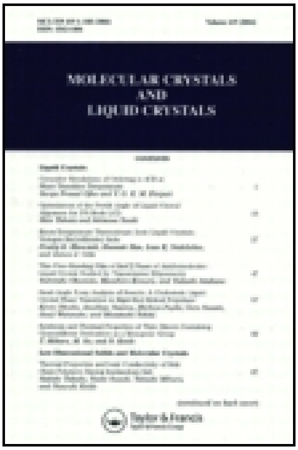

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Molecular Associations in Liquid Crystalline α-Cyanostylbenes

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Molecular Associations in Liquid Crystalline α-Cyanostylbenes

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The results of investigation of molecular association in liquid crystalline α-cyanostylbenes are reported. The dielectric dispersion of α-cyanostylbenes and it solutions doped weakly polar nematic mixture are investigated. The real and imaginary parts of dielectric permitivities $\varepsilon_\parallel$ and $\varepsilon_\perp$ of solutions with several concentrations have been measured in frequency range 1kHz-100MHz. The one dispersion region of $\varepsilon_\parallel$ and $\varepsilon_\perp$ of pure α-cyanostylbenes were observed. In contrast to pure α-cyanostylbenes two separate dispersions of Debye type were found for parallel component of the dielectric permitivity $\varepsilon_\parallel$ for solutions.

Keywords: α-cyanostylbenes; dispersion

An investigation of dielectric properties of the liquid crystalline α-cyanostylbenes (ACS)[1] revealed a dispersion of perpendicular component of the dielectric permitivity $\varepsilon_\perp$ in a frequency range 1,5MHz-30MHz. At the same frequencies a dispersion of parallel component of the dielectric permitivity $\varepsilon_\parallel$ was also observed. An analysis of the experimental data shows that frequency dependencies of both $\varepsilon_\parallel$ and $\varepsilon_\perp$ are described by Debye equations with similar relaxation times. Consequently, a single relaxation mechanism is responsible for these dependencies. It has been established that this mechanism is an exclusion from the dipole polarization of an orientational contribution due to the rotation of the molecules around their long axes. Such a contribution is quantitatively related to the transversal component of the molecular dipole moment. Since the ACS molecules possess significant longitudinal component of the dipole moment $\mu_l=\mu\cos\beta$ (μ=3.8D, β=64°)[1], one can expect to find the second "low-frequency" dispersion region for $\varepsilon_{||}$, which is intrinsic to the polar liquid crystals. This "low-frequency" dispersion is caused by an exclusion from the dipole polarization of the contribution due to the rotation of the molecules around their short axes. As a rule, the "low frequency" dispersion of $\varepsilon_{||}$ occurs at the frequencies one or two order lower than those for both dispersion of $\varepsilon_\perp$ and "high-frequency" dispersion of $\varepsilon_{||}$. For ACS, however, the "low-frequency" dispersion of $\varepsilon_{||}$ has not been found at frequencies ranging down to 0,01 Hz.[2] In addition, a quasistatic value of $\varepsilon_{||}$ appears to be smaller than that calculated in frame work of the theory of dielectric polarization of liquid crystals by using the molecular parameters μ and β[1]. Thus, it has been experimentally established that, for liquid crystalline α-cyanostylbenes, a dipolar contribution to a dielectric polarization along director due to the rotation of the molecules around their short axes is absent. This contribution should be quantitatively related to the longitudinal component of the molecular dipole moment $\mu_l=\mu\cos\beta$. Its absence and, as a result, an absence of the "low-frequency" dispersion of $\varepsilon_{||}$ as well as contradiction between values of $\varepsilon_{||}$ experimentally determined and those calculated by using the molecular parameters μ and β, can be caused by an intermolecular interaction. This interaction can, for example, give rise to compensation of the longitudinal component of the molecular dipole moment by creation of the molecular associations.

In this paper we present the results of an investigation of the dielectric relaxation in solutions of 4-n-hexoxy-4-n-amyl-α-cyanostylbene in a nonpolar LC solvent for different concentrations. A dissolution of ACS in the liquid crystalline solvent allows us to control the interaction between ACS molecules and, changing the concentration, one can vary a character of this interaction preserving simultaneously liquid crystalline state of the solution. It is clear, that such dissolution can make the longitudinal component of the ACS molecular dipole moment to be dielectrically active that should be, in turn, reflected in the frequency dependence of $\varepsilon_{||}$ for ACS solution. In addition, when a nonpolar LC solvent is used, only the ACS molecules contribute to the orientational dielectric polarization of the solution, and molecular mechanisms of the dipole polarization of the solution are the molecular mechanisms of the polarization of ACS.

A mixture of homologues of alkylcyclohexancarbones acids ($\varepsilon_{||}$=2,3; $\varepsilon_\perp$=2,3) has been chosen as a solvent. This investigation of dielectric properties of the ACS solutions have been performed for the samples containing 30%, 50% and 80% of ACS by weight. For these samples, the principal values of both dielectric permitivities $\varepsilon'_{||}$, $\varepsilon'_\perp$ and the dielectric losses $\varepsilon''_{||}$, $\varepsilon''_\perp$ have been measured in the frequency range 1kHz-100MHz in a whole temperature interval of existence of mesophase. The frequency dependencies of $\varepsilon'_{\parallel}$ and $\varepsilon'_{\perp}$ for the 30% ACS solution at the temperature 9°C are shown in Fig.1. In the same figure the dependence of $\varepsilon'_{\parallel}$ on the frequency f is plotted for pure ACS.

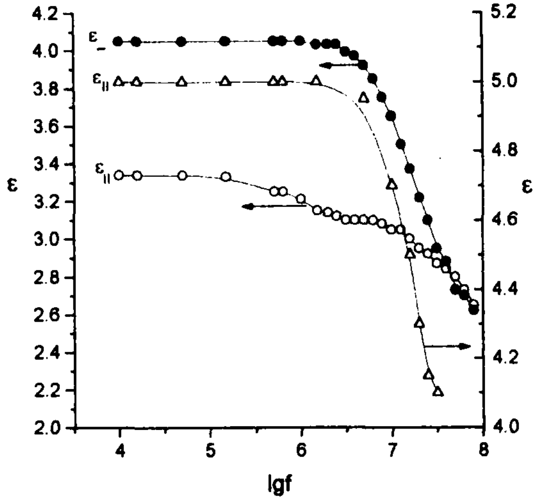

FIGURE 1 Frequency dependence of dielectric permittivities $\varepsilon'_{\parallel}$ - (Δ) for pure ACS at temperature 30°C and $\varepsilon'_{\parallel}$ - (o), $\varepsilon'_{\perp}$ - (•) for solution containing 30% ACS at 9°C.

From Fig.1 it is seen that $\varepsilon'_{\perp}$ has a single dispersion region for the solution. At the same time, unlike the pure ACS, for the ACS solution, the frequency dependence of $\varepsilon'_{\parallel}$ demonstrates two dispersion regions intrinsic to liquid crystals consisting of molecules with nonzero longitudinal and transversal components of the dipole moment. In addition, the "high-frequency" dispersion region of $\varepsilon'_{\parallel}$ occurs in the same interval as the dispersion of $\varepsilon'_{\perp}$. An occurrence of the "low-frequency" region of $\varepsilon_{\parallel}$ in the ACS solution can be considered as an evidence of the rotation of the ACS molecules around their short axes in the liquid crystalline solution. Consequently, the longitudinal component of the dipole moment contributes to the dielectric polarization. An analysis of the dispersion curves has been performed in the way proposed in Ref.[3] by using the relationship

$$\varepsilon'=\varepsilon_0-\tau 2\pi f\varepsilon'', \tag{1}$$

and plotting ε' versus $\varepsilon''\times 2\pi f$ (see Fig.2). One can see that, for 30% ACS concentration at 9°C, the dependence of ε' on $\varepsilon''\times 2\pi f$ can be approximated by two straight lines with different slopes. This fact confirms an existence of two dispersion regions of $\varepsilon_{\|}$ and indicates the Debye character of the relaxation processes. In Fig.2 the dependencies of ε' on $\varepsilon''\times 2\pi f$ for the solutions with 50% ACS (18°C), and 80% ACS (36°C), respectively, are also shown.

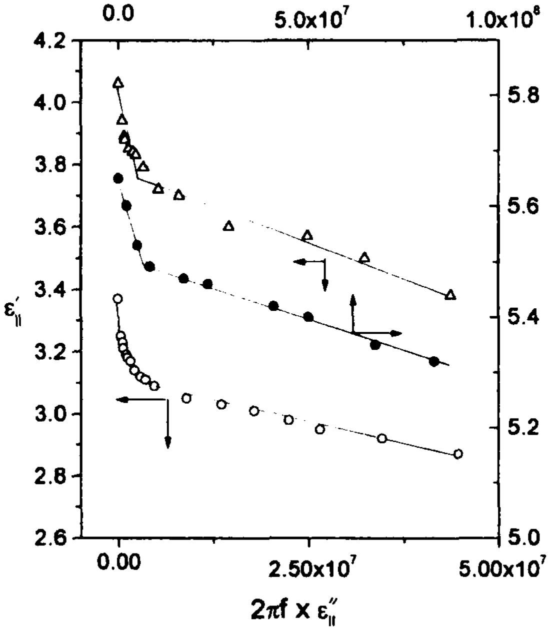

FIGURE 2 Variation of $\varepsilon'_{\|}$ vs. $2\pi f\times\varepsilon''_{\|}$ for ACS solutions: 30% - (o), 50% - (▵), 80% - (●).

It is clearly seen that, for these concentrations, two Debye relaxation processes are also observed. Analogous results have been obtained at different temperatures within an interval of existence of mesophase in the solutions under investigation. Thus, for the investigated frequency range, in the ACS solutions the dispersion of $\varepsilon_{\|}$ is related to two relaxation processes, which can be characterized by the relaxation times $\tau_{\|1}$ ("low-frequency" dispersion of $\varepsilon_{\|}$), and $\tau_{\|2}$ ("high-frequency" dispersion of $\varepsilon_{\|}$), respectively. These relaxation times can be determined from the slope of the dependence of $\varepsilon'_{\|}$ on $\varepsilon''_{\|}\times2\pi f$. In Fig.3, for the 80% ACS solution, the relaxation time $\tau_{\|1}$ is plotted in logarithmic scale versus an inverse temperature.

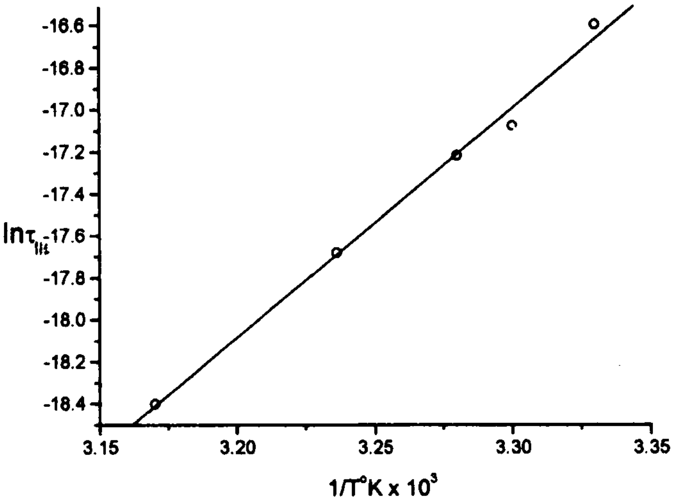

FIGURE 3 Variation of the relaxation time $\tau_{\|1}$ vs. an inverse temperature for 80% ACS solution.

This dependence is linear, and one can determine, according to Arrhenius relationship, an activation energy $U_{\|1}$ of the orientational dielectric polarization due to the rotation of the molecules around their short axes. The value $U_{\|1}$=84 kJ/mole determined in a such way is in a quantitative agreement with corresponding activation energy previously determined for several mesogenic liquids.

On the basis of the above-mentioned experimental results we can come to the following conclusions:

1. A dissolution of ACS in a nonpolar LC solvent gives rise to an appearance of a second ("low-frequency") dispersion region of $\varepsilon_{\parallel}$ which is not observed in the ACS.
2. An occurrence of the "low-frequency" dispersion of $\varepsilon_{\parallel}$ in the ACS solutions means that the ACS molecules, which are dissolved in the liquid crystalline solvent, possess a nonzero longitudinal component of the dipole moment, that is in agreement with results obtained for ACS solutions in the isotropic organic solvent (tetrachlormethan)[1].
3. A dielectric activity of the longitudinal component $\mu\cos\beta$ of the ACS molecular dipole moment, which is observed at the dissolution of ACS in the nonpolar LC-solvent, indicates an occurrence of the intermolecular interaction in ACS which gives rise to a formation of molecular associations with a compensation of the longitudinal component the dipole moment.

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