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Linear and Nonlinear Dielectric Properties of 4-Heptyl-4′-cyano-biphenyl Solutions in Benzene*

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Linear electric susceptibility and nonlinear dielectric effect (NDE) of the isotropic phase of the benzene solutions of 4-heptyl-4′-cyano-biphenyl (7CB4) are described in the whole concentration and temperature ranges. At the molar fraction above 0.85 strong, critical pre-transitional effects are observed, associated with the imminent nematic phase. The effects of the molecular reorientation and dipolar association, the latter manifesting itself by positive NDE and near the transition to the solid phase with a strong negative NDE, are taken into account. Otherwise, critical fluctuations occurring near the nematic phase transition lead to a strong, critical increase of the electric susceptibility change in electric field. The observed effects, with supplementary optical and microscopic studies, allow an accurate determination of the temperatures of phase transitions and setting up the phase diagram of these solutions.

Key words: molecular interactions, electric polarization, nonlinear polarization, nematic phase, phase diagram

Much attention has been paid to 4-heptyl-4′-cyano-biphenyls, the well known and important family of compounds which exhibit mesogenic properties. As a rule, in the literature on this subject, mainly the optical [1] and dielectric properties [2–7] have been described. Information on the optical polarizability, dipole moments and orientational ordering of molecules have been addressed in these studies. Nematic phase is known to occur in these compounds within a broad range of the alkyl chain lengths ($4 < n < 10$). In addition, with $n = 3$ and $n = 4$ a monotropic nematic phase has been observed; for $n > 7$ a smectic phase occurs.

We report the dielectric studies of *4-heptyl-4′-cyano-biphenyl* (7CB4) solutions in benzene in wide range of temperatures and for physically available concentrations. The aim is to obtain an information on the phase diagram and in a long outlook, to explore the mechanisms that lead to formation of mesophases. We focus on the application of *Nonlinear Dielectric Effects* (NDE), *i.e.* on the nonlinear dependence of electric polarization on the intensity of electric field E [8]. Orienting dipoles in the field E leads to a decrease of electric permittivity ε, thus, to a negative change of this

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*Dedicated to the memory of Professor Krzysztof Pigoń quantity ($\Delta\varepsilon < 0$). The effect is known as Langevin effect. Contrariwise, the increase of permittivity is observed in substances, where the *inter*- and *intramolecular* equilibria occur. Then, the electric field favours (energy-wise) the more polar components, increasing their population and consequently rising the electric permittivity ($\Delta\varepsilon > 0$). It is, the so called chemical effect. Magnitude of both, Langevin and chemical effects, is proportional to fourth power of the dipole moment [8], which explains the special role they play in the molecular phenomena. With a general theory of this phenomenon [9], one should be able to obtain an information about the dipole moments of unstable complexes and determine the energies of intermolecular interactions.

Much stronger increase of electric permittivity in electric field, known as *Pretransitional Dielectric Effect* (PNDE) is observed in systems exhibiting a partial miscibility at the point of *critical miscibility* [10–12]. Similar results are observed near the clearing point in nematics [13,14]. The interaction of electric field with the critical fluctuations is responsible for the effects in both cases [12,15].

Eearlier [16] we reported on studies of the diluted solutions of 4-heptyl-4′-cyano-biphenyl in benzene of the molar fraction $f < 0.4$. Simultaneous analysis of linear and nonlinear polarization has led to the determination of the energy of intermolecular interactions, the average association degree of cyclization and relative orientation of the polar cyanide groups in the unstable molecular complexes. The dipole moment $\mu_{exp} = 4.5$ D of the molecule agrees well with $\mu_{cal} = 4.56$ D, calculated by the semi-empirical PM3 method from the MOPAC 6 package. The energy minimum was achieved with dihedral angle $\phi = 0$ and the angle between the dipole moment and the axis of the least moment of inertia $\varphi = 12°$ (Fig. 1). Most significant result of the studies of the moderately diluted solutions was the conclusion that the antiparallel dimers are only a first step process of more complicated associations [16].

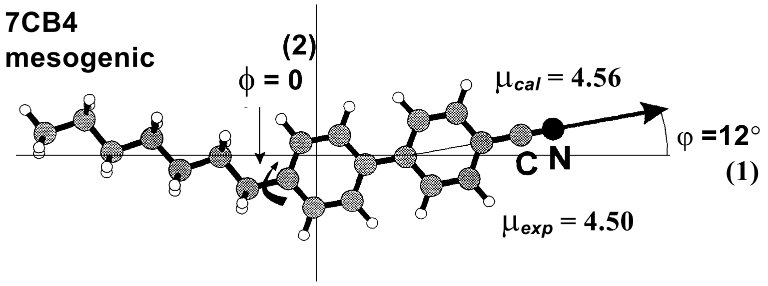

Figure 1. Molecule of 4-heptyl-4′-cyano-biphenyl. The dipole moment μ_{cal}, dihedral angle ϕ and orientation related to the principal axes of the moment of inertia calculated with the semi-empirical method PM3 from the MOPAC 6 package.

In this paper we focus particularly on the temperature dependence of electric permittivity and nonlinear dielectric effect near the phase transitions. Simultaneous studies of concentration dependence revealed that the nematic phase is also present in the concentrated 7CB4 solutions in benzene.

EXPERIMENTAL

It is prerequisite, with NDE measurements, that the sample exhibits possibly the lowest electric conductivity. With the instruments we used, reported previously [17,18], the conductivity should be less than 10^{-5} S/m. For that reason, all the materials were thoroughly purified and dried. Since the change of electric permittivity in isotropic liquids depends on square of the electric field E, the following quantity is the measure of NDE

$$\frac{\varepsilon^E - \varepsilon}{E^2} = \frac{\Delta\varepsilon}{E^2} \qquad (1)$$

Relative change of permittivity $\Delta\varepsilon/\varepsilon$, for the isotropic molecular liquids in the electric field limited by electric breakdown, is less than 10^{-3}–10^{-6}. These low values put extreme demands on the experimental apparatus. In our instrument, the electric field pulse had about 1 ms duration, permitting to measure $|\Delta\varepsilon/\varepsilon| > 10^{-6}$–$10^{-7}$ for the liquids of $\sigma < 10^{-5}$ S/m conductivity, to the accuracy around 3%.

Hewlett Packard 4192A LF impedance analyzer was used and the accuracy of the linear measurements of electric permittivity (ε) was 0.05% at 1 MHz frequency. Density (d) was measured with a hydrostatic densitometer and the refraction index with an Abbe refractometer at 0.01% precision.

RESULTS AND DISCUSSION

The results of electric permittivity (ε) and its variations ($\Delta\varepsilon/E^2$) in a strong external electric field were used to set up a phase diagram of the solutions. In Fig. 2 the electric permittivity of benzene solutions of 7CB4 is shown as a function of concentration (molar fraction). For a better readability, the results for only three temperatures 15°C, 30°C and 55°C are displayed. However, all these measurements were

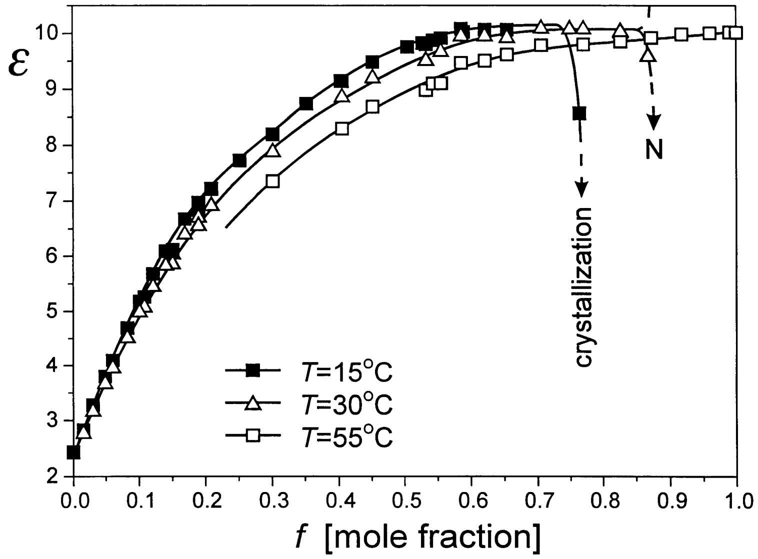

Figure 2. Dependence of the electric permittivity of benzene solutions of 7CB4 on the mole fraction at three temperatures. Transition points to the nematic phase (N) and solid phase are marked.

performed at larger number of temperatures, decreasing the temperature step near the phase transitions, which will be seen in the successive Figures. Temperature range was extended up to 80°C for the pure 7CB4.

The relevant concentration curves of the nonlinear effect, measured at six temperatures, are presented in Fig. 3. In the whole concentration range we observe a strong temperature dependence of $\Delta\varepsilon/E^2$. In diluted solutions ($f < 0.1$, Fig. 3; inset) the orientation of 7CB4 monomers in electric field, *i.e.* Langevin effect, results in negative values of NDE. On the increasing the molar fraction the nonlinear effect changes sign from negative to positive (chemical effect). As shown previously [16], after a detailed, quantitative analysis for non-concentrated solutions ($f < 0.4$), this is directly associated with dipolar interactions, leading to dimers and higher multimers. Here, we are interested in phase transitions from the isotropic liquid to a solid, including the nematic phase at higher concentrations ($f < 0.85$).

These processes may be easier to observe and analyse when changing temperature. Figs. 4 and 5 display the curves $\varepsilon(T)$ and $\Delta\varepsilon(T)/E^2$, respectively. Even in Fig. 2, one can distinguish a plateau at the level $\varepsilon \approx 10$. This is rather uncommon in isotropic systems of unlimited miscibility. We believe that this is associated with an approach to the nematic phase, *i.e.* an evident ordering of the long polar axes of 7CB4 molecules. Successive temperature runs of the nonlinear dielectric effect clearly illustrate the approaching to the nematic phase with a critical increase of the $\Delta\varepsilon/E^2$. Phenomenological description of this and other phenomena, associated with critical fluc-

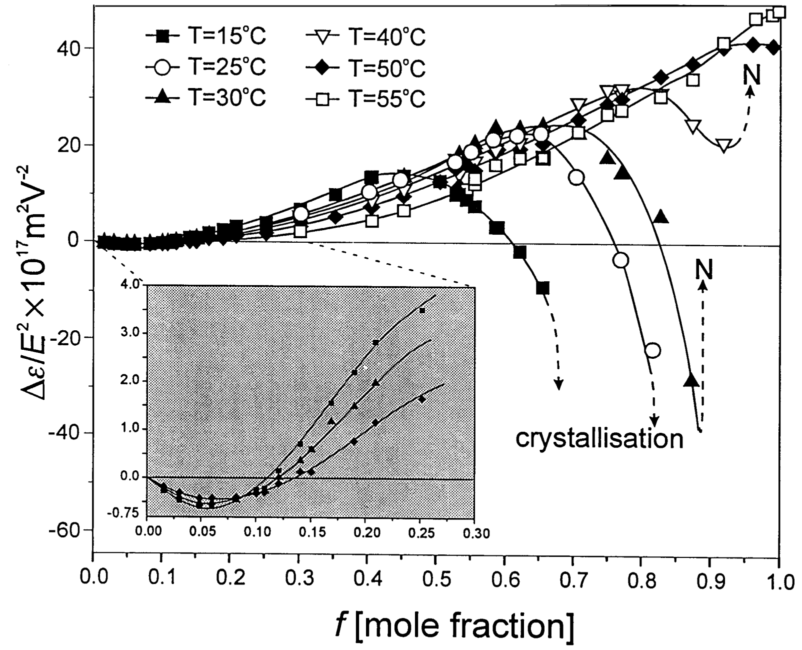

Figure 3. Nonlinear dielectric effect $\Delta\varepsilon/E^2$ of 7CB4 solutions as a function of mole fraction in benzene for six temperatures. Transition points to the nematic phase (N) and solid phase are marked with arrows.

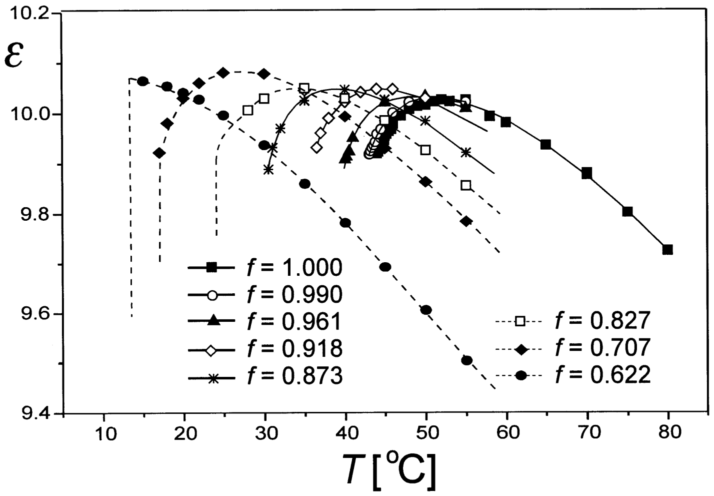

Figure 4. Temperature dependence of electrical permittivity ε for benzene solutions of 7CB4 at eight selected concentrations.

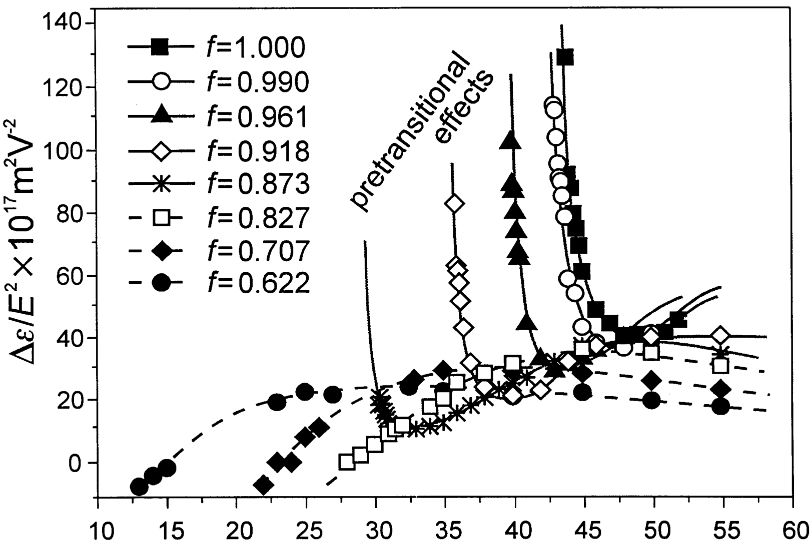

Figure 5. Nonlinear dielectric effect $\Delta\varepsilon/E^2$ of 7CB4 solutions as a function of temperature T at eight selected concentrations in benzene.

tuations, like light scattering or Kerr effect, has been proposed by de Gennes [19], who explained it by the phenomenological theory of Landau (LdG model). The strong electric field induces a deformation of the critical fluctuations and changes the range of the critical correlations. Both effects lead to a critical rise of the permittivity variations in the electric field observed as a large positive value of $\Delta\varepsilon/E^2$. LdG model provides the quantitative description of these features by means of the field theory and for $T > T_c$ yields the following formula [15,20]

$$\frac{\Delta\varepsilon}{E^2} = \frac{A}{T - T^*}, \qquad \text{where} \qquad A = \frac{2\varepsilon}{3a}\Delta\varepsilon_o \Delta\varepsilon_f \tag{2}$$

and a denotes the amplitude of the second term in the series expansion of LdG, whereas $\Delta\varepsilon_o$ and $\Delta\varepsilon_f$ – the anisotropies of electric permittivity of the nematic phase at zero-frequency and the frequency, at which the NDE experiment is run (usually a few MHz), respectively. $T^* = T_c - \Delta T$ is the extrapolated temperature of the (assumed,) hypothetical, continuous second order phase transition. Small deviation from this model, observed in the vicinity of the nematic phase [21,22], are explained as caused by non-classical fluctuations near T^*.

For the molar fraction of 7CB4 in benzene $f < 0.85$ one does not observe the critical increase of NDE as before: on lowering the temperature, the solution passes to a region of the liquid–solid phase equilibrium, leaving the nematic phase. This is accompanied by the sign change followed by a salient rise of the negative NDE (Fig. 2 and Fig. 5). Most likely, this effect is due to a significant shift of molecular equilibrium to larger molecular clusters of a notable dipole moment, where again, the negative Langevin effect dominates. Soon after the first microcrystals of 7CB4 appear, strong disturbances, related to their motion in the electric field, make the measurement of NDE impossible. After solidification of the sample the nonlinear effect becomes non-measurable, due to the immobility of electric dipoles.

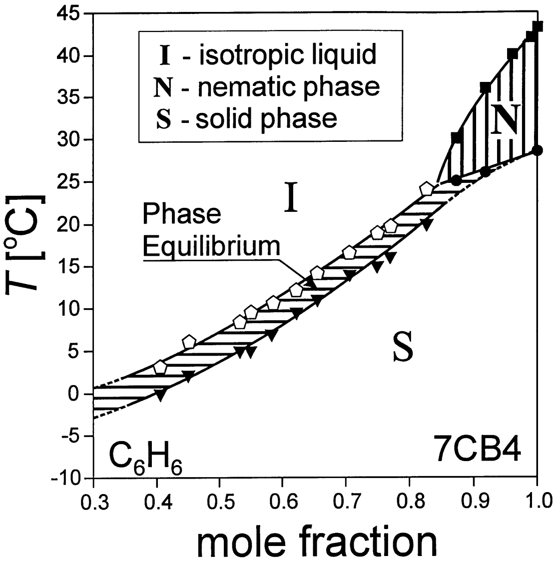

Figure 6. Phase diagram of 4-heptyl-4′-cyano-biphenyl in benzene.

The results shown in Figs. 2–5, as well as direct optical and microscopic observations, enable to set up a phase diagram (Fig. 6). Notably, there is a wide range of 7CB4 concentrations ($0.85 < f \leq 1$), where the nematic phase exists. At lower concentrations, on decrease of the temperature of the homogeneous, isotropic solution, crystals of 7CB4 start to precipitate. Virtually, the phase equilibrium range is approximately 6°C in the whole studied range of concentration.

It is worth mentioning here that similar studies have been made earlier for the 4-heptyl-4′-cyano-biphenyl isomer with cyano group at position 3 (7CB3) [23]. This compound does not exhibit nematic phase, despite the fact that both, the shape of the molecule and the magnitude of the dipole moment ($\mu_{7CB3} = 4.4$ D) are very similar to those of 7CB4. Furthermore, the processes of dipolar association are less emphasized in this compound. It turns out that the experimental results in the whole concentration range can be accounted for with a simple dimerization model with nearly antiparallel dimers [23]. In addition, a study is being made recently of the solutions of 4-heptyl-4′-nitro-biphenyl (7NB4), where the cyano group in position 4 is replaced with nitro group. Consequently, being so similar ($\mu_{7NB4} = 5.1$ D), this compound appeared non-mesogenic. It means that the magnitude of the dipole moment, and chemical resemblance have no definitive effect on the evolution of the dipolar association and occurrence of nematic phase. The search of the constitutive factors, such as the details of chemical structure, responsible for the molecular interactions, hence for the form of phase diagram, is still challenging.

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