Shear Viscosity of the Homologous Series of *n*CHBT ($n = 0 \div 12$) in the Isotropic and Nematic Phases

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The paper presents results of shear viscosity measurements performed on nematogenic 4-(*trans*-4′-*n*-alkylcyclohexyl)isothiocyanatobenzenes (C_nH_{2n+1}–CyHx–Ph–N=C=S, *n*CHBT) in the isotropic ($n = 0 \div 12$) and nematic ($n = 4 \div 12$) phases. The viscosity measured in the nematic phase is, due to the flow alignment phenomenon, close to the Męsowicz η_2 viscosity coefficient. An odd-even effect in the *n* dependence of the viscosity-activation energy is observed both in the nematic and isotropic phases of *n*CHBT.

Key words: Shear Viscosity, *n*CHBT, Isotropic Phase, Nematic Phase.

1. Introduction

The transport processes in fluids are intensively studied by computer simulation using non-equilibrium molecular dynamics [1–6]. The majority of these papers deals with the momentum transfer because this phenomenon contains the most essential features of the process. From the macroscopic point of view, the momentum transfer can be described by the shear viscosity.

The paper presents the shear viscosity measurements performed on thirteen members of the *n*CHBT homologous series ($n = 0 \div 12$). The influence of the molecular length on the viscosity of the liquids composed of molecules of the same polarity and the same structure is shown.

2. Experimental

The compounds *n*CHBT, $n = 0 \div 12$, were synthesized and purified at the Institute of Chemistry, Military University of Technology, Warsaw. The compounds are nematogenic for $n \geq 2$; for $n = 2$, 4 and 5 the nematic phase is monotropic [7]. Figure 1 presents the *n* dependence of the nematic to isotropic phase transition temperature (T_{NI}) of *n*CHBT. The melting points of the compounds are also shown in the picture.

The viscosity was determined with a Haake viscometer Rotovisco RV 20 with the measuring system CV 100, the share rate being 275 s^{-1}. The measuring system consists of a rotary beaker filled with a cylindrical sensor of the Mooney-Ewart type (ME 15), placed in the centre of the beaker. The liquid gap was 0.5 mm. The accuracy of the viscosity determination was $\pm 5 \cdot 10^{-2}$ mPa · s.

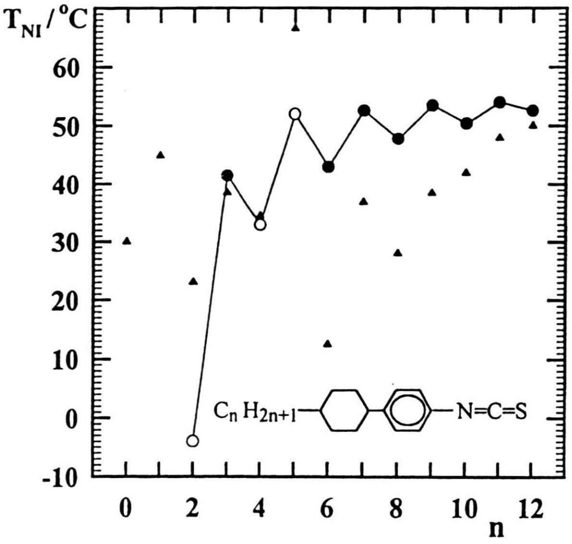

Fig. 1. The *n* dependence of the nematic (N) to isotropic (I) phase transition temperature of the homologous series *n*CHBT. The transition is monotropic for $n = 2$, 4 and 5. The triangles denote the melting points.

3. Results and Discussion

Figure 2 presents the temperature dependence of the viscosity measured in the isotropic phase of *n*CHBT. In Fig. 3 these results are presented in the form of Arrhenius plots. Two conclusions can be derived from the data: *i*) at constant temperature the viscosity depends monotonously on the *n* number, i.e. on the length of the molecules; *ii*) for a given *n* the temperature dependence of the viscosity shows the activation character, i.e.

$$\eta(T) = \eta_0 \exp(E_A/RT)\,. \tag{1}$$

At the isotropic to nematic phase transition temperature the viscosity decreases abruptly as shown in Figure 2.

For anisotropic liquids (like nematic liquid crystals) in flow, two phenomena are typical: *i*) the viscosity is anisotropic and *ii*) the flow brings about a molecular alignment [8].

The anisotropy of the viscosity of nematic liquid crystals results from the possibility of different mutual orientations of the director $\boldsymbol{n}$, the velocity of the flow $\boldsymbol{v}$ and the velocity gradient $\boldsymbol{grad}v$. Figure 4 shows the three principal orientations of these vectors, as proposed by M. Męsowicz [9]. According to this picture, three indepen-

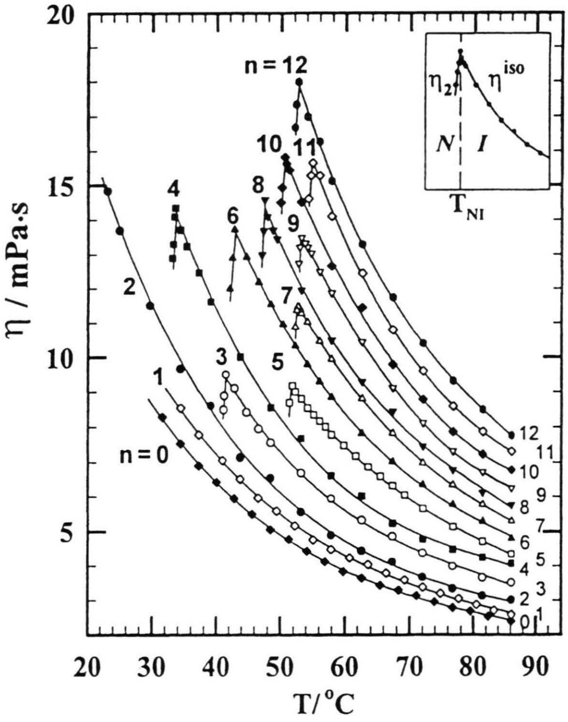

Fig. 2. The temperature dependences of the viscosity of *n*CHBT ($n = 0 \div 12$) in the isotropic phase. A sharp decrease of η is observed at the isotropic (I) to nematic (N) phase transition (see insert).

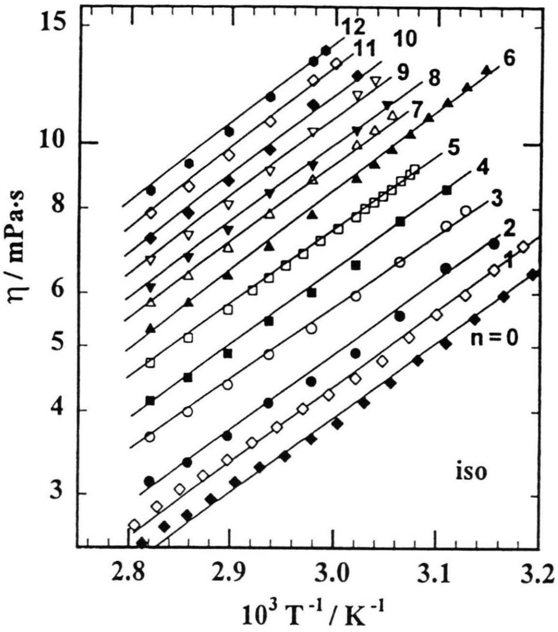

Fig. 3. Arrhenius plots for the viscosity of *n*CHBT ($n = 0 \div 12$) in the isotropic phase.

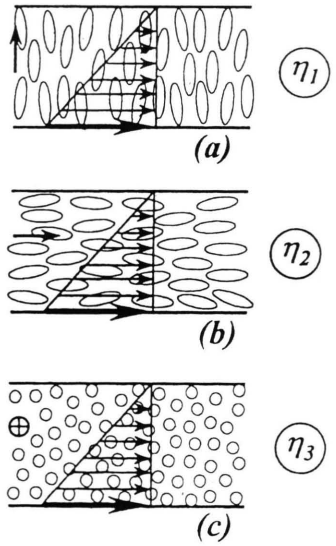

Fig. 4. The experimental conditions for measurements of the three Męsowicz shear viscosity coefficients in the nematics: a) $\boldsymbol{n} \perp \boldsymbol{v}$, $\boldsymbol{n} \parallel \boldsymbol{grad}v$; b) $\boldsymbol{n} \parallel \boldsymbol{v}$, $\boldsymbol{n} \perp \boldsymbol{grad}v$; c) $\boldsymbol{n} \perp \boldsymbol{v}$, $\boldsymbol{n} \perp \boldsymbol{grad}v$.

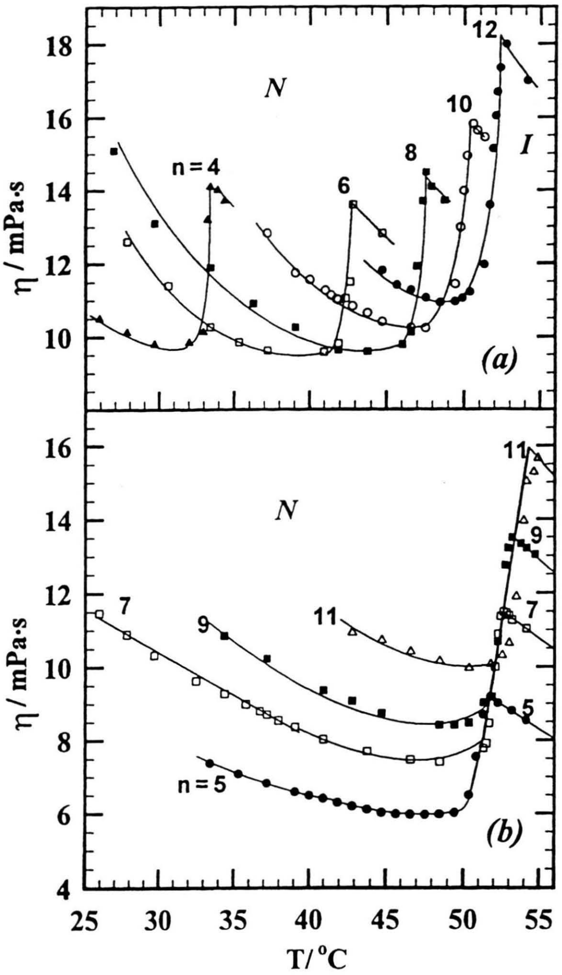

Fig. 5. The temperature dependences of the viscosity measured in the nematic phase of *n*CHBT with even (a) and odd (b) number *n*. In the vicinity of the N-I transition, the viscosity of the isotropic phase is marked (see insert in Fig. 2).

dent shear viscosities can be measured, provided an external orienting force (magnetic field, for example) can be applied to the nematic sample in the three perpendicular directions. For nematics consisting of elongated molecules the following inequalities hold:

$$\eta_2 < \eta_3 < \eta_1 \, , \qquad (2)$$

with an exception of the nematic to smectic A pretransitional region [10, 11].

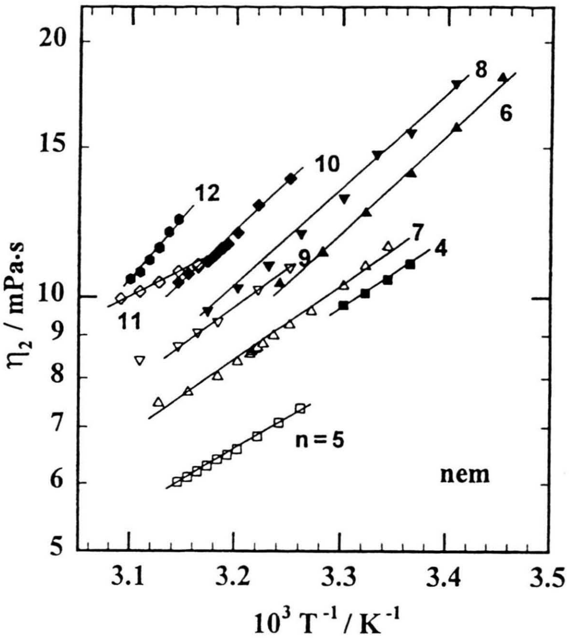

Fig. 6. Arrhenius plots for the viscosity coefficient η_2 measured in the nematic phase of *n*CHBT ($n = 4 \div 12$).

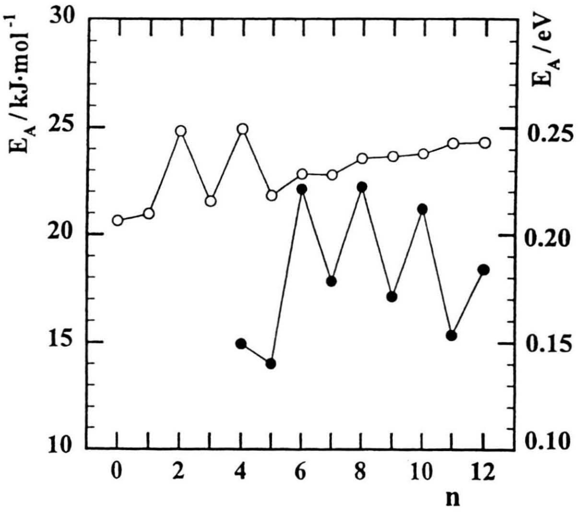

Fig. 7. The odd-even effect in the viscosity activation energy for the isotropic and nematic phases of *n*CHBT. ○: iso; ●: nem.

It has been shown many years ago [8] that in the absence of external forces the flow of a nematic consisting of elongated molecules causes a molecular orientation very similar to that presented in Figure 4b. This flow-aligning corresponds to the minimal viscosity. However, the final molecular alignment due to the nematic steady shear flow must fulfil the condition of vanishing of the torque at the

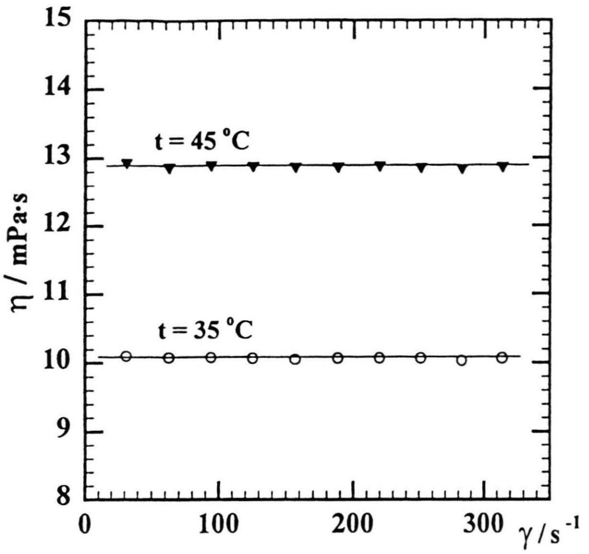

Fig. 8. The newtonian behaviour of 6CHBT in the isotropic and nematic phases. γ denotes the shear rate (velocity gradient). ▼: iso; ○: nem.

director ***n***. The torque vanishes for a specific angle φ between the flow direction ***v*** and the director ***n*** [12]. As can be seen in Fig. 4b, the angle φ for the determination of η_2 is zero. Therefore, the viscosity coefficient measured for freely flowing nematics is only close to the η_2 Mięsowicz coefficient [13] and the interpretation and the conclusions should be considered here with care.

Figures 5 and 6 present the temperature dependences of the viscosity measured in the nematic phase of *n*CHBT. If one omits the temperature region of a few degrees below the transition to the nematic phase, the viscosity η_2 shows the activation behaviour presented in Figure 6. However, for most of the *n*CHBT's the temperature range of the existence of the nematic phase is too short for the verification of this type of η_2 (T) dependence.

Figure 7 presents the *n* dependence of the viscosity activation energy for *n*CHBT calculated according to (1). The odd-even effect and the quite reasonable values of the activation energy seem to confirm the activation behaviour of the Arrhenius type of the viscosity of the series of *n*CHBT both in the isotropic and nematic phases.

Within the available range of the shear rate ($30 \div 320$ s^{-1}), the studied compounds show the newtonian behaviour, i.e. the viscosity does not depend on the velocity gradient both in the isotropic and nematic phases. As an example, Fig. 8 presents the newtonian behaviour of 6CHBT in the two phases.

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