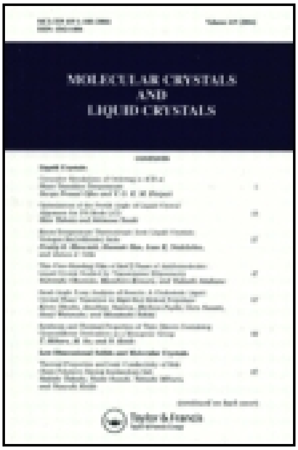

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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To cite this article: D. Demus, A. Hauser, M. Keil & W. Wedler (1990): On the Temperature Dependence of the Shear Viscosity of Nematic Liquid Crystals, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 191:1, 153-161

To link to this article: http://dx.doi.org/10.1080/00268949008038587

Mol. Cryst. Liq. Cryst. 1990, Vol. 191, pp. 153–161
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Printed in the United States of America

On the Temperature Dependence of the Shear Viscosity of Nematic Liquid Crystals

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Different theories describing the temperature behavior of the viscosity are compared. Correlations between viscosities and glass temperatures are discussed. The influences of molecular shape and packing fraction on the viscosity are studied.

INTRODUCTION

In many display applications[1,2] the viscosity plays an important role and is determining the switching times. Especially the strong temperature dependence of the viscosity causes problems for the display working at low temperatures and nowadays for outdoor applications. The temperature behavior of the viscosity in the nematic phase shows also interesting theoretical aspects. In nematic liquid crystals the viscosity is of tensorial character. Different coefficient models are discussed.[3] The Miesowicz coefficients[4] η_1, η_2 and η_3 in the notation of Helfrich[5] for the geometries which are described in Reference 6 are defined by the following three equations:

$$\eta_1 = \eta + \xi_1; \qquad \eta_2 = \eta + \xi_2; \qquad \eta_3 = \eta \tag{1}$$

The temperature dependence of the Miesowicz viscosities is mainly determined by that of η.[6] An additional temperature dependence will come into play due to the dependence of ξ_i on the orientational order. The temperature dependence of the orientation order, however, is weak compared with that of η[6] and is neglected in the following discussion.

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†Part of Plenary lecture at the 8th Liquid Crystal Conference of Soc. Countries, Krakow, August 1989.

THEORETICAL ASPECTS

The theory of Macedo and Litovitz[7] is based on the assumption of a quasicrystalline liquid structure. A molecule is pictured as vibrating about an equilibrium position until the combination of two events occurs: (1) the molecule attains sufficient energy to overcome the attractive forces holding it to its neighbors, and (2) an empty site is available into which the molecule can jump. The probability p_j of a transition or jump from one site to another is given by the expression

$$p_j = p_E p_V \tag{2}$$

where p_E is the probability of attaining sufficient energy to break away from neighbors and p_V is the probability that there is sufficient local free volume for a jump to occur. Assuming that some minimum local free volume v^* is necessary for a jump to occur one can calculate the probability of finding v^* and thus the jump probability p_v

$$p_V \cong \exp(-\gamma v^*/v_f) \tag{3}$$

where v_f is the average free volume per molecule. The constant γ is a numerical factor needed to correct for the overlap of free volume and lies between $\frac{1}{2}$ and 1. The quantity v^* should be close to v_0, the close-packed molecule volume.

In all quasicrystalline theories of the viscosity of liquids it is presumed that the viscosity is inversely proportional to the diffusional jump probability p_j and since

$$p_E \cong \exp(-E_v/RT) \text{ and } p_V \cong \exp(-\gamma v_0/v_f) \tag{4}$$

this would lead to an expression of the form

$$\eta = A_0/(p_E p_V) = A_0 \exp(\gamma v_0/v_f + E_V/RT) \tag{5}$$

where A_0 varies with temperature but usually far less than the exponential term; E_V is the height of the potential barrier between equilibrium positions; R, the gas constant and T the absolute temperature.

The free volume v_f is defined as the actual molecular volume minus v_0, thus $v_f = v - v_0$. These molecular volumes are related to the corresponding molar quantities by $v = V/N_A$, $v_0 = V_0/N_A$ and $v_f = V_f/N_A$ where N_A is Avogadro's constant. The free volume V_f can be approximated by

$$V_f = \alpha V(T - T_0) \tag{6}$$

where T_0 is the extrapolated temperature where the free volume becomes zero and α is the thermal expansion coefficient.

Combining Equations (5) and (6) we have

$$\eta = A_0 \exp(\gamma V_0/(\alpha V(T - T_0)) + E_V/RT) \tag{7}$$

Equation (7) can be simplified for those liquids where $E_v/RT << V_0/V_f$ to the form

$$\eta = A_0 \exp(\gamma V_0/(\alpha V(T - T_0))) \tag{8}$$

An empirical equation corresponding to Equation (8) with $\gamma V_0/\alpha V$ = const. has been used to fit the viscosity of glass forming media and is known as Vogel-Fulcher-Tammann (VFT) equation.[8] If in the contrary, $E_V/RT >> V_0/V_f$, Equation (7) reduces to the Arrhenius equation (9)

$$\eta = \eta_0 \exp(E_V/RT) \tag{9}$$

Kneppe *et al.*[10] have been extended the VFT equation by an order parameter term for the rotational viscosity γ_1

$$\gamma_1 = (1 - T/T^*)^{2\beta} \exp(B/(T - T_0)) \tag{10}$$

to describe the temperature dependence of the order parameter with the exponent β and the characteristic temperature T^*.

Diogo and Martins[11] gave an analogous equation

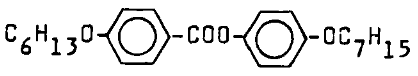
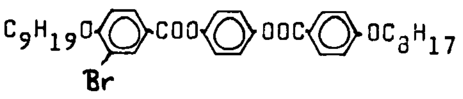
$$\gamma_1 = AS^2 \exp(BS^2/(T - T_0)) \tag{11}$$

with an additional term S^2 in the exponent. A critical discussion of this equation is given in Reference 9. Assuming that the temperature dependence of γ_1 is comparable to that of η we obtain the equation

$$\eta = A(1 - T/T_{NI})^C \exp(B/(T - T_0)) \tag{12}$$

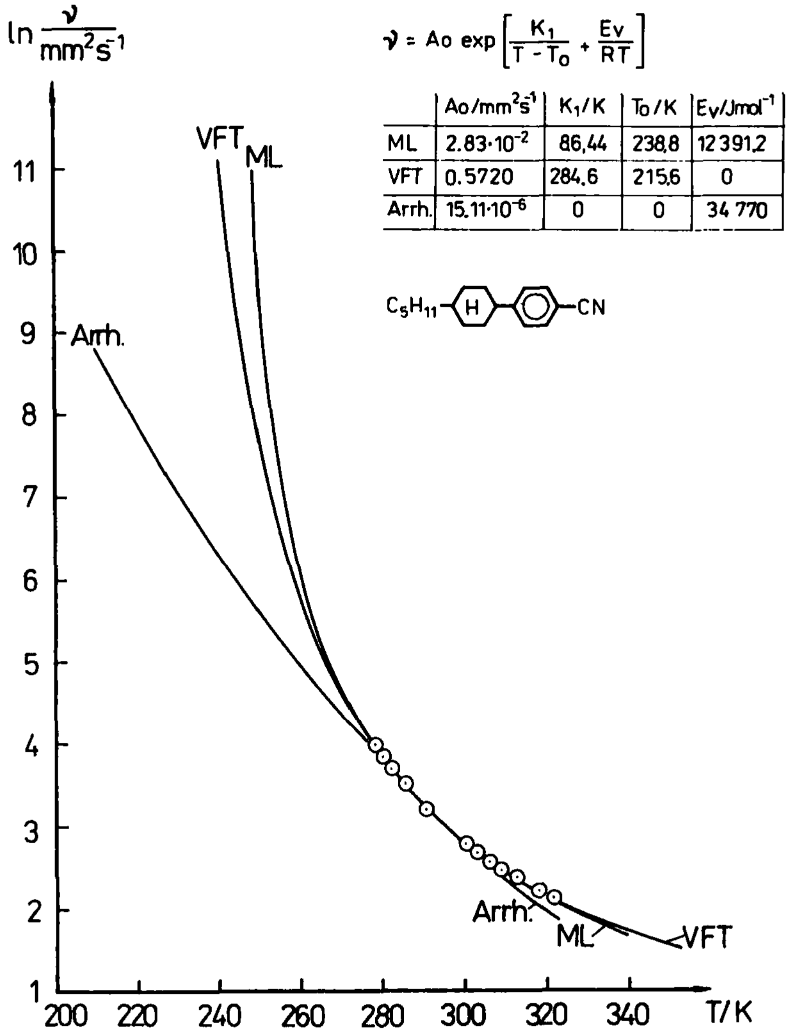
where A, B, C are adjustable parameters and T_{NI} is the clearing temperature. By fitting Equation (12) to the experimental values we have obtained the data given in Table I. As can be seen the parameter C is very small. Then Equation (12) reduces to the VFT equation (8) which is used in the following.

Table 1

	A/cP	C	B/K
	0.346	-0.050	368
	0.067	-0.027	797
	0.214	-0.027	611

DISCUSSION

The Arrhenius plot is not successful for viscosities of liquid crystals as shown in References 9 and 10. In Figure 1 viscosity data obtained from Reference 12 are fitted with the Equations (7), (8), (9). The Arrhenius plots according to Equation (9) cannot reflect the strong increase of viscosity by approaching the glass transition. The VFT-Equation (8) is a good approximation for experimental viscosities. The



$$\nu = A_0 \exp\left[\frac{K_1}{T - T_0} + \frac{E_V}{RT}\right]$$

	$A_0/mm^2 s^{-1}$	K_1/K	T_0/K	$E_V/Jmol^{-1}$
ML	$2.83 \cdot 10^{-2}$	86,44	238,8	12391,2
VFT	0.5720	284,6	215,6	0
Arrh.	$15.11 \cdot 10^{-6}$	0	0	34 770

FIGURE 1 Comparison of the fitting behavior of Equation (7) from the Macedo-Litovitz theory (ML) with the VFT equation and the Arrhenius equation (Arrh.) for experimental values given in Reference 12.

nonlinear least squares fit of Equation (7) with four parameters gives a little better accordance (Figure 1) than the VFT-Equation. Near to T_{NI} the influence of the order parameter on the temperature dependence of η becomes stronger, on the other hand the shear orientation may be disturbed in this temperature region. Therefore strong deviations from Equations (7), (8), (9) may occur.

Schad and Zeller[13] have claimed that the temperature dependence of the viscosity is a universal function of $T - T_g$ where T_g is the glass transition temperature. According to Reference 13 T_g can be approximated by a linear function

$$T_g = \alpha E_{\mathrm{coh}}/z + \beta \tag{13}$$

with E_{coh} equal to the cohesive energy increment at room temperature, z equal to degrees of freedom per increment and α and β are constants. E_{coh} can be computed from a group contribution method[14] which assigns an incremental value to each atom or group in the molecule. E_{coh} is simply the sum of all group contributions and the degree of freedom is defined by $z = 5 + (\Sigma_1 z_1 - 1)$ where five external degrees of freedom have to be added to the internal ones.

The assumption of a linear correlation between the cohesive energy E_{coh} and the glass transition temperature according to Reference 13 is not found for strongly different compounds as shown in Figure 2. That means that T_g is not only determined by the attractive forces expressed by E_{coh}. In the contrary, as it is known for the structure of liquids in general, also the occurence of the glass structure is mainly governed by repulsive forces or in other words by the free volume. On the other hand, specialities of the molecular structure (symmetry, bulkiness) have a considerable influence on the glass temperature. A linear correlation between the measured viscosity and the calculated values of the effective intermolecular potentials for several rod-like compounds in the liquid crystalline state is shown in Reference 15. In general, however, there is also no correlation between the logarithmic viscosity and the cohesive energy E_{coh}/z as demonstrated in Figure 3 for many substances. The cohesive energy is not the dominating factor controlling the temperature dependence of the viscosity which is emphasized by the fact that the VFT equation gives a much better approximation to the experimental data than the Arrhenius equation. The "universal" viscosity function claimed by Schadt and Zeller[13] may be due to the fact that they restricted their experimental material to rod-like compounds.

Of course, the attraction energy has a strong influence on the packing fraction at 74°C, V_B/V_{74} which can be seen in Figure 4 where V_B is the Bondi[16] volume without any free volume. There is no simple correlation but in compounds of comparable molecular shape a clear increase of the packing fraction with the cohesion energy. By this indirect way via the volumina, the attraction energies in the sense of Equation (8) also strongly influence the viscosities.

Summarizing we can say that in the past the role of the attractive forces in nematic liquid crystals has been overemphasized. The repulsive forces are more important in determining the structure of the liquids and also their viscosity.

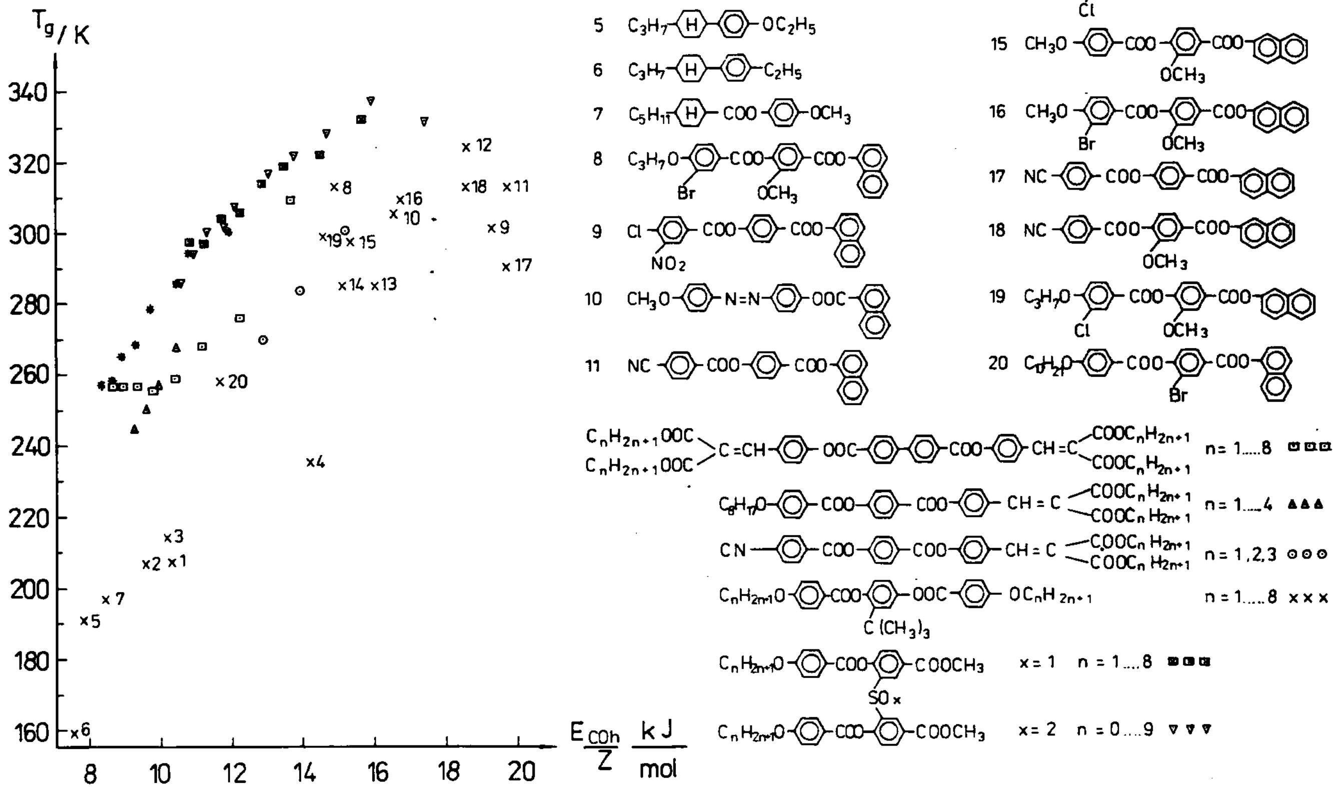


FIGURE 2 Experimental glass transition temperatures T_g versus the cohesive energy E_{coh}/z calculated from increments of Fedors.[14] The T_g of the compounds 1–7 are given by Reference 13.

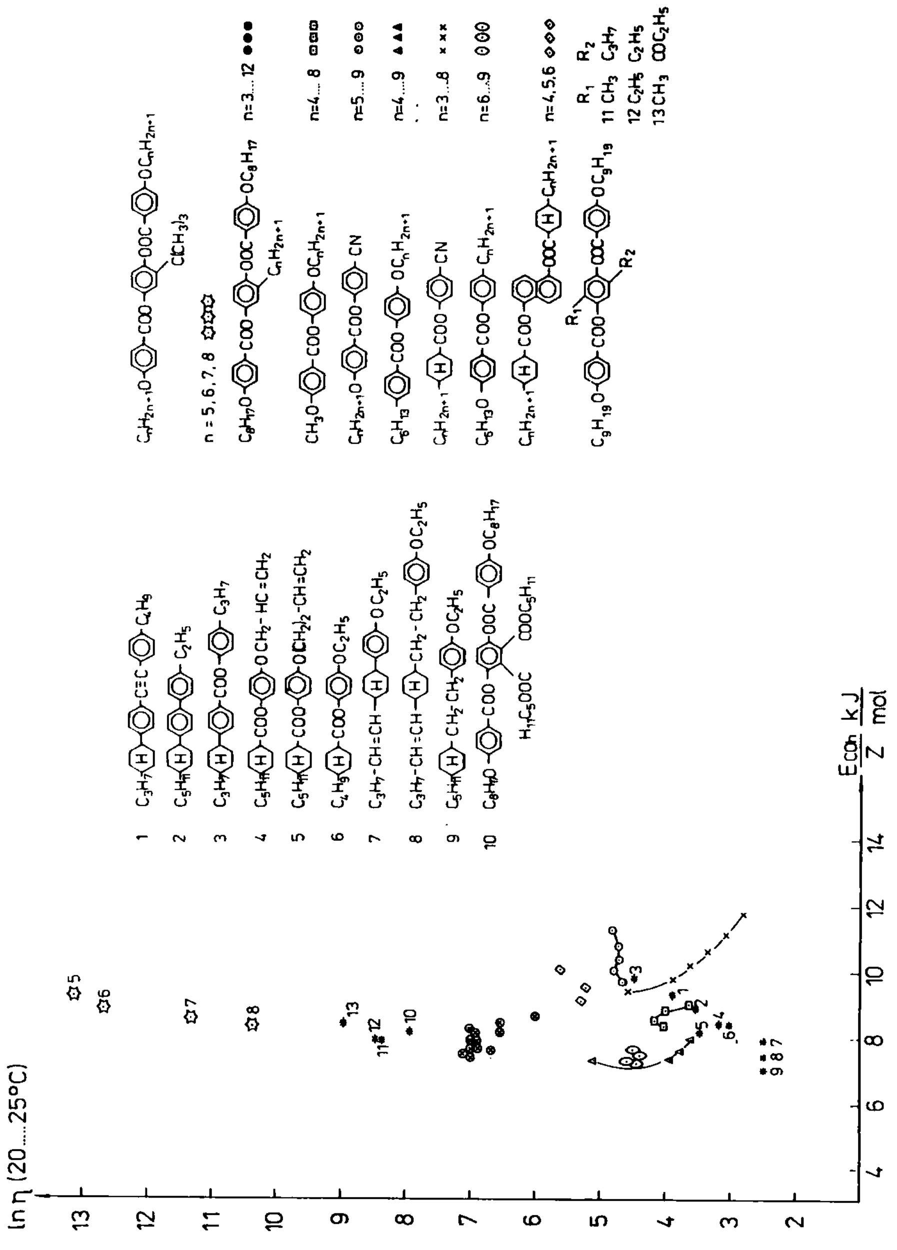


FIGURE 3 The logarithmic viscosity versus the cohesive energy E_{coh}/z. The viscosities of the compounds 1–9 are taken from Reference 17.

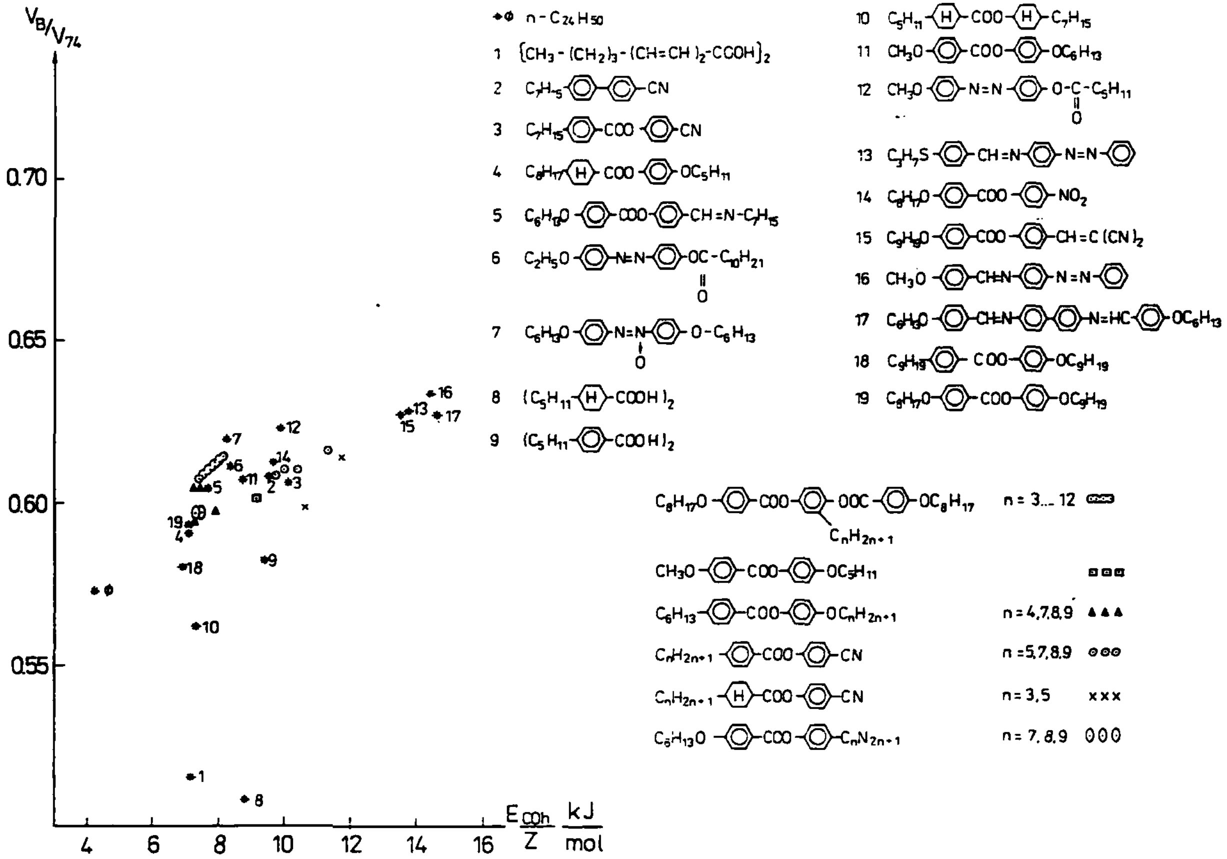


FIGURE 4 Packing fraction V_B/V_{74} versus the cohesive energy.

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