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Order parameter and temperature dependence of the hydrodynamic viscosities of nematic liquid crystals (*)

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Résumé. — Une analyse théorique de la dépendance des cinq viscosités hydrodynamiques d'un cristal liquide nématique incompressible, en fonction du paramètre d'ordre et de la température est présentée. Cette analyse est la généralisation d'une théorie moléculaire de la viscosité rotationnelle γ_1 proposée récemment par les auteurs (*Port. Phys.* 9 (1975) 129 et *Mol. Cryst. Liq. Cryst.* 66 (1981) 133); elle est basée sur le concept de volume libre et sur la théorie des processus cinétiques. Des formules théoriques sont proposées pour chacune des cinq viscosités en fonction de huit paramètres moléculaires, du paramètre d'ordre $S(T)$, de la température T , et d'une température fixe T_0 au-dessous de laquelle le mouvement visqueux des molécules n'est plus possible par manque de volume libre suffisant. Ces formules sont comparées avec les résultats expérimentaux disponibles pour le M.B.B.A. et on constate un assez bon accord dans tout le domaine de la phase nématique.

Abstract. — A theoretical analysis of the order parameter and temperature dependence of the complete set of five independent viscosities of incompressible nematic liquid crystals is presented. It is an extension of a previous theory by the authors on the thermal dependence of the twist viscosity in nematics (*Port. Phys.* 9 (1975) 129 and *Mol. Cryst. Liq. Cryst.* 66 (1981) 133) and develops from the concept of free volume and the theory of rate processes. Theoretical expressions are derived for each of the five viscosities in terms of the order parameter $S(T)$, the current temperature T , eight parameters which depend on molecular properties, and some fixed temperature T_0 below which viscous molecular motion is not possible due to the lack of enough free volume. These expressions are contrasted with the experimental data available for M.B.B.A. and all of them are found to be in good agreement with the data, over the full nematic range of this material.

1. **Introduction.** — The order parameter of the nematic liquid crystal phase is given by a symmetric traceless tensor formed with the components n_i of the director \mathbf{n} :

$$Q_{ij}(T) = S(T) \cdot (n_i n_j - \frac{1}{3} \delta_{ij}), \quad (1.1)$$

where S is the degree of order expressed by

$$S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle, \quad (1.2)$$

θ is the angle between \mathbf{n} and the long molecular axis, and $\langle \dots \rangle$ is an ensemble average [1].

An incompressible nematic has five independent viscosity coefficients [2, 3], depending in general on the temperature and on the order parameter, itself temperature dependent.

Up to now, various expressions have been proposed to account for the order parameter dependence of the nematic viscosities [4, 5], but less attention has been paid to the explicit temperature dependence of these viscosities. The twist viscosity γ_1 is an exception, and its temperature and order parameter dependence have already been considered in different ways [6, 7, 8].

The aim of this paper is to derive theoretically both the order parameter and the temperature dependence of the complete set of nematic viscosities : $\alpha_1, \alpha_4, \gamma_1, \gamma_2,$ and γ_3 (defined below). The order parameter dependence of these viscosities is derived in the next section. In section 3 we discuss their temperature dependence, starting from a generalization of our previous theory [8] of the temperature dependence of γ_1 . To lowest order in Q , our new results are :

$$\alpha_1(T) = c_1 S^2 \cdot \exp\left(\frac{\theta_3 S^2}{T - T_0}\right) \quad (1.3)$$

$$\alpha_4(T) = \left(a - \frac{b}{3} S\right) \cdot \exp\left(\frac{\theta_3 S^2}{T - T_0}\right) \quad (1.4)$$

(*) A preliminary account of some of the results in this paper was first presented as an oral communication at the III International Conference on Physico-Chemical Hydrodynamics, PCH, 80, Madrid (Spain), March, 30-April 2, 1980.

$$\gamma_1(T) \equiv \alpha_3(T) - \alpha_2(T) = g_1 S^2 \cdot \exp\left(\frac{\theta_1 S^2}{T - T_0}\right) \quad (1.5)$$

$$\begin{aligned} \gamma_2(T) \equiv \alpha_3(T) + \alpha_2(T) &= \alpha_6(T) - \alpha_5(T) = \\ &= g_2 S \cdot \exp\left(\frac{\theta_2 S^2}{T - T_0}\right) \quad (1.6) \end{aligned}$$

$$\gamma_3(T) \equiv \alpha_6(T) + \alpha_5(T) = bS \cdot \exp\left(\frac{\theta_3 S^2}{T - T_0}\right) \quad (1.7)$$

where the $\alpha_i(T)$ are the nematic viscosities as defined in [9], S is the degree of order, T is the temperature, and the other symbols represent parameters that are (nearly) temperature independent. These expressions are contrasted in section 4 with the experimental data available for the nematic material M.B.B.A. (4-methoxybenzilidene-4', n-butylaniline), and they are found to be in fairly good agreement with the data, over the full nematic range of this material. Finally, in section 5, we present the main conclusions of this paper.

2. Order parameter dependence of the nematic viscosities. — The hydrodynamic equations of motion of an incompressible and isothermal nematic liquid crystal may be written :

$$\partial_i v_i = 0 \quad (2.1)$$

$$\rho \frac{dv_i}{dt} = \partial_j \sigma_{ji} \quad (2.2)$$

$$\varepsilon_{ijk}(\sigma'_{jk} + n_j h_k) = 0, \quad (2.3)$$

where ρ is the density, σ_{ji} is the stress tensor, σ'_{ji} is the viscous stress tensor, and h_i is the molecular field [2, 3, 9]. The molecular field is the functional derivative of the free energy density f with respect to the director :

$$h_i = - \frac{\delta f}{\delta n_i}, \quad (2.4)$$

and the stress tensor is the functional derivative of f with respect to the strain tensor $\partial_j u_i$, where u_i is the displacement along the direction i ,

$$\sigma_{ji} = - \frac{\delta f}{\delta(\partial_j u_i)}. \quad (2.5)$$

The entropy production $\dot{\Sigma}$ is given by [9] :

$$T \dot{\Sigma} = \int d^3 \mathbf{r} \{ h_i N_i + \bar{\sigma}'_{ji} A_{ij} \} \quad (2.6)$$

where N_i is the director velocity with respect to the enviroing fluid :

$$N_i = \frac{dn_i}{dt} - \frac{1}{2} (\text{rot } \mathbf{v} \times \mathbf{n})_i, \quad (2.7)$$

$\bar{\sigma}'_{ji}$ is the symmetric part of the viscous stress tensor, and A_{ij} is the symmetric part of the velocity gradient tensor :

$$A_{ij} = \frac{1}{2} (\partial_i v_j + \partial_j v_i). \quad (2.8)$$

Expressions (2.4) and (2.6) may be re-written in a more convenient way, if we consider the free energy density f as a functional of Q_{ij} (instead of n_i) and $\partial_j u_i$.

Expression (2.6) then reads :

$$T \dot{\Sigma} = \int d^3 \mathbf{r} \left\{ - \frac{\delta f}{\delta Q_{ij}} \cdot \frac{\delta Q_{ij}}{\delta t} + \bar{\sigma}'_{ji} A_{ij} \right\}, \quad (2.9)$$

where the time derivative is evaluated along one flow line and with respect to the enviroing fluid, i.e.

$$\frac{\delta Q_{ij}}{\delta t} = S \cdot (n_i N_j + N_i n_j). \quad (2.10)$$

A direct comparison of equations (2.6) and (2.9) gives :

$$h_i = - 2 S \cdot \frac{\delta f}{\delta Q_{ij}} \cdot n_j. \quad (2.11)$$

Returning back to equation (2.9), we see that $-\delta f/\delta Q$ and $\bar{\sigma}'$ may be chosen as thermodynamic forces, and $\delta Q/\delta t$ and A as the corresponding fluxes. Then, if the linear response theory holds, we may write

$$- \frac{V}{kT} \frac{\delta f}{\delta Q_{ij}} = R_{ijkl} \cdot \left(\tau_1 \cdot \frac{\delta Q_{kl}}{\delta t} + \tau_{13} \cdot A_{kl} \right) \quad (2.12)$$

$$\frac{V}{kT} \bar{\sigma}'_{ij} = R_{ijkl} \cdot \left(\tau_{31} \cdot \frac{\delta Q_{kl}}{\delta t} + \tau_3 \cdot A_{kl} \right) \quad (2.13)$$

where V is a volume, τ_1 , τ_{13} , τ_{31} and τ_3 have the dimensions of time, and R is a tensor with the symmetry of the nematic phase. The Onsager relations impose further

$$\tau_{13} = \tau_{31} = \tau_2. \quad (2.14)$$

Equations (2.12) and (2.13) may be considered as the relaxation equations respectively for orientation stresses and shear stresses. Thus, τ_1 and τ_3 are the characteristic times for the relaxation of orientation stresses and shear stresses, respectively, and τ_2 is a mixed time for the coupling between orientation and flow. These relaxation times were first considered by Hess [5].

The tensor R of equations (2.12) and (2.13) must be symmetric in i, j and k, l because it links two symmetric tensors. In addition it should reflect the ordered character of the medium, and therefore we assume it to be a function of Q which we may expand as follows, up to order Q^2 :

$$\begin{aligned} R_{ijkl} &= a_1 \cdot \frac{1}{2} (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) + \\ &+ a_2 \cdot \frac{1}{4} (\delta_{ik} Q_{jl} + Q_{ik} \delta_{jl} + \delta_{il} Q_{jk} + Q_{il} \delta_{jk}) \\ &+ a_3 \cdot \frac{1}{2} (Q_{ik} Q_{jl} + Q_{il} Q_{jk}) + a_4 \cdot Q_{ij} Q_{kl} \\ &+ a_5 \cdot \frac{1}{4} (Q_{is} Q_{sk} \delta_{jl} + \delta_{ik} Q_{js} Q_{sl} + Q_{is} Q_{sl} \delta_{jk} \\ &+ \delta_{il} Q_{js} Q_{sk}) + a_6 \cdot Q_{rs} Q_{sr} \cdot \frac{1}{2} (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \\ &+ \mathcal{O}(Q^3) \quad (2.15) \end{aligned}$$

where the a_i are numerical coefficients. In the expansion (2.15) we have omitted the terms containing δ_{ij} or δ_{ki} for the following reasons. First both σ_{ij} and $\delta f/\delta Q_{ij}$ are indeterminate to arbitrary terms of the form $-p\delta_{ij}$ (the scalar pressure) or $-\lambda\delta_{ij}$ (the director stress), so that terms containing δ_{ij} may be included in σ_{ij} or $\delta f/\delta Q_{ij}$. Second, the terms containing δ_{ki} vanish for both Q (by definition) and A (because the fluid is incompressible) have zero trace. Substituting (2.15) into equations (2.12) and (2.13), and using (2.10) and (2.11) we find :

$$h_i = 2 \frac{kT}{V} \cdot \left(B_1 + \frac{1}{2} B_2 \right) \cdot [\tau_1 S^2 N_i + \tau_2 S A_{ij} n_j] \quad (2.16)$$

$$\begin{aligned} \bar{\sigma}'_{ij} = & 2 \frac{kT}{V} \cdot \tau_2 \cdot \left(B_1 + \frac{1}{2} B_2 \right) \cdot \frac{1}{2} (n_i N_j + N_i n_j) + \\ & + \frac{kT}{V} \cdot \tau_3 \cdot \left[B_1 A_{ij} + \frac{1}{2} B_2 (A_{ik} n_k n_j + n_i n_k A_{kj}) \right. \\ & \left. + B_3 n_i n_j (n_k A_{kp} n_p) \right] \quad (2.17) \end{aligned}$$

where

$$B_1 = a_1 - \frac{1}{3} a_2 S + \frac{1}{9} S^2 (a_3 + a_5 + 6 a_6) \quad (2.18a)$$

$$B_2 = a_2 S + \frac{1}{3} S^2 (a_5 - 2 a_3) \quad (2.18b)$$

$$B_3 = (a_3 + a_4) S^2. \quad (2.18c)$$

Equations (2.16) and (2.17) reduce to the Leslie equations [2, 3, 9] by putting :

$$\begin{aligned} \gamma_1 = & 2 \frac{kT}{V} \cdot \left(B_1 + \frac{1}{2} B_2 \right) \cdot \tau_1 \cdot S^2 \simeq 2 a_1 \times \\ & \times \frac{kT}{V} \cdot \tau_1 \cdot S^2 + \mathcal{O}(S^3) \quad (2.19) \end{aligned}$$

$$\begin{aligned} \gamma_2 = & 2 \frac{kT}{V} \cdot \left(B_1 + \frac{1}{2} B_2 \right) \tau_2 \cdot S \simeq 2 \frac{kT}{V} \times \\ & \times \tau_2 \cdot \left(a_1 S + \frac{1}{6} a_2 S^2 \right) + \mathcal{O}(S^3) \quad (2.20) \end{aligned}$$

$$\gamma_3 = \frac{kT}{V} B_2 \tau_3 \simeq \frac{kT}{V} \cdot \tau_3 \cdot \left[a_2 S + \frac{1}{3} (a_5 - 2 a_3) S^2 \right] \quad (2.21)$$

$$\alpha_1 = \frac{kT}{V} B_3 \tau_3 = \frac{kT}{V} \cdot \tau_3 \cdot (a_3 + a_4) S^2 \quad (2.22)$$

$$\begin{aligned} \alpha_4 = & \frac{kT}{V} B_1 \tau_3 = \frac{kT}{V} \cdot \tau_3 \cdot \left[a_1 - \frac{1}{3} a_2 S + \right. \\ & \left. + \frac{1}{9} (a_3 + a_5 + 6 a_6) S^2 \right]. \quad (2.23) \end{aligned}$$

For $S = 0$, i.e. in the isotropic phase, only α_4 is non-zero and its value is twice the ordinary isotropic viscosity η_{isov} as seen from equation (2.23).

Equations (2.19)-(2.23) display the order parameter dependence of a complete set of independent nematic viscosities. They agree with those of Hess [5],

except for the S^2 -terms in γ_3 and α_4 which are missing in his expressions. Imura and Okano [4] proposed an analogous expansion of the viscosities in powers of Q , but they assumed that the coefficients of S were « weakly temperature dependent » [4]. By comparison of our expressions (2.19)-(2.23) with those of reference [4] we find that they are in general agreement except that Imura and Okano wrote

$$\gamma_1 = 2 C_1 S + 2 C_2 S^2$$

and from our expressions $C_1 = 0$. The proportionality of γ_1 to S^2 may also be proved from a general thermodynamic argument [10]. On the other hand, as we shall see below, the coefficients of S (i.e. the relaxation times τ_i) show a strong temperature dependence, in contrast to what has been assumed by Imura and Okano [4].

3. Thermal dependence of the viscosities of nematic liquid crystals. — Besides the degree of order S , itself temperature dependent, the relaxation times τ_1 , τ_2 and τ_3 are functions of temperature and show a strong contribution to the overall thermal dependence of the nematic viscosities. On the other hand, the parameters a_i are « geometrical », rather than dynamical parameters, and their temperature dependence (if any) may be neglected. In the following we shall only consider the thermal dependence of τ_1 , τ_2 and τ_3 .

Recently we have shown that the twist viscosity γ_1 may be related to the equilibrium frequency ν_0 of reorientational jumps of π radians performed by the molecules against the intermolecular potential. The relation is :

$$\gamma_1 = \frac{kT}{\pi^2 V_i} \cdot \frac{1}{\nu_0} \quad (3.1)$$

where $1/V_i \sim S^2$ (this volume V_i is the molecular volume as extrapolated from the isotropic phase to the temperature T and should not be confused with the volume V in expression (2.19) — see reference [6]). The frequency ν_0 was computed in references [6] and [8], and may be expressed as :

$$\nu_0 \sim \frac{kT}{h} \exp(-\epsilon S/kT) \cdot \exp[-\theta_1 S^2/(T - T_0)] \quad (3.2)$$

where kT/h is a fundamental frequency, $\exp(-\epsilon S/kT)$ is proportional to the probability that the reorientating particle (one molecule or a small group of them) has enough energy to overcome the potential barrier due to the molecular field created by the other molecules, and $\exp[-\theta_1 S^2/(T - T_0)]$ is proportional to the probability that the particle finds enough free volume to jump. (For details see Ref. [8].)

By comparison of (2.19) with (3.1) and (3.2) we find :

$$\tau_1 \sim \frac{h}{kT} \cdot \exp\left(\frac{\theta_1 S^2}{T - T_0}\right). \quad (3.3)$$

In this expression, and in the following, we ignore the factor $\exp(\varepsilon S/kT)$ because the temperature variation of $S^2/(T - T_0)$ dominates that of S/T in most practical cases (see Ref. [8]).

The same type of argument may be used to find the thermal dependence of τ_3 . One must then consider the translational jumps between two equilibrium positions instead of the rotational jumps of π . The result is

$$\tau_3 \sim \frac{h}{kT} \cdot \exp\left(\frac{\theta_3 S^2}{T - T_0}\right). \quad (3.4)$$

In view of (3.3) and (3.4) it seems reasonable to assume a similar thermal dependence for the mixed parameter τ_2 , i.e. :

$$\tau_2 \sim \frac{h}{kT} \cdot \exp\left(\frac{\theta_2 S^2}{T - T_0}\right). \quad (3.5)$$

Finally, by substitution of (3.3), (3.4), and (3.5) into (2.19)-(2.23) we find the results (1.3)-(1.7) announced in the Introduction (section 1) to this paper.

We do not give here a detailed derivation of equation (3.4) because it is analogous to that presented in [8] for the case of $\gamma_1(T)$. Instead, we shall discuss briefly the free volume factor, $\exp[\theta_k S^2/(T - T_0)]$. This factor dominates the thermal dependence of the relaxation times considered, and may be written as [8]

$$\frac{\theta_k S^2}{T - T_0} = \frac{\Delta V_k}{V_0 \alpha \cdot (T - T_0)} \quad (3.6)$$

where V_0 is the molar volume of the nematic phase at $T = T_0$ and α is a thermal expansion coefficient, so that $V_0 \cdot \alpha \cdot (T - T_0)$ is the free volume available per molecule; it vanishes when $T = T_0$ so that T_0 is the temperature at which ceases the particle mobility related to free volume. ΔV_k ($k = 1, 2, 3$) is the increase in free volume needed by one particle to jump; a crude estimate of ΔV_k can be made by noting that near the crystal-nematic and near the nematic-isotropic transition temperatures, ΔV_3 and ΔV_1 may be compared respectively to the volume jumps observed at these transitions. These relations, of course, are not rigorous, but they are expected to be roughly correct.

4. Comparison of this theory with experimental data about M.B.B.A. — The measurement of a complete set of nematic viscosities was first done by Gähwiller on M.B.B.A. [11]. He measured the thermal dependence of the so-called Miesowicz viscosities, η_a , η_b and η_c , and of the flow alignment angle ψ . The Miesowicz viscosities are the apparent viscosities measured in a flow experiment between two parallel plates, and correspond to the following geometries (we use here the notation of Ref. [9]) :

a) director perpendicular to the direction of flow and to the velocity gradient :

$$\eta_a = \frac{1}{2} \alpha_4, \quad (4.1)$$

b) director parallel to the direction of flow :

$$\eta_b = \eta_a + \frac{1}{4}(\gamma_1 + \gamma_3 + 2\gamma_2), \quad (4.2)$$

c) director parallel to the velocity gradient :

$$\eta_c = \eta_a + \frac{1}{4}(\gamma_1 + \gamma_3 - 2\gamma_2) = \eta_b - \gamma_2. \quad (4.3)$$

The flow alignment angle ψ is the angle between \mathbf{n} and \mathbf{v} when a similar flow experiment is performed without any external field imposing a given orientation to \mathbf{n} ; then ψ is given by :

$$\cos(2\psi) = -\frac{\gamma_1}{\gamma_2}. \quad (4.4)$$

A direct test of our theory with the data of [11] is probably not meaningful because the reported values of η_c were questioned by different authors [12, 13], suggesting that they were underestimated. This is corroborated by new and more precise measurements recently performed by Knepe and Schneider [14]. Thus, we preferred to take together the data reported up to now by different authors [11-23] and perform our analysis on each viscosity over all the corresponding data. For $S(T)$ we have used the data of reference [24].

This analysis may be summarized as follows :

1) First, the twist viscosity $\gamma_1(T)$ was computed by a least squares fit of equation (1.5) to the data reported in references [11], [13], and [15-22]. The best parameters found are $g_1 = 1.066$ P, $\theta_1 = 115.81$ K, and $T_0 = 255 \pm 5$ K. Figure 1 displays the best fit of $\gamma_1(T_{NI} - T)$ so obtained, together with the experimental points; we remark the good agreement between our equation (1.5) and the experimental data.

2) Data about $\gamma_2(T)$ were then obtained from two different sources : one set of data was computed from the $\psi(T)$ values of reference [11] and the previously evaluated curve of $\gamma_1(T)$, using equation (4.4); the other set of data was computed using equation (4.3) and the data about $\eta_b(T)$ and $\eta_c(T)$ of reference [14]. A least squares fit of equation (1.6) to all the data so obtained gave $T_0 = 255 \pm 5$ K, as in the preceding case, $g_2 = -0.440$ P, and $\theta_2 = 166.60$ K. Figure 2 shows the experimental data together with the $\gamma_2(T_{NI} - T)$ fitting curve; the agreement is again very good.

3) Data on $\gamma_3(T)$ were obtained from the experimental data [11, 14] on η_a and η_b and the preceding computed curves of γ_1 and γ_2 through the relation

$$\gamma_3 = 4(\eta_b - \eta_a) - (\gamma_1 + 2\gamma_2). \quad (4.5)$$

The parameters b , θ_3 and T_0 could then be directly obtained by a least squares fit of equation (1.7) to these data. We did not use this procedure, however, because the data are too disperse (see Fig. 3). Instead,

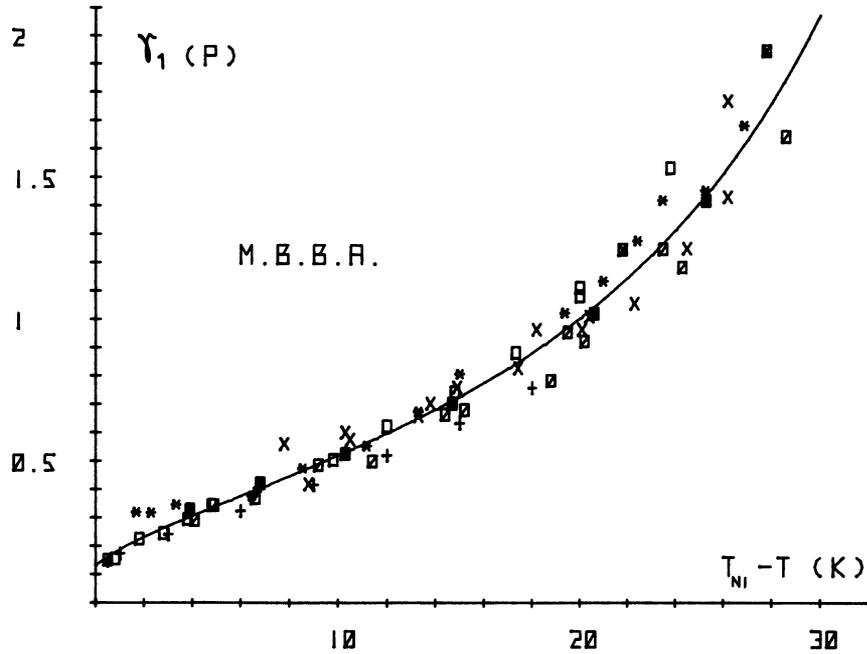


Fig. 1. — Twist viscosity γ_1 versus $T_{Ni} - T$ for M.B.B.A. The full curve is a least squares fit of equation (1.5) to the experimental data, giving $g_1 = 1.066$ P, $\theta_1 = 115.81$ K and $T_0 = 255$ K. Data points : + : from Ref. [11]; x : from Ref. [15]; \boxtimes : from Ref. [16]; \boxminus : from Ref. [17]; \blacksquare : from Ref. [18]; \square : from Ref. [19]; * : from Ref. [13] using the data of references [19], [20] and [21].

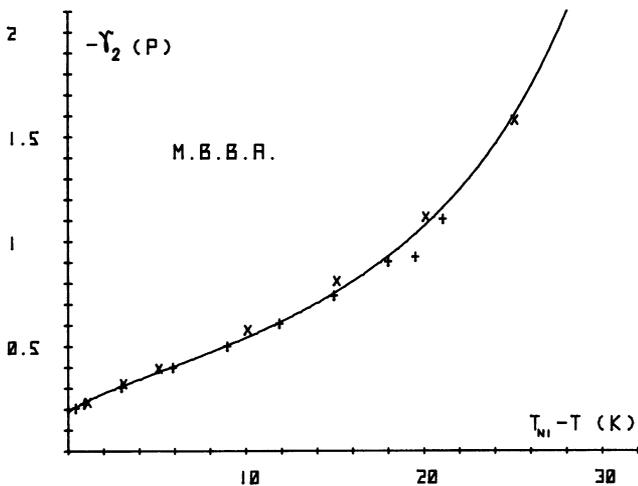


Fig. 2. — γ_2 versus $T_{Ni} - T$ for M.B.B.A. The full curve is a least squares fit of equation (1.6) to the experimental data, giving $g_2 = -0.440$ P, $\theta_2 = 166.60$ K and $T_0 = 255$ K. Data points : + : computed from Ref. [11]; x : computed from Ref. [14].

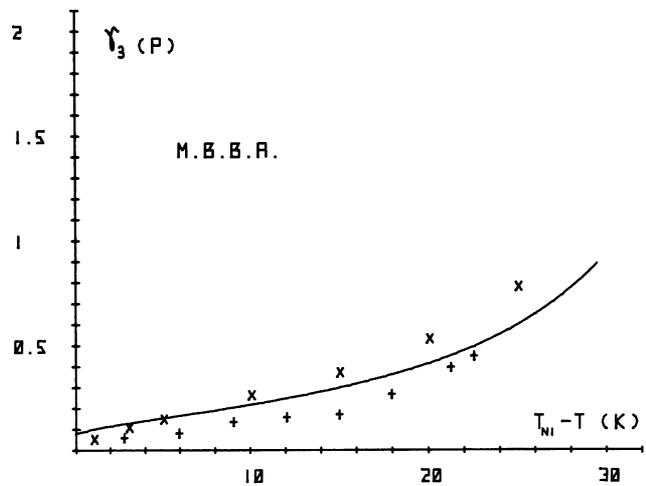


Fig. 3. — γ_3 versus $T_{Ni} - T$ for M.B.B.A. The full curve is a least squares fit of equation (1.7) to the experimental data, giving $b = 0.188$ P, $\theta_3 = 153.82$ K and $T_0 = 255$ K. Data points : + from Ref. [11]; x from Ref. [14].

we considered together these data on γ_3 and on α_4 [11, 14], and using the equation

$$\alpha_4 + \frac{1}{3} \gamma_3 = a \cdot \exp\left(\frac{\theta_3 S^2}{T - T_0}\right) \quad (4.6)$$

(which is obtained from equations (1.4) and (1.7)), we got, by the least squares method, $a = 0.268$ P, $\theta_3 = 153.82$ K and $T_0 = 255$ K (again). The value of a was checked through the relation

$$\alpha_4(T_{Ni}^-) = 2 \eta_{iso}(T_{Ni}^+) - \frac{1}{3} \gamma_3(T_{Ni}^-) \quad (4.7)$$

where $\eta_{iso}(T_{Ni}^+)$ and $\gamma_3(T_{Ni}^-)$ were obtained by extrapolation to T_{Ni} of the curves fitting the (rather precise) data in references [11] and [14]. We found $a = 0.296$ P, a value that is only 10 % higher than the previous one, which is reasonable in view of the data available.

Then, with the values of θ_3 and T_0 fixed, we used equation (1.7) and the data on $\gamma_3(T)$ to get $b = 0.1884$ P.

Finally, with the foregoing values of b , θ_3 and T_0 we computed the complete curve $\gamma_3(T_{Ni} - T)$ which is shown in figure 3 together with the experimental data ;

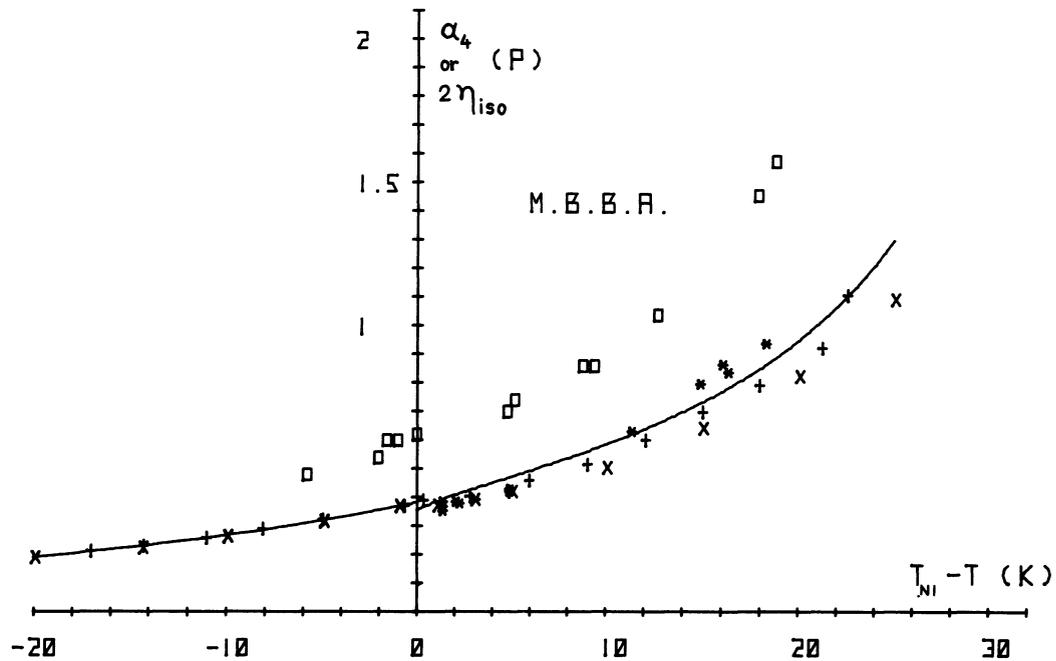


Fig. 4. — α_4 and $2 \eta_{iso}$ versus $T_{NI} - T$ for M.B.B.A. The full curve $\alpha_4(T_{NI} - T)$ was computed using equations (4.7) and (1.4) as explained in the text. The parameters in equation (1.4) are : $a = 0.296$ P, $b = 0.188$ P, $\theta_3 = 153.82$ K and $T_0 = 255$ K. Data points : + from Ref. [11]; \square from Ref. [12]; \times from Ref. [14]; * from Ref. [23]. The full curve $2 \eta_{iso}(T_{NI} - T)$ was computed by a least squares fit procedure over the data of references [11] and [14]; its analytical form is

$$2 \eta_{iso}(P) = 3.198 \times 10^{-6} \times \exp(3708.06/T).$$

in spite of the dispersion of the data, the agreement found appears to be rather satisfactory.

4) At this point we already knew all the parameters needed to compute $\alpha_4(T)$ through equation (1.4). Choosing the second value of a , we computed the curve $\alpha_4(T_{NI} - T)$ shown in figure 4, to which we superimposed the experimental points quoted from references [11, 12, 14, 23]. No least squares fit was used here. The agreement found was again very good, except for one set of data (from Ref. [12]), which is certainly overestimated.

5) To compute $\alpha_1(T)$ from equation (1.3) only one more parameter (c_1) was needed. We took the appropriate experimental data from reference [14] and using the previously computed values of θ_3 and T_0 we got $c_1 = -0.1466$ P by the least squares method; the corresponding curve is shown in figure 5 together with the data. Good agreement is found again (note that the ordinate scale in figure 5 is five times expanded relatively to that used in the other figures). However a word of caution is necessary in this case. As pointed out by different authors [11, 14], $\alpha_1(T)$ is hard to get in a flow experiment because it is obtained through the difference between two nearly equal terms, i.e.

$$\alpha_1 = 4 \eta_{45} - 2(\eta_b + \eta_c) \quad (4.8)$$

where η_{45} is the apparent viscosity measured when the director is normal to the velocity gradient and makes

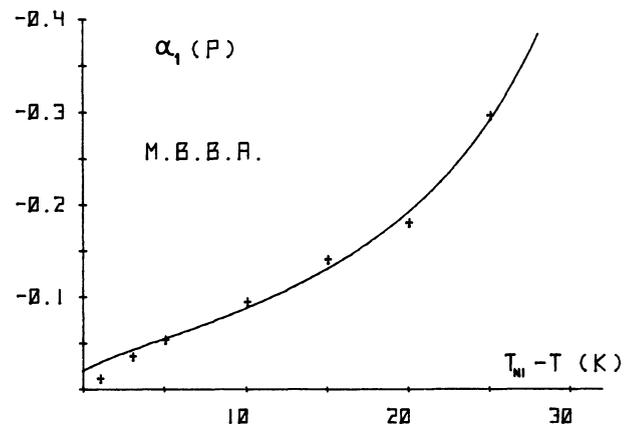


Fig. 5. — α_1 versus $T_{NI} - T$. The full curve is a least squares fit of equation (1.3), with the previously computed values of θ_3 and T_0 , to the experimental data in reference [14], giving $c_1 = -0.147$ P.

an angle of 45° with the velocity vector. The absolute values of $\alpha_1(T)$ so obtained may thus contain significant errors. For example, Gähwiler [11] reports the (single) value $\alpha_1 = 6 \pm 4$ cP at $T_{NI} - T = 18$ K, which is at strong variance with the Kneppé and Schneider's [14] value $\alpha_1 = -16.4$ cP at the same $T_{NI} - T$ (Fig. 5). Both values were obtained through the measurement of η_{45} , η_b and η_c , and application of equation (4.8). But, as mentioned above, and as shown by figure 7, Gähwiler's data about η_c are

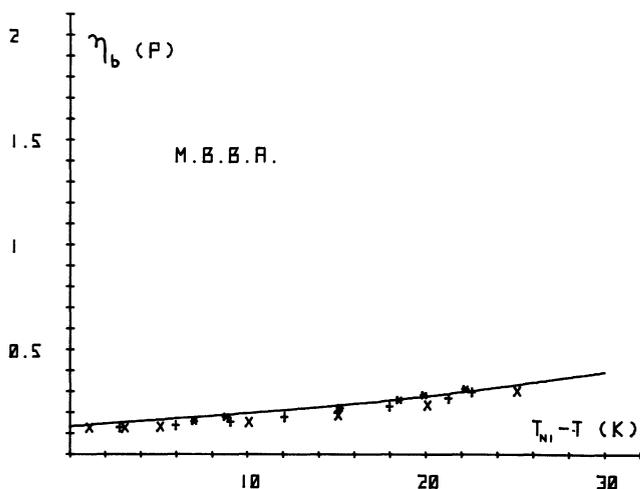


Fig. 6. — η_b versus $T_{NI} - T$. The full curve was computed through expression (4.2) and the previously evaluated expressions for $\gamma_1(T)$, $\gamma_2(T)$, $\gamma_3(T)$ and $\alpha_4(T)$. Data points : + from Ref. [11]; x from Ref. [14]; * from Ref. [23].

underestimated (≈ 15 cP from Fig. 7). If we use in equation (4.8) our value of $\eta_c(T_{NI} - 18)$ from figure 7, Gähwiler's estimate of α_1 becomes $\alpha_1(T_{NI} - 18) \approx -24 \pm 4$ cP which is now compatible with the results in figure 5 (Gähwiler's estimated error should not be taken too seriously).

6) Finally, to conclude the analysis of the experimental data, we computed $\eta_b(T)$ and $\eta_c(T)$ from equations (4.1)-(4.3) and the theoretical curves of $\gamma_1(T)$, $\gamma_2(T)$, $\gamma_3(T)$ and $\alpha_4(T)$ previously obtained. Figures 6 and 7 display the computed curves superimposed to the experimental data available, showing again good agreement and proving the self-consistency of our analysis. Note that these curves are not least squares fits.

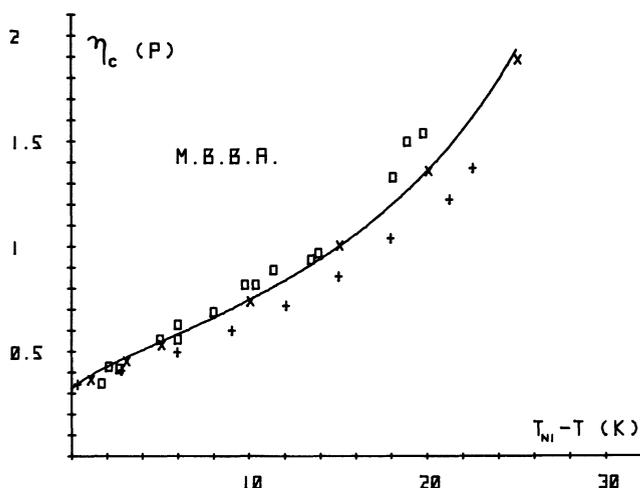


Fig. 7. — η_c versus $T_{NI} - T$. The full curve was computed through expression (4.3) and the previously evaluated expressions for $\gamma_1(T)$, $\gamma_2(T)$, $\gamma_3(T)$ and $\alpha_4(T)$. Data points : + from [11]; \square from [12]; x from [14].

5. Discussion. — The analysis performed in the preceding section leads us to the conclusion that equations (1.3)-(1.7) agree fairly well with the experimental data reported about the nematic viscosities of M.B.B.A. Our analysis also supports the suggestion [12, 13] that the η_c values of reference [11] are underestimated, as it is seen from figure 7.

We remark that with only nine parameters ($g_1, g_2, a, b, c_1, \theta_1, \theta_2, \theta_3$, and T_0) we were able to compute the temperature variation of the five viscosities $\gamma_1, \gamma_2, \gamma_3, \alpha_4$, and α_1 in a fairly good agreement with the experiment. In principle, according to our equations (2.19)-(2.23) twelve parameters are needed to determine completely the thermal dependence of five independent viscosities of a nematic liquid crystal. However, as α_1 is comparatively negligible, we may drop the S^2 -terms in equations (2.21) and (2.23) and yet compute the parameters $g_1, g_2, a, b, c_1, \theta_1, \theta_2, \theta_3$, and T_0 with excellent accuracy (just as done above). Moreover, if the experimental values of η_{iso} and α_4 near T_{NI} are known with enough accuracy, one of the two parameters a or b can be directly computed from the size of the discontinuity in α_4 for $T = T_{NI}$ (see Eq. (4.7)), therefore reducing the number of free parameters to eight. If T_0 can be measured by a different technique, the free parameters reduce to seven when α_1 can be measured or to six when α_1 lies within the experimental error and is neglected.

It is interesting to note that our value of T_0 is close to one of the two transitions that have been found in the supercooled nematic phase of M.B.B.A. around 200 K and 248-258 K [26].

Another (rough) check of our results can be done by considering the values obtained for the parameters θ_1 and θ_3 . As remarked before, it is expected that for $T \approx T_{NI}$:

$$\theta_1 S^2 \sim \frac{\Delta V_{NI}}{V_0 \cdot \alpha}, \tag{5.1}$$

where ΔV_{NI} is the volume jump at T_{NI} . Taking $\alpha \approx \alpha_N = 6.7 \times 10^{-4} \text{ K}^{-1}$ [25] and $V_N(T_{NI}) \approx 259 \text{ cm}^3/\text{mole}$ [25], we computed $V_0 \approx 248 \text{ cm}^3/\text{mole}$. As $S(T_{NI}) \approx 0.325$ [24] we found $\theta_1 \cdot V_0 \cdot \alpha \cdot S^2 \approx 2 \text{ cm}^3/\text{mole}$ which is somewhat greater than the experimental value $\Delta V_{NI} = 0.4 \text{ cm}^3/\text{mole}$ [25]. But α is actually the thermal expansion coefficient of the free volume which is necessarily smaller than the nematic one, i.e., $\alpha \approx \alpha_N - \alpha_K$. On the other hand, we also expect that for $T \approx T_{KN}$:

$$\theta_3 S^2 \sim \frac{\Delta V_{KN}}{V_0 \cdot \alpha}, \tag{5.2}$$

where the subscript KN refers to the crystal-nematic phase transition. For $T = 293 \text{ K}$ we find now $\theta_3 \cdot V_0 \cdot \alpha \cdot S^2 \approx 10 \text{ cm}^3/\text{mole}$ which is close to the experimental value $\Delta V_{KN} = 12 \text{ cm}^3/\text{mole}$ [25].

6. Conclusion. — We propose in this paper expressions to account for the order parameter and tempe-

perature dependence of five independent viscosities of nematic liquid crystals. We have shown that besides their thermal dependence on the order parameter, the temperature dependence of the five viscosities is mainly due to three relaxation times, respectively for shear stresses, orientation stresses, and the coupling between them, and that the thermal dependence of these times is mainly a free-volume effect.

All our expressions are in fairly good agreement with the corresponding experimental data so far reported for M.B.B.A., over the full nematic range of this material. Similar data on Merck-IV and pentylcyanobiphenyl

are currently being investigated and will be shown to support as well the theory in this paper (Diogo, A. C. and Martins, A. F., work in preparation).

New experimental data on the viscosities of other nematic materials would be very welcome in order to test the generality of the expressions proposed in this paper. On the other hand, it would be interesting to get a better insight into the meaning of the parameter T_0 either by this technique or by any other.

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