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MOLECULAR DYNAMICS OF 4-(*trans*-4′-*n*-HEPTYLCYCLOHEXYL)-ISOTHIOCYANATOBENZENE STUDIED WITH DIELECTRIC RELAXATION SPECTROSCOPY

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Dielectric relaxation study was carried out for the nematic and isotropic phases of 4-(*trans*-4′-*n*-heptylcyclohexyl)isothiocyanatobenzene in the frequency range from 100 kHz to 1 GHz. In the nematic phase two relaxation processes were recorded for the electric permittivity component measured parallel to the molecular orientation (director $\boldsymbol{n}$) and three relaxation processes — for the perpendicular permittivity component. The strength of the nematic potential and the nematic order parameter were estimated.

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1. Introduction

A variety of experimental methods have been used to study of molecular motions in liquids and liquid crystals. Among these methods the dielectric relaxation spectroscopy (DRS) seems to be the most convenient one because it probes the motion of any permanent dipole presented in the molecule. Due to its wide frequency ranges DRS gives the possibility to follow the reorientational movements of both dipolar groups and the whole molecules [1, 2].

Relaxation of dielectric materials can be described by means of the complex permittivity

$$\varepsilon^* = \varepsilon'(\omega) - \mathrm{i}\varepsilon''(\omega). \tag{1}$$

The real (ε') and imaginary (ε'') parts of the permittivity are functions of the frequency ω only in the relaxation region.

In liquid crystals the relaxation process is anisotropic. The difference in the dielectric behavior of the components $\varepsilon_{\parallel}^{*}(\omega)$ and $\varepsilon_{\perp}^{*}(\omega)$ measured, respectively, parallel and perpendicular to the direction of the macroscopic molecular orientation (described by the director $\boldsymbol{n}$), can give the additional information about the reorientational processes in comparison to the data obtained in the isotropic phase. For calamitic liquid crystals, if one neglects the librational movements, the molecular dynamics can be described in terms of three following rotational modes [3]: (i) the rotation of the molecule around its short axis (ω_1), (ii) the molecular precessional motion about the director $\boldsymbol{n}$ (ω_2), and (iii) the rotation around long molecular axis (ω_3). The experiment shows that the following relation is fulfilled: $\omega_1 < \omega_2 < \omega_3$. The low-frequency dispersion of $\varepsilon_{\parallel}^{*}$ (at ω_1) is of a special interest. The nematic potential causes the long-range orientational order and hinders the rotation of the molecules around the short axis, so the corresponding relaxation time is significantly longer than that in the isotropic phase. This fact allows one to determine the height of the nematic potential barrier and thus the orientational order parameter from the dielectric data [4–8].

In this work we investigated the dielectric relaxation processes for nematogenic liquid crystal 4-(*trans*-4′-*n*-heptylcyclohexyl)isothiocyanatobenzene (C_7H_{15}–CyHx–Ph–N=C=S, 7CHBT) in a large temperature range, covering the nematic and isotropic phases. Comparing the relaxation time corresponding to the molecular rotation around the short axis in the two phases, the retardation factor, the height of the nematic potential barrier, and the order parameter of 7CHBT as a function of temperature [9] were determined. Additionally, the viscosity and dielectric relaxation activation energies are compared.

2. Experimental

The nematogenic 7CHBT was synthesized and purified at the Institute of Chemistry, Military Academy of Technology, Warsaw. The temperatures of the phase transitions of the compound (Cr 36.9°C N 52.5°C I) are in agreement with the literature data [10].

The measurements of the complex permittivity versus temperature were performed in the frequency range from 100 kHz to 1 GHz. The measuring cell was a plane capacitor located at the end of the coaxial line [11]. Depending on the frequency region, two impedance analyzers HP 4192A (100 kHz ÷ 13 MHz) and HP 4191A (1 MHz ÷ 1 GHz) were used. In the nematic phase the sample was oriented by magnetic field $\boldsymbol{B}$ of about 1 T. The permittivity measurements were performed for two orientations of the measuring electric field $\boldsymbol{E}$ and orienting magnetic field $\boldsymbol{B}$: $\boldsymbol{E} \parallel \boldsymbol{B}$ ($\varepsilon_{\parallel}^{*}$) and $\boldsymbol{E} \perp \boldsymbol{B}$ ($\varepsilon_{\perp}^{*}$). The accuracy of the results was better than 2% for ε' and 5% for ε''. The temperature of the sample was stabilized within ±0.1°C.

The viscosity was measured with a Haake viscometer Rotovisco RV20 with the measuring system CV100; the shear rate was 140 s^{-1}. The system consists of the rotary beaker filled with the substance investigated and the cylindrical sensor of the Mooney–Evart type (ME15), placed in the centre of beaker. The gap for the substance was 0.5 mm.

3. Results

We measured the dielectric properties of 7CHBT over the temperature range between 90°C and 35°C. Figures 1a and b present the typical frequency dependence of the real (ε') and imaginary (ε'') parts of the electric permittivity, whereas Fig. 1c shows plots of ε'' versus ε' (Cole–Cole plots) for 7CHBT in the nematic and isotropic phases. It is seen that in the nematic phase the most dominant dielectric relaxation process occurs in the low frequency range (several MHz) and is observed distinctly in the parallel component of the electric permittivity.

In order to determine the relaxation times connected with all the relaxation processes, it is necessary to resolve the recorded spectra into elementary components. We used the empirical Cole–Cole formula [12]:

$$\varepsilon'(\omega) = \varepsilon_\infty + \sum_{i=1}^{3} A_i \frac{1}{1+(\omega^2\tau_i^2)^{1-k_i}}, \tag{2a}$$

$$\varepsilon''(\omega) = \sum_{i=1}^{3} A_i \frac{\omega\tau_i}{1+(\omega^2\tau_i^2)^{1-k_i}}, \tag{2b}$$

where A_i is the dielectric strength and τ_i is the relaxation time, related to a given relaxation process. Parameter k_i characterizes the distribution of the relaxation times and reduces to 0 for the processes described by the Debye equation [13]. A_i, τ_i and k_i are the adjustable parameters in the fitting of Eqs. (2) to the experimental data. The fitting was made by using the least squares method.

Figure 2 shows the examples of the best fitting of Eqs. (2a) and (2b) to the experimental points, presented in the form of the Cole–Cole plots. It was found that the k_i ($i = 1, 2, 3$) parameters were equal to about 0.01, which means that all the relaxation processes occurring in the dielectric spectrum of 7CHBT can be considered as the Debye-type. Similar results were previously found for other liquid crystals [14, 15]. The values of A_i and τ_i resulting from the resolution of the experimental spectra into elementary contributions are presented in Fig. 3, as a function of the temperature.

Knowing the relaxation times in the nematic and isotropic phases for the process corresponding to the molecular rotation around the short axis (ω_1) one can determine the orientational order parameter of 7CHBT as a function of temperature using the theory proposed by Martin et al. [9, 16]. According to the theory, the relaxation time in the presence of the nematic potential (τ_1) is longer than that in the absence of the nematic potential (τ_0) by a factor

$$g = \frac{\tau_1(q \neq 0)}{\tau_0(q = 0)}, \tag{3}$$

called the retardation factor. Here q is the height of the nematic potential barrier and τ_0 is the value of the relaxation time extrapolated from the $\tau_1(T)$ dependence in the isotropic phase to a given temperature in the nematic phase.

According to the Maier–Saupe mean field theory [17], the nematic potential can be presented in the following form:

$$U(\Theta) = qP_2(\cos\Theta), \tag{4}$$

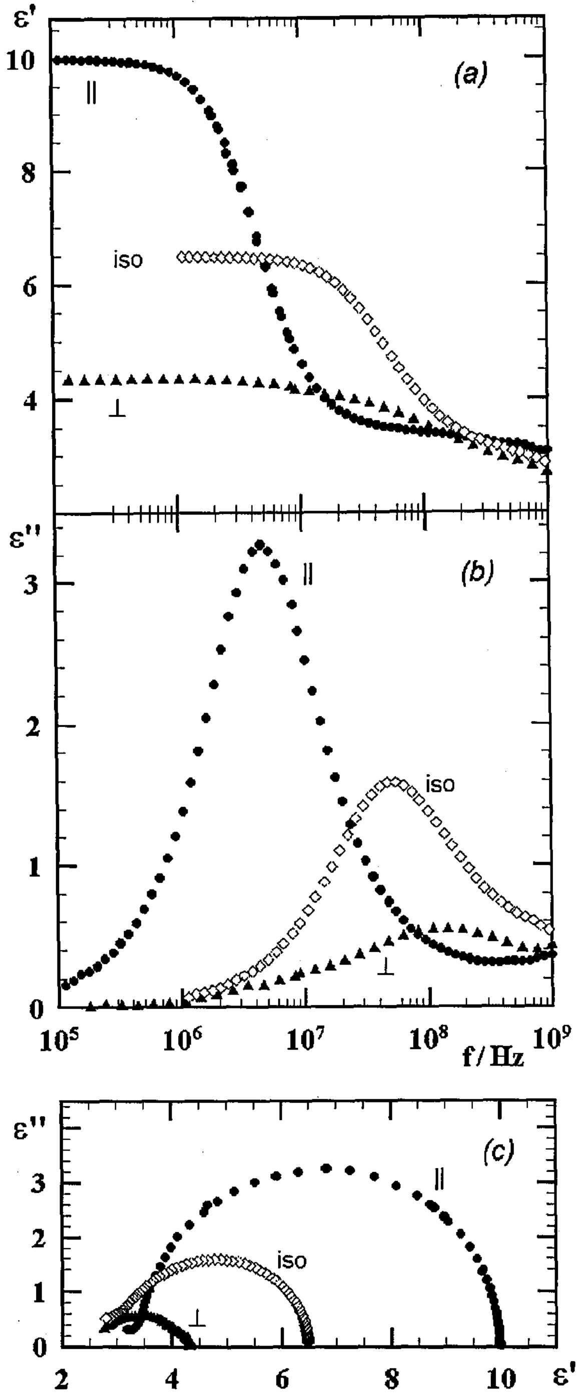

Fig. 1. Experimental results of measurements of the complex electric permittivity as a function of the frequency for 7CHBT in the nematic ($T = 45°C$) and isotropic ($T = 60°C$) phases: (a) real part of permittivity, (b) imaginary part, (c) Cole–Cole plots.

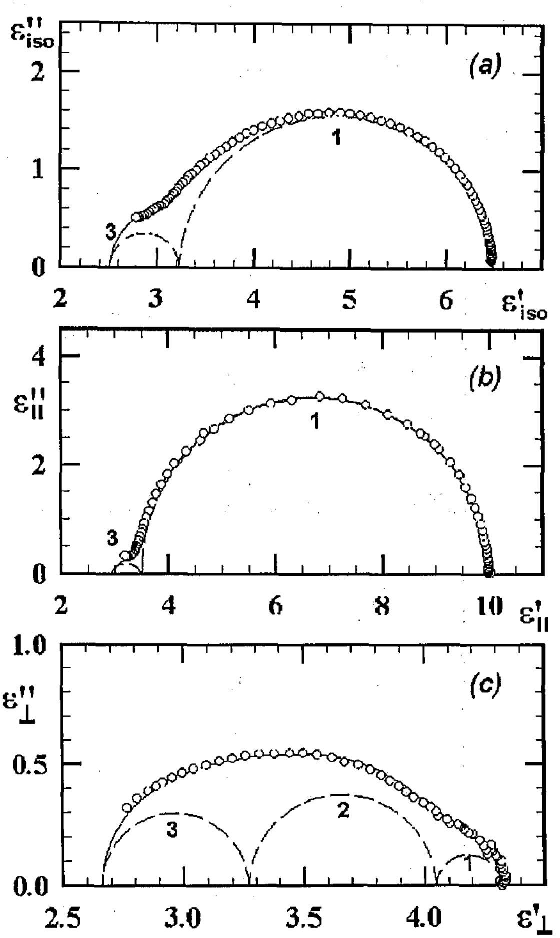

Fig. 2. The dashed lines represent the elementary contributions to the total dielectric absorption corresponding to the different modes of the molecular rotation in the isotropic (a) and nematic (b, c) phases of 7CHBT. The numbers of semicircles correspond to the frequency ω_1, ω_2 and ω_3, respectively.

where $P_2(\cos\Theta)$ is the second Legendre polynomial and Θ is the angle between the long molecular axis and the director n.

The long-range orientational order is defined as the averaged second Legendre polynomial

$$\langle P_2(\cos\Theta)\rangle = \left\langle \frac{3}{2}\cos^2\Theta - \frac{1}{2}\right\rangle = \frac{\int_0^{\pi/2}\left(\frac{3}{2}\cos^2\Theta - \frac{1}{2}\right) f(\Theta)\sin\Theta \mathrm{d}\Theta}{\int_0^{\pi/2} f(\Theta)\sin\Theta \mathrm{d}\Theta}, \tag{5}$$

where the angular bracket means the averaging over the all possible positions of the molecules in the time and the space. Here $f(\Theta)$ is the undisturbed distribution function of the nematic order and can be presented in the following form [9, 16]:

$$f(\Theta) = f(0)\exp\left(-\frac{q}{kT}\sin^2\Theta\right). \tag{6}$$

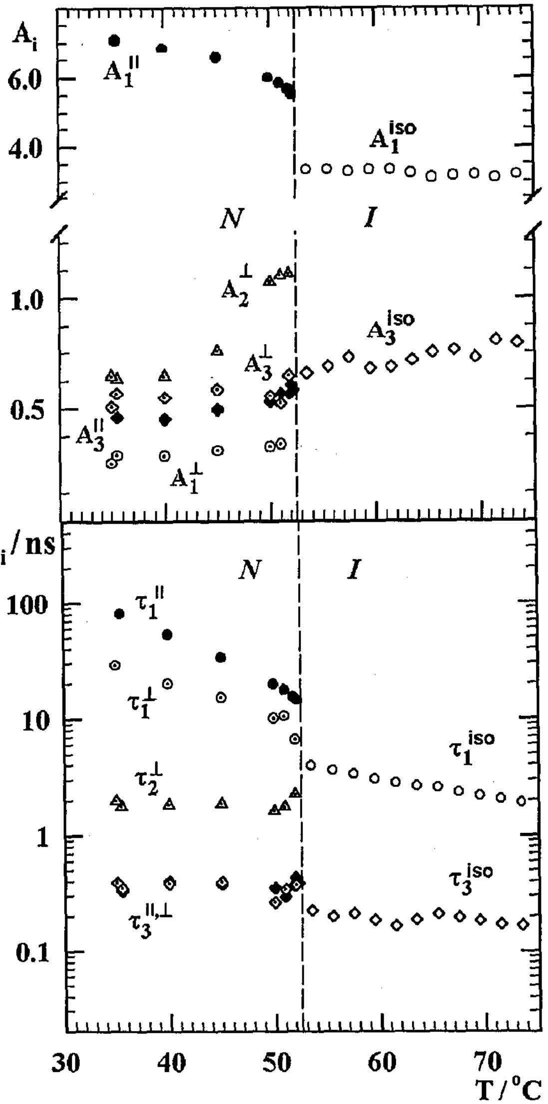

Fig. 3. Temperature dependence of the dielectric strengths and relaxation times corresponding to the different modes of rotation of 7CHBT molecules in the nematic and isotropic phases.

On the basis of the retardation factor g value, the height of the potential barrier can be determined using the method proposed by Martin et al. [9]. The values of τ_0, g, and q for 7CHBT at various temperatures are gathered in Table. Figure 4 shows the order parameter $\langle P_2 \rangle$, calculated from Eqs. (5) and (6), as a function of reduced temperature $T^* = T/T_{\mathrm{NI}}$, where T_{NI} is the nematic to isotropic phase transition temperature. The solid line in the figure represents the temperature dependence of $\langle P_2 \rangle$ resulting from Maier–Saupe theory [17].

TABLE

Relaxation time τ_0, retardation factor g and height of the potential barrier q for rotation around the molecular short axis for 7CHBT.

T [°C]	τ_0 [ns]	g	q	
			[eV]	[kJ/mol]
35.0	7.69	10.55	0.121	11.66
39.5	6.43	8.32	0.111	10.66
44.5	5.31	6.36	0.102	9.84
49.5	4.41	4.55	0.088	8.52
50.5	4.25	4.14	0.085	8.21
51.3	4.13	3.72	0.077	7.42
51.5	4.10	3.68	0.076	7.29
51.7	4.07	3.54	0.074	7.09

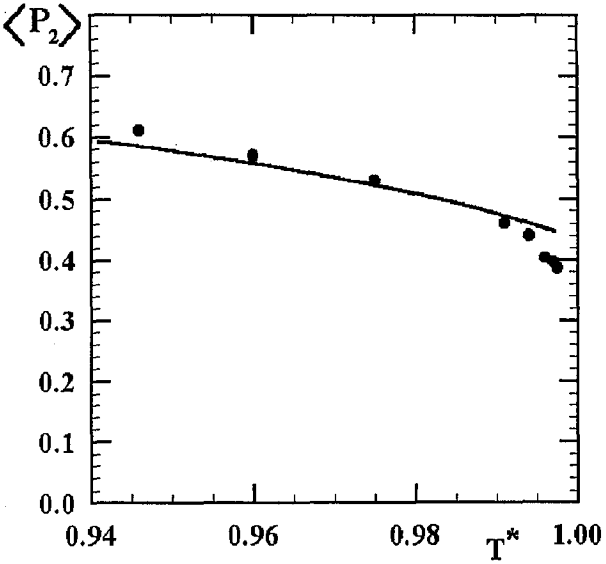

Fig. 4. Temperature dependence of the order parameter $\langle P_2 \rangle$ for 7CHBT. Solid curve corresponds to the Maier–Saupe theory [17].

Figure 5 presents the shear viscosity versus temperature measured in the isotropic and nematic phases of 7CHBT. At the isotropic to nematic phase transition a sharp decrease in the viscosity occurs, which is connected with the alignment of the long molecular axes parallel to the flow velocity direction. Thus, the viscosity coefficient measured in our experiment in the nematic phase is close to the Mięsowicz η_2 viscosity coefficient [18].

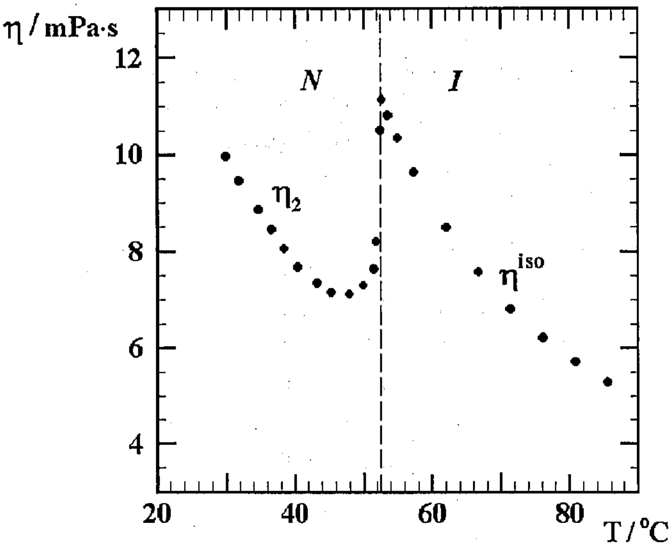

Fig. 5. The shear viscosity measured in the isotropic and nematic phase of 7CHBT.

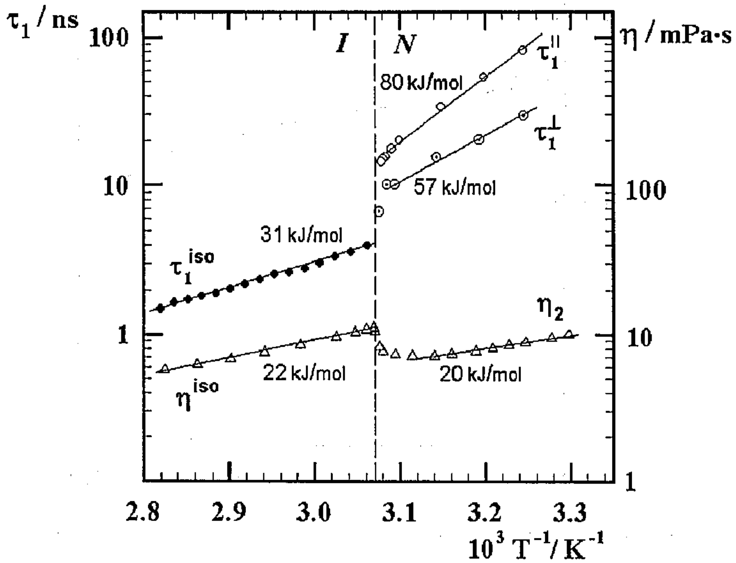

Fig. 6. Arrhenius plots for the relaxation time τ_1 and the viscosity of 7CHBT.

Figure 6 shows the Arrhenius plots for the viscosity coefficient and the relaxation time τ_1 for 7CHBT in the nematic and isotropic phases. The values of the corresponding activation energy are given in the figure.

4. Discussion

The dielectric anisotropy $\Delta\varepsilon$ of 7CHBT in the static fields is positive and relatively large ($\Delta\varepsilon = 5.5$ at 40°C), which indicates that the longitudinal component of the permanent dipole moment is significantly higher than the transverse one.

In the parallel component of the electric permittivity $\varepsilon^*_{\|}(\omega)$ only two relaxation processes (at ω_1 and ω_3) are observed. The lack of the contribution from the process at ω_2 is rather exceptional [14] and suggests that the orientation of 7CHBT molecules, resulting from the acting of two factors: the magnetic field $\boldsymbol{B}$ and the surfaces anchoring forces, gives (accidentally) the zero perpendicular dipole moment component to the measuring electric field $\boldsymbol{E}$ direction. In the isotropic phase the processes at ω_1 and ω_3 are found. The dielectric strength $A_1^{\|}$ is significantly higher than A_1^{iso} and decreases with the rise of temperature. The relaxation time $\tau_1^{\|}$ behaves similarly, which indicates the strong effect of the nematic potential on the rotation of the permanent dipole moment around the molecular short axis. The relaxation strength $A_3^{\|}$ is very small in comparison to $A_1^{\|}$ and its magnitude is of the order of A_3^{iso}. The relaxation time $\tau_3^{\|}$ remains constant within the experimental uncertainties over the whole temperature range of the nematic phase, because the rotation around the long axis is not influenced by the nematic order.

In the detailed analysis of the dielectric data for the perpendicular component of the permittivity it should be always realized that we are dealing with relatively small amplitude of the dielectric response of the system. Nevertheless, the occurrence of the three relaxation processes in $\varepsilon^*_{\perp}(\omega)$ spectrum is doubtless. The magnitude and the temperature dependence of the dielectric strengths and the relaxation times are in agreement with the relaxation model proposed previously [3, 14].

The temperature dependence of the order parameter $\langle P_2 \rangle$ of 7CHBT (Fig. 4) obtained on the basis of the relaxation times $\tau_1^{\|}$ and τ_1^{iso} is very close to that resulting from the Maier–Saupe theory [17]. With the increasing temperature $\langle P_2 \rangle$ decreases and drops to zero at the transition to the isotropic phase. The liquid crystal 7CHBT has a very good orienting ability ($\langle P_2 \rangle \approx 0.57$ at 40°C), which means that together with the relatively large dielectric anisotropy, the compound can be useful in the liquid crystal mixtures of practical significance.

The activation energy for the rotational movement of the molecule around its short axis obtained from $\tau_1^{\|}$ is greater than that determined from $\tau_1^{\perp}$ (see Fig. 6). Similar result was obtained for 6CHBT [14] and it was explained in terms of the additional coupling between the permanent dipole moment of the rotating molecule and the probing electric field for $\boldsymbol{E} \parallel \boldsymbol{n}$.

Figure 6 shows that the viscosity activation energy both in the nematic and isotropic phases is approximately of the same value, which means that the nematic order does not significantly influence the dynamics of the viscous flow of the liquid crystal 7CHBT. The difference between the activation energy determined from $\tau_1^{\text{iso}}(T)$ with respect to that obtained from $\eta^{\text{iso}}(T)$ seems to suggest that although in the isotropic phase the main factor determining the molecular motion is the

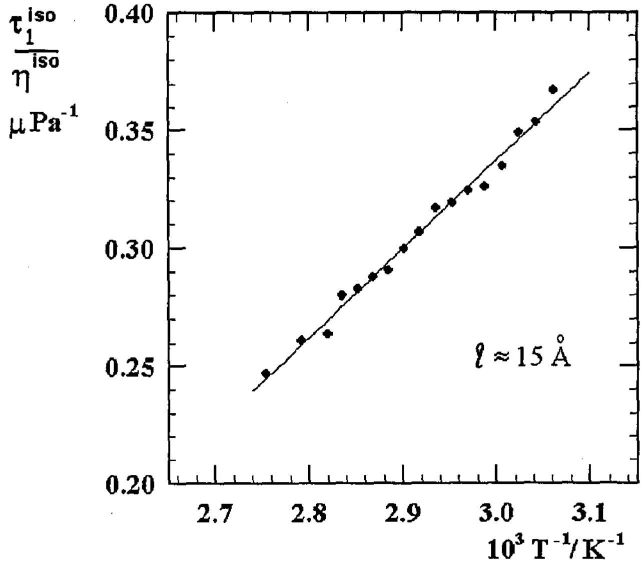

Fig. 7. Ratio $\tau_1^{\text{iso}}/\eta^{\text{iso}}$ as a function of the temperature reciprocal corresponding to the Debye model (Eq. (7)). ℓ denotes the apparent length of 7CHBT molecule rotating around its short axis.

viscosity, also other factors can play some role. Such a factor may be, for example, the short-range orientational order of polar molecules.

The data of $\tau_1^{\text{iso}}(T)$ and $\eta^{\text{iso}}(T)$ obtained for the isotropic phase of 7CHBT can be used for the evaluation of the length of the nematogen molecule in the frame of the Debye model [13]. In the model, the sphere of a radius a represents the rotating dipolar, rigid and axially symmetric molecule of an effective length $\ell = 2a$. The relation between the dielectric relaxation time, corresponding to the molecular rotation around its short axis, and the viscosity of the medium in which the sphere are moving, has a following form:

$$\tau_1^{\text{iso}} = \frac{4\pi\eta^{\text{iso}}a^3}{kT}, \tag{7}$$

where k is the Boltzmann constant and T is the absolute temperature. The slope of the dependence $\tau_1^{\text{iso}}/\eta^{\text{iso}}$ on T^{-1} is proportional to a^3. As can be seen in Fig. 7, the dependence is quite good in linearity and the slope gives a reasonable value $\ell \approx 15$ Å for the effective length of the 7CHBT molecule.

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