Nonlinear Dielectric Relaxation in Solutions of 6CHBT in Nonpolar Medium

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The frequency dependence of the nonlinear dielectric increment was studied for benzene solutions of the nematogenic molecule 4-(*trans*-4'-*n*-hexylcyclohexyl)isothiocyanatobenzene (C_6H_{13}CyHx-Ph-N=C=S, 6CHBT) at 25°C. The increment was induced by a quasi-static electric field of high strength (10^7 V/m), and its relaxation was detected by an alternating field of low strength (10^2 V/m) in the frequency range 1 MHz–3 GHz. The results are discussed in the framework of Coffey's theory.

Key words: Dielectrics; Nonlinear Dielectric Increment; Nonlinear Relaxation.

1. Introduction

Nonlinearity in the dielectric behavior of isotropic liquids refers to the relation between the electric field strength E and the charge density (dielectric polarization) induced by the field on the liquid surfaces adjoining the capacitor's electrodes. In the fields of small and moderate intensity the polarization P is proportional to the field strength:

$$P = \varepsilon_0(\varepsilon - 1)E, \qquad (1)$$

where $\varepsilon_0 = 8.85$ pF/m and ε is the (relative) electric permittivity of the liquid. This linear relation means that the permittivity ε, determined as

$$\partial P/\partial E = \varepsilon_0(\varepsilon - 1), \qquad (2)$$

does not depend on the electric field strength (Figure 1). Only for this reason can ε be called the "dielectric constant", because it depends on the temperature (density) and on the frequency of the measuring field. Linear dielectric spectroscopy is one of the basic methods for investigations of the molecular dynamics in liquids and liquid crystals [1]. The molecular interpretation of the experimental results is based on the Smoluchowski-Debye model of rotational diffusion of the dipoles [2–5].

High electric fields (10^6 V/m, or higher) applied to polar liquids cause a deviation from the linear dependence (1) (see Figure 1). There are two main molecular phenomena which can be responsible for this nonlinearity. First of all, the Langevin saturation of the orientation of the dipoles is due to the strong electric field. This effect leads to a decrease in the permittivity of polar liquids.

In the experiment one determines the nonlinear dielectric increment $\Delta\varepsilon$, which is defined as the difference between the permittivity measured by an a.c. electric field of small amplitude $E(\omega)$ in the presence (ε_{E_0}) and the absence (ε) of a biasing field E_0 of high amplitude:

$$\Delta\varepsilon = \varepsilon_{E_0} - \varepsilon. \qquad (3)$$
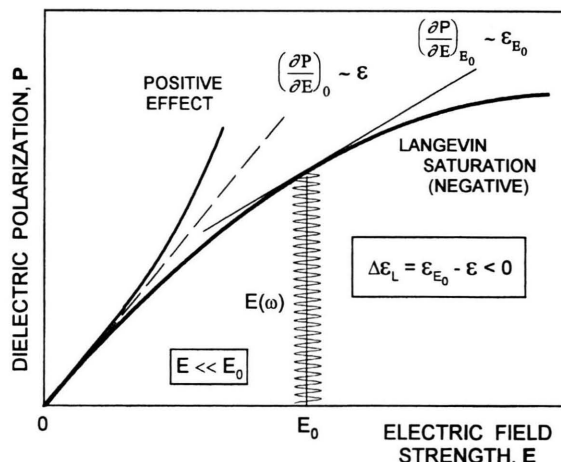

Fig. 1. A strong electric field E_0 causes a nonlinearity in the dielectric polarization vs. field strength dependence. The nonlinearity can lead to the increase (positive effect) or to the decrease (negative effect) of the permittivity measured by a.c. field $E(\omega)$ of small strength.

In case of the Langevin saturation the increment $\Delta\varepsilon$ is negative. $\Delta\varepsilon$ is proportional to the square of the field strength E_0.

The nonlinear dielectric increment due to the Langevin saturation shows the relaxation occurring in the same frequency region as the linear dielectric relaxation [6] (at least for small values of the ratio of the electric dipolar energy (μE_0) to the thermal energy (kT) [7]), and can be presented in the complex form:

$$\Delta\varepsilon^*(\omega) = \Delta\varepsilon'(\omega) - i\Delta\varepsilon''(\omega), \qquad (4)$$

where $\Delta\varepsilon'$ and $\Delta\varepsilon''$ are the real and imaginery parts of the nonlinear dielectric increment, respectively.

The second phenomenon, which can also cause a nonlinearity in the dependence of the polarization on the field strength, occurs 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) involve the change of molecular polarity. 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. These effects cause an increase of the permittivity of liquids, i.e. the increment (3) is positive. It shows the relaxation in the frequency region dependent on the rate of the chemical process occurring in the liquid studied.

Since the nonlinear dielectric increment measured for dipolar liquids is, in general, a sum of the two effects mentioned above, 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 the aggregation processes in liquids, is a unique method of detecting the intermolecular interactions and studying their kinetics. This spectroscopy has been used for the investigation of the kinetics of cis-lactams cyclic dimerization [8, 9] and cholesterol aggregation [10, 11] in nonpolar media.

In this paper we analyze the frequency dependence of the dielectric nonlinear effect measured for solutions of the nematogenic polar molecules of 4-(*trans*-4'-*n*-hexyl-cyclohexyl)isothiocyanatobenzene in benzene.

2. Experimental

Materials. 4-(*trans*-4'-*n*-hexylcyclohexyl)isothiocyanatobenzene ($C_6H_{13}CyHx-Ph-N=C=S$, 6CHBT) was synthesized and purifed at the Institute of Chemistry, Military University of Technology, Warsaw. 6CHBT is a liquid crystalline substance with a nematic to isotropic phase transition at 43.1 °C. Benzene was dried with metallic sodium, distilled and stored over molecular sieves of 4 Å.

Apparatus. The nonlinear dielectric effect measurements were carried out using a stationary relaxation method in which a quasi-static electric field (85 Hz) of high amplitude ($E_0 = 1.1 \times 10^7$ V/m) is superimposed on a field $E(\omega)$ of weak amplitude and variable frequency. In the frequency range from 1 to 100 MHz the nonlinear dielectric data can be collected by measuring the changes in the resonance parameters of a classical LC-resonance circuit. To obtain a dielectric spectrum, the resonance frequency is selected by changing the inductance coils connected in parallel to the measuring capacitor. In the frequency range from 100 MHz up to about 3 GHz a coaxial resonant cavity was used. The details concerning the apparatus and measuring procedure have been described in [8, 12].

3. 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 a strong electric field can give a positive contribution to the nonlinear dielectric increment.

The experimental results presented in Fig. 2 have been obtained for very dilute solutions of 6CHBT in benzene. Dilution of a dipolar substance in a nonpolar medium is an efficient way for the reduction of dipole-dipole interactions. Unfortunately, a decrease of the number of dipoles per unit volume leads to a decrease of the measured signal amplitude. The concentration of dipoles in our experiment ($c = 0.118$ M (= mole/dm^3), ~ 1% in molar fraction) is a compromise between the reduction of dipole-dipole interactions and the sensitivity of the measuring apparatus [13].

A theoretical description of the frequency dependence of the nonlinear dielectric phenomenon caused by the saturation of the dipole-orientation in strong electric fields has been proposed by Coffey and Paranjape [14], Kasprowicz-Kielich and coworkers [15–18] and Kimura and Hayakawa [19]. The theories concern isotropic dielectrics containing N mutually non-interacting dipolar, axially symmetric molecules, with the dipole moment vector parallel to the axis of symmetry. The rotational re-
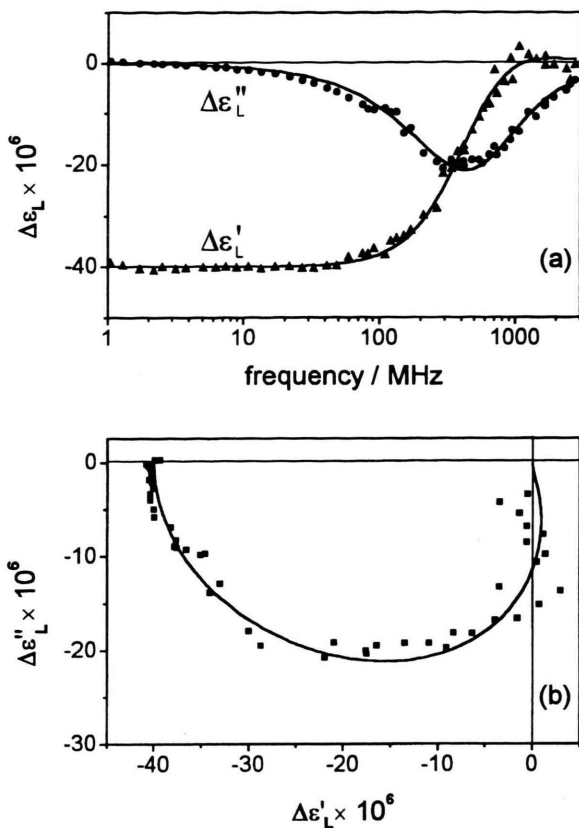
Fig. 2. Frequency dependence of the real $\Delta\varepsilon_L'$ and imaginary $\Delta\varepsilon_L''$ parts of the nonlinear dielectric increment due to the Langevin saturation of the dipoles (a) and the nonlinear Cole-Cole plot (b) for 6CHBT solution. Molar concentration of 6CHBT: $c = 0.118$ M, $E_0 = 1.1 \times 10^7$ V/m, $T = 25\,°C$. Solid lines represent the Coffey Eqs. (5) for $L = -0.40 \times 10^{-4}$ and $\tau = 0.254$ ns.
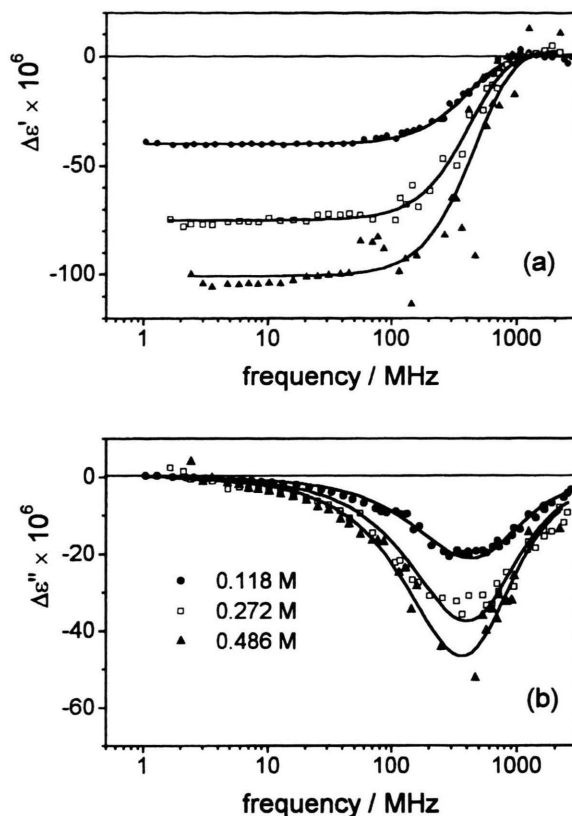
Fig. 3. Frequency dependence of the real (a) and imaginary (b) parts of the nonlinear dielectric increment for different molar concentration of 6CHBT in benzene at $25\,°C$ and $E_0 = 1.1 \times 10^7$ V/m, Solid lines represent the Coffey Eqs. (5).

Table 1. Values of the apparent nonlinear relaxation time and nonlinear dielectric strength for 6CHBT molecules dissolved in benzene ($T = 25\,°C$, $E_0 = 1.1 \times 10^7$ V/m).

Concentration/M	τ/ns	$\Delta\varepsilon_s \times 10^3$
0.118	0.254	−0.037
0.272	0.272	−0.066
0.486	0.296	−0.082

laxation of such an assembly, placed in a strong electric field, is described by the extended Debye rotational diffusion model [4, 20].

Here we will use Coffey's equations [14]:

$$\Delta\varepsilon_L' = L \frac{1}{1 + \omega^2 \tau^2} F_1(\omega),$$

$$\Delta\varepsilon_L'' = L \frac{\omega \tau}{1 + \omega^2 \tau^2} F_2(\omega), \tag{5}$$

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

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

$$F_2(\omega) = \frac{42 + 19\omega^2 \tau^2 + \omega^4 \tau^4}{3(1 + \omega^2 \tau^2)(9 + \omega^2 \tau^2)}. \tag{6}$$

L in (5) denotes the strength of the nonlinear dielectric increment and is equal to the static value of the increment ($\Delta\varepsilon_{L_s}$) (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 [21]:

$$L = \Delta\varepsilon_{Ls} = -\frac{N \mu^4}{45\varepsilon_0 (kT)^3} E_0^2 F(\varepsilon_s, \varepsilon_\infty), \tag{7}$$
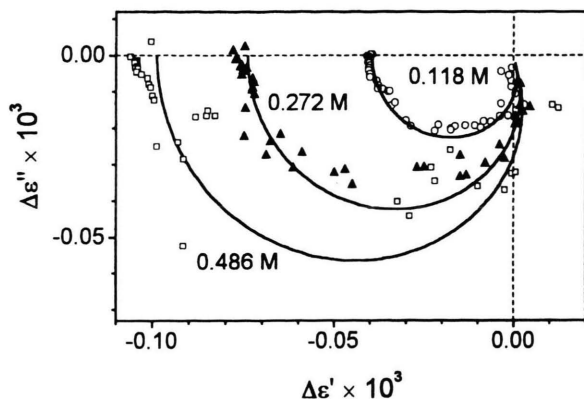
Fig. 4. Nonlinear Cole-Cole plots for solutions of 6CHBT in benzene. Solid lines represent the Coffey Eqs. (5).
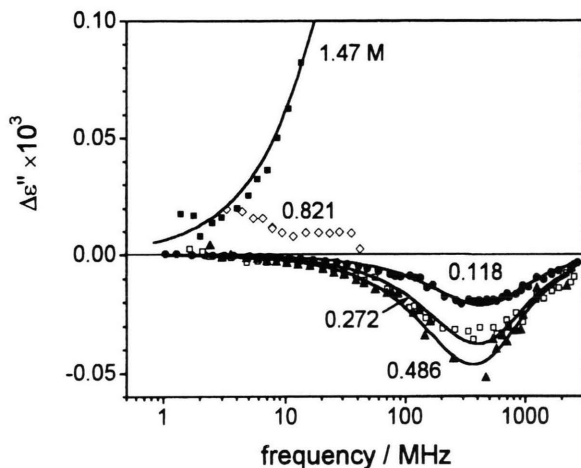

Fig. 5. For 6CHBT concentration of about 8% (in mol. fraction) the measured nonlinear dielectric increment changes the sign and the amplitude strongly increases with the increase of 6CHBT concentration in benzene solutions.
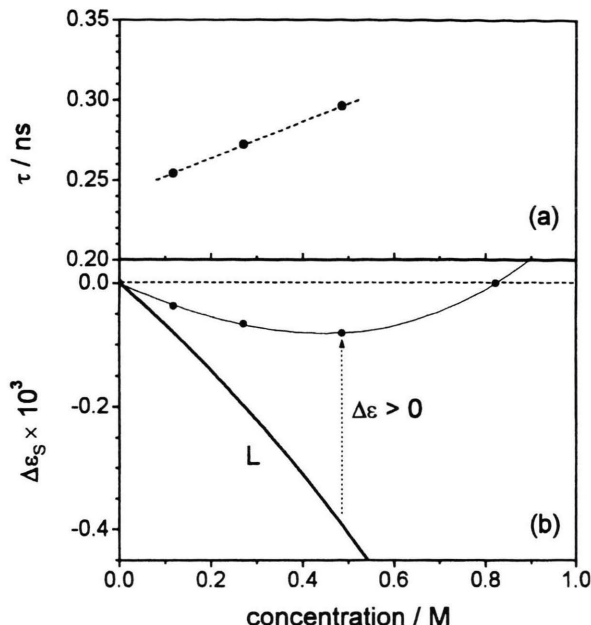

Fig. 6. Apparent nonlinear relaxation time $\tau(a)$ and nonlinear dielectric strength $\Delta\varepsilon_s$ (points in (b)) as a function of 6CHBT concentration in benzene solutions. L is the nonlinear strength calculated (Eq. (7)) for non-interacting dipoles (Langevin saturation).

where N is the number of dipoles per unit volume and μ the molecular dipole moment. L is negative and depends on the square of the biasing electric field strength E_0 and the fourth power of the molecular dipoles moment.

The function $F(\varepsilon_s, \varepsilon_\infty)$ expresses the fact that the dipoles are immersed in a 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 [22] for the Onsager model [23], is given by

$$F(\varepsilon_s, \varepsilon_\infty) = \frac{\varepsilon_s^4(\varepsilon_\infty + 2)^4}{(2\varepsilon_s + \varepsilon_\infty)^2(2\varepsilon_s + \varepsilon_\infty^2)}. \qquad (8)$$

The solid lines in Fig. 2 present the best fitting of the theoretical predictions given by (5) to the experimental results (points). The values of the fitting parameters (L and τ) are gathered in Table 1.

Figures 3 and 4 show the evolution of the nonlinear dielectric properties of 6CHBT in benzene solutions as the number of dipoles per unit volume increases. The experimental results can still be described by the Coffey equations, however when the concentration of the solutions is increased, one observes a considerable drop in the sensitivity of the measuring circuits in the frequency range between 100 MHz and 1 GHz. As a consequence, one records in the relaxation region an abnormal scattering of the experimental points, which is exceptionally intense for the solution of 0.486 M. For higher 6CHBT concentrations (Fig. 5) the results cannot be recorded in the frequency region above 100 MHz, and simultaneously the measured nonlinear dielectric increment becomes positive. For the concentration 1.47 M of 6CHBT in benzene the positive increment $\Delta\varepsilon$ becomes immense compared to the Langevin effect.

Figure 6 shows that with increase of the dipole concentration, the strength $\Delta\varepsilon_s$ deviates considerably from the dependence predicted for non-interacting dipoles.
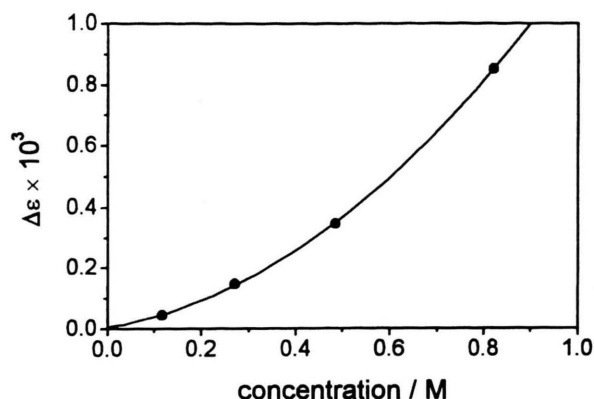
Fig. 7. Positive contribution to the nonlinear dielectric increment as a function of 6CHBT concentration in benzene solutions.

The dependence, denoted in the figure as L, results from (7) for the dipole moment 3.5 D, characteristic of the single 6CHBT molecules [24]. The difference between L and $\Delta \varepsilon_s$ refers to the positive contribution ($\Delta \varepsilon$) to the total nonlinear increment. The dependence of $\Delta \varepsilon$ on the 6CHBT concentration is depicted in Figure 7.

The positive contribution to the nonlinear dielectric effect measured in dilute dipolar solutions corresponds most probably to the field-induced shift of the equilibrium between the simplest dipolar aggregates (i.e. dimers) and single molecules. The polarity of the dimers is considerably reduced (due to the antiparallel arrangement of dipoles) and a strong electric field shifts the equilibrium toward the (more polar) monomers. The experimental data presented in Fig. 3 suggest that the relaxation of the nonlinear positive effect occurs in a frequency region close to that corresponding to the Langevin saturation relaxation. The apparent relaxation time determined in the experiment depends weakly on the 6CHBT concentration (Fig. 6a), although at the same time the strength of the positive increment increases quite strongly (Figure 7).

Acknowledgement

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