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Shear viscosity of nematic liquid crystals in the vicinity of the smectic-*A* phase in alkyloxycyanobiphenyl mixtures

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The paper presents a singular temperature behavior of the shear viscosity measured for freely flowing nematic liquid crystals in vicinity to smectic-*A* phase in *n*-octyloxycyanobiphenyl and *n*-hexyloxycyanobiphenyl mixtures—a system exhibiting the reentrant nematic phase.

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I. INTRODUCTION

In a recent paper [1] we presented the results of the shear viscosity measurements performed for freely flowing (i.e., without external ordering forces) mesogenic compounds of different polymorphism: *n*-hexyloxycyanobiphenyl ($C_6H_{13}O$ Ph Ph CN, 6OCB) with the simplest possible sequence of phase transitions: isotropic–nematic–crystal, and *n*-octyloxycyanobiphenyl ($C_8H_{17}O$ Ph Ph CN, 8OCB) with the isotropic–nematic–smectic-*A* (I–N–S_A)–crystal transitions. Essentially different temperature behavior of the viscosity measured in nematic phase of the compounds, collated with the Miesowicz viscosity coefficients, was the basis for formulation of a simple principle connecting the fluid flow with its viscosity: *a free fluid adopts such a manner (or way) of flow, that corresponds to the minimum of its viscosity at given conditions* [1].

The Miesowicz shear viscosity coefficients [2] correspond to the nematic liquid crystal flow with different mutual orientations of three vectors: the macroscopic molecular ordering, which usually is forced by magnetic field, (the director **n**), the flow velocity (**v**), and the velocity gradient. For elongated mesogenic molecules, the lowest resistance for the nematic flow, i.e., the lowest viscosity value, is expected for $\mathbf{n} \parallel \mathbf{v}$. Indeed, when the orienting magnetic field is parallel to the nematic flow velocity, the lowest viscosity (η_2) is recorded. Among the two remaining viscosities, η_1 is the highest and η_3 is close to the viscosity measured in the isotropic phase of the compound studied.

In case of *freely flowing nematics*, the viscosity measurements give, according to the principle of the viscosity minimum, the values very close to η_2 Miesowicz coefficient, as shown in Fig. 1(a) for 6OCB.

The above picture of the nematic viscosity is strongly disturbed for compounds exhibiting the transition from the nematic to smectic-*A* phase [3–5], as 8OCB. Due to the presmectic effects, the η_2 viscosity goes to infinity at the nematic to smectic-*A* transition. Because η_1 and η_3 viscosities are practically unaffected by the transition to smectic *A* phase, the viscosities $\eta_2(T)$ and $\eta_3(T)$ intersect themselves a few degrees before the transition.

Such a case is presented in Fig. 1(b), where the results of $\eta_2(T)$ and $\eta_3(T)$ measurements performed for 8OCB with the use of the orienting magnetic field [3] are compared with the viscosity measured for freely flowing 8OCB (full points) [1]. The results clearly show that at about 72 °C, the freely flowing nematic 8OCB changes the manner of flow from that corresponding to η_2 ($\mathbf{n} \parallel \mathbf{v}$) to that corresponding to η_3 ($\mathbf{n} \perp \mathbf{v}$). In brief, at a given temperature the flow of 8OCB is related to the minimum of its viscosity.

In Fig. 1(b) and in the following figures, the temperature range where the viscosity of freely flowing nematic liquid crystal (N) corresponds to η_2 Miesowicz coefficient is, in short, denoted as N_2 and that of η_3 as N_3.

The subject of this paper is the mixtures of 8OCB and

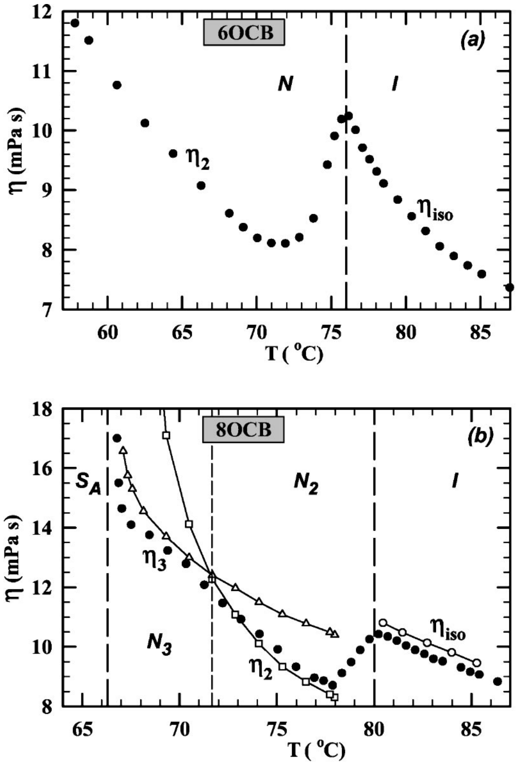

FIG. 1. Temperature dependence of the shear viscosity measured for free flow of isotropic (I) and nematic (N) phases of 6OCB and 8OCB. In (b) the open points present the η_2 and η_3 Miesowicz viscosities measured by Graf *et al.* [3] for the sample oriented with magnetic field.

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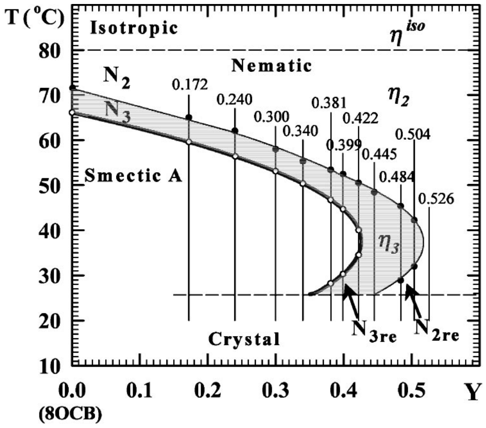

FIG. 2. The phase diagram for 8OCB/6OCB mixtures. Y denotes the molecules ratio $N_{6\mathrm{OCB}}/N_{8\mathrm{OCB}}$. The viscosity was measured for Y values marked in the diagram. The area of the anomalous behavior of the nematic shear viscosity (presmectic effects) is marked in gray.

6OCB—a classical system, already, which exhibits the phenomenon of reentrance of the nematic phase [6–17].

II. EXPERIMENT

n-hexyloxycyanobiphenyl (melting point $= 58\,^\circ\mathrm{C}$, the transition from the nematic to isotropic phase at $T_{NI} = 76\,^\circ\mathrm{C}$) and n-octyloxycyanobiphenyl (melting point $= 54.5\,^\circ\mathrm{C}$, the transition from the smectic A to nematic phase at $T_{S_AN} = 66\,^\circ\mathrm{C}$ and $T_{NI} = 80\,^\circ\mathrm{C}$) were synthesized and purified at the Institute of Chemistry, Military University of Technology, Warsaw. The purity of the compounds, checked by the chromatography, was 99.9%.

The viscosity was measured with a Haake viscometer RV 20 with the measuring system CV 100. The system consists of a rotary beaker filled with the studied liquid and a cylindrical sensor of Mooney-Ewart-type, placed in the center of the beaker. The liquid gap was 0.5 mm. The accuracy of the viscosity determination was 0.5%. In the available range of the shear rates $30\ \mathrm{s}^{-1}--300\ \mathrm{s}^{-1}$ the nematics studied show a Newtonian behavior. The temperature of the sample was controlled with an accuracy of $0.1\,^\circ\mathrm{C}$.

III. RESULTS AND DISCUSSION

Figure 2 presents the phase diagram for 8OCB and 6OCB mixtures. The following features of the diagram are the most important. The addition of 6OCB molecules to 8OCB manifests itself in a decrease of the nematic to smectic-A phase transition temperature. Since the transition from the isotropic to nematic phase in pure 6OCB and 8OCB occurs at temperatures (T_{NI}) quite close to each other ($76\,^\circ\mathrm{C}$ and $80\,^\circ\mathrm{C}$), the value of T_{NI} for studied 8OCB and 6OCB mixtures is practically independent on their composition. So, it can be seen in the diagram that the increase of the molecules ratio $Y = N_{6\mathrm{OCB}}/N_{8\mathrm{OCB}}$ leads to an essential increase of the temperature range of the nematic phase existence: from about 14° in pure 8OCB ($Y=0$) to about 40° in the solution of $Y=0.422$. The most fascinating is the range of the molecules ratios between 0.35 and 0.43, where the reentrance of the nematic phase occurs. The shape of the nematic–smectic-A boundary is close to the parabola with the maximum at $Y = 0.43$ and $T = 38\,^\circ\mathrm{C}$. For $Y > 0.43$ the mixtures show the isotropic and nematic phases only. The presented diagram agrees well with that published previously [7,8].

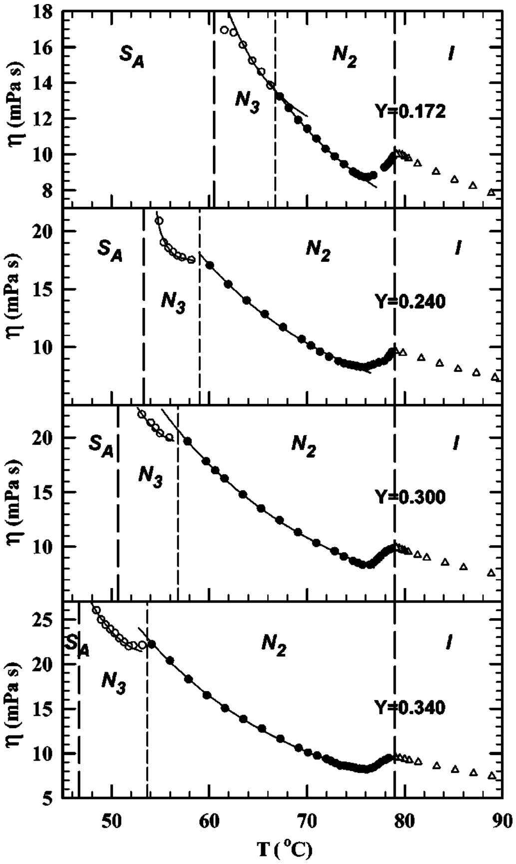

FIG. 3. Temperature dependence of the shear viscosity of the 8OCB/6OCB mixtures of low concentrations of 6OCB.

The viscosity measurements were performed for the compositions of the 8OCB and 6OCB mixtures shown in the diagram. The mixtures are divided into three groups and the viscosity of each of them as a function of temperature is presented in separate pictures (Figs. 3–6).

The mixtures of the first group (Fig. 3) correspond to the part of the diagram in which the I–N–S_A transitions occur ($Y = 0.172$–0.340); here the crystallization prevents studying the smectic-A–reentrant nematic transition. Two observations concerning the viscosity behavior for these mixtures seem to be important: (i) as the concentration of 6OCB increases, the change of the viscosity from η_2 to η_3 becomes more-and-more pronounced, if compared with pure 8OCB; (ii) the change from η_2 to η_3 occurs in the mixtures (and in pure 8OCB) at, more-or-less, constant temperature distance to the nematic to smectic-A transition.

Figure 4 presents the viscosity on temperature dependence for three mixtures in which the reentrant nematic phase occurs. The main experimental result is the following. The viscosity of the reentrant nematic corresponds to the η_3 viscosity coefficient, in the whole possible for measurements

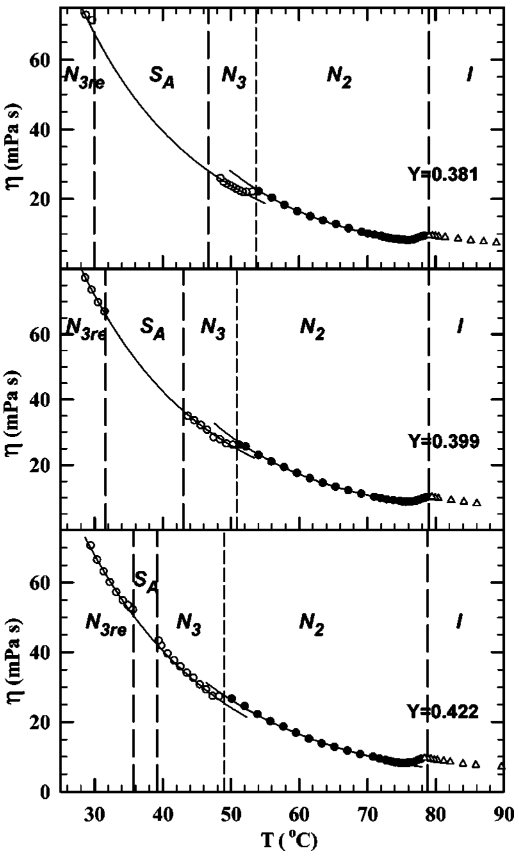

FIG. 4. Temperature dependence of the shear viscosity of the 8OCB/6OCB mixtures with ''classical'' reentrant nematic phase. The reentrance of η_3 viscosity occurs.

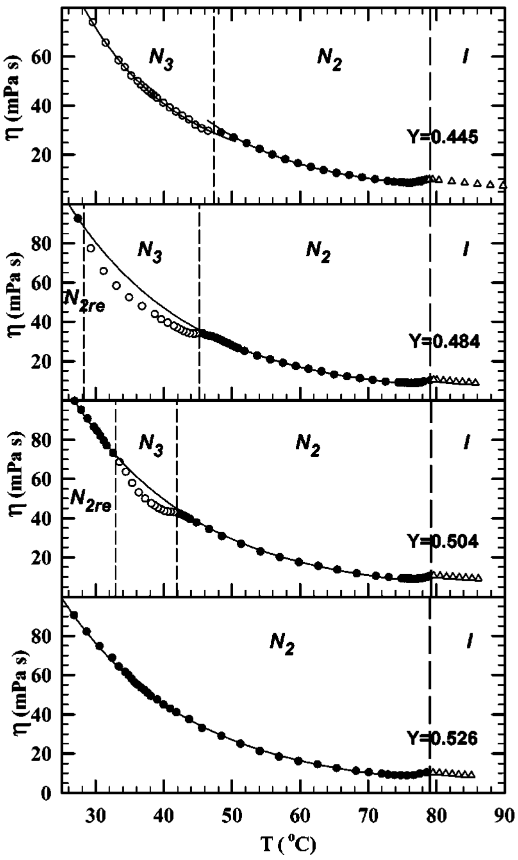

FIG. 6. Temperature dependence of the shear viscosity of the 8OCB/6OCB mixtures beyond the parabola of existence of the smectic-*A* phase. The reentrance of η_2 viscosity occurs.

temperature range. This is clearly seen in Fig. 5, where the viscosity of the mixture of $Y=0.399$ is presented in a form of Arrhenius plot. The calculated viscosity activation energies for η_2 and η_3 are closed to each other, but as shown in [1], the values of the energies are so strongly influenced by the presmectic effects that the discussion on them would be hazardous.

The last four 8OCB and 6OCB mixtures studied are beyond the parabola of the existence of smectic-*A* phase. The results presented in Fig. 6 show without doubt that the presmectic effects are extended along the Y axis and appear for $Y>0.43$. Although the smectic-like short range order was detected for $Y>0.43$ with many different experimental methods, such as a high resolution x-ray scattering [8] or an ionic conductivity [11], it is surprising that the order is strong enough for forcing the change of the manner of nematic free flow. As seen in Fig. 6, the temperature range of the η_3 viscosity appearance in the region of $Y > 0.43$ decreases symmetrically with respect to the median temperature 38 °C of the parabolic phase boundary of S_A existence. In lower temperatures the viscosity returns to its ''normal'' value, η_2. So, from the viscosity point of view we are dealing with the second phenomenon of the reentrance in the 8OCB and 6OCB mixtures.

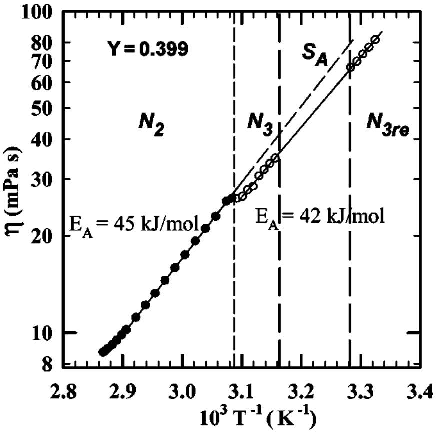

FIG. 5. Arrhenius plot for the viscosity measured for the mixture of $Y=0.399$.

The main conclusion resulting from the presented studies is the following. The shear viscosity of freely flowing nematic liquid crystal is surprisingly sensitive to the presmectic molecular arrangements. However, the presmectic change in the viscosity from η_2 to η_3 occurs at a quite good defined temperature and it concerns also the mixtures really without the smectic phase but the concentration of which is not far from the critical 6OCB concentration ($Y = 0.43$). The set of the temperatures of η_2 to η_3 transitions in all studied mixtures (full points in Fig. 2) forms the parabola with the same median temperature as the parabola describing the smectic-*A* phase boundary: the two curves are only shifted horizontally by $\Delta Y \cong 0.1$. In such circumstances, from the viscosity point of view, two nematic reentrant phenomena can be distinguished in 8OCB and 6OCB mixtures (see Fig. 2). The first one is the reentrant nematic with η_3 viscosity coefficient (N_{3re}) reappearing after crossing the smectic-A boundary. The second one (N_{2re}) concerns the η_2 viscosity that reappears after crossing the boundary of the area of presmectic short range ordering of mesogenic molecules.

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