Dielectric pretransitional effects in the isotropic phase of chiral liquid crystals

J. Leys[a]; C. Glorieux[a]; M. Wübbenhorst[a]; J. Thoen[a]

[a] Laboratorium voor Akoestiek en Thermische Fysica, Departement Natuurkunde en Sterrenkunde, Katholieke Universiteit Leuven, B-3001 Leuven, Belgium

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J. LEYS*, C. GLORIEUX, M. WÜBBENHORST and J. THOEN

Laboratorium voor Akoestiek en Thermische Fysica, Departement Natuurkunde en Sterrenkunde, Katholieke Universiteit Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium

We have performed dielectric measurements on chiral liquid crystalline systems. From the values of the static dielectric permittivity, it is observed that the dielectric pretransitional effect in the isotropic phase on approaching the isotropic to cholesteric or isotropic to blue phase transition is virtually not influenced by the chirality of the system. The relaxation times do not show anomalous behaviour near the transition, although a small overall slowing down is observed in mixtures with increasing chirality.

1. Introduction

Liquid crystals are regarded as model systems for testing theories of phase transitions, because of the diversity of transitions found: first-order, weakly first-order and continuous transitions can all be present in one system. First-order transitions are characterized by the presence of discontinuities in the first derivatives of the relevant thermodynamic potentials, for example steps in specific volume or entropy. Continuous transitions do not have these steps. Quite often, several physical properties exhibit pretransitional or so-called critical fluctuation effects. These fluctuations can be present in either of the phases. Here we want to focus on the isotropic (I) to nematic (N) and isotropic to cholesteric or chiral nematic (N*) transitions, approached from the isotropic side. In general these transitions are weakly first order, meaning that small discontinuities as well as critical fluctuations are present.

The fluctuations in the isotropic phase upon approaching the weakly first-order NI phase transition manifest themselves by the formation of domains with local nematic order. The size of these domains is given by a correlation length ξ that diverges at T^*, the absolute limit of the (supercooled) isotropic phase:

$$\xi(T) = \xi_0 t^{-v},$$

with $t = |T - T^*|/T^*$, v a positive universal exponent for the relevant universality class and ξ_0 a system-dependent amplitude.

With dielectric spectroscopy these fluctuations can be seen indirectly via the static value of the dielectric permittivity for compounds having a strong dipole moment along the long molecular axis, as for example the alkylcyanobiphenyls (nCBs). These molecules dynamically form antiparallel correlated pairs, which results in a reduced effective dipole moment. These pairs are formed more easily in the mesophases than in the isotropic phase. In the prenematic fluctuations this is also the case and on approaching the NI transition when lowering the temperature, the static value first increases slower than far from the transition, then reaches a maximum and finally decreases [1, 2].

Both presence and absence of pretransitional effects depending on the order of the transition can be well illustrated in the nCB series. The mesogenic members of this group (those with isotropic to nematic as well as those with an isotropic to smectic transition, both weakly first-order transitions) clearly show such a maximum and decrease. Opposed to this, there is no pretransitional effect for the non-mesogenic members (that have a strongly first-order isotropic to crystal transition) [3].

For some other liquid crystals, the pretransitional effect does not appear as a maximum and decrease, but only as a bending down of the curve. This occurs for example in compounds having a smaller dipole moment along the long molecular axis.

There is also a large number of liquid crystals for which no dielectric pretransitional effect can be seen. There can be two reasons for this: a dipole moment is absent or the location or orientation of the dipole moment makes the dipole coupling geometrically difficult.

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*Corresponding author. Email: jan.leys@fys.kuleuven.be

The absence of a dielectric pretransitional effect is not an indication for the absence of the nematic pretransitional fluctuations. This was recently clearly demonstrated in a comparison of the dielectric pretransitional effect of non-chiral liquid crystals with the thermal pretransitional effects and the latent heats [4].

Chiral liquid crystals form a nematic phase in which the director rotates throughout the sample. On a large scale this results in a helical structure. Typically pitches of hundreds of nanometres are seen; this is to be compared to a typical molecular length of a few nanometres. One can see that the local order in this cholesteric phase is very like the nematic one, although there should be some influence from the helix.
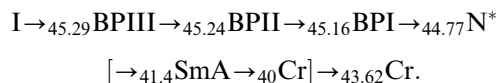
In view of these observations, it might be interesting to study the dielectric pretransitional effect in chiral systems. In particular we want to verify if there are systematic dependencies of the strength of the dielectric pretransitional effect on chirality. We are aware of a single study on the dielectric pretransitional effect in cholesteric liquid crystals [5]. There, the pretransitional effect in CB15 was discussed.

We studied the dielectric properties of two chiral systems. The first one is S-(+)-4-(2-methylbutyl)phenyl-4-decyloxybenzoate (CE6). The chiral centre is situated in the methylbutyl tail. This chiral tail is the same as that of 4-(2-methylbutyl)-cyanobiphenyl (CB15) that we will mix with 4-pentyl-cyanobiphenyl (5CB) to obtain a system with adjustable chirality. The choice of the two systems is motivated by (i) the identical chiral tail, (ii) the short pitches of CE6 and CB15, which are amongst the molecules with the highest chirality, and (iii) the possibility of using two well-known isomeric molecules in a mixture. The mixing of a molecule with a chiral isomer is one of the best possibilities to change the chirality in a system, apart from mixing both enantiomers.

2. Experiment

S-(+)-4-(2-methylbutyl)phenyl-4-decyloxybenzoate (CE6), 4-pentyl-cyanobiphenyl (5CB) and 4-(2-methylbutyl)-cyanobiphenyl (CB15) were obtained from Merck and used without further purification.

CE6, shown in figure 1, is a highly chiral molecule with blue phases intervening between the isotropic and the cholesteric phase. The phase sequence upon cooling of the pure chiral compound, according to Voets [6], with transition temperatures in °C, is

$$I \rightarrow_{45.29} BPIII \rightarrow_{45.24} BPII \rightarrow_{45.16} BPI \rightarrow_{44.77} N^*$$

$$[\rightarrow_{41.4} SmA \rightarrow_{40} Cr] \rightarrow_{43.62} Cr.$$

The dipole moment is calculated to be 2.4 D, having an angle of 76° with the long molecular axis [7]. Additional information on the molecule can be found in a series of conference proceedings [8–10].

5CB and CB15 have well-known properties. 5CB shows an isotropic to nematic transition at 35.3°C and crystallizes around 22.5°C, but it can fairly easily be supercooled. CB15 crystallizes at 4°C, but can be supercooled as well. Then a monotropic phase sequence appears, with a cholesteric phase starting at −30°C and a smectic A phase at −54°C [11]. A glass transition is reported at about −63°C [12]. CB15 might have (monotropic) blue phases.

We determined the dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ of CE6 in the frequency range $1–10^7$ Hz using a Novocontrol Alpha Dielectric Spectrometer. Temperature control was assured by a Novocontrol Quatro controller, giving a stability of 50 mK or better. The data were obtained in a slow cooling run (0.1 K/6–10 min). The sample was placed between two brass electrodes that were covered with a polyimide coating inducing homeotropic alignment. The electrodes were separated by two 100 μm glass fibres. The coating was used to determine unambiguously the phase transition and should not influence the isotropic phase.

The mixtures of 5CB and CB15 were prepared by simple blending of the required amount of LC in the isotropic phase of the mixture. Then the sample was placed in a parallel plate capacitor where the permittivity was measured by a HP4284A LCR Meter (20 Hz to 1 MHz) and a HP4291B Impedance Analyzer (1 MHz to 1 GHz). Both measurements were performed without having to move or open the measurement cell.
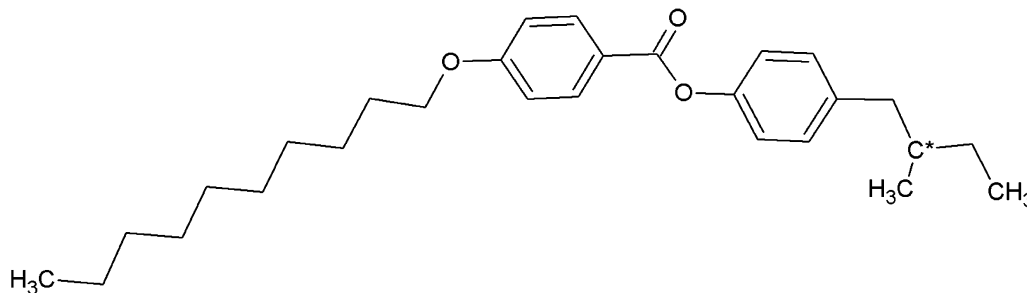

Figure 1.   Chemical structure of CE6.

Temperature control was assured by a home-made system, where a temperature controlled fluid is circulated through the walls of an oven surrounding the cell. A strong permanent magnet (0.4 T) was used to induce the alignment for observing the phase transition.

Results for the static permittivity of 5CB were taken from a PhD thesis [13]. Results for the relaxation times of 5CB were taken from an unpublished measurement in our lab that was done under the same circumstances as for the mixtures. Corresponding data for CB15 were taken from a previous publication [14]. The permittivity data of CB15 were also measured with the Novocontrol setup and will be discussed later in more detail.

All data were analysed in terms of two quantities: the static values of the permittivity and the relaxation times. To determine the static value a fixed frequency was chosen where there is neither a contribution from relaxation processes nor strong losses due to electrical conductivity. We will illustrate the choice of the frequency in Section 4.1. At this frequency, the real part of the permittivity is regarded as the static value. This frequency is not the same for all systems, since the relaxation processes can be at different frequencies and the purity can differ, causing higher conductivity. For CE6 and for the mixtures 5 kHz was used, pure 5CB was measured at 1 kHz, and for pure CB15 a slightly lower value of 91 Hz was taken. Because of a small change in the cell geometry at about 18°C, caused by a phase transition in Teflon® [15, 16], a correction procedure was applied to the extracted static values.

For the analysis of the static value, we will present a normalized result[1]

$$\frac{\varepsilon' - \varepsilon'_{\text{MI}}}{\varepsilon'_{\text{MI}}},$$

to make sure that any small change in the calibration does not contribute to the magnitude of the considered effect.

The relaxation times were determined from a fitting procedure using the WinFIT program from Novocontrol. For the quantitative analysis of the dielectric spectra we used the Havriliak–Negami function [17]. In case of more than one relaxation process the Havriliak–Negami function in the frequency domain is given as

$$\varepsilon^* = \varepsilon_\infty + \sum_j \frac{\Delta\varepsilon_j}{\left[1 + \left(i2\pi f \tau_j\right)^{\alpha_j}\right]^{\beta_j}} - i\frac{\sigma_0}{\varepsilon_0 2\pi f},$$

where ε_∞ is the high-frequency limit of the permittivity,

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[1] The actual mesophase (M) following the isotropic phase is not clearly identified for all the samples. Therefore the transition will be written as MI.

$\Delta\varepsilon_j$ the dielectric strength, τ_j the mean relaxation time, and j the number of the relaxation process. The exponents α_j and β_j describe the symmetric and asymmetric distribution of relaxation times. The last term accounts for the low-frequency contribution of the conductivity σ_0.

For CE6 two processes were used, of which the fastest one was at the edge of the measurement range. Both processes were found to be close to a single relaxation time (Debye) process ($\alpha = \beta = 1$). For the mixtures one process with both α and β as free parameters was used. CB15 was fitted using one Cole–Davidson process, meaning β free and α fixed to 1; 5CB with a Cole–Cole process, α free and β fixed to 1.

3. Static dielectric properties

3.1 CE6

The static value of the dielectric permittivity of CE6 at 5 kHz is given in figure 2. The permittivity follows a straight line, until the isotropic-blue phase transition at T_{MI} is encountered. Also the mesophases have been probed, but from the dielectric results alone, it is difficult to identify the phases. It is also not relevant for the subject discussed in this paper.

The linear dependence in the isotropic phase is in contrast with the behaviour in case of a dielectric pretransitional effect, which would give a curvature or bending down of the curve near the transition. This linear dependence resembles the pretransitional behaviour for MBBA as reported in [4] and is very different from the curvature and bending reported in [1, 2] for nCBs and also for part of the molecules in [4]. So the conclusion is that a dielectric pretransitional effect is absent in CE6.

3.2 CB15

Since CB15 has a monotropic phase sequence, considerable attention was given to the determination of the static value of the dielectric permittivity of this liquid crystal. The appearance of the cholesteric phase apparently coincides with the start of the crystallization process. This makes an accurate determination of ε'_{MI} and T_{MI} in this case rather difficult.

To obtain the best possible result, parameters like thickness, cooling rate, surface treatment and DC-bias were varied and also an effort was made to increase the purity of the CB15 sample. We noted that the phase transition temperature was nearly independent of the cooling rate, if the transition was reached before the sample had crystallized. CB15 always crystallized upon heating, if it had not already done so during cooling. DC-bias and surface treatment did not improve the results.
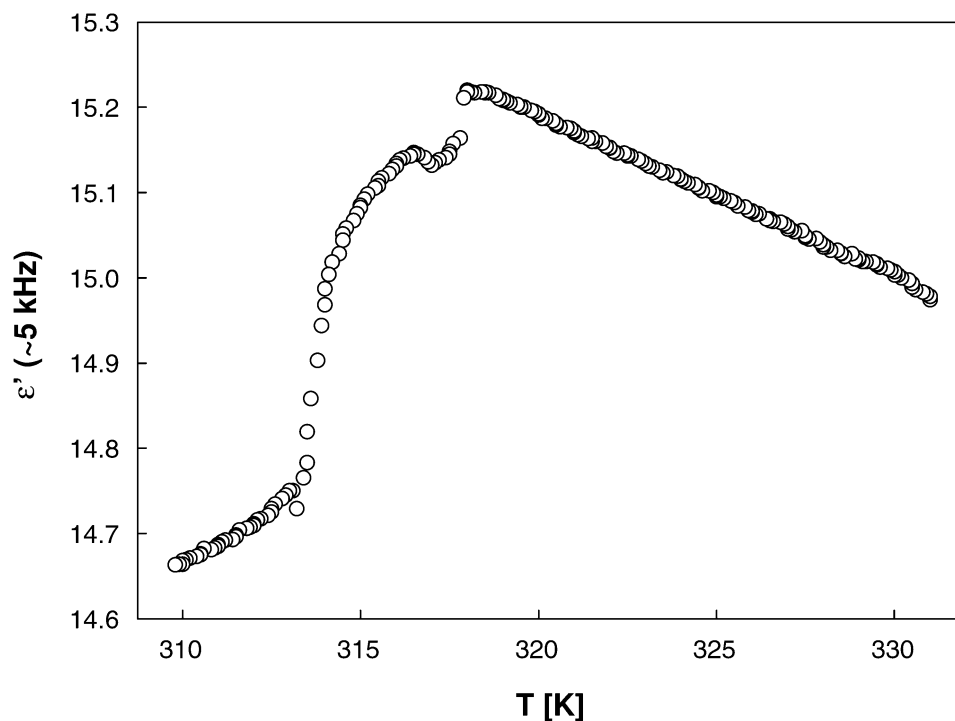
Figure 2.   The static value of the dielectric permittivity of CE6 at 5 kHz.

To improve the purity of the sample an amount of CB15 was heated under reduced pressure (~0.25 bar) for several hours at about 75°C. The sample was placed between polished and untreated brass electrodes, separated by 50 μm fibers. A short spectrum was measured at a fixed temperature and stabilization times were taken as short as possible. The phase transition temperature was determined from careful examination of fitting results and the static value itself. The value found was −31°C, consistent with those in the literature [11, 12, 14]. A fixed frequency of 91 Hz was chosen. At this frequency the influence of electrode polarization is quite small and nearly constant for the given temperature range as a function of temperature. Overall, the effect is an increase of the absolute value of the permittivity by about 0.1. This was verified by an analysis of the fitting results and comparison with the behaviour of the real part of the permittivity at other frequencies. In short, due to not correcting for electrode polarization, we might have introduced a systematic error as small as 1% on the absolute value, but we have verified that this error does not influence the temperature dependence of the static value. On the other hand the influence of the relaxation process on the static permittivity is negligable at this frequency. As a final check, the results of CB15 were compared with those of other liquid crystals with a comparable structure and dipole moment. This leads to the result presented in figure 3.

Here we see that the behaviour of CB15 is comparable to that of other molecules having the same basic structure, namely a (short) alkyl chain, a two-ring core and a –CN terminal group. Results for 5CB, 5PCH (4-pentylcyclohexyl-4′-cyanophenyl) and 8CB (4-octyl-cyanobiphenyl) are taken from [13], results for 5CN (1-(4-pentylcyclohexyl)-2-(4-cyanophenyl)ethane) are taken from [18]. On the ground of all these considerations, we think that the permittivity values presented for CB15 are amongst the best possible for this molecule. They also compare well to those of reference [5] and are not contradictory to those of [19].

3.3   *Mixtures of 5CB and CB15*

It is known [20] that the pitch in a mixture of a nematic with a chiral compound is a linear function of the concentration of the chiral compound. So we can consider the concentration of CB15 as a measure of the chirality of the mixtures of 5CB and CB15.

Before we start our discussion of the dielectric results, we note that the transition temperatures of the mixtures are consistent with a linear interpolation between the T_{MI}[2]

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[2] T_{MI} is the temperature of the last data point that belongs to the isotropic phase. Subsequent data points at lower temperatures belong to the cholesteric phase or eventually the two phase region. Since we used small temperature steps, T_{MI} can be regarded as the upper limit of the two phase region.
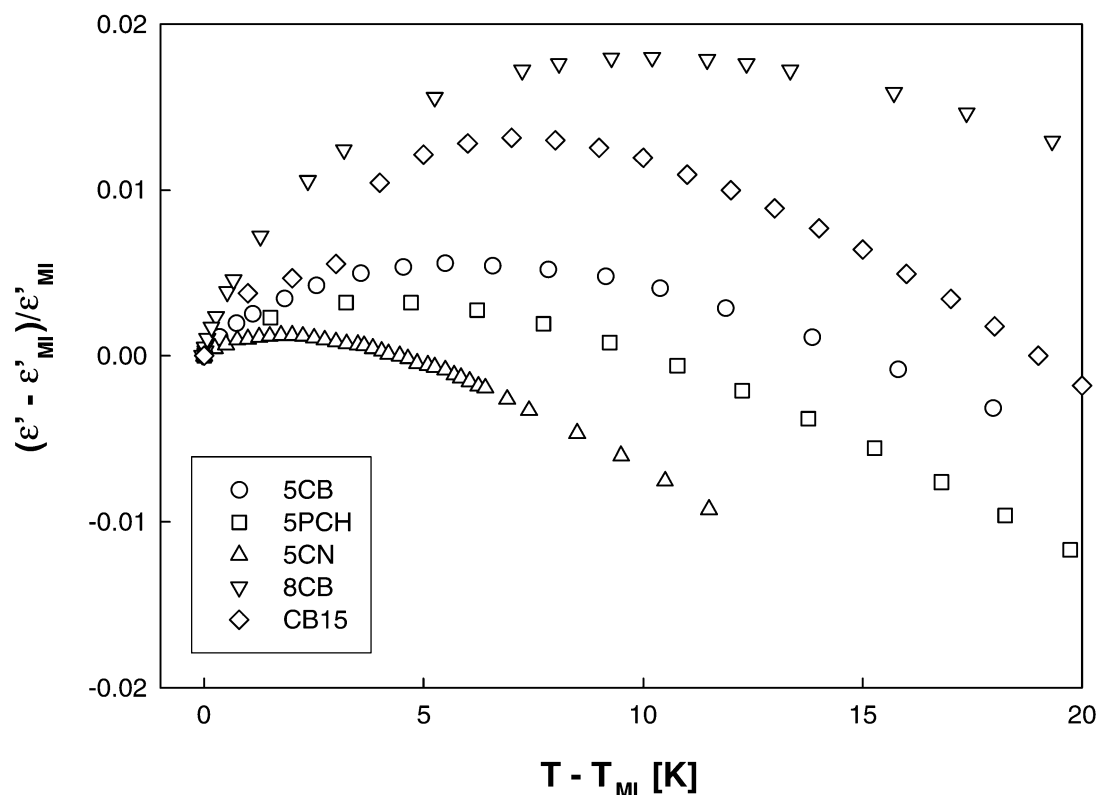
Figure 3.   Pretransitional effect in 5CB, CB15 and comparable molecules.

of 5CB and CB15. This is shown in figure 4. In figure 5 we have plotted $(\varepsilon' - \varepsilon'_{\mathrm{MI}})/\varepsilon'_{\mathrm{MI}}$ versus $T - T_{\mathrm{MI}}$. The reason for the quantity on the Y-axis is given in Section 2; $T - T_{\mathrm{MI}}$ rescales the temperatures to a common reference. So this plot shows the pure pretransitional effect on a relative scale. For the mixtures only data from the heating run are presented, as those of the cooling contain the same information, but they are more scattered.

Pure 5CB, the 20% mixture and pure CB15 show a maximum in the static permittivity. In all other cases the values do not become positive and only a curvature is observed. The degree at which the strength drops (the slope of the linear part of the curves) becomes larger with increasing concentration of the chiral component.

Finally we present in figure 6 five vertical slices of figure 5, resulting in a plot of $(\varepsilon' - \varepsilon'_{\mathrm{MI}})/\varepsilon'_{\mathrm{MI}}$ versus concentration for a number of $T - T_{\mathrm{MI}}$ values. As not all $T - T_{\mathrm{MI}}$ values were measured, cubic spline interpolation was used to obtain the values plotted in the figure. Dashed lines are a guide to the eye. A few features can be seen more clearly in this figure. First of all, 5CB, CB15 and the 20% mixture show positive values for the normalized ε'. They are the only three systems having a maximum in the corresponding curve in figure 5. For the 65% mixture there seems to be an unexpected

maximum that is probably a consequence of the experimental uncertainty and not a real effect.

Clearly visible for $T - T_{\mathrm{MI}} = 10\,\mathrm{K}$ and $= 20\,\mathrm{K}$ is the non-linear behaviour of $(\varepsilon' - \varepsilon'_{\mathrm{MI}})/\varepsilon'_{\mathrm{MI}}$ with concentration. The curve shows a minimum somewhere above 50%. Here we have spotted a non-trivial effect of the mixing of 5CB and CB15: the strength of the pretransitional effect does not follow a linear dependence with concentration. Even if one argues that the effect under consideration is small and the values for 5CB and CB15 were obtained with different experimental set-ups, the conclusion still holds by considering the mixtures alone.

4.   Dynamic dielectric properties

4.1   *CE6*

For completeness we present the spectrum of CE6 in the isotropic phase in figure 7 at T = 65°C. The graph illustrates our motivation for choosing 5 kHz as the frequency to extract the static value of the dielectric permittivity. Normally this is done in that part of the spectrum where ε'' is nearly equal to zero. Since there is no such region here, we decided to take the frequency slightly below the minimum in ε'', to make sure that we did not probe any influence from the relaxation
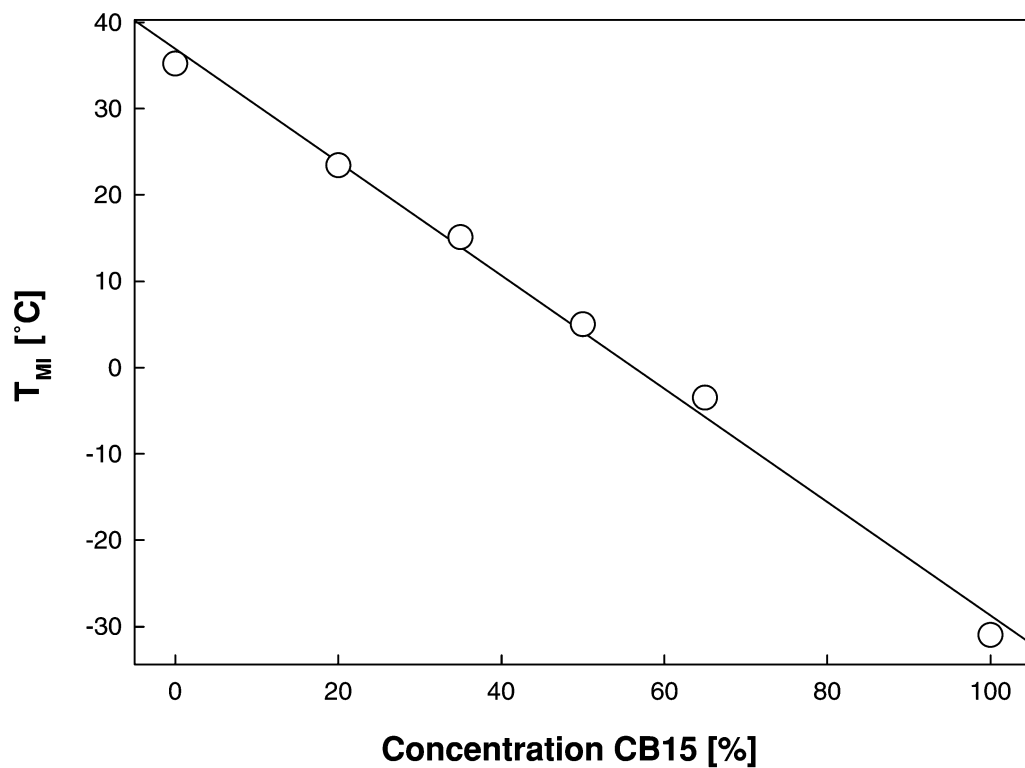
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Figure 4. Transition temperatures T_{MI} for mixtures of CB15 and 5CB and of the pure compounds. The line is a linear fit to the points.
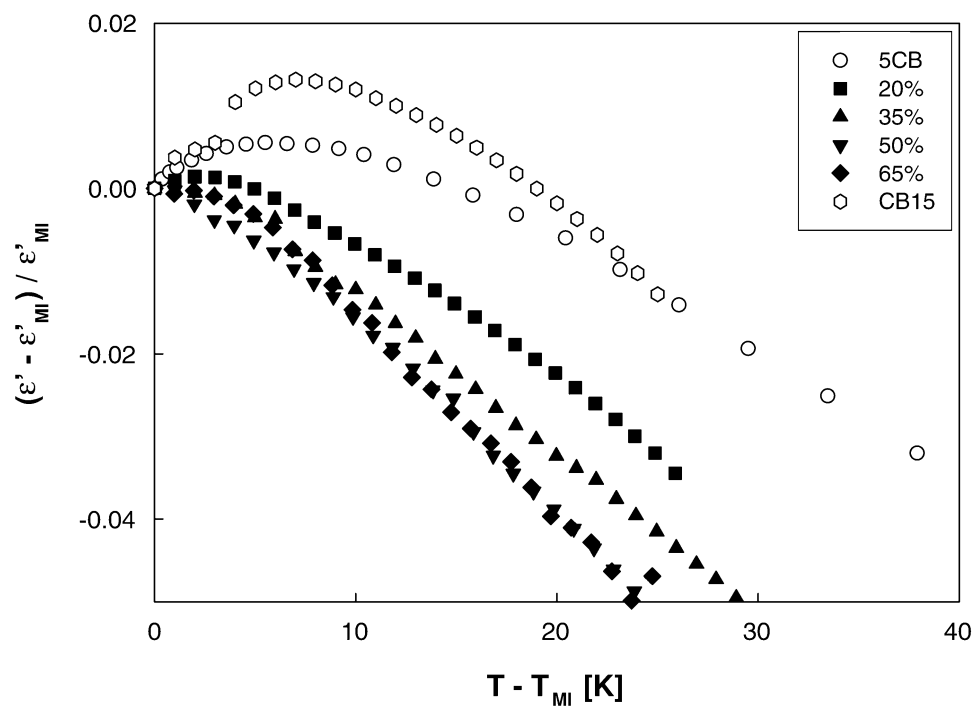

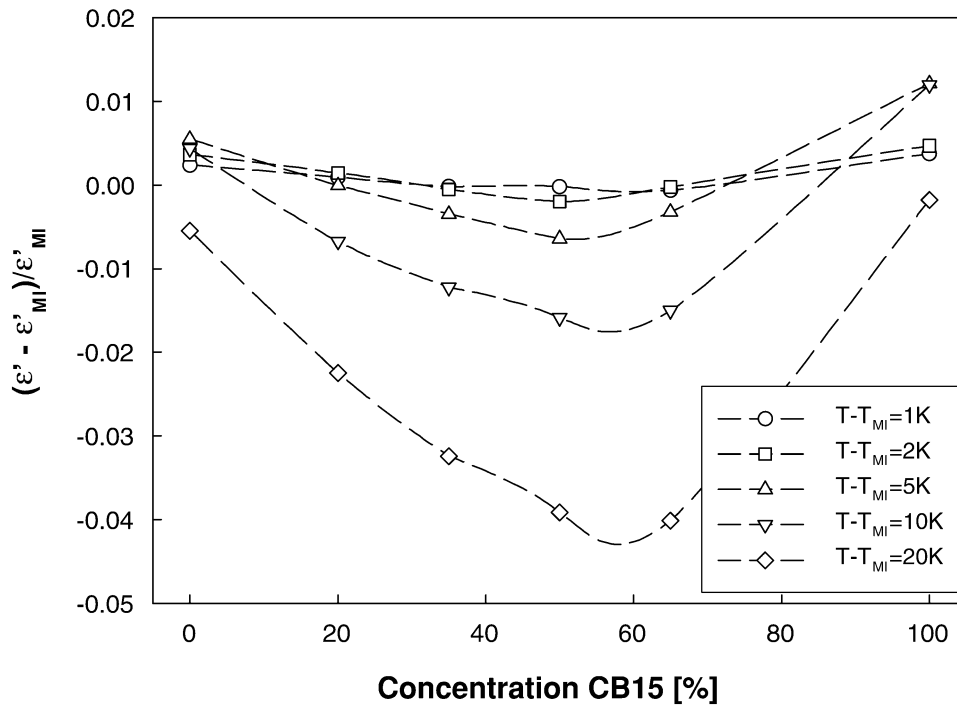Figure 5. Pretransitional effect in the heating runs of mixtures of 5CB and CB15.

Figure 6. Concentration dependence of the pretransitional effect in mixtures of 5CB and CB15.
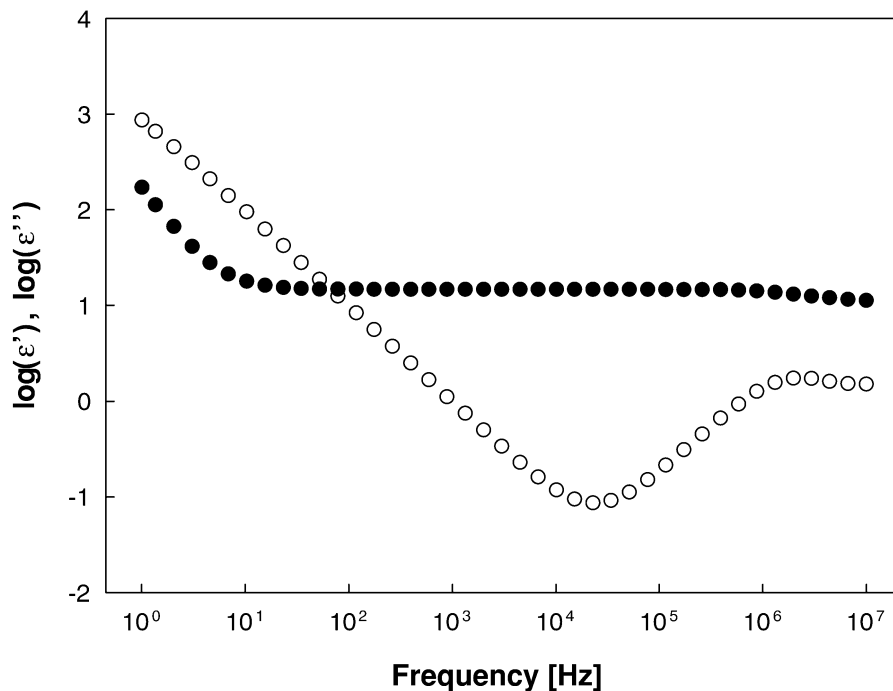
Figure 7. Dielectric spectrum of CE6 in the isotropic phase at T=65°C: real (●) and imaginary (○) part of the permittivity.

processes (at higher frequencies) and such that the influence from the conductivity (at lower frequencies) is as small as possible.

The relaxation time dependencies of CE6 (figure 8) do not show remarkable features. As the fastest process was at the end of the observed frequency range, fitting
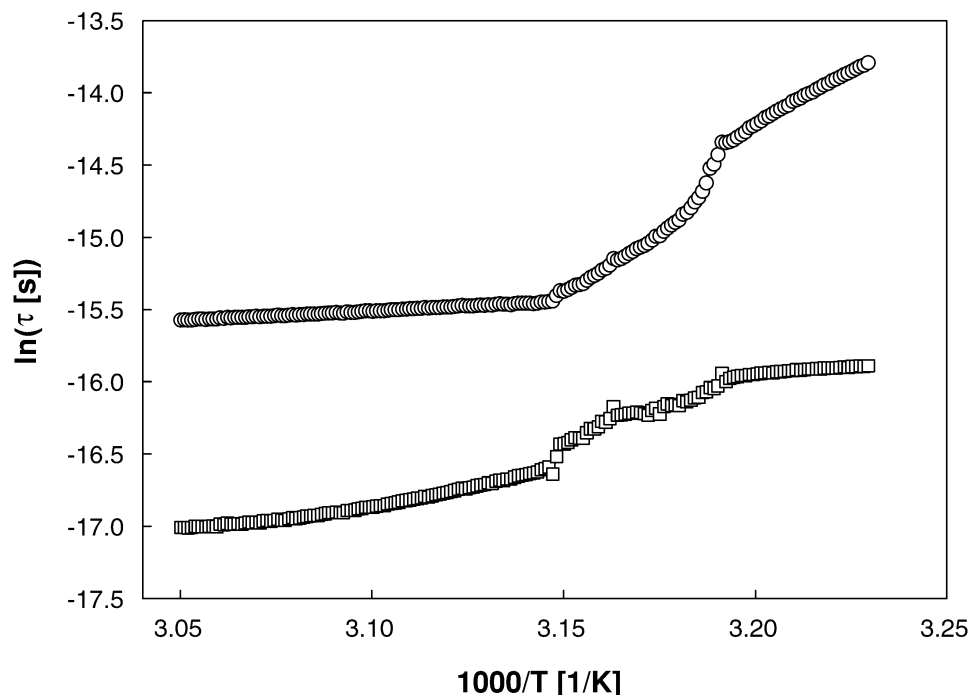
Figure 8.   Temperature dependence of the relaxation times of both relaxation processes in CE6.

this process resulted in less accurate relaxation time data. We identify the slowest relaxation as the rotation around the short molecular axis and the faster process as the rotation around the long molecular axis.

One can identify three regions in the temperature dependence of relaxation time behaviour, corresponding to the isotropic phase, to the region of the blue and cholesteric phases and to the smectic phase. However, for the molecule under consideration, from dielectric spectroscopy it is difficult to make a clear distinction between the blue phases and the cholesteric phase. This observation can serve as evidence that the local structure, which is relevant for the relaxation processes, is not too different in the blue phases from that of a cholesteric phase.

4.2   *Mixtures of 5CB and CB15*

We also performed a straightforward analysis of the relaxation times of 5CB, CB15 and their mixtures. The relaxation times were extracted from the spectra and a Vogel–Fulcher–Tamman (VFT) temperature dependence was fitted through the points in the isotropic phase. We want to compare the dependence on chirality of the relaxation times with that of the static value of the permittivity.

In figure 9, we present the relaxation times versus inverse temperature. From the curves, two observations are easily made. The first one is the increase of the

relaxation time with increasing CB15 concentration. The second observation is that to a certain extent, the curves from the isotropic phase all have a very comparable curvature. This must of course be confirmed from more quantitative methods, in this case, a fit with the VFT equation.

First we present in figure 10 three vertical cuts of figure 9, with the same purpose as in figure 6. The filled points represent interpolated values using the VFT equation that fits the experimental data very well. There is no temperature at which relaxation times were available for all concentrations, so the graph contains points obtained by extrapolation (the open symbols). This means that for 5CB and 20%, the isotropic relaxation times have been extrapolated in the mesophase temperature range. From figure 10, we see that at a given temperature, the relaxation times increase monotonically, though not linearly, with CB15 concentration.

The results of a fit with the VFT equation

$$\tau = \tau_\infty \exp\left(\frac{B}{T - T_0}\right),$$

are presented in figure 11. The actual fit was performed on the linearization of the relation between $\log\tau$ and $1/(T-T_0)$:

$$\log\tau = \log\tau_\infty + \frac{B}{T - T_0}.$$

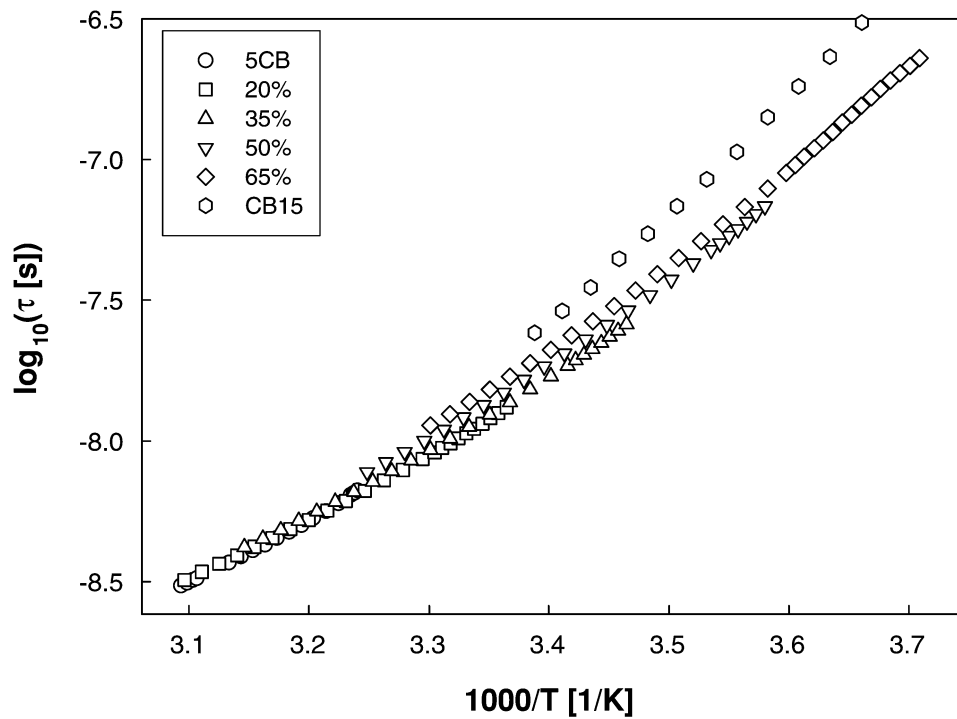The Vogel temperature T_0 was varied over a temperature

Figure 9. Temperature dependence of the relaxation times for the isotropic phases of CB15, 5CB and the mixtures.
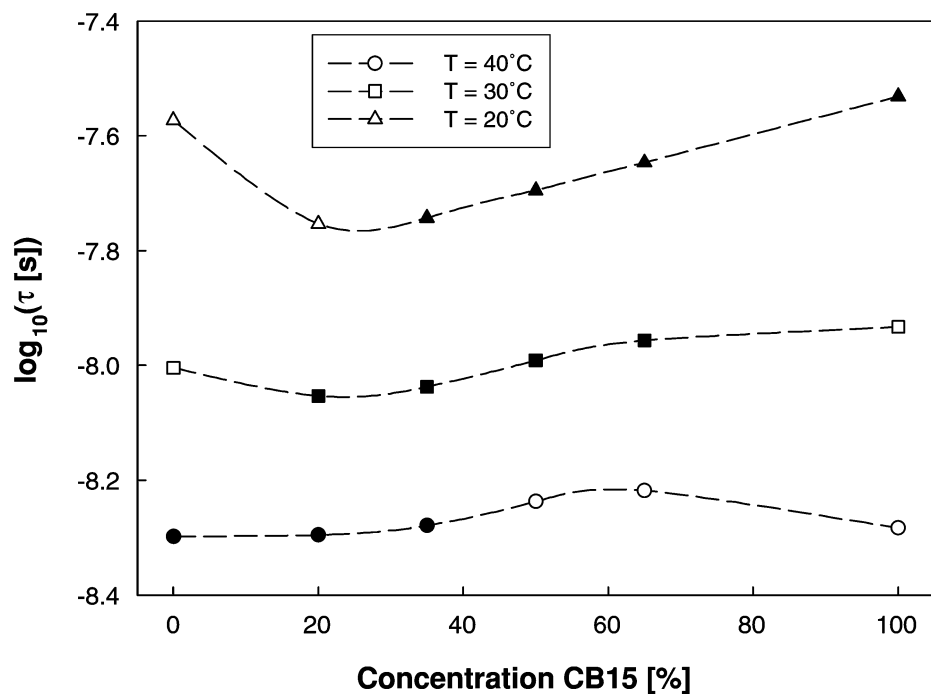

Figure 10. Relaxation times versus CB15 concentration in the 5CB+CB15 mixtures at selected temperatures. Full symbols correspond to data points, open symbols are extrapolation from the VFT fit.

range, and the temperature where the quadratic deviation (χ^2) of the resulting linear fit was minimal, was taken as the value for T_0. When the Vogel temperature is zero, this equation reduces to the Arrhenius equation. Here again we see a non-linear dependence of the fitting parameters on the concentration of CB15.
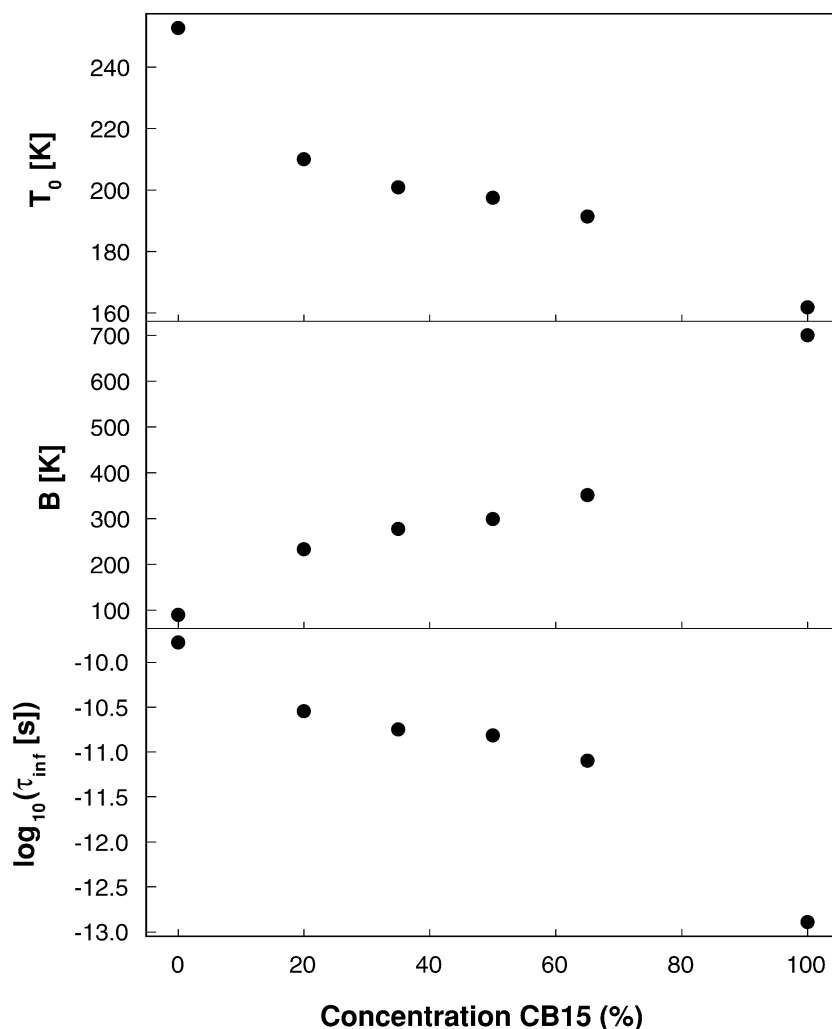
Figure 11. VFT parameters of CB15, 5CB and the mixtures.

5. Discussion and conclusion

We have studied the dielectric properties of two chiral systems, focussing on the behaviour related with the presence of the isotropic to cholesteric or blue phase transition. We have paid specific attention to the pretransitional effect in the static dielectric permittivity in the isotropic phase.

The absence of a dielectric pretransition in CE6 can be explained by the same argument as applicable to MBBA [4]. If the position and orientation of the dipole moment make it geometrically unlikely that the molecules form a dynamically antiparallel correlated pair, then no pretransitional effect can be expected. As the dipole moment of CE6 is in size and position comparable to that of MBBA, the obtained result for CE6 can, indeed, be expected.

The situation is more interesting for the mixtures of 5CB and CB15. Apart from the pretransitional behaviour,

we have results on other properties, namely relaxation times and transition temperatures. They can be compared, looking for systematic effects in their dependence on the concentration of CB15 and thus on the chirality.

1. The transition temperatures have a linear dependence with concentration.
2. The relaxation time evolves towards that of CB15 with increasing concentration of CB15. But the evolution is not linear, as can be seen directly from figure 9, where the step from the 65% mixture to CB15 is much larger than the step from 5CB to the 35% mixture. This becomes more clear after fitting the relaxation times in the isotropic phase with the VFT equation. Here clearly a non-linear behaviour for the parameters can be observed, together with a monotonic evolution.
3. In this paper, we are mainly interested in the pretransitional effect in the static dielectric permittivity.

In figure 6, for example for $T-T_{\mathrm{MI}}=20\,\mathrm{K}$, there is a clear but small (order of a few percent) minimum in the concentration dependence. Since this minimum is located near the 50% concentration, it is unlikely that it is related to chirality.

Combining these observations, we see that although all the properties depend on the concentration, this dependence is not the same. For the transition temperatures and the relaxation times it is monotonic, but only linear for the temperatures. And in case of the dielectric pretransitional effect there is a minimum around 50%. This indicates that the changing chirality of the sample is not the most important factor controlling the behaviour of the mentioned physical properties. Specifically for the dielectric pretransitional effect, probably a difference in the intermolecular potential between a 5CB molecule and a CB15 molecule and between two 5CB or CB15 molecules is responsible for the minimum at about 50%: this difference can influence the dipole correlation responsible for this effect. For the relaxation times and the transition temperatures, it is less obvious how the observed dependence can be explained.

We conclude that (i) chirality does not play an important role in the static dielectric pretransitional effect of the molecules we have probed, and (ii) the physical properties of the mixtures of 5CB and CB15 depend on the concentration, but are most likely the result of (small) differences in intermolecular interactions and not much influenced by chirality.

Acknowledgements

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