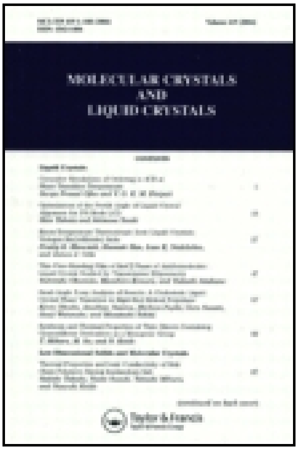

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Longin N. Lisetski [a], Oleg Ts. Sidletski [a], Nikolai V. Moshel [b], Vitali Ya. Malikov [a] & Pyotr E. Stadnik [a]

[a] Institute for Single Crystals, 60 Lenin Ave., 61001, Kharkov, Ukraine

[b] Chernihiv State Pedagogical University, 53 Sverdlova st., 14038, Chernihiv, Ukraine

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Dielectrometry Studies of Intermolecular Interactions in Cyanobiphenyl-Azomethine Mixtures Forming Induced Smectic-B Phase

LONGIN N. LISETSKI[a], OLEG TS. SIDLETSKI[a],
NIKOLAI V. MOSHEL[b], VITALI YA. MALIKOV[a] and
PYOTR E. STADNIK[a]

[a]*Institute for Single Crystals, 60 Lenin Ave., 61001 Kharkov, Ukraine and*
[b]*Chernihiv State Pedagogical University, 53 Sverdlova st., 14038 Chernihiv, Ukraine*

For liquid crystalline system MBBA/EBBA + eutectic mixture of alkyl- and alkoxycyanobiphenyls, dielectric permittivity ε was measured in isotropic, nematic and induced smectic-B phases as function of temperature and concentration. Strong positive deviations of ε from additivity were reported in the concentration range where the induced S_B phase was formed. These deviations persisted in the nematic and isotropic phases, suggesting a clear picture of intermolecular interactions in the system responsible for the smectic-B phase formation.

Keywords: dielectric permittivity; cyanobiphenyls; azomethines; induced smectic phase

INTRODUCTION

Dielectric permittivity in mixtures of nematic liquid crystals commonly used in electrooptics is generally believed to vary linearly (or almost linearly) with concentration. However, it has been long known that substantial deviations can occur if the compounds involved are of different chemical nature (e.g., mixtures of polar and non-polar substances [1, 2]). Studies of such deviations can be used as a 'liquid crystal' variant of dielectrometry (often used, as a standard method of physico-chemical analysis, for studies of intermolecular interactions in binary or quasibinary organic systems [3]). Examples of such an approach can be noted, e.g., for systems 4-alkyl-4'-cyanobiphenyl (nCB) + 4,4'-dialkylazoxybenzene [4] or mixtures of nematics and cholesterol esters [5]. Since specific intermolecular interactions leading to non-trivial concentration behavior of ε are generally known to worsen characteristics of electrooptical mixtures, the use of such systems was usually avoided by most workers in this field. This situation is a probable reason why papers on dielectrometric studies of liquid crystalline mixtures has not been numerous [6,7]. However, some of the most recent papers [8, 9] show a renewed interest in this subject.

In the 50:50 mol.% mixture of *p*-pentylphenyl-2-chloro-4-(*p*-pentylbenzoyloxy) benzoate (PCPB) and *p*-octylphenyl-2-chloro-4-(*p*-heptylbenzoyloxy) benzoate (OCHB) [8], anisotropy of dielectric permittivity in the nematic phase close to T_i was shown to be substantially lower than for each of the components involved, suggesting much smaller degree of antiparallel ordering in the mixture.

In mixtures of 5CB and 4-pentyl-4'-hexyloxybenzoate forming an induced smectic-A phase [9], substantial negative deviations from additivity were observed in the nematic phase for the concentration region where the induced phase was formed. In the isotropic phase of this system, the measured permittivity values were also noticeably lower than could be expected from the additivity rules.

In our paper we report dielectric permittivity studies for a relatively well known system comprising cyanobiphenyls and azomethines (Schiff bases). Since the pioneering work of Bak, Park and Labes [10], who observed formation of an induced translationally ordered phase for 5CB + MBBA , mixtures containing various homologues of these substances have been extensively studied, with the induced phase identified as smectic-B (accompanied by smectic-E) [11, 12], and a number of peculiar features upon introduction of chiral dopants reported [13, 14].

EXPERIMENTAL

Our aim was to detect dielectrometric evidence of specific effects in azomethine-cyanobiphenyl systems determined by interactions between central cores of these molecules. We used two eutectic mixtures as components of our binary system:

1) MBBA/EBBA (N-37), M_{ave}=274; 2) Standard eutectic mixture of alkyl- and alkoxycyanobiphenyls (CBM, ZhK-807), M_{ave}=258. As M_{ave}

values for N-37 and CBM were sufficiently close, difference between molar and molecular mass additivity could be neglected.

We used a three-electrode measurement cell of planar geometry, as previously described [15, 16]. The layer thickness (50 μm) was set by a Teflon-4 film. The cell temperature was controlled within ±0,2 ^{0}C. The sample was filled into a cell by capillary action (to avoid air bubbles formation) at temperatures exceeding the nematic-isotropic phase transition point by 15-20^0. The cell capacitance was measured at 1 KHz using an E8-4 capacitance meter at different temperatures on cooling; dielectric permittivity was determined as the ratio between capacitance values for the filled and emply cell.

RESULTS AND DISCUSSION

Phase diagram of system MBBA/EBBA + CBM obtained from DSC data (Mettler TA 3000) is shown in Fig. 1. Assignment of the mesophase types was made according to literature data on cyanobiphenyl-azomethine systems [12, 14] and checked by polarization micros-

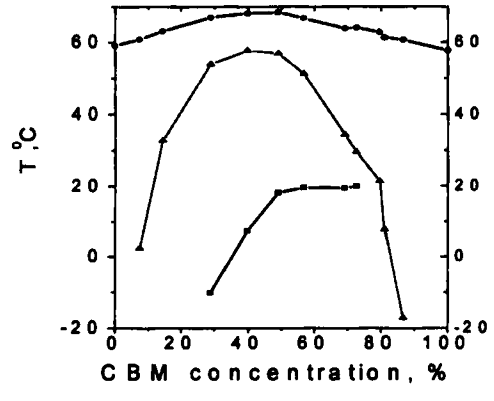

FIGURE 1 Phase diagram of the system MBBA/EBBA + CBM.

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The measured dielectric permittivity values are presented in Fig. 2 for different temperatures and concentrations.

Dielectric permittivity of CBM shows rather strong increase with temperature, which is related to weakening of dipole-dipole correlations of polar molecules. For much less polar azomethines, temperature variation of ε is substantially weaker. For the studied set of mixtures, $\frac{1}{\varepsilon}\frac{d\varepsilon}{dT}$ is rising rather smoothly with increased CBM concentration, with small steps or inflections on ε(T) plots corresponding to the phase transition points in agreement with DSC data.

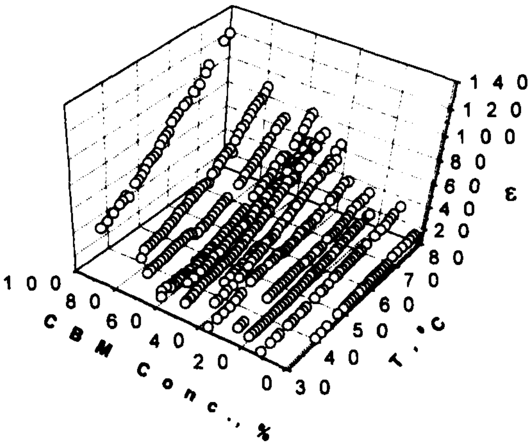

FIGURE 2 Dependence of dielectric permittivity vs. temperature and concentration of CBM.

The results obtained can be presented more clearly if, instead of isotherms conventionally used in physico-chemical analysis, we consider ε vs. concentration plots for equal reduced temperatures $\theta = \frac{T}{T_{S-N}}$ and $\tau = \frac{T}{T_{N-I}}$, where T_{S-N} and T_{N-I} are nematic-isotropic

(N→I) and induced smectic-nematic (S_B→N) phase transition temperatures (Fig. 3).

In all four cases, substantial positive deviations of ε from additivity are observed in the concentration region where induced S_B phase is formed. The effect is generally stronger at lower temperatures; no essential difference, however, could be noted between the temperature regions just above and below the phase transition. This strongly implies that the observed behavior of ε is not a direct function of phase state, but is determined by the short-range order and pair interactions of molecules of different kind.

Of special importance is the fact that the effect in question has been clearly observed in the isotropic phase. In our opinion, this allows to justify an apparent over-simplification of our experimental procedure. In fact, a more rigorous study should involve separate measurement of $\varepsilon_\perp$ and $\varepsilon_\parallel$ in the mesophases with appropriate control of textures and surface conditions. By the way, this can possibly explain the observed sharp decrease of ε when we go from pure CBM to CBM+20% MBBA/EBBA – for CBM, the measured ε is close to the literature values of $\varepsilon_\parallel$; upon addition of MBBA/EBBA, homeotropic texture deteriorates, and contributions from $\varepsilon_\perp$ become significant.

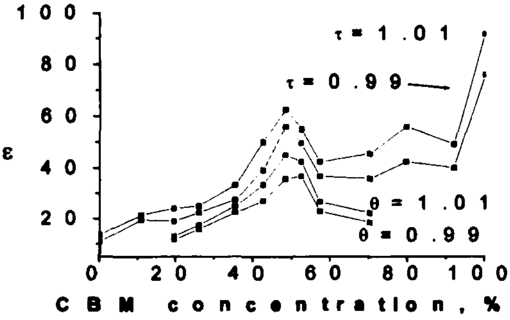

FIGURE 3 Dependence of dielectric permittivity on reduced temperature in MBBA/EBBA – CBM system

CONCLUSIONS

The following picture can be proposed to describe processes of induced phase formation in azomethine/cyanobiphenyl mixtures:

- Due to some specific interactions or just requirements of molecular packing (exact mechanism remains unknown), azomethine and cyanobiphenyl molecules show a tendency to form correlated 'pairs' (accompanied by dissociation of cyanobiphenyl 'dimers' as described in [17]). This leads to the observed increase in ε;
- Upon cooling, the short-range order induced by the correlated mixed 'pairs' is converted to the long range translational order of the S_B phase. From the methodological point of view, our dielectrometry procedures seem to be sensitive enough as a tool for studies of intermolecular interactions and mechanism of induced phase formation in liquid crystalline mixtures.

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