Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Simões, M. , Domiciano, S. M. and Alves, F. S.(2006) 'Scaling properties of the Miesowicz coefficients', Liquid Crystals, 33: 7, 849 — 854
To link to this Article: DOI: 10.1080/02678290600722858
URL: http://dx.doi.org/10.1080/02678290600722858

Liquid Crystals, Vol. 33, No. 7, July 2006, 849–854

Scaling properties of the Miesowicz coefficients

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(*Received 28 May 2005; in final form 25 January 2006; accepted 27 February 2006*)

In this work a set of experimental data points is used to study some scaling properties of Miesowicz coefficients. Using the fact that all the compounds studied present two critical points—the crystal–nematic and the nematic–isotropic phase transitions—a common temperature scale was defined. With the use of this unique temperature scale two relevant aspects that distinguish the viscosity of these materials can be simultaneously extracted and studied: (1) the molecular shape anisotropy and (2) the different strengths of molecular interaction of the different compounds. Through the study of the scaling properties associated with these properties, the existence of a common law connecting the Miesowicz coefficients with the associated decay time is proposed.

1. Introduction

The macroscopic anisotropy exhibited by some materials is among the most intriguing physical properties of matter. As a rule, it results from symmetries at the molecular level and constitutes a good guide to the comprehension of the microscopic structure of the material [1]. Particularly surprising is the fact that liquids can also present macroscopic anisotropic behaviour, nematic liquid crystals (NLCs) being the simplest of these substances [2]. In 1935, Miesowicz discovered that under the presence of an external magnetic field even their viscosity can become anisotropic [3]. Since then, an enormous amount of work has been devoted to the study of this property and research in this area remains active [4–18].

It is common to study the viscosity of these materials by considering the contribution of the alignment order through the explicit use of the order parameters S_2 and S_4 [2]. The kinetic approach of Doi and co-workers [9–12], and the conformational transformation of Hess and co-workers [14–17], are the most important approaches that follow these lines. Nevertheless, although having the great merit of producing an expression for viscosity free of free parameters [4], which captures the essence of the phenomena, (giving a semi-microscopic explanation to the origin of their anisotropy), both approaches show disagreements with the experimental data, mainly as the nematic–crystal phase transition is approached [7, 8]. The origin of such disagreements is yet to be studied [6]. So, a study of the nematic viscosity, which can combine the richness of the experimental data accumulated in the liquid crystal literature [18–25], with secure theoretical propositions, would be useful in the search for a microscopic theory that could describe the observed phenomena in the entire range of the nematic phase. That is the aim of this work.

Here, we will follow the essence of the conformational transformation approach of Hess *et al.* [14–17], which proposed that the viscosity of a nematic material can be computed by deforming the spherically symmetric molecules of an isotropic reference liquid in such a way that, once deformed, it assumes the ellipsoidal shape of a nematic molecule. Starting from the canonical expression for the viscosity of a liquid, two conform transformations similar to the one proposed by Hess will be applied to capture three kinds of distinct microscopic contributions to the macroscopic behaviour of these materials: (1) the molecular anisotropic shape, (2) the strength of the interaction between neighbouring molecules and (3) the decay time associated with the viscous process. A large set of experimental data on thermotropic liquid crystals will be compared with our results [18–25], and it will be shown that once the molecular shape and strength of the molecular interactions are separated from the global behaviours of the viscosity data, the resultant curves describe a closely regular behaviour, indicating that these parameters are important in distinguishing the viscosity of different compounds.

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Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2006 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290600722858

2. Time correlation approach

The anisotropy observed in viscosity coefficients is a macroscopic manifestation of the different geometrical orientations that the microscopic anisotropic liquid crystal molecules can acquire in a sample where the shear flow introduces a preferred orientation. The observation of such behaviour in the viscosity of a NLC, led to the following definition for the Miesowicz viscosity coefficients [3]: η_1, when the long axis of the molecules is parallel to the gradient of the velocity; η_2, when the long axis of the molecules is parallel to the direction of the flow; η_3, when the long axis of the molecules is simultaneously perpendicular to the direction of the flow and perpendicular to the velocity gradient (see figure 1).

In order to handle the explicit influence of the micellar anisotropy on the Miesowicz coefficients, the standard viscosity expression, given as a time correlation function [26, 27], will be used. According to the theory of the transport process, the shear viscosity is given by [26]:

$$\eta = \frac{1}{k_B T V} \int_0^\infty \mathrm{d}t \langle J^{xy}(0) J^{xy}(t) \rangle \tag{1}$$

where

$$J^{xy} = \sum_{a=1}^{N} \frac{p_a^x p_b^y}{m} + \frac{1}{2} \sum_{a,\, b=1}^{N} r_{ab}^x F_{ab}^y \tag{2}$$

is the transverse current, k_B is the Boltzmann constant, V is the volume of the sample, p_a^x is the cartesian component x of the of the momentum of the particle a, r_{ab}^x is the cartesian component x of the distance between the particles a and b, F_{ab}^y is the cartesian component y of the force between the particles a and b, and N is the total number of particles in the sample. In liquids, the viscosity is dominated by the term $r_{ab}^x F_{ab}^y$, which takes care of the transport of momentum through the direct interaction between the particles. This is the term that we will use here. The first term, containing $p_a^x p_a^y$, evolves the direct transport of momentum by the particles moving from one shear plane to another, being dominant for gases, but marginal for liquids.

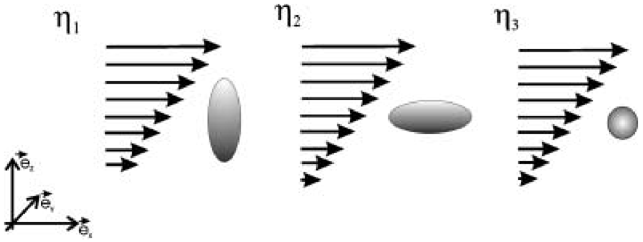

Figure 1. Geometry used to define each of the Miesowicz coefficients. The arrows give the direction of the fluid follow, and the continuous variation of their length represents variation of the fluid velocity. For each Miesowicz coefficient the molecular long axis has a different orientation relative to the direction of the fluid flow. For the coefficient η_1, the long axis of the molecules is parallel to the gradient of the velocity; for η_2, the long axis of the molecules is parallel to the direction of the flow; for η_3, the long axis of the molecules is perpendicular to the direction of the flow and also perpendicular to the velocity gradient.

Firstly, it will be assumed that the correlation between different instants decays exponentially, $\langle J^{xy}(0)\ J^{xy}(t) \rangle \sim J^{xy}(0)^2 \exp(-t/\tau)$, where τ is the correlation decay time [28, 27]. Hence,

$$\eta = \tau \frac{\langle J^{xy}(0)^2 \rangle}{k_B T V}. \tag{3}$$

Furthermore, as done by Hess, it is assumed that the force between the particles results from an interacting potential U_{ab}, which is invariant by a conformational transformation that changes it from a sphere to an ellipsoid having the shape of the nematic micelles (or molecules). So, we would have

$$F_{ab}^y = \frac{\mathrm{d}}{\mathrm{d}y} U_{ab} \tag{4}$$

and, using this equation to perform the Hess conform transformation,

$$r_{ab}^x \to l_x \bar{r}_{ab}^x \tag{5}$$

$$F_{ab}^y \to \frac{1}{l_y} \overline{F}_{ab}^y. \tag{6}$$

The term of equation (2) that is relevant for the viscosity of liquids becomes

$$\frac{1}{2} \sum_{a,\, b=1}^{N} r_{ab}^x F_{ab}^y \to \left(\frac{l_x}{l_y} \right) \frac{1}{2} \sum_{a,\, b=1}^{N} \bar{r}_{ab}^x \overline{F}_{ab}^y \tag{7}$$

where the bar over $\bar{r}_{ab}^x$ and $\overline{F}_{ab}^y$ is used to indicate that they have spherical symmetry and l_x and l_y are, respectively, the instantaneous projection of the molecular dimensions along the directions $\vec{e}_x$ and $\vec{e}_y$. Finally, assuming that the statistical average over the dynamical variables, position and momentum, is independent of the average over the effective molecular shape, we would arrive at

$$\eta = \left\langle \left(\frac{l_x}{l_y} \right)^2 \right\rangle \tau \frac{\langle \bar{J}^{xy}(0)^2 \rangle}{k_B T V}. \tag{8}$$

Consequently, as the different Miesowicz coefficients are distinguished by different geometry, the values of l_x and l and the decay times will vary accordingly. Using the definitions of the Miesowicz coefficients and the geometry shown in figure 1 it is found that

$$\eta_1 = \left\langle \left(\frac{h}{a}\right)^2 \right\rangle \tau_1 \frac{\langle \bar{J}^{xy}(0)^2 \rangle}{k_B T V} \tag{9}$$

$$\eta_2 = \left\langle \left(\frac{a}{h}\right)^2 \right\rangle \tau_2 \frac{\langle \bar{J}^{xy}(0)^2 \rangle}{k_B T V} \tag{10}$$

$$\eta_3 = \tau_3 \frac{\langle \bar{J}^{xy}(0)^2 \rangle}{k_B T V}. \tag{11}$$

See figure 2, where h is the instantaneous molecular projection along the director direction and a is the instantaneous molecular projection on the axis perpendicular to the director direction. In this equation the term $\langle \bar{J}^{xy}(0)^2 \rangle$ is, by construction, spherically symmetric, being, therefore, the same for all Miesowicz coefficients. Consequently, the orientational averages [9–13], usually expressed in terms of the order parameters S_2 and S_4, are contained in the averages $\langle (h/a)^2 \rangle$ and $\langle (a/h)^2 \rangle$ and in the decay times. So, it follows that the relations

$$\frac{\eta_1}{\eta_3} = \left\langle \left(\frac{h}{a}\right)^2 \right\rangle \frac{\tau_1}{\tau_3}, \qquad \frac{\eta_2}{\eta_3} = \left\langle \left(\frac{a}{h}\right)^2 \right\rangle \frac{\tau_2}{\tau_3} \tag{12}$$

would depend exclusively on the geometry of the nematic domains and in the decay times. In order to obtain an expression where the geometrical averages, $\langle (h/a)^2 \rangle$ and $\langle (a/h)^2 \rangle$, could be eliminated, let us assume that the rule,

$$\left\langle \left(\frac{h}{a}\right)^2 \right\rangle \left\langle \left(\frac{a}{h}\right)^2 \right\rangle \approx \left\langle \left(\frac{h}{a}\right)^2 \left(\frac{a}{h}\right)^2 \right\rangle = 1 \tag{13}$$

can be taken as an approximation. In general the product of averages is not exactly the average of the product. Nevertheless, such an approximation should be useful in the experimental investigation of the data corresponding to the expressions that appear in equation (12); in their product the terms having geometrical meaning become eliminated. Under such an approximation we have,

$$\frac{\eta_3^2}{\eta_1 \eta_2} = \frac{\tau_3^2}{\tau_1 \tau_2}. \tag{14}$$

In this equation any explicit contribution of the molecular dimensions to the viscosity has been eliminated, and a correlation between the Miesowicz coefficients and the respective decay times is all that remains. It will be shown that with a redefinition of the temperature scale it is possible to arrange experimental data in such a way that they all seem to lie on the same curve, suggesting the existence of a common general law.

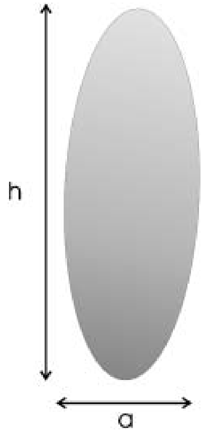

Figure 2. Ellipsoid exhibiting the geometry that leads to the results stated in equation (11). The parameter h measures the instantaneous projection of the molecular dimensions along the director direction; a is the instantaneous molecular projection on the direction perpendicular to the director that is contained in the plane defined by the velocity gradient and the velocity of the fluid.

3. Corresponding states and the nematic temperature scale

In the proceeding section, the contribution of the molecular size proportions to the liquid crystal viscosity was factorized. Nevertheless, there is another important physical aspect distinguishing viscosities of different compounds: the difference in the strength of the interaction between their constituent molecules. One consequence of such difference is that the temperatures at which the same kind of phase transition is observed in different materials depends on the material. So, if for all compounds the same and unique temperature could be attributed this critical point, at least around them part of the effects attributed to the diversity found in the strength of the interaction could be made uniform. Usually, this procedure is implemented with a rescaling in the temperature. Nevertheless, for some liquid crystals not just one critical point is found, but two: the nematic–isotropic and the nematic–crystal phase transition points. So, for these compounds we can go beyond a simple shift in the temperature value; the existences of two critical points permits the collective establishment of two fixed temperatures and, as a consequence, the definition of a new temperature scale, the nematic scale [7, 8]. Thus the effect of the homogenization of the interaction between molecules would not be restricted to the neighbourhood of a critical point, but it would be extended to the whole range of the nematic phase. That is, for such compounds a nematic state could be defined in terms of this temperature scale and it will not describe the physical state of a particular compound but, more than that, collectively through a correspondence of states it would map the physical states of all them [30–32].

In order to compare the above results with experimental data, LC viscosity data exhibiting these two fixed points have been collected from the LC literature. The list of the compounds utilized in this analysis is: PAA (*p*-azoxyanisole); MBBA (*p*-methoxybenzylidene-*p*-*n*-butylaniline); N4 (eutectic mixture of the 4-methoxy-4-*n*-butylazoxybenzenes); EM (eutectic mixture of 4′-*n*-pentylphenyl 4-methoxybenzoate and 4-*n*-pentylphenyl 4-*n*-hexyloxybenzoate); 5CB (4-*n*-pentyl-4-cyanobiphenyl); HBAB (*p*-*n*-hexyloxybenzylidene-p-aminobenzonitrile); MIST (1:1:1-molar mixture of HBAB with *p*-*n*-butoxybenzylidene-p-aminobenzonitrile and *p*-*n*-octanoyloxybenzylidene-*p*′-aminobenzonitrile).

The researchers who performed the measurements used here are quoted in [18–25]. For all these compounds the nematic phases exist in different temperature intervals that have been rescaled to a new, and unique, temperature scale where to the crystal–nematic phase transition points given the temperature $T=0$, while for the nematic–isotropic phase transition point the temperature $T=1$ was assigned. Then, using these experimental data, the relations given in equations (12) and (14) were computed. The ratios η_3/η_1 and η_3/η_2 are displayed in a unique graphic form, see figure 3; their product is shown in figure 4. The distribution of these points is in complete accord with the reasoning developed previously [7, 8]. The sets of points corresponding to η_3/η_1 and η_3/η_2 are not randomly distributed. The values of η_3/η_1 fluctuate around $\eta_3/\eta_1 \approx 0.4$, being observed to increase slightly with rise of temperature. The values of η_3/η_2 fluctuate around 1.7, presenting a small decrease with rise of temperature. Furthermore, both sets of experimental data points seem to approach the value 1 as the temperature approaches the N–I transition. Even with significant fluctuations, it is clear that these experimental data points occupy two distinct regions. The regularity and agreement observed in their distribution seems to be in accord with the idea that they describe corresponding states; after a simple rescaling in the temperature, experimental data for different compounds, measured at different fimes in different studies, are clearly distributed along two distinct regions, suggesting that they could coalesce along two single

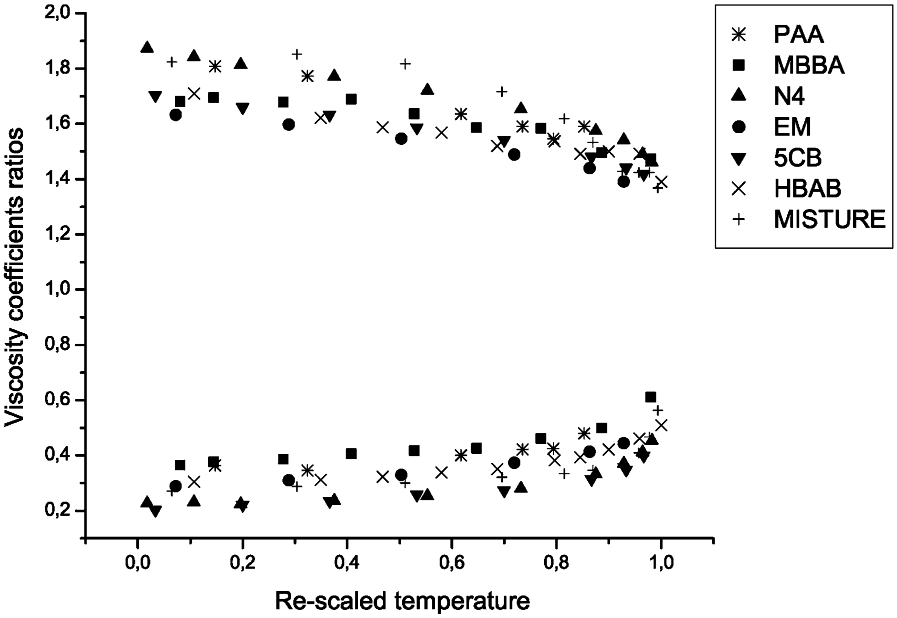

Figure 3. Experimental data points from different sources have been collected and used to furnish the ratios between the Miesowicz coefficients, η_3/η_2 and η_3/η_1 [18–25]. The temperature scale is the nematic temperature scale, defined in such a way that, for all compounds, the nematic–crystal transition point is associated with a reduced temperature $T=0$ [7, 8]. Additionally, the nematic–isotropic phase transition is associated with the reduced temperature $T=1$. The η_3/η_2 data appear in the upper half of the plot, showing a regularity that suggests a corresponding states curve. The data for η_3/η_1 appear in the lower half of the plot and also suggest a corresponding states curve.

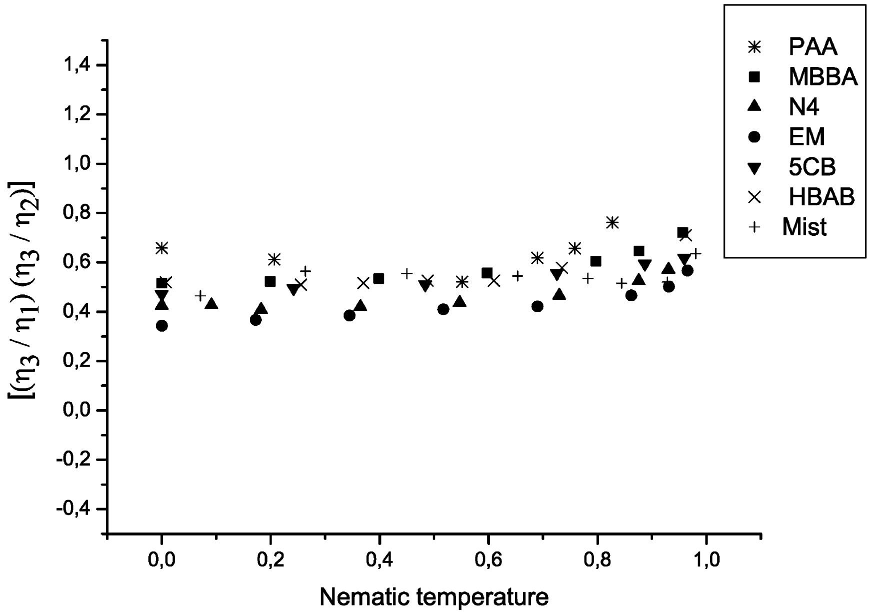

Figure 4. Distribution of the quantity $\eta_1\eta_2/\eta_3^2$, as a function of the reduced temperature (as defined in the text) for the experimental data exhibited in figure 3. According to the calculation developed in this paper, this quantity would represent the ratio $\tau_1\tau_2/\tau_3^2$, between the time relaxation rate and viscosity of each Miesowicz coefficient, equation (14). The distribution these experimental data suggest that a different decay time is associated with each Miesowicz coefficient, but, nevertheless, a common law connects them.

curves. Furthermore, the existence of these two distinct and characteristic lines of coalescence of the experimental data seems to be in agreement with the content of equation (12), revealing that indeed the geometric proportions and quotient between the decay times of the molecules are approximately the same for all compounds studied.

In figure 4, the nematic scale is again used to display the experimental data according to the relationship of equation (14). It is easy to see that the resulting curve presents the same regularity and consistency found for equation (12), also suggesting that a common law connects these data. Even with a non-negligible dispersion, the coherence of these data is sufficient to suggest the existence of a universality described by a curve of corresponding states, which according to our preceding scaling analysis would be a result of the approximate coincidence observed in the ratio, $\tau_3^2/(\tau_1\tau_2)$, of the decay times.

4. Final remarks and conclusion

Through the application of two rescalings on the correlation function that describes the viscosity of a liquid, the contribution of some parameters to the distinction between the viscosities of different thermotropic nematic liquid crystals has been determined. We have used a set of experimental data to test the hypotheses that sustain our study. It has been found that three parameters make relevant contributions to the nematic viscosity: (1) the ellipsoidal molecular shape, (2) the range of the molecular interaction and (3) the decay time associated with the viscosity process. When these parameters are analysed the ratio between the Miesowicz coefficients assumes the form of regular curves, showing apparently common behaviour for all the materials studied. So, by suggesting that the ratios given by equations (2) and (14) would be the same for all thermotropic compounds, these laws provide a criterion for seeking an efficient viscosity theory; when the nematic temperature scale is used, these three relationships provide a criterion to be satisfied by the results of any theory accounting for the Miesowicz coefficients. Furthermore, if these relations are verified, or even if their precision is determined, they would render the determination of the Miesowicz coefficients trivial; if the nematic–crystal and the nematic–isotropic temperatures of a given thermotropic compound are known, the nematic temperature scale could be constructed, and the determination of one of the Miesowicz coefficients at a unique point would be enough to determine all of them over the range of the nematic phase.

Acknowledgements

This work was supported by the Brazilian Agencies CAPES, Fundação Araucária and CNPq.

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