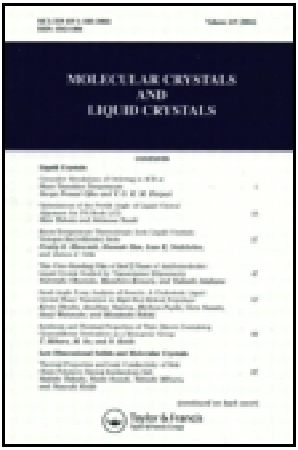

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NONLINEAR DIELECTRIC RELAXATION SPECTRA OF MESOGENIC MOLECULES IN BENZENE SOLUTIONS

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Nonlinear Dielectric Relaxation Spectra of Mesogenic Molecules in Benzene Solutions

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The frequency dependence of the nonlinear dielectric increment was studied for benzene solutions of 4,4′-*n*-hexylcyanobiphenyl (6CB), 4-(*trans*-4′-*n*-hexylcyclohexyl)-isothiocyanatobenzene (6CHBT) and 1-[3-*n*-decylbiphenyl]-2-[4-isothiocyanatophenyl]-ethane (10TPEB) molecules. In dilute solutions of these strongly dipolar nematogenic molecules (c < 1M) we observed the Langevin saturation related to nonlinear reorientation of dipoles in a strong electric field. The spectrum is described by the relaxation functions formulated by Coffey et al. [Proc. R. Ir. Acad. **78**, 17 (1978)]. For more concentrated solutions (c > 1M) of 6CB and 6CHBT in benzene large positive field-induced changes of permittivity are observed. Such a large nonlinearity in polarization is expected in the vicinity of the isotropic-nematic phase transition because the molecular correlation length of the nematic domains becomes unusually large.

Keywords: mesogenic molecules; liquid crystals; nonlinear dielectric spectroscopy; dipolar interactions; Langevin saturations

INTRODUCTION

Electric fields of high intensity applied to polar liquids produce a nonlinearity in the dependence of the polarization on the field strength.

The nonlinearity can be caused mainly by two molecular phenomena occurring in isotropic liquids. First of all, it is the Langevin ***saturation of the orientation of the dipoles*** forced by the strong electric field. This effect leads to a decrease in the permittivity of polar liquids. The nonlinear dielectric increment ($\Delta\varepsilon$), which is defined as a difference between the permittivity value measured by an a.c. electric field of small amplitude ($E(\omega) \approx 10^2$ V/m) in the presence (ε_{E_0}) and the absence (ε) of a d.c. field of very high amplitude ($E_0 \approx 10^7$ V/m):

$$\Delta\varepsilon = \varepsilon_{E_0} - \varepsilon, \tag{1}$$

has a negative value. The value of $\Delta\varepsilon$ is proportional to the square of the field strength E_0. The increment shows relaxational behavior (nonlinear dielectric relaxation) in the same frequency region as the linear dielectric relaxation [1] (at least for small values of the ratio of the electric dipolar energy (μE_0) to the thermal energy (kT) [2]), and can be presented in the complex form :

$$\Delta\varepsilon^*(\omega) = \Delta\varepsilon'(\omega) - i\Delta\varepsilon''(\omega), \tag{2}$$

where $\Delta\varepsilon'$ and $\Delta\varepsilon''$ are the real and imaginary parts of the nonlinear dielectric increment, respectively. The Langevin dielectric saturation occurs always, if the dipolar liquids are placed in a strong electric field.

The second phenomenon, which can also cause a nonlinearity in the dependence of the polarization on field strength, occurs only for systems in which (*i*) intermolecular interactions (e.g., dipole-dipole or hydrogen bonds) lead to the formation of aggregates with a compensated dipole moment or (*ii*) intramolecular processes (e.g., conformational change) produce new dipoles. Then, the strong electric field shifts the equilibrium between the aggregates and the monomers (or other aggregates) or between the conformers in favor of more polar species. This ***"chemical effect"*** causes an increase of the permittivity of liquids, i.e. the increment in Eq. (1) has a positive value. The increment shows a relaxation in a frequency region dependent on the rate of the chemical process occurring in the studied liquid.

Since the nonlinear dielectric increment measured for dipolar liquids is, in general, a sum of two effects : the orientational Langevin saturation (negative contribution) and the chemical effect (positive contribution), the interpretation of the experimental results is not a simple matter. However, the problem is worth the effort because the nonlinear dielectric spectroscopy, due to its exceptional sensitivity to various aggregation processes in liquids, is a unique method of detecting of the intermolecular interactions and studying their kinetics.

In this paper we analyze the results of the measurements of nonlinear dielectric effect (NDE) carried out for solutions of 4,4'-*n*-hexylcyanobiphenyl (6CB), 4-(*trans*-4'-*n*-hexyl-cyclohexyl)-isothiocyanatobenzene (6CHBT) and 1-[3-*n*-decylbiphenyl]-2-[4-isothiocyanatophenyl]-ethane (10TPEB) in benzene, what gave an opportunity for simultaneous studies of the two contributions to the NDE in the systems.

EXPERIMENTAL

Materials. 4,4'-*n*-Hexylcyanobiphenyl (C_6H_{13}-Ph-Ph-C≡N, 6-CB), 4-(*trans*-4'-*n*-hexyl-cyclohexyl)-isothiocyanatobenzene (C_6H_{13}-CyHx-Ph-N=C=S, 6CHBT) and 1-[3-*n*-decylbiphenyl]-2-[4-isothiocyanatophenyl]-ethane ($C_{10}H_{21}$-Ph-Ph-CH_2-CH_2-Ph-N=C=S, 10TPEB) of high purity was kindly supplied by R.Dąbrowski from the Institute of Chemistry, Military University of Technology, Warsaw. Benzene was dried with metallic sodium, distilled and stored over molecular sieves of 4A.

Apparatus. The nonlinear dielectric effect measurements were carried out with a stationary relaxation method in which the quasi-static electric field (~85 Hz) of high amplitude ($E_o = 1.1 \times 10^7$V/m) is superimposed on the field E(ω) of weak amplitude and variable frequency. In the frequency range from 1 MHz to 100 MHz nonlinear dielectric data can be collected by measuring the changes in the resonance parameters of a classical LC-resonance circuit. In the frequency range from 100 MHz up to about 3 GHz a partially coaxial resonant cavity was used. The frequency was selected by changing the cavity length. The details concerning the apparatus and measuring procedure have been described previously [3,4].

RESULTS AND DISCUSSION

The Langevin saturation phenomenon can be investigated only for non-interacting dipolar systems. As mentioned above, the dipolar interactions lead to molecular aggregates which, in the presence of strong electric field, can give a positive contribution to the nonlinear dielectric increment.

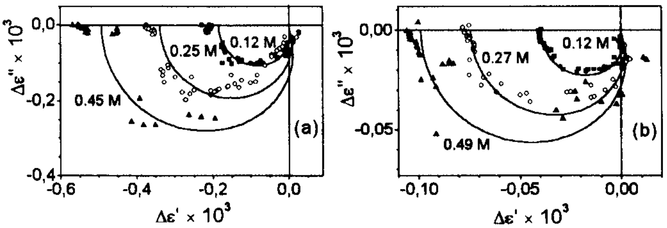

FIGURE 1. Nonlinear Cole-Cole plots for solutions of 6CB (a) and 6CHBT (b) in benzene. Solid lines represent the Coffey Eqs. (3).

The experimental results presented in Fig. 1 have been obtained for very dilute solutions of 6CB and 6CHBT in benzene. Dilution of a dipolar substance in nonpolar medium is an efficient way for the reduction of dipole-dipole interactions and, as has been shown in Ref.

[5], in the most diluted solutions, the dipole-dipole interactions are negligible. The figure shows the evolution of the nonlinear dielectric properties as the number of dipoles per unit volume increases.

For a theoretical description of the frequency dependence of the nonlinear dielectric phenomenon caused by the saturation of the dipoles orientation in strong electric field we use the Coffey and Paranjape equations [6], which are appropriate for our experimental method of measuring $\Delta\varepsilon$ (with the use of two electric fields : $E(\omega)$ and E_o). The equations have the following form :

$$\Delta\varepsilon'_L = L\cdot\frac{1}{1+\omega^2\tau^2}\cdot F_1(\omega)\ ,\qquad \Delta\varepsilon''_L = L\cdot\frac{\omega\tau}{1+\omega^2\tau^2}\cdot F_2(\omega), \tag{3}$$

where τ is the relaxation time and $F_1(\omega)$ and $F_2(\omega)$ refer to the nonlinearity of the dipolar relaxation process :

$$F_1(\omega)=\frac{27+\omega^2\tau^2-2\omega^4\tau^4}{3(1+\omega^2\tau^2)(9+\omega^2\tau^2)},\ F_2(\omega)=\frac{42+19\omega^2\tau^2+\omega^4\tau^4}{3(1+\omega^2\tau^2)(9+\omega^2\tau^2)}. \tag{4}$$

The quantity L in Eqs. (3) denotes the strength of the nonlinear dielectric increment and is equal to the static value of the increment ($\Delta\varepsilon_{Ls}$) (the high frequency value of the increment $\Delta\varepsilon_{L\infty}$ is equal to zero).

The strength L is related to the molecular quantities in the following way [7]:

$$L\equiv\Delta\varepsilon_{Ls}=-\frac{N\mu^4}{45\varepsilon_o k^3T^3}\cdot E_o^2\cdot F(\varepsilon_s,\varepsilon_\infty)\ , \tag{5}$$

where N is the number of dipoles per unit volume, μ - the molecular dipole moment, k - the Boltzmann constant and T - the absolute temperature. The value of L is negative and depends on the square of the biasing electric field strength E_o and the forth power of the molecular dipole moment.

The function $F(\varepsilon_s, \varepsilon_\infty)$ in Eq. (5) express the fact that the dipoles are immerged in the dielectric medium of the static permittivity ε_s and the high frequency permittivity ε_∞. The form of the function depends on the model of the local field in dielectrics and, as has been shown by Thiebaut [8] for the Onsager model [9], is given by

$$F(\varepsilon_s,\varepsilon_\infty)=\frac{\varepsilon_s^4(\varepsilon_\infty+2)^4}{(2\varepsilon_s+\varepsilon_\infty)^2(2\varepsilon_s+\varepsilon_\infty^2)}\,. \qquad (6)$$

The solid lines in Fig. 1 present the best fit of the theoretical predictions given by Eqs. (3) to the experimental results. As can be seen, the Coffey equations describe quite well the experimental results of the frequency dependence of the negative nonlinear dielectric increment including the change of the sign of the real part of the increment in the high-frequency region.

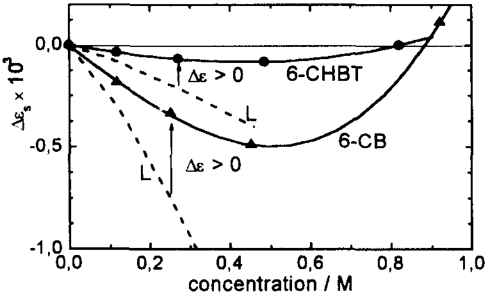

FIGURE 2. Nonlinear dielectric strength $\Delta\varepsilon_s$ as a function of 6CB (▲) and 6CHBT (●) concentration in benzene solutions. The dashed lines represent the nonlinear strength L calculated for non-interacting dipoles (Eq.(5)).

Figure 2 shows that with an increase of the dipole concentration, the strength $\Delta\varepsilon_s$ deviates considerably from the dependence predicted for non-interacting dipoles. This dependence, denoted in the figure as L, results from Eq. (5) for the dipole moments 4.7 and 3.5 D of the single 6CB [10,11] and 6CHBT [12] molecules, respectively.

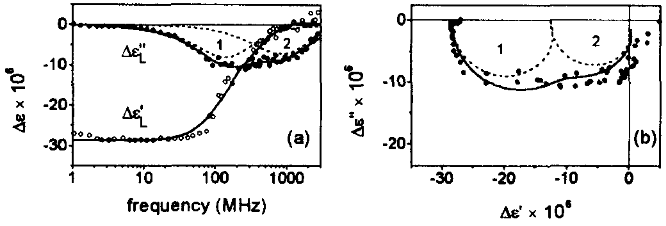

FIGURE 3. Frequency dependence of the real $\Delta\varepsilon_L$' and imaginary $\Delta\varepsilon_L$" parts of the nonlinear dielectric increment due to the Langevin saturation of the dipoles (a) and the nonlinear Cole-Cole plot (b) for 10TPEB solution. Molar fraction of 10TPEB: x = 0.0102, E_o = 1.1×10^7 V/m, T = 25°C. Solid lines represent the best fitting of the Coffey Eqs. (3), extended to the case of the two simultaneous nonlinear relaxation processes [13], to the experimental results (points). Dashed lines 1 and 2 represent the nonlinear dielectric absorption components corresponding to molecular rotation around the short and long axes, respectively.

Fig. 3 presents the nonlinear dielectric relaxation spectra of a dilute solution of 10TPEB in benzene, at 25°C. Two absorption bands, recorded in the experiment, can be connected with the rotations of single molecules around their principal molecular axes. For the 10TPEB molecules the angle between the dipole moment vector and the long axis is markedly different from zero. For this type of molecules the dipole moment component perpendicular to the long axis is quite large, so that the molecular rotation around the long axis, leads to a large contribution to the total dielectric absorption [14].

Figures 4 shows the evolution of the nonlinear dielectric properties of 6CB and 6CHBT in benzene solutions as the number of dipoles per unit volume increases. For solutions of 6CB and 6CHBT of concentration about 1M the nonlinear dielectric increment Δε changes the sign to the positive and becomes immense if compared to the negative Langevin effect. The experimental results can be described by the single Debye relaxation function (solid lines in Fig. 4). The values of the fitting parameters (τ and Δε) are depicted in Fig. 5.

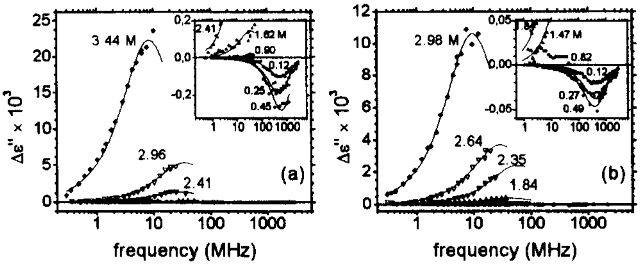

FIGURE 4. Frequency dependence of the imaginary part of the nonlinear dielectric increment for solutions of 6CB (a) and 6CHBT (b) in benzene at 25°C. The inset shows frequency dependence of Δε" for diluted solutions.

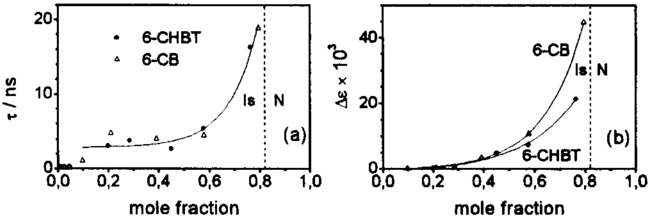

FIGURE 5. Variation of the relaxation time τ (a) and nonlinear dielectric strength Δε (b) with the concentration of 6CB and 6CHBT derived from the nonlinear dielectric spectra presented in Fig. 4.

The experimental data presented in the insets of Fig.4 suggest that the relaxation of the nonlinear positive effect for diluted solutions (c < 1M) occurs in a frequency region close to that corresponding to the

Langevin saturation relaxation. *The positive contribution* to the *nonlinear dielectric effect* shows a critical behaviour of relaxation time in extremaly concentrated solutions i.e. in vicinity of the isotropic-nematic phase transition (Fig.5). Such a large pretransitional increasing of the relaxation time is expected in the vicinity of the isotropic-nematic phase transition because the molecular correlation length of the domains becomes unusually large [15].

ACKNOWLEDGMENTS

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