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# Dielectric Permittivity on Commensurate and Incommensurate Smectic Phases†

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Dielectric permittivity and calorimetric data are presented on mixtures at the nematic–smectic A phase transitions. The permittivity change was found to be linearly dependent on the McMillan temperature ratio $T_{NA}/T_{NI}$. The experimental data obtained on the induced $S_{A1}$ and the incommensurate $S_{A2}$ phases have shown a similar behaviour.

## INTRODUCTION

In recent years considerable attention has been paid to the study of binary mixtures forming bimolecular smectic A ($S_{A2}$) and monomolecular smectic A ($S_{A1}$) layers. At least one of the components of these mixtures was a cyano or nitro derivative. The layer spacing (d) and the phase transitions were studied by Hardouin[1] and Leadbetter[2] and anomalous behaviour of the $d/l$ ratio (where $l$ is the molecular length) and reentrant phases was found. The experimental results were analysed by Prost[3] on the basis of the free energy method.

The origin of the bimolecular layer formation was assigned to the interaction of the strong terminal dipoles. But in the induced $S_A$ phase a monomolecular layer was always found. In the induced phases the specific intermolecular interaction energy determined from the nonlinearity of the nematic–isotropic phase boundary yielded $E_{AB}$ = 1.5–2.5 kJ mole$^{-1}$.[4] The role of the charge redistribution contribution to the

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$E_{AB}$ has been studied by Fourier Transformed Infrared Spectroscopy, but because we found no new or disappearing spectral band or strong shift any possible effect will be neglected here.

The dielectric permittivity study proved to be a sensitive method of investigating the dipole–dipole correlation in one component systems. In the static permittivity ($\epsilon_{\parallel}$) a sharp decrease was found at the nematic–smectic A phase transition in a few members of the *p,p'*-di-*n*-alkylazoxybenzenes.[5] This effect was interpreted by the antiparallel short range ordering of the terminal dipole moments. The dipole–dipole correlation was calculated by Bordewijk[5] and Benguigui.[6] The observed anomalous temperature dependence of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ measured around the nematic–smectic A phase transition was qualitatively interpreted as the result of the increased dipole–dipole interaction in the smectic A phase.

Recently a considerable amount of experimental data has become available on compounds with a smectic A phase whose magnitude and direction of the molecular dipole moments differed.[7] The conclusion can be drawn that in all cases $\epsilon_{\parallel}$ decreases at the nematic–smectic A transition indicating the increasing antiparallel dipole–dipole ordering in the layered structure. But $\epsilon_{\perp}$ does not behave uniformly at the nematic-smectic A of different compounds. By studying the temperature dependence of the static permittivity in binary mixtures it is possible to determine the role of the dipole–dipole interaction; the variation of the concentration leads to a continuous change of the neighbourhood of a dipole.

The purpose of the present work is to investigate the static permittivity of a liquid crystalline mixture versus concentration and to determine the dependence of the permittivity change at the nematic–smectic A phase transition on reduced temperature.

## EXPERIMENTAL

Mixtures of 8OCB and EBBA were investigated by means of dielectric permittivity and differential scanning calorimetry. The state diagram of the mixture is given in Figure 1 which was taken from the work of Schneider and Sharma.[8] The phase boundaries shown in the figure were confirmed.

One can see an incommensurate double layered smectic A phase in the 0.91–1.0 concentration region, denoted by $S_{A2}$. The layer thickness of 8OCB is $d \cong 1.4 \cdot l = 3.2$ nm.[2] The $S_{A1}$ region denotes a mono-

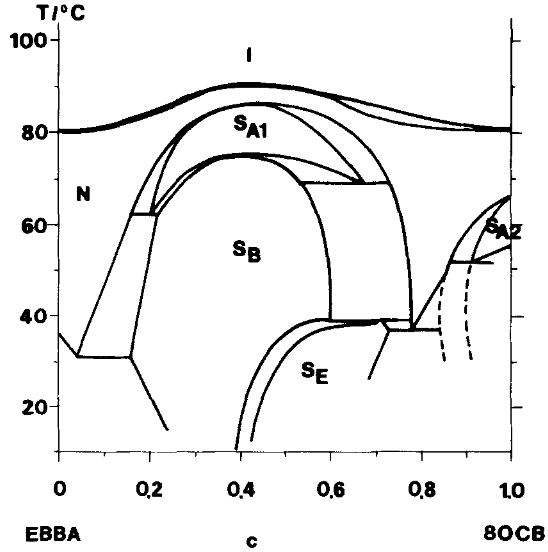


FIGURE 1 State diagram of EBBA/8OCB system.[8]

layered smectic A phase, between the 0.20 and 0.66 mole fraction of 8OCB. For the 50–50 mixture the layer thickness

$$d = \frac{l(\text{8OCB}) + l(\text{EBBA})}{2} = 2.25 \text{ nm}$$

was determined.[8]

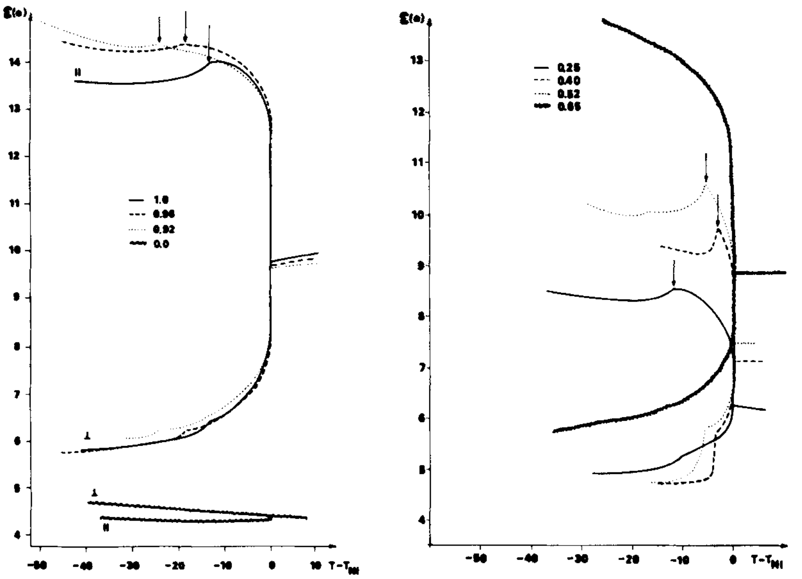
The dielectric permittivity study was made at 1.0; 0.96; 0.92; 0.65; 0.52; 0.40; 0.25 and 0, the calorimetric study at 1; 0.96; 0.92; 0.60; 0.52; 0.40; 0.33; 0.25 mole fraction of 8OCB.

## RESULTS AND DISCUSSION

In Figure 2a, b we show the static dielectric permittivity versus temperature for the above mentioned concentrations. In Figure 2a the two components are demonstrated separately: $c = 1.0$ and 0; and the curves for the $S_{A2}$ region of the mixture. We will mainly concentrate on the behaviour of $\epsilon_{\parallel}$ at the nematic–smectic A phase transition. 8OCB has a decrease of $\epsilon_{\parallel}$ at N–$S_{A2}$. The step decreases with increasing EBBA content, and diminishes when the $S_{A2}$ phase disappears. It is the only remarkable difference in the dielectric behaviour of the mixture in this concentration region. Figure 2b shows the lower concentrations of 8OCB, the region where the induced $S_{A1}$ phase is present. The step of $\epsilon_{\parallel}$ at N–$S_{A1}$ reappears and has a maximum value around $c = 0.40$, where the smectic A induction is maximal.

A feature deserving attention is the behaviour of $\epsilon_{\perp}$. We can conclude from Figure 2a, b that $\epsilon_{\perp}$ has a similar temperature dependence at nematic–smectic A to that of $\epsilon_{\parallel}$, contrary to the *p*,*p*′-di-*n*-alkylazoxybenzenes.[5] This results in a nearly constant $\epsilon_a$ below the nematic–smectic A transition for all concentrations studied, that is why we analyze quantitatively only $\epsilon_{\parallel}$.

The nematic–smectic A phase transition was investigated by differential scanning calorimetry as well. The thermograms indicate the N–$S_{A1}$ phase transition to be definitely of first order type whereas the N–$S_{A2}$ is only weakly first order one, as far as the ΔH values were found small but not negligible. Corresponding transition enthalpies versus concentration are given in Figure 3a. The shaded areas represent regions without the $S_A$ phase (or mixed phases). We suggest the quantity $\delta''_{NA}$ to characterize the change of $\epsilon_{\parallel}$ at the N–$S_A$ transition.



(a) (b)

FIGURE 2 Static dielectric permittivity vs. $T - T_{NI}$ of EBBA/8OCB mixture. Values represent the mole fraction of 8OCB, arrows indicate the N–$S_A$ phase transition.

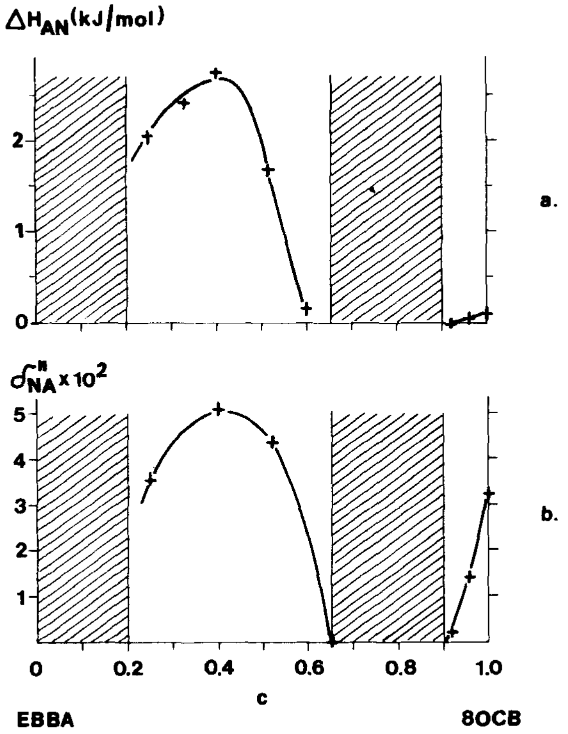


FIGURE 3 Transition enthalpy and permittivity change at the nematic–smectic A phase transition.

We introduce:

$$\delta''_{NA} = 1 - \frac{\min \epsilon_{\parallel}\,(\text{in } S_A)}{\epsilon_{\parallel}\,(T = T_{NA})}$$

In Figure 3b we demonstrate the value of $\delta''_{NA}$ versus concentration. Lines connecting the experimental points for both $\Delta H_{NA}$ and $\delta''_{NA}$ versus concentration follow the shape of the N–$S_A$ phase boundary (see Figure 1). This phase transition can be analysed by the McMillan-Lee theory[9] based on long-range dispersive interactions. On that basis these authors predicted a universal critical value of $T_{NA}/T_{NI}$, below which the N–$S_A$ transition becomes of second order type. This suggests the plot of $\delta''_{NA}$ versus $T_{NA}/T_{NI}$, represented in Figure 4. $\delta''_{NA}$ shows a linear dependence on $T_{NA}/T_{NI}$ reaching zero at $T_{NA}/T_{NI}$ = 0.93.

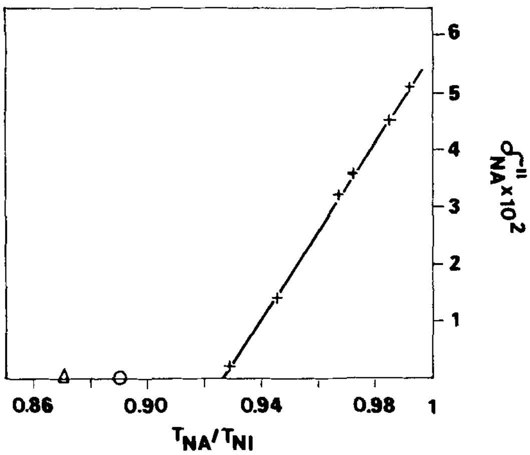


FIGURE 4 Permittivity change at nematic–smectic A phase transition vs. $T_{NA}/T_{NI}$. △—McMillan's theory;[9] ○—Lee's theory.[9]

We found here that $\delta''_{NA}$, which used to be interpreted as a measure of the short range dipole–dipole interaction, was governed by the nature of the phase transition: the more second order the transition, the less pronounced the change of the dipole contribution to $\epsilon_{\parallel}$ at the nematic–smectic A phase transition.

As is mentioned, $\delta''_{NA}$ is linearly dependent on $T_{NA}/T_{NI}$, but one can express it as a function of the length of the nematic range $\Delta T = T_{NI} - T_{NA}$ as well, that is,

$$\delta''_{NA}(\Delta T) = \delta''_{NA}(\mathrm{O})\left[1 - \frac{\Delta T}{\Delta T_c}\right]$$

where

$$\Delta T_c = \Delta T|_{T_{NA}/T_{NI}=0.93} = 0.07T_{NI}$$

We draw attention to the result that $\delta''_{NA}$ follows the same rule in both the mono- and the bilayer systems.

## CONCLUSION

The measurements presented here show that the permittivity change at the N–$S_A$ phase transition decreases linearly (within the limits of experimental errors) with $T_{NA}/T_{NI}$, the McMillan temperature ratio. It is especially interesting that the data measured at the induced $S_{A1}$ phase are on the same line as that of the incommensurate $S_{A2}$ phase. These results show that the permittivity change is governed not only by the nearest neighbour interactions but by macroscopic thermodynamic effects as well.

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