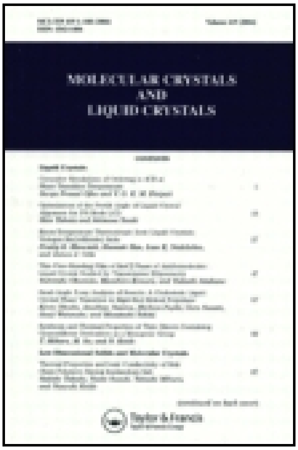

Molecular Crystals and Liquid Crystals

Viscous Properties of Nematic Mixture at Variation of PVT-State Parameters

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Version of record first published: 18 Oct 2010

To cite this article: A. N. Larionov, N. N. Larionova & S. V. Pasechnik (2004): Viscous Properties of Nematic Mixture at Variation of PVT-State Parameters, Molecular Crystals and Liquid Crystals, 409:1, 459-466

To link to this article: http://dx.doi.org/10.1080/15421400490434009

Mol. Cryst. Liq. Cryst., Vol. 409, pp. 459–466, 2004
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490434009

VISCOUS PROPERTIES OF NEMATIC MIXTURE AT VARIATION OF PVT-STATE PARAMETERS

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The results of acoustic investigations of the viscous properties of a nematic liquid crystal mixture with wide temperature range at varying PVT-state parameters are presented. The original ultrasonic set-up was elaborated to provide the determination of some dissipative parameters including the ratio of twist viscosity γ_1 *to magnetic susceptibility anisotropy* $\Delta\chi$ *as a function of pressure (P) and temperature (T) at constant volume (V). It is found that the ratio* $\gamma_1/\Delta\chi$ *exponentially decreases with increasing temperature or with decreasing pressure. This agrees with the free volume theory. According to our calculation free volume increases with temperature or decreasing pressure. The energies of activation* (E_v, E_p) *of the twist viscosity at constant volume and pressure are calculated. The dependence of Leslie viscosity coefficient* α_1 *on temperature is determined too.*

Keywords: PVT-state parameters; twist viscosity; ultrasonic set-up

INTRODUCTION

It is well known that ultrasonic measurements provide a lot of information about viscous and elastic properties of liquid crystals [1]. In particular, the dependence of the ultrasonic attenuation coefficient α on the angle θ between the wave vector of a longitudinal ultrasonic wave and the director can be described as:

$$\frac{\Delta\alpha}{f^2} = a \cdot \cos^2\theta + b \cdot \cos^4\theta, \tag{1}$$

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where f is the ultrasonic frequency, $\Delta\alpha = \alpha(\theta) - \alpha(\theta = \pi/2)$,

$$a = \frac{2\pi^2}{\rho c^3} \times (\mu_2 + \mu_3 + \alpha_5 + \alpha_6 - \gamma_1\lambda^2), \tag{2}$$

$$b = \frac{2\pi^2}{\rho c^3} \times (\alpha_1 + \gamma_1\lambda^2), \tag{3}$$

α_i are the Leslie's coefficients for an incompressible nematic and μ_i the dissipative parameters of a compressible nematic, describing different relaxation processes. One can see that ultrasonic investigations provide additional information about material parameters of LC, in particular about the Leslie coefficient α_1, which was determined only for rare nematics. The second parameter, namely the twist viscosity coefficient γ_1, which enters in the combinations is of a great importance for practical applications and was studied intensively both experimentally and theoretically [2]. In particular, some microscopic approaches were proposed to describe the temperature dependence of this parameter. Earlier it was shown [3], that the measurements of ultrasonic attenuation coefficient in a rotating magnetic field can provide the determination of the ratio $\gamma_1/\Delta\chi$ ($\Delta\chi$ – the magnetic susceptibility anisotropy). Such measurements are especially important in the case of pressure variations [4], as only rare experiments were performed under these conditions with the help of an alternative technique [5]. At the same time the usage of the additional thermodynamic parameter (pressure) provides a better understanding of the molecular reorientational processes, which take place in a nematic phase.

In this paper the new ultrasonic technique intended to account the influence of specific volume variations on the viscous behavior of nematics is described. The main attention is devoted to the PVT - dependence of the twist viscosity in a wide-range nematic mixture. It is shown, that in this case the influence of temperature and specific volume variations on the phenomena under consideration can be separated. Detailed experimental data obtained by this technique for another nematic mixture will be presented elsewhere.

EXPERIMENTAL

An ultrasonic set-up based on the pulse method for two fixed distances was used to measure the complex of acoustic parameters ultrasound velocity c and attenuation α at different angles θ between LC director and the wave vector) and the density ρ of LC under varying pressure and temperature. So the dependencies of viscous and elastic parameters of liquid crystals upon PVT-thermodynamic state parameters have been studied.

The ultrasonic cell contains three electroacoustic transducers (Fig. 1). A radio-frequency pulse of amplitude A_0 is applied to the transducer 4 immersed in the liquid crystal sample 7. The sound pulse travels to the transducers 1 and 5, where it is transformed into the radio-frequency pulses of amplitude A_1 and A_2 accordingly:

$$A_1 = k_1 \cdot A_0 \cdot exp(-\alpha l_1), \qquad A_2 = k_2 \cdot A_0 \cdot exp(-\alpha l_2),$$

where k_1 and k_2 are the sound transmission coefficients of acoustic channels, l is the distance between piezocrystals 4 and 1, which is the function of temperature and pressure, l_2 is the distance between piezocrystals 4 and 5, which is constant. The velocity and absorption of sound were measured at frequencies of 2.67 MHz and 500 kHz. The accuracy of measurements is 0.02% and 0.08% for the velocities at 2.67 MHz and 500 kHz accordingly and 2% for the absorption coefficient. By comparing the time duration of sound pulses between piezocrystals both 4 and 1 and 4 and 5, we determined the density of liquid crystal under varying pressure and temperature. After filling and sealing, the acoustic cell was inserted into a pressure vessel made from diamagnetic steel. Experiments were performed in the pressure range 1...600 bar and in the temperature range 290...365 K. The accuracy of the pressure determination is within ±5 bar. The temperature of the ultrasonic cell was controlled to within ±0.01 K with the help of a thermostat. The uniform orientation of the nematic director was obtained by the usual way [3,4] using a static magnetic field and a rotating one with 0.15 T induction. In the latter case the ratio $\gamma_1/\Delta\chi$ can be determine from the analysis of the time dependencies of the ultrasonic attenuation [3,4].

In these experiments the mixture (LC-440) of p-n-butyl-p-methoxy-azoxy-benzene and n-butyl-p-heptanoyloxyazoxybenzene (2 : 1) has been

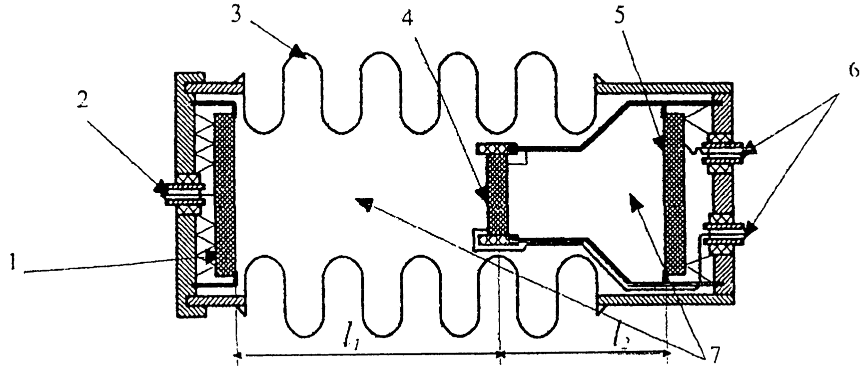

FIGURE 1 Ultrasonic cell, 1,4,5-piezocrystals; 2,6-lead-in; 3-separating diaphragm, 7-liquid crystal.

studied. This compound was chosen in order to get a broad nematic phase, which takes place in the mixture mentioned above. The additional information obtained by different methods for the mixture and the single components [6,7] is of importance too.

RESULTS AND DISCUSSION

The angular dependency of the attenuation coefficient, obtained in a static magnetic field (director oriented in the direction of the magnetic field) is shown in Figure 2.

The experimental data are well described by the expression (1) (curves in Figure 2). So one can calculate the parameter b, which is proportional to the combination $(\alpha_1 + \gamma_1 \lambda^2)$ of material parameters of an incompressible nematic (under neglecting of the possible relaxation contribution to this combination [8]). In the rotating magnetic field the angular dependence has the same form at low frequencies (ω_H) of rotation (a synchronous regime), but there is a phase gap (ϕ) between the field and the director, which depends on the twist viscosity coefficient γ_1 and can be used to calculate this parameter:

$$\gamma_1 = \frac{H^2 \cdot \Delta\chi \cdot \sin 2\varphi}{2\omega_H} \tag{4}$$

So the phase gap and the ratio $\gamma_1/\Delta\chi$ can be determined from the comparison between dynamic and the static experiments. The twist viscosity coefficient γ_1 can be determined if $\Delta\chi$ is known. Though the latter parameter was only measured at atmospheric pressure [9] it can be reasonably calculated at different pressures too. The connection $\Delta\chi \sim S$ (where S – the order parameter, which is assumed to depend only on the difference between clearing temperature Tc and the given temperature T) is taken into account

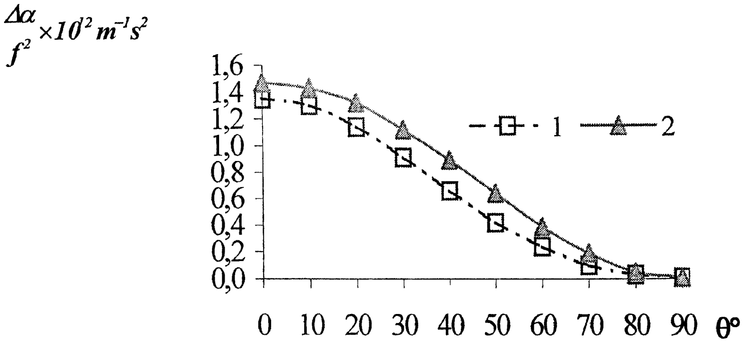

FIGURE 2 Angular dependence of $\Delta\alpha/f^2$ at 295.0 K(1); 343.0 K(2) at 0.1 MPa.

in this calculation. The pressure dependence of the clearing temperature T_c was obtained from the ultrasonic measurements of $\Delta\alpha$, which goes to zero at the clearing point. Accordingly to our results:

$$T_c(P) = T_{oc} + k_c \cdot P, \tag{5}$$

where the clearing point temperature at atmospheric pressure is $T_{oc} = 345.7\,K$ and the coefficient k_c is equal to $3.28\cdot10^{-7}\,Pa^{-1}\cdot K$

The dependencies of parameters b and γ_1 on pressure are presented in Table 1. Two other parameters (ρ and c) included in this table and determined in our experiments are necessary for the calculation of viscous parameters from the angular dependence of an ultrasonic attenuation coefficient (see Eq. (1)).

An equation governing the dependence of the twist viscosity upon pressure and temperature was proposed in [10]:

$$\gamma_1 = A_1\left(1 - \frac{T}{T^*}\right)^{2\beta} \cdot \exp\left(\frac{B}{T - T_0}\right), \tag{6}$$

where

$$T^* = T_0^*\left(\frac{P}{a} + 1\right)^{C}, \tag{7}$$

Our results are described by this formula quite well at the next values of parameters:

$$T_0^* = 353.7\,K; \quad a = 4.757 \cdot 10^8 Pa \cdot s; \quad c = 0.6; \quad A_1 = 0.0269\,Pa \cdot s;$$
$$\beta = 0.3536; \quad B = 243.26K; \quad T_0^* = 213.04\,K.$$

Using the data on ρ and c, obtained at varying pressure and temperature (see Table 1) one can get the dependence of γ_1 upon pressure and temperature at constant volume (Fig. 3).

TABLE 1 Pressure Dependencies of the Material Parameters of LC-440

T, K	P, MPa	0.1	10	20	30	40	60
297.0	γ_1, Pa·s	0.1333	—	—	0.1425	0.1457	0.1560
	ρ, kg/m^3	1106.8	—	—	1117.8	1120.3	1126.1
	c, m/s	1553.9	—	—	1660.1	1685.5	1729.5
	b·10^{14}, m^{-1}s^2	53.4	—	—	76.0	81.0	95.0
337.0	γ_1,Pa·s	0.0222	0.0252	0.0289	0.0319	0.0354	0.0418
	ρ, kg/m^3	1088.7	1093.3	1097.9	1102.8	1107.5	1115.5
	c, m/s	1392.3	1442.9	1496.2	1533.3	1571.8	1632.5
	b·10^{14}, m^{-1}s^2	−7.4	0.1	6.5	10.3	15.8	24.3

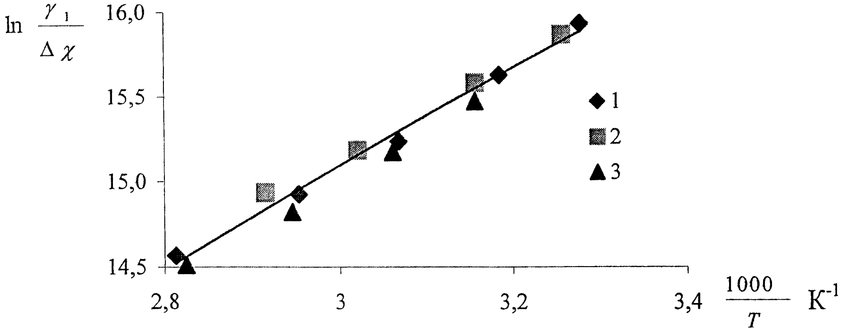

FIGURE 3 Dependence of ln $(\gamma_1/\Delta\chi)$ upon T^{-1} at specific volume $v \cdot 10^4$ [m^3/kg]: 9.03 (1); 8.99 (2); 9.08 (3).

The presented dependence is nearly exponentially, so the activation energy at constant volume:

$$E_V = R \cdot \left(\frac{\partial(\ln\gamma_1)}{\partial(1/T)}\right)_V, \tag{8}$$

was calculated. This parameter reflects the sole influence of temperature without superimposed influence of density. The value of the activation energy E_V does not depend on the density of liquid crystal and is equal to 23 kJ/mol in the temperature interval $\Delta T_c = T_c - T = 0\ldots35$ K. Far from the clearing point ($\Delta T_c = 35\ldots55$ K) some increasing of E_V (about 20%) takes place. It may be connected to the decrease of the activation energy at constant pressure E_p when the pressure is increasing (Table 2).

The dependence of the activation energy E_p upon pressure may be explained by means of thermodynamic Ex. [11]:

$$E_V = E_P - RT^2\left(\frac{\partial P}{\partial T}\right)_V \cdot \alpha^*_{visc}, \tag{9}$$

where α^*_{visc} – is the slope of the ln $\gamma_1 \sim P$ isotherms. While E_p should be proportional to the total molecule energy paid to jump over a potential barrier and to form the hole, E_V is connected only with the former part. So the ratio (E_p/E_V) has to be more than one, which is in accordance with our results. This parameter decreases in nematic phase at increasing pressure (Table 3).

TABLE 2 Activation Energy E_p at Different Pressures

P, MPa	0.1	10	20	30	40	50	60
E_p, kJ/mol	31.7	31.4	30.3	27.8	26.7	24.6	23.3

TABLE 3 Pressure Dependence of the Ratio (E_p/E_V), $\Delta T_c = 0\ldots35\,K$

P, MPa	0.1	10	20	30	40	50	60
E_p/E_V	1.38	1.37	1.32	1.21	1.16	1.07	1.02

It is of interest if this ratio can be lower than 1 at higher pressure. To answer this question additional experiments have to be fulfilled.

Using the presented results we have calculated the hole volume ΔV (Table 4). This parameter increases with increasing temperature, which seems to be quite reasonable.

The order of magnitude of the hole volume is the same as the "volume of molecule" estimated previously for MBBA : EBBA mixtures [12] using the results of dielectric measurements. Nevertheless the temperature dependence of this parameter is opposite to the dependence reported in the work mentioned above. Obviously additional results for the investigated mixture have to be obtained to explain this discrepancy.

It is of interest to estimate the Leslie coefficient α_1 from the ultrasonic measurements using Eq. (2). The only unknown parameter λ^2 is close to 1 if the flow orientation angle β is about zero. We have used the measured values of this angle in the first component of our mixture [7] to calculate α_1 assuming that β depends on the difference $T - T_c$. The result of this calculation is presented in Table 5.

One can see that this coefficient has a negative sign and is essentially smaller than the rotational viscosity coefficient, at least far from the clearing point, which is in accordance with data, obtained for MBBA [2]. Nevertheless, additional experiments using independent techniques are needed to be sure hat the ultrasonic method gives the correct values of this parameter in the whole nematic range.

TABLE 4 Temperature Dependence of the Hole Volume

T, K	309	319	323	327	331	335	339	347
$\Delta V \cdot 10^5 m^3/mol$	0.64	0.82	1.05	1.30	1.60	1.84	2.08	2.42

TABLE 5 Temperature Dependence of α_1

T, K	297,0	315,0	323,0	333,0	337,0	340,5	342,0
α_1, Pa·s	– 0,0055	– 0,0073	– 0.0111	– 0,0172	– 0,0167	– 0,0194	– 0,0185

CONCLUSION

The new ultrasonic set-up, which can be used for the study of liquid crystals under variable PVT state parameters is described. The dissipative parameters of a nematic mixture are determined using the angular dependencies of the ultrasonic attenuation coefficient, obtained in static and rotating magnetic field. The temperature dependencies of the twist viscosity coefficient at constant pressure and specific volume are obtained and analyzed. In particular, it is shown that the activation energy of this coefficient at constant pressure E_p exceeds the analogous energy E_v at constant volume. The obtained results are discussed in the framework of the hole theory. The obtained results can be also used to calculate the Leslie coefficient α_1.

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