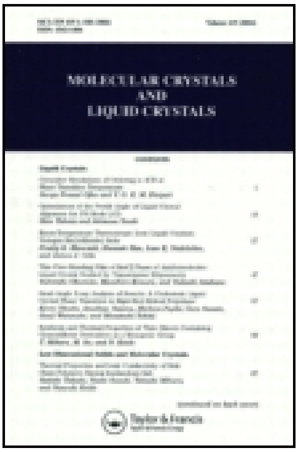

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The Influence of Natural and Model Nanoinclusions on the Properties of Nematic Phase

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The present work is focused on the investigation of the influence of a small volume fraction of nanoinclusions on the Miesowicz viscosity coefficient η_2 *of the nematic phase. Two kinds of nanoinclusions in the nematic phase have been studied: natural (smectic cybotactic clusters) and solid impurities (AEROSIL® 380). The volume fraction of nanoinclusions was estimated using the Batchelor model. This allowed in turn for calculating their number density. For cybotactic clusters, we found that their number in the nematic phase of octyloxycyanbiphenyl (8OCB) goes over the maximum when approaching the nematic-smectic phase transition. To shed some light on that finding we also studied* η_2 *for a number of different AEROSIL® 380 suspensions in the nematic host of 4-trans-4′-n-hexylcyclohexyl isothiocyanatobenzene (6CHBT).*

Keywords Aerosil nanoparticles; cybotactic groups; Miesowicz viscosity coefficients

1. Introduction

Heterogenic inclusion strongly affects bulk properties of the host system. Considerable experimental [1–4] and theoretical efforts [5–7] are made to understand modifications of different properties of liquid crystalline phases caused by different kinds of inclusions. Inclusion of silica nanoparticles introduces significant disorder to a host liquid crystal phase [2,3,8,9]. For example, magnetic properties of a liquid crystal depend on the shape of the doped magnetic nanoparticles [9]. Surface interactions between the inclusions and the liquid crystalline molecules modify also the system dynamic behaviour [3]. Among others, aerosil particles dispersed in a liquid crystal change the phase transitions temperatures [4,8]. NMR [10], ESR [2], dielectric spectroscopy [3,11] and other studies showed that dynamic properties of the host phase are also altered.

Aerosil or magnetic solid nanoparticles are "guest" intrusions in a liquid crystalline phase. If a liquid crystal features both the nematic and smectic phases, substantial

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Address correspondence to Józef K. Mościcki, Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Kraków, Poland. Tel.: +48-12663 5674; Fax: +48-126337086; E-mail: jkmoscic@gmail.com modification of the nematic phase bulk properties on approaching the nematic-smectic phase transition is caused by the presence of natural heterogeneities – the so called smectic cybotactic groups, short-living smectic order fluctuations. The theory of the critical behavior of cybotactic nematic was given by Jähnig and Brochard [12]. Although these smectic cybotactic intrusions are not solid, but under favourable conditions could act like solid-like ones, which manifests in, e.g., twist and bend elastic constants K_{22} and K_{33} [13,14], rotational viscosity coefficient γ_1 [13,15] and Miesowicz viscosity coefficient η_2 (director $\hat{n}$ is parallel to the flow viscosity $\vec{v}$, $\hat{n} \| \vec{v}$) [13,16–21].

This work concentrates on influence the inclusions have on the Miesowicz viscosity coefficient η_2 [16] in the liquid crystalline nematic phase. We show that η_2 in the nematic phase in the proximity of the N-SmA phase transition allows estimation of the cybotactic groups' volume fraction and the number of groups, if we treat them as heterogeneous inclusions. Appropriateness of such approach is verified by a complementary study of an aerosil nanoparticles doped nematic phase.

2. Experimental Methods

The Miesowicz viscosity coefficient η_2 was measured using the pendulum viscometer [22]. The viscometer heart is a glass plate attached to a long pendulum arm, and submersed in a studied liquid. Due to the viscous force, the pendulum arm with the plate performs damped oscillations from which the viscosity coefficient is calculated. Liquid crystalline phase under study was oriented with a 0.5 T horizontal magnetic field generated by a classic electromagnet [22].

The temperature of the sample was controlled with the Unipan 650H temperature controller with the accuracy of 0.01°C. The temperature was measured to within 0.1°C with a diode temperature sensor.

Effects due to the presence of smectic cybotactic groups were studied in a nematic phase of octyloxycyanbiphenyl (8OCB, from AWAT, Military University of Technology, Warsaw, Poland). 8OCB has nearly second order transition at $T_{NA} = 67.5°C$, and the temperature range of the nematic phase is large enough for cybotactic groups being present only close to the nematic-smectic phase transition.

Effects due to aerosil nanoinclusions were studied for AEROSIL® 380 (Evonik Degussa) suspended in a standard nematogen, 4-trans-4′-n-hexylcyclohexyl isothiocyanatobenzene (6CHBT, $T_{NI} = 42.8°C$.) (from AWAT, Military University of Technology, Warsaw, Poland). The suspensions were prepared by keeping the mixture, 6CHBT and desired amount of the aerosil nanoparticles (w/w) in an ultrasonic bath for one hour at temperatures well above the clearing point of the host material (bath temperature ca. 50°C). The suspension had tendency to precipitate after a series of measurements, manifested by a drop in η_2 values; in each such case the sample was sonicated again before continuing the measurements.

3. Results and Discussion

3.1. *Volume Fraction of Inclusions*

The Batchelor model has been used to calculate both the volume fraction of the smectic cybotactic groups and of aerosil nanoparticles. The viscosity coefficient of the suspension of hard spheres in a solvent is given by [23]:

$$\eta = \eta_h \cdot (1 + 2.5\varphi + 6.2\varphi^2 + \cdots) \tag{1}$$

where η and η_h are viscosity coefficients of the suspension and host solvent respectively, and φ is the volume fraction of the spheres.

For cybotactic groups Eq. (1) can be put into service since η_2 in the smectic phase has essentially "infinite" value in comparison with the nematic one, so it can be safely assumed for the flow in which $\hat{n}$ is maintained parallel to $\vec{v}$ that the cybotactic nematic is a suspension of "solid", the smectic cybotactic groups, in a nematic "solvent". Furthermore, η_2 in the nematic phase has a finite, measurable value and follows well the Arrhenius law. In such the system, thus, apparent η_2 can be identified with η in Eq. (1), with η_h being the viscosity coefficient of the pure nematic. φ is the volume fraction of the cybotactic groups in the system. It can be argued that the nematic solvent viscosity coefficient at any given temperature T, can be estimated using the Arrhenius equation [21]:

$$\eta_n = \eta_o \exp\left(\frac{E_A}{k_B T}\right) \tag{2}$$

with E_A and k_B being the activation energy and the Boltzmann constant, respectively.

Calculation of the cybotactic groups volume fraction using the Batchelor's formula is only some reasonable estimation, due to different reasons discussed in detail elsewhere [21].

Equation (1) was used also to calculate the effective volume fraction of the aerosil nanoparticles doped into the liquid crystal, φ being now the effective volume fraction of the aerosil particles and η_h the η_2 Miesowicz viscosity coefficient of the pure liquid crystal (6CHBT).

3.2. *Cybotactic Groups*

The temperature dependence of the cybotactic groups volume fraction is given in Figure 1.

The inset in the Figure 1 shows the same data redrawn in semi-log scale to emphasize the fact that the volume fraction of cybotactic groups follows the Arrhenius law. This result is not obvious, since the volume, V_1, of a single cybotactic group, which we may assume to be proportional to the product of correlation lengths $V_1 = \xi_{||}\xi_{\perp}^2$ should then obey the power law [24–26]:

$$V_1 \sim \left(\frac{T - T_{NA}}{T_{NA}}\right)^{-\nu_{||} - 2\nu_{\perp}} \tag{3}$$

where $\xi_{||}$, $\xi_{\perp}$, $\nu_{||}$, and $\nu_{\perp}$ are longitudinal and transverse correlation lengths and appropriate critical coefficients, respectively. The observed difference in the character of the temperature dependence of the cybotactic group volume, most probably results from the temperature behavior of the number of cybotactic groups [21]. The number can be estimated by dividing the cybotactic groups volume fraction, ϕ_{cyb}, by the single cybotactic group volume: $\varphi_{cyb}/(T - T_{NA}/T_{NA})^{-\nu_{||} - 2\nu_{\perp}}$. As shown

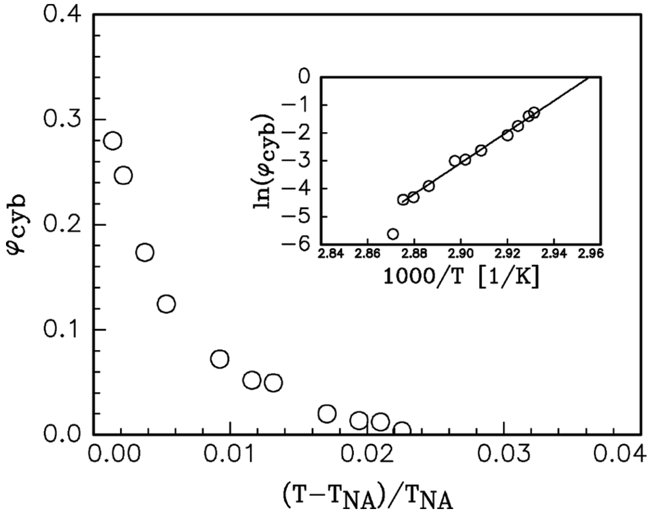

Figure 1. Volume fraction of the smectic cybotactic groups versus the reduced temperature, $(T-T_{NA})/T_{NA}$ (T_{NA} is the nematic-smectic A transition temperature), in nematic phase of 8OCB [21]. In the inset, the same data are redrawn in semilogarithmic scale. Arrhenius' character of the dependence, with $E_A = 0.46\,\mathrm{kJ/mol}$ is clearly visible.

in Figure 2, with reduced temperature decreasing the number of cybotactic groups grows initially to a maximum. The maximum presence suggests situation when it becomes energetically more favorable for the system to support coalescence of small-volume smectic-like fluctuations into larger smectic-like entities, e.g., by reduction of the entity effective surface area. Thus, after reaching the maximum the number

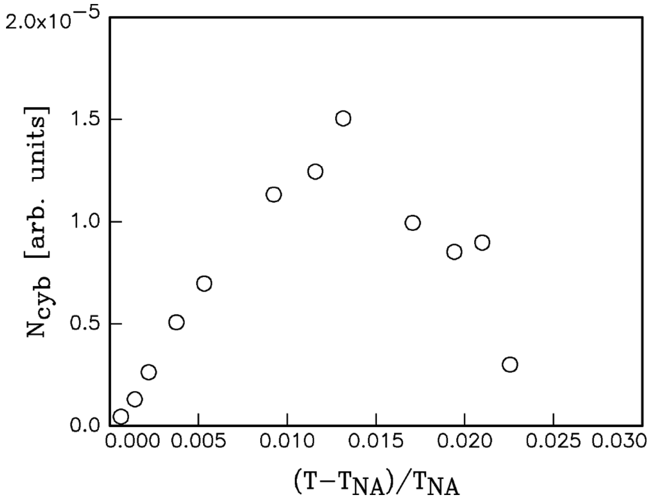

Figure 2. The number of smectic cybotactic groups as a function of the reduced temperature, $(T-T_{NA})/T_{NA}$ (T_{NA} is the nematic-smectic A transition temperature), for 8OCB [21]. With decreasing of the reduced temperature the number is rising to reach the maximum and diminish afterwards.

of groups decreases on further approaching the phase transition, as the new phase takes over the sample volume.

3.3. *Aerosil Inclusions*

The Miesowicz viscosity coefficient η_2 for several suspensions of AEROSIL® 380 in 6CHBT are given in Figure 3.

Clearly, the presence of AEROSIL® 380 nanoparticles increases the viscosity coefficient η_2. The temperature behavior of η_2 in the nematic phase far from the clearing point for both pure 6CHBT and for all the studied volume fractions of nanoinclusions is of the Arrhenius type. The activation energy for η_2 in nematic goes over minimum on continuous increase of the inclusion effective volume fraction. For each case the effective volume fraction of inclusions was calculated with aid of Eq. (1). However, to draw more definite conclusions concerning this result, measurements for other concentrations of nanoparticles should be performed.

The results of η_2 versus the effective volume fraction of aerosil nanoparticles for a few temperatures are shown in Figure 4. Addition of the aerosil changes the clearing point, but the change is smaller than 1°C for small concentrations of aerosil [8]. Therefore, the results are shown not for the reduced temperatures, but for a set temperatures, 25, 30 and 35°C. The rise in η_2 viscosity coefficient is rather moderate for the volume fractions smaller than 10%. For the highest effective volume fraction of aerosil studied, the rise is considerable for each of those temperatures. It seems to be slightly larger for 25°C than for higher temperatures (30 and 35°C). This kind of behavior may be indicative of the aerosil particle cluster formation. It is also possible that the Batchelor's formula [23] is no longer valid for these concentrations. We are not able to answer definitely this question at the present stage of the investigation,

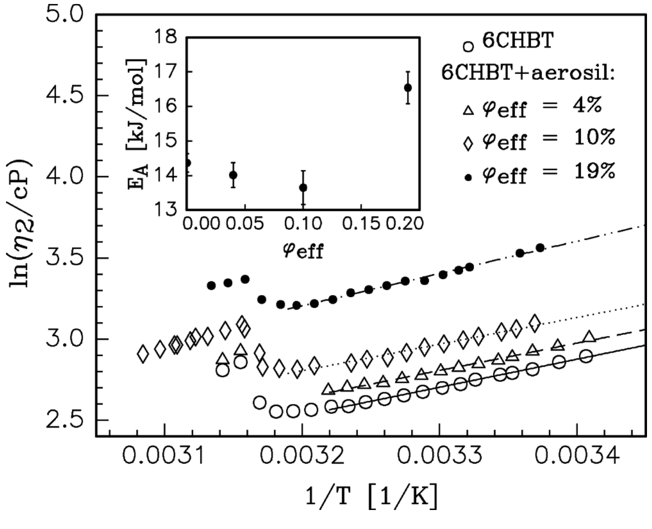

Figure 3. Temperature dependence of the Miesowicz viscosity coefficient η_2 for 6CHBT and its mixtures with different concentrations of aerosil 380 (open circles –6CHBT, triangles – $\varphi_{eff} = 0.04$, diamonds – $\varphi_{eff} = 0.10$, full circles – $\varphi_{eff} = 0.19$). In the inset the activation energy dependence on the effective volume fraction, φ_{eff}, of aerosil nanoinclusions is shown.

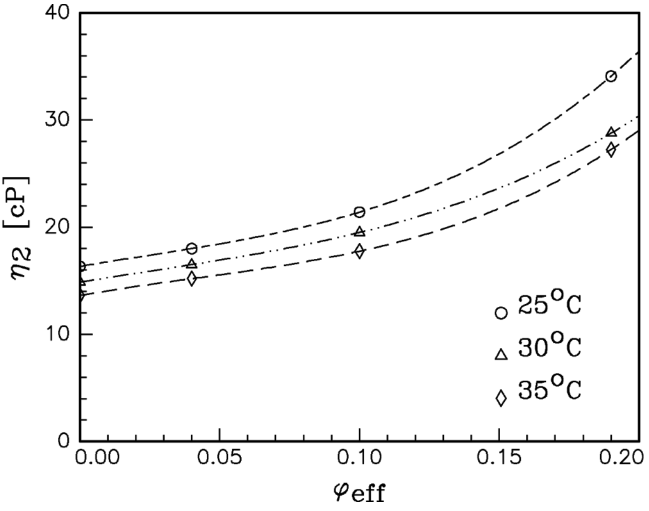

Figure 4. Miesowicz viscosity coefficient η_2 for different effective volume fraction, φ_{eff}, of the aerosil 380 doped into a nematic 6CHBT at temperatures 25 (circles), 30 (triangles) and 35°C (diamonds). The dashed lines are guides to the eye.

because more data especially for inclusions of volume fractions higher than 10% needs to be collected.

4. Summary

Behavior of Miesowicz viscosity coefficient η_2 in the nematic phase doped with natural and artificial inclusions was studied. For natural inclusions (smectic cybotactic groups) the viscosity data can be interpreted in terms of the cybotactic groups' volume fraction and the number of those groups. The estimated volume fraction temperature dependence is of the Arrhenius type in opposition to the suggested by the critical phenomena power–law dependence for the single group. The calculated number of cybotactic groups goes through maximum with decreasing the reduced temperature. This probably reflects fact that at some point on approaching the transition temperature the system begins to favor energetically larger volumes with the smectic order at the expense of smaller cybotactic molecular swarms.

The temperature behavior of η_2 for all studied concentrations of artificial nanoinclusions in the nematic liquid crystal phase is of the Arrhenius type. The activation energies are going through a minimum with the increase of effective volume fraction of aerosil particles.

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