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## Liquid Crystals

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# Kerr effect studies on mixtures of liquid crystals

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The electro-optical Kerr effect was studied for mixtures of low molar mass liquid crystals within the isotropic phase in the neighbourhood of the nematic phase. The mixtures are characterized by components having similar or antagonistic dipole configurations, as well as different molecular geometries (calamitic and discotic). The investigations reveal that simple mixing rules can be applied for the description of the Kerr response of the mixtures in spite of the fact that the Kerr response displays a set of unusual features, among them a temperature induced sign inversion and synergistic effects.

## 1. Introduction

Mixtures of low molar mass liquid crystals, in particular of nematic materials, are used in display applications where dielectric and optical properties of the system control the coupling to the external fields and the optical response [1–3]. This contribution is concerned with electro-optical studies involving the Kerr effect in such mixtures. It is the aim of the investigations to obtain a better understanding of intermolecular correlation effects occurring in such mixtures.

Nematic liquid crystals are known to display unusual electro-optical properties within the isotropic phase as the nematic–isotropic transition temperature is approached [4–6]. The electric field induced birefringence,  $\Delta n$ , which increases proportionally to the square of the electric field  $\mathbf{E}$  (see equation (1)) diverges at a temperature  $T^*$  which in the majority of cases is located slightly below the transition temperature  $T_{\text{NI}}$ .

$$\Delta n = B\lambda\mathbf{E}^2 \quad (1)$$

where  $B$  is the Kerr constant and  $\lambda$  the wavelength of the light.

De Gennes [7] has treated this phenomenon using a Landau expansion of the free energy of the system with respect to the orientational order parameter  $S$ . He argues that the phase transition is first order for symmetry reasons, yet that it is only weakly so, and pretransitional fluctuations are thus observable. The magnitude of such fluctuations grows with decreasing temperature similarly to the case for critical systems. Using the approach described above, one may represent the temperature

dependence of the Kerr constant  $B$  as follows:

$$B \propto \frac{1}{(T - T^*)^\gamma} \quad (2)$$

with  $\gamma = 1$ .

Using a statistical mechanical treatment, we may trace back the divergence of the Kerr constant to the divergence of the orientational correlation factor  $g_2$  defined as [8]

$$g_2 = 1 + \frac{1}{2} \sum_{i,j} \langle 3 \cos^2 \theta_{ij} - 1 \rangle \quad (3)$$

i.e.

$$g_2 \propto \frac{1}{(T - T^*)^\gamma} \quad (4)$$

The expression obtained from such a treatment is

$$B \propto \left\{ \Delta\alpha g_2 + f_c \frac{\mu^2}{kT} [2(g_1 - 1) + g_2] \right\} \quad (5)$$

with the geometric factor

$$f_c = \frac{1}{2} (3 \cos^2 \beta - 1). \quad (6)$$

where  $\beta$  is the angle between the dipole direction and the principal axis of polarizability and  $g_1$  is the Kirkwood correlation factor which is usually below 1. A common finding is that the correlation factor  $g_2$  is of the order of  $10^2$  at the transition temperature  $T_{\text{NI}}$ . The sign of the Kerr constant is controlled by the angle  $\beta$ , i.e. by the electronic configuration of the molecules. It changes from positive to negative values as the angle  $\beta$  grows from  $0^\circ$  to  $90^\circ$ . The sign and magnitude of the Kerr constant are thus controlled predominantly by the

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orientation correlation factor  $g_2$  and a geometrical factor.

We consider in this contribution the electro-optical properties of binary mixtures of liquid crystalline materials within the isotropic phase [9–12]. We may envision two different situations as far as the electronic configurations of the components of the blends are concerned:

- One limiting case is that the two components show a similar electronic configuration in that the dipoles are approximately parallel (or perpendicular) to the polarizability axis and the geometric axis, which defines the order parameter. We may expect simple mixing laws for this case.
- The other limiting case is the one where one of the components has the dipole moment perpendicular to the principal axis of the polarizability and the other parallel to it (antagonistic dipole configurations). The orientational order fluctuations should be characterized for both components by a preferred orientation of the long axes. The electric field couples differently, however, to the two components. It will tend to orient the long axis of the first component along the field direction and that of the second component perpendicular to the field direction. It seems possible that the applied field couples independently to the two components in the blends, and we may even expect to observe the induction of a phase separation of the two components at a sufficiently strong field.

## 2. Experimental

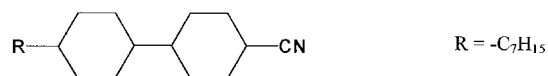
### 2.1. Sample

The compounds which were selected for the investigations are displayed in the Scheme. The transition temperatures and their electronic properties as obtained from quantum mechanical calculations [13] are shown in the table. PCH7 and CCH7 are characterized by dipole moments which are, to a first approximation, parallel to the principal axis of polarization; the magnitudes of the dipole moments are similar and the compounds differ with respect to the magnitude of the anisotropy of polarization. The compound CCN47, on the other hand, has a dipole moment which is oriented approximately perpendicular to the principal axis of polarizability. Furthermore, we will consider the compound BCH32 characterized by a vanishing dipole moment, and a discotic system with a negative birefringence and having not a nematic phase, but a columnar phase [14, 15].

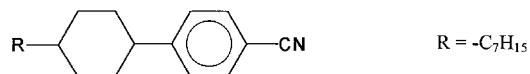
### 2.2. Experimental set-up

The experimental set-up has been described in previous papers [16, 17]. It is sufficient to state than an

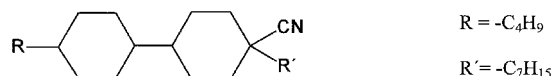
### CCH7



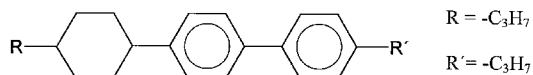
### PCH7



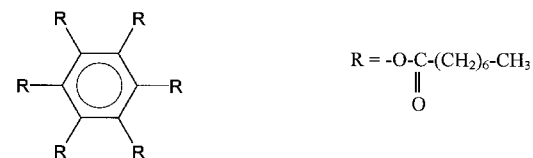
### CCN47



### BCH32



### Discotic system



Scheme. Structures of the liquid crystal compounds studied in this contribution.

electric field is applied to the mixtures in a cell fitted with a thermostat. A light beam passes through the cell perpendicular to the direction of the applied field. A linear detection system, including a quarter wave device was used. The polarizer was oriented at an angle of 45° with respect to the electric field and the analyser was rotated precisely by a known angle  $\alpha$  relative to the direction of extinction.

## 3. Results and discussions

### 3.1. Phase diagrams of the mixtures

We will consider only the phase diagrams of two mixtures namely of PCH7 and CCH7, with similar dipole configurations, and of CCN47 and PCH7 with antagonistic dipole configurations. Figures 1 and 2 display the corresponding phase diagrams. The mixture

Table. Transition temperatures and physical parameters for the materials shown in the scheme.

Substance	$M/\text{g mol}^{-1}$	$T_{\text{NI}}/^\circ\text{C}$	$T^*/^\circ\text{C}$	$\Delta\alpha/10\text{E-}40 (\text{Cm})^2/\text{J}$	$ p D$	$\beta/^\circ$
CCH7	289.51	84	82.5	9.01	3.00	10.0
PCH7	283.46	55	53.5	18.09	3.56	4.5
CCN47	345.62	58	57	8.38	2.69	80.6
BCH32	306.50	166	164.5	25.21	0.039	—
Discotic system	930	82	25	-21.51	0.01	—

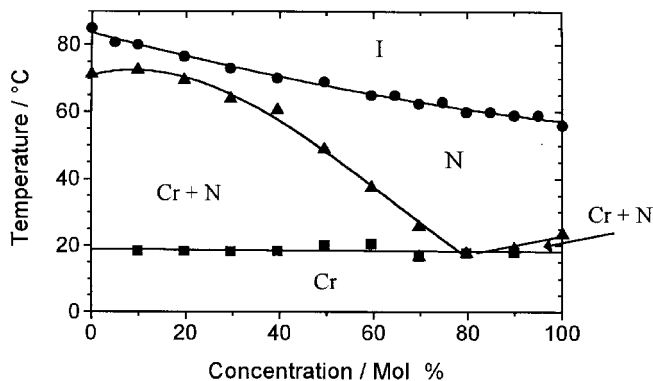


Figure 1. Phase diagram of the mixture PCH7/CCH7.

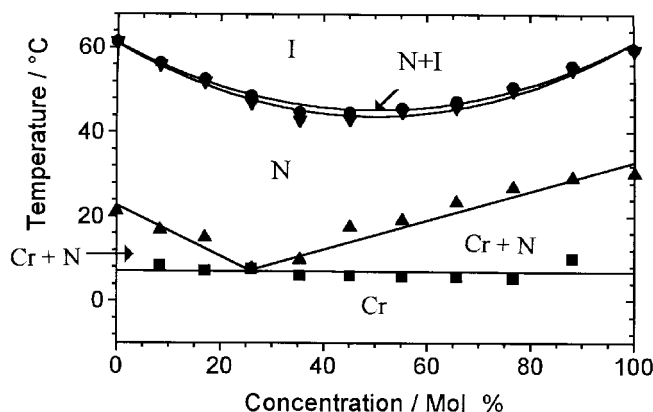


Figure 2. Phase diagram of the mixture CCN47/PCH7.

PCH7/CCH7 is characterized by a clearing temperature which varies linearly with composition and by a eutectic behaviour with respect to the nematic/crystal transition. The mixture CCN47/PCH7, on the other hand, shows a very strong depression of the clearing temperature at intermediate concentrations and again a eutectic behaviour for the nematic/crystal transition. It is apparent that the antagonistic dipole configurations affect the phase behaviour considerably in the latter case.

### 3.2. Kerr effect in mixtures of PCH7 and CCH7

The two components display a Kerr response which obeys the Landau–de Gennes description in an ideal way. The Kerr constant is found to diverge in both cases

at a temperature about 1 K below the clearing temperature.

The Kerr responses of the mixture also behave ideally as is apparent from figure 3, which displays plots of the inverse of the Kerr constants as a function of the temperature. The parameter is the composition of the blends. The characteristic temperature  $T^*$  is found in all cases to be located about 1 K below the clearing temperatures of the mixtures. The different slopes reflect the differences in the electronic properties of the compounds. The Kerr response of the mixtures of the two compounds considered so far is thus ideal, as expected.

### 3.3. Kerr effect in mixtures of PCH7 and CCN47

The two pure compounds differ with respect to sign of their Kerr constants. It is positive for PCH7 and negative for CCN47. Yet both pure compounds show an ideal Kerr response: the inverse of each Kerr constant varies linearly with temperature and the characteristic temperature  $T^*$  is located about 1 K below the clearing temperature.

The experimental observation on the Kerr behaviour is that the mixtures behave ideally in the way defined above, as long as the concentration of the respective second component is small. Deviations from this behaviour occur, however, as the concentration of the second component increases. A characteristic set of examples is

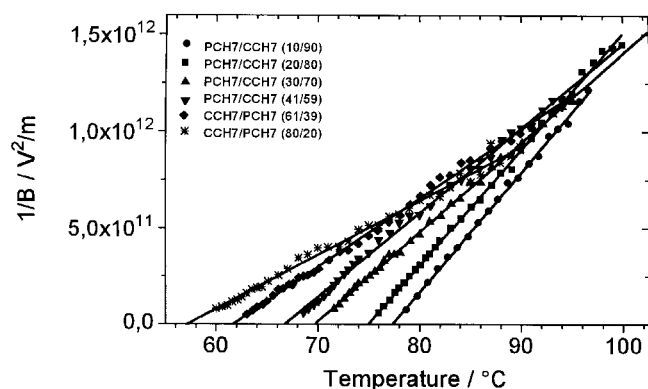


Figure 3. Kerr response of the mixture PCH7/CCH7 for various compositions. Plotted is the inverse of the Kerr constant versus the temperature.

shown in figures 4(a) and 4(b), where the concentration is in the intermediate range. Deviations from a linear variation are observed and for concentrations above 66 mol %, we find a very unexpected variation of the inverse of the Kerr constant with temperature as apparent from figure 4(b). A similar variation of the shape of the response curves is observed as one starts from the pure compound CCN47 and adds PCH7.

The reason for the behaviour shown in figure 4(b) is that the Kerr constants change sign as a function of the temperature: this effect dominates the whole temperature dependence. The temperature at which the inversion of the sign takes place is found to depend strongly on the composition, as is obvious from figure 5. The experimental results indicate that the Kerr response of the binary mixtures may become quite complex and it seems that the sign inversion dominates the Kerr response for selected mixtures even in the neighbourhood of the divergence temperature.

We will discuss in the following the possible origin of a temperature induced sign reversal. A temperature

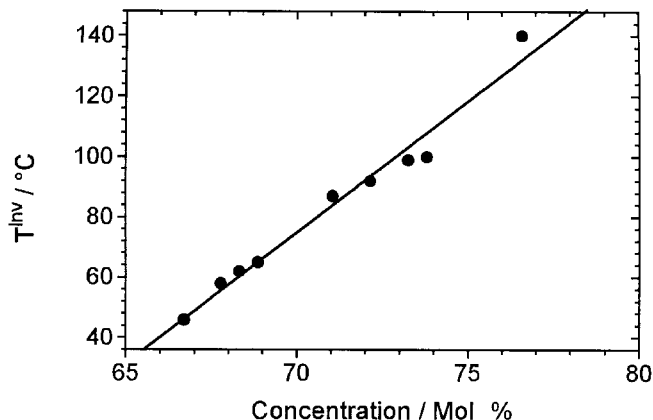


Figure 5. Dependence of the inversion temperature on the composition of the mixtures of CCN47/PCH7.

dependent sign reversal can take place when the contribution coming from the anisotropy of polarization (which is always positive) and that coming from the dipolar configuration are of equal magnitude and of different sign. The system has to be characterized in this case by an angle  $\beta$  larger than the magic angle. Small changes of the temperature will give rise to a sign inversion in this case, since the second term gets smaller with increasing temperature, whereas the first term is temperature independent. The starting point for the discussion is the general equation derived by statistical mechanics which can be written in a simplified form as follows:

$$B(T - T^*) = C \left(1 - \frac{T_0}{T}\right) \quad (7)$$

where the inversion temperature  $T_0$  and the constant  $C$  are given by

$$T_0 = -\frac{f_c \mu^2}{k \Delta \alpha} \quad \text{and} \quad C \propto \Delta \alpha \quad (8)$$

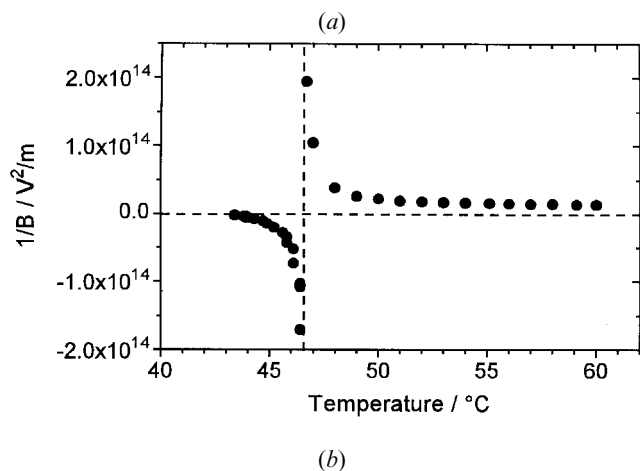
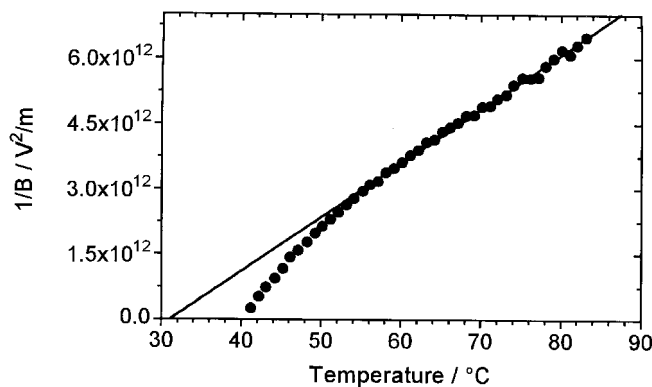
(The magnitude of the Kirkwood correlation factor is usually of the order of 0.5, so that we can neglect the corresponding contribution.)

This equation suggests a plot

$$B(T - T^*) \text{ versus } \left(1 - \frac{T_0}{T}\right) \quad (9)$$

since  $g_2 \propto 1/(T - T^*)^2$ , see above.

It is apparent from figures 6(a) and 6(b) that one obtains a linear plot in all cases, i.e. in those cases where a sign reversal takes place and in those cases where deviations from the usual Kerr plot are observed. The Kerr response of the mixtures considered here are thus characterized by a superposition of sign reversal and a critical divergence. An important conclusion from this



Figures 4(a) and 4(b). Kerr response of the mixtures CCN47/PCH7 for various compositions (60 and 67 mol % CCN47). Plotted is the inverse of the Kerr constant versus the temperature.

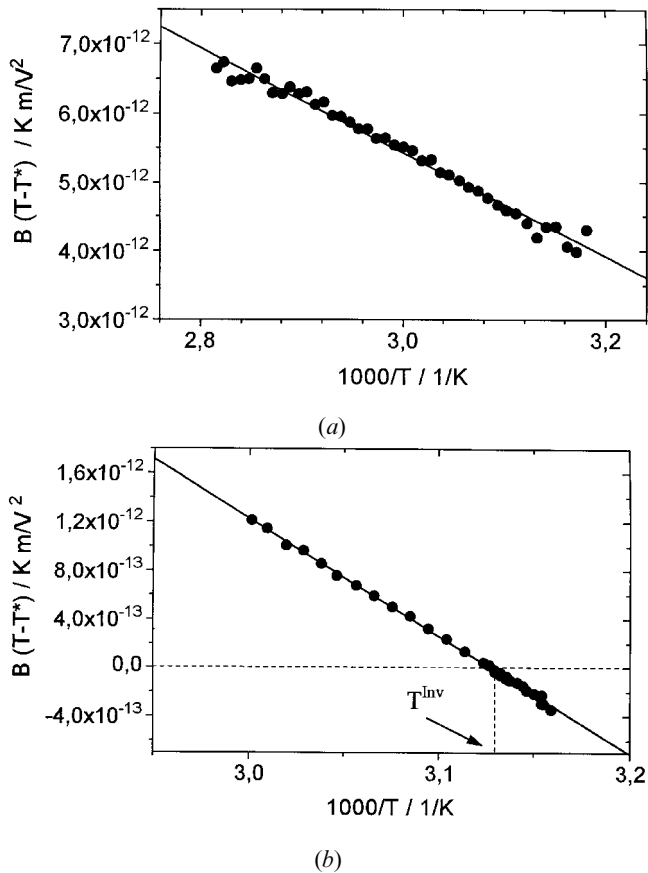


Figure 6(a). Plot of  $B(T - T^*)$  versus  $1/T$  for a concentration of 60 mol % CCN47. (b) Plot of  $B(T - T^*)$  versus  $1/T$  for a concentration of 67 mol % CCN47.

analysis is that the sign reversal can occur in only one direction, namely from negative to positive values with increasing temperatures. All mixtures studied so far show this direction experimentally. The constants  $T_0$  and  $C$  which are obtained from this plot are directly related to electronic properties as shown above.

Any further evaluation depends thus on our choice of the model for the character of the orientational correlations occurring in the mixtures. It is sufficient to point out that we were not able to fit the data by assuming that a phase separation takes place in the field and that each component contributes independently to the applied field. We were able, on the other hand, to obtain reasonable results, even on a quantitative basis, by assuming that the compounds remain mixed, that the orientations of the long axes of both compounds together define the total orientational correlations as depicted in figure 7, and that these clusters couple to the external field.

The major problem to be discussed next is in which way we have to translate the equations given above for the case of the binary mixtures. We assumed to a first

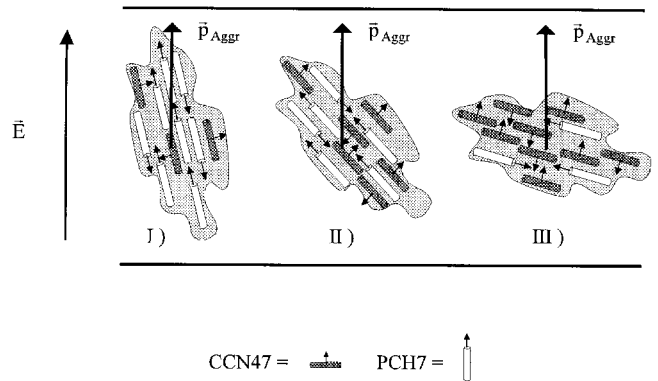


Figure 7. Schematic representation of the orientational correlations in the mixtures (I), (II) and (III) corresponding to a coupled response to the external electric field and an increase in concentration of CCN47.

approximation that we can calculate the mean anisotropy  $\Delta\alpha_M$  per molecule of the cluster from simple mixing rules

$$\Delta\alpha_M = \Phi \cdot \Delta\alpha_A + (1 - \Phi) \cdot \Delta\alpha_B \quad (10)$$

where  $\Phi$  is the concentration, and that we can proceed in a similar way for the dipolar contributions  $\mu_A$  and  $\mu_B$  considering, however, the parallel and perpendicular components separately.

$$|\mu_M| = [(\Phi \cdot \mu_{\parallel,A} + (1 - \Phi) \cdot \mu_{\parallel,B})^2 + (\Phi \cdot \mu_{\perp,A} + (1 - \Phi) \cdot \mu_{\perp,B})^2]^{1/2} \quad (11)$$

We obtain in this case for the absolute value  $B_M$  and the angle  $\beta$

$$B_M \propto \left\{ \Delta\alpha_m g_{2,M} + \frac{\mu_M^2 F}{2k_B T} (3 \cos^2 \beta_M - 1) \times [2(g_{1,M} - 1) + g_{2,M}] \right\} \quad (12)$$

$$\beta_M = \tan^{-1} \left( \frac{\Phi \cdot \mu_{\perp,A} + (1 - \Phi) \cdot \mu_{\perp,B}}{\Phi \cdot \mu_{\parallel,A} + (1 - \Phi) \cdot \mu_{\parallel,B}} \right) \quad (13)$$

We will discuss the consequences of this assumption, first on a qualitative level. The addition of the component CCN47 to PCH7 will lead on average to an increase of the angle  $\beta$  as depicted in figure 7. The sign inversion will occur as the magic angle is crossed. Actually there is a simple way of testing whether this is correct, since the internal structure of the lower temperature nematic phase should reflect that of the clusters, due to orientational correlations, and the only difference is the absolute value of the order parameter. The test involved the orientation of the mixtures in an electric field as analysed by flat camera X-ray experiments. The results are shown in figure 8 for various compositions of the blends. The

azimuthal distribution of the scattering intensity reflects the orientational distribution of the molecular axis. The diagrams displayed in figure 8 show that the director is continuously rotated with respect to the co-ordinate system defined by the electric field with increasing concentration of the second component. The distribution becomes random at an intermediate concentration, as expected for clusters where the angle  $\beta$  corresponds to the magic angle.

Using the simple mixing laws given above (see equations (10), (11) and (13)), we are actually able to account for the Kerr results even on a quantitative scale (see equation (12)). This is obvious from figure 9 which compares experimental values with those calculated from the data characteristic of the pure components (see the

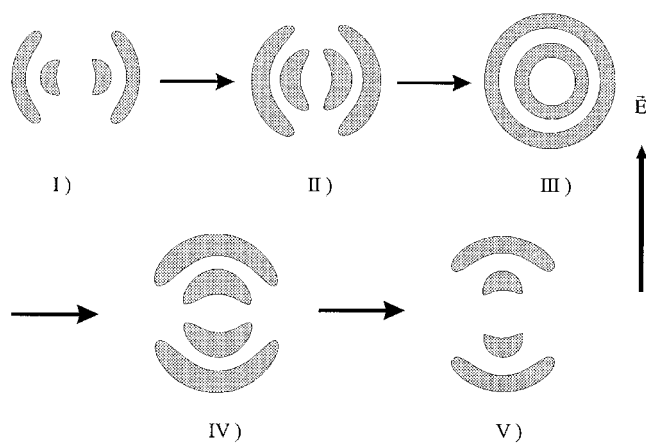


Figure 8. Schematic drawings of the experimental results of flat camera X-ray studies on mixtures in an electric field. The parameter is the composition of the mixtures of CCN47/PCH7. (I) 100 mol% PCH7, (II) 20 mol% CCN47, (III) 70 mol% CCN47, (IV) 80 mol% CCN47, (V) 100 mol% CCN47.

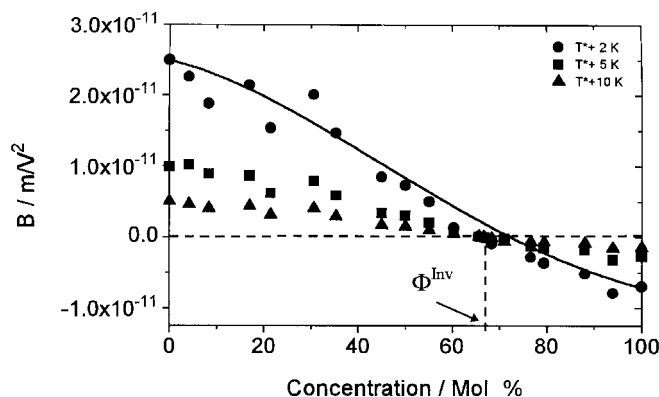


Figure 9. Comparison of experimental and calculated Kerr constants (see equation (12)) for the mixtures CCN47/PCH7.

table) and a correlation factor  $g_{2,M} \cong 300$ . A similar agreement was obtained for all mixtures studied.

### 3.4. Variation of dipole configurations and molecular geometry

Finally we will consider mixtures where one of the components has a vanishing dipole moment, but a strong anisotropy of the polarizability (BCH 32), and one where the second component is discotic. The results are shown in figures 10 and 11. The discotic system is characterized by a  $T^*$  which is located much more than 1 K below the clearing temperature of the mixture as shown in figure 12. We observe as a common feature that the absolute values of the Kerr constants are larger than those of the pure components at intermediate concentrations. These synergistic effects are caused by the fact that the molecular axes tend to align parallel in the clusters and that the clusters couple jointly to the electric field by dipolar interactions. We observed similar effects for a large number of other systems not described here.

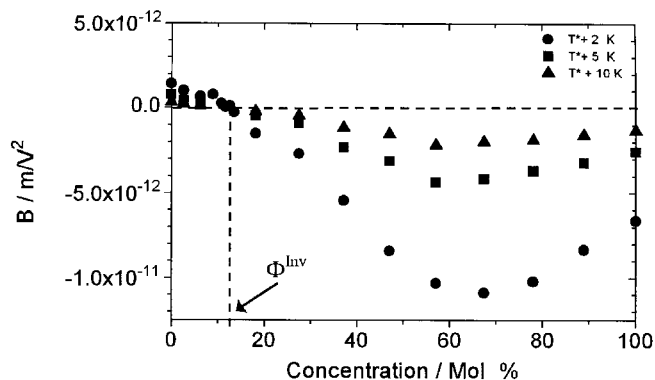


Figure 10. Kerr response of the mixture of BCH32 and CCN47 for various compositions. Plotted is the Kerr constant versus the concentration.

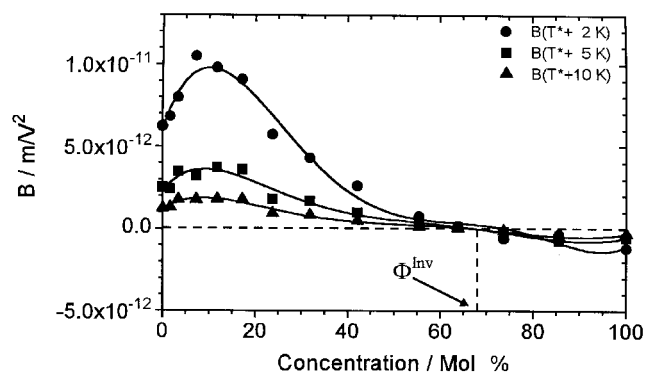


Figure 11. Kerr response of the mixture of the discotic system with CCH7 for various compositions. Plotted is the Kerr constant versus the concentration.

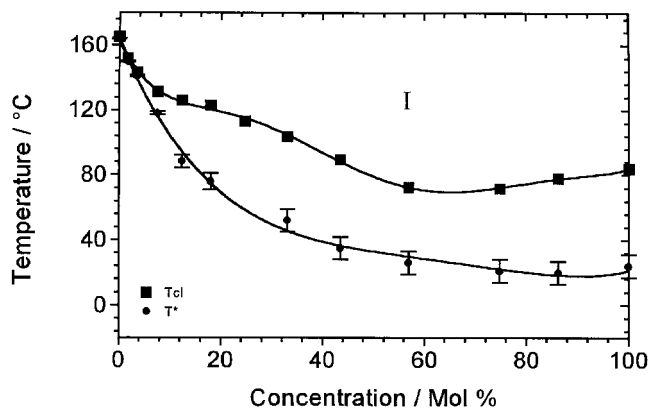


Figure 12. Phase diagram of the mixture discotic system/CCH7 for various compositions. Plotted is the clearing transition and  $T^*$  versus the concentration.

#### 4. Conclusions

Mixtures of liquid crystalline compounds display pre-transitional effects within the isotropic phase close to the nematic phase which can be accounted for on the basis of the Landau–de Gennes treatment. Simple mixing laws can be applied even to the case of an antagonistic dipolar configuration of the components of the blends, despite the fact that the Kerr response of the blends may be dominated by a sign inversion.

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