Miesowicz viscosities study of a two-component thermotropic mixture

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The order parameter and the temperature dependence of the Miesowicz viscosity coefficients of different mixtures of mesogenic 4-cyan-4′-octyloxybiphenyl (8OCB) and 4-butylbenzoate 4′-isothiocyanatephenyl (4TPB) are studied. Measurements were performed with the aid of a home-built Miesowicz viscometer. The data are analyzed by means of the relations of Kneppe *et al.* and critically compared with the predictions of available theoretical models. [S1063-651X(98)01109-X]

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I. INTRODUCTION

Liquid crystal hydrodynamics has been studied for nearly 90 years [1–11]. However, there are still two interrelated and important problems concerning the hydrodynamics of liquid crystals, which still lack a satisfying explanation. First, the temperature and order parameter dependence of the viscosity coefficients: It is well known that far from the clearing point, T_{NI} and the nematic-smectic transition temperature, T_{SN}, the Miesowicz viscosity coefficients, η_1, η_2, and η_3, cf. Fig. 1, exhibit Arrhenius behavior. However, near the transitions the order parameter, which itself is also temperature dependent, plays a significant role in their temperature dependence, which remains to be understood. This is inevitably associated with an adequate answer to the second intriguing problem of the dependence of the viscous stress tensor on the microscopic parameters of the system, i.e. the development of the microscopic theory of the hydrodynamics of liquid crystals.

There are two popular approaches to these questions. One of them uses the thermodynamics of irreversible processes [12–16] while the other starts from the molecular properties [17–22]. Some of these theories are of historical interest only and cannot be used in the interpretation of experimental data. However, lately a few theories [17–19,21,22] have appeared, the results of which substantially motivated the present work. Those results, though similar, differ from one another and we found it interesting to evaluate those theories by comparing them with experimental results.

In Sec. II we briefly review the key theories. The experimental technique and results for mixtures of 4-cyan-4′-octyloxybiphenyl (8OCB) and 4-butylbenzoate 4-isothiocyanatephenyl (4TPB) are discussed with the aid of phenomenological diagrams of Kneppe *et al.* [23,24] (KSS) in Secs. III and IV. The applicability of Kuzuu-Doi (KD) and Osipov Terentjev (OT) theories to our experimental data will be discussed in Sec. V.

II. TEMPERATURE DEPENDENCE OF THE VISCOSITY TENSOR

The Kuzuu-Doi theory [17] relates the macroscopic viscous stress tensor $\underline{\sigma}$ to microscopic parameters. The theory is a generalization of a theory of Doi [25] for lyotropic liquid crystals of rodlike polymers. Starting from the time evolution of the orientational distribution function, and calculating the change of the free energy per unit volume, they derived the stress tensor $\underline{\sigma}$ for the monomer thermotropic liquid crystal, which leads to the Miesowicz viscosities:

$$\eta_1^{\mathrm{KD}}=\frac{ckT}{4D_r}\frac{p^2-1}{p^2+1}\left\{\frac{1}{35}\frac{p^2-1}{p^2+1}(14+5S+16S_4)+S(2+1/\lambda)\right\}, \tag{1}$$

$$\eta_2^{\mathrm{KD}}=\frac{ckT}{4D_r}\frac{p^2-1}{p^2+1}\left\{\frac{1}{35}\frac{p^2-1}{p^2+1}(14+5S+16S_4)-S(2-1/\lambda)\right\}, \tag{2}$$

$$\eta_3^{\mathrm{KD}}=\frac{ckT}{4D_r}\left(\frac{p^2-1}{p^2+1}\right)^2\frac{2}{35}(7-5S-2S_4), \tag{3}$$

where D_r is the effective rotational diffusion coefficient, c the number density, p the molecular length-to-diameter ratio, λ a constant, S, S_4 order parameters, $S=\langle P_2[\cos(\theta)]\rangle$ and $S_4=\langle P_4\rangle$, respectively, and the superscript ''KD'' refers to Kuzuu and Doi and is introduced for clarity of presentation.

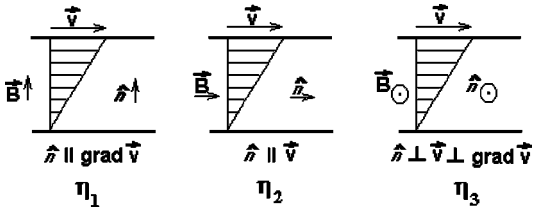

FIG. 1. Definition of principal flow geometries and the corresponding Miesowicz viscosity coefficients.

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Equations (1)–(3) predict the temperature and order parameter dependence of Miesowicz viscosities. One has to keep in mind that D_r is also temperature dependent, so for comparison with experimental results this dependence has to be either known or assumed. We note that λ is not related to microscopic parameters. To bypass this inconvenience and eliminate λ and D_r, one can take an appropriate combination of the Miesowicz viscosities, cf. Eqs. (1)–(3):

$$\frac{\eta_3}{\eta_1-\eta_2}\approx\frac{p^2-1}{p^2+1}\left(\frac{1}{10}\frac{1}{S}-\frac{1}{14}\right). \tag{4}$$

Since $S_4\approx[1-(1-S)^{0.6}]$ the following strict inequality holds: $S_4<S$ [26].

The correctness of Eq. (4) can thus be verified by a linear relation between $\eta_3/(\eta_1-\eta_2)$ and S^{-1} from the experimental results.

If one considers the usual Arrhenius temperature dependence of D_r, $D_r=C\exp(-B/T)$, the following additional relation should follow:

$$\ln\left(\frac{\eta_1-\eta_2}{S}\right)=\ln(T)+a\frac{1}{T}+b. \tag{5}$$

The validity of Eqs. (4) and (5) will be tested in detail in Sec. V.

An attempt to eliminate the shortcomings of KD theory was provided by Osipov and Terentjev [18,19]. They used the microscopic stress tensor and kinetic equation to derive the temperature and order parameter dependence of the viscosity coefficients. Their goal was to express the friction coefficient λ' ($\lambda'\sim 1/D_r$), which is a model parameter of the kinetic equation, in terms of molecular parameters. They used the general formula taken from the fluctuation-dissipation theorem:

$$\lambda'=\frac{1}{3kT}\int_0^\infty\langle\Gamma(t)\Gamma(0)\rangle_{\mathrm{eq}}dt, \tag{6}$$

where $\Gamma(t)$ is the total torque exerted on a molecule, $\langle\Gamma\rangle_{\mathrm{eq}}=0$; and arrived at the following expression for the microscopic friction coefficient λ':

$$\lambda'\simeq 100(1-\Phi)c^2d^6\left(\frac{d}{L}\right)^2\frac{(kT)^5}{G_0^3}\sqrt{\frac{I_\perp}{kT}}\exp\left(3\frac{G_0+G_a}{kT}\right), \tag{7}$$

where Φ and c are the volume fraction and the number density of molecules, respectively; G_0 and G_a are constants describing, respectively, the isotropic and anisotropic contributions to the attractive part of the intermolecular interaction potential, $G_a\ll G_0$; and $I_\perp$ is the transverse moment of inertia of the molecules.

Equation (7) ensures the Arrhenius behavior of the viscosity coefficients, with the activation energy determined mainly by the isotropic intermolecular attraction ($\sim G_0$).

Another problem not addressed by KD is the relation of λ to molecular parameters. This is evaluated from the explicit expression for the anisotropic part of the microscopic stress tensor:

$$\sigma_a^{ij}=\frac{1}{2}c\frac{\partial U}{\partial\theta}\left(h_s(n_in_\mu A^{\mu j}-n_jn_\mu A^{\mu i})-\frac{1}{2}h_a(n_iN_j-n_jN_i)\right). \tag{8}$$

The scalar functions h_s and h_a depend only on θ, where θ is the angle between the director and the unit vector in the direction of the long molecular axis, **u**, and can be derived from the kinetic equation. They are subsequently averaged over the angle θ. Thus OT relate λ to molecular parameters via

$$\lambda\sim kTS\frac{p^2-1}{p^2+1}\left(\frac{J_0}{kT}\right)^{-1/2}\exp\left(-\frac{J_0}{kT}\right), \tag{9}$$

where J_0 is a constant, which according to mean field theory is equal to $4.5kT_{NI}$, with T_{NI} being the clearing point.

The Leslie coefficients derived by Osipov and Terentjev lead to the following temperature and order parameter dependence of the Miesowicz viscosity coefficients:

$$\eta_1^{\mathrm{OT}}=\frac{1}{2}\left(\frac{3\sqrt{3}}{16}+\frac{J_0S}{kT}\right)\frac{\pi c\lambda'}{e}\left(\frac{J_0S}{kT}\right)^{-3/2}\exp\left(\frac{J_0S}{kT}\right), \tag{10}$$

$$\eta_2^{\mathrm{OT}}=\eta_3^{\mathrm{OT}}=\frac{1}{2}\frac{3\sqrt{3}}{16}\frac{\pi c\lambda'}{e}\left(\frac{J_0S}{kT}\right)^{-3/2}\exp\left(\frac{J_0S}{kT}\right). \tag{11}$$

It follows from Eq. (10) and Eq. (11) that the ratios $\eta_1^{\mathrm{OT}}/\eta_2^{\mathrm{OT}}=\eta_1^{\mathrm{OT}}/\eta_3^{\mathrm{OT}}$ should be linearly dependent on S/T. The theory predicts the equity of η_2^{OT} and η_3^{OT} in contradiction to the experimental results, $\eta_2\neq\eta_3$ [2,23,24,27–29]. However, one may think of $\eta_2^{\mathrm{OT}}/\eta_3^{\mathrm{OT}}=1$ as a constraint that the ratio should be constant and independent of the substance, which we will explore later in this paper.

All the Leslie coefficients, from which Eqs. (10) and (11) were obtained, are proportional to $\exp[(J_0S)/(kT)]$, as a result of a too drastic approximation in the calculation of the symmetrical part of the stress tensor [18]. This approximation was corrected later [19], and the following Miesowicz coefficients can be obtained from the new set of Leslie coefficients:

$$\eta_1^{\mathrm{OT}*}=\frac{c\lambda'}{2}\left\{\frac{1}{14}\frac{p^2-1}{p^2+1}(3S+4S_4)+\frac{6}{14}S+\frac{7}{35}+\frac{1}{12}\left(\frac{J_0}{kT}\right)^{1/2}\exp\left(\frac{J_0}{kT}\right)S\right\}, \tag{12}$$

$$\eta_2^{\mathrm{OT}*}=\frac{c\lambda'}{2}\left\{\frac{1}{14}\frac{p^2-1}{p^2+1}(3S+4S_4)-\frac{8}{14}S+\frac{7}{35}+\frac{1}{12}\left(\frac{J_0}{kT}\right)^{1/2}\exp\left(\frac{J_0}{kT}\right)S\right\}, \tag{13}$$

$$\eta_3^{\mathrm{OT}*}=\frac{c\lambda'}{70}(7-5S-2S_4). \tag{14}$$

The OT* viscosity coefficients produce the same relation between the combination $\eta_3/(\eta_1-\eta_2)$ and the order parameter as KD, cf. Eq. (4). The other relation, however, is some-

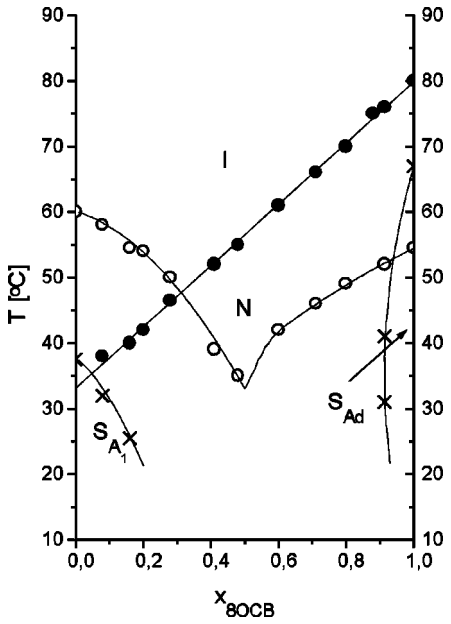

FIG. 2. Temperature—composition phase diagram of 4TPB and 8OCB mixture; (●)—T_{NI}, (×)—T_{NA}, (○)—melting temperatures [30].

what different and follows without any additional assumptions from Eq. (12) to Eq. (14):

$$\ln\left(\frac{\eta_1^{\mathrm{OT}*}-\eta_2^{\mathrm{OT}*}}{ST^{4.5}}\right)=a_{\mathrm{OT}}\frac{1}{T}+b_{\mathrm{OT}}. \tag{15}$$

The validity of Eq. (15) will be discussed in Sec. V.

Finally, a molecular theory of Chrzanowska and Sokalski [21], and Fialkowski [22] (CSF) appeared recently. The Leslie coefficients are derived for the biaxial nematic but in the uniaxial limit they reduce to formulas quite similar to those of KD, in particular, they lead to the same relations as Eq. (4) and Eq. (5). Therefore their findings will be addressed in this paper in conjunction with KD only.

III. EXPERIMENT

The mesogenic substances 8OCB (4-cyan-4′-octyloxybiphenyl) and 4TPB (4-butyl benzoate 4′-isothiocyanatephenyl) were synthesized at the Technical Military Academy in Warsaw [30] and used without any further purification. The phase diagram of an 8OCB+4TPB mixture is shown in Fig. 2. Samples with the weight percent of 8OCB, $x_{8\mathrm{OCB}}=0.40$, 0.50, 0.60, 0.70, 0.80, 0.90, 0.91, 0.92, and 1.00, denoted in bold in what follows, were used for measurements. On increasing temperature the mixtures **0.40**–**0.91** have the phase sequence Cr-*N*-*I*, while the phase sequence of **0.92** and **1.00** is Cr-A_d-*N*-*I*, where *I*, *N*, A_d, and Cr stand for the isotropic, nematic, smectic A_d, and crystal phase, respectively.

The viscosity coefficients are measured with the aid of a home-built Miesowicz viscometer [31] with the accuracy of 5% to 10%. An external magnetic field of 0.5 T allowed measurements of $\eta_1(\mathbf{n}\|\mathrm{grad}\,\mathbf{v})$ and $\eta_3(\mathbf{n}\perp\mathbf{v}\perp\mathrm{grad}\,\mathbf{v})$, while the orientation $\mathbf{n}\|\mathbf{v}(\eta_2)$ is achieved to a good approximation by flow [3,32]. The temperature is controlled to within 0.1 K.

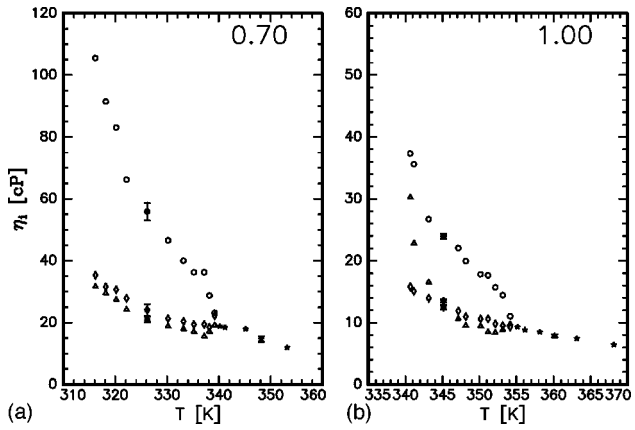

FIG. 3. Typical Miesowicz viscosity coefficient dependence on temperature for **0.70** (a) and **1.00** (b) mixtures; (○)—η_1, (△)—η_2, (◇)—η_3, and (⋆)—η_{iso}.

The order parameter is related to Δn via [33]

$$\Delta n\sim\rho^{1/2}S, \tag{16}$$

where ρ is density, and hence the temperature dependence of the order parameter is dominated by that of the birefringence Δn. We took advantage of this property to measure $\Delta n(T)$ in a supplemental experiment and use it instead of S in what follows. $\Delta n(T)$ measurements were performed on the Abbe refractometer with an accuracy of 3×10^{-4}.

IV. RESULTS AND DISCUSSION

Illustrative results for $\eta_i(T)$ for the **0.70** and **1.00** mixtures, and of $\Delta n(T)$ for **0.70** are given in Fig. 3 and Fig. 4, respectively. Results for other samples exhibiting only the nematic phase are similar to that for **0.70**. The behavior of **1.00** is typical for a group of mixtures which has both the nematic and smectic *A* phase. Therefore, results are shown in what follows for **0.70** and **1.00** only, unless stated otherwise. We plan to publish a detailed study of the concentration dependence of viscosity coefficients in the future.

In order to systematize the viscosity results, the phenomenological relations of Kneppe *et al.* [23,24] between the Miesowicz viscosities in the nematic phase, referred to hereafter as KSS, can be used:

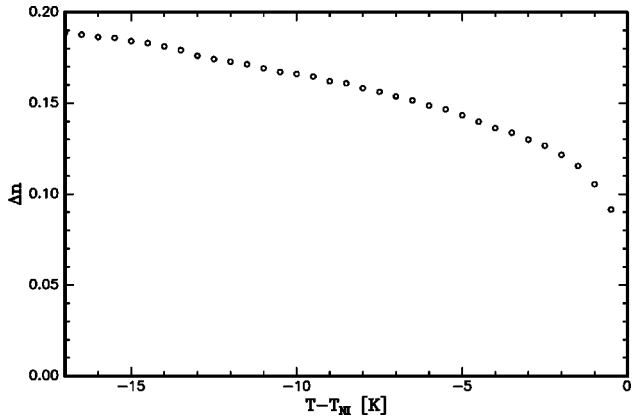

FIG. 4. Typical temperature dependence of birefringence for **0.70**; T_{NI} is the clearing point, cf. Fig. 2.

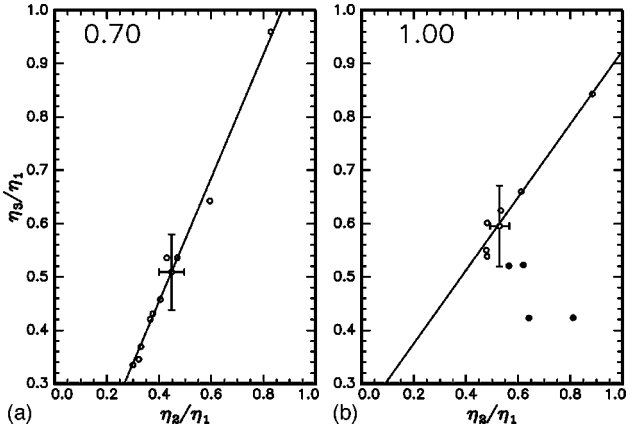

FIG. 5. Plots of η_3/η_1 vs η_2/η_1 for **0.70** (a) and **1.00** (b) mixtures. Full symbols indicate the pretransitional effects.

$$\frac{\eta_3}{\eta_1}=a\frac{\eta_2}{\eta_1}+b \tag{17}$$

and for any two viscosity coefficients:

$$\eta_i=a_{ij}\eta_j+b_{ij}, \quad i=1,2,3 \tag{18}$$

a_{ij} and b_{ij} being numerical constants. For single-component nematogens Eq. (17) should hold across the whole nematic phase temperature range except for a region of pretransitional effects at the nematic–smectic-*A* (*NA*) transition, whereas Eq. (18) should be valid only far from both phase transitions [23,24].

The temperature dependence of viscosity coefficients results from a combination of two effects. On the one hand, it is almost entirely Arrhenius in behavior:

$$\eta_i=\eta_{0_i}\exp(-E_{A_i}/kT). \tag{19}$$

On the other hand, near the clearing point the significant temperature dependence of the order parameter exerts a profound influence on the viscosity, i.e., the temperature dependence of reduced viscosities $\eta_i^{\mathrm{red}}=\eta_i/\eta_{iso}$ reflects strongly the temperature dependence of the order parameter [23,24]:

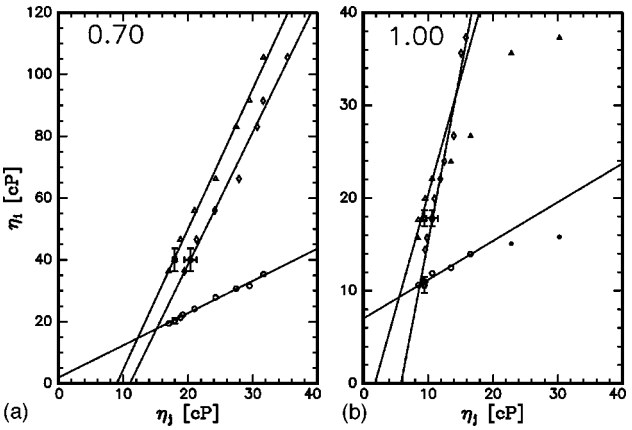

FIG. 6. Plots of η_i vs η_j for **0.70** (a) and **1.00** (b) mixtures; symbols △, ◇, and ○ correspond to $\eta_1=f(\eta_2)$, $\eta_1=f(\eta_3)$, and $\eta_3=f(\eta_2)$, respectively. Pretransitional effects are emphasized by full symbols.

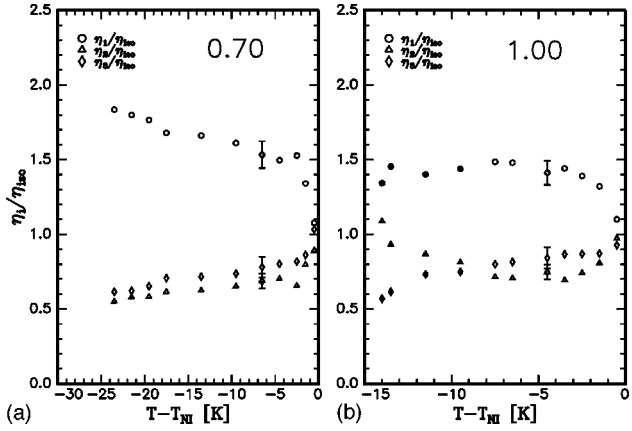

FIG. 7. Plot of η_i^{red} vs $(T-T_{NI})$ for **0.70** (a) and **1.00** (b) mixtures; (○)—η_1, (△)—η_2, (◇)—η_3. Full symbols indicate the presence of pretransitional effects.

$$\eta_i^{\mathrm{red}}=\frac{\eta_i}{\eta_{iso}}=1+\left(\frac{\eta_i^1}{\eta_{iso}}-1\right)S, \tag{20}$$

where η_i^1, η_{iso} are viscosity coefficients in the limit $S=1$ and $S=0$, respectively.

The phenomenological equations (19) and (20) attempt to rationalize the temperature and order parameter behavior of the viscosity coefficients.

In order to verify the universality of KSS phenomenological relations, we replotted our raw data in terms of Eq. (17), Eq. (18), and the following relations, cf. Fig. 5 to Fig. 8:

$$\eta_i^{(\mathrm{red})}=f(T-T_{NI}), \tag{21}$$

$$\eta_i^{(\mathrm{red})}=a_i\Delta n+b_i. \tag{22}$$

For samples exhibiting only the nematic phase, we find the ratio η_3/η_1 is indeed a linear function of η_2/η_1, cf. Eq. (17). Typical results for this group are given in Fig. 5(a). Furthermore, the coefficients *a* and *b* for all these nematic mixtures have similar values to those obtained for single-component liquid crystals [24]. In the case of **0.92** and **1.00**, on approaching the smectic phase, Eq. (17) does not hold, cf.

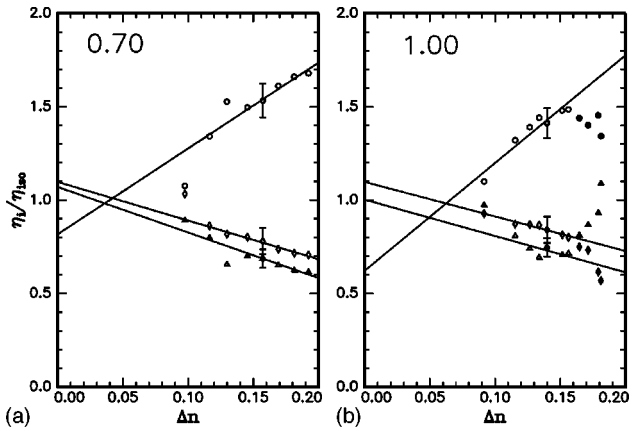

FIG. 8. Plot of η_i^{red} vs Δn for **0.70** (a) and **1.00** (b). Symbol codes as in Fig. 7.

Fig. 5(b). However, besides pretransitional effects, far from the smectic phase *a* and *b* still have values typical for the former.

Results of $\eta_i = f(\eta_j)$ for **0.70** and **1.00** are shown in Fig. 6. For samples **0.92** and **1.00** only $\eta_1 = f(\eta_3)$ is linear in the whole temperature range, in agreement with a theoretical prediction of [34]. A completely different situation is found for the case of η_i vs η_2 and it manifests itself in the diagram as a deviation from linearity of η_1 vs η_2 and η_3 vs η_2, cf. full symbols in Fig. 6(b).

It is instructive to compare the values of a_{ij} of Eq. (18) for samples exhibiting nematic and smectic phases with those which are only nematogenic. a_{32} values are typical for other nematic liquid crystals [24], $a_{32} > 1$, and are comparable to each other for mixtures **0.40**–**0.91**. In the case of liquid crystals exhibiting a smectic phase, a_{32} is much smaller, i.e., 0.830 for **0.92** and 0.418 for **1.00**, even in the linear region of the nematic phase. Values of a_{13} and a_{12} are similar for all of the samples investigated, whether or not the smectic phase is exhibited. It is not surprising in the case of a_{13}, where no pretransitional effects are present, but in the case of a_{12} the qualitative behavior of $\eta_1 = f(\eta_2)$ is different for those two groups of the investigated samples.

The diagrams of η_i^{red} vs $T - T_{NI}$, cf. Eq. (21), for **0.70** and **1.00** are shown in Fig. 7. Again, mixtures **0.40**–**0.91** show a typical temperature dependence of reduced viscosities closely reflecting the temperature behavior of the order parameter, whereas *NA* pretransitional effects are visible for samples **0.92** and **1.00**. For the latter samples, the resemblance to the order parameter behavior is visible only in the limited region far from the nematic-smectic transition temperature. Pretransitional behavior is visible for all three viscosity coefficients because of an arbitrary choice of η_{iso} as the arithmetic average, $(\eta_1 + \eta_2 + \eta_3)/3$, cf. full symbols in Fig. 7.

To verify the viscosity dependence on the nematic order, reduced viscosities versus the anisotropy of the refractive index Δn are plotted in Fig. 8, cf. Eq. (22). The $\eta_i / \eta_{iso} = f(\Delta n)$ dependence is nearly linear for samples **0.40**–**0.90**, but the agreement deteriorates on approaching the clearing point. Note that the coefficient b_i of Eq. (22) should be equal to one, which is not always the case, cf. Eq. (20). For samples **0.92** and **1.00** deviations from the linearity are again visible, cf. full symbols in Fig. 8.

In summary, we find KSS diagrams a good and universal way of presenting experimental results. Induced nematics obey the phenomenological rules typical for single-component materials. Discrepancies are visible, however, for substances which exhibit both nematic as well as smectic phases, in agreement with McMillan theory [34].

V. COMPARISON WITH THEORETICAL RESULTS

We find it instructive to look at our results in terms of existing theories. To facilitate comparison with KD [17] and CSF [21,22] theories in terms of Eqs. (16), (4), and (5), we replotted our raw data in the form

$$\frac{\eta_3}{\eta_1 - \eta_2} = a_{\mathrm{KD}} \frac{1}{\Delta n} + b_{\mathrm{KD}}, \tag{23}$$

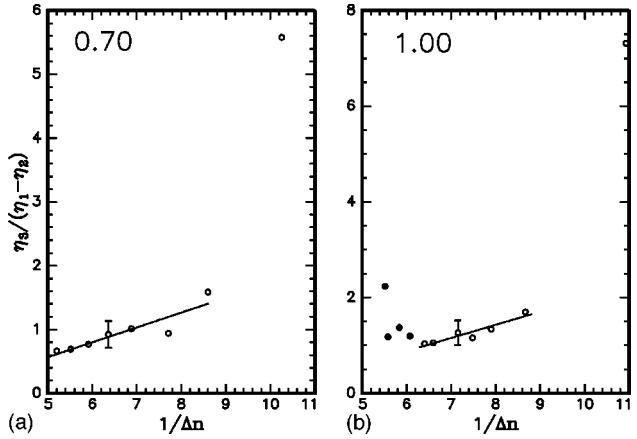

FIG. 9. Plot of $\eta_3/(\eta_1 - \eta_2)$ vs Δn^{-1} for **0.70** (a) and **1.00** (b). The fitted curves are shown. Pretransitional effects are marked with full symbols.

$$\ln\left(\frac{\eta_1 - \eta_2}{\Delta n T}\right) = a'_{\mathrm{KD}} \frac{1}{T} + b'_{\mathrm{KD}}. \tag{24}$$

Experimental results for **0.70** and **1.00**, together with fit to Eq. (23) curves are given in Fig. 9. Near the clearing point $(\eta_1 - \eta_2) \to 0$ and $\eta_3/(\eta_1 - \eta_2) \to \infty$, for all samples. Far below the clearing temperature, experimental points lie on straight lines except for the *NA* pretransitional region for **0.92** and **1.00**, cf. full circles in Fig. 9. Close to the *NA* transition, the $\eta_3/(\eta_1 - \eta_2)$ vs Δn^{-1} plot indicates the divergence of η_2, cf. the full circles in Fig. 9. Note that the coefficient $b_{\mathrm{KD}} = -\frac{1}{14}(p^2-1)/(p^2+1)$ should depend only on the molecular axial (length-to-diameter) ratio *p* and vary from $-\frac{1}{14}$ to $\frac{1}{14}$, cf. Eq. (4). Unfortunately, establishing a reasonably precise value of b_{KD} would require high accuracy of the η_i measurements and experimental coverage of a substantial range of $1/\Delta n$. We found that in only three cases (**0.40**, **0.90**, **0.91**) was b_{KD} within the range, but even then the error bounds were large compared with the narrow theoretical range allowed. Consequently, it is not possible to verify if the results are consistent with, e.g., the mean value of the axial ratio in the mixtures studied, cf. Eq. (4). CSF theory predicts an even smaller value for their *b* coefficient in Eq. (23), i.e., $b \approx 0.43 b_{\mathrm{KD}}$, so the above uncertainty holds in this case as well.

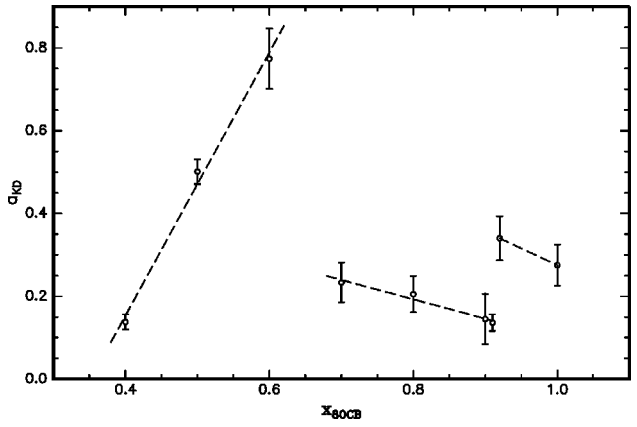

FIG. 10. The concentration dependence of a_{KD} factor in Eq. (23). Typical error bars are also shown.

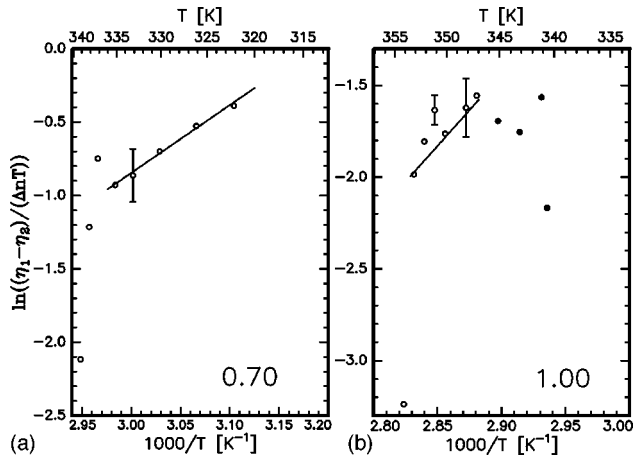

FIG. 11. Plot of $\ln[(\eta_1-\eta_2)/(\Delta nT)]$ as a function of $1/T$ for **0.70** and **1.00**; together with fitted lines. Pretransitional effects are marked with full circles.

As far as the coefficient a_{KD} is concerned, it is instructive to follow the change of a_{KD} with concentration of 8OCB in the mixture, cf. Fig. 10. Initially a_{KD} increases until it reaches a maximum at about $x_{8\mathrm{OCB}}=60\%$, to fall abruptly over the next 10%, followed by a further slow decrease towards a minimum at about $x_{8\mathrm{OCB}}=91\%$. For the concentration of 8OCB in the range from 91% to 92% there is a nearly stepwise change in a_{KD}, which is most probably related to a change in the molecular ordering. The coefficient a_{KD} depends on p, the density and the polarizability, cf. Eq. (4). For the **0.92** sample there is a smectic and reentrant nematic phase in addition to the nematic phase, cf. Fig. 2. Since no dramatic change in the density is observed on changing the concentration from 91% to 92%, the rise in a_{KD} must result from the behavior of other quantities, e.g., as a result of dimer formation. Note that this trend is already visible in the nematic phase, cf. Fig. 10.

Normalized experimental data together with fitted straight lines corresponding to Eq. (24) are shown in Fig. 11. Near the clearing point $\ln[(\eta_1-\eta_2)/\Delta nT]$ drops abruptly. A similar drop is also observed close to the smectic phase (full symbols), due to the divergence of $(\eta_1-\eta_2)$, which follows the above mentioned divergence of η_2. According to the OT theory, the ratio η_2/η_3 should be constant $(=1)$ and independent of the substance, cf. Eq. (11). From the summary plot of η_2/η_3 versus $\Delta n/T$ for all mixtures given in Fig. 12 it follows that our data seem to be in qualitative agreement with OT predictions, i.e., the viscosity ratio is indeed constant to within experimental error over the nematic phase and independent of the mixture. For mixtures **0.92** and **1.00** close to the *NA* transition, pretransitional effects are present, but the value of η_2/η_3 calculated far from the smectic phase is the same as for other mixtures studied.

The constancy of the ratio $\eta_2/\eta_3\approx 0.9$, in agreement with prediction of OT theory, is an important result. An important contradiction between the theory and measured viscosity coefficients rests in relative magnitudes of η_2 and η_3. The theory predicts the equity of these viscosity coeffficients, while for all our experimental data $\eta_2<\eta_3$. One can easily verify that the latter relation is consistently satisfied by available experimental data for different neat and composite rodlike liquid crystals [3,23,24,27–29].

An interesting insight into the source of this contradiction at the molecular level emerges if one attempts to identify molecular dynamics modes associated with the Miesowicz viscosities, e.g., via the classic Stokes-Einstein-Debye (SED) proportionality relation between rotational correlation time of a particle and the local viscosity [35–38]. This relation has already been explored by Diogo and Martins to link

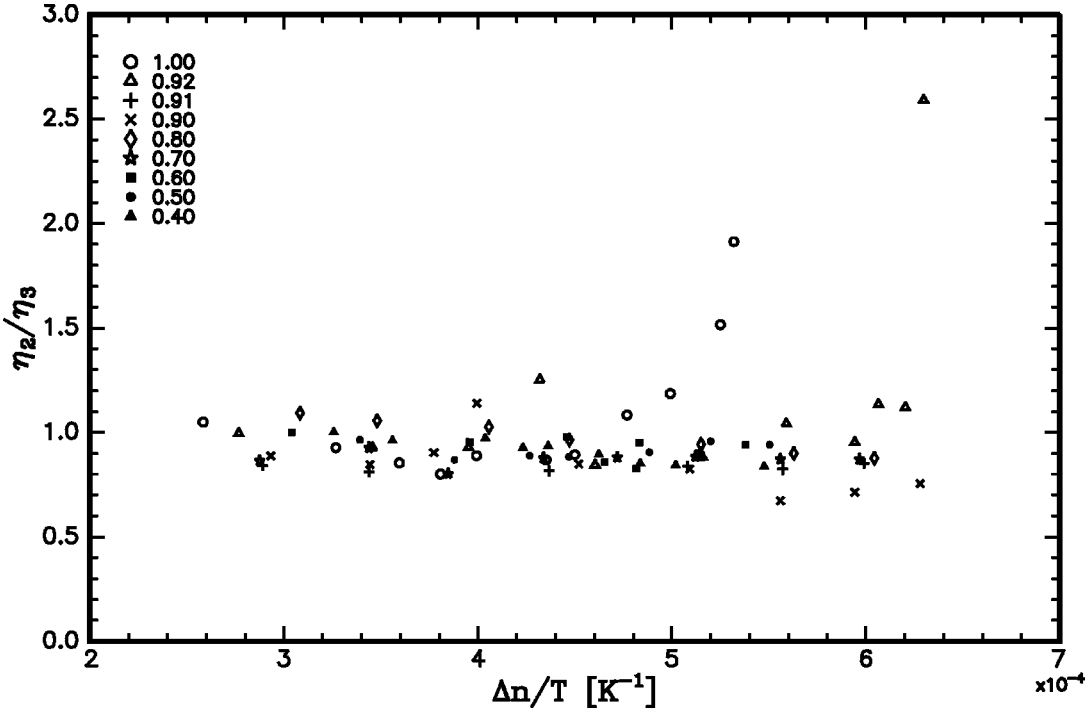

FIG. 12. Summary plot of η_2/η_3 as a function of $\Delta n/T$ for all the mixtures studied.

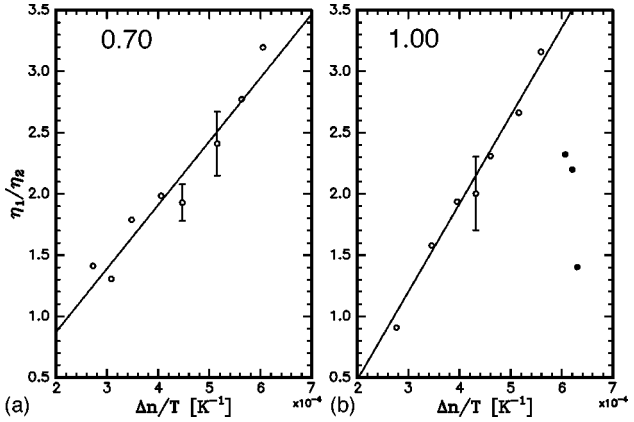

FIG. 13. η_1/η_2 vs $\Delta n/T$ for **0.70** (a) and **1.00** (b); full symbols indicate pretransitional effects.

semiempirically the nematic rotational viscosity coefficient, γ_1 to end-over-end molecular reorientation [15,16]. It follows from SED that molecular reorientation linked to η_2^{OT} end η_3^{OT} should be the same, while experimental results imply somewhat faster dynamics for η_2 than for η_3. It is commonly accepted from dielectric spectroscopy studies that effectively three modes dominate molecular rotational dynamics in the nematic phase: (i) a remarkably retarded, by comparison to molecular dynamics of the isotropic phase, end-over-end tumbling of the long molecular axis over the nematic potential barrier, (ii) at least an order of magnitude faster reorientations about the long molecular axis, and (iii) even faster fluctuations of the long axis in the nematic potential well which are either precessions or small-angle reorientations about the short axis [39,40]. From the flow geometry considerations, cf. Fig. 1, one finds that the shear strain of Couette flow in the case of η_3, when the director is pointing normal to the direction of flow and velocity gradient, is relaxed by either dynamics modes (ii) or (iii). In the case of η_2, the director is along the flow direction. The shear strain produces thus torques which may, in principle, force tumbling of the long molecular axis [(i) mode] or enhance the order [(iii) mode]. The same order of magnitude of η_2 and η_3 values in both the experiment and OT theory clearly excludes the slow (i) dynamic mode as the relief mechanism in η_2^{OT}.

Equity of η_2^{OT} and η_3^{OT} is a direct consequence of the strong OT assumption $I_\perp \gg I_\parallel$, which leaves the (ii) mode out of consideration [18]. Spectroscopic methods attest, however, that molecules spend a substantial amount of time rotating rapidly about the long axis, and the viscous strain in the η_3 geometry must also be effectively relaxed via this dynamical mode. The presence of such a mechanism is the only means which leads to relaxation times that are longer than those implied by mechanism (iii) thus ensuring that $\eta_2 < \eta_3$, as observed experimentally. Now, identifying η_2 and η_3 simply with modes (iii) and (ii), respectively, we estimate from SED and, e.g., results of Nordio *et al.* [39] $\eta_2/\eta_3 \sim \tau_{\mathrm{iii}}/\tau_{\mathrm{ii}} \sim \tau_{10}/\tau_{11} \approx 0.4$ for typical values of the order parameter ($S=0.5$). If η_3 is more realistically associated with some effective relaxation time due to modes (ii) and (iii), e.g., $\propto(\tau_{\mathrm{iii}}^{-1}+\tau_{\mathrm{ii}}^{-1})^{-1}$, then we obtain $\eta_2/\eta_3 \approx 0.7$. Although such estimation is only tentative, these values are indeed close to experimental results in nematics, 0.5–0.7 [3,23,24,27–29].

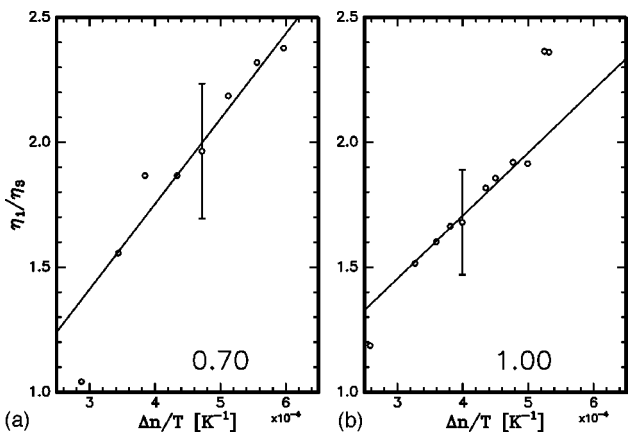

FIG. 14. η_1/η_3 vs $\Delta n/T$ for **0.70** (a) and **1.00** (b).

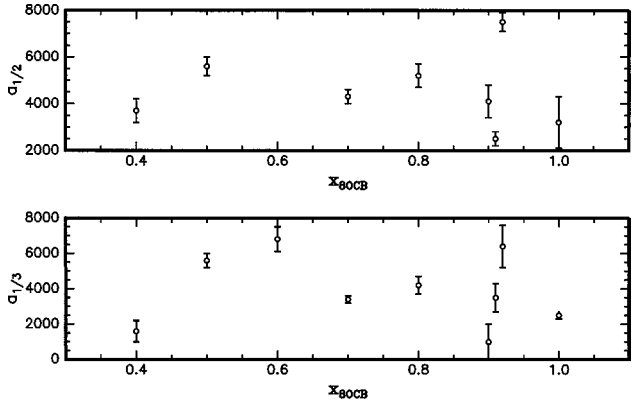

FIG. 15. The dependence of $a_{1/2}$ and $a_{1/3}$ vs composition $x_{8\mathrm{OCB}}$.

η_1/η_2 and η_1/η_3 versus $\Delta n/T$ plots are shown in Fig. 13 and Fig. 14. The ratios should be linear in $\Delta n/T$, cf. Eq. (10) to Eq. (11). The tangents $a_{1/2}$ and $a_{1/3}$ are proportional to T_{NI}, therefore they should be linear and increasing with the composition $x_{8\mathrm{OCB}}$, cf. Fig. 2. The composition dependence of $a_{1/2}$ and $a_{1/3}$ is given in Fig. 15. As one can see, there is no linear dependence on the composition for those tangents. We suppose that instead of approximate expressions for α_i (and consequently η_i) the exact equations given later by Osipov and Terentjev [19] should be used. Relations between the different Miesowicz viscosities [Eqs. (12)–(14)] are then much the same as those obtained by Kuzuu and Doi [17], and Eq. (24) takes the form

$$\ln\left(\frac{\eta_1^{\mathrm{OT}}-\eta_2^{\mathrm{OT}}}{\Delta n T^{4.5}}\right)=a_{\mathrm{OT}}\frac{1}{T}+b_{\mathrm{OT}}. \tag{25}$$

Unfortunately it is not possible to discern at the moment which of those two equations (24) and (25) better describes reality. The curves fit to Eq. (24) and Eq. (25) are indistinguishable to within experimental error and also the fit errors are much the same. The value of a which should be associated with the activation energy of the effective rotational diffusion coefficient, obtained in both cases (a_{KD} and a_{OT}) is somewhat different. Therefore to answer this question the activation energy has to be known from an independent experiment.

VI. CONCLUSIONS

The viscosity coefficients for several mixtures of 8OCB and 4TPB were measured. Experimental data were analyzed using Kneppe *et al*. relations. KSS diagrams proved to be a convenient way of presenting the viscosity results for liquid crystal mixtures. In particular, the difference in behavior for the samples exhibiting only the nematic phase and for those which have also a smectic phase is emphasized. One of the KSS coefficients, a_{32}, is greater than one for substances with only a nematic phase and smaller than one in the nematic phase of substances with both phases. No such difference is observed for a_{12} and a_{13}, although the qualitative behavior is completely different for those two groups of samples. Theories of Kuzuu and Doi and Osipov and Terentjev were also tested with our results. As it turns out, one of the most interesting results of the application of KD theory is the behavior of a_{KD} [Eq. (23)], which seems to be strongly sensitive to the kind of ordering and dimerization. We have shown also that some results of OT theory are at odds with experimental findings, namely, OT predicts higher values for η_2 than those found in nematics.

ACKNOWLEDGMENT

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