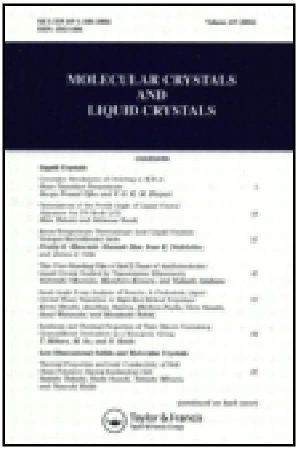

# Molecular Crystals and Liquid Crystals

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# Rotational Viscosity Coefficients $\gamma_1$ for Mixtures of Nematic Liquid Crystals

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# Rotational Viscosity Coefficients $\gamma_1$ for Mixtures of Nematic Liquid Crystals[†]

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The rotational viscosity coefficients $\gamma_1$ for mixtures of nematic liquid crystals have been determined as a function of temperature and composition. Mixtures of two components with equal clearing temperatures but different molecular lengths, of two homologues, and of a mesogenic and a nonmesogenic compound, together with a system which exhibits an induced smectic phase have been studied. The dependence on composition is understood qualitatively. Far away from the clearing point, the dependence on composition is similar to that of the shear viscosity coefficients in isotropic liquids. At high temperatures, the concentration dependence of $\gamma_1$ is influenced by the order parameter which strongly depends on concentration in systems with different clearing temperatures.

## INTRODUCTION

The viscous behavior of nematic liquid crystals can be described by four shear viscosity coefficients and a rotational viscosity coefficient which has no counterpart in isotropic liquids. As the rotational viscosity coefficient $\gamma_1$ determines the response times of liquid crystal displays, it has achieved special interest in recent years. In contrast to the shear viscosity coefficients, the rotational viscosity coefficients of nematic liquid crystals can be measured by two comparatively simple and precise methods: the rotating magnetic field method[1-3] and the relaxation method.[4-6] A large number of papers with experimental results on $\gamma_1$ is therefore to be found in the literature: *e.g.* $\gamma_1$ as function of temperature,[7] as function of molecular

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structure[8] and for a homologous series of liquid crystals.[9] Contrarily, a systematic investigation of the dependence of $\gamma_1$ on composition in mixtures of nematic liquid crystals is missing. Information on this dependence is especially important for liquid crystals which are used in display devices.

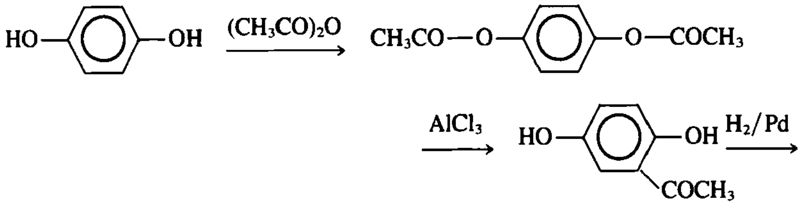
We have therefore measured the rotational viscosity as a function of concentration and temperature for four systems with different properties. The systems consist of the following components:

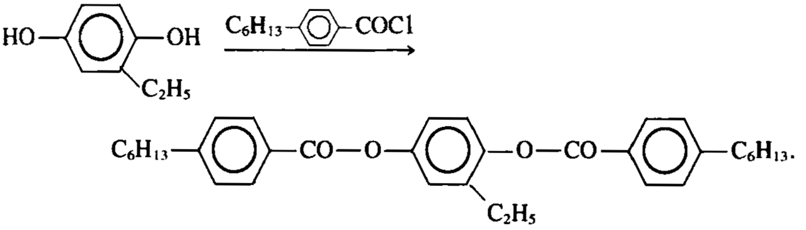
1. ethylhydroquinone di-4-n-hexylbenzoate and the 50 wt.% mixture of 4-n-pentyloxyphenyl 4-methoxybenzoate and 4-n-octyloxyphenyl 4-n-propyloxybenzoate exhibit equal clearing points but very different rotational viscosities;
2. 4'-methoxybenzylidene-4-n-butylaniline and 4'-ethoxybenzylidene-4-n-butylaniline are homologous compounds with different clearing temperatures and viscosities;
3. 4'-methoxybenzylidene-4-n-butylaniline and 4'-cyano-4-n-pentylbiphenyl, with similar viscosities, exhibit an induced smectic phase in their mixtures. This system was chosen because of the possible influence of molecular association on the concentration dependence of $\gamma_1$.
4. 4'-ethoxybenzylidene-4-n-butylaniline and the nonmesogenic compound biphenyl form a system in which a strong dependence of clearing temperature and rotational viscosity on concentration was expected. Nonmesogenic or smectic additives are often used in liquid crystal materials for displays in order to diminish the rotational viscosity.

## EXPERIMENTAL

The experimental setup for the measurement of $\gamma_1$ has been described in detail previously.[7]

4'-methoxybenzylidene-4-n-butylaniline (MBBA; $T_{NI}$ = 45.8°C), 4'-ethoxybenzylidene-4-n-butylaniline (EBBA; $T_{NI}$ = 79.3°C) and 4'-cyano-4-n-pentylbiphenyl (5CBP; $T_{NI}$ = 34.8°C) were synthesized according to well-known reactions. Biphenyl (BP; $T_{CI}$ = 69.9°C) was a commercial product which was recrystallized several times. Ethylhydroquinone di-4-n-hexylbenzoate[10] (ESTER 3; $T_{NI}$ = 75.9°C) was synthesized according to the reaction scheme





4-n-pentyloxyphenyl 4-methoxybenzoate and 4-n-octyloxyphenyl 4-n-propyloxybenzoate were synthesized according to well-known reactions. The 50 wt.% mixture (ESTER 2) exhibits the same clearing temperature as ESTER 3.

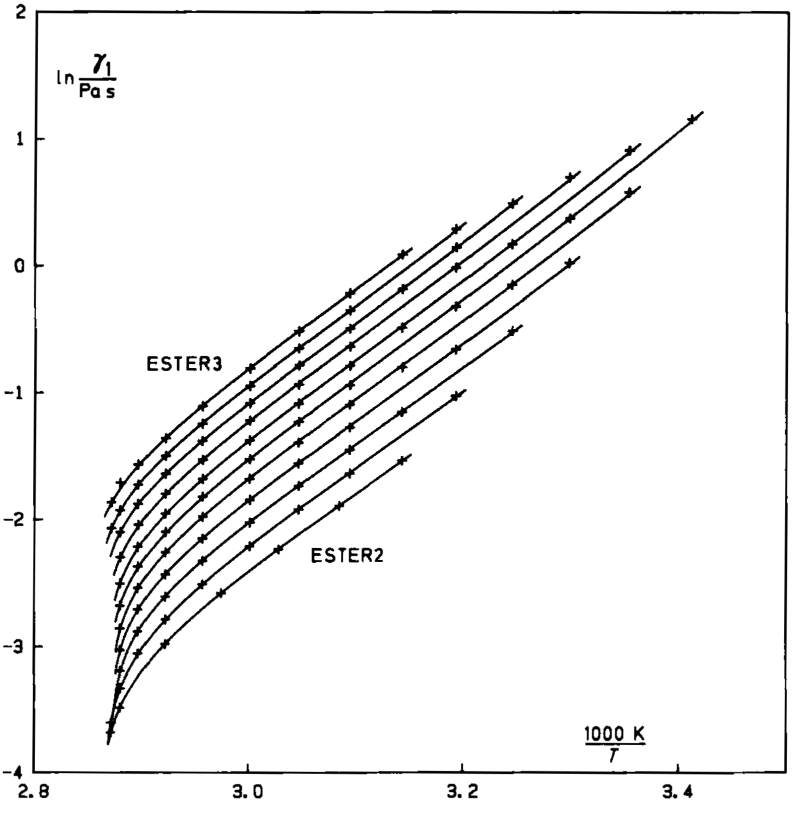


FIGURE 1 Logarithm of the rotational viscosity coefficient $\gamma_1$ for ESTER 3/ESTER 2 mixtures as a function of the inverse temperature $T$. The values for pure ESTER 2 are shown in the lowest curve. The concentration of ESTER 3 is increased by 10 mole % for each curve. The solid lines are calculated according to Eq. (1).

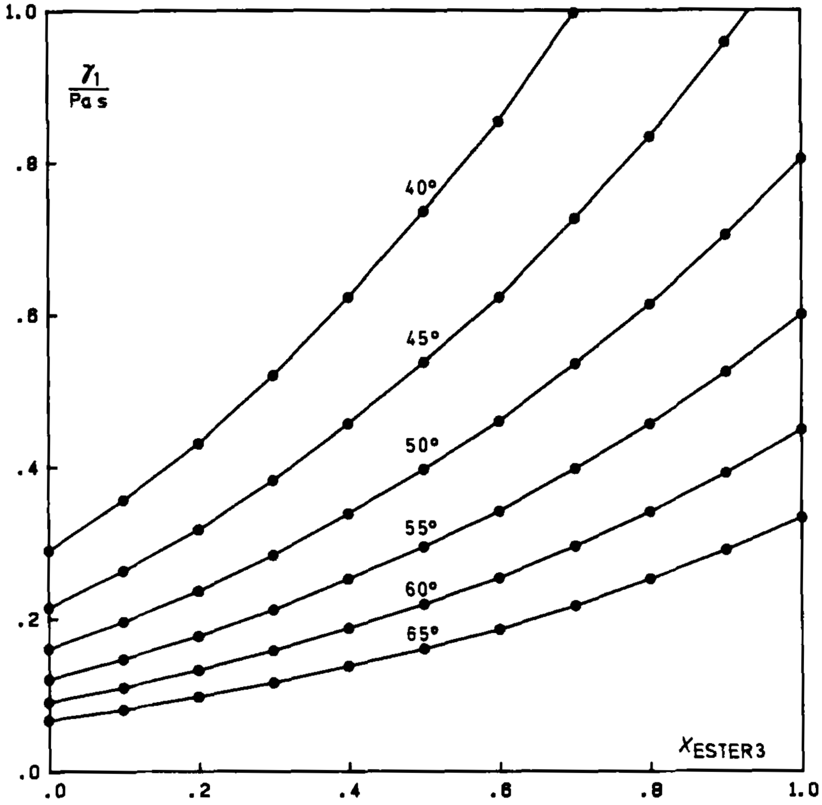


FIGURE 2 Rotational viscosity coefficient $\gamma_1$ for ESTER 3/ESTER 2 mixtures vs mole fraction $x$ of ESTER 3 for different temperatures (°C).

## RESULTS AND DISCUSSION

The dependence of the rotational viscosity on composition will generally be influenced by two effects. Similarly to the shear viscosity of isotropic mixtures, the dependence on composition is nonlinear and influenced by volume effects and intermolecular forces. In addition, the rotational viscosity depends on the order parameter which is generally a function of composition. In order to separate these two effects, we have investigated the ester mixture ESTER 3/ESTER 2 for which the clearing temperatures of the components are nearly equal and the mixtures exhibit only a weak minimum ($\Delta T$ = 1.5 K) in the clearing point curve at intermediate concen-

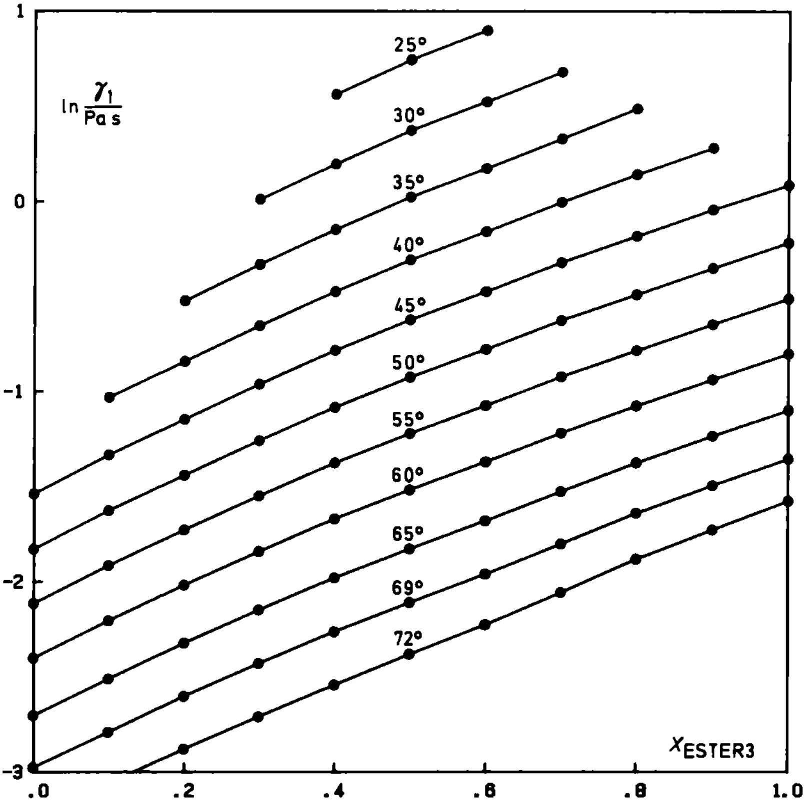


FIGURE 3 Logarithm of $\gamma_1$ for ESTER 3/ESTER 2 mixtures vs mole fraction of ESTER 3.

trations. Assuming that the temperature dependence of the order parameter is a universal function of the reduced temperature, there should be no concentration dependence of the order parameter in this system.

Figure 1 shows the rotational viscosity coefficients for this system as a function of temperature. The rotational viscosity coefficients of the pure components are very different (5:1). The larger part of this ratio will probably be caused by the different molecular lengths. The influence of the lateral ethyl group in the central ring on the rotational viscosity is unknown. The $\gamma_1$ curves look very similar and show an approximately constant shift with concentration in the logarithmic plot. The curves can be described by functions of the type[11]

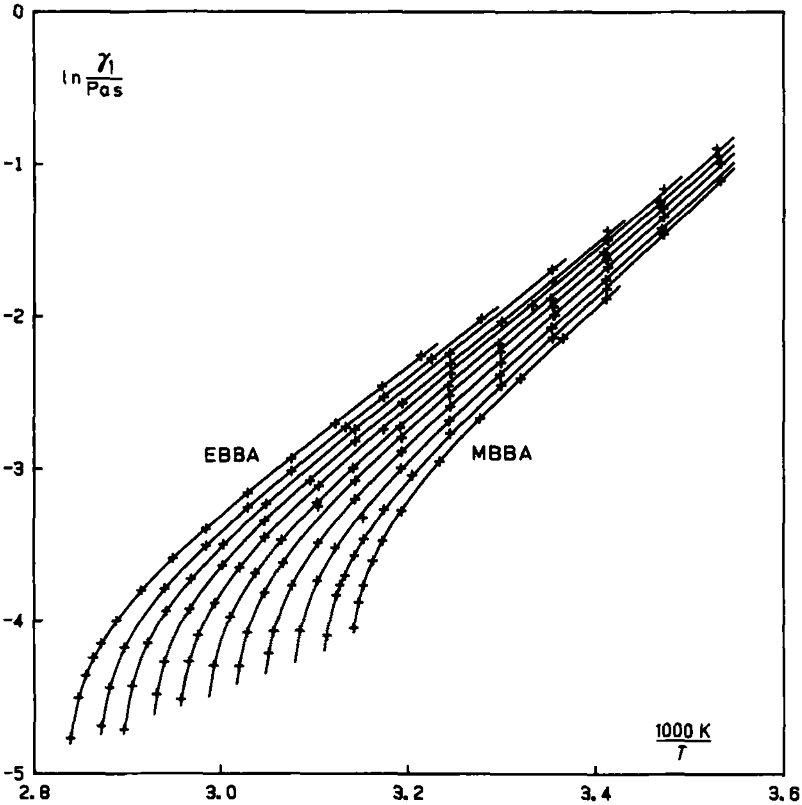


FIGURE 4 Logarithm of $\gamma_1$ for EBBA/MBBA mixtures vs inverse temperature. Mole fractions as in Figure 1.

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

within experimental error (2–3%). The strong decrease in the neighborhood of the clearing point is caused by the decreasing order parameter. This influence is described by the term $(1 - T/T^*)^B$ in Eq. (1). The slight increase in the slope at low temperatures can be explained by a free volume model which leads to the temperature difference $T - T_0$ in the exponential term.

The parameters in Eq. (1) were determined for each mixture with a least squares fit. In this way, it was possible to calculate the rotational viscosity coefficients as a function of concentration at constant temperatures.

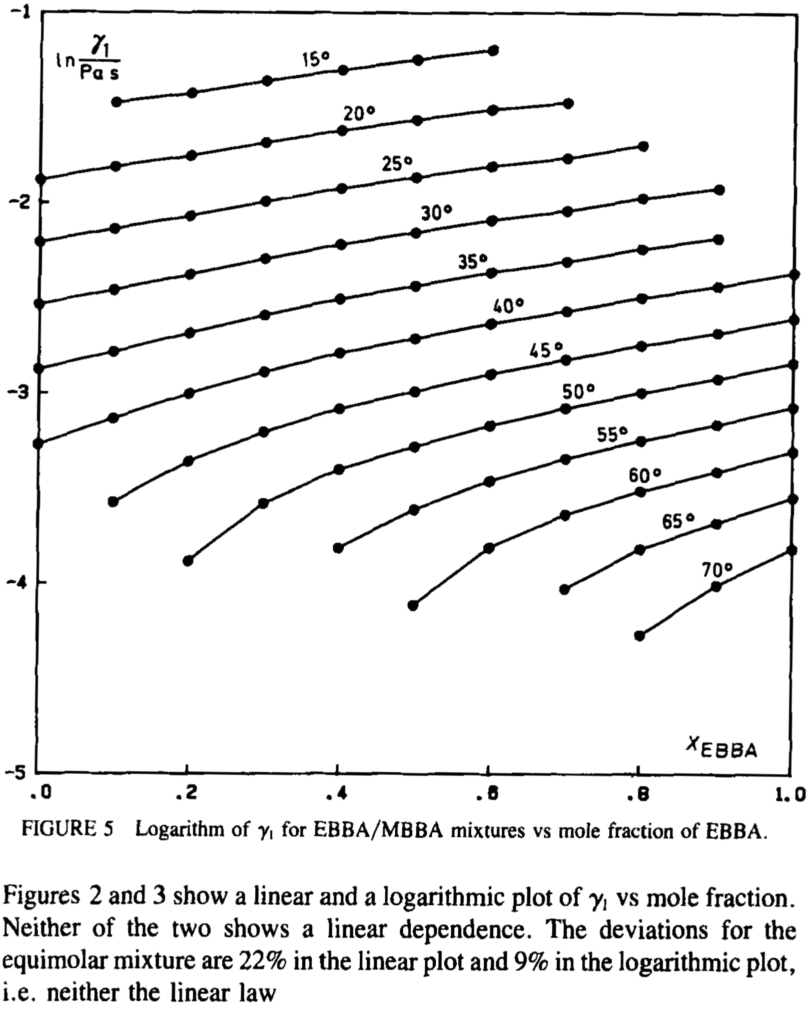


FIGURE 5 Logarithm of $\gamma_1$ for EBBA/MBBA mixtures vs mole fraction of EBBA.

Figures 2 and 3 show a linear and a logarithmic plot of $\gamma_1$ vs mole fraction. Neither of the two shows a linear dependence. The deviations for the equimolar mixture are 22% in the linear plot and 9% in the logarithmic plot, i.e. neither the linear law

$$\gamma_1 = x_A \gamma_{1,A} + x_B \gamma_{1,B} \tag{2}$$

nor the logarithmic law

$$\ln \gamma_1 = x_A \ln \gamma_{1,A} + x_B \ln {}_{1,B} \quad \text{or} \quad \gamma_1 = \gamma_{1,A}{}^{x_A} \cdot \gamma_{1,B}{}^{x_B} \tag{3}$$

is strictly fulfilled. Other plots such as $\gamma_1$ vs volume fraction or $\gamma_1^{-1}$ vs mole fraction result in lines that are more strongly curved. It is possible, of course, to find equations for the concentration dependence which contain an adjustable parameter, as for example, the equation of Hill.[12] The situa-

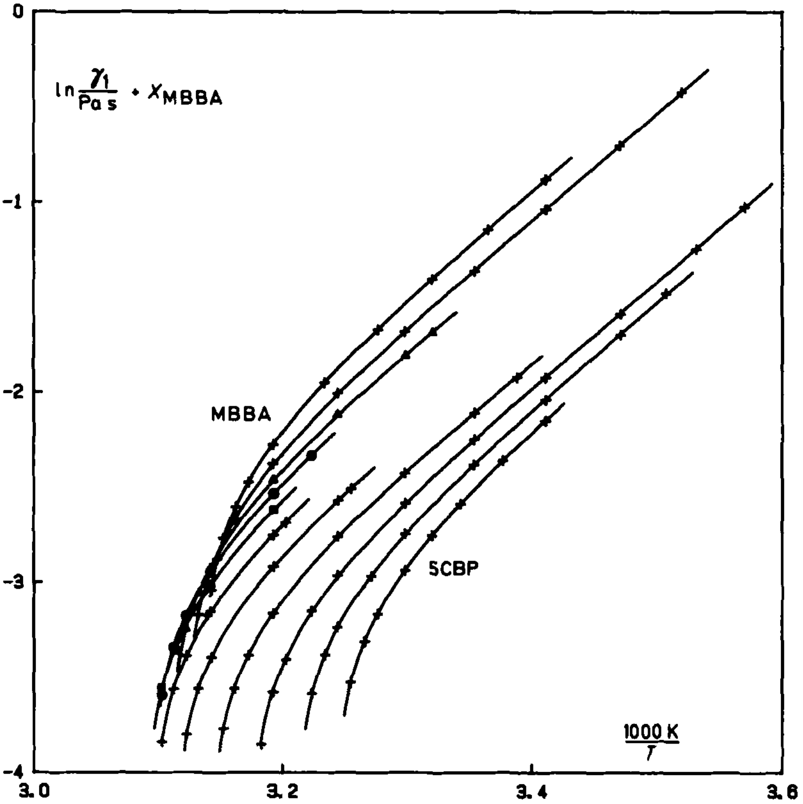


FIGURE 6 Logarithm of $\gamma_l$ for MBBA/5CBP mixtures vs inverse temperature. Mole fractions as in Figure 1. The curves are shifted in the ordinate direction by the term $x_{\mathrm{MBBA}}$ for a better representation.

tion seems to be very similar to that of the shear viscosity coefficients of isotropic liquids for which no parameter-free equation was found which is valid for a large number of systems.[13]

Figure 4 shows the $\gamma_1$ values for the mixtures of the two homologues MBBA and EBBA. The EBBA curve is shifted to the upper left side because of the higher clearing point and the larger molecular length of this component. Apart from the absolute values, the curves are very similar to the $\gamma_1$ curves of the esters. The least squares fits according to Eq. (1) result in nearly equal activation energies $C \cdot R$ ($\approx 1100 \cdot R$), exponents $B$ (.25–.28), glass temperatures $T_0$ (150–200 K) and temperature differences $T^* - T_{\mathrm{NI}}$ (0.3–1.0 K). At low temperatures, ln $\gamma_1$ depends almost linearly on mole fraction (Figure 5). As the rotational viscosity coefficients of the

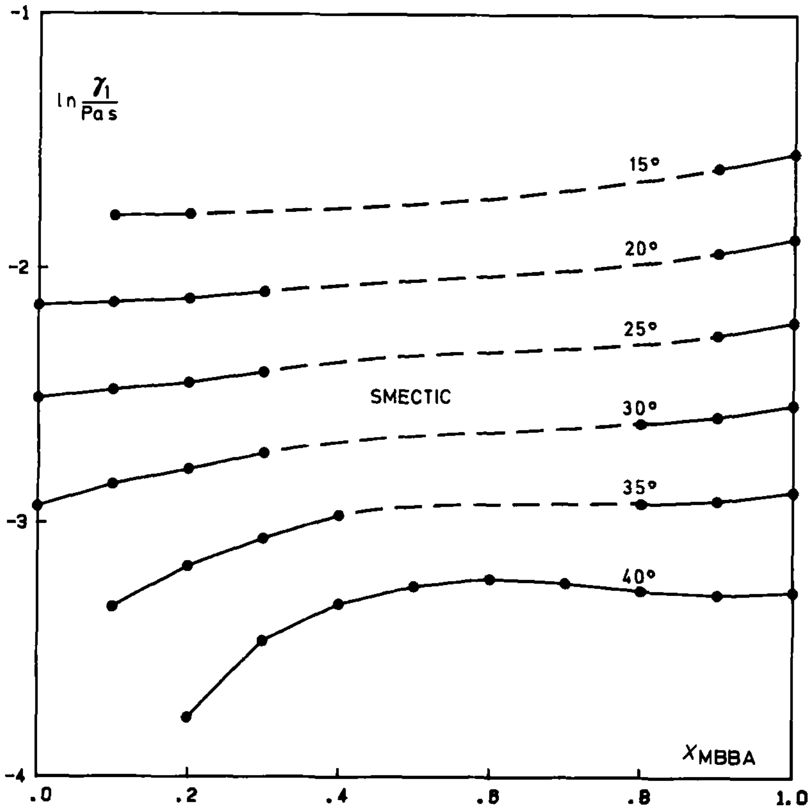


FIGURE 7 Logarithm of $\gamma_1$ for MBBA/5CBP mixtures vs mole fraction of MBBA. Broken lines are a guide for the eye.

two components are only slightly different, this result cannot be taken as further proof for a more or less logarithmic dependence on concentration. Due to the different clearing temperatures, the order parameter depends on concentration at higher temperatures and this results in a nonlinear dependence of $\gamma_1$ on concentration.

The system MBBA/5CBP (Figure 6) exhibits an induced smectic phase at intermediate concentrations; an $S_B$ phase is shown at high temperature and an $S_E$ phase at low temperature.[14,15] Therefore, the temperature range of the nematic phase is rather limited at intermediate concentrations. Pretransitional phenomena, which would lead to a divergence of $\gamma_1$ at the nematic-smectic phase transition, are not observed. Obviously, the highly ordered smectic phases exhibit first order transitions to the nematic phase. Pretransitional phenomena should also cause divergences in the com-

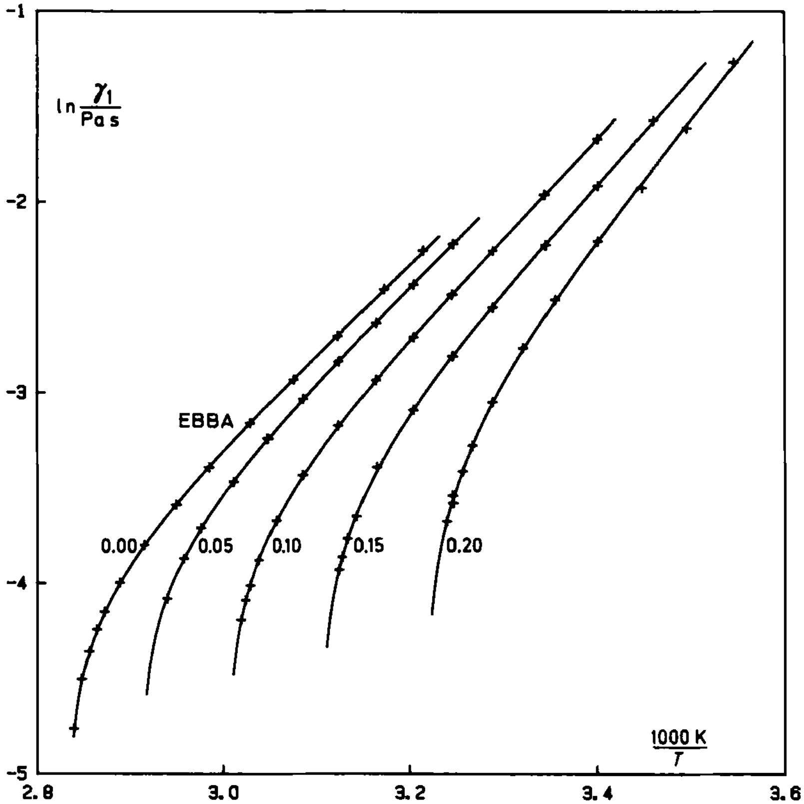


FIGURE 8 Logarithm of $\gamma_1$ for MBBA/BP mixtures vs inverse temperature for different mole fractions of BP.

position diagram (Figure 7); these are not observed. $\gamma_1$ is not defined in the smectic phase and the broken lines are only a guide for the eye. The smooth continuation of the curves on the other side of the smectic region without any indication of an extremum may be taken as a further proof for the assumption[7] that the association in 5CBP[16] does not influence the rotational viscosity to a large extent. Because of a maximum of the nematic-isotropic transition temperature at intermediate concentrations and the low clearing temperature of 5CBP, the curves in Figure 7 become bent for high temperatures where the order parameter depends strongly on concentration.

In the system EBBA/BP, only mixtures with low BP content could be investigated as the clearing temperature drops below room temperature at higher BP concentration. The curves in Figure 8 exhibit an increase in slope with increasing BP concentration. Whether this increase is due to a variation of the activation energy, of the exponent $B$ in Eq. (1) or the glass temperature, could not be evaluated. Especially at higher BP concentrations, the temperature range for the $\gamma_1$ measurements becomes too small for an unambiguous determination of these parameters. The admixture of BP for the purpose of viscosity reduction does not seem to be advantageous. Of course, there is a strong reduction, but the decrease in clearing temperature and the increase in temperature dependence seem to cancel this advantage. Materials for this purpose must be mesogenic in order to keep the clearing temperature constant and must be as small and nonpolar as possible in order to give a low viscosity. The alkyl- and alkoxy-substituted cyclohexylbenzenes and biphenyls which are used for this purpose[17] seem to fit into this scheme.

## Acknowledgments

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