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Experimental Study of the Twist Viscosity in Nematic Liquid Crystals†

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Magnetic measurements of the twist viscosity in 24 nematic liquid crystals as a function of temperature show that the activation energy is $5.5 + 0.5 \times 10^3$ K; it does not depend strongly on the nematic-to-isotropic transition temperature or on any other obvious parameter.

INTRODUCTION

Rotating field torque experiments[1–4] were made on 24 doped and undoped commercial nematic liquid crystal compounds and mixtures to measure the twist viscosity $\gamma_1/\rho(\text{cm}^2/\text{sec})$ from the crystallization temperature to the nematic-to-isotropic transition temperature. When molecules rotate at frequency ω(rad/sec) about a normal to their long axis, the torque about this normal on a vessel containing a unit mass of sample is

$$L = (\gamma_1/\rho)\omega \tag{1}$$

Molecules rotate in synchronism with a d.c. magnetic field H (Oe) which spins at ω if the following expression is satisfied,

$$(\Delta\chi S H^2/2) > (\omega\gamma_1/\rho) \tag{2}$$

where S is the order parameter and $\Delta\chi$(cgs/g) is the difference between the susceptibilities along the long and short molecular axes. When molecules rotate at the same frequency as the field, they lag H by an angle α because of

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their twist viscosity; α is contained in the expression defining torque equilibrium where

$$\sin \alpha = \frac{2\gamma_1 \omega}{\rho \Delta\chi S H^2} \tag{3}$$

The origin of $\Delta\chi$ in nematics is their benzene ring type structure; long molecular axes lie in the plane of these rings which have respective inplane and normal susceptibilities of -37×10^{-6} and -91×10^{-6} cgs/mole.[5,1]

EXPERIMENTAL

In these experiments the field was produced by a U-shaped electromagnet with 6-inch diameter poles and tapered pole caps spaced for a $1\frac{1}{2}$ inch working gap. The magnet could be rotated, up to 1 rev/sec, either clockwise or counterclockwise on an 8-inch diameter thrust-bearing through gears and a belt which was driven by a 0 to ± 600 rev/sec, 1/50 h.p. variable-speed motor. Electrical power to the magnet coils was supplied at constant current through carbon brushes and a pair of 10-inch diameter copper slip-rings mounted on the magnet.

Samples were contained in either glass or gelatin capsules, 0.5 cm diameter by 1 cm long; these were suspended from an automatic recording torque magnetometer[6] having 10^{-3} dyne-cm sensitivity. All measurements were made in air on commercial materials with no additional purification.

As shown by Eq. (1), at $2\pi/15$ rad/sec a 10^{-3} dyne-cm sensitivity was sufficient for detecting a change in γ_1/ρ of 0.005 cm^2/sec for a 0.5 g sample. In practice there were additional sources of torque if the rotation axis of the magnet did not coincide with the center line of the suspension and sample or any ferromagnetic impurities contained therein; the resulting torques increased with field and were generally periodic in 2ω so that their contributions could be reduced by filtering the magnetometer output. At fields as high as 10 kOe, $\gamma_1/\rho(T)$ values were reproducible to within 5% for different runs in the range from 0.1 to 5.0 cm^2/sec.

A heating coil wound on a 1 cm diameter glass tube, surrounded the sample and suspension, and this was in turn enclosed in a glass Dewar so that the temperature could be changed smoothly as the sample was cooled. Temperature was measured using 0.001-inch diameter copper-constantin thermocouple wire which extended into the sample; the wires were twisted to reduce inductive pick-up and brought out through the magnetometer head.

RESULTS

For EBBA, [N-(p-Ethoxybenzylidene)-p-p-butylaniline], a plot of $\Delta\chi S H^2/2$ and $\omega\gamma_1/\rho$ against T is shown in Figure 1 with $\Delta\chi S$ measured at 6 kOe by a

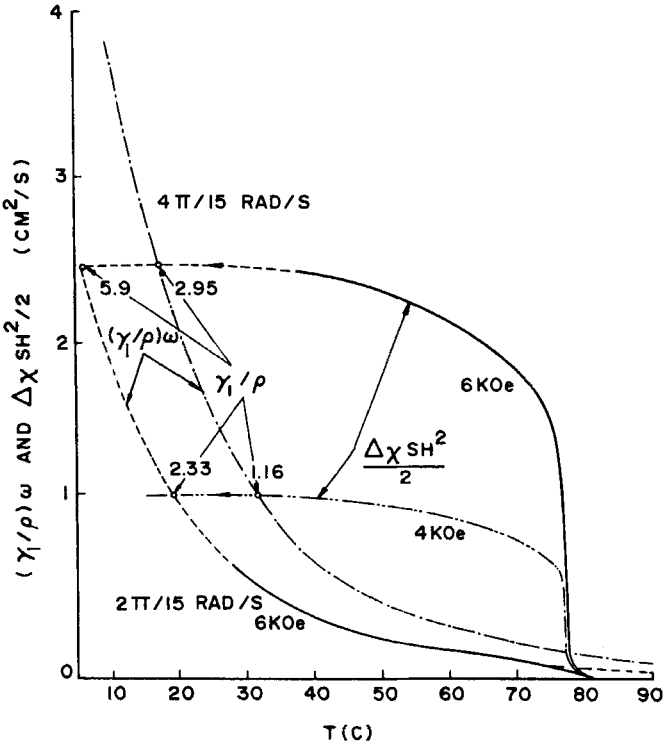

FIGURE 1 The temperature dependence of $(\gamma_1/\rho)\omega$ and $\Delta\chi SH^2/2$ for EBBA.

gradient force method and $\omega\gamma_1/\rho$ at $2\pi/15$ rad/sec and 6 kOe measured with the torque magnetometer. To show regions in which Eq. (2) is satisfied we plot both $\Delta\chi SH^2/2$ and $\omega\gamma_1/\rho$ for two values of ω and H. We assume a logarithmic behavior for γ_1/ρ against T to show that for a $\Delta\chi S$ of 1.4×10^{-7} cgs/g, the upper limit of γ_1/ρ that we can measure is 5.9 cm^2/sec when a 6 kOe field rotates at $2\pi/15$ rad/sec. Just below T_c where S goes rapidly to zero this method breaks down since Eq. (2) can no longer be satisfied; as a consequence of this, L/ω becomes less than γ_1/ρ and goes to zero at the nematic-to-isotropic transition temperature T_c.

Experimental plots of L/ω against T at 6 kOe and $2\pi/15$ rad/sec have been made with L/ω expressed as γ_1/ρ. In Figure 2 these data are plotted on a logarithmic scale for γ_1/ρ and we find a linear dependence against inverse temperature for T more than 5° below T_c; above these temperatures the falloff is presumingly due to small values of S which prevent molecules from rotating as fast as the field.

TABLE I

Transition temperature (T_c), twist viscosity extrapolated to T_c, $(\gamma_1/\rho)_{T_c}$, and activation energy, (B), in nematic materials.

Catalog Number[a]	Chemical	T_c (°C)	$(\gamma_1/\rho)_{T_c}$(exp) (cm^2/s)	$(\gamma_1/\rho)_{T_c}$(Eq. 5) (cm^2/s)	B(exp) $\times 10^{-3}$ (°K)
VL 1047–N	Standard MBBA	40	0.31	0.325	6.0
VL MBBA	p-Methoxybenzylidene-p-n-butylaniline	45	0.325	0.29	5.3
VL 1:1 (MBBA:EBBA)	1:1 Mixture MBBA:EBBA	63	0.16	0.205	5.3
VL 3268–N	Standard EBBA	71	0.165	0.18	5.3
M 10535	Mixture, phase VA (Dynamic scattering, with dopant)	74	0.185	0.176	4.6
M 10206	Mixture, phase V (Dynamic scattering, without dopant)	75	0.15	0.173	4.4
M 10105	Mixture, phase IV	76	0.115	0.171	5.1
VL EBBA	N-(p-Ethoxybenzylidene)-p-n-butylaniline	80	0.14	0.162	4.8
M 10598	Mixture, phase VI (Dynamic scattering, with dopant)	82.5	0.14	0.158	4.8
E 10482	Butyl p-(p-Ethoxyphenoxycarbonyl)-phenyl Carbonate	84	0.29	0.154	6.5

E 11900	Mixture (Field effect)	88	0.14	0.148	6.2
E 11643	Mixture (Dynamic scattering)	89	0.12	0.146	6.0
E 11880	p-[(p-Ethoxybenzylidene)amino] benzonitrile	90	0.19	0.144	5.75
E 9960	p-[N-(p-Methoxybenzylidene)-amino]phenyl Acetate	93	0.2	0.14	6.1
VL 74110-N	anisylidene-p-aminophenylacetate	96	0.18	0.135	6.6
E 10541	p-(p-Ethoxyphenylazo)phenyl Undecylenate	110	0.18	0.118	5.8
E 10573	p-(p-Ethoxyphenylazo)phenyl Heptanoate	115	0.115	0.113	4.55
E 10120	4,4′-Bis(hexyloxy)azoxybenzene	125	0.156	0.104	5.75
E 10890	p-[(p-Methoxybenzylidene)-amino]benzonitrile	125	0.087	0.104	6.4
E 9723	4,4′-Azoxydianisole	135	0.075	0.097	3.7
VL 146176-N	———	160	0.125	0.081	7.8
E 9781	p,p′-Azoxydiphenetole	165	0.05	0.079	5.5
E 10836	p-(p-Ethoxyphenylazo)phenyl Crotonate	186	0.06	0.07	5.3
TBBA (Nematic phase)	terephthal-bis-(butylaniline)	225	0.05	0.058	5.1

[a] E–Eastman Kodak Company, Rochester, N.Y. 14650
M–E. Merck, Darmstadt, Germany
VL–Vari-light Corporation, Cincinnati, Ohio 45242

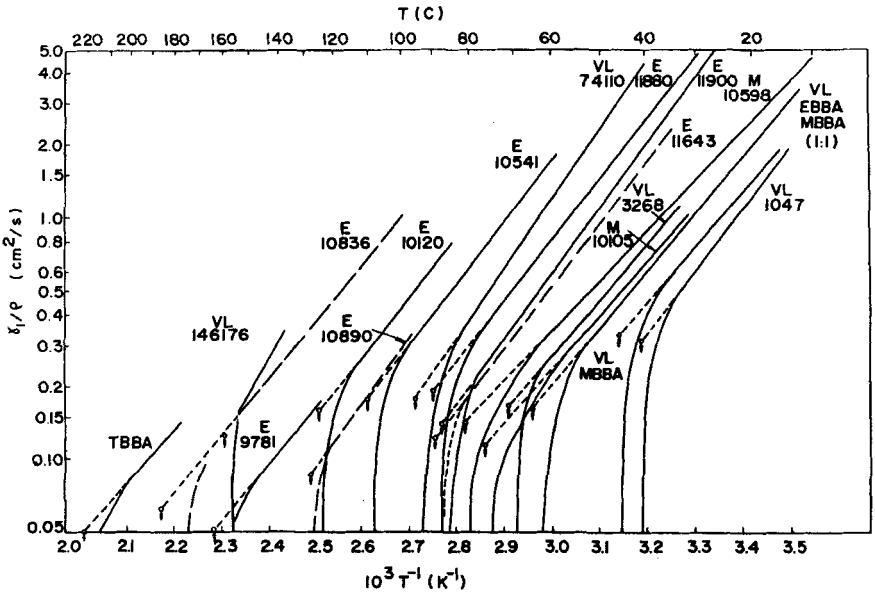

FIGURE 2 Plots of γ_1/ρ on a logarithmic scale against inverse temperature using data taken at 6 kOe and $2\pi/15$ rad/sec.

DISCUSSION

We can express twist viscosity as a function of temperature by the equation

$$\gamma_1/\rho = Ae^{(B/T)} \tag{4}$$

where the activation energy B is $5.5 \pm 0.5 \times 10^3$ K and does not depend strongly on T_c or on any other obvious parameter; this value agrees with previous measurements reported on 3 materials.[4]

Table I lists the materials we have measured and their following properties: T_c (the temperature at which L goes to zero), values of $\gamma_1/\rho(T_c)$ and B that are determined from the curves in Figure 2.

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