ON THE VISCOSITY COEFFICIENTS OF NEMATIC MBBA AND THE VALIDITY OF THE ONSAGER–PARODI RELATION

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From a critical review of the experimental viscosity data for nematic MBBA a complete set of viscosity coefficients is proposed, for which the Onsager–Parodi relation is valid. The temperature dependence of γ_1 can be described by $\gamma_1 \sim S \exp(E/kT)$.

In this letter viscosity data for N-(*p*-methoxybenzylidene)-*p*-*n*-butylaniline, MBBA, in the nematic phase are critically reviewed. It is shown that the rotational viscosity γ_1 derived from Gähwiller's complete set of data is in disagreement with results from other measurements. A new complete set of viscosity data is proposed, for which the Onsager–Parodi relation is valid.

The expression for the viscous stress tensor of an incompressible nematic contains six coefficients with the dimension of a viscosity: $\alpha_1, \dots, \alpha_6$ (Leslie coefficients) [1]. Parodi has shown that from Onsager's reciprocal relations, which reflect the time reversal invariance of the microscopic motions, one can derive [2]

$$\alpha_6 - \alpha_5 = \alpha_2 + \alpha_3 . \tag{1}$$

As the validity of this relation in the case of nematic liquid crystals has been questioned, it would be useful to have experimental tests. This would require many independent measurements, which are usually not available, in which case eq. (1) is simply assumed to be true.

The viscosities that are measured experimentally are usually combinations of the α's. In a simple shear experiment for a nematic with a uniform director pattern one can measure the three Miesowicz viscosities (fig. 1a,b,c):

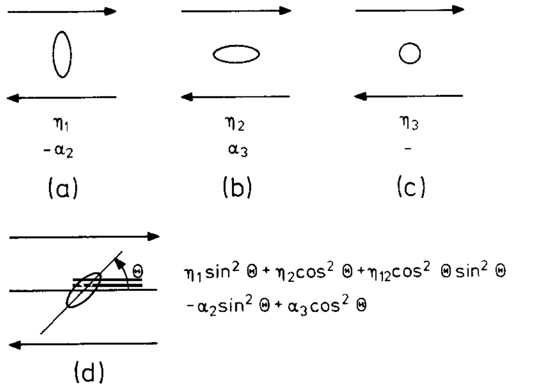

Fig. 1. The three main geometries (a), (b), (c) for shear with the corresponding viscosity and shear torque coefficient; (d) the same when the director is in the shear plane at an angle θ with the flow direction.

η_1: director parallel to velocity gradient,
η_2: director parallel to flow direction,
η_3: director normal to shear plane.

In Miesowicz' original papers on PAA [3] the definitions of η_1 and η_2 are interchanged; we have retained here the notation of Helfrich [4]. These viscosities are related to the α's by

$$\begin{aligned} &\eta_1 = \tfrac{1}{2}(-\alpha_2 + \alpha_4 + \alpha_5), \\ &\eta_2 = \tfrac{1}{2}(\alpha_3 + \alpha_4 + \alpha_6), \quad \eta_3 = \tfrac{1}{2}\alpha_4 . \end{aligned} \tag{2}$$

If the director is in the shear plane at an arbitrary angle

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with the flow direction a fourth coefficient $\eta_{12} = \alpha_1$ comes into play, that is symmetric in the coordinates (see fig. 1d). If the director is in the shear plane the flow leads to a torque on the director and thus changes the orientation of the director. The corresponding shear-torque coefficients are $-\alpha_2$ and α_3 if the director is parallel to the velocity gradient and to the flow, respectively (fig. 1a,b). For an arbitrary angle θ between the director and the flow direction (fig. 1d), there is a specific angle θ_0 (flow alignment angle) where the shear torque vanishes, given by

$$\tan^2\theta_0 = \alpha_3/\alpha_2 = (\gamma_2 + \gamma_1)/(\gamma_2 - \gamma_1). \quad (3)$$

In this expression we have introduced

$$\gamma_1 = \alpha_3 - \alpha_2, \quad \gamma_2 = \alpha_6 - \alpha_5. \quad (4)$$

The viscosities γ_1 and γ_2 can often be measured directly in experiments where the director is made to rotate. In terms of the experimental viscosities eq. (1) can be written as

$$\eta_2 - \eta_1 = \alpha_3 + \alpha_2. \quad (5)$$

Gähwiller has reported on the viscosities of MBBA [5]. From his results a complete set of coefficients can be calculated assuming that eq. (1) is valid. The results are given in table 1. In addition various authors have reported values for γ_1, which are collected in fig. 2. These results from several different methods indicate at $T_{NI}-T = 18°$ a value $\gamma_1 \approx 95$ cP, which is considerably larger than Gähwiller's result. Considering the Onsager–Parodi relation as stated in eq. (5), we must conclude that either this relation does not hold

Table 1
Viscosity coefficients for MBBA at 25°C ($T_{NI} - T = 18$°C) in cP.

Experimental a)	Calculated
η_1 = 103.5 ± 1.5	α_1 = 6.5 ± 4
η_2 = 23.8 ± 0.3	α_2 = −79 ± 2
η_3 = 41.6 ± 0.7	α_3 = − 0.9 ± 0.3
η_{12} = 6.5 ± 4	α_4 = 83.2 ± 1.5
θ_0 = 6° ± 1°	α_5 = 45 ± 5
	α_6 = −34 ± 2
	γ_1 = 78 ± 2
	γ_2 = −80 ± 2

a) Ref. [5].

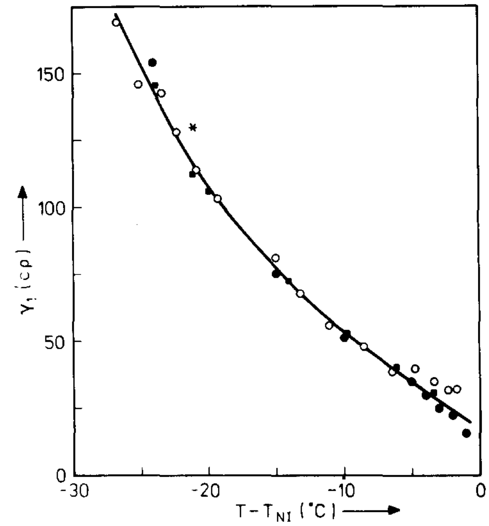

Fig. 2. The rotational viscosity γ_1 versus reduced temperature for MBBA; ●■: rotating magnetic field [6,7]; ★: motion of walls [8]; ○: light scattering [10]. (This method gives K_{22}/γ_1, from which γ_1 is calculated with $K_{22}/\Delta\chi$ from ref. [11], and $\Delta\chi$ from ref. [12].)

or that $|\eta_2 - \eta_1|$ as given by Gähwiller is too small. Therefore we shall compare these shear flow results in detail with those of some other methods.

Using the attenuation of ultrasound Martinoty and Candau [13] have measured the quantities

$$\tilde{\eta}_2 = \eta_2 - \tfrac{1}{3}\alpha_3(1 + \gamma_2/\gamma_1), \quad \tilde{\eta}_3 = \eta_3. \quad (6)$$

Because of the small value of θ_0 one has $|\alpha_3| \ll |\alpha_2|$, and consequently $\tilde{\eta}_2 \approx \eta_2$. The experimental results are $\tilde{\eta}_2 = 27$ cP and $\tilde{\eta}_3 = 42$ cP, in good agreement with the results of table 1. Summerford et al. [14] have argued that Gähwiller's result for η_1 is too small. To maintain a uniform director pattern the torque due to the applied magnetic field must be much larger than the shear torque. In this particular configuration (director parallel to velocity gradient) this means

$$\Delta\chi H^2 \gg -\alpha_2 s, \quad (7)$$

where s is the shear rate. With the fields and shear rates used by Gähwiller this condition is only approximately fulfilled. However, the results of Summerford et al. are probably not trustworthy, because they also report rather high values for η_3 and for the viscosity in the isotropic phase, for which quantities this argument

Table 2
Revised viscosity coefficients for MBBA at $T_{NI} - T = 18°C$ (cP).

Experimental	Calculated
$\eta_2 = 23.8 \pm 0.3$ a)	$\alpha_1 = 6.5 \pm 4$
$\eta_3 = 41.6 \pm 0.7$ a)	$\alpha_2 = -96 \pm 3$
$\eta_{12} = 6.5 \pm 4$ a)	$\alpha_3 = -1.1 \pm 0.2$
$\theta_0 = 6° \pm 1°$ a)	$\alpha_4 = 83.2 \pm 1.5$
$\gamma_1 = 95 \pm 3$ b)	$\alpha_5 = 63 \pm 12$
	$\alpha_6 = -34 \pm 2$
	$\eta_1 = 121 \pm 4$
	$\gamma_2 = -97 \pm 3$

a) Ref. [5]. b) From fig. 2.

does not hold. Nevertheless, their objection to the value of η_1 seems to be correct. Not including η_1 in experimental results, but still assuming that the Onsager–Parodi relation is valid, we have therefore recalculated the viscosity coefficients of MBBA (see table 2). The new higher value of η_1 would influence the result for η_{12}. However, in the absence of sufficient experimental information, we shall not attempt to recalculate η_{12}.

Now a further check on the results of table 2 is possible using viscosity data from light scattering experiments. From table 2 we calculate

$$\eta_{\text{bend}} = \gamma_1 - \alpha_2^2/\eta_1 = 19 \text{ cP}. \tag{8}$$

Experimental results for this quantity range from 19 to 21 cP [15,16]. Although these results are not very accurate, because they depend on the value chosen for K_{33}, which is somewhat uncertain, we see that the agreement is excellent. Hence we can conclude that within the experimental accuracy the Onsager–Parodi relation has been verified for MBBA.

There has been some controversy regarding the temperature dependence of γ_1 [17,18]. From the present results we can calculate $\gamma_1/\Delta\chi^m$, where $\Delta\chi^m = \Delta\chi/\rho$ is the anisotropy of the mass susceptibility. Assuming that the molecules are effectively axially symmetric around their long axis, one has $\Delta\chi^m \sim S$, where S is the nematic order parameter. From the plot in fig. 3 we see that the temperature dependence of γ_1 can be described by

$$\gamma_1 \sim S \exp(E/kT). \tag{9}$$

Because the nematic temperature range of MBBA is

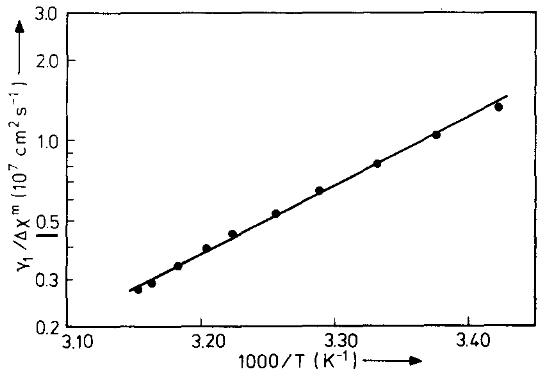

Fig. 3. Logarithmic plot of $\gamma_1/\Delta\chi^m$ versus $1000/T$ using interpolated data for γ_1 from fig. 2 (full line) and the susceptibilities from ref. [12].

rather limited, other pre-exponential factors like 1 or S^2, although less probable, cannot be completely ruled out. Eq. (9) is in agreement with results of Prost et al. [18] for a different nematic compound with a much wider nematic range.

[1] See, e.g., P.G. de Gennes, The physics of liquid crystals (Clarendon, Oxford, 1974) Ch. 5, where references can can also be found to the original literature.
[2] O. Parodi, J. Phys. 31 (1970) 581.
[3] M. Miesowicz, Bull. Acad. Polon. A229 (1936); Nature 158 (1946) 27.
[4] W. Helfrich, J. Chem. Phys. 50 (1969) 100; 53 (1970) 2267.
[5] Ch. Gähwiller, Phys. Lett. 36A (1971) 311; Mol. Cryst. Liquid Cryst. 20 (1973) 301.
[6] H. Gasparoux and J. Prost, J. Phys. 32 (1971) 953.
[7] G. Heppke and F. Schneider, Z. Naturforsch. 27a (1972) 976.
[8] L. Léger, Solid State Commun. 11 (1972) 1499.
[9] P. Pieranski, F. Brochard and E. Guyon, J. Phys. 34 (1973) 35.
[10] S.A. Shaya and H. Yu, J. Chem. Phys. 63 (1975) 221.
[11] F. Leenhouts, F. van der Woude and A.J. Dekker, Phys. Lett. 58A (1976) 242.
[12] W.H. de Jeu, W.A.P. Claassen and A.M.J. Spruyt, Mol. Cryst. Liquid Cryst. 31 (1976) 269.
[13] P. Martinoty and S. Candau, Mol. Cryst. Liquid Cryst. 14 (1971) 243.
[14] J.W. Summerford, J. Boyd and B.A. Lowry, J. Appl. Phys. 46 (1975) 970.
[15] I. Haller, J. Chem. Phys. 57 (1972) 1400.
[16] J.L. Martinand and G. Durand, Solid State Commun. 10 (1972) 815.
[17] A.F. Martins, Port. Phys. 9 (1974) 1.
[18] J. Prost, G. Sigaud and B. Regaya, J. Physique Lett. 37 (1976) L-341.