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Liquid Crystals

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Dielectric properties of the nematic liquid crystal 4-*n*-pentyl-4′-cyanobiphenyl in porous membranes

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Broadband dielectric spectroscopy (up to 10^9 Hz) is employed to study the molecular dynamics of the liquid crystal 4-*n*-pentyl-4′-cyanobiphenyl (5CB) in the free bulk phase and confined in cylindrical channels of Anopore membranes having a diameter of 0.2 μm and length of about 60 μm. The bulk samples of 5CB orient almost homeotropically between the untreated metal electrodes of the measurement set-up, and two relaxation processes are observed: the slower δ-relaxation is assigned to hindered rotation (180° flips) of the molecules around their molecular short axis, and a faster second process is attributed to the tumbling of the molecules about this axis. In the confined 5CB samples, the membrane pores align the nematic director axially or radially depending upon their surface preparation. Planar (axial) alignment is always found in untreated membranes, whereas radial alignment was achieved by treatment with decanoic acid. Consequently the director field is fixed perpendicular or parallel to the electric field and we are able to study each of the two relaxation processes separately by appropriate surface treatment of the pores. The frequencies of both processes are found to be unchanged with respect to the bulk phase. We extract the frequency dependence of the dielectric anisotropy $\delta\varepsilon$ from the dispersion curves of $\varepsilon_{\|}$ and $\varepsilon_{\perp}$. Two changes of sign of $\delta\varepsilon = (\varepsilon_{\|} - \varepsilon_{\perp})$ are detected as predicted in the literature.

1. Introduction

In recent years, a substantial amount of research has been devoted to the elucidation of anchoring and ordering mechanisms of liquid crystal molecules near solid surfaces [1–4]. The interaction of a liquid crystalline compound with a solid surface depends on the nature of both the surface and the liquid crystal material. Nematic liquid crystals (NLC) in restricted geometries represent simple examples of complex systems where orientational ordering and surface interactions can be studied easily. The characteristic distance l_o in which LC–surface interactions may be observed is in the order of about 10^3 Å [5]. The behaviour of NLC in pores of diameters in the order of l_o gives information about the nature of the LC–surface interactions.

Crawford *et al.* [6] have examined the role of surface coupling agents on alignment and ordering mechanisms at the liquid crystal–solid interface by means of deuterium nuclear magnetic resonance. The nearly cylindrical channels of Anopore membranes are modified chemically using an aliphatic acid ($C_nH_{2n+1}COOH$) as surface coupling agent before they are filled with the nematic liquid crystal. The homeotropic anchoring condition leading to planar or escaped radial director structures is stable for surfactants with $n \geqslant 7$, while chain lengths of $n \leqslant 6$ support homogeneous anchoring at the cavity walls with a uniform axial configuration of the director in the pores. Interactions between the long alkyl chains and the liquid crystal molecules are predominantly steric, resulting in homeotropic ordering while, for short chain lengths, strong interactions between the alumina surface and the core of the liquid crystal molecules dominate and enforce planar ordering [7].

Dielectric studies of NLC have proved to be a valuable source of information on the mesomorphic, liquid crystalline phase. Oriented samples of liquid crystals are dielectrically anisotropic, and both the real and imaginary parts of the permittivity tensor yield two independent principal components. The frequency dependent dielectric anisotropy is governed by permanent and induced

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dipole moments at low frequencies, and at the short-wave side of the dispersion steps (first $\varepsilon_{\parallel}$, then $\varepsilon_{\perp}$) only by the molecular polarizability.

Often in nematic liquid crystals, the relaxation of the longitudinal dielectric constant $\varepsilon_{\parallel}$ connected with molecular flips about their short axes occurs in the MHz region, where the transverse component $\varepsilon_{\perp}$ still remains constant [8–10]. For nematics with a low frequency $\delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} < 0$†, this leads to a continuous increase of $|\delta\varepsilon|$, whereas for nematics with $\delta\varepsilon > 0$, the anisotropy is predicted to change its sign twice in the dispersion curve [11]. Stieb *et al.* [12] and de Jeu *et al.* [13] were the first who discovered a change of sign of $\delta\varepsilon$ in nematic mixtures experimentally; Attard *et al.* [14] reported two-frequency switching in siloxane side chain polymers. Similar behaviour has been reported for some Schiff's bases [15]. It has been demonstrated that solely a change in temperature may be sufficient to change the sign of dielectric anisotropy of certain nematics [16], and the effect has been applied in two-frequency driven LC displays.

Dielectric properties of liquid crystals in porous materials have been only briefly explored [17, 18]. By means of broadband dielectric spectroscopy the frequency and temperature dependence of the complex dielectric function is measured in this work. Fixed alignment of the nematic in the regular pores allows a separate study of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ over the whole frequency range and conclusions can be reached on molecular dynamics.

2. Experimental

The liquid crystal investigated was the commercially available compound 4-*n*-pentyl-4′-cyanobiphenyl (5CB). This compound exhibits a nematic phase within the temperature range from 295 to 308 K. The nematic phase could be easily supercooled and dielectric measurements could be performed down to approximately 270 K without problems. The dipolar moment and polarizability of the 5CB molecule are mainly determined by the cyano group which in a rather good approximation can be considered to be along the molecular long axis. Therefore, 5CB is a compound of relatively high dielectric anisotropy in the nematic mesophase which makes it particularly suitable for dielectric studies.

Anopore filters are composed of aluminum oxide films with cylindrical pores penetrating the 60 μm thick membrane sheets normally. Three types of filter, 0·2, 0·1 and 0·02 μm with porosities of 50, 40 and 35 per cent, respectively, have been filled with the liquid crystal 5CB. The pores have diameters of 0·2 μm for each filter type; filter sizes are determined by thin sieve coatings on one side of the membrane which may be neglected in the dielectric studies. The high surface-to-volume ratio of the membranes allows for the investigation of confined nematics by dielectric spectroscopy directly in the filters sandwiched between the electrodes of the dielectric spectrometer. Thus the pore axes are strictly normal to the electrode plane and therefore parallel to the electric field.

Untreated membranes are well known to align the nematic director in a planar axial manner at their surfaces [6]. In pure samples, we always observe a nematic director field fixed parallel to the external electric field. The orientation changes qualitatively if the membranes are treated with a 2·0 wt % solution of decanoic acid ($C_9H_{19}COOH$) in methanol. The membranes are dipped into the solution for approximately one minute and then quickly pressed between the filters in order to remove the solvent from the outer membrane surface. Then they are placed in a vacuum oven for one hour to evaporate the methanol. The acid head group binds chemically to the surface and the aliphatic chains form a compact array perpendicular to the cavity wall. The liquid crystal is introduced into the membranes in its isotropic phase and heated for several hours to ensure complete filling. Afterwards, the excess of liquid crystal is removed by pressing the sample membrane between filter papers.

The quality of the samples obtained was controlled by polarizing microscopy. The conoscopic method was used to determine the alignment of the 5CB molecules inside the Anopore channels. The two types of surface preparation give strikingly different conoscopic images. In the absence of aliphatic acid surface treatment, a black Maltese cross characteristic of a uniaxial crystal cut perpendicular to its optical axis is observed. The nematic director is aligned parallel to the channels. The Anopore membranes filled with NLC are optically uniaxial with the optical axis oriented along their channels. After the insertion of a λ-plate, the conoscopic images of the samples allow the determination of the birefringence $\Delta n = (n_e - n_o)$ where n_e and n_o denote the effective extraordinary and the ordinary refractive indices of the system. The sign of Δn is positive over the whole temperature range for the 5CB/Anopore system.

In the membranes chemically modified with the aliphatic acid, strong scattering of light is observed. The aliphatic acid coating induces homeotropic orientation of the director at the walls, which may lead to three basic types of nematic director field configuration, i.e. the planar-radial, planar-polar and escaped radial configurations [19]. In the plane of the filter sheets, the director orientation is inhomogeneous for both types of homeotropic director configurations, and the resulting

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† The dielectric anisotropy of nematic liquid crystals is conventionally denoted by $\Delta\varepsilon$. We use the notation $\delta\varepsilon$ here in order to avoid confusion with the dielectric relaxation strength $\Delta\varepsilon$.

inhomogeneous refractive index profile introduces strong static scattering of the transmitted light.

From the dielectric spectra we conclude that the director alignment was very much planar in the pore cross-sections. The dielectric spectra cannot distinguish between planar polar and radial orientations of the director field.

3. Results and discussion

For a comparison of the confined and free phase, we measured the dielectric spectra of 5CB in the bulk and adsorbed in Anopore membranes. In bulk nematic 5CB, two relaxation processes may be observed simultaneously [17]. The first process, the slower one, is assigned to the hindered rotation of the molecules around their molecular short axes (molecular flips of 180°); its relaxation time is in the range of about $2{\cdot}3\times10^{-8}$ to $5{\cdot}3\times10^{-8}$ s, depending on the temperature. This process affects the longitudinal component (along the director) of the dipolar moments. As we will show below, it is theoretically established that this process is most efficient when the director is aligned parallel to the electrical field, but does not affect dielectric relaxation when the director is perpendicular. The second, faster process originates from tumbling of the molecules around the director axis with relaxation times in the range 4 to $5{\cdot}6\times10^{-9}$ s in the temperature range from 294 to 304 K. It affects mainly the lateral dipolar moment (perpendicular to the local director orientation) and is consequently most effective when the director is perpendicular to the sensing electric field. In the isotropic phase, where the hindering nematic potential is absent, only one single relaxation process can be observed.

The Havriliak–Negami [20] analysis was applied for the quantitative interpretation of the dielectric data to determine the corresponding relaxation time distributions and dielectric strengths of the relaxation processes.

$$\varepsilon''(\omega)=\sum_{k=1}^{2}\mathrm{Im}\,\{(\Delta\varepsilon_k)/(1+i\omega\tau_k)^{\alpha_k})^{\gamma_k}\}\qquad(1)$$

gives the frequency dependence of the imaginary part of the dielectric permittivity (usually denoted as dielectric loss). Here, $\Delta\varepsilon_k=(\varepsilon_s-\varepsilon_\infty)k$ is the dielectric strength of the kth process, ε_s and ε_∞ describe the values of ε' at the low frequency and high frequency side of the relaxation, respectively, and α and γ are constants characterizing width and asymmetry of the relaxation time distribution.

At first we checked the dielectric properties of the empty Anopore membrane. Figure 1 displays the real and imaginary part of the dielectric function at 297 K. The open symbols represent the data for the empty membrane; the real part (ε') of the dielectric function is constant in the measured frequency range and accordingly no loss peak can be observed in ε''. Hence in the filled Anopore membrane only the 5CB contributes to the imaginary part of the dielectric function.

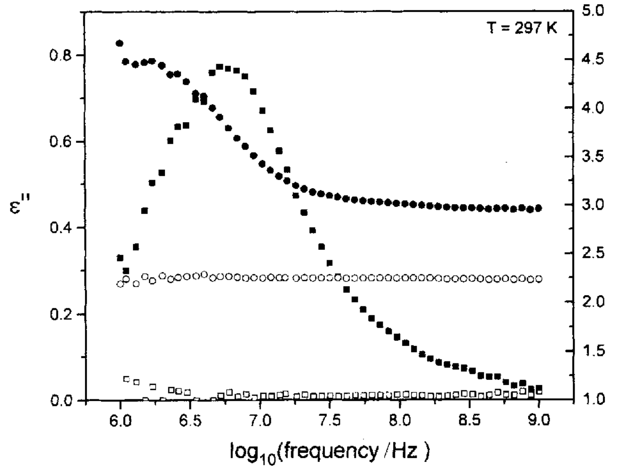


Figure 1. Real- and imaginary parts of the dielectic function for empty Anopore membrane (open symbols) and Anopore membrane filled with 5CB (solid symbols). ○, ●: real part (ε'); □, ■: imaginary part (ε'').

Figures 2 (*a*) and (*b*) show typical experimental dielectric loss curves versus frequency in the nematic phase. Figure 2(*a*) gives a comparison between the frequency dependencies of dielectric loss ε'' for the bulk 5CB sample and 5CB confined to untreated Anopore membranes of different filter types. Spectra measured at one particular temperature (297 K) are shown. In the bulk phase, two processes are seen; the slower one is much larger in amplitude, whereas the high frequency process is indicated only by a shoulder in the dielectric loss spectrum. In the confined nematic, the dielectric loss peak of the slow process is slightly shifted towards higher frequencies with respect to the free phase. It is independent of the type of filter. This should not be surprising because the basic effect of confinement is the director alignment at the pore surfaces. In the confined mesophase, the nematic director is aligned perfectly parallel to the pore walls of the filters (axial configuration). The fast process is suppressed in the dielectric spectra of the axially confined NLC samples. In this configuration, only the process connected with flips of the molecules around their short axes is effective.

Figure 2 (*b*) shows the frequency dependence of the dielectric loss ε'' for 5CB in Anopore membranes chemically modified using decanoic acid ($C_9H_{19}COOH$). Two curves of the homeotropic bulk data taken at different temperatures are shown for comparison. The dominating low frequency peak in the bulk curve shifts towards lower frequencies with decreasing temperature. In the confined sample, this first, slow process is remarkably suppressed; despite its higher absolute dielectric strength in the bulk, it drops almost below experimental reso-

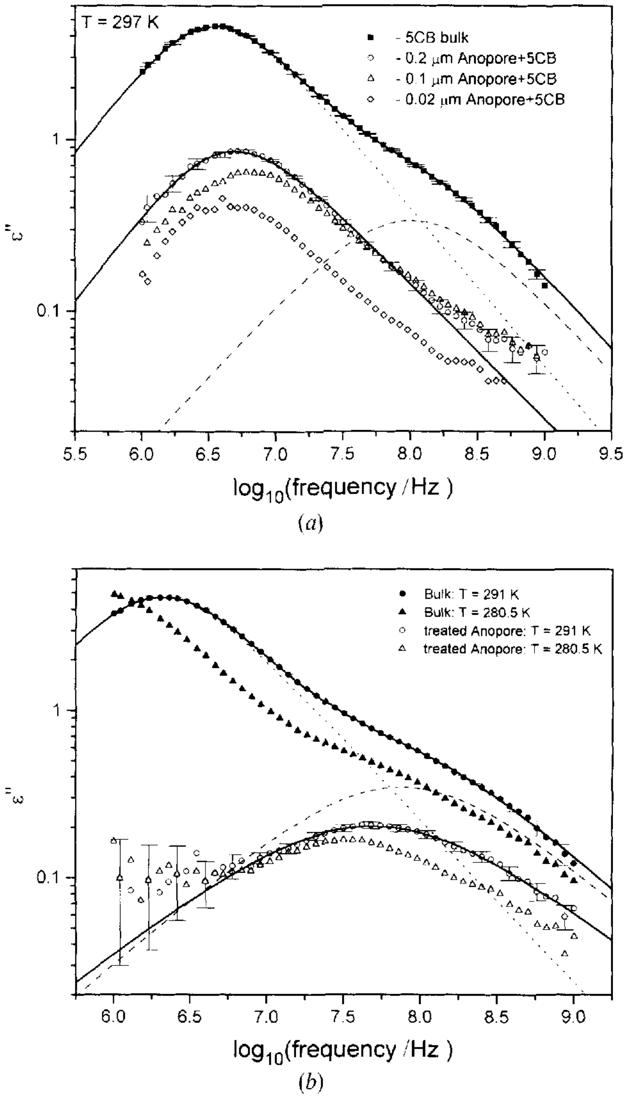


Figure 2. (*a*) Frequency dependence of the dielectric loss ε'' for 5CB in the bulk (solid symbols) and confined to untreated Anopore filters of different types (open symbols) at $T = 297$ K in the nematic mesophase. The solid curves are fits to superposed Havriliak–Negami processes (equation (1)). The dashed and dotted lines indicate the contributions of the high and low frequency processes, respectively, in the bulk experiment. (*b*) Frequency dependence of the dielectric loss ε'' for 5CB in the bulk (solid symbols) and confined to Anopore filters of porosity 0.2 μm treated with decanoic acid (open circles). The solid lines are Havriliak–Negami fit curves. Curves corresponding to two temperatures are shown.

lution in the treated Anopore sample as seen in the figure. This gives strong evidence that the nematic director inside the filters is oriented nearly perpendicular to the axes of the channels (planar-polar or planar-radial configuration) and does not observably escape the planar orientation, at least at high temperatures in the nematic phase. A slight reappearance of the slow frequency process is indicated, however, at very low temperatures.

A quantitative evaluation has been performed by fitting the dielectric data to superpositions of Havriliak–Negami processes as given in equation (1). Fit curves corresponding to a superposition of two processes as given in equation (1) are drawn as solid lines. The dashed and dotted lines indicate the contributions of the two individual processes to the bulk curve. Dielectric strengths and relaxation times versus temperature have been retrieved from the fits of data sets.

The temperature dependence of the dielectric strength $\Delta\varepsilon_1$ for axially confined 5CB is shown in figure 3 (*a*) together with the data for the homeotropic bulk sample. The dielectric strength in the porous media is one order of magnitude lower than in the bulk, and it decreases with smaller filter size. Due to the different filling factors, absolute magnitudes cannot be compared directly. The main influence comes from the different amounts of liquid crystal inside the pores which prevent a comparison of the absolute values of the dielectric losses measured in different samples. In the isotropic phase, the ratio of dielectric strengths of different samples should depend on the filling factor only. Assuming that this filling factor is temperature independent, we can try to scale absolute data from experiments on different samples by adjusting the dielectric strength of the process in the isotropic phase. This allows a comparison of the absolute dielectric losses for different samples in the nematic phase.

The dielectric medium is not homogeneous, and effective dielectric coefficients measured in the experiment with confined NLC are a mixture of the dielectric coefficients of the filter and NLC materials. However, we do not observe loss processes in the filter material; therefore dielectric loss data can be attributed to the nematic LC completely.

The ratio of the effective dielectric strengths of the two molecular processes in the bulk sample is defined mainly by the sample geometry, i.e. the orientation of the director field with respect to the external electrical field in the sample container. The slow process attributed to the molecular flips around the short axis is particularly effective in the geometry used in our experiment. The dielectric strength of the second process is one order of magnitude lower than the first one. This gives strong evidence that the director arrangement is almost homeotropic. The uncovered metal surfaces of the electrodes of the sample container align the nematic normal to their surfaces and the surface alignment is maintained in the bulk of the NLC layer in a thickness of approximately 50 μm. The director is therefore nearly (not perfectly) aligned to the external electric field. The meas-

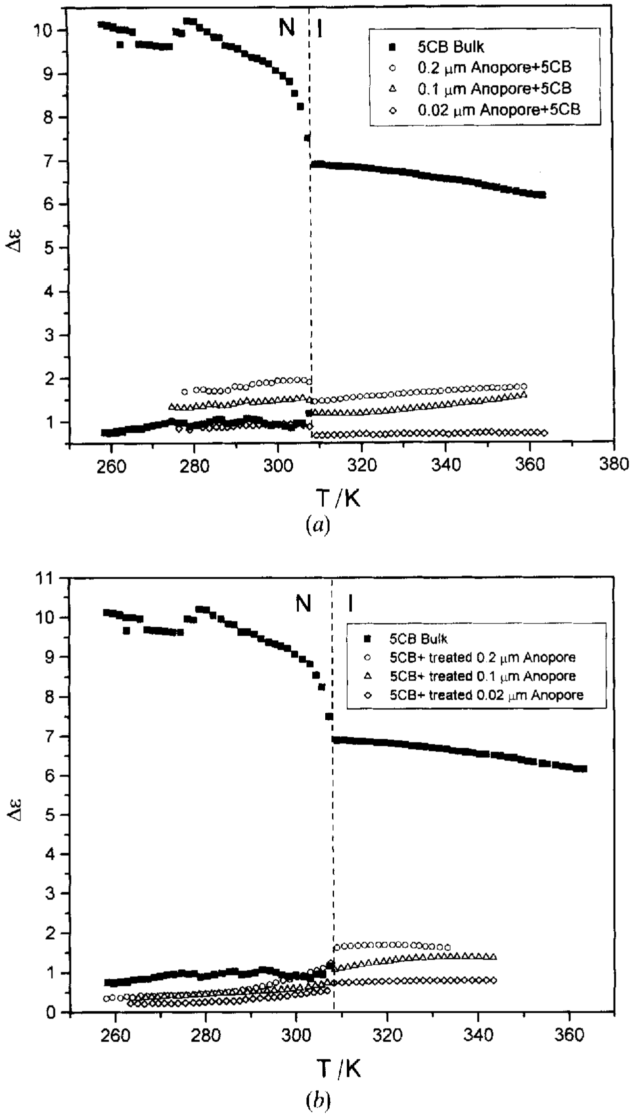


Figure 3. (*a*) Temperature dependence of the dielectric strength $\Delta\varepsilon$ for the process observed in 5CB confined to untreated filters (open symbols). The dielectric strengths for both processes observed in the bulk (homeotropic orientation) are given for comparison (full symbols). (*b*) Same as in figure 2 (*a*) for 5CB in filter pores treated with decanoic acid $C_9H_{19}COOH$.

uring field of less than 0·5 V is smaller than the critical Fréedericksz threshold for 5CB (approx. 1 V), but may support the homeotropic orientation induced by the surface. One further piece of evidence for this assumption is that no Fréedericksz reorientation was observed after application of a bias electric field.

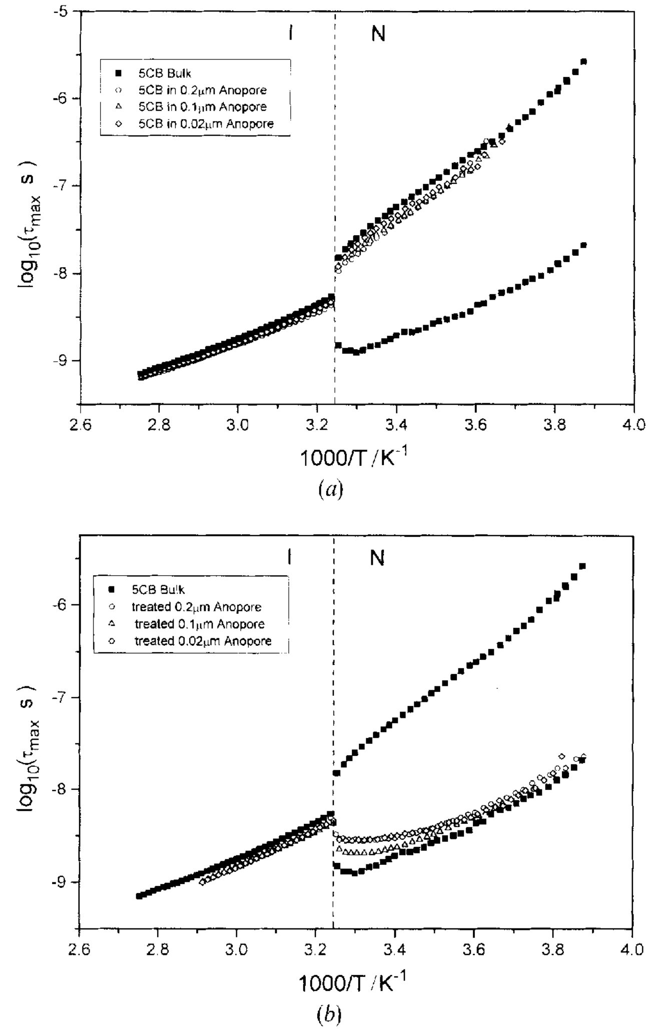
The dielectric strength of the first process $\Delta\varepsilon_1$ is comparable in magnitude with the static dielectric coefficient of 5CB. However, the decrease in the real part of dielectric function in the dispersion curve is greater than the static dielectric anisotropy $\varepsilon_{\parallel} - \varepsilon_{\perp}$, where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ denote the components of the dielectric tensor measured parallel and perpendicular to the director, respectively.

The temperature dependence of the dielectric strength $\Delta\varepsilon_2$ for 5CB confined to surface treated Anopore membranes is presented in figure 3 (*b*). The dielectric strengths observed in the nematic phase are lower than in the isotropic phase. Differences of the dielectric strengths in the isotropic phase of the different samples again are due to the variation in the filling factors.

Figure 3 (*b*) compares the dielectric strength of 5CB in treated filters with the bulk processes. Only the fast process can be extracted from the confined LC data. However, as is seen in the figure, the strength of the fast process seems to decrease towards lower temperatures. It seems reasonable to assume that the decreasing relaxation strength of the fast process is connected with a slight escape of the director field towards an axial orientation in the centre of the filter channels, although a low frequency contribution from the escaped configuration in the pore centres (director along the electric field direction) is not resolvable in the relaxation curves within experimental uncertainty.

No differences between the relaxation frequencies are observed for different filter sizes. A pronounced broadening of the relaxation time distribution is observed for the liquid crystal in the pores chemically modified using aliphatic acid. In contrast to the measurements in untreated membranes, we observe now the tumbling of the molecules around their molecular short axis. In this configuration, we can separate the dispersion of the real part of $\varepsilon_{\perp}$. The Anopore filters provide an excellent means to achieve oriented nematic samples in dielectric experiments without the necessity of applying additional magnetic fields which would make the experimental set-up more complicated.

The relaxation rates are independent of the filling factor and thus easier to compare for all samples. Figures 4 (*a*) and (*b*) present Arrhenius plots of the relaxation times $\tau_{\max}$ for bulk 5CB and the confined 5CB samples. The temperature dependence of the mean relaxation time $\tau_{\max}$ exhibits Arrhenius-like behaviour in the isotropic phase and, except for the range in the vicinity of T_{NI}, also in the nematic phase. In the isotropic phase, the relaxation rates of all samples coincide; an influence of the inner surfaces on dielectric relaxation is not noticeable. The relaxation frequency decreases with decreasing temperature down to the phase transition at $T_{\mathrm{NI}} = 308$ K. The activation energy retrieved from the relaxation time data in the isotropic phase is about 36·7 kJ mol^{-1}. In the nematic phase the situation is more complicated. The relaxation time of the slow process observed in the axially oriented (untreated) systems is



(*a*)

(*b*)

Figure 4. (*a*) Arrhenius plot of the temperature dependence of the relaxation time τ_{max} for the slow process observed in 5CB in untreated filters (open symbols) and the first and second region of dispersion in bulk 5CB (solid symbols). (*b*) Same as in figure 3(*a*) for 5CB in filter pores treated with decanoic acid $C_9H_{19}COOH$ (open symbols). Bulk data are again given for comparison.

slightly faster in the porous materials as compared to the bulk, but the differences are not significant and might be attributed to slightly changed order parameters. Its activation energy in the nematic state of 64·6 kJ mol^{-1} is comparable with data from other experiments [21, 22]. The relaxation rate of the process observed in the planar orientation of the confined nematic (homeotropic to the pore walls treated with aliphatic acid) is faster by about two orders of magnitude, and its relaxation frequency coincides roughly with that of the fast bulk process. For this fast process, an Arrhenius plot far below the phase transition yields the activation energy of about 46·3 kJ mol^{-1}, whereas near the phase transition the behaviour cannot be described in terms of an Arrhenius formula. The influence of different filter materials is insignificant as expected.

The orientation of the nematic molecules inside the treated and untreated Anopore membranes allows for separate measurements of the dielectric dispersion curves for the real parts of both $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ of the permittivity tensor in 5CB. Figure 5 shows the ratio of the relaxation times of the tumbling and flipping processes for different temperatures in the nematic phase. Whereas the temperature characteristics of the fast process are not very different from the isotropic relaxation process with comparable activation energies, the slow flip process is strongly influenced by the nematic potential. The corresponding relaxation time ratio is determined by the potential barrier separating the two energetically equivalent opposite orientations of the molecule with respect to the director axis. If a simple ansatz of rotational diffusion in a cosine potential $V = V_0 \cos(\theta)$ (see e.g. [23]) is assumed, where θ is the angle between director and molecular long axis (roughly the direction of the dipolar moment of 5CB), one can estimate the ratio between the dynamics of the fast process (in the potential minimum) and the slow process (crossing of the potential barrier). $\tau_{slow}/\tau_{fast} = I_0{}^2\ (V_0/(k_bT))$ decreases with the square of the modified Bessel function of order zero. The corresponding values for V_0 which yield the experimental ratios depicted in figure 6 are 2·44 k_bT at the high temperature end ($\tau_{slow}/\tau_{fast} = 0{\cdot}1$) and 4·0 k_bT at the low temperature end ($\tau_{slow}/\tau_{fast} = 0{\cdot}08$). In Maier–Saupe theory, one would expect order parameters of 0·638 and 0·793, respectively, with these values for the mean field potentials. Compared to order parameters from other

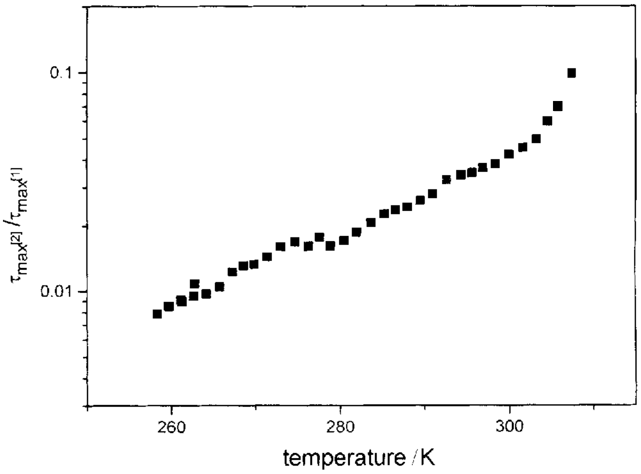


Figure 5. Ratio of the dielectric relaxation times of the slow and fast processes in 5CB as a function of temperature in the nematic phase. Their increasing ratio at lower temperatures is a measure of the higher hindering potential for the flip process.

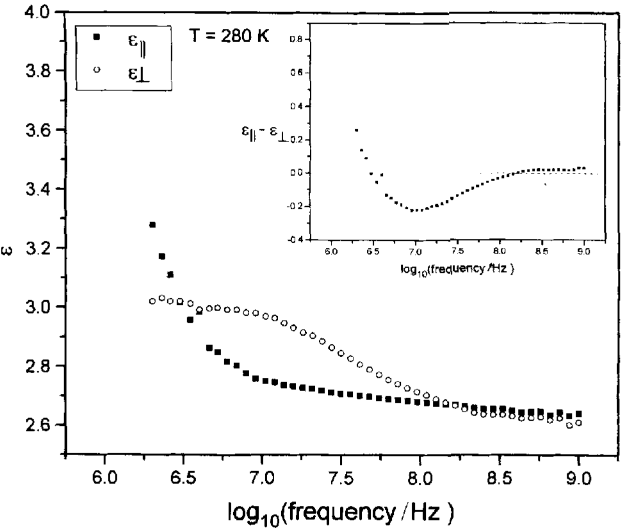


Figure 6. Frequency dependence of the dielectric permittivities $\varepsilon_{\parallel}$ parallel and $\varepsilon_{\perp}$ perpendicular to the director for 5CB, measured in untreated (■) and treated (○) Anopore membranes (diameter 0·2 µm), respectively. The inset shows the frequency dependence of the dielectric anisotropy $\delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$ at a temperature of 280 K. At frequencies 3·2 and 174 MHz, the anisotropy changes its sign.

experiments (e.g. [24]), the potential barriers estimated from the relaxation time ratios are slightly too high but, in view of the rough estimates, in a reasonable order of magnitude. Moreover, in the polar liquid crystal 5CB, short range dipolar antiparallel ordering may be responsible for a deviation from Maier–Saupe mean field predictions.

Figure 6 shows the frequency dependence of the real parts of the dielectric permittivities $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, of 5CB measured in untreated and treated 0·2 µm Anopore membranes, respectively. As data for different Anopore samples cannot be compared directly, the curves have been scaled with the filling factor retrieved from the isotropic loss slightly above the phase transition T_{NI}. Both curves intersect at two frequencies, 3·2 and 174 MHz. This is direct experimental evidence that the dielectric anisotropy changes its sign twice over the complete frequency range. The static dielectric anisotropy, as well as the optical anisotropy n_e–n_o are positive, and the dielectric loss of the slower process is larger than the static anisotropy; therefore this behaviour should be expected. The inset in figure 6 gives the frequency dependence of the dielectric anisotropy $\delta\varepsilon$ which illustrates our conclusion. The change of sign in $\delta\varepsilon$ would imply that the nematic director will align parallel to the external electric field in the low and high frequency limits, whereas it orients perpendicular to the field at some intermediate frequency range.

This behaviour was already predicted earlier [21], but this paper seems to be the first where dielectric relaxation measurements of 5CB are reported in the frequency range where both relaxation processes are effective.

The theoretical description of molecular order in the nematic phase allows us to connect the measured dielectric losses with the nematic order parameter S. The low frequency dielectric anisotropy of a molecule is determined by two factors: (i) the polarizability anisotropy α_a, which for the elongated molecules of nematogenic compounds yields a positive contribution, (ii) the static dipole orientation. The sign of the latter contribution is positive if the net permanent dipole moment of the molecule makes a small angle β with its long axis. In the 5CB molecule, the strong static dipole of the cyano group is almost parallel to the molecular long axis, and $\beta \approx 0$. Maier and Meier [25–27] took into account the polarization field in the medium by applying Onsager theory [28]. The effective induced dipole moments per molecule along and perpendicular to the unique axis (director) of the NLC are given by the expressions:

$$\bar{m}_1 = (\bar{\alpha} + \tfrac{2}{3}\alpha_a S)FhE_1 \qquad (2a)$$

$$\bar{m}_2 = (\bar{\alpha} + \tfrac{1}{3}\alpha_a S)FhE_2 \qquad (2b)$$

where $h = 3\bar{\varepsilon}/(2\bar{\varepsilon}+1)$ is the cavity field factor, $\bar{\varepsilon} = \frac{1}{3}(\varepsilon_{\parallel} + 2\varepsilon_{\perp})$ stands for an average dielectric constant, $F = 1/(1-\bar{\alpha}f)$ is the reaction field factor, $\bar{\alpha}$ the mean polarizability, and α_a the polarizability anisotropy. The factor f is given by $f = (2\bar{\varepsilon}-2)/4\pi\varepsilon_0 a^3(2\bar{\varepsilon}+1)$ with a being the molecular radius, S is the nematic order parameter and E is the applied electric field. The indices 1 and 2 designate the field components parallel and perpendicular to the director. The relations of the effective permanent dipole moments to the electric field are [29]:

$$\bar{\mu}_1 = \frac{\mu^2}{3k_B T} hF^2 E_1[1+2S] \qquad (3a)$$

$$\bar{\mu}_2 = \frac{\mu^2}{3k_B T} hF^2 E_1[1-S] \qquad (3b)$$

From equations (2) and (3) one can calculate the order parameter S if the dielectric strengths of processes assigned to hindered rotation about the molecular short axis, $\Delta\varepsilon_{\parallel}$, and tumbling around this axis, $\Delta\varepsilon_{\perp}$, are known:

$$S = \frac{\Delta\varepsilon_{\parallel} - \Delta\varepsilon_{\perp}}{2\Delta\varepsilon_{\perp} + \Delta\varepsilon_{\parallel}} \left[\frac{\bar{\alpha} + F\mu^2/3k_B T}{\alpha_a/3 + F\mu^2/3k_B T} \right] \qquad (4)$$

We have used data available in the literature for 5CB at $T = 298$ K: $\mu = 1{\cdot}1 \times 10^{-29}$ Cm, $\bar{\alpha} = 3{\cdot}62 \times 10^{-39}$ C^{2}m^2 J^{-1}, $\alpha_a = 3{\cdot}02 \times 10^{-39}$ C^{2}m^2 J^{-1}, $\varepsilon_{\parallel} = 18{\cdot}5$, $\varepsilon_{\perp} = 7$, $M = 249$ g mol^{-1}, $\rho = 1{\cdot}022$ g cm^{-3}. The dielectric strengths (scaled by the isotropic values to account for the filling factors) give a ratio of $\Delta\varepsilon_{\parallel}/\Delta\varepsilon_{\perp} = 2{\cdot}0$ at this temperature which yields the unrealistically low value of $S=0{\cdot}29$ for the nematic order parameter, i.e. for an order parameter of $\approx 0{\cdot}5$, the ratio $\Delta\varepsilon_{\|}/\Delta\varepsilon_{\perp}$ should be 3·25. It is interesting, however, that Buka and Price [30] from measurements on a homologous compound came to a comparably low value.

4. Conclusions

The dielectric properties of nematic liquid crystal 5CB confined to treated and untreated Anopore membranes have been measured in the frequency range from 10^6 to 10^9 Hz at temperatures between 270 and 320 K. It has been shown that the confinement of NLC to inorganic filters with regular pores provides a convenient tool for the orientation of the sample in dielectric experiments. We have measured separately the dispersion curves for the slow and fast dielectric relaxation process in the nematic. In bulk 5CB, with the boundary conditions imposed by our experimental set-up, two relaxation processes are observed. The first, slower one is assigned to the hindered rotation of the molecules around their short axes. It is very effective in the bulk sample which indicates that the nematic aligns quite well homeotropically at the untreated metal electrodes of the set-up. The second process is faster by approximately two orders of magnitude; it is connected with tumbling of the molecules around the molecular short axis. In the Anopore membranes, a separation of the two processes is possible. The nematic order parameter calculated from the ratio of the dielectric losses connected with both processes using Maier–Meier theory yields too low values compared with data from other experiments.

The relaxation rate in the isotropic phase is not influenced by the presence of the inner surfaces in the confined systems. The weakening of the dielectric strength of the observed processes for the 5CB/Anopore system, as compared to the bulk, is mainly caused by the filling factor and is in the order of 0·35–0·5.

From the observed dispersion curves of $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ we could show experimentally that the dielectric anisotropy $(\varepsilon_{\|}-\varepsilon_{\perp})$ of 5CB changes its sign twice over the frequency range covered by our experiments. The dielectric measurements in untreated Anopore membranes confirm the planar axial order of nematic molecules; in membranes treated by decanoic acid, a polar-radial or polar-planar orientation of the molecules is very likely, although a slight escaped director structure at least at low temperatures seems to be indicated in the dielectric data.

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