Nonlinear Dielectric Relaxation in Solutions of Rodlike Nonpolar Dimers of Mesogenic and Nonmesogenic Carboxylic Acids

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The nonlinear dielectric spectra of mesogenic 4-*n*-butylcyclohexanecarboxylic acid ($C_4H_9CyHxCOOH$, BCHA) and nonmesogenic 4-methylcyclohexanecarboxylic acid ($CH_3CyHxCOOH$, MCHA) in cyclohexane solutions were recorded in the frequency range of 1−100 MHz in the presence of the strong static electric field $E_0 = 1.1 \times 10^7$ V/m, at 25 °C. An essential difference in the nonlinear dielectric behavior of the compounds composed of the hydrogen-bonded nonpolar cyclic dimers with different length of the hydrocarbon tails was discussed. The dynamic pretransitional phenomena revealed for nematogenic BCHA were interpreted in the frame of the Landau−de Gennes theory.

Introduction

The transition from the isotropic liquid to the liquid crystalline nematic phase shows features of both the first and the second order phase transitions. The latent heat and a jump in the molar volume observed at the transition together with a spectacular pretransitional phenomena observed in the isotropic nematogenic liquids were the reasons for the classification of the isotropic to nematic phase transition as a weakly first order or close to second order.[1]

The pretransitional phenomena are due to the existence of a short-range orientational order of the mesogenic molecules leading to the formation of the pseudonematic domains in the isotropic liquid. The size of the domains increases as the temperature of pure nematic liquid[2−7] or as the concentration of the mesogenic molecules in solutions approaches to the transition to the nematic phase.[8] It should be emphasized that the pretransitional phenomena appear nearly exclusively in the nonlinear studies, i.e., when an external stimulus is sufficiently strong. It concerns certainly the dynamics of the phenomena. The linear methods, the linear dielectric spectroscopy in particular, are not able to detect the dynamic pretransitional effects. Only when a strong electric field is applied to the mesogenic liquid does a *new dielectric absorption band* appears in the frequency region about 1 order of magnitude lower than that recorded in the linear spectroscopy as a band corresponding to the rotation of individual mesogenic molecules around their short axis.

In recent papers,[7,8] we presented the results of the nonlinear dielectric relaxation studies performed for the mesogenic polar compound 4-(*trans*-4′-*n*-hexylcyclohexyl)isothiocyanatobenzene ($C_6H_{13}CyHxPhNCS$, 6CHBT) in the vicinity of the isotropic to nematic phase transition. Both in case of decreasing temperature of the pure mesogenic compound and in case of the increasing of its concentration in nonpolar medium at constant

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temperature, an approaching to the phase transition manifests itself by a critical-like behavior of the nonlinear dielectric strength and the nonlinear relaxation time.

It was shown in ref 8 that the nonlinear relaxation time τ measured as a function of concentration of the mesogenic compound fulfills the equation

$$\tau(X) = \frac{V^*_{eff}\eta(X)}{kT(X^* - X)^\alpha} \qquad (1)$$

analogous to that resulting from the Landau−de Gennes theory for dependence of the relaxation time on temperature.[1] In eq 1, X denotes the molar fraction of the mesogenic solute, η denotes the viscosity of the solution, V^*_{eff} denotes the effective volume of the relaxing entity, and k denotes the Boltzmann constant. X^* stands for the concentration of virtual transition of the second order, in analogy to T^* in the Landau−de Gennes theory, and α is the critical exponent. For solutions of 6CHBT in benzene,[8] within the experimental errors, the value of the exponent α is close to unity, similarly to that obtained in temperature dependence of the nonlinear relaxation time measured for pure isotropic 6CHBT[7] and that obtained with other methods, such as the light scattering[9,10] and the optical Kerr effect[2,3,11−14] for other mesogens.

Hitherto, the prenematic effects were studied for the dipolar mesogenic compounds only. As shown in refs 8 and 7, in case of the nonlinear dielectric spectroscopy, the polarity of mesogenic molecules sometimes brings about some problems in a full detection of the absorption band corresponding to the randomization of the pseudonematic domains directors, after their partial orientation by the electric field of high intensity. When the band occurs in the frequency region not too far from the absorption band due to rotation of the individual molecules, an interference of the two dielectric absorptions can lead to considerable reduction of the spectrometer sensibility, until measurements are unable to be made. It is the reason that the nonlinear dielectric spectra recorded for the polar mesogenic

Nonlinear Dielectric Relaxation in Carboxylic Acids

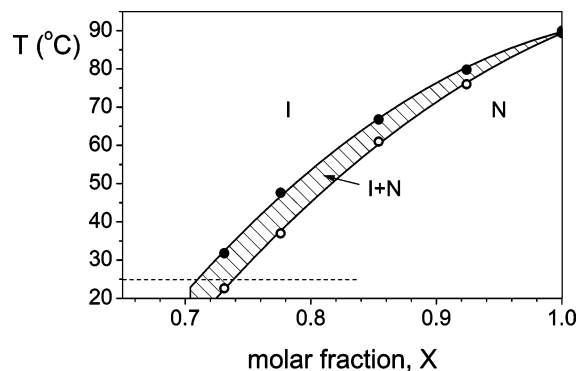*J. Phys. Chem. A, Vol. 107, No. 30, 2003* **5651**

Figure 1. Phase diagram for BCHA + cyclohexane mixtures. *X* denotes the molar fraction of BCHA. The nonlinear dielectric spectra were recorded at 25 °C. The hatched area denotes the isotropic + nematic (I + N) two-phase region.

compound 6CHBT[8,7] are discontinued at tens of megahertz, depending on temperature or concentration.

Presented in this paper are the results of the investigations of the pretransitional effects in the isotropic phase of mesogenic liquid consisting of the *nonpolar* molecules, which are fascinating for many reasons. First of all, it is quite an interesting question whether the intermolecular interactions, reduced to the anisotropic polarizability interactions, lead to the nematic phase through the pseudonematic domains of the features analogous to those observed for dipolar mesogenic molecules. From the experimental point of view, the situation here is advantageous, because the lack of the dielectric absorption due to the molecular reorientations creates the circumstance where the whole band corresponding to the prenematic effects can be recorded.

For comparison, the results obtained for the nonpolar and nonmesogenic compound of the same structure are presented.

Experimental Section

Two carboxylic acids, 4-*n*-butylcyclohexanecarboxylic acid (BCHA) and 4-methylcyclohexanecarboxylic acid (MCHA), were synthesized and purified at the Institute of Chemistry, Military University of Technology, Warsaw. Mesogenic BCHA has the following sequence of phases: crystal −36 °C − nematic −90 °C − isotropic. The nonmesogenic MCHA melts at 25 °C. Cyclohexane was distilled and stored over molecular sieves of 0.4 nm. The purity of the compounds, checked by chromatography, was better than 99%.

Figure 1 presents the phase diagram for the BCHA + cyclohexane mixtures. The nonlinear dielectric measurements were performed at 25 °C.

In the experimental method, we used the electric field of high strength $E_0 = 1.1 \times 10^7$ V/m and low frequency (85 Hz) perturbs the system periodically, and the permittivity change

$$\Delta\epsilon = \epsilon_{E_0} - \epsilon, \qquad (2)$$

is measured with a weak field $E(\omega)$ of high frequency. The nonlinear dielectric data are obtained by monitoring the modulation of the parameters of a resonant circuit induced by the application of a high field to the capacitor of the circuit, filled with the liquid studied. An LC resonance circuit with exchangeable coils covers the frequency range from 100 kHz to 100 MHz. The sample is subjected to the resultant of two fields: one static of high amplitude and the other of low amplitude at selected high frequency. As soon as the impedance of the liquid is modified by the action of the periodic high field, the amplitude modulation of the high-frequency resonant voltage occurs. The
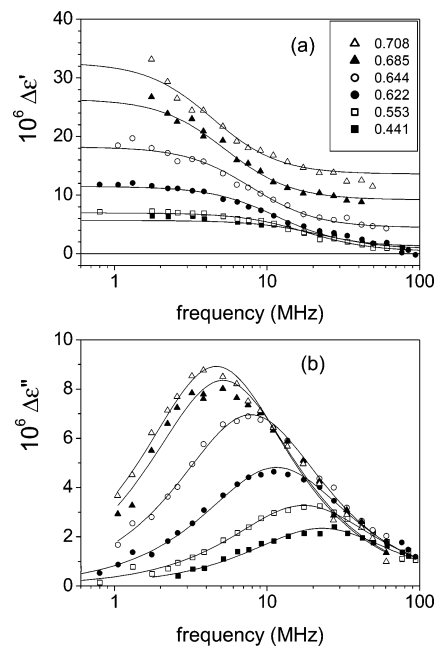

Figure 2. Frequency dependence of the real (a) and imaginary (b) parts of the nonlinear dielectric increment measured for different molar fraction of mesogenic BCHA in cyclohexane at 25 °C, $E_0 = 1.1 \times 10^7$ V/m. The values of the molar fraction of BCHA are given in the inset. The solid lines correspond to the Debye-type function (4) with a single relaxation time. In the real part of the effect, the solvent contribution was subtracted.

modulation depth reflects the difference between the resonance curves at peak field strength and at zero field. Demodulation and consecutive amplification provide the signals which are recorded as function of the swept frequency. The signals reveal a shift of the resonant frequency together with changes of bandwidth and resonant voltage. A fit of the data to the derivative of the expression relating the voltage to the resonance parameters yields the field-induced changes of the complex impedance.[15]

Results and Discussion

Figures 2 and 3 present the nonlinear dielectric spectra recorded for solutions of the mesogenic carboxylic acid (BCHA) and nonmesogenic acid (MCHA), respectively.

The standard recording of the linear dielectric spectra shows no absorption bands in the frequency region of 50 kHz to 100 MHz for carboxylic acids studied, both in pure state and in solutions, for BCHA both in the isotropic and nematic phases. The permittivity value is about 3 and very weakly depends on temperature and concentration of the acid. Besides, in the nematic phase of BCHA, the permittivity does not respond to application of the biasing d.c. voltage, usually used for orientation of the nematic liquid crystals. All of these facts undoubtedly prove that the linkage of two polar molecules of carboxylic acid by two hydrogen bonds leads to the cyclic dimers (3) with compensated dipole moment.
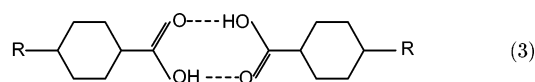
A qualitative analysis of the experimental results presented in Figures 2 and 3 leads to the following conclusions. (i) The strong electric field applied to the solutions of carboxylic acid, both mesogenic and nonmesogenic, induces an increase of the electric permittivity, i.e., the increment (2) is positive. (ii) The
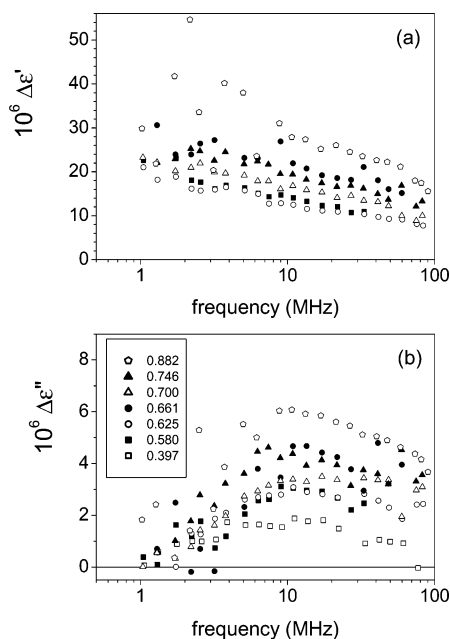
Figure 3. Real (a) and imaginary (b) parts of the dielectric increment of nonmesogenic MCHA dissolved in cyclohexane, at 25 °C, as a function of frequency. $E_0 = 1.1 \times 10^7$ V/m. The values of the molar fraction of MCHA are given in the insert.

value of the increment is on the order of 10^{-6}, i.e., about 3 orders of magnitude lower than that measured for polar 6CHBT.[8,7] The nonlinear dielectric increment on order of 10^{-6} touches the limit of the possibilities of the experimental method used. For pure cyclohexane, the increment is about 3×10^{-6}. (iii) The most striking difference in the nonlinear dielectric behavior of the mesogenic and nonmesogenic compounds studied is observed in frequency dependence of the dielectric increment $\Delta\epsilon$.

The positive nonlinear dielectric increment is observed in a system in which the intermolecular aggregates, susceptible to the strong electric field, exist. In the case of carboxylic acids, one can think at once about the equilibrium between nonpolar dimers and polar monomers. The strong electric field can shift the equilibrium toward the polar monomers, and it gives an increase of the permittivity of solution. However, it is not the case, because the dimerization process is here so efficient that in the concentrated solutions the equilibrium is practically totally shifted toward the nonpolar dimers. In the infrared spectrum of the concentrated solutions of carboxylic acids, there are no traces of the band corresponding to the stretching vibration of the free O−H groups.[16] In such a situation, the nonlinear dielectric spectroscopy can detect the monomer−dimer equilibrium only in very diluted solutions of the hydrogen-bonded compound in nonpolar medium.[17] Unfortunately, for the diluted solutions of carboxylic acids studied, the effect due to the application of the strong electric field was beyond the sensitivity of the set up used.

The nonlinear dielectric spectra presented in Figures 2 and 3 illustrate a quite different molecular organization in mesogenic and nonmesogenic liquids consisting of the molecules of the same structure and polarity. Both of the acids studied are composed of the nonpolar dimers, so the intermolecular (interdimers) interactions are of the same type, resulted from the significant anisotropy of the dimers' polarizability. The difference is in the length of the hydrocarbon tails at the ends of the dimers. The shortest possible tail (−CH₃) in the MCHA molecule makes the compound nonmesogenic. The nonlinear
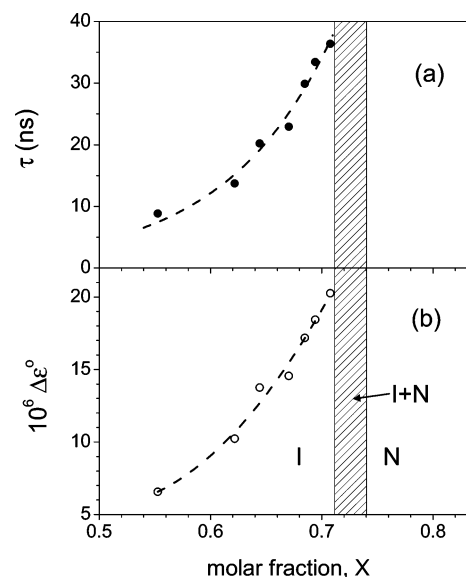

Figure 4. BCHA in cyclohexane molar fraction dependence of the nonlinear relaxation time (a) and the strength of the nonlinear dielectric increment (b), at 25 °C.

dielectric spectra show (Figure 3) that in such a case the interactions lead to formation of the interdimeric entities of partially compensated anisotropy of polarizability which are in equilibrium with the free dimers of MCHA. The strong electric field shifts the equilibrium toward the more anisotropic entities, i.e., the dimers. A great variety of interdimeric entities formed makes the spectrum very broad but with a quite distinct frequency dependence of the real and imaginary parts of the nonlinear dielectric increment. From the spectra presented in Figure 3, one can roughly estimate the frequency maximum (about 10 MHz) corresponding to the kinetics of the formation of the interdimeric entities in the nonmesogenic isotropic liquid composed of the nonpolar, anisotropically polarizable dimers.

On the contrary to the discussed above case of nonmesogenic acid solutions, the nonlinear dielectric spectra of mesogenic BCHA solutions (Figure 2) point out for a quite well organized molecular system, which in the strong electric field relaxes with a well-defined relaxation time. The solid lines in Figure 2 correspond to the best fit of the Debye-type function

$$\Delta\epsilon^* = \Delta\epsilon' - i\Delta\epsilon'' = \frac{\Delta\epsilon^0}{1 + i\omega\tau} \qquad (4)$$

with the single relaxation time (τ). $\Delta\epsilon''$ and $\Delta\epsilon''$ denote, respectively, the real and imaginary parts of the nonlinear dielectric increment, $\Delta\epsilon^0$ denotes the strength of the nonlinear effect, and ω denotes the angular frequency. Both the strength and the relaxation time show a critical-like behavior as the acid concentration approaches to the two-phase (isotropic+nematic) region (Figure 4). One can assume that the nonlinear relaxation observed in BCHA solutions is due to the randomization of the pseudonematic domains. So, as for the solutions of previously studied polar 6CHBT,[8] one can use the eq 1 for determination of the concentration X^* of the virtual transition of the second order, provided the experimental dependence η/τ on molar fraction X is linear. As seen in Figure 5, the dependence is quite good linear and the value of X^* obtained from the extrapolation of η/τ to zero is equal to 0.81. This value of the molar fraction corresponds to the nematic phase of the mixture BCHA + cyclohexane. The next step of the evaluation of experimental data is the determination of the value of the critical exponent
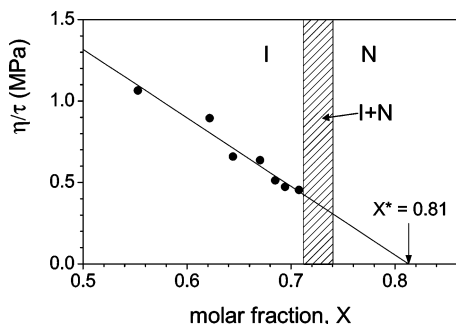
Nonlinear Dielectric Relaxation in Carboxylic Acids

J. Phys. Chem. A, Vol. 107, No. 30, 2003 **5653**

Figure 5. Determination of the virtual molar fraction X^* of nematogenic BCHA dissolved in cyclohexane.
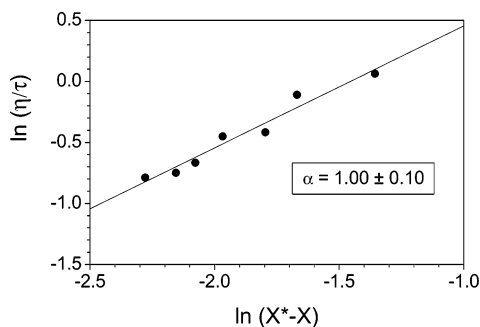

Figure 6. Determination of the critical exponent α for the nonlinear relaxation time dependence on the BCHA concentration in cyclohexane in vicinity of the transition isotropic $-$ two-phase (I $+$ N) region.

α. Predicted by eq 1, the linear relation of $\ln(\eta/\tau)$ vs $\ln(X^* - X)$ is here well fulfilled, as shown in Figure 6. The slope of the line gives for the exponent α the value of 1.0 ± 0.1, which, within the experimental errors, coincides with the value of the critical exponent obtained for polar mesogens both in a pure state and in solutions with the use of the nonlinear dielectric spectroscopy[8,7] and other nonlinear methods.[2,3,11,13,14,18,19]

Conclusions

We presented the results of the nonlinear dielectric studies performed for mesogenic and nonmesogenic compounds composed of the nonpolar rodlike entities (cyclic dimers of carboxylic acids). Two important conclusions result from the studies. (i) The nonlinear dielectric spectroscopy, despite an extremely low strength of the nonpolar system response to an application of the strong electric field, is able to exhibit an essential difference in the molecular organization in mesogenic and nonmesogenic liquids. (ii) The nonpolar mesogenic liquid, in the vicinity of the transition to the nematic phase, manifests the pretransitional dynamic effects which can be interpreted within the same theory, as for strongly polar mesogens. In particular, the critical exponent, corresponding to the nonlinear relaxation time dependence on nonpolar mesogen concentration, has the same value as that determined for temperature and concentration dependence for strongly polar mesogen.

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