Viscosity Behavior at the Nematic to Smectic A Phase Transition in Freely Flowing Compounds

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The paper shows that the shear viscosity at the nematic to smectic A phase transition in freely flowing n-hexyloxycyanobiphenyl + n-octyloxy-cyanobiphenyl mixtures (a system exhibiting the reentrant nematic phase) corresponds to the Mięsowicz η_3 viscosity coefficient and its temperature behavior is analogous (but strongly enhanced) to that observed for the η_2 viscosity coefficient at the isotropic to nematic phase transition.

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1. Introduction

In our recent papers [1, 2] we analyzed some peculiarities in the viscous properties of freely flowing mesogenic compounds. In particular, a lack of the external ordering forces allowed us to observe a phenomenon of the spontaneous molecular rearrangement in flowing nematic liquid crystals in the vicinity of the nematic to smectic A phase transition.

A molecular alignment caused by the nematic free flow in which the molecular ordering (the director n) is parallel to the flow velocity v and the both vectors are perpendicular to **grad** v, is a well-known phenomenon. The temperature dependence of the viscosity measured in such cases is practically identical to that measured as the Mięsowicz η_2 viscosity coefficient ($n \parallel v, n \perp$ **grad** v) [3] with the use of the ordering magnetic field (see Fig. 1). The convergence of these two viscosities is not hazardous at all, because "a free fluid adopts such a manner of flow that corresponds to the minimum of its viscosity at given conditions" [2]. There is no less viscosity of nematic liquid crystals than the Mięsowicz η_2 viscosity. An exam-
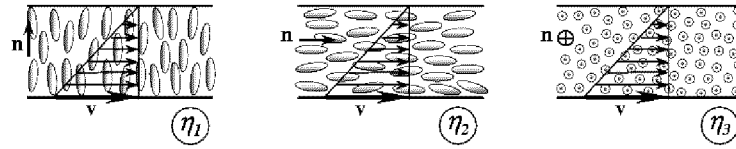
Fig. 1. The experimental conditions for measurements of the three Mięsowicz shear viscosity coefficients of nematic liquid crystals.
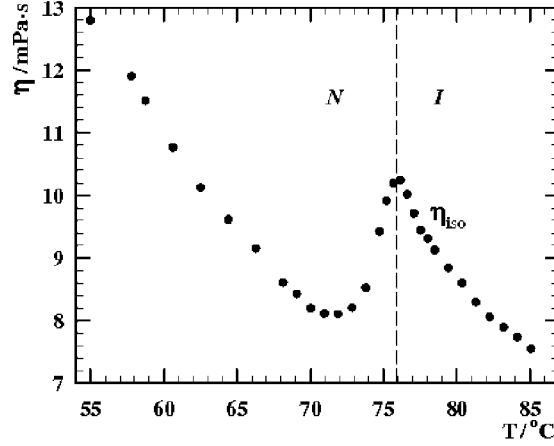

Fig. 2. Temperature dependence of the shear viscosity measured for freely flowing n-hexyloxycyanobiphenyl (6OCB) in the isotropic (I) and nematic (N) phases. In the nematic phase the viscosity is very close to the Mięsowicz η_2 viscosity coefficient.

ple of such a viscosity behavior is presented in Fig. 2 for n-hexyloxycyanobiphenyl (6OCB). Among the two remaining Mięsowicz viscosities, η_1 ($n \perp v$, $n \parallel \mathbf{grad}\, v$) is the highest and η_3 ($n \perp v$, $n \perp \mathbf{grad}\, v$) is close to the viscosity measured in the isotropic phase of the compound studied.

The situation begins somehow complicated when the transition from the nematic (N) to smectic A (S_A) phase occurs. Then, due to the formation of precursors of smectic layers, the molecular mobility corresponding to the η_2 viscosity begins to be restricted. So, in the vicinity of $N-S_A$ transition the viscosity η_2 shows a strong increase and goes to infinity at the transition. As the η_1 and η_3 viscosities are practically not affected by the $N-S_A$ transition, at the temperature of a few degrees before the transition, the viscosities η_2 and η_3 intersect each other and from then the lowest nematic viscosity is η_3 [4]. It was shown in our papers [1, 2] that in case of freely flowing nematic liquid crystal, according to the principle of the viscosity minimum, that effect leads to a spontaneous change of the molecular alignment direction from this corresponding to η_2 ($n \parallel v$) to that corresponding to η_3 ($n \perp v$). Figure 3 presents such a type of the viscosity temperature dependence for the compound with $I-N-S_A$ sequence of the phase transitions (n-octyloxycyanobiphenyl, 8OCB). In the figure, the results obtained
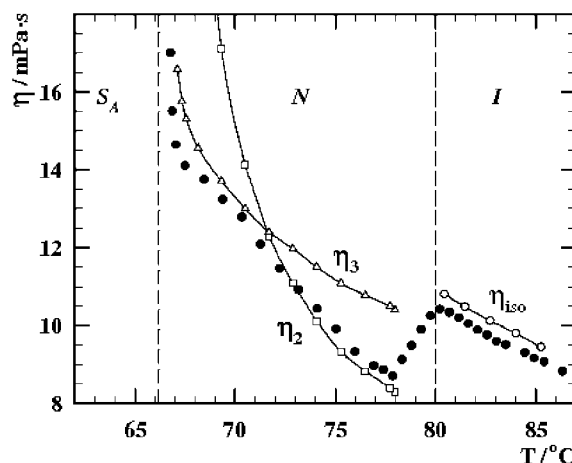
Fig. 3. Temperature dependence of the share viscosity measured for freely flowing *n*-octyloxycyanobiphenyl (8OCB) in isotropic and nematic phases. The open points present the $\eta_2(T)$ and $\eta_3(T)$ Męsowicz viscosity coefficients measured by Graf et al. [4] for the sample oriented with magnetic field.

for the sample oriented with magnetic field [4] are compared to those obtained for a freely flowing sample.

In that scope, the viscosity behavior at the nematic to smectic *A* transition and in the smectic *A* phase itself, is of a special interest. In this paper we present the results of the viscosity measurements performed in the smectic *A* phase of 8OCB + 6OCB mixtures. This system was chosen for investigations because the smectic *A* phase of pure compounds is rather "solid-like" without any possibilities for measurements of its viscosity. Numerous experimental data show that the smectic *A* phase of the above-mentioned mixtures exhibits some degree of fluidity [5–10], dependent, however, upon the concentration of 6OCB molecules.

2. Experimental

n-Hexyloxycyanobiphenyl ($C_6H_{13}O-Ph-Ph-C\equiv N$, 6OCB) with the following sequence of the phase transitions: crystal (Cr)$-58°$C–nematic (N) $-76°$C–isotropic (I) and *n*-octyloxycyanobiphenyl ($C_8H_{17}O-Ph-Ph-C\equiv N$, 8OCB): (Cr)$-54.5°$C–smectic *A* ($S_A$)$-66°C-(N)-80°C-(I)$, were synthesized and purified at the Institute of Chemistry, Military University of Technology, Warsaw. The purity of the compounds, checked by the chromatography, was better than 99.5%.

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 compound 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 measurements was 0.5%. The temperature of the sample was controlled with an accuracy of 0.1°C.

3. Results and discussion

Figure 4 presents the phase diagram for 8OCB and 6OCB mixtures. It is a classical already system in which the reentrant nematic phase (N_R) occurs. As seen in the diagram, the N_R phase appears for the molecules ratio $Y = N_{6OCB}/N_{8OCB}$ between about 0.36 and 0.43. For $Y < 0.36$, the crystallization of the mixtures prevents an appearance of N_R phase. The smectic A phase disappears when there is more than two nematogenic 6OCB molecules by about five smectogenic 8OCB molecules ($Y > 0.43$). In the mixtures of less number of 6OCB molecules than that, a stable smectic A phase exists, although its physical properties gradually evolve from these characteristic for the "solid-like" S_A phase in pure 8OCB to those close to the properties of the nematic phase, in case of the mixtures at the end of the parabola from Fig. 4.
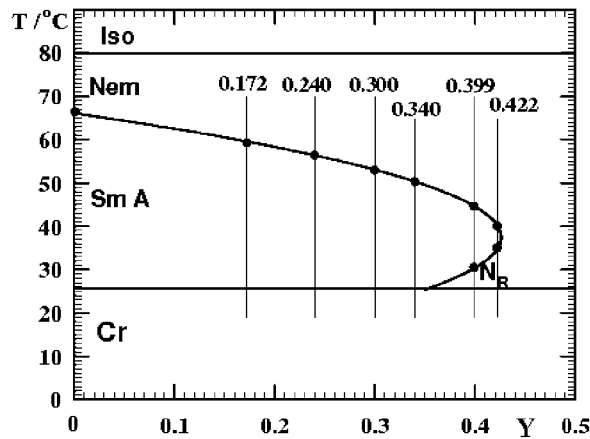

Fig. 4. The phase diagram for 8OCB/6OCB mixtures. Y denotes the molecules ratio N_{6OCB}/N_{8OCB}. The viscosity was measured for Y values marked in the diagram.

Figure 5 shows that an effect which is impossible in pure 8OCB begins possible in 8OCB/6OCB mixtures. In the smectic A phase composed of mixture of 8OCB and 6OCB molecules, the shear viscosity can be measured and its behavior at the nematic to smectic A phase can be investigated. As can be seen in Fig. 5, the transition to the smectic A phase manifests itself in a considerable increase in viscosity, but the effect strongly depends on the 6OCB concentration in the mixture. A huge effect is observed for the mixtures of a low value of Y, for which just after the $N-S_A$ transition, the viscosity increases to the value of about one order
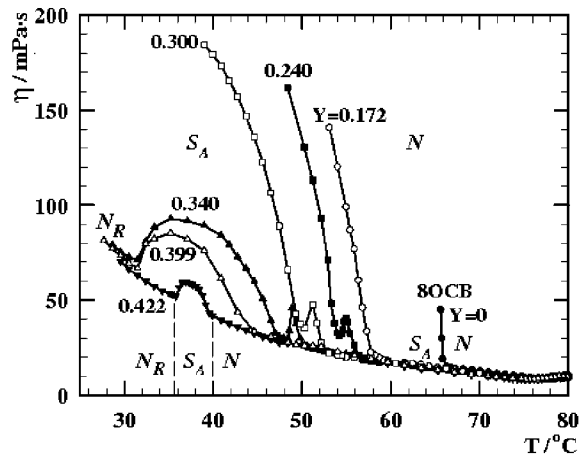
Fig. 5. The viscosity measured in the smectic A phase of 8OCB/6OCB mixtures as a function of temperature.

of magnitude higher than that in the nematic phase. For higher values of Y, it was possible to perform the viscosity measurements in the whole temperature range of existence of the smectic A phase. It is worth to notice that for the mixture of the highest concentration studied ($Y = 0.422$), although the viscosity of S_A phase is not too different from that of the nematic and reentrant nematic phases, the boundary of the S_A phase existence stands out still very distinctly.

At the nematic to smectic A phase transition in 8OCB/6OCB mixtures of the medium values of Y, one observes a peak of the viscosity. Figure 6 presents
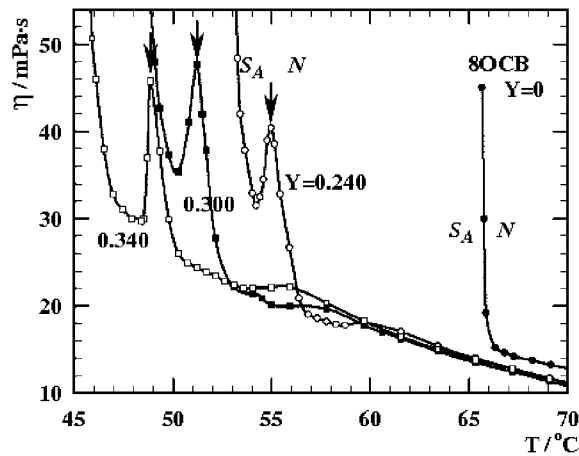

Fig. 6. The viscosity temperature behavior in the vicinity of the nematic to smectic A phase transition in 8OCB/6OCB mixtures. The arrow denotes the temperature of $N - S_A$ transition in a given mixture.

the effect in details. Similarly to the viscosity behavior at the isotropic to nematic phase transition, at the nematic to smectic A transition the viscosity attains its maximum, next, with decreasing temperature, the viscosity strongly decreases and afterwards a "normal" increase is observed.

On the basis of hitherto obtained experimental results on temperature dependence of the viscosity of mesogenic compounds being in a free flow, i.e. without external orienting forces, the following molecular picture of the process can be drawn (see Fig. 7). The phase transition from the isotropic to nematic phase manifests itself as a decrease in viscosity and its temperature dependence in the nematic phase is analogous to that measured as the η_2 viscosity. The fact is in agreement with our intuition because the lowest resistance to the nematic flow, i.e. the lowest viscosity value, is expected in the situation when the molecular alignment (vector n) is parallel to the velocity v of the flow. It always happens for the nematic liquid crystals in the absence of the pretransitional effects.
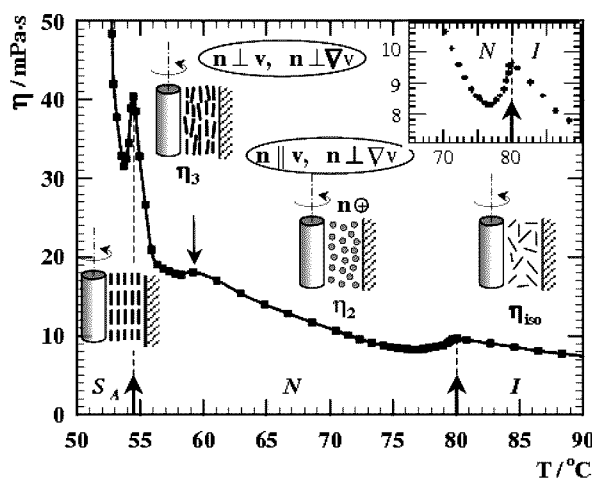

Fig. 7. The sketch presenting different modes of the molecular alignment due to free flow of the mesogenic compound in different phases. The experimental viscosity data concern 8OCB/6OCB mixture of $Y = 0.240$. The inset shows the viscosity behavior in the vicinity of the isotropic to nematic phase transition of the mixture.

An approaching of the smectic A phase reveals as an anomaly in the viscosity dependence of temperature, which is observed a few degrees before the nematic to smectic A transition. In Fig. 7 the anomaly is clearly seen at about 60°C, i.e. about 5 degree before the transition. At this temperature in the freely flowing nematic compound, the molecular orientation undergoes a change. The molecular alignment caused by the flow, which up to now was the "natural and obvious" ($n \parallel v$), changes at the temperature of about 60°C and becomes ($n \perp v$), as shown in Fig. 7, i.e. now corresponds to the Mięsowicz η_3 viscosity coefficient.

From the point of view of a layered structure as the liquid crystalline smectic A phase, only such a change on the molecular level makes possible a free flow of the S_A phase on the macroscopic scale. As a consequence, at the temperature of the transition to the smectic A phase, the layers formed make the flow of the smectic sample much more easier than in the nematic phase with the precursors of the layers only. Hence, at the $N-S_A$ transition one observes a strong decrease in viscosity. The decrease is similar to that observed in the isotropic to nematic phase transition (see the inset in Fig. 7), but the strength of the change in case of the $N-S_A$ transition is about one order of magnitude higher than that observed at the $I-N$ phase transition.

Acknowledgment

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