Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Dörrer, H. L. , Kneppe, H. and Schneider, F.(1992) 'Rotational viscosity γ_1 of nematic liquid crystals as a function of temperature, pressure and density', Liquid Crystals, 11: 6, 905 — 915
To link to this Article: DOI: 10.1080/02678299208030694
URL: http://dx.doi.org/10.1080/02678299208030694

LIQUID CRYSTALS, 1992, VOL. 11, NO. 6, 905–915

Rotational viscosity γ_1 of nematic liquid crystals as a function of temperature, pressure and density

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(*Received 21 November 1991; accepted 28 December 1991*)

Measurements of the rotational viscosity γ_1 and the density are presented for a mixture of 4′-methoxybenzylidenebutylaniline (MBBA) and its ethoxy homologue EBBA and a mixture of cyclohexylphenylnitriles (ZLI 2413 from Merck AG) as a function of temperature and pressure. A new set-up for the measurement of densities under pressures of up to 3 kbar is described. It is shown that the pressure dependence of the kinematic rotational viscosity γ_1/ρ and the temperature dependence of γ_1 under isobaric and isochoric conditions have common features with that of the shear viscosity of isotropic liquids. Furthermore, it is found that the curves $\gamma_1 = f(1/T)$ for constant p and $\gamma_1 = g(\rho)$ for constant T can be shifted one onto another by an appropriate shift of the scale of the independent variable.

1. Introduction

The decrease of the shear viscosity coefficient of isotropic liquids with increasing temperature is caused by two effects. First, there is the direct influence of temperature via the Boltzmann term and, secondly, the indirect influence of the density variation with temperature. Both effects can be separated by application of pressure on the sample. In particular, the isochoric temperature dependence of the viscosity coefficient can be measured if pressure is used to compensate for the density change with temperature. Kuss [1] has studied the isobaric and isochoric temperature dependence of the shear viscosity coefficients of a series of isotropic liquids and observed that the influence of both effects is of the same order of magnitude.

In this paper, we want to extend such measurements to nematic liquid crystals. However, the determination of the shear viscosity coefficients of nematics under pressure is not yet possible with sufficient precision. We have, therefore, studied the rotational viscosity γ_1, for which the necessary precision can be obtained [2]. This quantity describes the momentum which has to be exerted on the director during rotation of the director. The rotational viscosity depends on the degree of order S, which itself is a function of temperature and pressure. This leads to a complicated dependence of the rotational viscosity on these quantities. In an earlier paper [2], we have presented measurements of γ_1 under high pressure for MBBA and a commercially available mixture of cyclohexylphenylnitriles (ZLI 2413 from Merck AG) with a broad nematic range from −24 to 32°C at atmospheric pressure. Density measurements for ZLI 2413 have not yet been performed. The density of MBBA has been measured by Kuss [3] as a function of temperature and pressure. Unfortunately, the clearing point temperatures of Kuss's and our MBBA sample do not agree. Here, we present γ_1 and density measurements for an MBBA/EBBA mixture and density measurements for ZLI 2413 for the same batch for which the γ_1 measurements have been performed.

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2. Experimental

The measurement of γ_1 under high pressure was performed in the set-up which has been described in the earlier paper [2]. Measurement of the densities were performed in a dilatometer which is shown schematically in figure 1 (*a*). The dilatometer D with a volume of approximately 14 cm^3 is shown in detail in figure 1 (*b*). It is surrounded by the autoclave A1 which is manufactured from the high performance steel 1·6582 with a tensile strength of 910 N mm^{-2}. Two high pressure windows W1 allow us to observe the mercury meniscus in the capillary C (inner diameter 1·2 mm) of the dilatometer. At the same height, there are two windows W2 in the outer jacket J, in which water from a thermostat is circulated. After a temperature or pressure change, it is necessary to move the dilatometer to a position where the mercury meniscus is visible through the windows. For this purpose, two steel wires SW, which are connected to an iron counter weight CW in the autoclave A2, are attached to the dilatometer. The magnetic coil MC allows us to move the counter weight and the dilatometer up and down. The autoclave A2 is manufactured from the non-magnetic steel Amanox PN 1852 with a tensile strength of 900 N mm^{-2}. The filling procedure of this dilatometer with the liquid crystal LC and mercury M through the capillary is somewhat complicated; but it is possible with the aid of small tubes and vacuum. The reservoir R at the end of the capillary serves as the storage volume for excess mercury during the filling procedure. The sintered glass disc GD prevents small particles in the high pressure oil from falling into the capillary and disturbing the form of the mercury meniscus.

The thermal expansion and the compressibility of the dilatometer and the mercury were taken into account in the evaluation of the density values. The volume V of the liquid crystal is determined by

$$V = V_0(1 - ap - \tfrac{1}{2}bp^2)(1 + 3\alpha(t - t_0)) - m_{\mathrm{Hg}}/\rho_{\mathrm{Hg}}, \tag{1}$$

where V_0 is determined from the readings on the capillary. V_0 was shown to be a linear function of the readings within $\Delta V = \pm 3 \times 10^{-4}$ cm^3 by a calibration with mercury. The term in the first bracket describes the influence of the compressibility

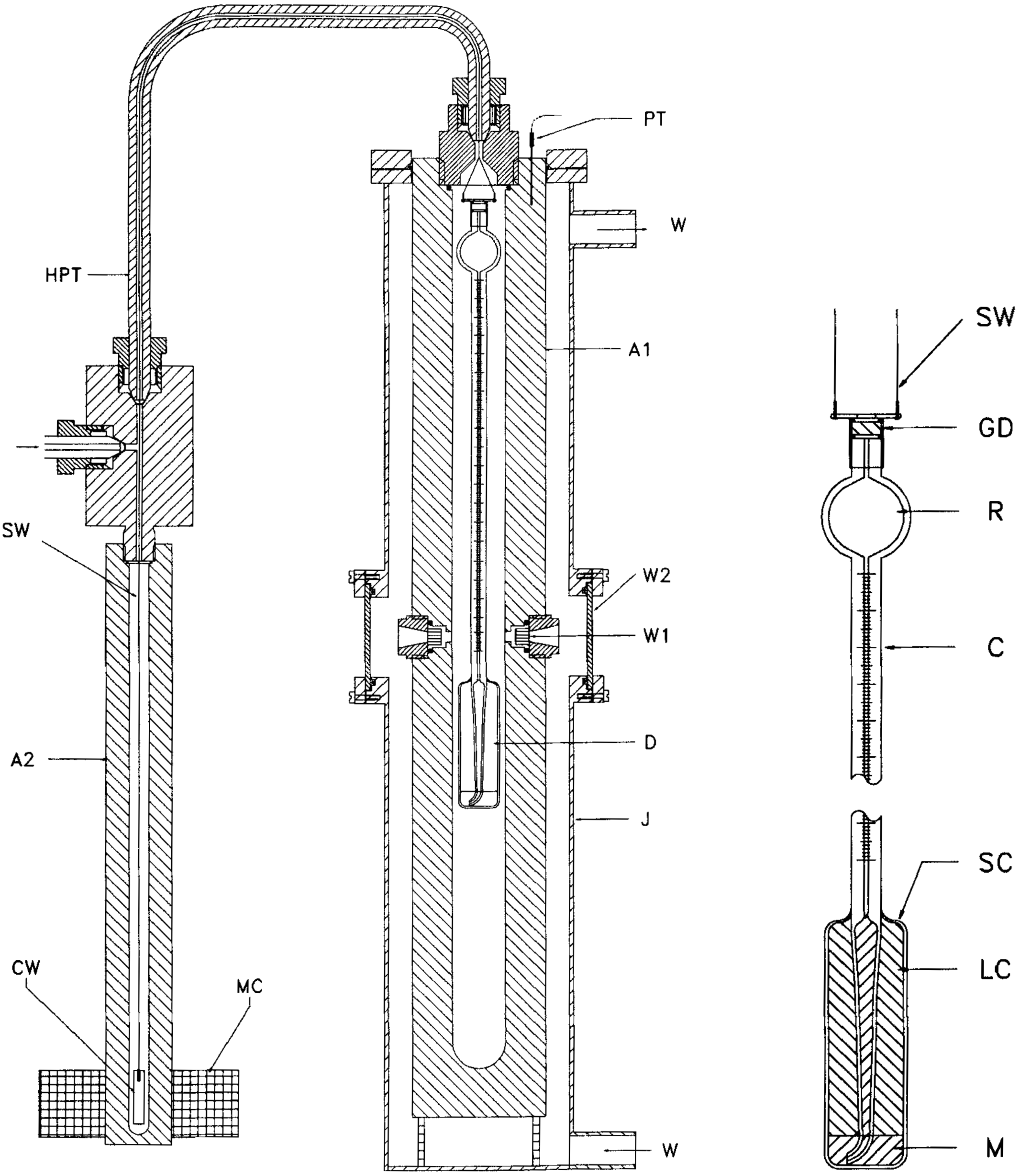
$$\kappa = a + bp \tag{2}$$

of the glass and the second its thermal expansion. The parameters for Duran are $a = 2{\cdot}986 \times 10^{-6}\,\mathrm{bar}^{-1}$, $b = -6{\cdot}8 \times 10^{-12}\,\mathrm{bar}^{-2}$ [4], and $\alpha = 3{\cdot}25 \times 10^{-6}\,\mathrm{K}^{-1}$. The density ρ_{Hg} of mercury was determined with the aid of the equation of state described by Grindley and Lind [5]. A test measurement with toluene, for which precise density data as a function of temperature and pressure are known [6], showed that the relative precision is in the order of 2×10^{-4}. The precise method used for toluene determines the compressibility via a measurement of the ultrasound velocity. It cannot be used for liquid crystals as the ultrasound velocity depends on the unknown alignment of the director in the sample.

ZLI 2413 was kindly supplied by the Merck AG. MBBA (4′-methoxy-benzylidene-4-*n*-butylaniline) and its ethoxy homologue EBBA were synthesized in our laboratory. The MBBA/EBBA mixture contained the components in a molar ratio of 2:1. This mixture is nearly a eutectic one [7] and gives a nematic range from <0 to 55°C at atmospheric pressure.

3. Experimental results

Figures 2 to 4 contain the experimental results for the γ_1 and the density measurements. The family of curves is limited by the clearing (for the rotational



(*a*) (*b*)

Figure 1. (*a*) Schematic diagram of the autoclaves and the dilatometer. PT: platinum thermometer; HPT: high pressure tubing; HP: high pressure connection to the high pressure generator; W: water from and to a thermostat. (*b*) Schematic diagram of the dilatometer. SC: sample container.

viscosity) and melting points, by the temperature limits 15/20 and 95/100°C and the pressure limits 1 and 2400/2500 bar. The γ_1 curves were fitted to the function

$$\gamma_1 = A(1-T/T^*)^{2\beta} \exp C\frac{T^*-T_0}{T-T_0}, \tag{3}$$

which proved to be a good fitting function for the temperature and pressure dependence in our earlier study [2]. $T^*(p)$ is the temperature where the order parameter and the rotational viscosity would vanish for a hypothetical liquid crystal. A pressure dependence of the form

$$T^*(p) = T_0^*(1+p/a)^c \tag{4}$$

is assumed for this quantity. This equation has been proposed for the pressure dependence of transition temperatures by Simon and Glatzel [8] as well as Feyz and Kuss [9]. $(1-T/T^*)^\beta$ is a well-known fit for the order parameter as a function of temperature. The exponential term in equation (3) is a Vogel-type expression which includes a divergence at the temperature T_0 which is assumed to be independent of pressure.

The density values were mainly fitted by a special form of the Tait equation. A small additional term describes the influence of the orientational order.

$$\rho = \frac{\rho_0}{1-D\ln(1+p/B)} + E(1-T/T^*)^\gamma. \tag{5}$$

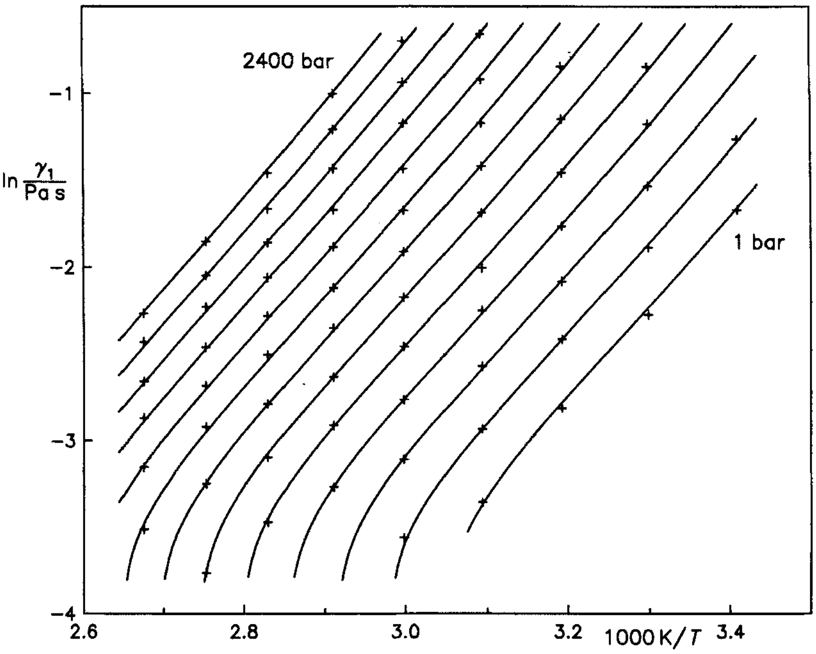


Figure 2. The rotational viscosity γ_1 as a function of temperature at pressures between 1 and 2400 bar (1, 200, 400 bar...) for the MBBA/EBBA mixture. The solid curves were calculated with the aid of equation (3); the parameters are given in the text.

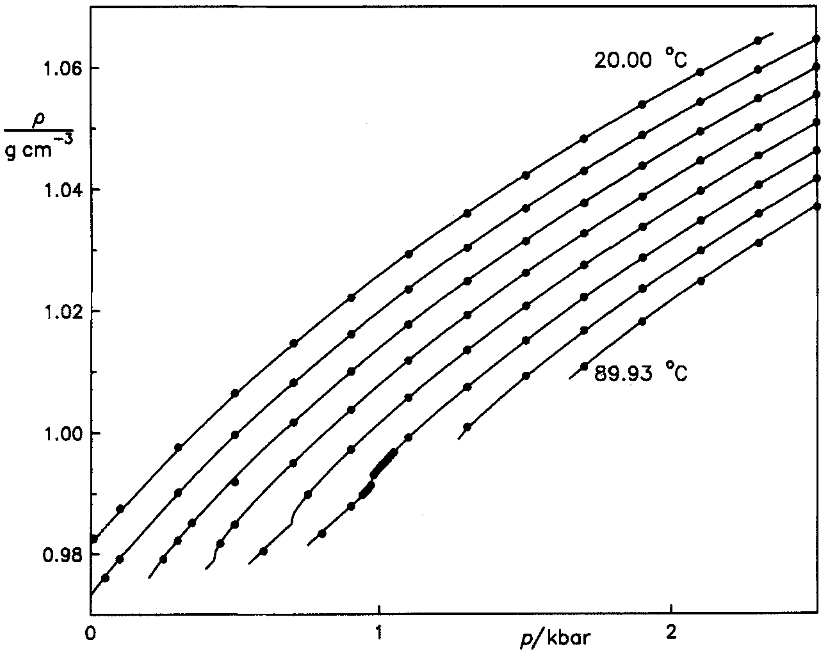


Figure 3. Density ρ as a function of pressure at different temperatures (20·00, 30·04, 39·97, 49·81, 59·78, 69·83, 79·94, and 89·93°C) for the mixture ZLI 2413. The solid curves were calculated with the aid of equation (5); the parameters are given in the text.

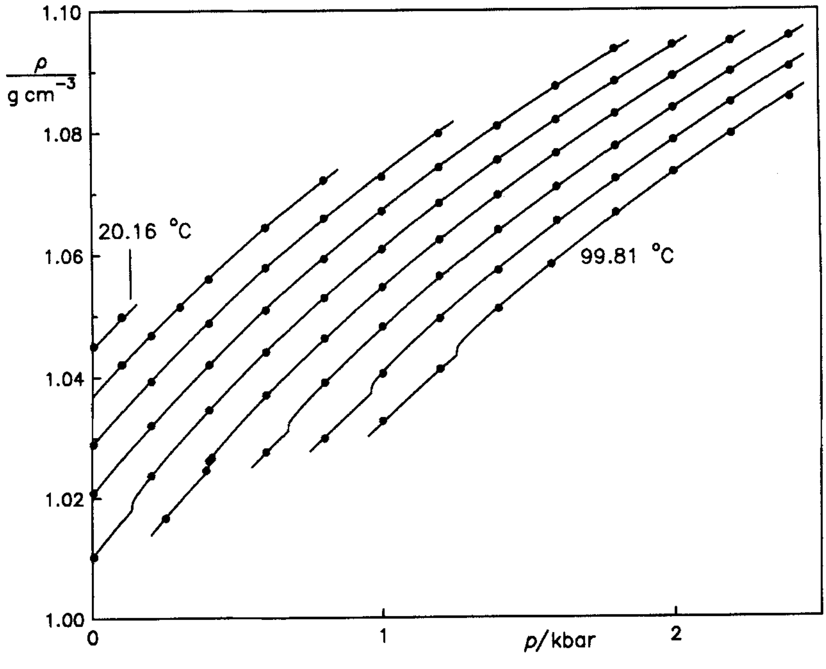


Figure 4. Density ρ as a function of pressure at different temperatures (20·16, 30·18, 40·19, 49·95, 59·90, 69·84, 79·83, 89·94, and 99·81°C) for the MBBA/EBBA mixture. The solid curves were calculated with the aid of equation (5); the parameters are given in the text.

The parameters ρ_0, D, and B of the Tait equation were assumed to depend on temperature according to

$$\rho_0 = r_1 + r_2 T + r_3 T^2, \tag{6}$$

$$D = d_1 + d_2 T, \tag{7}$$

$$B = b_1 + b_2 T. \tag{8}$$

E and γ in the last term (see equation (5)), which was used by van Hecke and Stecki [10] to describe the influence of the orientational order for their high precision density values at atmospheric pressure, were assumed to be independent of temperature and pressure. Whether this assumption is correct is not known. However, the influence of this term on the density (1 per cent for ZLI 2413 and 0·5 per cent for the MBBA/EBBA mixture, see later) is so small that significant changes are not expected.

Small differences in the temperatures T^* ($\Delta T^* \approx 0{\cdot}6$ K for ZLI 2413; no difference for the MBBA/EBBA mixture) between the γ_1 and ρ measurements were taken into account by different T_0^* values whereas the other parameters in equation (4) were assumed to be equal for both fits. The parameters of equations (3), (4) and (5) were determined with the Marquardt fitting procedure and the solid curves in figures 2 to 4 were calculated with these equations. The parameters are:

	ZLI 2413 mixture	MBBA/EBBA mixture
Density ρ	$r_1 = 1{\cdot}1265\,\mathrm{g\,cm^{-3}}$	$r_1 = 1{\cdot}1759\,\mathrm{g\,cm^{-3}}$
	$r_2 = -3{\cdot}198 \times 10^{-4}\,\mathrm{g\,cm^{-3}\,K^{-1}}$	$r_2 = -1{\cdot}6596 \times 10^{-4}\,\mathrm{g\,cm^{-3}\,K^{-1}}$
	$r_3 = -6{\cdot}432 \times 10^{-7}\,\mathrm{g\,cm^{-3}\,K^{-2}}$	$r_3 = -9{\cdot}954 \times 10^{-7}\,\mathrm{g\,cm^{-3}\,K^{-2}}$
	$d_1 = 6{\cdot}494 \times 10^{-2}$	$d_1 = 9{\cdot}768 \times 10^{-2}$
	$d_2 = 5{\cdot}800 \times 10^{-5}\,\mathrm{K^{-1}}$	$d_2 = 2{\cdot}113 \times 10^{-4}\,\mathrm{K^{-1}}$
	$b_1 = 3375\,\mathrm{bar}$	$b_1 = 2665\,\mathrm{bar}$
	$b_2 = -6{\cdot}326\,\mathrm{bar\,K^{-1}}$	$b_2 = -4{\cdot}033\,\mathrm{bar\,K^{-1}}$
	$E = 1{\cdot}0518 \times 10^{-2}\,\mathrm{g\,cm^{-3}}$	$E = 4{\cdot}369 \times 10^{-3}\,\mathrm{g\,cm^{-3}}$
	$\gamma = 0{\cdot}2821$	$\gamma = 0{\cdot}16488$
Rotational viscosity γ_1	$A = 2{\cdot}004 \times 10^{-4}\,\mathrm{Pa\,s}$	$A = 1{\cdot}2434 \times 10^{-4}\,\mathrm{Pa\,s}$
	$\beta = 0{\cdot}12177$	$\beta = 0{\cdot}08124$
	$C = 5{\cdot}775$	$C = 6{\cdot}143$
	$T_0 = 161{\cdot}99\,\mathrm{K}$	$T_0 = 156{\cdot}85\,\mathrm{K}$
	$T_0^* = 305{\cdot}4\,\mathrm{K}$	$T_0^* = 327{\cdot}8\,\mathrm{K}$
	$a = 3871\,\mathrm{bar}$	$a = 3702\,\mathrm{bar}$
	$c = 0{\cdot}5107$	$c = 0{\cdot}4417$.

The scatter in the density values, which is especially apparent for the MBBA/EBBA mixture at the highest temperature, is partly due to temperature differences of up to $\pm 0{\cdot}1$ K during the pressure variation. The solid curves were calculated for constant temperatures and do not take into account these temperature differences.

The Eyring theory for isotropic liquids leads to an equation between the kinematic shear viscosity ν and the pressure, namely

$$\frac{\partial \ln \nu}{\partial p} = \frac{\Delta V^{\ddagger}}{RT}, \tag{9}$$

where $\Delta V^{\ddagger}$ is the activation volume which is in the order of 1/6 to 1/8 [11] of the molar volume. We have tested the analogue of this equation for the rotational viscosity

$$\ln \gamma_1/\rho = \frac{\Delta V^{\ddagger}}{RT} p + C. \tag{10}$$

A plot of $\ln \gamma_1/\rho$ versus p/T should give straight lines at constant temperature. Figure 5 shows that this linear behaviour is observed if the orientational order does not change significantly, i.e. the pressure must be high enough. The slopes $m = \Delta V^{\ddagger}/R$ of the lines should be constant. We observe a slight increase with decreasing temperature. The mean slope of 0·43 K bar^{-1} gives $\Delta V^{\ddagger} = 36\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$. The ZLI mixture has a mean molar volume of 249 cm^3 mol^{-1}. Thus, $\Delta V^{\ddagger}/V \approx 1/6{\cdot}7$ falls in the range observed for the shear viscosity of isotropic liquids.

Furthermore, equations (3)–(5) allow a presentation of the rotational viscosity as a function of density. This presentation gives a better basis for theoretical considerations than a presentation as a function of pressure. It is known [1] that a plot of $\ln \eta$ versus density gives nearly straight lines for simple isotropic liquids. Figure 6 shows, therefore, the corresponding plot of $\ln \gamma_1$ versus density for the liquid crystal ZLI 2413. Besides the bending near the nematic–isotropic transition at low densities, the curves show this nearly linear behaviour.

The plot of γ_1 as a function of temperature under isochoric conditions requires the determination of the pressure for given densities and temperatures. This was performed with equation (5) by an iterative algorithm. Then, γ_1 was determined from equation (3) for this temperature and pressure and plotted in figures 7 and 8 as a function of temperature. Some isobaric curves are also shown for the purpose of comparison. The course of the isobars and the isochores is similar: a strong bending in the

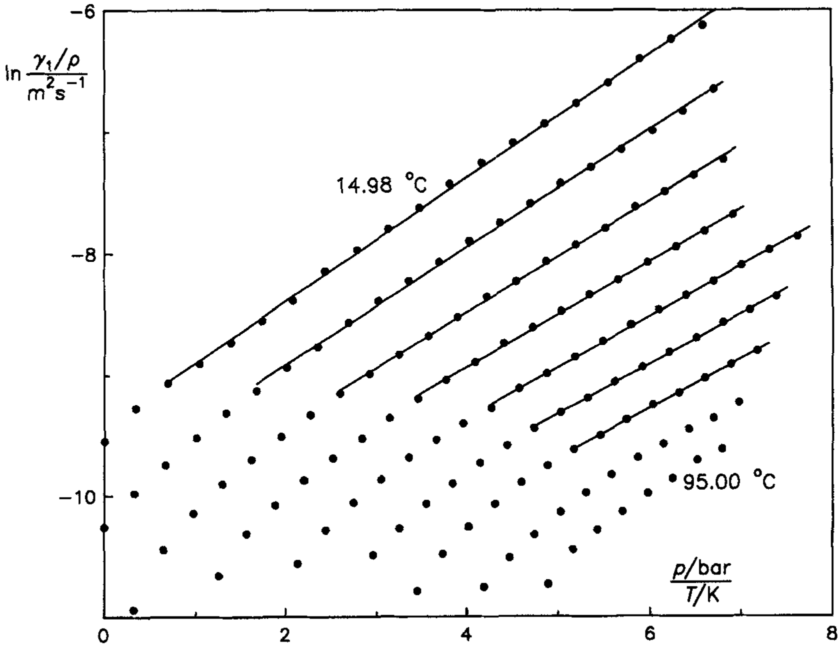


Figure 5. Kinematic rotational viscosity γ_1/ρ versus the pressure–temperature ratio p/T for the mixture ZLI 2413 at temperatures between 14·98 and 95·00°C.

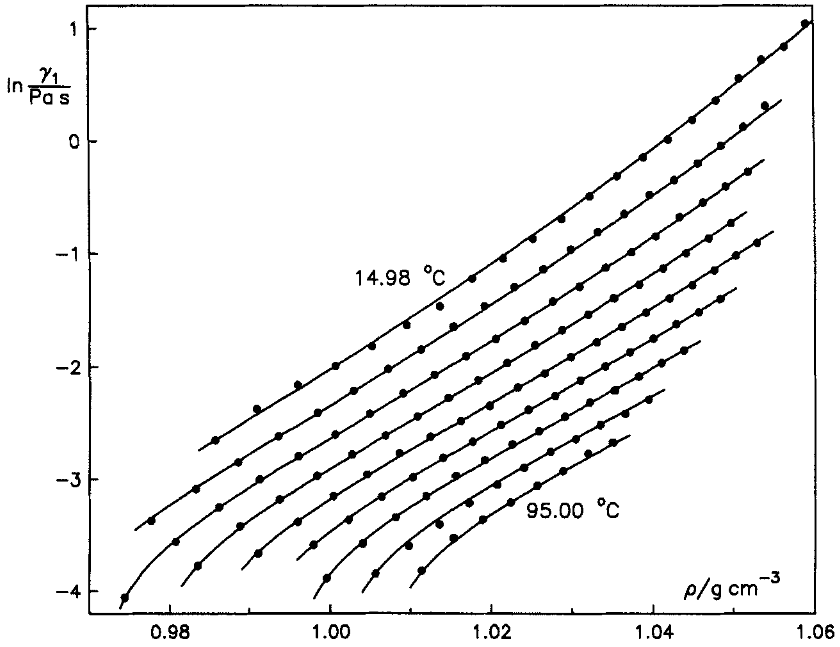


Figure 6. The rotational viscosity γ_1 as a function of density ρ at different temperatures for the mixture ZLI 2413. The solid curves were calculated with the aid of equations (3) and (5).

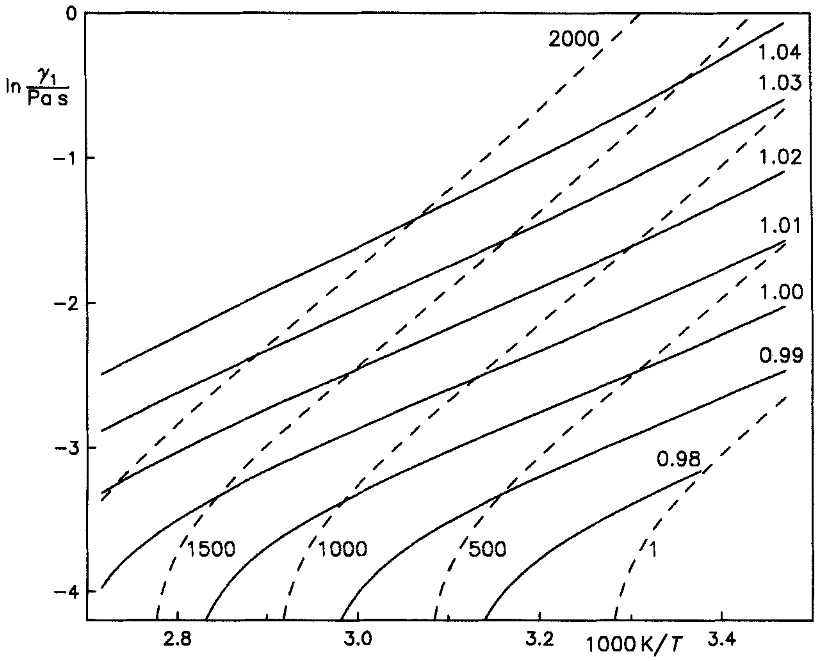


Figure 7. The rotational viscosity γ_1 as a function of temperature under isochoric conditions (——) for the mixture ZLI 2413. Some isobaric curves (– – –) are inserted for the purpose of comparison. The parameters in the figure are the densities in g cm^{-3} and the pressures in bar, respectively.

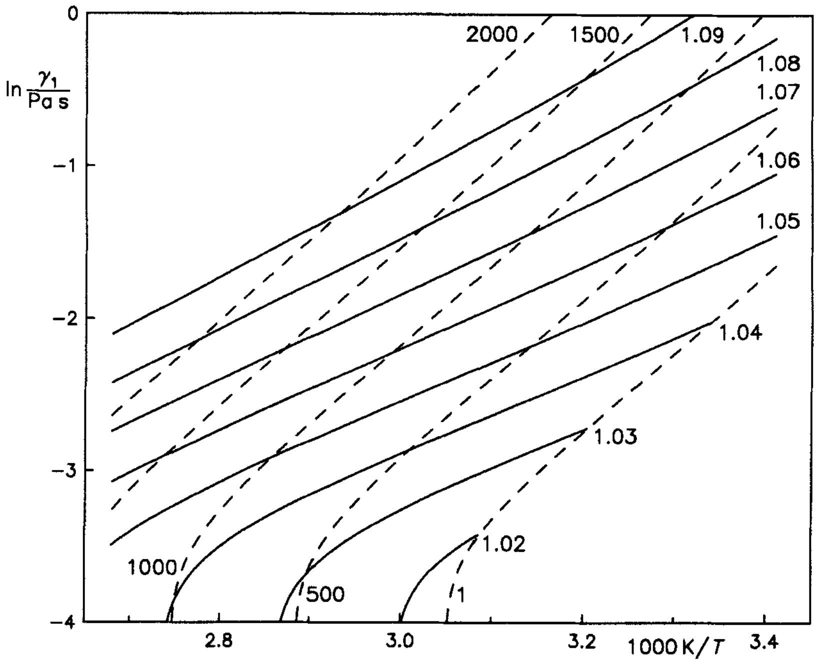


Figure 8. The rotational viscosity γ_1 as a function of temperature under isochoric conditions (——) for the MBBA/EBBA mixture. Some isobaric curves (– – –) are inserted for the purpose of comparison. The parameters in the figure are the densities in g cm^{-3} and the pressures in bar, respectively.

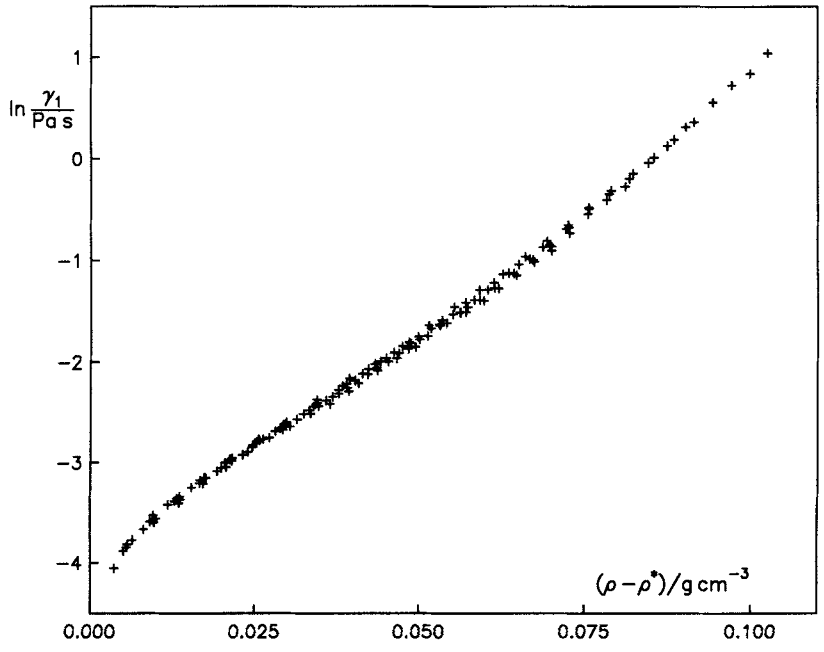


Figure 9. The rotational viscosity γ_1 as a function of the reduced density $\rho-\rho^*$ for the mixture ZLI 2413.

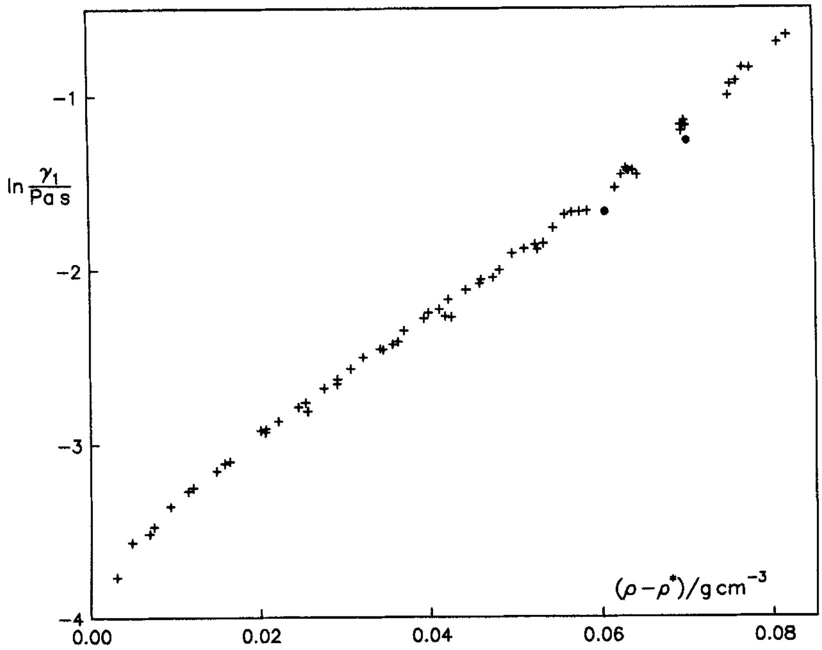


Figure 10. The rotational viscosity γ_1 as a function of the reduced density $\rho-\rho^*$ for the MBBA/EBBA mixture. The points denoted by full circles represent measurements at 20°C.

neighbourhood of the nematic–isotropic transition due to the strong change of the orientational order with temperature and a nearly linear dependence (for these scales) at lower temperatures. The deviation from the linear dependence is a slight increase in the slopes at low temperature. This effect is observed for the isochoric and the isobaric curves. The main differences are the reduced slopes of the isochores. The activation energies in the centre of figure 7 are $E_{A_p}=44{\cdot}2\,\mathrm{kJ\,mol^{-1}}$ and $E_{A_v}=22{\cdot}6\,\mathrm{kJ\,mol^{-1}}$ with nearly equal values for figure 8. The ratio $E_{A_p}/E_{A_v}\approx 2$ is usually observed for isotropic liquids [1] and for the shear viscosity of liquid crystals under flow alignment [12].

In an earlier paper [2], we observed that the form of the isobaric curves $\ln\gamma_1=f(1/T)$ for different pressures is very similar and that it was possible to shift the curves one onto another if $\ln\gamma_1$ is plotted as a function of the reduced reciprocal temperature $1/T-1/T^*(p)$ where $T^*(p)$ has the same meaning as in equation (4). Equation (3) is a consequence of this observation. The question arises whether it is possible to find a similar shift for the $\ln\gamma_1=g(\rho)$ curves. We found that such a shift is possible with a reduced density $\rho-\rho^*(T)$ (or $1/\rho-1/\rho^*$ with a slightly poorer result). $\rho^*(T)$ is the analogue to $T^*(p)$ and is the density at the pressure where the orientational order vanishes. Figures 9 and 10 show these plots for the two liquid crystal mixtures studied. It should be noted that the scatter of values is slightly larger for the MBBA/EBBA mixture than for the ZLI 2413 mixture. Most of the deviating points represent measurements at low temperatures and, accordingly, low pressures. The corresponding nematic–isotropic transitional pressures are very low, for example this pressure amounts to -800 bar for the 20°C/1 bar measurement. Obviously, it is not possible to measure the density for this pressure and we assume that the extrapolation with the Tait equation leads to the deviation. It is even astonishing that this procedure gives such a good result for the low temperature values. For the ZLI 2413 mixture, the deviations should be smaller as the differences between the low lying nematic–isotropic transition temperature and the temperatures of measurement are smaller.

The question arises as to whether it is possible to extract the function $\gamma_1 = f(p, T)$ from the observation that $\ln \gamma_1$ is a universal function of $1/T - 1/T^*(p)$ and $\rho - \rho^*(T)$, respectively. This is surely impossible, but these results allow a considerable reduction of the complexity of the problem. If the rotational viscosity is known as a function of temperature at one pressure, for example at atmospheric pressure, it is possible to evaluate $\gamma_1 = f(p, T)$ if T^* (or the clearing point temperature) is known as a function of pressure. A similar evaluation is possible with the aid of the density representation.

Financial support by the Deutsche Forschungsgemeinschaft is gratefully appreciated.

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