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Dielectric Relaxation and Viscosity of Mesogenic *n*-Heptylcyanobiphenyl

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Molecular dynamics of *n*-heptylcyanobiphenyl (C_7H_{15}-Ph-Ph-C=N, 7CB) in the isotropic and nematic phases was studied with the use of dielectric spectroscopy. In the measuring frequency range (from 100 kHz to 100 MHz) the absorption band corresponding to the molecular rotation around the short axis dominates in the dielectric spectrum. On the basis of temperature dependences of the relaxation time and the shear viscosity of 7CB, the strength of the nematic potential and the effective length of the rotating 7CB molecule were estimated.

Key words: dielectric relaxation, 7CB, nematic liquid crystal, viscosity

Dielectric relaxation spectroscopy is a very convenient method for studying the molecular dynamics in polar liquids and liquid crystals. The data resulting from the studies may concern both the individual polar molecules, as in diluted solutions in non-polar medium, and the whole molecular aggregates in which the molecules are involved by strong interactions, as in some hydrogen-bonded systems, for example [1]. From the molecular physics point of view, the studies of nematic liquid crystals are of a special interest. The macroscopic orientation of nematic molecules within the whole sample can be achieved by an appropriate preparation of the measuring capacitor electrodes or by applying an external electric or magnetic field. This fact gives a unique opportunity for studies of the molecular dynamics in correlation to the principle axes of the molecules. It was shown in [2], that in the oriented nematic sample the nematogenic molecules rotate around three axes: two of them concern the molecule itself and they are the long and short molecular axes, and the third axis is the direction of the macroscopic molecular orientation – the director **n**. The long and short axes correspond, respectively, to the minimum and maximum of momentum of inertia of the molecule and, of course, they are the axes of molecular rotation on the isotropic phase, too. The dielectric relaxation studies performed for numerous mesogenic com-

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pounds showed [3–10] that the absorption band, corresponding to the molecular rotation around the long axis is, in practice, not sensible to the isotropic to nematic phase transition. The most informative is the behavior of the dielectric absorption band related to the molecular rotation around the short axis. The studies of this type of rotation, performed for mesogenic *n*-heptylcyanobiphenyl molecules, are the subject of the present paper. For the first time in the literature the dielectric relaxation data obtained for the studied compound are interpreted together with the viscosity data, giving important quantities concerning the nematic phase (strength of the nematic potential) and the mesogenic molecule itself (in the isotropic phase).

EXPERIMENTAL

n-Heptylcyanobiphenyl (7CB) was synthesized and purified at the Institute of Chemistry, Military Technical University, Warsaw. The compound exhibits the following sequence of phase transitions: crystal – (30°C) – nematic (N) – (42.9°C) – isotropic (I). The dielectric relaxation spectra were recorded with a HP4194A Impedance/Gain-Phase Analyzer in the frequency range 100 kHz to 100 MHz. A three-electrodes plane capacitor was used and an external biasing d.c. electric field (5 V/0.5 mm) was applied for the nematic ordering. In such a case, the $\varepsilon^*_{||}(\omega)$ dielectric spectrum can be recorded only. The strength of the probing a.c. electric field was 500 mV/0.5 mm. The shear viscosity was measured with a Haake viscometer Rotovisco RV20 with the measuring system CV100. The system consists of the rotary beaker filled with the studied compound and the cylindrical sensor of the Mooney-Evart type (ME15), placed in the center of the beaker. The liquid gap was 0.5 mm. In the available range of the shear rates (30 s^{-1}–300 s^{-1}) 7CB, both the isotropic and nematic phases, exhibit the Newtonian behavior.

RESULTS AND DISCUSSION

Fig. 1 presents the dielectric relaxation spectra recorded in the isotropic and nematic phases of 7CB. As mentioned above, in the nematic phase the measurements were carried out for **E** || **n**. Fig. 2 shows, that the dielectric relaxation spectra of 7CB in the two phases can be perfectly described by Debye formula:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega) = \varepsilon_\infty + \frac{A}{1 + j\omega\tau} \tag{1}$$

where A and τ denote, respectively, the dielectric strength and the relaxation time. ε_∞ is the permittivity measured for so high frequency to prevent the orientational dielectric polarization and often it is taken as the refraction index square. A trace of the dielectric absorption, due to the molecular rotation around the long axis, which can be seen in Fig. 2 (b) in the frequency region around 100 MHz, was neglected in further discussion.

Fig. 3 presents the temperature dependences of the dielectric strength (A) and the relaxation time (τ) for the rotation of 7CB molecules around the short axis in the isotropic and nematic phases. In general, the values of the relaxation time agree with the data obtained previously for 7CB by Davies *et al.* [9], Bose *et al.* [10] and Lippens *et al.* [11]. However, the requirements of high precision in the τ determination, imposed by the procedure of its interpretation together with the viscosity data, were the reasons for the re-measurement of the dynamic dielectric properties of 7CB.

Both A and τ exhibit a jump at the phase transition. The strong increase of the dielectric strength in the nematic phase is due to the alignment effect of the biasing d.c. electric field, causing an increase of the projection of the dipole moment of rotating molecules on the probing (a.c.) electric field direction (the dielectric strength is proportional to the square of the projection). A jump of the relaxation time reflects the appearance of the nematic potential. In principle, the difference in the activation energy for the rotation of mesogenic molecules around the short axis in the isotropic and nematic phases can be a measure of the nematic potential strength, provided the viscosity effect is not too different in both phases.

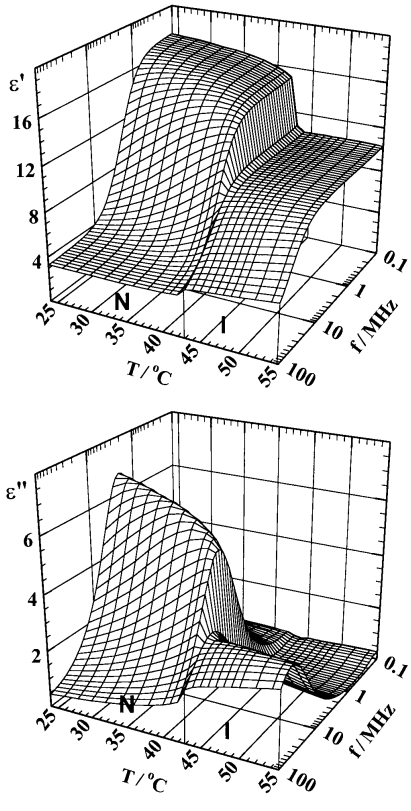

Figure 1. Frequency and temperature dependences of the real (ε') and the imaginary (ε'') parts of the electric permittivity of 7CB in the isotropic and nematic phases. In nematic phase the permittivity $\varepsilon^*_{||}(\omega, T)$ was measured.

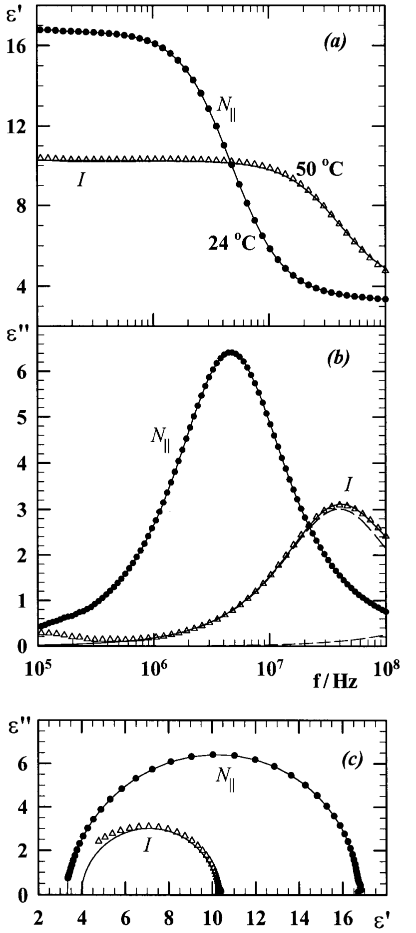

Figure 2. An example of frequency dependence of the real (*a*) and imaginary (*b*) parts of the electric permittivity and Cole-Cole plots (*c*) for 7CB in the isotropic and nematic (**n** || **E**) phases. The solid lines correspond to the Debye-type dependences, see Eq. (1).

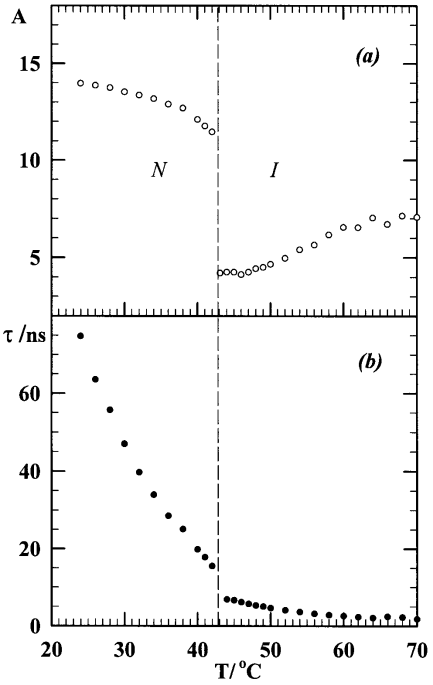

Figure 3. Temperature dependence of the dielectric strength (*a*) and the relaxation time (*b*) corresponding to 7CB molecular rotation around the short axis.

The problem is that the viscosity of nematic liquid crystals is an anisotropic quantity and at least three different viscosity coefficients have to be taken into account, as proposed by Męsowicz [12]. Three Męsowicz shear viscosity coefficients of nematics correspond to three principal mutual orientations of the macroscopic molecular ordering (the director **n**), the flow velocity (**v**) and the velocity gradient (**grad** v) (Fig. 4). In a typical experiment the magnetic field is used for molecular alignment in the nematic sample. One can expect that for strongly elongated mesogenic molecules, the lowest resistance to the nematic flow corresponds to the situation shown in Fig. 4 (b). Indeed, when the ordering magnetic field, *i.e.* the director **n** is parallel to the velocity of the nematic flow, the lowest viscosity (η_2)) is measured. Among two remaining viscosity coefficients, η_1 has the highest value and η_3 is close to the viscosity measured in the isotropic phase of the compound. If one excludes the temperature range in proximity of the isotropic to nematic phase transition, the dependences $\eta_1(T)$, $\eta_2(T)$ and $\eta_3(T)$ are roughly parallel to each other [13–15]. This means that the viscosity activation energies, corresponding to the coefficients η_1, η_2 and η_3, are not too different and for the purpose of our discussion, the temperature behavior of the one of η_i coefficients can be considered as representative for the nematic liquid crystal studied.

Experiment shows that in the absence of external forces, the flow of a nematic liquid crystal (consisting of elongated molecules) causes a molecular orientation, very similar to that presented in Fig. 4 (b). Fig. 5 presents the results of the shear viscosity measurements for freely flowing 7CB in the isotropic and nematic phases. At the temperature of the phase transition, a sharp decrease of the viscosity is observed. It is due to the flow alignment effect [16–20], which leads to the macroscopic alignment of the mesogenic molecules more or less parallel to the velocity **v** and perpendicular to the velocity gradient, so, the viscosity measured in this experiment is close to η_2 Mięsowicz coefficient.

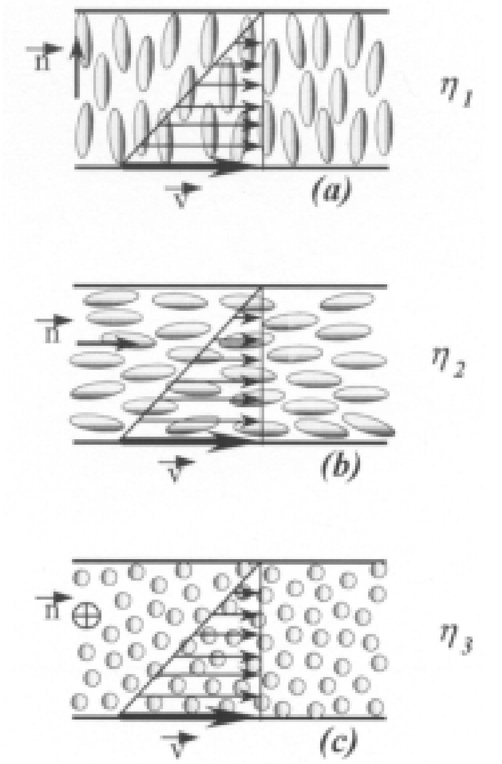

Figure 4. The experimental conditions for measurements of the three Mięsowicz shear viscosity coefficients of nematic liquid crystals: a) **n** ⊥ **v**, **n** || **grad** v; b) **n** || **v**, **n** ⊥ **grad** v; c) **n** ⊥ **v**, **n** ⊥ **grad** v.

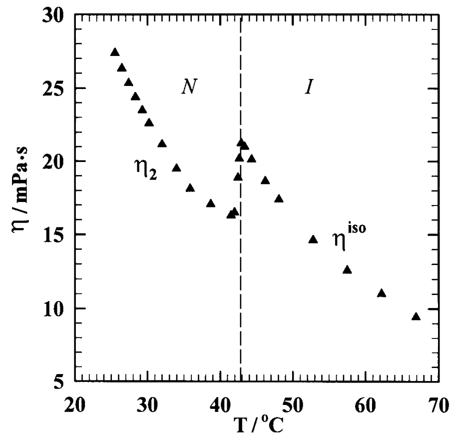

Figure 5. Temperature dependence of the shear viscosity of freely flowing 7CB in isotropic and nematic phases.

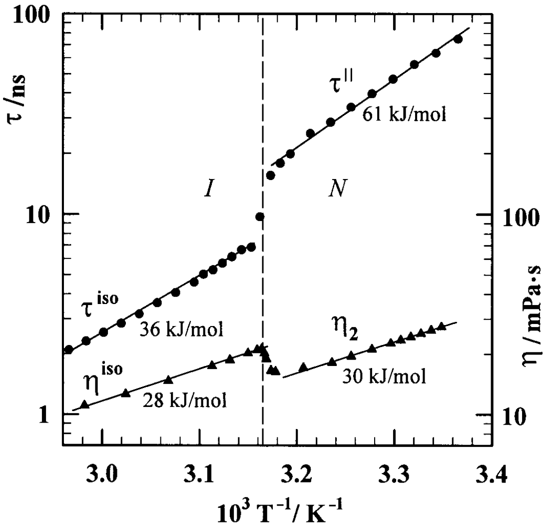

Figure 6. Arrhenius plots for the relaxation time corresponding to the molecular rotation around the short axis and for the shear viscosity of freely flowing 7CB. The values of the activation energy are given in the picture.

Fig. 6 presents the Arrhenius plots for the dielectric relaxation time and the viscosity of 7CB. The important observation concerns the viscosity: both in the isotropic and nematic phases the values of the activation energy are practically the same. Hence, the result allows one to conclude that the difference in the activation energies for the dielectric relaxation time in the nematic and isotropic phases of 7CB is connected mainly to the existence of the nematic potential. As seen in Fig. 6, the strength of the 7CB nematic potential estimated in this way equals 25 kJ/mol. Quite close values of the activation energies of the viscosity and the relaxation time in the isotropic phase (Fig. 6) indicate that the viscosity is the main factor, which determines the dynamics of 7CB molecules in the disordered medium. If so, one can use here the simple hydrodynamic model of Stokes-Einstein-Debye, which links the relaxation time τ and the viscosity η of isotropic liquids [1]:

$$\tau^{\text{iso}} = \frac{\pi \ell^3 \eta^{\text{iso}}}{2kT} \tag{2}$$

where T is the absolute temperature and k is the Boltzmann constant. In the model, the sphere of a diameter ℓ represents a dipolar, rigid and axially symmetric rotating molecule. Fig. 7 shows that the linear relation between $\tau^{\text{iso}}/\eta^{\text{iso}}$ and T^{-1}, predicted by (2), is quite good fulfilled in the case of 7CB. The slope of the linear dependence is proportional to the effective length ℓ of the rotating molecule. For 7CB the molecular length estimated in such a way equals to about 18 Å and is very close to the quantum-chemical estimation (19 Å).

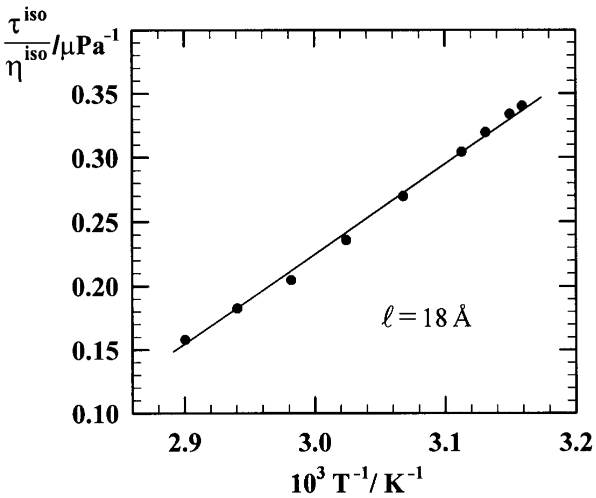

Figure 7. τ/η on T^{-1} dependence for 7CB in the isotropic phase [see Eq. (2)].

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