## Liquid Crystals

Publication details, including instructions for authors and subscription information:
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**To cite this Article** Janik-Kokoszka, Joanna(2010) 'On the smectic cybotactic groups and pretransition effects in the Miesowicz viscosity coefficient $\eta_2$', Liquid Crystals, 37: 1, 77 — 84
**To link to this Article: DOI:** 10.1080/02678290903377467
**URL:** http://dx.doi.org/10.1080/02678290903377467

*Liquid Crystals,*
Vol. 37, No. 1, January 2010, 77–84

# On the smectic cybotactic groups and pretransition effects in the Miesowicz viscosity coefficient $\eta_2$

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*(Received 15 April 2009; accepted 30 September 2009)*

A new method of investigation of smectic cybotactic groups is proposed. Cybotactic nematic is considered to be a heterogeneous mixture of smectic cybotactic groups in 'nematic' solvent. In the first approximation, the cybotactic groups were treated as hard spheres and their volume fraction $\phi_{cyb}$ was calculated using the formula for the viscosity of a hard sphere suspension out of the Miesowicz viscosity coefficient $\eta_2$. The reduced temperature $(T_{cyb} - T_{NA})/T_{NA}$ at which the cybotactic groups start to influence the behaviour of $\eta_2$ was found to be constant for all the liquid crystals under investigation (the results of our measurements for octyloxycyanobiphenyl were compared with other data for smectogenic liquid crystals). The temperature dependence of $\phi_{cyb}$ is discussed. The number of cybotactic groups was estimated. This number increased with decreasing temperature, and diminished after reaching a maximum. This behaviour seems to be universal, with a maximum at similar reduced temperatures for the liquid crystals investigated.

**Keywords:** cybotactic groups; viscosity

## 1. Introduction

It is well known that the behaviour of a liquid crystal in a nematic phase differs significantly depending on the phase sequence of a given liquid crystal [1–3]. Thermotropic liquid crystals are divided into two main groups: nematics and smectics. In a nematic phase the centres of mass of molecules are not ordered, but there is an orientational ordering of the long (for calamitic liquid crystals) axes of molecules. All the smectic phases are characterised by a one-dimensional translational order in addition to the orientational order. In the simplest of the smectic phases, smectic A, the long molecular axes are normal to the layer. If a nematic phase is not the only liquid crystalline phase present for a given substance, but additionally a smectic phase appears, then pretransitional effects are observed in the vicinity of a nematic-smectic phase transition. The pretransitional behaviour is observed for those properties which differ significantly in the nematic and smectic phases. Among others a qualitative difference in the nematic and smectic phases, and thus pretransitional phenomena are observed for such properties as, for example, twist and bend elastic constants $K_{22}$ and $K_{33}$ [3, 4], rotational viscosity coefficient $\gamma_1$ [3, 5–8] and Miesowicz viscosity coefficient $\eta_2$ (director $\hat{n}$ is parallel to the flow velocity $\vec{v}$, $\hat{n}\|\vec{v}$) [3, 9–12]. Such behaviour can be attributed to the presence of regions of smectic ordering in a nematic phase and has been theoretically investigated by Jähnig and Brochard [13], who studied in particular the critical behaviour on approach of the nematic–smectic A phase transition. Those smectic regions appearing in the vicinity of the nematic-smectic phase transition are called smectic cybotactic groups. The evidence for the existence of such clusters is found in the results of X-ray measurements [14–16], Mössbauer investigations [17] and in the analysis of textures with image processing methods [18].

The aim of the present paper is to investigate the behaviour of smectic cybotactic groups and their influence on the viscosity of smectogenic liquid crystals.

Cybotactic groups are considered to be anisotropic and their shape to be ellipsoidal [15, 19]. The average dimension along the long axis is of the order of the longitudinal correlation length, $\xi_{||}$, while along the short axis it is of the order of the transversal correlation length $\xi_{\perp}$. Therefore, the size of cybotactic groups should diverge at the transition, and the temperature dependence of their axes lengths follow equations: $\xi_{||} \propto t^{-\nu_{||}}$, $\xi_{\perp} \propto t^{-\nu_{\perp}}$, where $t$ is the reduced temperature: $t = (T - T_{NA})/T_{NA}$, while $\nu_{||}$ and $\nu_{\perp}$ are critical exponents. However, analysing the nuclear magnetic resonance data, Phani Kumar *et al.* [20] argue that cybotactic clusters are anisotropic only close to the nematic-smectic phase transition, while for temperatures at which cybotactic groups start to appear in nematic phase, their shape is isotropic.

The best candidates for the investigation of cybotactic groups are those properties which differ significantly in the nematic and smectic phases. One of these properties is the viscosity coefficient in the Miesowicz geometry of $\eta_2$ $(\hat{n}\|\vec{v})$. In the nematic phase it has a finite value [11, 21–24], while in the smectic one its value is infinite [9, 12] due to the fact that shear flow,

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ISSN 0267-8292 print/ISSN 1366-5855 online

DOI: 10.1080/02678290903377467
http://www.informaworld.com

which cuts smectic layers, is impossible. This essential difference in $\eta_2$ demonstrates itself in completely different behaviour in the nematic phase of nematogenic and smectogenic liquid crystals. For a liquid crystal exhibiting only a nematic liquid crystalline phase, the temperature dependence of $\eta_2$ is of the activation (Arrhenius) type in the whole nematic phase, with the exception of a small region close to the clearing point. For smectogenic liquid crystals, the Arrhenius-like behaviour can be observed (if at all) only far away from the phase transitions. On approaching the nematic-smectic transition temperature a pretransitional divergence of $\eta_2$ is observed. It seems obvious that this behaviour is a result of the presence of regions with smectic ordering in a nematic phase [25]. Therefore, it should be possible to extract information on smectic cybotactic groups starting from viscosity data. A new method for finding the volume fraction of smectic cybotactic groups is proposed. Namely, the cybotactic nematic is treated as a 'mixture' of smectic cybotactic groups dissolved in a nematic solvent.

The plan of this paper is as follows. The method for extracting the volume fraction of smectic cybotactic groups out of the temperature results of $\eta_2$ is shown in Section 2. The behaviour of smectic cybotactic clusters is discussed in Section 3 and the change in number of clusters with temperature is shown. The summary and perspectives for further research are given in Section 4.

## 2. The volume fraction of smectic cybotactic groups

Studies were started with the problem of how to extract the information concerning smectic cybotactic groups out of the Miesowicz viscosity coefficient $\eta_2$ data. To answer this question a novel approach to the problem of divergence of this viscosity coefficient was proposed. A liquid crystal at temperatures not far from the nematic-smectic phase transition was considered as a heterogenous mixture of smectic cybotactic groups dissolved in a nematic solvent. To calculate the volume fraction of cybotactic groups at a given temperature the hard sphere suspension model was used [26]. The viscosity coefficient $\eta_2$ of cybotactic groups is infinite and, therefore, in the first approximation they can be considered as hard spheres. The viscosity coefficient of such a suspension is related to the volume fraction of the spheres, $\phi$, through the equation [26, 27]:

$$\eta = \eta_h \cdot \left(1 + 2.5\varphi + 6.2\varphi^2 + \ldots\right), \tag{1}$$

where $\eta$ and $\eta_h$ are viscosity coefficients of the suspension and solvent, respectively.

The use of the above equation for calculating the volume fraction of the cybotactic groups can be treated only as the first approximation for a few reasons. Firstly, the liquid crystalline cybotactic groups are ellipsoidal rather than spherical in shape, while the equation is derived for spheres. Secondly, Equation (1) was obtained for spheres of equal size [26], while at a given temperature a distribution of sizes of cybotactic groups can be expected. The polydispersity results in lowering the viscosity of a suspension with respect to that of single sized spheres [28, 29]. Therefore, the volume fraction calculated according to Equation (1) is underestimated. However, it is argued [28, 29], that the effect is rather small even for quite large polydispersity. Thirdly, the equation is derived for the isotropic solvent, and the anisotropic one is much more complicated. Some numerical studies of the friction coefficient of ellipsoidal particles suspended in nematic liquid crystals have been made [30], but the results obtained are not yet sufficient to quantify the dependence on shape or solvent viscosity anisotropy for the purpose of the present investigation. Fourthly, for larger ratios of $\eta/\eta_h$ the quadratic term is not sufficient and the next order term should be used. Unfortunately, no theoretical work, which would give a reliable value for the coefficient of this order, is available. However, the results obtained with Equation (1) are a good first approximation of the behaviour of cybotactic groups not too close to the nematic-smectic phase transition. This temperature region, where the groups first start to appear, was the most interesting in this work. The results hopefully will prove an incentive for theoretical work to obtain more realistic formulae.

In the present work $\eta$ of Equation (1) is equal to viscosity coefficient $\eta_2$ measured at a given temperature, while $\eta_h$ has the meaning of a viscosity coefficient of the nematic phase, if the smectic cybotactic groups were absent. Obviously as the cybotactic groups cannot be removed, so $\eta_h$ cannot be measured directly, but a quantitative estimate can be given. In order to do that, it was considered that coefficient $\eta_2$ in the nematic phase of a smectogenic liquid crystal consisted of two parts: regular, $\eta_n$, and irregular, $\eta_s$, the latter resulting from the influence of smectic ordering. The regular part can be considered to be the viscosity coefficient of a nematic without smectic cybotactic groups, that is, $\eta_h = \eta_n$. There are various ways in which one can estimate $\eta_n$. However, care is necessary with the way in which the regular part is chosen because it can influence the obtained results, for example, the value of the critical exponent for viscosity depends strongly on this choice [31]$^1$. In the discussion of $\eta_2$ data, three different ways of dealing with the problem of the regular part are usually undertaken. First, the regular part can be considered as negligible when compared with the divergent term [7]. The second option is to use as a regular part an Arrhenius (activation) equation, that is

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

where $E_A$ is the activation energy and $k_B$ the Boltzmann constant. Equation (2) seems to be the most obvious description of the temperature dependence of the regular part [7, 12], since both the viscosity coefficient of isotropic liquids and $\eta_2$ of nematogenic liquid crystals follow that formula. The third possibility, introduced by Graf *et al.* [32], is based on the KSS relation [2, 32]:

$$\frac{\eta_2}{\eta_1} = a \cdot \frac{\eta_3}{\eta_1} + b, \tag{3}$$

where $\eta_1$, $\eta_2$ and $\eta_3$ are Mięsowicz viscosity coefficients. (We used Helfrich [33] notation for the Mięsowicz viscosity coefficients, that is, $\eta_1$ is measured in the geometry of $\hat{n} \| grad\ v$ and $\eta_3$ in $\hat{n} \perp \vec{v} \perp grad\ v$.)

It is argued that $a$ is nearly the same for all the liquid crystals and is equal to 0.865, while the parameter $b$ can be evaluated [32]. The reason Graf *et al.* [32] used this procedure is that according to them, the separation of the regular and irregular parts by extrapolation of Equation (2) into the divergent part is impossible since divergence already begins at the clearing point. Results in the present work do not support completely this last hypothesis (see below).

In the present paper the second approach was chosen for the evaluation of the regular part, since it is valid for $\eta_2$ of nematogens, that is, for nematics without smectic cybotactic groups. Due to the fact that for the temperatures close to the nematic-smectic phase transition, the temperature dependence of the irregular part of the Miesowicz viscosity coefficient $\eta_2$ is equal to

$$\eta_s = B\left(\frac{T - T_{NA}}{T_{NA}}\right)^{-x} \tag{4}$$

then the equation

$$\eta_2 = \eta_0 \exp\left(\frac{E_A}{k_B T}\right) + B\left(\frac{T - T_{NA}}{T_{NA}}\right)^{-x} \tag{5}$$

can be fitted to the experimental data [7, 10, 13]. This procedure is used mainly to obtain the critical exponent $x$. The same procedure might be attempted to obtain $\eta_0$ and $E_A$ values far from the nematic-smectic phase transition. However, it is not obvious that the temperature dependence of the irregular part far from the nematic-smectic phase transition temperature, which is the region of most interest for the present work, should be the same as in Equation (4). Also, when Equation (5) is fitted to the experimental data, a substantial irregular part in the whole range of the nematic phase is obtained. However, Montrucchio *et al.* [18] have shown that for several nematics, there is a temperature region where cybotactic groups exist, as well as a region closer to the clearing point, where they are absent. Therefore, one can expect the typical for classical nematics Arrhenius-like behaviour without an irregular part in a certain temperature range, and both regular and irregular contributions in a region closer to the nematic-smectic phase transition. Of course, as will be discussed below, there are also liquid crystals, for example, octylcyanobiphenyl (8CB), for which it is not possible to find any temperature range where only an Arrhenius-like part is present. For such liquid crystals Equation (5) should be used in the whole nematic temperature range. (Unfortunately, we could not use this procedure to analyse the Kneppe *et al.* [6] data for 8CB due to an insufficient number of points.)

Thus the regular part is calculated by extrapolating Equation (2) to the given temperature ($E_A$ and $\eta_o$ are fit parameters in the non-divergent temperature region). Knowing both the value of $\eta_h$ and measuring $\eta_2$ at a given temperature, the volume fraction of smectic cybotactic groups at this temperature can be calculated with the help of Equation (1).

## 3. Results and discussion

Before discussing the results of the temperature dependence of the volume fraction of smectic cybotactic groups, the plot of the ratio of $\eta_2/\eta_n$ versus the reduced temperature (see Figure 1) for several liquid crystals is discussed first.

For this paper the viscosity coefficient $\eta_2$ for 8OCB (octyloxycyanobiphenyl) was measured with a newly constructed pendulum viscometer [34] (compare Figure 2). The results were compared with other data for different liquid crystalline substances exhibiting both nematic and smectic phases measured with different techniques, namely 8OCB [7, 32], CBOOA (n-cyanobenzylidene-n′-octyloxyaniline) [9], 8CB [2] and a mixture of 7CB (heptylcyanobiphenyl), 8OCB and 5CT (pentylcyanoterphenyl) [12] (this mixture also exhibits a re-entrant nematic phase).

The ratio $\eta_2/\eta_n$ provides information on the temperature at which smectic cybotactic groups start to appear. It can be seen that the character of its behaviour is similar for all the substances under consideration. This means that the influence of the smectic phase seems to commence at similar reduced temperatures, namely

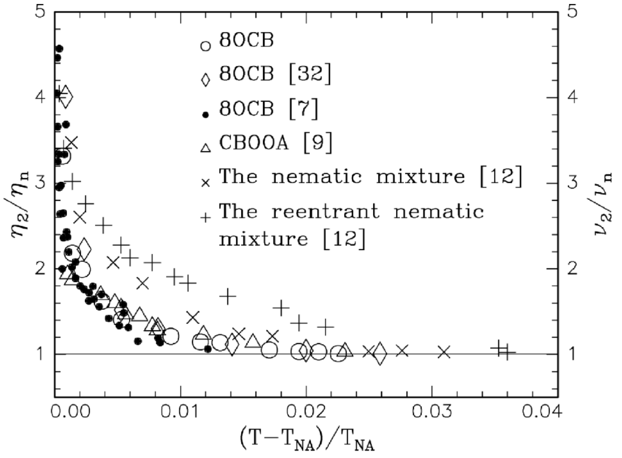

Figure 1. Summary plot of $\eta_2/\eta_n$ versus reduced temperature for: octyloxycyanobiphenyl (8OCB) open circles (present work), diamonds [32], dots [7]; n-cyanobenzylidene-n′-octyloxyaniline (CBOOA) triangles [9]; a nematic mixture (x) [12]; a re-entrant nematic mixture (+) [12]. Note that for the Bhattacharya and Letcher [12] mixture (x, +), the ratios are for the kinetic viscosity coefficients and not the dynamic coefficients (the right-hand axis). $181\times126$ mm$^2$ ($300\times300$).

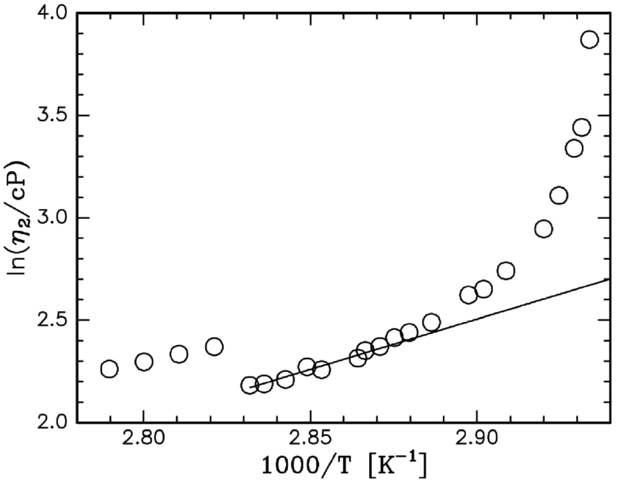

Figure 2. The temperature dependence of the Miesowicz viscosity coefficient $\eta_2$ for octyloxycyanobiphenyl [present work]. The straight line is a fit for the Arrhenius equation (Equation (2)) in the temperature range 348–353 K. The activation energy is 40.8 kJ mol$^{-1}$. $166\times126$ mm$^2$ ($300\times300$).

$$0.021 \le \left|\frac{T-T_{NA}}{T_{NA}}\right| \approx const \le 0.025 \qquad (6)$$

for all the considered liquid crystals in a nematic phase and 0.036 for the re-entrant nematic one. The Leger and Martinet [7] results had to be excluded because their high temperature viscosity results did not allow estimation of this temperature with sufficient accuracy. (The main aim of Leger and Martinet [7] measurements was to investigate the critical behaviour of $\eta_2$, therefore they concentrated on the results close to $T_{NA}$, while in the present work the other region is most important.) However, the other sets of data [present work, 32] for the same liquid crystal (8OCB) gave consistent results. This temperature, at which smectic cybotactic groups start to appear, is $T_{cyb}$ and the reduced one, $t_{cyb} = \left|\frac{T_{cyb}-T_{NA}}{T_{NA}}\right|$. The onset of cybotactic groups is obtained in the following way: $T_{\mathrm{cyb}}$ is the temperature for which a deviation of $\eta_2/\eta_n$ (or $\nu_2/\nu_n$) from 1, is less than 3%. This value is an estimate on which experimental level we can be more or less sure that this effect is present.

It is interesting to compare the range of influence of smectic cybotactic groups in nematic and re-entrant nematic phases. Unfortunately hardly any data are available, the kinetic viscosity ($\nu_2$) results of a mixture studied by Bhattacharya and Letcher [12], exhibiting both nematic and reentrant nematic phases, had to be used. The results of $\nu_2/\nu_n$ versus reduced temperature are included in the same figure as the ratios of the dynamic viscosities (i.e. in Figure 1). For the re-entrant nematic phase, the reduced temperature has to be defined as: $t = (T_{RNA} - T)/T_{RNA}$. It can be seen that the results for the ratio of kinematic viscosities do not differ much from the ratios of the dynamic viscosities. The values of the $\nu_2/\nu_n$ ratios are a little higher than those for $\eta_2/\eta_n$. It is not possible now to discern if it was due to the fact that a mixture as opposed to a single component liquid crystals was involved or if the difference results from the ratio of densities ($\rho_n/\rho_2$, the relation between the dynamic and kinetic viscosity coefficients is $\eta = \rho\nu$). Nevertheless, there is no significant difference between the temperatures at which smectic groups start to be observable, $t_{cyb}$, for the nematic phase of the mixture and single component compounds. However, it seems that the influence of cybotactic groups goes further in the re-entrant nematic phase than in the nematic one. As seen in Figure 1, in the nematic phase $t \simeq 0.025$, while in the re-entrant nematic phase of the same mixture $t \simeq 0.036$.

Another observation concerns the relation between $T_{cyb}$ and $T_{NI}$. It is possible to find the value of the defined by McMillan ratio [35, 36] $R_M = T_{NA}/T_{NI}$, for which the temperature at which the cybotactic groups start to appear, $T_{cyb}$, is equal to the clearing temperature $T_{NI}$. Simple calculation shows that the condition $T_{cyb} = T_{NI}$ is met for liquid crystals with $R_M \approx 0.97-0.98$. For liquid crystals characterised by those or higher values of $R_M$, the smectic cybotactic groups are present in the whole temperature range of the nematic phase. An example of such a liquid crystal is 8CB ($R_M = 0.978$). The nematic-smectic A transition temperature for this liquid crystal is $T_{NA} \simeq 306.7$K. Assuming that Equation (6) is universal, the temperature for which the irregular part starts to be present was calculated. The obtained value $T_{cyb} = 313.1 - 314.4$ K is very close or only slightly higher than the clearing point (the values of $T_{NI}$ reported for 8CB are equal to $313.6 - 314.05$ K) [2, 37]. Thus, there is no temperature range of nematic phase of 8CB without smectic cybotactic groups. This result is in agreement with the argument of Graf *et al.* [32], that the divergent part starts at the clearing point. However, for other liquid crystals studied (8OCB, CBOOA, the mixture of 7CB, 8OCB and 5CT) $T_{cyb}$ was lower than $T_{NI}$. That means that for some liquid crystals, there are two kinds of nematics, with and without cybotactic groups, separated by an order transition at a temperature equal to $T_{cyb}$. This kind of transition has already been investigated by Montrucchio *et al.* [18], with picture analysis methods, for other liquid crystals.

Another presentation of the obtained results is given in Figure 3, which shows the percentage of the cybotactic nematic phase $(T_{cyb}–T_{NA})$ to the whole nematic range $(T_{NI}–T_{NA})$ versus the McMillan parameter, $R_M = T_{NA}/T_{NI}$. If the assumption is true that the reduced temperature at which those groups begin to appear is constant (compare Equation (6)), than the equation

$$t'_{cyb} = \frac{const \cdot R_M}{1 - R_M}, \tag{7}$$

should hold.

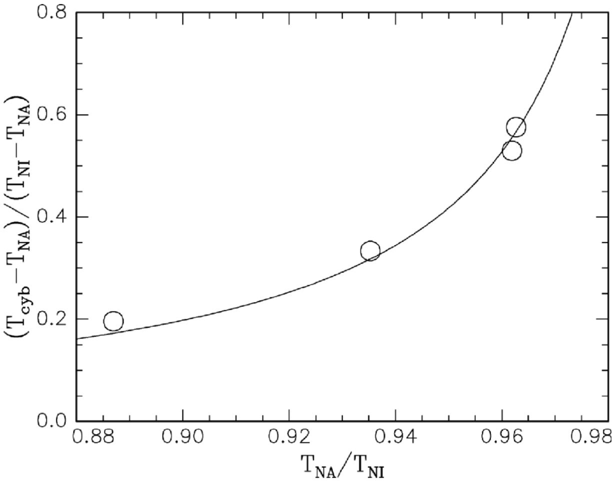

Figure 3. A plot of scaled temperature at which smectic cybotactic groups start to appear $t'_{cyb} = \frac{T_{cyb}-T_{NA}}{T_{NI}-T_{NA}}$ versus the McMillan parameter $R_M = T_{NA}/T_{NI}$ for octyloxycyanobiphenyl [present work, [32], n-cyanobenzylidene-n′-octyloxyaniline [9] and the mixture of heptylcyanobiphenyl, octyloxycyanobiphenyl and pentylcyanoterphenyl [12] (nematic phase). The curve is fitted to Equation (7), *const* = 0.022 ± 0.001. The results for Leger and Martinet [7] data for octyloxycyanobiphenyl are not included due to insufficient accuracy in determining $T_{cyb}$. 167 × 126 mm$^2$ (300 × 300).

Experimental results of $t'_{cyb}$ versus $R_M$, together with the fitted to the Equation (7) curve, are given in Figure 3. ($T_{cyb}$ is obtained from the data shown in Figure 1. However we had to exclude from our considerations the re-entrant nematic mixture [12] due to the obvious lack of $T_{NI}$, and Leger and Martinet [7] 8OCB results, because of large uncertainty about the obtained $T_{cyb}$ value.) The value of const obtained in this fit is equal to 0.022 ± 0.001. However, in order to draw more definite conclusions, more data for other liquid crystals should be investigated.

After discussing the temperature range of the appearance of cybotactic groups in nematic and re-entrant nematic phases, the temperature dependence of the volume fraction of smectic cybotactic groups calculated with the help of Equation (1), according to the procedure described in Section 2 can be discussed. The results for 8CB had to be excluded due to an insufficient number of data points. Please note that in the case of the nematic and re-entrant nematic phases of the mixture [12], $\rho$ was unknown, hence results for this mixture show only a general tendency. The results are given in Figure 4. The character of temperature dependence for all the liquid crystals under consideration [7, 9, 12, 32] was quite similar. Now the question arises which mathematical formula describes this dependence in the best way.

First, it was necessary to check if the volume fraction of smectic cybotactic groups is characterised by the same temperature behaviour as a single cybotactic group. An average cybotactic group has a volume equal to [15, 19, 36]

$$V_1 = \xi_{||}\xi_{\perp}^2, \tag{8}$$

thus its temperature dependence is described by the equation

$$V_1 \sim t^{-\nu_{||}-2\nu_{\perp}}. \tag{9}$$

Therefore, the results were plotted in the log–log scale to check if the power law holds (see Figure 5):

$$\varphi_{cyb} \approx |T - T_{NA}|^{-y}. \tag{10}$$

As can be seen, there are two regions for the temperatures closer and farther from the phase transition.

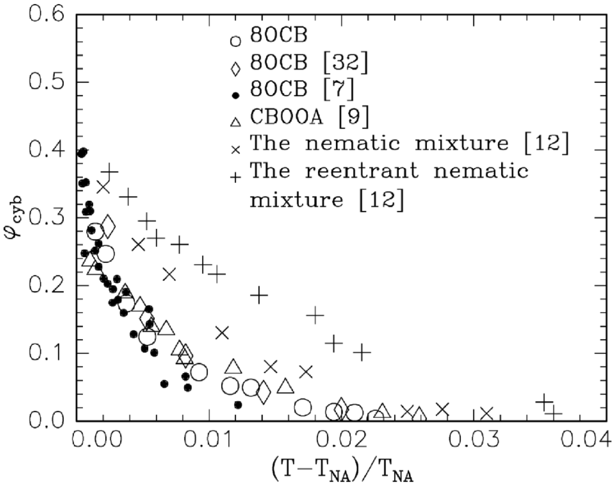

Figure 4. The temperature dependence of the volume fraction of smectic cybotactic groups for octyloxycyanobiphenyl (8OCB) open circles (present work), diamonds [32], dots [7]; n-cyanobenzylidene-n′-octyloxyaniline (CBOOA) triangles [9]; a nematic mixture (x) [12]; a re-entrant nematic mixture (+) [12]. Note that for the Bhattacharya and Letcher [12] mixture (x, +), the ratios are for the kinetic viscosity coefficients and not the dynamic coefficients and thus the above plot shows only a tendency of the behaviour of $\phi_{cyb}$. 167×128 mm² (300×300).

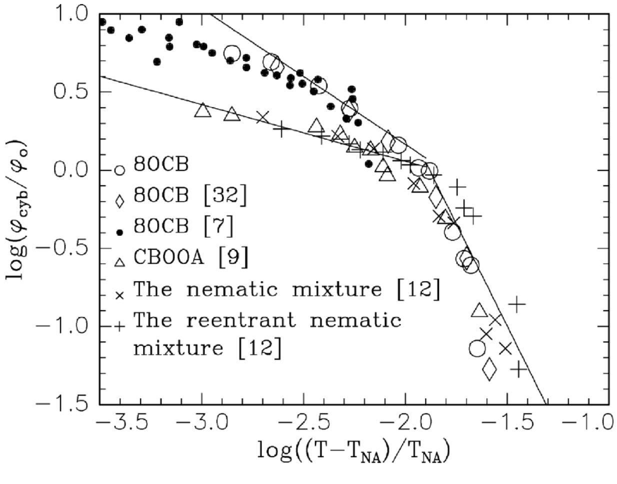

Figure 5. Temperature dependence of the volume fraction of smectic cybotactic groups in log-log scale. Symbol codes as in Figure1. The lines are sample fits to Equation (10) in 'closer' and 'farther' temperature regions meant to guide the eye. $\phi_o$ is an arbitrary constant. 167 × 128 mm (300 × 300).

The exponents are equal to $y_1 = 0.36$–$0.86$ for nematic liquid crystals in the 'closer temperatures' region. In the 'farther temperatures' region, this value is much higher and is of the order $y_2 = 2$–$5$.

Table 1. The values of the exponent $y$ in the low ($y_1$) and high ($y_2$) temperature regions for the substances under investigation.

| Substance | $y_1$ | $R^2$ | $y_2$ | $R^2$ |
|---|---|---|---|---|
| Re-entrant nematic phase of the mixture of heptylcyanobiphenyl, octyloxycyanobiphenyl and pentylcyanoterphenyl [12] | 0.36 | 0.975 | 3.6 | 0.847 |
| Heptylcyanobiphenyl, octyloxycyanobiphenyl and pentylcyanoterphenyl [12] | 0.37 | 0.993 | 2.8 | 0.937 |
| n-Cyanobenzylidene-n′-octyloxyaniline [9] | 0.39 | 0.821 | 2.8 | 0.961 |
| Octyloxycyanobiphenyl [7] | 0.36 | 0.853 | 2.0 | 0.697 |
| Octyloxycyanobiphenyl [32] | 0.86 | 0.995 | 4.1 | 0.938 |
| Octyloxycyanobiphenyl [present work] | 0.73 | 0.961 | 5.0 | 0.816 |

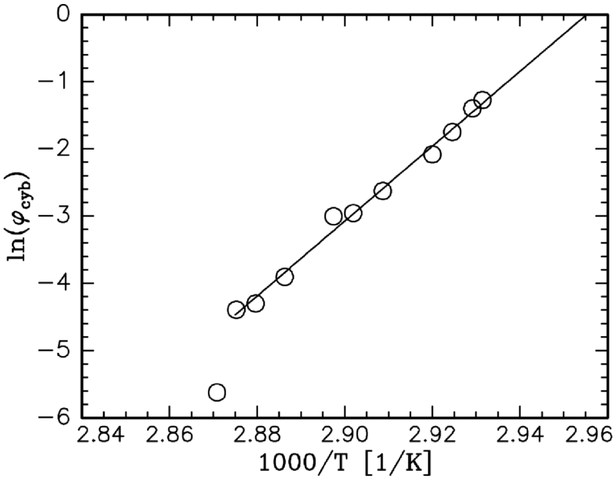

Figure 6. The results of the present work data for octyloxycyanobiphenyl in a semi-logarithmic scale. The line is a result of fit to Equation (11). 167×126 mm² (300×300).

As is seen from the Table 1, the fits are not completely satisfactory, therefore, the results were replotted in still another representation, namely, $\ln \varphi_{cyb} = f(1/T)$. As an example, the plot of data for 8OCB is presented in Figure 6. As can be seen a straight line was obtained here, as well as for other cases, with $R^2$ better than 0.993 (compare Table 2). So the volume fraction of smectic cybotactic groups is described with the activation equation:

$$\varphi_{cyb} = \varphi_o \cdot \exp\left(\frac{E_{A_1}}{k_B T}\right), \tag{11}$$

rather than with the power law of a single cybotactic group (Equation (9)). The calculated activation energies are given in Table 2.

The question to answer now is: what is the reason for the different temperature behaviour of a single group and the volume fraction of all the groups? The

Table 2. The values of the activation energies for the volume fraction of cybotactic groups for the liquid crystals under investigation.

| Substance | $E_A$ [J] | $R^2$ |
|---|---|---|
| Re-entrant nematic phase of the mixture of heptylcyanobiphenyl, octyloxycyanobiphenyl and pentylcyanoterphenyl [12] | $(-)2.39 \cdot 10^{-22}$ | 0.978 |
| Nematic phase of the mixture of heptylcyanobiphenyl, octyloxycyanobiphenyl and pentylcyanoterphenyl [12] | $5.32 \cdot 10^{-22}$ | 0.980 |
| n-Cyanobenzylidene-n′-octyloxyaniline [9] | $5.42 \cdot 10^{-22}$ | 0.977 |
| Octyloxycyanobiphenyl [7] | $11.1 \cdot 10^{-22}$ | 0.938 |
| Octyloxycyanobiphenyl [32] | $7.45 \cdot 10^{-22}$ | 0.996 |
| Octyloxycyanobiphenyl [present work] | $7.69 \cdot 10^{-22}$ | 0.993 |

volume fraction of smectic cybotactic groups $\phi_{cyb}$, is proportional to the volume of a single group $V_I$ and to the number of the groups, $N_{cyb}$:

$$\varphi_{cyb} = N_{cyb} \cdot V_1 / V, \tag{12}$$

where $V$ is the total volume.

Knowing the temperature dependence of the volume of a single group (compare Equation (9)) and the volume fraction of cybotactic groups gives an insight into the temperature dependence of the number of cybotactic groups. A plot of $N_{cyb}$ in arbitrary units (i.e. $\varphi_{cyb}/t^{-\nu_{\|}-2\nu_{\perp}}$) versus the reduced temperature is given in Figure 7. (The values of the critical exponents $\nu_{\|}$ and $\nu_{\perp}$ are taken from the paper of Garland and Nounesis [36].) The results for the Bhattacharya and Letcher mixture [12] are not included, since critical coefficients $\nu_{\|}$ and $\nu_{\perp}$ were not available.

It is interesting that the temperature behaviour of $N_{cyb}$ seems to be universal. Two regions of different character of behaviour can be distinguished in the plot. First at higher temperatures, just after the cybotactic groups start to appear, the number of cybotactic groups increases with decreasing temperature. At a certain reduced temperature, $t \approx 0.013$, the number $N_{cyb}$ reaches maximum. When the temperature is further lowered, $N_{cyb}$ starts to decrease. This result can be explained in the following way: at the start when the cybotactic groups are still small, there is no restriction on the appearance of new groups. However, when the size of a cybotactic group reaches certain dimensions, it might be more favourable for the groups to combine forming one group instead of two. So then the total number of cybotactic groups diminishes.

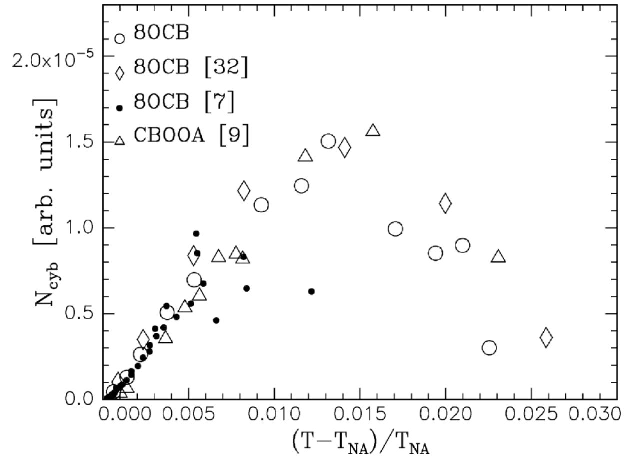

Figure 7. The number of smectic cybotactic groups versus the reduced temperature for octyloxycyanobiphenyl (8OCB) open circles (present work), diamonds [32], dots [7]; n-cyanobenzylidene-n′-octyloxyaniline (CBOOA) triangles [9]. The results for the Bhattacharya and Letcher [12] mixture are not included since the critical coefficients $\nu_{\|}$ and $\nu_{\perp}$ for this mixture were not available. 167×124 mm$^2$ (300×300).

The above description has to be treated as a first approximation of the behaviour of cybotactic groups because of the approximate character of our calculations. The volume fraction of smectic cybotactic groups was calculated assuming them to have a spherical shape. According to Phani Kumar *et al.* [20], this idea is valid at higher temperatures, while at lower temperatures they are ellipsoidal. (Other authors [15, 19] consider the cybotactic groups to be ellipsoidal, although they were interested in the low temperature region close to the nematic-smectic phase transition.) However, no data are available yet as to the temperature at which their shape changes. It would be interesting to see if this temperature could be connected to, for example, a maximum of $N_{cyb}$. It might be also useful to include the anisotropy of the shape of cybotactic groups into the calculation of the volume fraction of the groups, and to check what correction this would impose on the presented results.

## 4. Summary

The present paper describes studies of the temperature behaviour of smectic cybotactic groups and their influence on the Miesowicz viscosity coefficient $\eta_2$. It was found that smectic ordering begins to exert an influence on the $\eta_2$ coefficient at nearly the same reduced temperature for a number of liquid crystals, that is, 8OCB [present paper, 32], CBOOA [9] and the nematic phase of the mixture of 7CB, 8OCB and 5CT [12]. This influence reaches further in the re-entrant nematic phase than in the nematic one. The dependence of the temperature at which the cybotactic groups start to appear $T_{cyb}$ on the McMillan parameter $R_M$ was also investigated. For a certain value of $R_M$ ($R_M \geq 0.97 - 0.98$), smectic groups are present in the whole range of the nematic phase starting from the clearing temperature.

The novelty of this work is centred on treating a nematic with smectic cybotactic groups as a mixture of 'hard spheres' – the cybotactic groups in a 'solvent' – a liquid of purely nematic ordering. The model of viscosity of such a suspension, although used with a few simplifying assumptions, allowed the calculation of the volume fraction of smectic cybotactic groups out of the Miesowicz viscosity coefficient $\eta_2$ data. It was shown that the temperature behaviour of this volume fraction has an activational character.

The number of cybotactic groups in a cybotactic nematic was estimated. After the groups start to appear, their number grows with decreasing temperature until it reaches a maximum. At that temperature the conditions for a combination of two groups start to become more favourable than for the formation of a new group, and the number of the groups starts to diminish.

This model has only an approximate character and requires further elaboration. Further investigations of viscosity coefficients of smectogenic liquid crystals in a nematic phase are necessary. Also the influence of the anisotropy of the shape of cybotactic groups on the calculation of their volume fraction should be taken into account in further research.

## Note

1. The critical coefficient $\nu$ for the same data set of the rotational viscosity coefficient $\gamma_1$ for 8OCB was equal to 0.51 and 0.35 [5] depending on the choice of the regular part. Note, however, that for the viscosity coefficient $\gamma_1$ the regular part is much more important than for $\eta_2$ [7].

## Acknowledgements

Financial support from the Polish State Committee for Scientific Research (KBN) under Project No. 2 P03B 086 23 is acknowledged. I would like to thank Professor Józef K. Mościcki for drawing my attention to this interesting subject and for discussions.

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