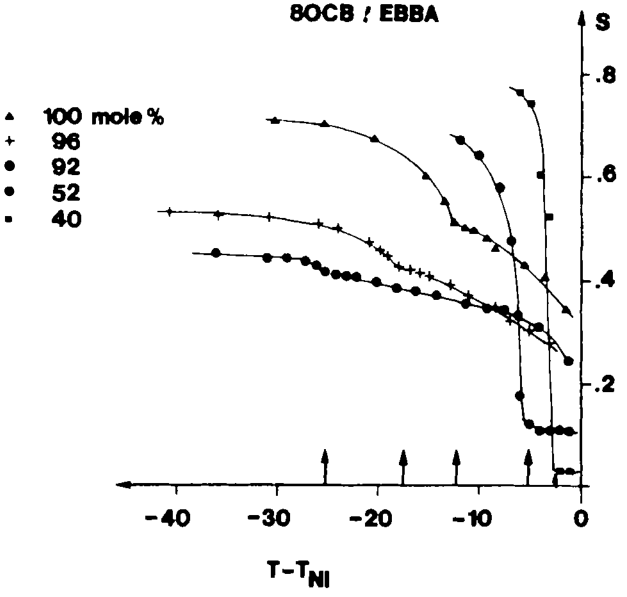

FIGURE 12 Order parameter *vs*. temperature of mixture I.

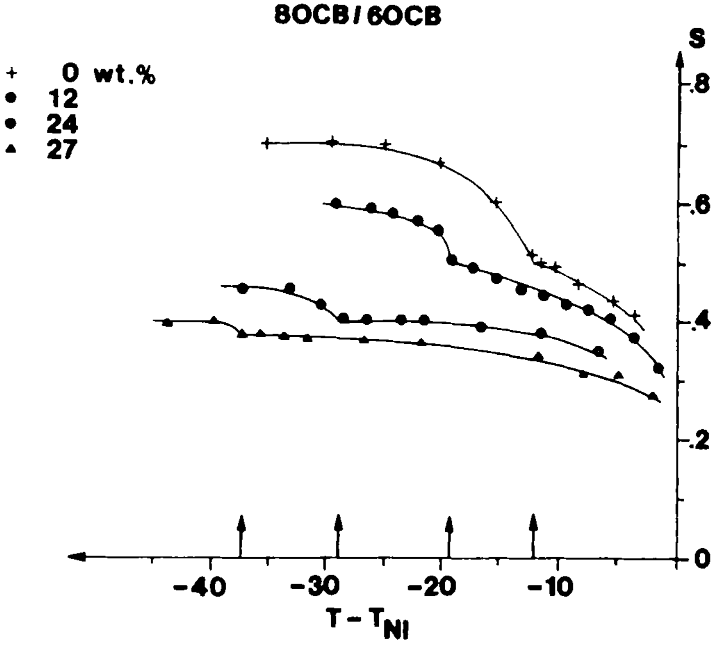

FIGURE 13 Order parameter *vs*. temperature of mixture II.

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sotropy. In these cases the polarisability anisotropy term is comparable with the dipolar one and can not be neglected. In the absence of careful measurement of the refractive indices it is impossible to check the calculations on substances with low dipole moments.

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