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Determination of Viscosity Coefficients of a Nematic Liquid Crystal Using a Shear Waves Reflectance Technique†

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Abstract—Dispersion equations for shear waves propagating in a nematic liquid crystal are derived from the Ericksen and Leslie's hydrodynamic equations. The complex reflection coefficient of a shear wave at a solid-nematic liquid crystal interface is related to effective viscosity coefficients depending on the orientation of the molecules with respect to the polarization of the wave.

Some experimental results relative to paramethoxybenzilidene-butylanilin are presented.

Résumé—On établit à partir des équations hydrodynamiques d'Ericksen et de Leslie les équations de dispersion d'ondes de cisaillement se propageant dans un cristal liquide nématique orienté. On donne les relations entre le coefficient de réflection d'une onde de cisaillement sur un interface solide-liquide nématique et les coefficients de viscosité effectifs obtenus pour différentes orientations du nématique par rapport au plan de polarisation de l'onde.

On expose des résultats expérimentaux obtenus sur un échantillon de paraméthoxybenzylidènebutylaniline.

Introduction

The dynamical behaviour of nematic liquid crystals at low frequencies and long wavelengths is well described by the continuum theory introduced by Ericksen⁽¹⁾ and Leslie⁽²⁾. The fundamental hydrodynamic equations involve six frictional coefficients. In order to obtain these coefficients, different types of techniques can be used (Inelastic light scattering,⁽³⁾ Viscosimetry⁽⁴·⁵⁾).

In this paper we are dealing with ultrasonic attenuation of shear

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waves which provides another useful method for measuring viscosity coefficients.

At first, we derive from the hydrodynamic equations, the expressions of the shear attenuation relative to different orientations of the preferred axis of the molecules with respect to the polarization of the wave.

Then, we show how effective viscosity coefficients can be obtained by a reflectance technique which has been already used successfully for viscous and viscoelastic liquids.(6,7,8)

We also present some experimental results obtained for nematic methoxybenzylidenebutylanilin (MBBA).

1. Hydrodynamic Equations for a Nematic Liquid Crystal

For small amplitude motions, the general equation describing the motion of an incompressible nematic fluid was given by Ericksen(1) and Leslie(2)

$$\rho \dot{V}_i = \frac{\partial}{\partial x_j}\sigma_{ji} - \frac{\partial p}{\partial x_j}\delta_{ij} \tag{1}$$

where:

—ρ is the density

—V the hydrodynamic velocity of components V_i

—p the pressure

—σ_{ij} the non-symmetric stress tensor

$$\sigma_{ij} = \alpha_1 n_k n_p A_{kp} n_i n_j + \alpha_2 n_i N_j + \alpha_3 n_j N_i + \alpha_4 A_{ij} + \alpha_5 n_i n_k A_{kj} + \alpha_6 n_j n_k A_{ki} \tag{2}$$

with:

$$A_{ij} = \tfrac{1}{2}\left(\frac{\partial V_i}{\partial x_j} + \frac{\partial V_j}{\partial x_i}\right) \quad \text{and} \quad \mathbf{N} = \frac{\mathrm{d}\mathbf{n}}{\mathrm{d}t} - \tfrac{1}{2}\,\mathbf{rot}\,\mathbf{V}\wedge\mathbf{n} \tag{3}$$

The α_i coefficients have the dimension and the order of magnitude of a viscosity. At each point **r** in space the preferred direction of the molecules is described by an unit vector **n** (director) of components n_i.

As the molecules exert on the hydrodynamic motion a torque $\mathbf{\Gamma}$, there is a supplementary equation of motion for the internal rotation

$$I\frac{\mathrm{d}\mathbf{\Omega}}{\mathrm{d}t} = \mathbf{n}\wedge\mathbf{h} - \mathbf{\Gamma} \tag{4}$$

where:

—$\mathbf{\Omega} = \mathbf{n}\Lambda\frac{d\mathbf{n}}{dt}$ is the internal rotational velocity.

—I is the moment of inertia by unit volume.

—$\mathbf{n}\Lambda\mathbf{h}$ is the torque on one molecule due to its coupling with neighbours ($\mathbf{h}$ is a molecular field derived from the free energy expression of Franck).⁽¹¹⁾

—$\mathbf{\Gamma}$ is the frictional torque associated with the hydrodynamic motion.

$$\mathbf{\Gamma} = \mathbf{n}\Lambda[\gamma_1\mathbf{N} + \gamma_2 A\mathbf{n}] \tag{5}$$

with

$$\gamma_1 = \alpha_3 - \alpha_2$$
$$\gamma_2 = \alpha_6 - \alpha_5$$

Moreover, there are only five independent coefficients according to the Parodi's relation⁽⁹⁾

$$\alpha_2 + \alpha_3 = \alpha_6 - \alpha_5$$

We assume that:

(a) The medium is incompressible

(b) The Franck's constants are all equal ($K_{ii} = K$); in which case:

$$\mathbf{h} = K\Delta\mathbf{n} \tag{6}$$

(c) The inertia term is negligible in equation (4) which becomes

$$\mathbf{\Gamma} = \mathbf{n}\Lambda\mathbf{h} \tag{7}$$

2. Shear Waves Propagation in a Nematic Liquid Crystal

I. GENERAL EQUATIONS

Let us consider a system of rectangular x_1, x_2, x_3 coordinates (Fig. 1). Let $\theta_1, \theta_2, \theta_3$, be the angles between the director and the three axis.

We consider a shear wave with the displacement in the x_1 direction and we assume that this displacement is independent of x_1 but may vary along x_2 and x_3. In this case, the only non zero components in the stress tensor are:

$$A_{12} = A_{21} = \tfrac{1}{2}\frac{\partial V_1}{\partial x_2} \quad \text{and} \quad A_{13} = A_{31} = \tfrac{1}{2}\frac{\partial V_1}{\partial x_3}$$

The equation of motion is:

$$\rho\dot{V}_1 = \frac{\partial}{\partial x_2}\sigma_{21} + \frac{\partial}{\partial x_3}\sigma_{31}$$

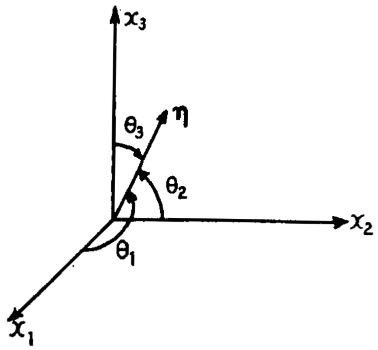

Figure 1.

with:

$$\sigma_{31} = \frac{A}{2}\frac{\partial V_1}{\partial x_2} + \frac{B}{2}\frac{\partial V_1}{\partial x_3} + \alpha_2 n_3 \frac{\mathrm{d}n_1}{\mathrm{d}t} + \alpha_3 n_1 \frac{\mathrm{d}n_3}{\mathrm{d}t}$$

$$\sigma_{21} = \frac{A'}{2}\frac{\partial V_1}{\partial x_2} + \frac{B'}{2}\frac{\partial V_1}{\partial x_3} + \alpha_2 n_2 \frac{\mathrm{d}n_1}{\mathrm{d}t} + \alpha_3 n_1 \frac{\mathrm{d}n_2}{\mathrm{d}t}$$

and:

$$\begin{aligned} A &= n_3 n_2 (2\alpha_1 n_1^2 + \alpha_5 - \alpha_2) \\ B &= 2\alpha_1 n_1^2 n_3^2 + n_1^2(\alpha_3 + \alpha_6) + n_3^2(\alpha_5 - \alpha_2) + \alpha_4 \\ A' &= 2\alpha_1 n_1^2 n_2^2 + n_1^2(\alpha_3 + \alpha_6) + n_2^2(\alpha_5 - \alpha_2) + \alpha_4 \\ B' &= A \end{aligned} \tag{8}$$

According to Eq. (5) the components of Γ are:

$$\begin{aligned} \Gamma_1 &= \gamma_1\left(n_2 \frac{\mathrm{d}n_3}{\mathrm{d}t} - n_3 \frac{\mathrm{d}n_2}{\mathrm{d}t}\right) + \tfrac{1}{2}\frac{\partial V_1}{\partial x_3} n_1 n_2 (\gamma_1 + \gamma_2) \\ &\quad - \tfrac{1}{2}\frac{\partial V_1}{\partial x_2} n_1 n_3 (\gamma_1 + \gamma_2) \\ \Gamma_2 &= \gamma_1\left(n_3 \frac{\mathrm{d}n_1}{\mathrm{d}t} - n_1 \frac{\mathrm{d}n_3}{\mathrm{d}t}\right) + \tfrac{1}{2}\frac{\partial V_1}{\partial x_3}[n_3^2(\gamma_2 - \gamma_1) - n_1^2(\gamma_1 + \gamma_2)] \\ &\quad + \tfrac{1}{2}\frac{\partial V_1}{\partial x_2} n_2 n_3 (\gamma_2 - \gamma_1) \\ \Gamma_3 &= \gamma_1\left(n_1 \frac{\mathrm{d}n_2}{\mathrm{d}t} - n_2 \frac{\mathrm{d}n_1}{\mathrm{d}t}\right) + \tfrac{1}{2}\frac{\partial V_1}{\partial x_3} n_2 n_3 (\gamma_1 - \gamma_2) \\ &\quad + \tfrac{1}{2}\frac{\partial V_1}{\partial x_2}[n_1^2(\gamma_1 + \gamma_2) + n_2^2(\gamma_1 - \gamma_2)] \end{aligned} \tag{5'}$$

and using Eq. (7)

$$\Gamma_1 = K\left\{\sin\theta_2\cos\theta_3\,\nabla^2\theta_2 - \sin\theta_3\cos\theta_2\,\nabla^2\theta_3 + \cos\theta_2\cos\theta_3\left[\left(\frac{\partial\theta_2}{\partial x_2}\right)^2 + \left(\frac{\partial\theta_2}{\partial x_3}\right)^2 - \left(\frac{\partial\theta_3}{\partial x_2}\right)^2 - \left(\frac{\partial\theta_3}{\partial x_3}\right)^2\right]\right\} \tag{7'}$$

Γ_2 and Γ_3 being obtained by circular permutation on the indices.

In the study of the propagation of shear waves, we are concerned with the deviations of variables from their values at rest.

Considering only first order variations we can write:

$$\theta_i = \theta_{i,0} + \epsilon_i$$

Assuming that the variations are small it is possible in Eqs. (8) (5′) (7′) to neglect powers of small quantities higher than the first and their products.

We consider the three following orientations of the director with respect to the plane of polarization of the shear wave:

(a) Molecules parallel to ox_1.

The equation of motion is:

$$\rho\dot{V}_1 = \tfrac{1}{2}(\alpha_3+\alpha_4+\alpha_6)\left(\frac{\partial^2 V_1}{\partial x_2^2} + \frac{\partial^2 V_1}{\partial x_3^2}\right) - \alpha_3\left(\frac{\partial}{\partial x_3}\epsilon_3 + \frac{\partial}{\partial x_2}\epsilon_2\right)$$

The expressions of $\dot{\epsilon}_3$ and $\dot{\epsilon}_2$ can be derived from the Eqs. (5′) and (7′)

$$\begin{aligned}\dot{\epsilon}_3 &= \frac{K}{\gamma_1}\nabla^2\epsilon_3 + \tfrac{1}{2}\frac{\partial V_1}{\partial x_3}\left(1+\frac{\gamma_2}{\gamma_1}\right)\\ \dot{\epsilon}_2 &= \frac{K}{\gamma_1}\nabla^2\epsilon_2 + \tfrac{1}{2}\frac{\partial V_1}{\partial x_2}\left(1+\frac{\gamma_2}{\gamma_1}\right)\end{aligned} \tag{9a}$$

(b) Molecules parallel to ox_2

$$\rho\dot{V}_1 = \frac{(\alpha_4+\alpha_5-\alpha_2)}{2}\frac{\partial^2 V_1}{\partial x_2^2} + \frac{\alpha_4}{2}\frac{\partial^2 V_1}{\partial x_3^2} - \alpha_2\frac{\partial}{\partial x_2}\dot{\epsilon}_1$$

with:

$$\dot{\epsilon}_1 = \frac{K}{\gamma_1}\nabla^2\epsilon_1 - \tfrac{1}{2}\frac{\partial V_1}{\partial x_2}\left(1-\frac{\gamma_2}{\gamma_1}\right) \tag{9b}$$

(c) Molecules parallel to ox_3

$$\begin{aligned}\rho\dot{V}_1 &= \frac{\alpha_4}{2}\frac{\partial^2 V_1}{\partial x_2^2} + \frac{(\alpha_5-\alpha_2+\alpha_4)}{2}\frac{\partial^2 V_1}{\partial x_3^2} - \alpha_2\frac{\partial}{\partial x_3}\dot{\epsilon}_1\\ \dot{\epsilon}_1 &= \frac{K}{\gamma_1}\nabla^2\epsilon_1 - \tfrac{1}{2}\left(1-\frac{\gamma_2}{\gamma_1}\right)\frac{\partial V_1}{\partial x_3}\end{aligned} \tag{9c}$$

II. SHEAR WAVE PROPAGATION ALONG x_3 AXIS WITH DISPLACEMENT ALONG x_1

(a) Molecules parallel to ox_1 (i.e. parallel to the flow).

The equation of motion is:

$$\rho \dot{V}_1 = \frac{(\alpha_3+\alpha_4+\alpha_6)}{2}\frac{\partial^2 V_1}{\partial x_3^2} - \alpha_3 \frac{\partial}{\partial x_3}\dot{\epsilon}_3 \tag{10}$$

with:

$$\dot{\epsilon}_3 = \frac{K}{\gamma_1}\frac{\partial^2 \epsilon_3}{\partial x_3^2} + \tfrac{1}{2}\left(1+\frac{\gamma_2}{\gamma_1}\right)\frac{\partial V_1}{\partial x_3} \tag{11}$$

We look for solutions of the form:

$$V_1 = A\,\mathrm{e}^{i\omega t}\,\mathrm{e}^{-\Gamma x_3}$$

$$\epsilon_3 = \epsilon_{3,0}\,\mathrm{e}^{i\omega t}\,\mathrm{e}^{-\Gamma x_3}$$

Γ being the complex constant of propagation of the wave. As we are concerned with small amplitude variations we can assume that $\mathrm{d}/\mathrm{d}t = \partial/\partial t = i\omega$.

Combining (10) and (11) we obtain the dispersion equation:

$$\frac{EK}{\gamma_1}\Gamma^4 - i\omega\Gamma^2\left(J+\frac{K\rho}{\gamma_1}\right) - \omega^2\rho = 0 \tag{12}$$

with:

$$E = \frac{\alpha_3+\alpha_4+\alpha_6}{2}$$

$$J = E - \frac{\alpha_3}{2}\left(1+\frac{\gamma_2}{\gamma_1}\right)$$

E and J are both positive.(10)

The solutions of (12) are:

$$\Gamma'^2 = \frac{i\omega\gamma_1}{2EK}\left(J+\frac{K\rho}{\gamma_1}\right)\left[1+\left(1-\frac{4\rho EK}{\gamma_1[J+(K\rho/\gamma_1)]^2}\right)^{1/2}\right]$$

$$\Gamma''^2 = \frac{i\omega\gamma_1}{2EK}\left(J+\frac{K\rho}{\gamma_1}\right)\left[1-\left(1-\frac{4\rho EK}{\gamma_1[J+(K\rho/\gamma_1)]^2}\right)^{1/2}\right]$$

The term $4\rho EK/\gamma_1[J+(K\rho/\gamma_1)]^2$ is positive and in most cases much smaller than 1. ($K{\sim}10^{-6}$ dyne, $J{\sim}E{\sim}\gamma_1{\sim}0{,}1$ poise, $\rho{\sim}1$ gr/cc) Then:

$$\Gamma'^2 = \frac{i\omega J\gamma_1}{EK}$$

$$\Gamma''^2 = \frac{i\omega\rho}{J} \tag{13'}$$

There are two solutions of (13′) having physical meaning

$$\Gamma' = (1+i)\left(\frac{\omega J\gamma_1}{2EK}\right)^{1/2}$$

$$\Gamma'' = (1+i)\left(\frac{\omega\rho}{2J}\right)^{1/2}$$

The shear attenuation is given by the real part of Γ.

Γ' refers to an essentially orientational mode characterized by a very high attenuation.

Γ'' represents a mode similar to the one found for pure viscous liquids. In what follows we will refer to Γ' as an " orientational " mode and Γ'' as a " hydrodynamic " mode.

(b) Molecules parallel to ox_3 (i.e. to the shear gradient)

As above one finds two propagating modes characterized by:

$$\Gamma' = (1+i)\left(\frac{\omega J\gamma_1}{2EK}\right)^{1/2}$$
$$\Gamma'' = (1+i)\left(\frac{\omega\rho}{2J}\right)^{1/2} \tag{15}$$

with:

$$J = \tfrac{1}{2}(\alpha_5 - \alpha_2 + \alpha_4) + \frac{\alpha_2}{2}\left(1 - \frac{\gamma_2}{\gamma_1}\right)$$

$$E = \frac{\alpha_5 - \alpha_2 + \alpha_4}{2}$$

(c) Molecules parallel to ox_2 (i.e. perpendicular to both flow and shear gradient).

There is no coupling between orientation of molecules and hydrodynamic velocity.

From the equation of motion:

$$\rho\dot{V}_1 = \frac{\alpha_4}{2}\frac{\partial^2 V_1}{\partial x_3^2}$$

We derive only one solution:

$$\Gamma = (1+i)\left(\frac{\omega\rho}{\alpha_4}\right)^{1/2}$$

3. Reflection and Refraction of Plane Shear Waves at a Plane Interface of a Glass and a Nematic Liquid Crystal

I. NORMAL INCIDENCE

A. Reflection coefficient and effective viscosity coefficients

The expression of the complex reflection coefficient is obtained by writing the conditions of continuity for velocities and stresses at the interface.

The plane $x_3 = 0$ is taken as the common boundary of the two media (Fig. 2).

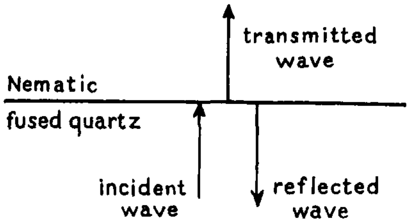

Figure 2.

The index s refers to the solid ($x_3 < 0$), index n to the nematic ($x_3 > 0$).

Let us consider an incident plane wave

$$V_i = A_i e^{i\omega t} e^{-\Gamma_s x_3}$$

Both reflected and refracted waves are transverse because the displacement at the interface due to the incident wave is parallel to the x_1 axis and independent of x_1.

The velocities associated with these waves are:

$$V_r = A_r e^{i\omega t} e^{+\Gamma_s x_3}$$

$$V_t = A_t e^{i\omega t} e^{-\Gamma_n x_3}$$

As there are two propagating modes in the nematic medium, we can write

$$V_t = V_t' + V_t''$$

with:

$$V_t' = A_t' e^{i\omega t} e^{-\Gamma_n' x_3}$$

$$V_t'' = A_t'' e^{i\omega t} e^{-\Gamma_n'' x_3}$$

At the interface the sum of the primary and reflected particle velocities must be equal to the sum of the refracted particle velocities:

$$A_i + A_r = A_t' + A_t'' \qquad (16)$$

The stress σ_{31} across planes parallel to the interface must also be continuous at the interface.

In the solid

$$\sigma_{31} = -Z_s(A_i e^{-\Gamma_s x_3} - A_r e^{+\Gamma_s x_3})$$

where Z_s is the mechanical impedance of the medium.

At the interface:

$$(\sigma_{31})_{x_3=0} = -Z_s(A_i - A_r)$$

In the nematic liquid crystal σ_{31} is a function of the orientation of the director. We consider again successively the three principal orientations.

(a) Molecules parallel to ox_1

σ_{31} is then given by

$$\sigma_{31} = \frac{B}{2}\left(\frac{\partial V_t}{\partial x_3}\right) - \alpha_3 \dot{\epsilon}_3 \qquad (18)$$

with:

$$B = \alpha_3 + \alpha_4 + \alpha_6$$

If the orientation of the nematic has been obtained by wall action, we may assume that at the surface of the solid the orientation is rigid

$$(\epsilon_3)_{x_3=0} = (\epsilon_3' + \epsilon_3'')_{x_3=0} = 0 \qquad (19)$$

Then the stress at the interface is given by:

$$(\sigma_{31})_{x_3=0} = \frac{B}{2}\left(\frac{\partial V_t}{\partial x_3}\right)_{x_3=0}$$

And the boundary condition gives:

$$\frac{B}{2}(\Gamma_n' A_t' + \Gamma_n'' A_t'') = Z_s(A_i - A_r) \qquad (20)$$

Combining Eqs. (16) and (20) we obtain the complex reflection coefficient r

$$r = \frac{A_r}{A_i} = \frac{Z_s - Z_n}{Z_s + Z_n} \tag{21}$$

with:

$$(Z_n)_{x_3=0} = \frac{B\Gamma''_n[1 + (A'_t\Gamma'_n/A''_t\Gamma''_n)]}{2[1 + (A'_t/A''_t)]} \tag{22}$$

Z_n represents the mechanical impedance of the nematic.

On the other hand, by using Eqs. (11) and (19) we can derive the expression for A'_t/A''_t.

$$\frac{A'_t}{A''_t} = -\frac{\alpha''_n}{\alpha'_n}\frac{1 - (2K/\gamma_1\omega)(\alpha'_n)^2}{1 - (2K/\gamma_1\omega)(\alpha''_n)^2} = \left(\frac{EK\rho}{J^2\gamma_1}\right)^{1/2} \frac{2J/B - 1}{1 - (K\rho/\gamma_1 J)}$$

Since $\Gamma_n = (1 + i)\alpha_n$

Accounting for the order of magnitude of the different terms we found that $A'_t/A''_t \leqslant 1$ and:

$$1 + \frac{A'_t}{A''_t}\frac{\Gamma'_n}{\Gamma''_n} \sim 2J/B$$

Therefore, Z_n becomes:

$$(Z_n)_{x_3=0} = (1 + i)\left(\frac{\omega\rho J}{2}\right)^{1/2} \tag{25}$$

with:

$$J = \frac{\alpha_3 + \alpha_4 + \alpha_6}{2} - \frac{\alpha_3}{2}\left(1 + \frac{\gamma_2}{\gamma_1}\right)$$

The knowledge of the mechanical impedance $Z_n (Z_n = R_n + iX_n)$ leads to the dynamic viscosity $(\eta = \eta^{(1)} - i\eta^{(2)})$ through the relations(6)

$$\eta^{(1)} = \frac{2R_nX_n}{\rho\omega} \qquad \eta^{(2)} = \frac{R_n^2 - X_n^2}{\rho\omega} \tag{26}$$

As $R_n = X_n$

$$\eta_a^{(1)} = \frac{2R_n^2}{\rho\omega} = \frac{\alpha_3 + \alpha_4 + \alpha_6}{2} - \frac{\alpha_3}{2}\left(1 + \frac{\gamma_2}{\gamma_1}\right)$$

$$\eta_a^{(2)} = 0$$

(b) Molecules parallel to ox_3

Then

$$\sigma_{31} = \frac{B}{2}\frac{\partial V_t}{\partial x_3} - \alpha_2\dot{\epsilon}_1 \quad \text{with} \quad B = \alpha_5 + \alpha_4 - \alpha_2$$

As above, one finds:

$$(Z_n)_{x_3=0} = (1+i)\left(\frac{\omega\rho J}{2}\right)^{1/2} \tag{27}$$

with:

$$J = \frac{\alpha_4+\alpha_5-\alpha_2}{2} + \frac{\alpha_2}{2}\left(1-\frac{\gamma_2}{\gamma_1}\right)$$

and

$$\eta_b^{(1)} = \frac{\alpha_4+\alpha_5-\alpha_2}{2} + \frac{\alpha_2}{2}\left(1-\frac{\gamma_2}{\gamma_1}\right)$$

$$\eta_b^{(2)} = 0$$

(c) Molecules parallel to ox_2

In this case: $\sigma_{31} = \frac{B}{2}\frac{\partial V_t}{\partial x_3}$

$$Z_n = \frac{B}{2}\Gamma_n \tag{28}$$

with: $B = \alpha_4$

The effective viscosity coefficient is:

$$\eta_c^{(1)} = \frac{\alpha_4}{2}$$

B. Relationship between complex reflection coefficient and shear mechanical impedance

From the Eq. (21)

$$Z_n = Z_s\frac{1-r}{1+r} \tag{29}$$

The value of Z_s is known. By measuring r it is possible to determine the shear mechanical impedance of the nematic at the interface and then, using Eqs. (25) (27) and (28), the effective viscosity coefficients.

The complex reflection coefficient can be written:

$$r = |r|\,e^{-i\theta}$$

where $|r|$ is the ratio of the amplitudes of the reflected and incident waves and θ the phase shift of the reflected waves caused by the presence of the nematic.

The Eq. (29) becomes:

$$Z_n = R_n + iX_n = Z_s \frac{1-|r|^2+2i|r|\sin\theta}{1+|r|^2+2|r|\cos\theta} \tag{30}$$

As in the case considered $R_n = X_n$, it is sufficient to measure $|r|$, θ being given by the relation

$$\sin\theta = \frac{1-|r|^2}{2|r|}$$

II. OBLIQUE INCIDENCE

The refracted disturbance is of a different nature than an ordinary plane wave. Nevertheless we can still write the boundary conditions and obtain expressions for the complex reflection coefficient.†

In the solid medium. For shear waves such that the motion in the x_1 direction is independent of x_1 the particle velocity satisfies the equation:

$$\left(\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial x_3^2}\right)V_i = \Gamma_s^2 V_i \tag{31}$$

A typical solution of this equation is:

$$V_i = A_0 e^{-G_s x_2 - H_s x_3} = A_0 e^{-\Gamma_s(mx_2+nx_3)}$$

where:

$$G_s^2 + H_s^2 = \Gamma_s^2$$

$$m^2 + n^2 = 1$$

m and n can be represented by $m = \sin\phi$ and $n = \cos\phi$. If ϕ is real $mx_2 + nx_3$ represents the distance to the origin in the direction of propagation. Then ϕ is the incidence angle.

In the nematic medium. We start from the general Eqs. (9a) (9b) (9c) and we look for solutions of the form:

$$V_t = A\, e^{i\omega t} e^{-G_n x_2 - H_n x_3}$$

$$\epsilon_i = \epsilon_{i0} e^{i\omega t} e^{-G_n x_2 - H_n x_3}$$

where G_n and H_n represent complex propagation constants along x_2 and x_3.

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† A detailed derivation of the reflection coefficient at the interface of two isotropic viscoelastic media, for oblique incidence has been made by H. T. O'Neil.(12)

We consider again three orientations.

(a) Molecules parallel to ox_1

Accounting for the equality $G_n = G_s$ (implied by continuity conditions for velocities at the interface), the dispersion equation is:

$$\frac{EK}{\gamma_1}H_n^4 - H_n^2\left[-\frac{2EK}{\gamma_1}G_s^2 + i\omega\left(J+\frac{K\rho}{\gamma_1}\right)\right] + \frac{K}{\gamma_1}EG_s^4 - i\omega G_s^2\left(J+\frac{K\rho}{\gamma_1}\right) - \omega^2\rho = 0 \tag{32}$$

Solving this equation we obtain as in the case of normal incidence two modes characterized by the following approximate expressions of the propagation constants.

$$\begin{aligned} (H'_n)^2 &= \frac{i\omega\gamma_1 J}{EK} - G_s^2 \\ (H''_n)^2 &= \frac{i\omega\rho}{J} - G_s^2 \end{aligned} \tag{33}$$

The boundary conditions for velocities and stresses lead to the relation

$$r = \frac{Z_s\cos\phi - Z_n}{Z_s\cos\phi + Z_n} \tag{34}$$

where: $Z_n = JH''_n$

with: $H''_n = \alpha'' + i\beta''$

and: $(\alpha'')^2 - (\beta'')^2 = -G_s^2$

$$\alpha''\beta'' = \frac{\omega\rho}{2J}$$

The real and imaginary parts of the shear impedance Z_n are then given by:

$$R_n = J\alpha''$$

$$X_n = J\beta''$$

And the real and imaginary parts of the dynamic viscosity are:

$$\eta_a^{(1)} = \frac{2R_nX_n}{\rho\omega} = J \tag{35}$$

$$\eta_a^{(2)} = \frac{R_n^2 - X_n^2}{\rho\omega} = -J^2G_s^2/\rho\omega \tag{36}$$

In the solid medium we may assume that the attenuation of shear waves is negligible, therefore:

$$G_s = \sin\phi\Gamma_s = i\sin\phi\frac{\omega}{C_s}$$

Then:

$$\eta_a^{(2)} = \frac{J^2}{\rho}\sin^2\phi\frac{\omega}{C_s^2}$$

C_s being the propagation velocity in the fused quartz.

In fact for frequencies smaller than 10^9 Hz $\eta_a^{(2)} \to 0$; therefore we may use the approximation $R_n = X_n$ to evaluate $\eta_a^{(1)}$. As we have seen previously, we obtain $\eta_a^{(1)}$ by measuring $|r|$.

For the two other orientations, the derivation is very similar and leads to the following viscosity coefficients.

(b) Molecules parallel to ox_3

$$\eta_b^{(1)} = \frac{\alpha_4+\alpha_5-\alpha_2}{2} + \frac{\alpha_2}{2}\left(1-\frac{\gamma_2}{\gamma_1}\right)$$

(c) Molecules parallel to ox_2

$$\eta_c^{(1)} = \frac{\alpha_4}{2}$$

4. Remarks

I. Normal Incidence and Oblique Incidence

At normal incidence the refracted disturbance consists of two plane shear waves propagating along the same direction as the incident wave.

On the contrary for oblique incidence, the disturbance is of a different type as an ordinary plane wave, the refracted angle being complex.

For instance, if the molecules are oriented along ox_1 (i.e. the case we have considered in detail in part (3. II. a) the complex refracted angle ψ'' of the hydrodynamic mode is given by:

$$\cos^2\psi'' = \frac{J}{i\omega\rho}(H_n'')^2 = 1 - i\frac{\omega J\sin^2\phi}{\rho C_s^2}$$

$$\sin^2\psi'' = \frac{J}{i\omega\rho}G_s^2 = i\frac{\omega J\sin^2\phi}{\rho C_s^2}$$

In fact, we have seen that because of the very small shear attenuation in the fused quartz, the calculation leads to effective viscosity coefficients identical to the rigorous solutions found for normal incidence.

Nevertheless oblique incidence method results in an enhanced effect on $|r|$. The mechanical impedance Z_s being multiplied by $\cos\phi$ (see Eq. 34).

II. Penetration Depth

The wave amplitude drops to 1/e times the initial value in the penetration depth l.

For instance in the case of normal incidence and molecules parallel to ox_1 or ox_3.

$$l' = \left(\frac{2EK}{\omega J\gamma_1}\right)^{1/2} \qquad \text{(orientational mode)}$$

$$l'' = \left(\frac{2J}{\omega\rho}\right)^{1/2} \qquad \text{(hydrodynamic mode)}$$

Typically $l''/l' \sim 100$
In a frequency range 10–100 MHz, the orders of magnitude of l' and l'' are:

$$6\ 10^{-3}\mu > l' > 2\ 10^{-3}\mu$$

$$0.6\mu > l'' > 0.2\mu$$

The penetration depth associated with the most attenuated mode is of the order of magnitude of a few molecular lengths. On the contrary, the hydrodynamic mode propagates in a non negligible distance and it may be possible to perform shear waves attenuation measurements by a transmission technique.

III. Spatial Variation of the Director's Deflection

Except for the case where the nematic is oriented along x_2 the shear gradient induces a deflection of the director. (see Eq. 11), although the boundary conditions imply that the molecules are strongly anchored at the surface.

The spatial variation of angular deviation in case of nematic orientation parallel to ox_1 axis is plotted on Fig. 3.

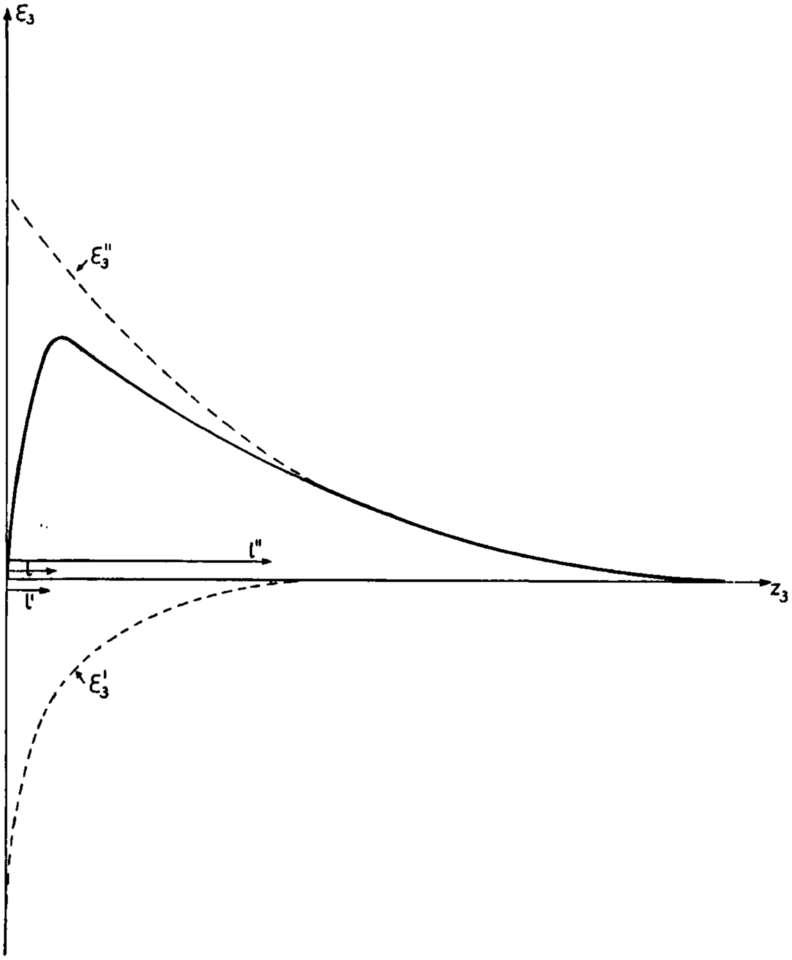

Figure 3.

The deflection is maximum for a distance l :

$$l = \frac{1}{2\alpha'} \log \frac{J^2\gamma_1}{EK\rho}$$

In terms of penetration depth

$$l \simeq 4{,}6\ l'$$

IV. INFLUENCE OF INERTIAL TERMS

So far we have neglected the inertial term in the equation of motion for internal rotation. If we account for this term the dispersion equation becomes more complicated. For instance in the case (a) (normal incidence), we have:

$$\frac{EK}{\gamma_1}\Gamma^4 - \Gamma^2\left(\frac{EI\omega^2}{\gamma_1} + i\omega\left(J + \frac{K\rho}{\gamma_1}\right)\right) - \omega^2\rho - \frac{i\omega^3 I\rho}{\gamma_1} = 0$$

The solutions of this equation depend critically on the value of the parameter: $I\omega/\tilde{\alpha}$ where $\tilde{\alpha}$ represents coefficients of the order of magnitude of a viscosity.

Typically $I \sim 10^{-14}$ gr cm^{-1} for MBBA.

Then we have

$$\frac{I\omega}{\tilde{\alpha}} \ll 1.$$

If $$\omega < 10^{10}\,\text{Hz}.$$

With this assumption, the solutions are identical to the ones found by neglecting inertial effects:

$$\begin{aligned}\Gamma' &= \left(\frac{\omega J\gamma_1}{2EK}\right)^{1/2}\left\{\left(1 + \frac{I\omega E}{2J\gamma_1}\right) + i\left(1 - \frac{I\omega E}{2J\gamma_1}\right)\right\}\\ &\sim \left(\frac{\omega J\gamma_1}{2EK}\right)^{1/2}(1+i)\\ \Gamma'' &= \left(\frac{\omega\rho}{2J}\right)^{1/2}\left\{\left[1 - \frac{I\omega}{2\gamma_1}\left(1 + \frac{E}{J}\right)\right] + i\left[1 + \frac{I\omega}{2\gamma_1}\left(1 + \frac{E}{J}\right)\right]\right\}\\ &\sim \left(\frac{\omega\rho}{2J}\right)^{1/2}(1+i)\end{aligned}$$

Writing as in part (3. I. A) boundary conditions, we found in the same approximation the same expression of the effective viscosity coefficients.

V. COMPARISON BETWEEN VISCOSITY COEFFICIENTS OBTAINED FROM CAPILLARY FLOW AND SHEAR WAVES REFLECTANCE EXPERIMENTS

The theory of laminar flow has been derived by Ericksen and Leslie. These authors show that the behaviour depends on the ratio $|\gamma_2/\gamma_1|$.

Far from the walls, if $|\gamma_1/\gamma_2| < 1$, the director tends toward a steady value lying on the plane of the shear. The angle between the direction of the flow and the director is such that

$$\cos(2\delta) = -\frac{\gamma_1}{\gamma_2}$$

The effective viscosity coefficient is given by

$$\eta^* = \tfrac{1}{2}[2\alpha_1 \cos^2\delta \sin^2\delta + (\alpha_3+\alpha_6)\cos^2\delta + \sin^2\delta(\alpha_5-\alpha_2)+\alpha_4]$$

The experiments of Porter, Johnson, Barrall⁽⁵⁾ seem to prove that $\gamma_2/\gamma_1 \sim -1$ (i.e. $\delta = 0$, molecules aligned along the flow)

Then

$$\eta^* \sim \tfrac{1}{2}(\alpha_3+\alpha_4+\alpha_6)$$

Using $\gamma_2/\gamma_1 \sim -1$ the effective viscosity coefficients measured by shear waves reflectance technique become:

$$\eta_a \sim \tfrac{1}{2}(\alpha_3+\alpha_4+\alpha_6) \sim \eta^*$$

$$\eta_b \sim \tfrac{1}{2}(\alpha_4+\alpha_5+\alpha_2)$$

$$\eta_c \sim \tfrac{1}{2}\alpha_4$$

$$\frac{\gamma_2}{\gamma_1} \sim -1 \text{ leads to } (\alpha_6-\alpha_5) \sim (\alpha_2-\alpha_3)$$

It follows:

$$\eta_a \sim \eta_b \sim \eta^* \ \dagger$$

5. Experimental Results

I. EXPERIMENTAL METHOD

We have used the standard two crystals radiofrequencies pulse technique which has been described by Mason⁽⁸⁾ and MacSkimin.⁽¹³⁾ A thin layer of nematic sample is placed on the top surface (plane $x_3 = 0$) of a fused quartz rod (impedometer) with obliquely cut ends (Fig. 4). The angle of incidence ($\phi = 77° 39'$) is determined from the dimensions of the bar ($A = 76.5$ mm, $B = 16.0$ mm, $C = 21.5$ mm).

A B.T. cut quartz crystal suitably bonded to one end of the bar and resonant in a thickness shear mode generates a pulsed ultrasonic

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† Indeed Rapini has shown by using the Parodi's relation that η_a is equal to η_b independently of the value of the ratio γ_2/γ_1. (Private communication).

shear wave with displacement in the x_1 direction. The transducer vibrates on the fundamental of 4.9 MHz and odd harmonics. The pulse is repeated every two milliseconds and its duration ($5\mu s$) is less than the time of travel through the bar.

At the interface there are a transmitted wave which is rapidly damped out and a reflected wave which is received at the other end of the bar by a second quartz crystal. This wave is reflected repeatedly at the interface and at both ends of the rod, creating a pulse echo pattern which can be displayed on an oscilloscope.

The reflection coefficient is obtained by measuring with a variable attenuator the amplitudes of waves reflected from the solid–liquid interface, and from the same surface when the refracting medium is absent.

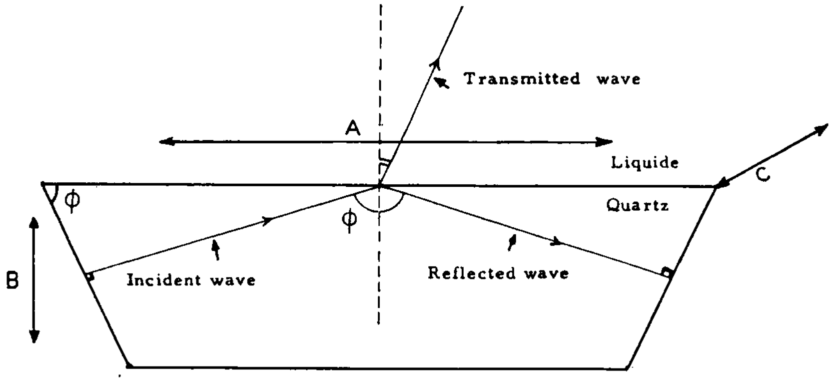

Figure 4.

If D (decibels) is the decrease of echo amplitude upon application of the test material, we have the relation.(7)

$$D = (-40 \log |r|)n + 20 \log |r| \qquad (37)$$

where n is the number of echoes.

The slope of the plot $D = f(n)$ allows us to determine the reflection coefficient.

Measurements have been performed as a function of temperature from 21 °C to 53 °C in the frequency range 15–80 MHz. The viscosity coefficients were obtained with an accuracy of 5 %.

II. MATERIALS

The nematic liquid crystal sample was the Methoxybenzylidenebutylaniline (MBBA). The clearing point was 41 °C. Some experiments done with samples characterized by higher transition temperature (45 °C) showed that the curve of viscosity versus temperature was simply displaced along the temperature axis.

The orientations of the MBBA were obtained by the method of Chatelain,(14) the plane surface of the bar being polished with kleenex.

III. EXPERIMENTAL RESULTS

A. Capillary viscosimetry

Viscosity of MBBA was measured as a function of temperature using capillary viscosimeters of three different diameters.

The results are shown in the Fig. 5. There is no influence of the diameter. The jump observed at the isotropic nematic transition has been observed by Porter, Johnson and Barral(5) for a PAA sample. This behaviour has been discussed by Papoular.(15)

B. Ultrasonic impedometry

We have realized two perpendicular orientations in the plane of the test surface along x_1 and x_3. The corresponding viscosity coefficients are given by the equations

– Molecules parallel to ox_1 $$\eta_a = \frac{\alpha_3 + \alpha_4 + \alpha_6}{2} - \frac{\alpha_3}{2}\left(1 + \frac{\gamma_2}{\gamma_1}\right)$$

–Molecules parallel to ox_2 $$\eta_c = \frac{\alpha_4}{2}.$$

Results obtained for D as a function of n at 25 °C are shown in Fig. 6 for the two orientations.

The viscosity coefficients evaluated from the slopes of the two straight lines are

$$\eta_a = 27 \text{ cp}$$

$$\eta_c = 42 \text{ cp}$$

Measurements have also been made as a function of temperature. Fig. 7 shows the results obtained for a molecular orientation parallel to ox_2.

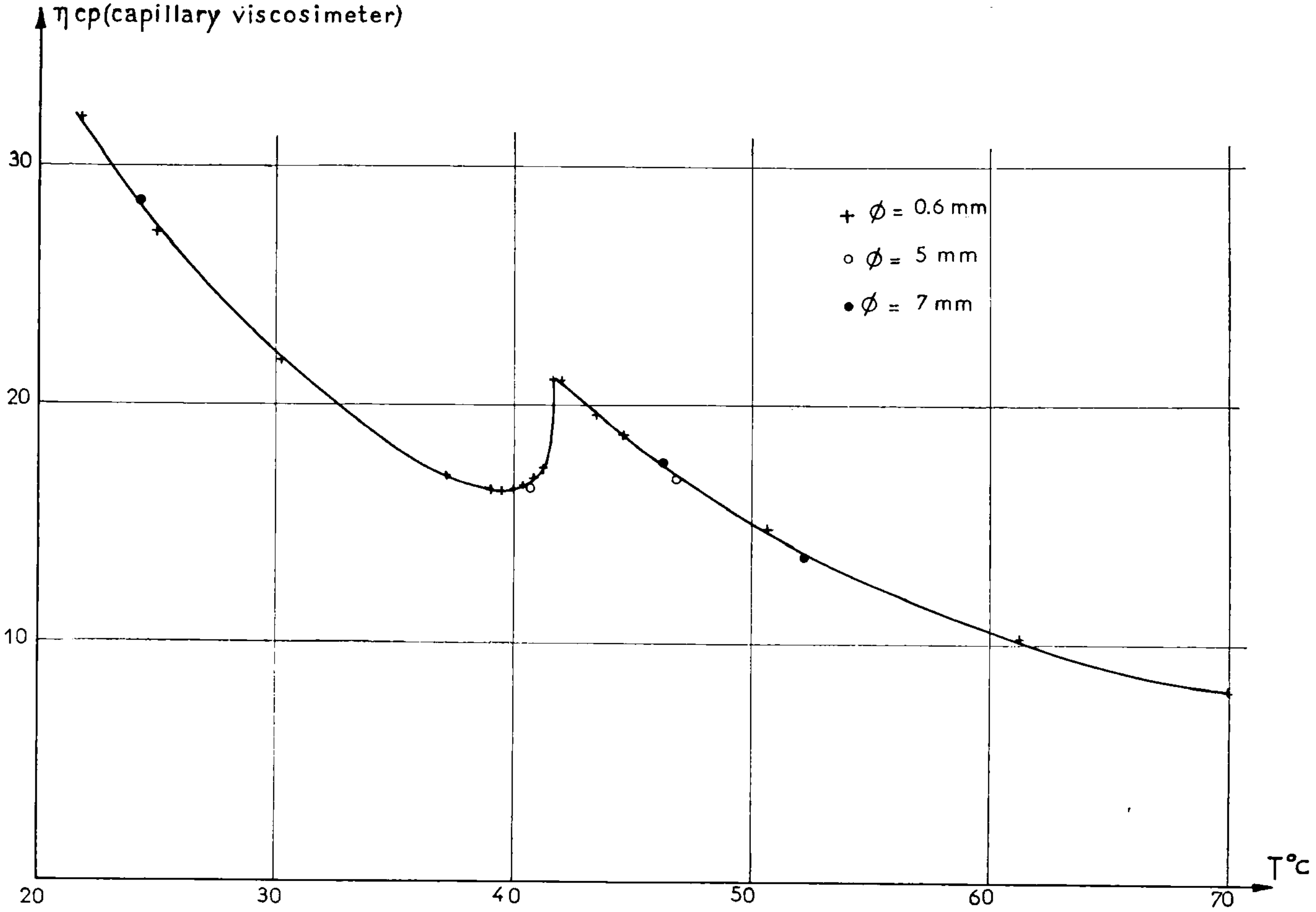
η cp(capillary viscosimeter)
30
20
10
20
30
40
50
60
70
T°C
+ Ø = 0.6 mm
o Ø = 5 mm
● Ø = 7 mm

Figure 5

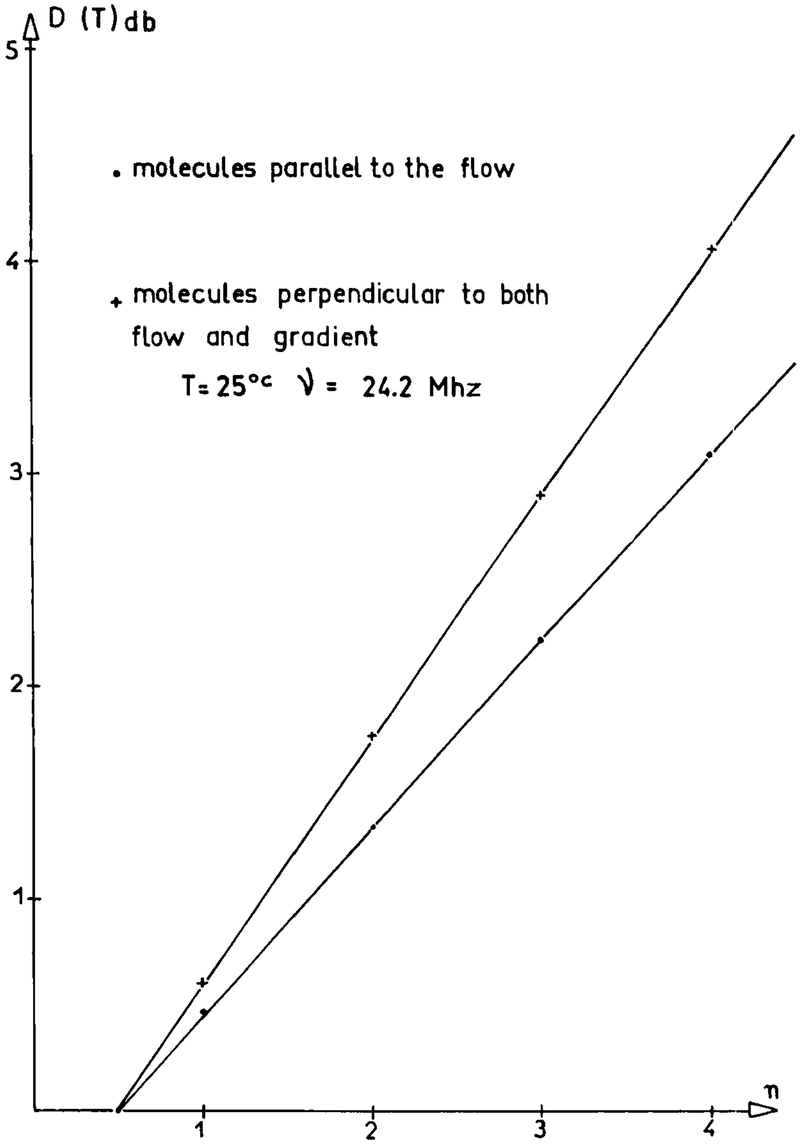
D (T) db
5
4
3
2
1
• molecules parallel to the flow
+ molecules perpendicular to both flow and gradient
T = 25°c ν = 24.2 Mhz
η
1
2
3
4

Figure 6.

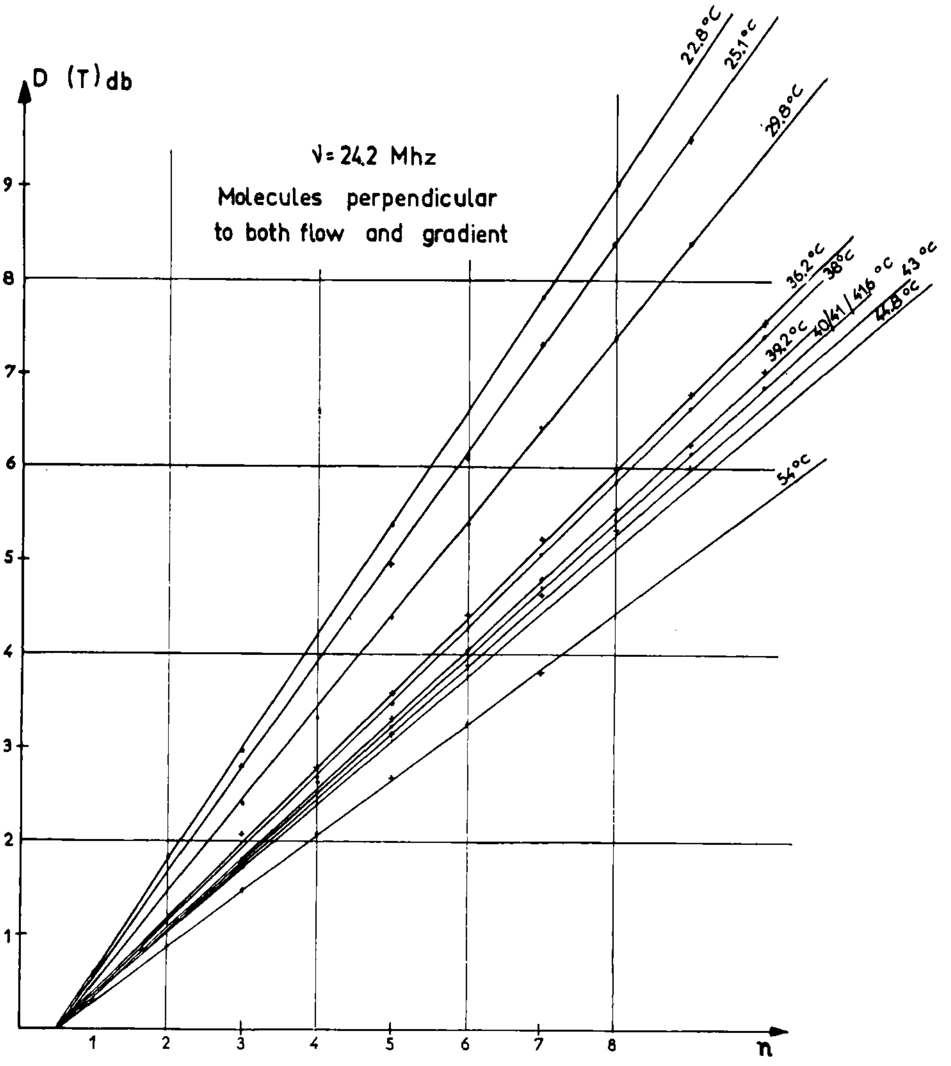

Figure 7.

The viscosity coefficients η_a and η_c are plotted versus temperature in Fig. 8 together with η_0 (high frequencies viscosity of the isotropic phase) and capillary viscosity results.

No frequency dependence in the range 15–80 MHz has been observed (Fig. 9) for (η_a), (η_c), (η_0 impedometer).

IV. Discussion

A. Comparison between viscosity coefficients obtained from capillary flow and shear waves reflectance experiments

As shown in Fig. 8, there is no difference between η_a and the viscosity η^* measured by capillary viscosimeter except for temperatures close to the transition-temperature.

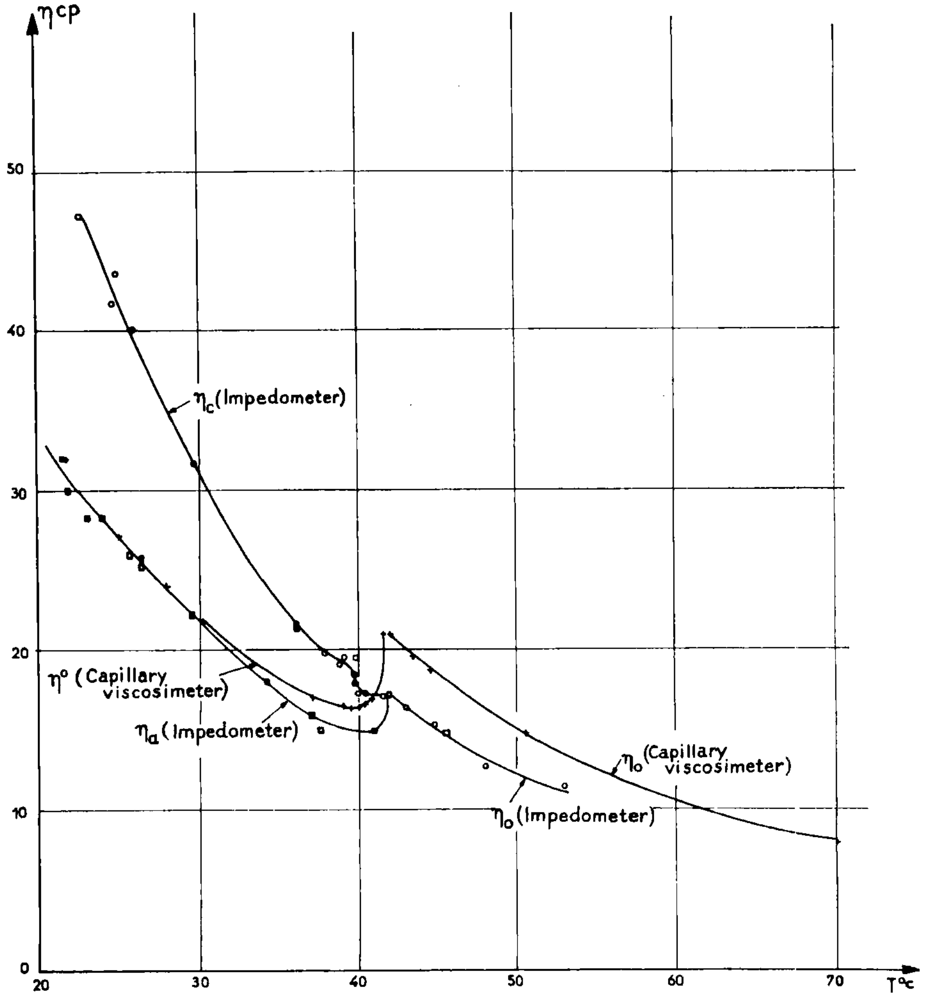

Figure 8.

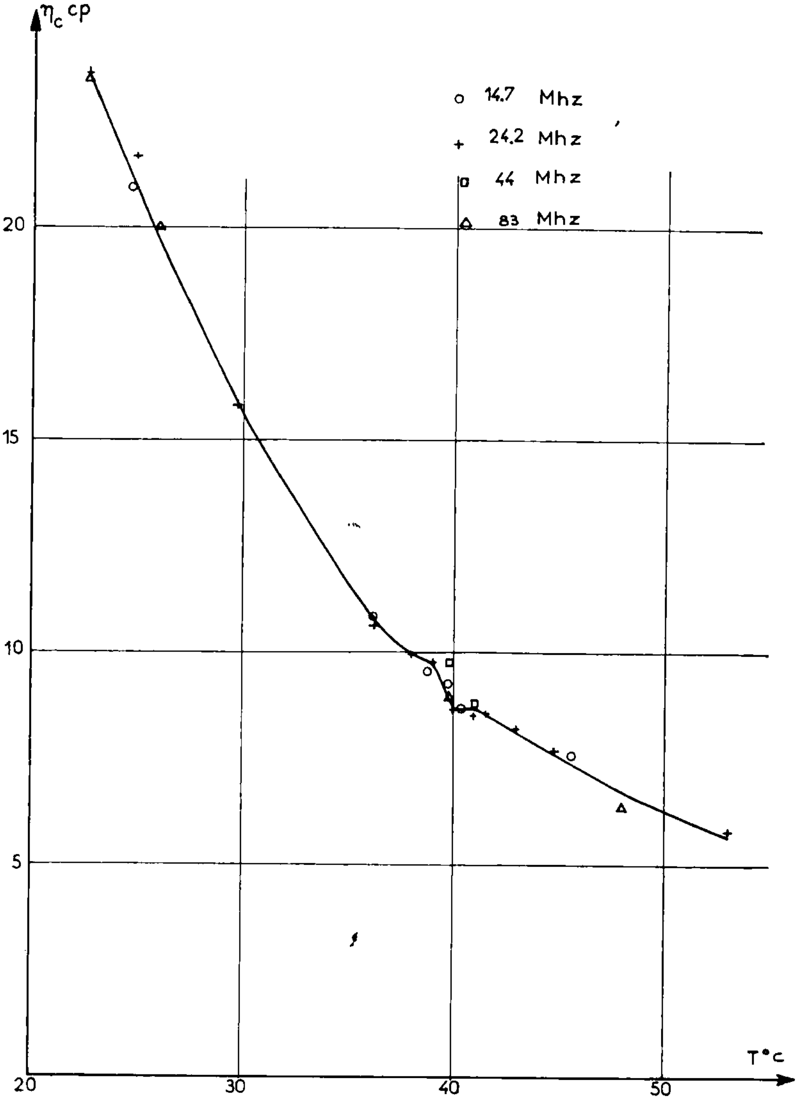

Figure 9.

According to the remark (4. v) this result indicates that

$$\frac{\gamma_2}{\gamma_1} \sim -1$$

Close to the transition it seems that the director makes an angle different from zero with the flow direction.

B. Viscosity coefficients anisotropy (far from the transition)

As $\gamma_2/\gamma_1 \simeq -1$ the viscosity coefficients are given by

$$\eta_a = \tfrac{1}{2}(\alpha_3 + \alpha_4 + \alpha_6)$$

$$\eta_c = \frac{\alpha_4}{2}$$

As seen in remark (4. v) $\eta_b \sim \eta_a$.

Therefore an experiment with a molecular orientation parallel to ox_3 (difficult to realize for MBBA) would not give supplementary informations.

C. Activation Energy

The viscosity obeys the usual exponential law.

$$\eta \sim \exp\,(W/RT)$$

We found:

$$W_a \sim 7.7 \text{ kcal/mole}$$

$$W_c \sim 10.2 \text{ kcal/mole}$$

D. Inertial term

The non frequency dependence (Fig. 9) shows that the inertial term is still negligible in this frequency range (see remark 4. IV).

E. Isotropic phase

The dispersion observed for viscosity (Fig. 8) is indicative of a structural relaxation related to the short range order. In a recent paper, De Gennes(16,17) describes the local state of order by a symmetric traceless tensor $Q_{\alpha\beta}$ proportional to the anisotropic part of the dielectric or magnetic susceptibility tensor. The hydrodynamic behaviour is discussed in terms of three viscosity coefficients η_0, μ, ν. De Gennes finds a simplified acceleration equation in the form:

$$\rho\dot{V} = \eta(\omega)\frac{\partial^2 V}{\partial z^2}$$

where

$$\eta(\omega) = \eta_0 - \frac{2\mu^2}{\nu}\frac{i\omega}{\Gamma + i\omega} = \eta' - i\eta''$$

Therefore

$$\eta'(\omega) = \eta_0 - \frac{2\mu^2}{\nu[1 + (\Gamma^2/\omega^2)]}$$

$$\eta''(\omega) = \frac{2\mu^2\Gamma}{\nu\omega[1 + (\Gamma^2/\omega^2)]}$$

Γ is the inverse of the relaxation time of the order parameter $Q_{\alpha\beta}$. Values of Γ have been obtained for MBBA by Litster and Stinson(18) from the width of the spectrum of inelastic scattered light.

In a temperature range 41°–53 °C, $\Gamma/2\pi$ varies from 0,15 MHz to 3,5 MHz. Therefore we can use safely the assumption $\omega^2 \gg \Gamma^2$ for frequencies ranging from 15 MHz to 85 MHz.

Then

$$\eta'(\omega) \sim \eta_0 - \frac{2\mu^2}{\nu}$$

$$\eta''(\omega) \sim \frac{2\mu^2}{\nu}\frac{\Gamma}{\omega}$$

Starting from:

$$RX = \rho\omega\eta'/2$$

$$R^2 - X^2 = \rho\omega\eta''$$

We obtain:

$$R^2 = \frac{\rho\omega}{2}(\eta'' + (\eta'^2 + \eta''^2)^{1/2})$$

$$X^2 = \frac{\rho\omega}{2}((\eta'^2 + \eta''^2)^{1/2} - \eta'')$$

$$R^2 - X^2 = \rho\omega\eta''$$

Assuming that $\omega \gg \Gamma$

$$R^2 = \frac{\rho\omega}{2}\left\{\frac{2\mu^2\Gamma}{\nu\omega} + \left[\left(\eta_0 - \frac{2\mu^2}{\nu}\right)^2 + \frac{4\mu^2\Gamma^2}{\nu^2\omega^2}\right]^{1/2}\right\}$$

$$X^2 = \frac{\rho\omega}{2}\left\{\left[\left(\eta_0 - \frac{2\mu^2}{\nu}\right)^2 + \left(\frac{4\mu^2\Gamma^2}{\nu^2\omega^2}\right)\right]^{1/2} - \frac{2\mu^2\Gamma}{\nu\omega}\right\}$$

If

$$\omega \gg \frac{2\mu^2\Gamma}{\nu[\eta_0 - (2\mu^2/\nu)]} \tag{38}$$

We have

$$R^2 \sim X^2 \sim \frac{\rho\omega}{2}\left(\eta_0 - \frac{2\mu^2}{\nu}\right)$$

In this case

$$\eta'' = 0$$

$$\eta' = \frac{2R^2}{\rho\omega} \sim \eta_0 - \frac{2\mu^2}{\nu}$$

When the condition (38) is fulfilled the ratio R^2/ω should be frequency independent. We have checked experimentally this behaviour (Fig. 9). Then, the difference between (η_0 capillary viscosimeter) and (η_0 impedometer) (Fig. 8) measures the ratio $2\mu^2/\nu$. This ratio is plotted versus temperature in Fig. 10.

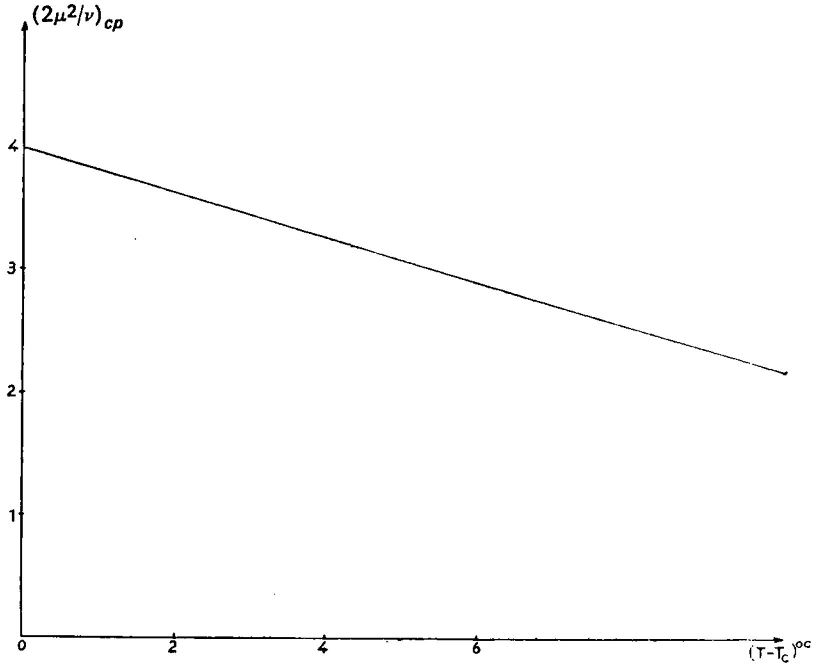

Figure 10.

Acknowledgements

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