Viscosity of nematic mixtures: A free-volume approach

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The five Leslie viscosities for a mixture of two nematic materials are computed as functions of the temperature, composition and order parameter. It is shown that, for a nematic mixture of A and B, the equations describing the composition and temperature behaviour of the Leslie viscosities have the same form as those for the pure components, provided that composition-averaged values of the parameters are used. For the case where the free volume is additive, the relaxation times for the mixtures can be directly expressed as functions of the parameters for the pure components. These results are compared with the experimental data on γ_1 for MBBA/EBBA mixtures, and fairly good agreement is found.

1. Introduction

Liquid crystal mixtures have been the subject of considerable interest over the last 20 years for a number of reasons, including attempts to increase the nematic range and lower the melting point of nematic materials, as well as improving the performances of electro-optic displays. Most work on this subject has been carried out on equilibrium properties [1] such as the prediction of phase diagrams and of the orientational order in such systems [2–7]. Dynamic properties like viscosities have been less studied, and most of the work presented up to now has been mainly concerned with the experimental determination of these properties [8–12].

The main purpose of this paper is to present a model to compute the five Leslie viscosities of a nematic mixture as functions of the viscosities of the components. This model is a generalization of previous work on the order parameter and temperature dependence of the viscosities of nematic materials [13], and it is based upon a suitable generalization of the Cohen–Grest theory of free volume [14]. The resulting expressions are

$$\gamma_1 = g_1(x)S^2\tau_1(x, S, T), \tag{1}$$

$$\gamma_2 = g_2(x)S\tau_2(x, S, T), \tag{2}$$

$$\gamma_3 = g_3(x)S\tau_3(x, S, T), \tag{3}$$

$$\alpha_4 = [g_4(x) - \tfrac{1}{3}g_3(x)S]\tau_3(x, S, T), \tag{4}$$

$$\alpha_1 = g_5(x)S^2\tau_3(x, S, T), \tag{5}$$

where $\gamma_1 = \alpha_3 - \alpha_2$, $\gamma_2 = \alpha_3 + \alpha_2 = \alpha_6 - \alpha_5$, $\gamma_3 = \alpha_6 + \alpha_5$, α_4 and α_1 are nematic viscosities, x is the composition variable (mole fraction), and the relaxation times τ_i can be expressed as

$$\tau_i(x, S, T) = \exp\left\{\frac{\beta_i[U_0(x) + U_1(x)S^2]}{(T - T_0)I}\right\}. \tag{6}$$

The parameters $g_1, \ldots, g_4$, as well as U_0, U_1, I and T_0, depend on the composition and the corresponding parameters for the pure components. Explicit expressions for these parameters will be presented below.

The structure of this paper is as follows. In the next section we shall present the main steps in the derivation of equations (1)–(6). Then, in §3, these results will be discussed and compared with the experimental data available on mixtures of MBBA (4-methoxybenzylidene-4'n-butylaniline) and EBBA (4-ethoxybenzylidene-4'-n-butylaniline) [11, 12]. Finally, in §4, the main conclusions of this paper will be presented, together with some suggestions for further work.

2. Main theoretical results

A set of equations essentially analogous to (1)–(5) (except for the composition dependence) were previously derived by one of us [15–17] for pure nematic materials. They are essentially based on the possibility of decomposing the 'viscosity tensor' relating thermodynamic forces and fluxes into the product of two tensors: one describing the dynamics and the other describing the symmetry of the nematic phase. The dynamics is described by the three characteristic times τ_1, τ_3 and τ_2, which are the relaxation times for orientation stresses, shear stresses and the coupling between orientation and flow. The coefficients $g_1, \ldots, g_5$ come from the symmetry of the nematic phase and are assumed to be (nearly) temperature independent. As long as this decomposition remains valid for nematic mixtures, equations (1)–(5) also remain valid for mixtures, but now the coefficients $g_1, \ldots, g_5$ and the relaxation times τ_i become dependent on the composition of the mixture. The coefficients $g_1, \ldots, g_5$ must depend on x in such a way that for $x = 0$ or $x = 1$ one must recover the values for the pure components. Therefore for a mixture of A and B we expect that $(i = 1, \ldots, 5)$

$$g_i(x) = xg_{iA} + (1 - x)g_{iB} + x(1 - x)g_{iAB} + O(x^3). \tag{7}$$

For mixtures composed of similar molecules, the g_{AB} term is expected to be rather small. In fact, as shown below, for MBBA/EBBA mixtures this term gives a correction of less than 6 per cent to $g_1(x)$. However, in every case, the main contribution to the viscosity comes from the τ_i, factor which we shall now consider.

The temperature and composition dependence of the relaxation times τ_i can be derived following the main ideas of the Cohen–Grest model [14] and its generalization for nematic materials [13]. We assume that with every molecule there is associated a cell of volume v, which is the sum of the free volume $v_f = v - v_c$ and the molecular volume v_c. The exchange of free volume within a cluster of contiguous liquid-like cells (i.e. cells for which $v_f > 0$) is assumed to be free. The motion of one molecule is only possible if the free volume available in its cluster is greater than or equal to a minimum volume v_m of the order of a molecular volume. It is then easy to show that

$$\tau_i = \exp\left(\frac{v_{mi}}{\bar{v}_f}\right) = \exp\left(\frac{\beta_i v_m}{\bar{v}_f}\right), \tag{8}$$

where $\beta = v_{m1}/v_{m3}$, $\beta_2 = v_{m2}/v_{m3}$, $\beta_3 = 1$, and β_1 and β_2 are close to 1. For a pure material the average free volume $\bar{v}_f$ may be computed as follows [13, 14]. We take the free energy F to be a functional of the distribution functions for orientation, $\phi(\mathbf{\Omega})$,

and for free volume, $\varrho(v_f)$. The normalization of $\varrho(v_f)$ is such that

$$\int_0^\infty dv_f \, \varrho(v_f) \;=\; p, \tag{9}$$

where p is the fraction of liquid-like cells. For $p > p_c$ an infinite liquid-like cluster is present, so the material behaves as a liquid; $p = p_c$ gives the glass transition, where an infinite solid-like cluster appears, and its characteristic temperature is T_0. Minimization of F with the constraints introduced by the normalizations of $\phi(\Omega)$ and $\varrho(v_f)$ yields a pair of self-consistennt equations for $\phi(\Omega)$ and $\varrho(v_f)$. Knowing $\varrho(v_f)$, the average free volume $\bar{v}_f$ can easily be computed.

For a nematic mixture of components A and B we write the free energy as

$$F \;=\; \int \frac{d\Omega_A}{4\pi} \int dv \, \varrho(v)\phi_A(\Omega_A)f_A(\Omega_A, v)$$

$$+ \int \frac{d\Omega_B}{4\pi} \int dv \, \varrho(v)\phi_B(\Omega_B)f_B(\Omega_B, v) - T\Sigma_{\text{com}}, \tag{10}$$

where $d\Omega \equiv \sin\theta \, d\theta \, d\varphi$ is an element of solid angle, $\phi(\Omega)$ is the orientation distribution function and $\varrho(v)$ is the cell volume distribution function; ϕ_A and ϕ_B are normalized respectively to x and $1 - x$, and the normalization of $\varrho(v)$ is given by equation (9). $T\Sigma_{\text{com}}$ is the communal entropy.

We assume the following form for $f_A(\Omega_A, v)$

$$f_A(\Omega_A, v) \;=\; \zeta_{0A}(v - v_{cA}) + \frac{kT_{1A}}{v_{aA} + \bar{v}_f} (v - v_{cA})$$

$$+ kT(\ln\phi_A + \ln x + \ln\varrho)$$

$$- \varepsilon_{AA}\frac{1}{v}S_A P_2(\cos\theta_A) - \varepsilon_{AB}\frac{1}{v}S_B P_2(\cos\theta_A). \tag{11}$$

The first two terms on the right-hand side of equation (11) express the work done in expanding the cell from its average value to its actual value v minus the work done in removing a molecule from the interior of the cell; the second term depends on the average free volume. The third term gives the entropy and the last two terms correspond to the Maier–Saupe potential. An equation analogous to (11) can be written for $f_B(\Omega_B, v)$ by replacing x by $1 - x$ and interchanging the subscripts A and B.

One important point should be stressed here. If we define an average free volume v_f and an average order parameter S by

$$\zeta_0 v_f \;=\; x\zeta_{0A}(v - v_{cA}) + (1 - x)\zeta_{0B}(v - v_{cB}), \tag{12}$$

$$\frac{kT}{v_a + \bar{v}_f}v_f \;=\; x\frac{kT_{1A}}{v_{aA} + \bar{v}_f}(v - v_{cA}) + (1 - x)\frac{kT_{1B}}{v_{aB} + \bar{v}_f}(v - v_{cB}), \tag{13}$$

$$\varepsilon S^2 \;=\; \int \frac{d\Omega_A}{4\pi}[\varepsilon_{AA}S_A P_2(\cos\theta_A) + \varepsilon_{AB}S_B P_2(\cos\theta_A)]\phi_A$$

$$+ \int \frac{d\Omega_B}{4\pi}[\varepsilon_{BB}S_B P_2(\cos\theta_B) + \varepsilon_{AB}S_A P_2(\cos\theta_B)]\phi_B \tag{14}$$

then equation (10) is transformed to an equation that is formally *the same as* that for a pure component. Therefore we may write, as for pure nematic components [13],

$$\tau_i = \exp\left(\frac{\beta_i v_{\mathrm{m}}}{\bar{v}_{\mathrm{f}}}\right) = \exp\left[\frac{\beta_i(T_0 - T_1)}{(T - T_0)I}\frac{v_{\mathrm{m}}}{v_{\mathrm{a}}}\right], \tag{15}$$

where

$$k(T_0 - T_1) = v_{\mathrm{a}}\left(\zeta_0 + \frac{\varepsilon}{v_{\mathrm{c}}^2}S^2\right), \tag{16}$$

$$I = \frac{1}{2} + \left[\frac{1}{4} + \frac{T(T_0 - T_1)}{(T - T_0)^2}\right]^{1/2}, \tag{17}$$

but we now have

$$\beta_i v_{\mathrm{m}} = \beta_{i\mathrm{A}} x v_{\mathrm{mA}} + \beta_{i\mathrm{B}}(1 - x)v_{\mathrm{mB}}. \tag{18}$$

Equation (15) shows that the relaxation times τ_i for a nematic mixture have the same formal expression as those for pure components. The parameters T_0, T_1, ζ_0 and ε can, in principle, be computed from the relevant thermodynamic data for non-ideal mixtures.

Equations (15)–(17) can be transformed into a more convenient form. By defining

$$U_0 + U_1 S^2 = v_{\mathrm{m}}\frac{\zeta_0}{k} + \frac{\varepsilon v_{\mathrm{m}}}{v_{\mathrm{c}}^2}S^2, \tag{19}$$

equation (15) becomes identical with (6), where

$$I = \frac{1}{2} + \left[\frac{1}{4} + \frac{T}{(T - T_0)^2}\frac{v_{\mathrm{a}}}{v_{\mathrm{m}}}(U_0 + U_1 S^2)\right]^{1/2}. \tag{20}$$

Equations (6) and (20) hold for both pure materials and for nematic mixtures if, in the latter case, we take the averaged quantities defined by equations (12)–(14). However, an important simplification of equations (6) and (20) can be made for the case where free volume is additive.

Let us now consider the case of nematic mixtures composed of relatively similar molecules, so that, for example, the volume is additive to a good approximation. For this case we also have additivity of the free volume,

$$\bar{v}_{\mathrm{f}} = x\bar{v}_{\mathrm{fA}} + (1 - x)\bar{v}_{\mathrm{fB}}, \tag{21}$$

so the relaxation times τ_i can immediately be computed:

$$\tau_i = \exp\left[\frac{\beta_{i\mathrm{A}} x v_{\mathrm{mA}} + \beta_{i\mathrm{B}}(1 - x)v_{\mathrm{mB}}}{x\bar{v}_{\mathrm{fA}} + (1 - x)\bar{v}_{\mathrm{fB}}}\right]. \tag{22}$$

Equation (22) allows τ_i to be expressed directly in terms of the parameters for pure components. In this case any viscosity of a mixture can be computed directly from the viscosities of the pure components, leaving only $g_{i\mathrm{AB}}$ as a free parameter.

One final point should be made. As is apparent from equations (6) and (20), τ_i is finite for $T = T_0$, so all the nematic viscosities are finite at the glass transition, although they become very large. The viscosities only become infinite at 0 K. On the other hand, for $T \gg T_0$, I is close to unity, so we have

$$\tau_i \sim \exp\left(\frac{U_0 + U_1 S^2}{T - T_0}\right). \tag{23}$$

3. Analysis of experimental data and discussion

One of the few mixtures for which a reasonable amount of viscosity data has been reported is MBBA/EBBA [11, 12]. Unfortunately the data on the Miesowicz viscosities of pure MBBA presented in [11] do not agree with the generally accepted values (for a survey see [16] and references therein), so we decided to consider only the data on $\gamma_1(x, T)$ for this mixture reported in [12].
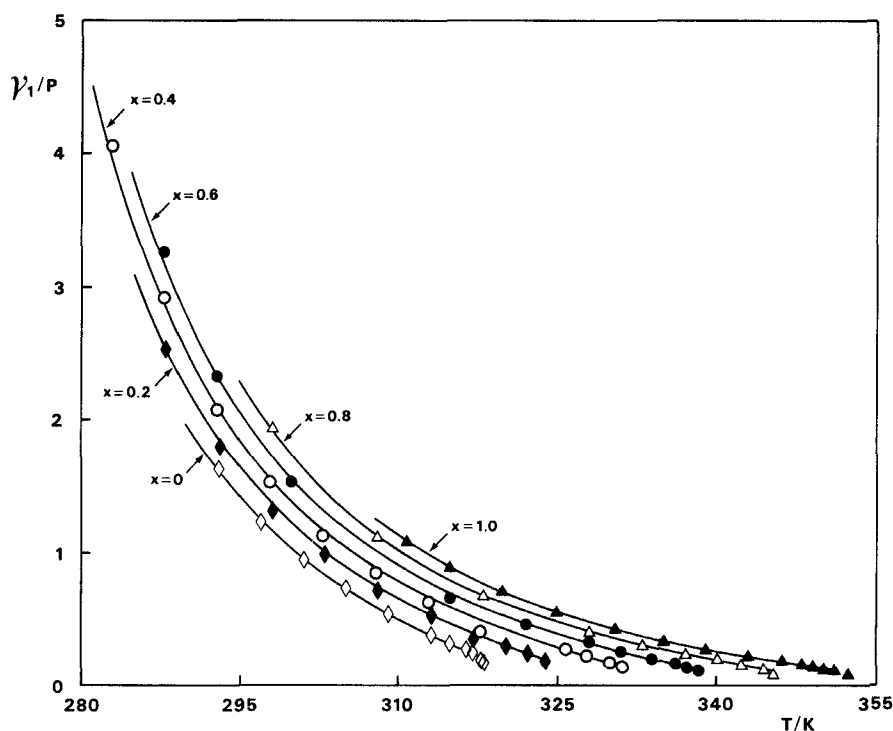

Figure 1. Rotational viscosity for mixtures of MBBA/EBBA, for $x_{EBBA} = 0, 0\cdot2, 0\cdot4, 0\cdot6, 0\cdot8, 1\cdot0$.

Figures 1 and 2 show data points taken from [12] as well as the theoretical curves calculated from equations (1) and (22), for MBBA/EBBA mixtures. Figure 3 shows the $g_1(x)$ values for each composition, and the other relevant parameters used in this calculation are given in the table (excluding g_{1AB}). As shown in figure 3, the calculated $g_1(x)$ values follow equation (7) to a good approximation; the g_{1AB} coefficient computed from figure 3 (shown in the table) is rather small. We also computed $\gamma_1(x, T)$ directly from the viscosities of the components by using equations (1) and (22) together with (7); the results are as good as those shown in figures 1 and 2: the r.m.s. error changes only from 3·35 cP to 3·85 cP, so we considered it unnecessary to show the corresponding plots.

The parameters given in the table for pure MBBA were computed from the $\gamma_1(T)$ data, and they are also compatible with other data on the same material relating to the remaining viscosities as well as to the pressure dependence of γ_1 [18]. The parameters for EBBA were computed from the $\gamma_1(T)$ data. The values of the order parameters were obtained from a fit of the magnetic susceptibility anisotropy data
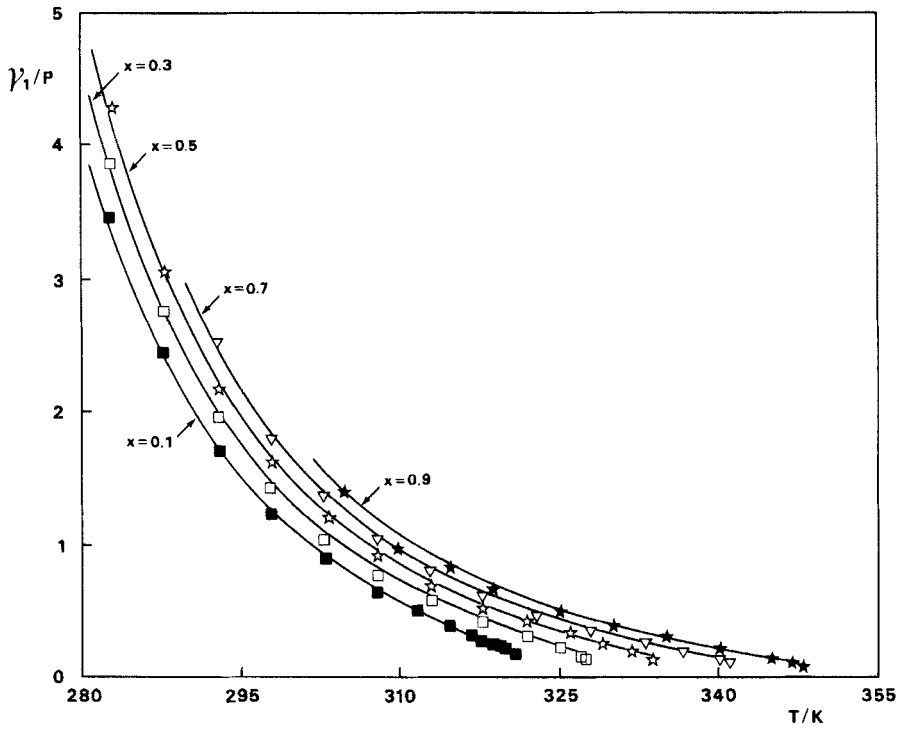
Figure 2.   Rotational viscosity for mixtures of MBBA/EBBA, for x_{EBBA} = 0·1, 0·3, 0·5, 0·7, 0·9.
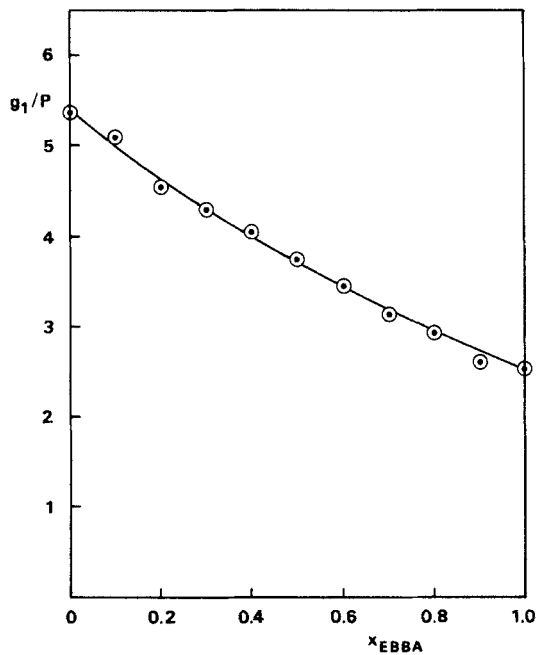

Figure 3.   Composition dependence of the parameter $g_1(x)$. The circles indicate the $g_1(x)$ values computed individually for every composition. The full curve is $g_1(x)$ as computed from equation (7).

Parameters for MBBA and EBBA.

	MBBA	EBBA
T_0/K	204	220
U_0/K	481·94	529·13
U_1/K	116·03	145·43
g_1/cP	5·3729	2·5367
β_1	0·8139	0·9169
v_a/v_m	$4·569 \times 10^{-3}$	$13·51 \times 10^{-3}$
v_m/cm^3	259	270
S_0	1	0·88
T_1/K	1·1	1·3
F	0·209	0·175
g_{1AB}	$-0·9914$	

reported in [19] using the empirical formula

$$S(T) = S_0 \left(1 - \frac{T}{T_{NI} + T_1} \right)^F. \qquad (24)$$

The order parameters for the mixtures were computed by assuming the additivity rule [7]

$$S_{AB}(x, T) = xS_A(T) + (1 - x)S_B(T), \qquad (25)$$

where $S_A(T)$ and $S_B(T)$ are given by equation (24) with T_{NI} replaced by the NI transition temperature of the mixture. All the numerical fits were made, using the MINUIT program [20].

The r.m.s. error of all the fits (130 points) is 3·4 cP and corresponds to a difference of less than 3 per cent between the experimental points and the computed ones over the full nematic and concentration ranges of MBBA/EBBA mixtures. The effect of the g_{1AB} term on $g_1(x)$ (see equation (7)) is less than 2·63 per cent, as can be seen from the table. Therefore the computation of the viscosity for any composition from the viscosities of the pure components by using equations (1), (7) and (22) but putting $g_{1AB} = 0$, i.e. *without free parameters*, yields an error of less than 5 per cent for γ_1 for the most unfavourable cases, i.e. for x close to 0·5. We believe that the regularity shown by the computed $g_1(x)$ values (as shown in figure 3) is a consequence of the fact that equation (22) describes quite correctly the temperature and concentration behaviour of the relaxation time τ_1.

One of the peculiarities of our model is the reduced number of free parameters needed in calculating the viscosities of nematic materials. For MBBA the glass transition temperature was measured [21], and its value (201 K) is in good agreement with our T_0; the value of v_m is, as expected, the molar volume in the nematic phase. Therefore only *ten* parameters $(g_1, \ldots, g_5, U_0, U_1, \beta_1, \beta_2, v_a)$ are needed in calculating the temperature behaviour of *six* viscosities of MBBA (the five Leslie viscosities plus the isotropic viscosity), and the agreement with the available experimental data has been found to be fairly good [18]. Moreover, as suggested by the above analysis of the MBBA/EBBA mixtures, it is possible to predict the viscosities of mixtures of relatively similar molecules from the viscosities of the pure components without any additional free parameter, provided that the additivity of free volume holds.

From the table the ratio U_1/U_0 has values 0·241 and 0·275 for MBBA and EBBA, respectively. It is expected that this ratio should be close to the ratio of the coefficients

of $P_2(\cos\theta)$ and the zeroth-order term in the expansion of the nematic pseudo-potential in Legendre polynomials

$$\psi(\theta) \;=\; A_0\varrho \,+\, A_2\varrho SP_2(\cos\theta) \,+\, \ldots \;. \tag{26}$$

This ratio has been calculated for the case of axially symmetric rods [22], and they have a value of about 0·2–0·3 for rods comparable to MBBA and EBBA, in good agreement with our values.

4. Conclusion

We have proposed in this paper a theory for the order parameter and temperature dependence of the Leslie viscosities of nematic mixtures, as a generalization of previous results on the temperature dependence of low molecular weight nematics [15–17] as well as nematic semi-flexible polymers [13]. One of the attractions of this model is the rather low number of free parameters used; for situations where the free volume is additive, even without any free parameters, it is possible to calculate the twist viscosity, for example, of one mixture from the viscosities of the pure components to a rather good approximation, as has been shown for MBBA/EBBA mixtures. The relative scarcity of experimental data on the temperature dependence of the Leslie viscosities for nematic mixtures does not allow us to compare our predictions with experimental results on the other Leslie viscosities. Therefore more experimental work is needed on this particular subject in order to test the theoretical predictions as well as in order to gain greater insight into the relationship between molecular parameters and Leslie viscosities of nematic materials.

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