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Measurement of the rotational viscosity, γ_1, of nematic liquid crystals under high pressure

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A method for the measurement of the rotational viscosity, γ_1, of nematic liquid crystals under high pressure is described. First measurements for the liquid crystals 4′-methoxybenzylidene-4-*n*-butylaniline, a broad range nematic mixture of substituted cyclohexyl-phenyls and a re-entrant nematic mixture are presented.

1. Introduction

The viscosity of a liquid exhibits a complicated dependence on temperature. The influence of temperature can be described roughly by two effects. First, the direct influence of temperature via the kinetic energy of the molecules and, secondly, the influence of density which also changes with temperature. Both effects have to be separated for a comparison between experimental and theoretical temperature dependencies as theories are usually developed for liquids at constant density. Viscosity values at constant density can be determined if the density variation with temperature is compensated by the application of pressure.

We have begun to study these effects on the rotational viscosity, γ_1, of nematic liquid crystals. This quantity describes the momentum which has to be exerted on the director during rotation. This is the first part of the study which describes the experimental set-up for the measurement of γ_1 under high pressure as well as the initial measurements. Our method of measurement allows a direct and precise determination of γ_1 in contrast to the method of Lagunov and Larionov [1] which gives only γ_1/χ_a where χ_a is the anisotropy of the magnetic susceptibility.

Measurements of γ_1 under high pressure were performed on 4′-methoxybenzylidene-4-*n*-butylaniline (MBBA), on a broad range nematic mixture which allows a temperature variation of nearly 100 K and on a re-entrant nematic mixture which allows us to study the divergence of γ_1 at the transition to a smectic phase.

The determination of the rotational viscosity at constant density cannot be performed at present as the corresponding density data under high pressure are not known. Kuss [2] has measured the density of MBBA under high pressure. However, the nematic–isotropic transition temperatures of our samples differ by up to 2 K from those of Kuss. Furthermore, the number of density values in the neighbourhood of the nematic–isotropic transition is too small for an evaluation of γ_1 at constant density in this temperature region.

2. Experimental

The rotational viscosity, γ_1, was determined by means of the rotating field method which is often used for measurements at normal pressure. The experimental set-up is

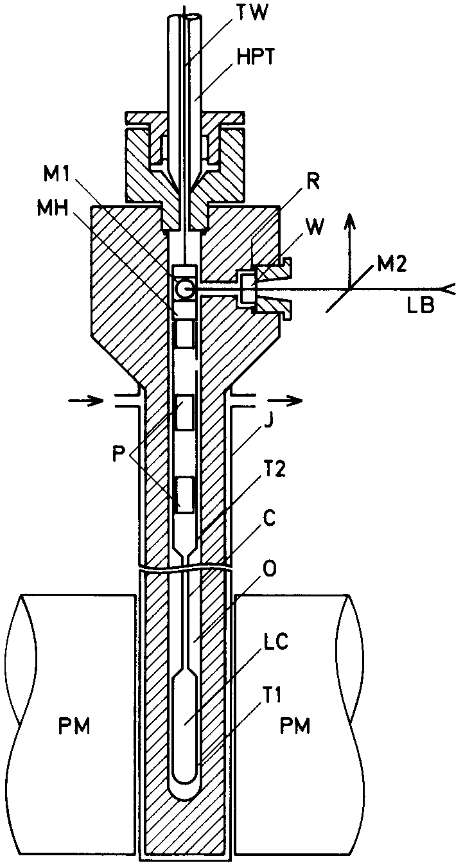

Figure 1. Experimental set-up.

shown in figure 1. The lower part of the sample container (part T1) contains 3 cm^3 of the liquid crystal (LC). It is connected via a glass capillary (C) (0·8 mm inner diameter) with a high precision glass tube (T2). Two glass pistons (P) separate the pressure transmitting oil (O) and the liquid crystal. This separation method allows a measuring time of 12 hours without a noticeable reduction of the nematic–isotropic transition temperature of the liquid crystal. The upper end of the tube (T2) is attached to the mirror holder (MH) with the mirror (M1) at which the laser beam (LB) is reflected. The reflected beam is observed after reflection at the semi-transparent mirror (M2). A glass window (W) is attached to the polished surface of a retaining ring which is sealed by a PTFE or a VITON O ring (R). The liquid crystal container is suspended from the torsion wire (TW) (spring steel wire, 30 μm diameter, 70 cm length) which is surrounded by a high pressure tube (HPT). The wire is attached to a fitting at the end of the high pressure tube. The high pressure generation and measuring system is also connected to this fitting. The autoclave is made from a non-magnetic steel with a yield strength of 900 N mm^{-2}. The set-up allows a maximum pressure of 3 kbar. The temperature of the autoclave is controlled by thermostatted oil which is circulating in the brass jacket (J). The rotating field is generated by a rotating permanent magnet (PM) (11 cm pole shoe diameter, 4 cm air gap, 0·3 T) which is driven by a stepping motor.

The definition of the rotational viscosity

$$\gamma_1 = M/\omega V \tag{1}$$

allows a very simple measurement of γ_1 with this device. The volume V of the liquid crystal is the volume of the lower part (T1) of the container which is nearly independent of temperature and pressure. M is the torque on the sample which can be calculated from the torsion of the wire. ω is the angular frequency of the director rotation with respect to the fluid at rest. This angular frequency is equal to the angular frequency of the rotating magnet if the director follows the field rotation. This is only possible at frequencies below

$$\omega_{\max} = \frac{\mu_0 \chi_a H^2}{2\gamma_1}. \tag{2}$$

As the field strength, H, decreases in the upper part of the autoclave, the angular frequency of the magnet exceeds $\omega_{\max}$ somewhere in the liquid crystal container. Therefore, this part of the container has a very small cross section and the upper part of the liquid crystal container is completely shielded by a thick iron plate against penetration of the magnetic field.

As the reflection of the laser beam can be observed only at two positions of the mirror (M1), measurements were performed as follows. At the beginning of the measurement, the upper end of the torsion wire is turned to a position in which the mirror (M1) is approximately perpendicular to the laser beam, the magnet being at rest. Then, the magnet is rotated with a frequency that leads to a 180° rotation of the sample. This measurement is repeated for the other sense of rotation and the rotational viscosity is calculated according to

$$\gamma_1 = \frac{(\phi_r - \phi_1)D}{(\omega_r - \omega_1)V} = \frac{2\pi D}{(\omega_r - \omega_1)V}. \tag{3}$$

Here ϕ is the torsion and D the torsion constant of the wire which is nearly independent of pressure (0·2 per cent/kbar [3]).

The liquid crystals studied were 4′-methoxybenzylidene-4-*n*-butylaniline (MBBA) with a nematic–isotropic transition temperature T_{NI} of 46·0°C at atmospheric pressure, ZLI 2413 (a mixture of substituted cyclohexyl-phenyls (Merck)) with T_{NI} = 32·3°C and a re-entrant nematic mixture CP (36·22 wt% 4′-cyano-4-*n*-heptylbiphenyl, 36·66 wt% 4′-cyano-4-*n*-octylbiphenyl, 18·08 wt% 4′-cyano-4-*n*-octyloxybiphenyl, 9·04 wt% 4″-cyano-4-*n*-pentylterphenyl) which is similar to a mixture described by Bhattacharya and Letcher [4] but which exhibits a higher maximum pressure for the nematic–smectic A transition.

3. Results

Figure 2 shows the rotational viscosity, γ_1, of MBBA as a function of pressure. The nearly logarithmic dependence at high pressure and the curvature at low pressure are very similar to the dependence on inverse temperature (see figure 3). The second effect is caused by the decrease of the nematic–isotropic transition temperature and the order parameter with decreasing pressure. In the region of nearly logarithmic dependence, we find $d\ln(\gamma_1/\mathrm{Pa\,s})/dp \approx 1{\cdot}2 \times 10^{-3}\,\mathrm{bar}^{-1}$ which is the same order of magnitude as for the shear viscosity of isotropic liquids. At lower temperatures this value increases as for isotropic liquids. The temperature dependence of γ_1 is shown in figure 3

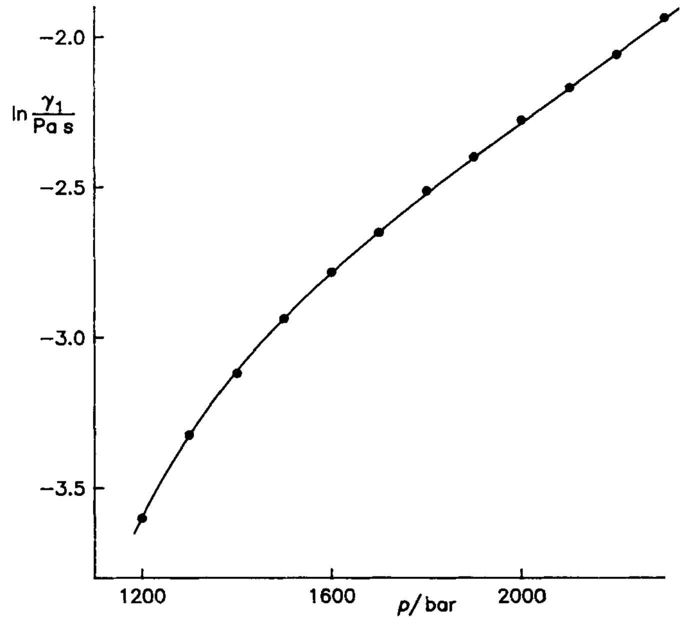

Figure 2. The pressure dependence of the rotational viscosity, γ_1, of MBBA at 85·24°C.

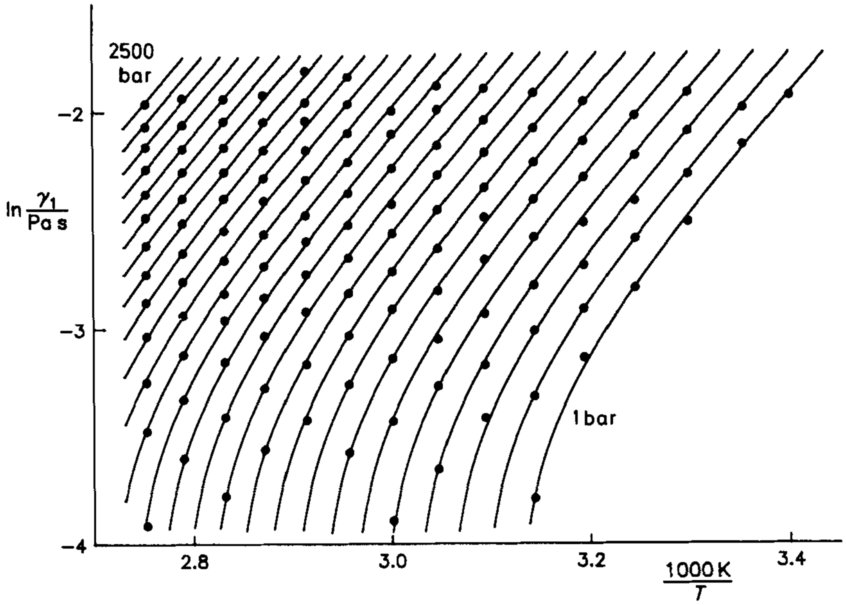

Figure 3. The temperature dependence of the rotational viscosity, γ_1, of MBBA for pressures between 1 and 2500 bar (1, 100, 200 bar, . . .). The solid curves were calculated from equation (7) with $A_1 = 1{\cdot}1239 \times 10^{-4}$ Pa s, $\beta = 0{\cdot}1486$, $B = 1235{\cdot}9$ K, $T_0 = 138{\cdot}1$ K. $T_0^* = 319{\cdot}8$ K, $a = 4239$ bar and $c = 0{\cdot}4950$. The parameters were obtained by fitting equation (7) to the experimental data with the Marquardt algorithm [6].

for pressures between 1 bar and 2·5 kbar. Values at 1 bar agree to within 2 per cent with published values [5]. The curves are limited by the rotational viscosity at the nematic–isotropic transition, at the melting point, at 1 bar and at an arbitrary chosen maximum temperature of 90°C.

Diogo [7] has presented the equation

$$\gamma_1 = AS^2\exp\left[\frac{BS^2}{\alpha(T - T_0) - \beta(p - p_0)}\right] \tag{4}$$

for the temperature and pressure dependence of γ_1. Theoretical [8] and experimental studies [9, 10] have shown that the relaxation time which is essentially the exponential term of equation (4) should be continuous across the clearing point. As the exponential term contains the order parameter, S, which vanishes at the nematic–isotropic transition equation (4) cannot be valid in general.

Because of the similar shape of the curves in figure 3 we have tried to superimpose the curves. Figure 4 shows the result for a shift in the abscissa direction by plotting $\ln\gamma_1$ versus $1/T - 1/T^*$ where T^* is the temperature for which the order parameter S and the rotational viscosity vanish. T^* was assumed to be

$$T^* = T_0^*\left(\frac{p}{a} + 1\right)^c. \tag{5}$$

This equation has been proposed for the pressure dependence of transition temperatures by Simon and Glatzel [11–13] and was used for the pressure dependence of nematic–isotropic transition temperatures by Feyz and Kuss [14]. Therefore this equation should also hold for the pressure dependence of T^* which is only slightly above the nematic–isotropic transition temperature. The temperature dependence of

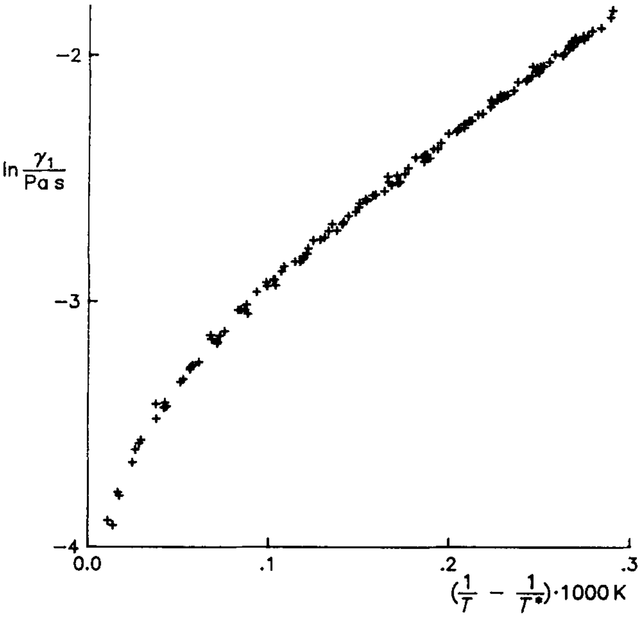

Figure 4. The rotational viscosity, γ_1, of MBBA as a function of the difference $1/T - 1/T^*$; T^* is the characteristic temperature.

γ_1 at atmospheric pressure can be described [10, 15] by

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

where the first term represents the temperature dependence of the order parameter squared. T_0 is the temperature at which γ_1 diverges and which depends on the glass transition temperature. It is possible therefore to describe the pressure and temperature dependence by

$$\gamma_1 = A_1\left(1 - \frac{T'}{T_1^*}\right)^2 \exp\left(\frac{B}{T' - T_0}\right),$$

with

$$\frac{1}{T'} = \frac{1}{T} - \frac{1}{T^*} + \frac{1}{T_1^*}, \tag{7}$$

if T_0 is assumed to be independent of pressure. T_1^* is the characteristic temperature at atmospheric pressure. Figure 3 shows that this equation describes our data very well and we deduce that T^* is a corresponding temperature for the reduced rotational viscosity

$$^1\gamma_1 = \frac{\gamma_1}{S^2}, \tag{8}$$

i.e. the reduced rotational viscosity at the characteristic temperature T^* does not depend on pressure

$$^1\gamma_1(T^*) = A_1 \exp\left(\frac{B}{T_1^* - T_0}\right). \tag{9}$$

It should be noted that T^* is a hypothetical temperature for a nematic liquid crystal.

As equation (7) is rather lengthy we have transformed it in the following way. The ratio T'/T_1^* in the S^2 term is nearly equal to T/T^*. The exponent $B/(T' - T_0)$ can be transformed with some approximations into $C(T^* - T_0)/(T - T_0)$ and a term which can be included in the constant A_1. The resulting equation

$$\gamma_1 = A_2\left(1 - \frac{T}{T^*}\right)^2 \exp\left(C\frac{T^* - T_0}{T - T_0}\right) \tag{10}$$

also exhibits the corresponding behaviour and describes our data very well (cf. figure 5). The reduced rotational viscosity at the characteristic temperature should be

$$^1\gamma_1(T^*) = A_2 \exp C. \tag{11}$$

Equations (9) and (11) lead to similar values for the reduced rotational viscosity at the characteristic temperature, 0·101 and 0·103 Pa s, respectively. The precision of our data is not sufficient to differentiate between equations (7) and (10).

In order to demonstrate the validity of equations (7) and (10) for a liquid crystal with a broad nematic phase range we have studied the rotational viscosity of the mixture ZLI 2413 which exhibits at 2 kbar a nematic phase between 100°C and less than 10°C as well as a comparatively sharp nematic–isotropic transition. Figure 6 shows that this liquid crystal exhibits strong deviations from a linear dependence in an Arrhenius diagram at low temperatures where the influence of the order parameter is small. Nevertheless, the temperature dependence can be described very well by equation (10) and by equation (7) although this is not shown here.

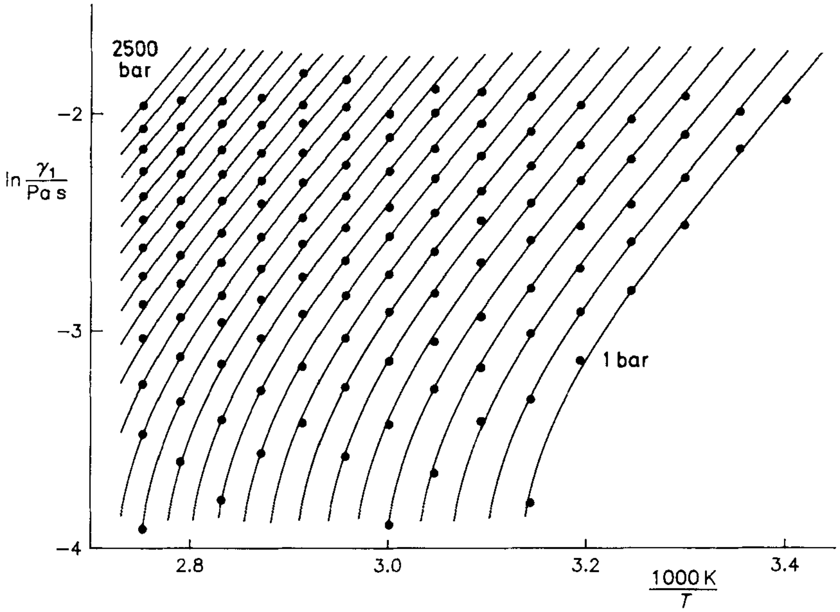

Figure 5. The temperature dependence of the rotational viscosity, γ_1, of MBBA for pressures between 1 and 2500 bar (1, 100, 200 bar, . . .). The solid curves are calculated from equation (10) with $A_2 = 4{\cdot}5160 \times 10^{-4}$ Pa s. $\beta = 0{\cdot}1520$, $C = 5{\cdot}4247$, $T_0 = 168{\cdot}3$ K, $T_0^* = 320{\cdot}0$ K, $a = 3827$ bar and $c = 0{\cdot}4486$.

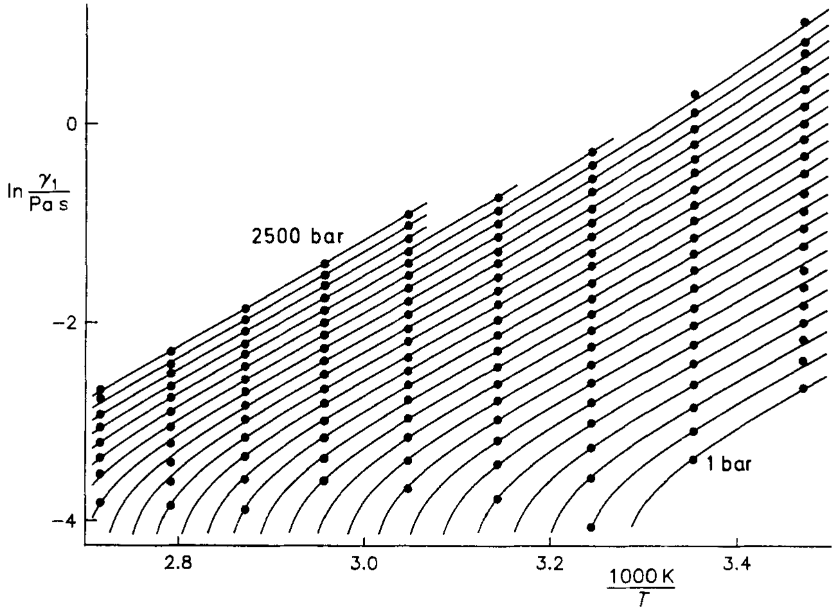

Figure 6. Temperature dependence of the rotational viscosity, γ_1, of ZLI 2413 for pressures between 1 and 2500 bar (1, 100, 200 bar, . . .). The solid curves are calculated from equation (10) with $A_2 = 1{\cdot}6837 \times 10^{-4}$ Pa s, $\beta = 0{\cdot}1203$, $C = 5{\cdot}9336$, $T_0 = 158{\cdot}8$ K, $T_0^* = 305{\cdot}3$ K, $a = 3602$ bar and $c = 0{\cdot}4819$.

Measurement of the rotational viscosity at high pressure allows a very simple solution of a problem which arises when studying the divergence of γ_1 at a nematic–smectic A phase transition. In this case, theory describes the rotational viscosity as a sum of a diverging part and a non-diverging part which shows the normal temperature dependence. In order to test theories these terms have to be separated. Generally, this separation cannot be performed unambiguously as the deviations from linearity in an Arrhenius plot by order parameter variation, the influence of the glass point and the divergence itself prevent a precise determination of the non-diverging part of γ_1. By application of high pressure, the smectic A phase of the liquid crystal can be suppressed very effectively although the variation of the rotational viscosity is only moderate.

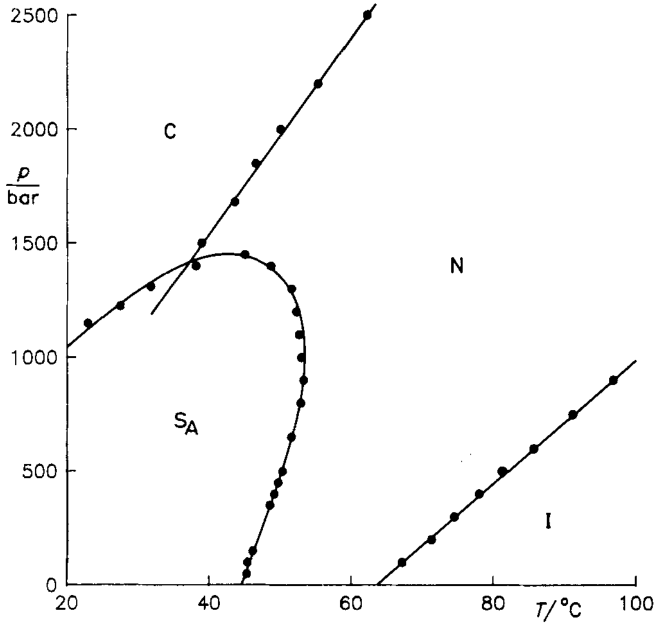

Figure 7. The phase diagram for the mixture CP.

As our measurements of γ_1 are performed with increasing pressure at constant temperature we have studied the divergence for pressure variations. Furthermore, the phase diagram of the mixture CP (cf. figure 7) shows that the re-entrant behaviour is more pronounced for pressure than for temperature variations. Figure 8 shows the pressure dependence of γ_1 for some of the temperatures for which measurements were performed. Equation (10) was fitted to the experimental values far away from the nematic–smectic transition. The difference to the experimental values, i.e. the diverging part of the rotational viscosity, is plotted in figure 9 as a function of pressure. At 53·63°C and above we only find a maximum value at about 1100 bar which is the pressure at maximum temperature for the nematic–smectic transition. At 52·99°C and below we observe divergences of γ_1' at the transitions. The precision of our values is not high enough for an evaluation of the critical coefficients. Some minor changes in our experimental set-up should lead to an accuracy which will allow this evaluation.

Further measurements of the rotational viscosity and of the density at high pressure are in progress. These measurements allow the determination of the rotational viscosity at constant density. We hope that these determinations will lead to a simpler comparison between experiment and theory.

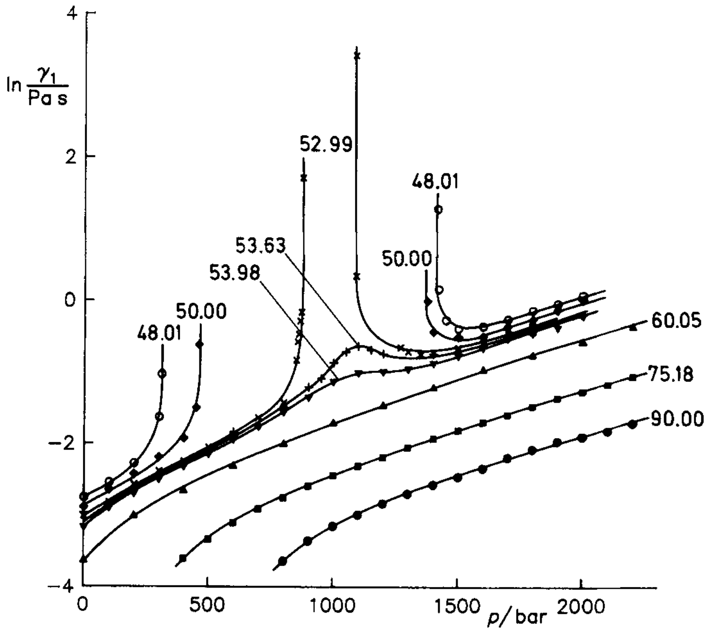

Figure 8. The pressure dependence of the rotational viscosity, γ_1, of the mixture CP for different temperatures.

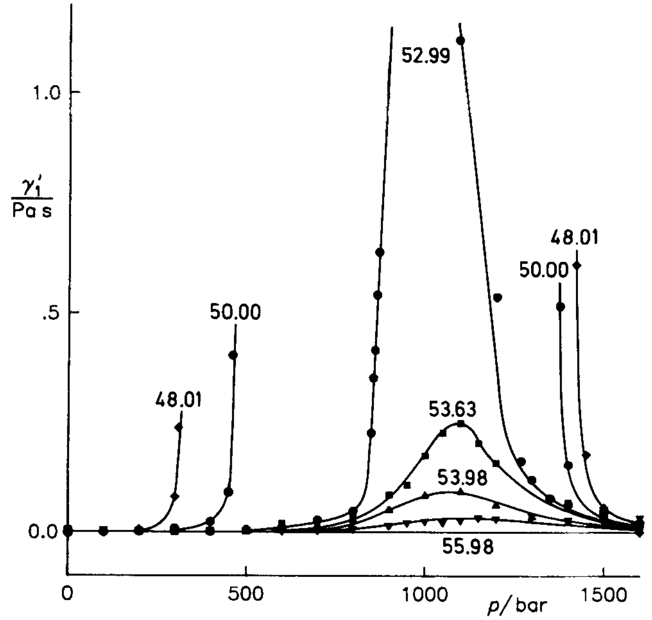

Figure 9. The diverging part γ_1' of the rotational viscosity of the mixture CP in the neighbourhood of the nematic–smectic transition as a function of pressure.

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