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 Blachnik, N. , Kneppe, H. and Schneider, F.(2000) 'Cotton-Mouton constants and pretransitional phenomena in the isotropic phase of liquid crystals', Liquid Crystals, 27: 9, 1219 — 1227
To link to this Article: DOI: 10.1080/02678290050122079
URL: http://dx.doi.org/10.1080/02678290050122079

Liquid Crystals, 2000, Vol. 27, No. 9, 1219–1227

Cotton–Mouton constants and pretransitional phenomena in the isotropic phase of liquid crystals

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(*Received 28 December 1999; accepted 23 March 2000*)

The Cotton–Mouton constants for three homologous series of liquid crystals were measured in the isotropic phase. Some of these measurements were performed with high temperature resolution. The results are compared with theories on pretransitional phenomena. The Landau–de Gennes theory proves to be inadequate to describe the data.

1. Introduction

The Cotton–Mouton effect in the isotropic phase of liquid crystal materials has been studied by several groups since the first measurements by Zadoc-Kahn in 1930 [1, 2]. De Gennes [3, 4] developed a theory for this effect by extending the Landau theory for continuous phase transitions with respect to pretransitional phenomena in liquid crystals. All subsequent experimental studies have used this Landau–de Gennes theory for the evaluation of the data. Though the results of some investigations did agree with this theory in a limited temperature range, it became apparent that it fails in the neighbourhood of the clearing point [5].

Our aim was to test the Landau–de Gennes theory and some new theories which have been developed in the meantime. We have developed an experimental set-up which allows the determination of the Cotton–Mouton (CM) constants and the temperature with a rather good precision. Three homologous series of liquid crystals were studied. Some measurements were performed with a high temperature resolution and more than 70 measurements at different temperatures for one component. The data are compared with the Landau–de Gennes theory and new theories.

The CM constant diverges in the isotropic phase when approaching the clearing point and ends with a finite value at this point. As there are some hints that this quasi-divergence depends on the transition enthalpies we have measured the latter and tried to correlate these with the strength of the divergence.

2. Experimental methods

The Cotton–Mouton constant

$$CM = \frac{\Delta n}{\lambda \mathbf{H}^2} \tag{1}$$

is determined from the magnetically induced birefringence

$$\Delta n = n_e - n_o \tag{2}$$

and the magnetic field strength $\mathbf{H}$. λ is the wavelength of light and n_e and n_o are the indices of refraction for parallel and perpendicular polarization with respect to the magnetic field.

A schematic diagram of the experimental set-up is shown in figure 1. The light of a He-Ne laser (632.8 nm, 5 mW, polarized) is passed through a polarizer (Glan–Thompson prism, extinction ratio 10^{-5}). Behind the Pockels cell (Gsänger, KD_2PO_4, longitudinal type, half-wave voltage 4 kV) and the sample, the light is passed through a crossed analyser of the same type. Thus there is almost no response of the detector (photodiode, Hamamatsu, S2386-18L) if no voltage is applied to the Pockels cell and the sample is isotropic.

If a magnetic field at 45° with respect to the polarization direction is applied to the sample, it becomes birefringent and the outcoming light is elliptically polarized. The phase retardation is compensated by applying a voltage to the Pockels cell until the light is extinguished by the crossed polarizer. The Pockels cell was thermostatted by means of a water thermostat within 0.1°C.

In order to enhance the sensitivity of measurement, the compensation voltage was modulated by a small a.c. voltage with a frequency of 7 kHz. The detector output

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Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2000 Taylor & Francis Ltd
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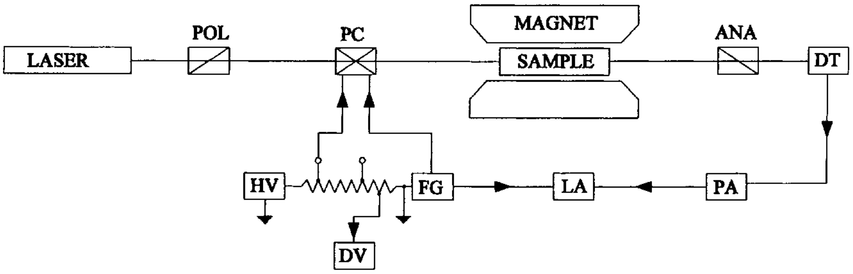

Figure 1. Schematic diagram of the experimental set-up. POL: polarizer, PC: Pockels cell, ANA: analyser, DT: detector, PA: preamplifier, LA: lock-in amplifier, FG: frequency generator, HV: high voltage source, DV: digital voltmeter.

passed a preamplifier and was measured with a lock-in amplifier (Stanford, SR810). The minimum of light intensity now corresponds to a zero crossing of the lock-in output.

The magnetic field was generated with an electromagnetic (Bruker, pole face diameter 25 cm) with an induction of 1.7 T at a pole face distance of 25 mm. The strength of the magnetic field was controlled by means of a Hall-effect device which was calibrated with a NMR gaussmeter.

The sample vessel was made of a quartz tube with optically plane windows at the ends (Hellma, 10 cm length, 5 mm inner diameter). The vessel was surrounded by a housing made of brass in which water or oil from a thermostat was circulating. The windows and the meniscus of the liquid crystal in the inlet were placed in the interior of the thermostatted part of the housing. Thus the temperature variation within the sample was very small. Two thermostats were used for the experiments. One thermostat (Haake, C6CP) permitted temperature control with 0.01–0.02 K; the other was developed in our laboratory and permitted control with 0.0004 K. The temperature measuring system of the latter was calibrated against a thermometer with an absolute deviation of ≈1 mK (Paar, MTK 25).

The Cotton–Mouton constant CM was determined according to

$$CM = \frac{1}{2lU_{1/2}} \frac{\Delta U}{\Delta \mathbf{H}^2} \tag{3}$$

where l is the length of the sample, $U_{1/2}$ the half-wave voltage of the Pockels cell and $\Delta U/\Delta \mathbf{H}^2$ the change of the voltage applied to the Pockels cell divided by the change in the field strength squared. This quotient was usually determined from measurements at inductions of 0 and 1.7 T. For these field strengths, the field dependence of the CM constant in the neighbourhood of the clearing point can be neglected [6].

Special attention was paid to the adjustment of the 45° angle of polarizer and analyser with respect to the field direction and the 90° angle between light ray and field direction. The latter angle was adjusted by means of the Faraday effect of a CCl_4 sample which exhibits nearly no CM effect [7], but a strong Faraday effect [8] which disappears at 90°.

Most of the liquid crystals were commercial products (alkyl- and alkyloxy-cyanobiphenyls from Merck Ltd, UK, alkylcyanophenylcyclohexanes from E. Merck, Darmstadt). They were used without further purification. Other liquid crystals were synthesized in our laboratory. We use the following abbreviations where *n* denotes the alkyl chain length:

alkylcyanobiphenyls	*n*CBP
alkyloxycyanobiphenyls	*n*OCBP
alkylcyanophenylcyclohexanes	*n*PCH
4-methyloxybenzylidene-4′-*n*-butylaniline	EBBA
4-ethyloxybenzylidene-4′-*n*-butylaniline	EBBA
4-*n*-butylbenzoic acid 4-*n*-hexyloxyphenyl ester	4-O6
4-*n*-butylbenzoic acid 4-*n*-heptyloxyphenyl ester	4-O7

The liquid crystals were filled into the sample vessel by means of a thermostatted and evacuated glass flask in which the liquid crystal was contained in the isotropic phase. Rotation of the bulb and injection of nitrogen allowed transfer of the liquid crystal into the sample vessel through a second neck. During measurements the sample was maintained under nitrogen. This filling method avoids any contact with ferromagnetic materials. The disastrous effect of some (!) ferromagnetic particles from a stainless steel needle which was used for filling with a syringe is shown in figure 2. We believe that some problems described in the literature [9, 10] are due to this magneto-optical Kerr effect of ferromagnetic particles.

The CM constants measured with our set-up for benzene (7.94×10^{-15} m A^{-2}) and toluene (8.28×10^{-15} m A^{-2}) at 25°C agree with the values of Battaglia and Ritchie [7] within 1%.

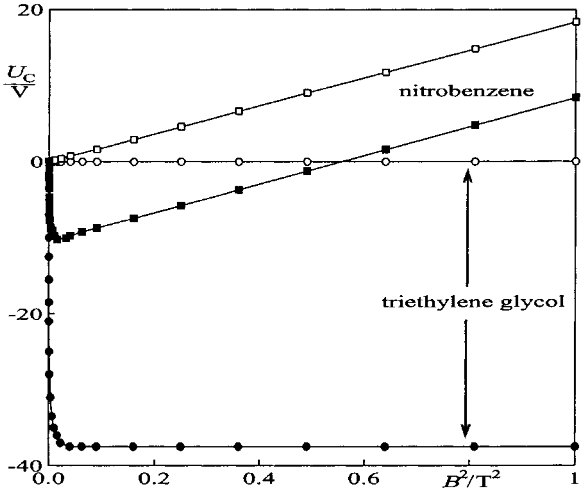

Figure 2. CM effect for nitrobenzene and triethylene glycol for pure compounds (open symbols) and contaminated with steel particles (full symbols). U_C is the compensation voltage at the Pockels cell.

Transition enthalpies were determined with a differential scanning calorimeter (Perkin Elmer, DSC7). The values, for which a comparison with earlier data from Thoen *et al.* [11–13] and Orwoll *et al.* [14] is possible, agree within 3%. Data are shown in table 1.

3. Experimental results and discussion

3.1. *Maximum CM constant and transition entropy*

As the isotropic–nematic transition is of first order, the CM constants in the isotropic phase remain finite and do not diverge as in the case of a continuous transition. There is a maximum value $CM_{\max}$ at the clearing point in the isotropic phase which can be measured with an accuracy of about 10% in spite of the extreme steepness of the CM curve as a function of temperature in that region. Figure 3 shows how this maximum value depends on the inverse of the transition entropy ΔS of isotropization. Within a homologous series we observe a rather good linear dependence. Even compounds with isotropic–smectic transitions lie on the corresponding line. The slopes of the lines are different for the various series as the anisotropies of the molecular magnetic susceptibilities and the polarisabilities exhibit different values

This observation is in agreement with the Landau–de Gennes theory if an additional assumption is made. The Landau–de Gennes ansatz for the free energy density is

$$F_N = F_0 + \frac{1}{2}a(T - T^*)Q^2 - \frac{1}{3}BQ^3 + \frac{1}{4}CQ^4 \quad (4)$$

Table 1. Phase sequences, transition entropies ΔS to the isotropic phases and maximum CM constants $CM_{\max}$.

Compound	Phase sequence[a]	$\frac{\Delta S}{\mathrm{J\,mol^{-1}\,K^{-1}}}$	$\frac{CM_{\max}}{10^{-15}\,\mathrm{m A^{-2}}}$
5CBP	Cr 22.5 N 34.8 I	1.20	3280
6CBP	Cr 13.5 N 29.1 I	0.91	4627
7CBP	Cr 28.5 N 42.6 I	1.78	2390
8CBP	Cr 21.0 SmA 32.5 N 40.5 I	1.94	2407
9CBP	Cr 40.5 SmA 44.5 N 49.7 I	3.56	1037
10CBP	Cr 44.0 SmA 51.6 I	8.59	394
11CBP	Cr 52.6 SmA 57.0 N 57.1 I	10.96	218
12CBP	Cr 43.5 SmA 58.5 I	12.42	147
5OCBP	Cr 53.0 N 68.1 I	0.54	7920
6OCBP	Cr 58.0 N 76.8 I	0.79	5621
7OCBP	Cr 53.5 N 74.6 I	0.72	6277
8OCBP	Cr 54.5 SmA 67.0 N 79.0 I	1.28	3812
9OCBP	Cr 65.0 SmA 76.0 N 78.8 I	1.87	2484
10OCBP	Cr 61.0 SmA 84.1 I	7.56	636
11OCBP	Cr 71.0 SmA 86.7 I	9.85	256
PCH3	Cr 36.0 N 46.3 I	2.64	196
PCH4	Cr 41.0 (N39.5) I	1.62	348
PCH5	Cr 31.0 N 54.6 I	2.31	259
PCH7	Cr 30.0 N 58.2 I	2.43	224
MBBA	Cr 21.8 N 45.7 I	1.57	5100
EBBA	Cr 37.0 N 79.9 I	1.27	2378
4-O6	Cr 29.1 N 48.0 I	1.74	1393
4-O7	Cr 35.0 N 43.3 I	1.60	1728

[a] Clearing temperatures from CM measurements; other transition temperatures from [15].

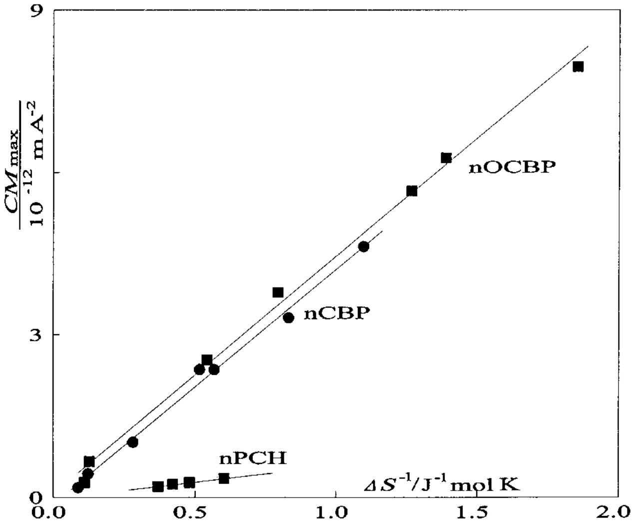

Figure 3. Maximum CM constant CM_{max} as a function of the inverse transition entropy.

with a, B, $C =$ const, Q is the order parameter and T^* is the temperature at which the isotropic phase would be transformed into the nematic phase by a continuous transition. This ansatz leads to the following equations

$$S_I - S_N = \Delta S = \frac{1}{2} a Q_{NI}^2 \qquad (5)$$

$$Q_{NI} = \frac{2B}{3C} \qquad (6)$$

$$T_c - T^* = \frac{2B^2}{9aC} \qquad (7)$$

where S is the entropy and T_c is the temperature of clearing.

According to Stinson and Litster [16] the CM constant of an isotropic sample of a liquid crystal is

$$CM = \frac{\mu_0 \varepsilon_a \chi_a}{6\lambda\sqrt{\bar{\varepsilon}}} \frac{1}{a(T - T^*)} \qquad (8)$$

where ε_a and χ_a are the anisotropies of the dielectric constant and the magnetic susceptibility for a completely ordered liquid crystal. $\bar{\varepsilon}$ is the trace of the dielectric constant tensor. Elimination of a and $T - T^*$ with equations (5), (6), and (7) gives

$$CM_{max} = \frac{\mu_0 \varepsilon_a \chi_a}{6\lambda\sqrt{\bar{\varepsilon}}} \frac{a}{C\Delta S} = \frac{K}{\Delta S}. \qquad (9)$$

Assuming K to be constant within a homologous series, this leads to the experimental observation. The slopes of the straight lines differ due to the different values of ε_a and χ_a.

Furthermore, we have tried to eliminate the variation of the slopes by using the half temperature values $T_{1/2}$ instead of CM_{max}. $T_{1/2}$ is the temperature difference in which CM decreases from the maximum to half the value. However, the corresponding diagram showed even within one series a greater scattering than the CM_{max} values.

3.2. *Temperature dependence of the CM constant*

3.2.1. *Landau–de Gennes theory*

First we repeated the measurements of Stinson and Litster [16, 17] who used the Landau–de Gennes theory for the evaluation of the temperature dependence of the CM constants for the first time. Figure 4 shows the CM constants of MBBA as measured by Stinson and Litster and by us.

The Landau–de Gennes theory predicts a temperature dependence of the form

$$CM^{-1} = C(T - T^*) \qquad (10)$$

for the CM constant of a nematic liquid crystal above the clearing point. Plotting CM^{-1} as a function of temperature should therefore give a straight line. Stinson and Litster have concluded from their data that this linear dependence is fulfilled except for a small temperature range directly above the clearing point. Our measurements on a purer sample show that the bent part of this plot extends over a greater temperature range. Even at high temperatures a slight bending is observed. The CM constant at the clearing point is considerably smaller than measured by Stinson and Litster.

For a detailed study of the Landau–de Gennes plot we used 4-O6 instead of the chemically unstable MBBA.

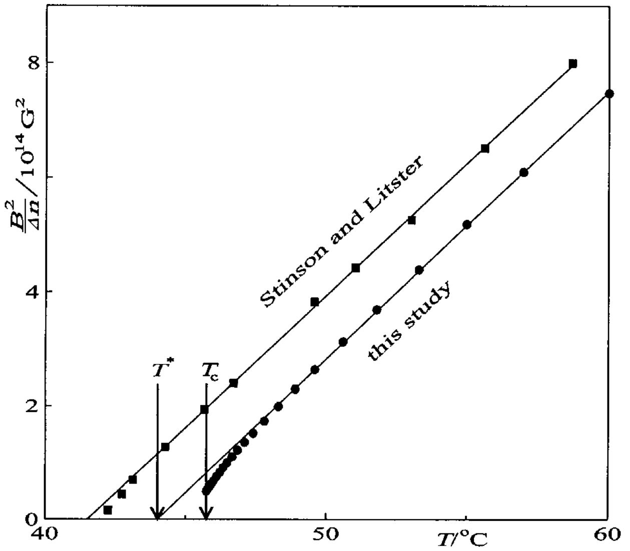

Figure 4. $B^2/\Delta n$ (inverse CM constant without λ) as a function of temperature for MBBA.

Both compounds are of medium polarity. Figure 5 shows the measurements on 4-O6 with high temperature resolution.

The deviations from the Landau–de Gennes line depend on the temperature range which is used for the linear regression. Figure 6 shows these deviations for a fit between 50 and 75°C. Other temperature ranges lead essentially to a rotation of the deviation curve without changing its form. As the deviation curve shows bending up to high temperatures, there is no temperature range in which a fit according to the Landau–de Gennes theory makes sense.

The often discussed temperature T^*, i.e. the intersection of the Landau–de Gennes line with the abscissa, depends strongly on the fit range. Table 2 shows this for the 4-O6 measurements. We have found $T_c - T^*$ values up to 10 K for other liquid crystals if the measurements are extended to higher temperatures and the high temperature range is used for the fit. Keeping this in mind, the long standing discussion, whether the difference $T_c - T^*$ is 1 K or not, makes no sense.

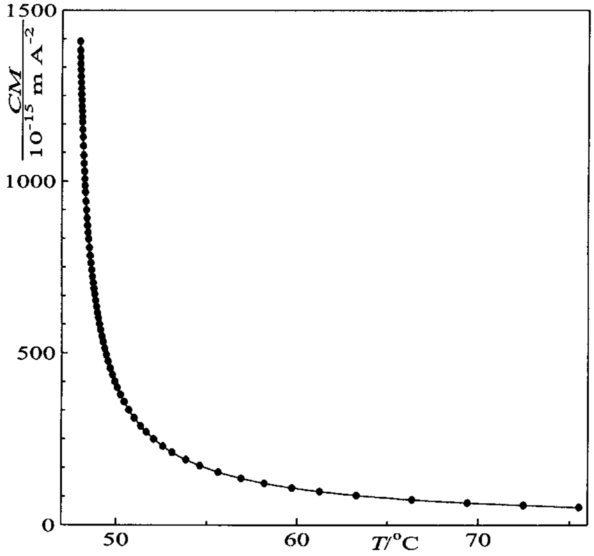

Figure 5. Cotton–Mouton constant of 4-O6 as a function of temperature.

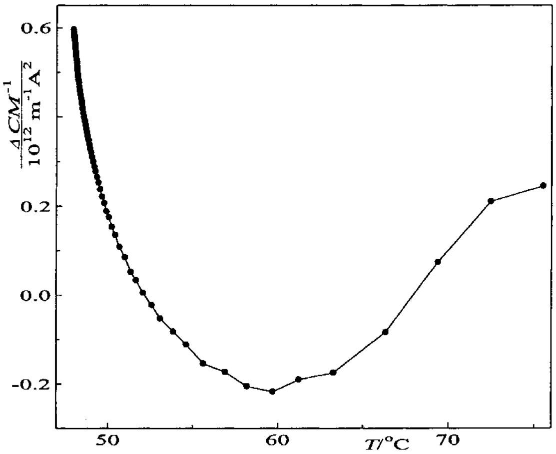

Figure 6. Residua of the Landau–de Gennes fit beween 50 and 75°C for 4-O6.

Finally, the plot of CM^{-1} versus temperature hides the errors of the Landau–de Gennes theory as the diverging quantity goes to zero and the temperature range in which the divergence takes place is rather small. The usual plot for diverging quantities at continuous transitions is the double logarithmic plot of the diverging quantity versus $T - T^*$. This is shown in figure 7.

From figure 7 diagram it is obvious that the Landau–de Gennes theory does not describe the temperature dependence of the CM constants in the isotropic phase of nematic liquid crystals very well. Due to the deficiencies of the Landau–de Gennes theory some improvements

Table 2. Differences $T_c - T^*$ and correlation coefficients as a function of the temperature range of the Landau–de Gennes fit for 4-O6.

Temperature range/°C	$(T_c - T^*)$/K	Correlation coefficient
57–76	2.85	0.999 904
52–76	2.27	709
49–76	1.75	440
52–61	1.78	886
49–61	1.46	647
52–57	1.63	946
49–52	1.18	833

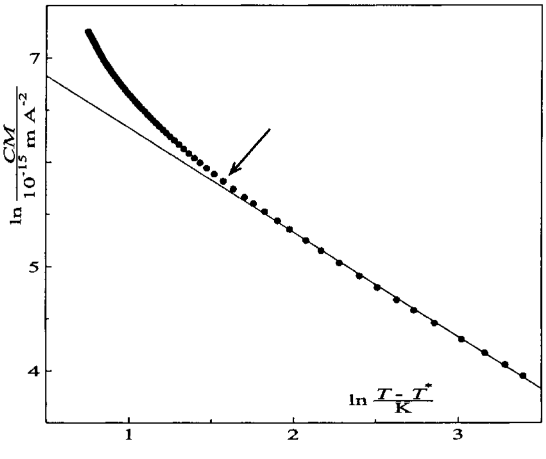

Figure 7. Double logarithmic plot of the CM constant of 4-O6 versus $T - T^*$. $T^* = 45.852$°C has been obtained by a linear fit of the values from the marked value up to high temperatures in a standard Landau–de Gennes plot (see figure 4). The straight line in this diagram corresponds to this linear fit.

have been suggested in recent years. These theories take into account nematic fluctuations [18], smectic fluctuations [19, 20] or adjustable exponents [3–5, 21] in the Landau–de Gennes equation, i.e. it is used like a critical law.

In order to test these theories we have studied the commercially available homologous series of liquid crystals *n*CBP, *n*OCBP and *n*PCH. Although the investigation of a series with non-polar molecules would be even more interesting, we have put this consideration aside because of the time required to produce such a series by synthesis.

Figures 8, 9 and 10 show the inverse CM constants as a function of temperature, i.e. Landau–de Gennes plots, for these series. It should be noted that phase transitions from the nematic to the isotropic phase as well as smectic–isotropic phase transitions are involved (see table 1).

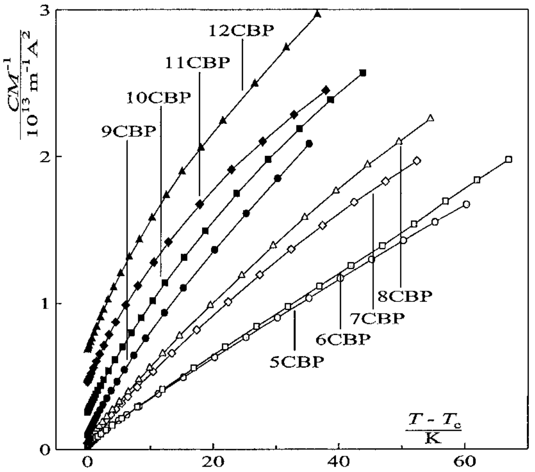

Figure 8. Inverse CM constant as a function of temperature for the homologous alkylcyanobiphenyls.

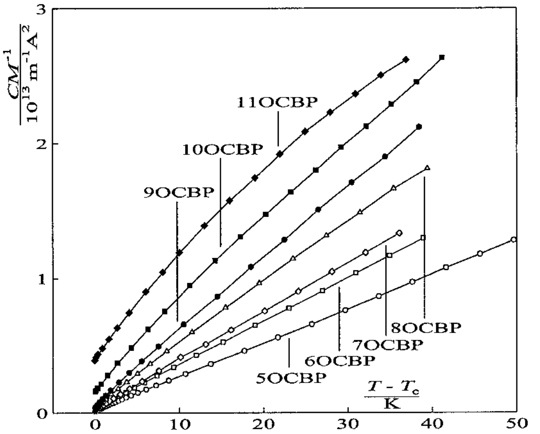

Figure 9. Inverse CM constant as a function of temperature for the homologous alkyloxycyanobiphenyls.

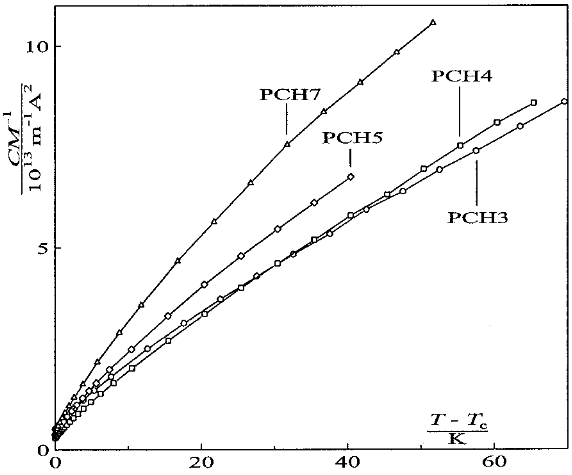

Figure 10. Inverse CM constant as a function of temperature for the homologous alkylcyanophenylcyclohexanes.

A comparison of figures 8, 9 and 10 leads to the following statements.

1. (1) The short homologues in the alkyl- and alkyloxy-cyanobiphenyl series show the smallest deviations from the Landau–de Gennes theory. The curves for the longer homologues are bent over the whole temperature range.
2. (2) There are no noticeable changes in the curves if the phase transition changes from nematic-isotropic to smectic-isotropic.
3. (3) The alkylcyanophenylcyclohexanes always show bent curves though there are no smectic phases present. The CM constants of the alkylcyanophenylcyclohexanes are smaller in comparison with the other series as the anisotropies of the magnetic susceptibilities are smaller.

From the above we can conclude that the presence of smectic phases cannot be the only reason for the deviations from the Landau–de Gennes theory. The short alkyl- and alkyloxy-cyanobiphenyls show an alternation of the proportionality constants between CM^{-1} and $T - T^{*}$ with chain length [10, 22, 23]. This is shown in detail in figure 11. The temperature range for the Landau–de Gennes fit was between 5 and 25 K above the clearing point. Probably, the PCH series also shows this effect. Unfortunately, the complete series of PCHs was not available to us.

3.2.2. *Theory of Fan and Stephen: nematic fluctuations*

The Landau–de Gennes theory is a static theory which does not take into account nematic fluctuations in the isotropic phase. Fan and Stephen [18] have incorporated these fluctuations into the theory and developed the following equation for the temperature dependence

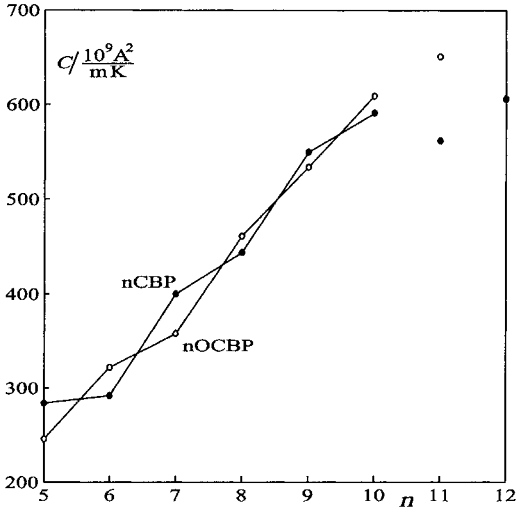

Figure 11. Proportionality constant C (see equation (10)) for the alkyl- and alkyloxy-cyanobiphenyls as a function of chain length. n is the number of carbon atoms in the chain.

which is shown in the form presented by Anisimov [24]

$$CM^{-1} \propto a\left(\frac{T-T^*}{T^*}\right)\left[1+\frac{7}{2\pi^2}\frac{c}{a^2}\frac{v_0}{\xi_0^3}\frac{T^{*1/2}}{(T-T^*)^{1/2}} - \frac{7}{4\pi^2}\frac{b^2}{a^3}\frac{v_0}{\xi_0^3}\frac{T^{*3/2}}{(T-T^*)^{3/2}}\right] \tag{11}$$

where a, b and c are the coefficients of the Landau expansion in dimensionless form. v_0 is the molecular volume and ξ_0 is the coherence length at 0 K. As these coefficients are not known with sufficient precision they are lumped together in the three new coefficients P_1, P_2, and P_3

$$CM^{-1} = P_1\left(\frac{T-T^*}{T^*}\right)\left[1+\frac{P_2}{(T-T^*)^{1/2}} - \frac{P_3}{(T-T^*)^{3/2}}\right] \tag{12}$$

i.e. the equation contains four adjustable parameters. We find from the transition enthalpy, the order parameter in the nematic phase at the clearing point, the difference $T_c - T^*$, and $v_0/\xi_0^3 \approx 2$ (according to Anisimov)

$$P_2 = (1\ \mathrm{K})^{1/2}; \qquad P_3 = (1\ \mathrm{K})^{3/2}$$

i.e. the terms in the bracket are of the same magnitude at the clearing point ($T - T^* \approx 1$ K) and no term can be neglected. Fits with our 4-O6 measurements showed however that the influence of the last term in equation (12) is comparably small, i.e. $P_2 = 1.16$ and $P_3 = 0.18$ for 4-O6, and that the standard deviation of the fit does not increase much if the three parameter equation

$$CM^{-1} = P_1\left(\frac{T-T^*}{T^*}\right)\left[1+\frac{P_2}{(T-T^*)^{1/2}}\right] \tag{13}$$

is used.

We have fitted this equation to the 4-O6 data on a logarithmic scale, i.e. the relative deviations between the data and equation (13) are minimized. The fitting parameters T^* and $P_2 = 1.27$ show the correct order of magnitude. As the remaining deviations are not observable on a plot, we have plotted the logarithmic residua in figure 12. The deviations show a systematic dependence on temperature. However, the mean relative deviation of 0.35% is only 10^{-4} of the total variation and can be caused by small errors of measurement or slight changes of the parameters over the temperature range of nearly 30 K.

The major part of the errors of the Landau–de Gennes theory is obviously removed by the Fan and Stephen equation with three parameters. The arguments for that are: (i) the precise fit, (ii) the reasonable values for T^* and P_2, (iii) similar precise fits for the lower homologues of the series studied. For the compounds with longer chain lengths the fits worsen with the chain length although the variation range of the CM constants becomes smaller. This may be caused by two effects: (i) the transition enthalpy increases with chain length, (ii) the influence of smectic phases increases with chain length, which will be discussed below. It is a difficult problem to separate the influence of these effects.

3.2.3. *Smectic fluctuations*

Anisimov *et al.* [19], as well as Gohin *et al.* [20], have independently developed a theory which takes into account the coupling of smectic and nematic fluctuations. There are experimental indications that this coupling

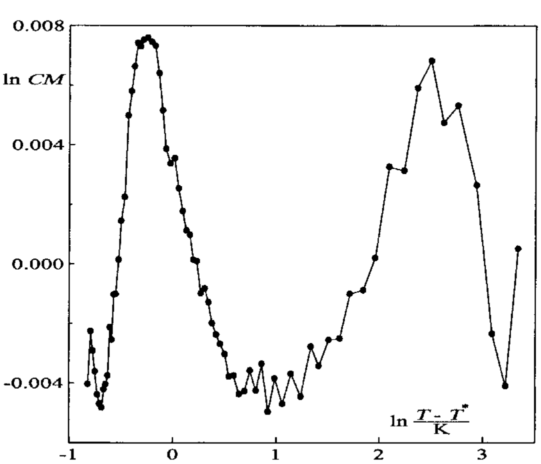

Figure 12. Logarithmic residua of a fit of the CM constant for 4-O6 with equation (13) as a function of temperature.

can give a contribution to the divergence of the CM constants. According to Gohin *et al.* the corresponding equation may be written as

$$CM^{-1} \propto a(T - T^*) + \frac{\chi}{(T - T^*_{\mathrm{SI}})^{1/2}} - \frac{\lambda^2}{(T - T^*_{\mathrm{SI}})^{3/2}} \qquad (14)$$

where χ and λ are the coupling constants between the smectic and nematic fluctuations and T^*_{SI} is the absolute stability limit for the isotropic phase against its transformation into the smectic phase without coupling. Gohin *et al.* have estimated that this coupling must lead to an experimentally observable effect. The equation is similar to equation (12), but it contains five adjustable parameters as the proportionality constant can be integrated into a, χ, and λ^2. As the two correcting terms have similar temperature dependences and three adjustable parameters, there is a clear risk that a fit leads to unreasonable values for χ, λ, and T^*_{SI}. Due to the similarity with equation (12) and the large number of adjustable parameters, (14) gives a perfect fit of the experimental data. Table 3 contains some data for the phase transitions and the difference $T^* - T^*_{\mathrm{SI}}$.

Despite all the dangers described above and the fact that T^*_{SI} is not an experimentally observable quantity (phase transition smectic–isotropic without coupling of the order parameters), the differences $T^* - T^*_{\mathrm{SI}}$ do not correspond to our expectations. The uncertainty of this statement cannot be improved by CM data on further liquid crystals as there is no possibility to change χ, λ and/or T^*_{SI} without changing $\Delta\mathbf{H}$, a, b, c, and T^*. Also, due to similar arguments the investigation of mixtures [25] will not lead to a solution of the problem.

3.2.4. *Using a critical law*

As the nematic–isotropic transition enthalpy for liquid crystals is usually rather small, it seems adequate to use the Landau–de Gennes equation (10) in the form of a critical law.

$$CM = c(T - T^*)^{-\gamma}. \qquad (15)$$

Table 3. Transition temperatures nematic/isotropic T_c, smectic/nematic T_S, and difference $T^* - T^*_{\mathrm{SI}}$ from the fit.

Compound	T_c/K	T_S/K	$(T^* - T^*_{\mathrm{SI}})$/K
8CBP	313.7	305.7	5.4
9CBP	322.9	317.7	10.8
11CBP	330.3	330.2	102.6
8OCBP	352.2	340.2	0.7
9OCBP	352.0	349.2	0.8
PCH3	319.5	—	19.2
PCH4	312.7	—	68.9
PCH5	327.8	—	11.9
PCH7	331.4	—	23.5

De Gennes also proposed this form and only mentioned that $\gamma = 1$ follows from a mean field theory such as the Maier–Saupe theory. Figure 13 shows the residua of a fit of this equation in logarithmic form to the 4-O6 data. There are systematic deviations up to 2%. Several reasons may lead to these deviations. The temperature range of nearly 30 K is by far too large for a reasonable fit with a critical law. The isotropic–nematic transition is not a continuous one. This will lead to restrictions concerning the critical behaviour. The exponent γ is supposed to be approximately 1.3 whereas the fit for the whole temperature range gives 0.855. Figure 14 shows that a smaller temperature range for the fit gives even smaller γ values.

These small exponents are shown by all liquid crystals studied. Figure 15 summarizes the results for fits over a temperature range of 1 K. The diagram does not contain the liquid crystals with the longest alkyl chains which exhibit only smectic phases and show a minor divergence with exponents of approximately 0.3.

Independent of the polarity and the alkyl chain length, the mean exponent is 0.75 ± 0.07, which is far from the

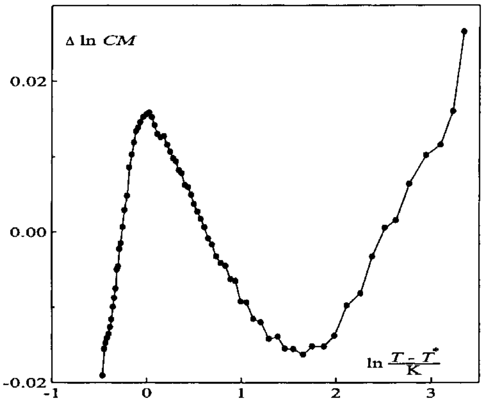

Figure 13. Logarithmic residua of a fit of the CM constant for 4-O6 with equation (15) as a function of temperature.

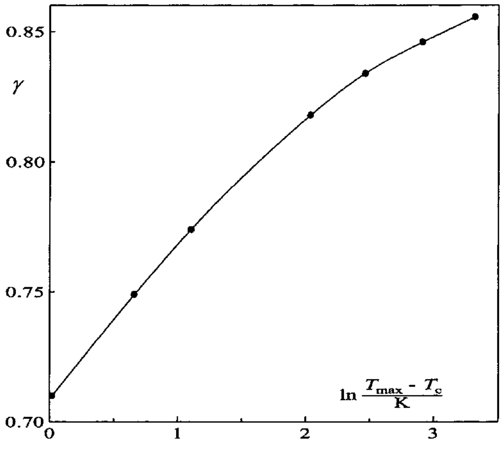

Figure 14. Exponent γ as a function of the fit range.

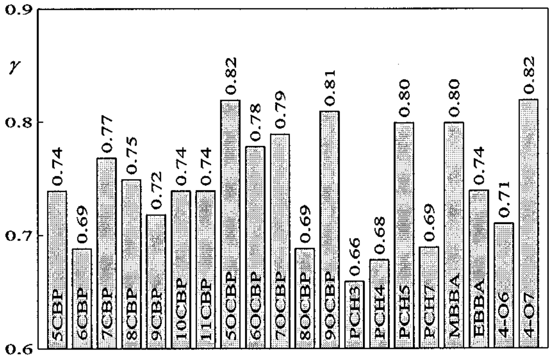

Figure 15. Exponents of the fit with equation (15) over a temperature range of 1 K for some liquid crystals.

theoretical value. The reason for this difference could be that the critical region is not accessible due to the first order transformation into the nematic phase or that there is a cross-over between critical and Landau–de Gennes behaviour [5] in the accessible temperature range. Finally Keyes [26] and Mukherjee [27] show that the behaviour of the NI transition can be tricritical. However, this should not change the values of the exponent very much.

4. Conclusion

The temperature dependence of the Cotton–Mouton constant has been determined for three homologous series of liquid crystals in their isotropic phases. The accuracy of the measurements allows an examination of the validity of theoretical predictions for the temperature dependence. The Landau–de Gennes theory describes the temperature dependence insufficiently well. Plotting the inverse Cotton–Mouton constant against the temperature results in bent curves. This bending is not limited to a region in the neighbourhood of the clearing point, but stretches across the whole isotropic phase. If equations which take nematic or smectic fluctuations into account are used, the residua in the fits decrease strongly. Especially, the equation of Fan and Stephen which takes into account nematic fluctuations gives a nearly perfect fit if three adjustable parameters are used.

A critical law gives a reasonable fit with three adjustable parameters. For all liquid crystals investigated, the critical exponent is smaller than unity which is far from theoretical predictions. We cannot find any systematic behaviour of the critical exponent from a comparison within and between the homologous series.

The maximum CM constant obtained at the clearing point was found to be proportional to the inverse transition entropy.

It is a pleasure for us to thank E. Merck, Darmstadt for supplying the alkylcyanophenylcyclohexanes. Financial support by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the Graduiertenkolleg Molekulare Ordnung und Reaktivität at the University of Siegen is gratefully appreciated.

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