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Dielectric relaxation in bulk and cylindrically confined octylcyanobiphenyl (8CB)

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The dielectric relaxation spectrum over the frequency range 10^2 to 1.8×10^9 Hz of 4-octyl-4′-cyanobiphenyl, 8CB, in bulk and confined to 200 nm diameter cylindrical pores is reported. We used matrices with parallel cylindrical pores, obtaining different alignments of the molecular director depending on the treatment. Results show that there are two relaxations in the isotropic phase and in the mesophases for parallel alignment and three for perpendicular alignment. The molecular origin of theses modes and the effect of the confinement on their dynamics are discussed. To compare properly the results for bulk and confined 8CB, a re-scaling of the experimental data is proposed.

1. Introduction

Dielectric spectroscopy is a powerful tool for the study of the dynamics of polar substances, for example, liquid crystals. Nematic liquid crystals, and above all the cyanobiphenyls, have been extensively studied by this technique [1]. However, some basic problems concerning the interpretation of the experimental results are still the source of controversy [2]. Recently, much attention has been paid to the effect of confinement of liquid crystals in porous matrices, with calorimetric and dielectric techniques very useful to analyse the changes in dynamic and static properties [3–10]. In this work we report a study on 8CB confined in untreated and treated cylindrical pores of Anopore membranes. We obtained configurations in which the molecules are aligned either parallel or perpendicular to the electric field, allowing us to measure both $\varepsilon_{\|}$ (probing electric field parallel to the director) and $\varepsilon_{\perp}$ (probing electric field perpendicular to the director). The experimental procedure is similar to that described in [3], where 8CB was also studied. However, our results have been treated in a different way. We propose a different analysis of the data, with two modes in the isotropic phase and in the mesophases for parallel alignment, and three for perpendicular alignment. For completeness, and in order to analyse properly the confinement effects, we also present results for bulk 8CB in both homeotropic-parallel and planar-perpendicular configurations.

A general theory for the dielectric relaxation of rigid dipolar molecules in nematic fluids has been developed by Nordio *et al.* [11]. Let us recall the main statements and assumptions of this theory. The frequency-dependent complex dielectric permittivity tensor, $\varepsilon_{\|}(\omega)$, $\varepsilon_{\perp}(\omega)$, can be related to the Laplace transform of the time autocorrelation functions for projections of the molecular dipole components parallel and perpendicular to the director:

$$C_{\|}(t) = \frac{\langle \mu_{\|}(0)\mu_{\|}(t)\rangle}{\langle \mu_{\|}^2\rangle} = \frac{1}{3\mu^2}\left[\mu_{\mathrm{l}}^2(1+2S)\phi_{00}^1(t) + \mu_{\mathrm{t}}^2(1-S)\phi_{01}^1(t)\right] \tag{1a}$$

$$C_{\perp}(t) = \frac{\langle \mu_{\perp}(0)\mu_{\perp}(t)\rangle}{\langle \mu_{\perp}^2\rangle} = \frac{1}{3\mu^2}\left[\mu_{\mathrm{l}}^2(1-S)\phi_{10}^1(t) + \mu_{\mathrm{t}}^2(1+S/2)\phi_{11}^1(t)\right] \tag{1b}$$

where μ_{l} and μ_{t} are components of the molecular dipole along and transverse to the long axis of the molecule, $\phi_{ij}^1(t)$ are time correlation functions of the first order Wigner rotation matrix, and S is the order parameter [12, 13]. The quantities $\phi_{ij}^1(t)$ describe the time dependence of angular functions representing different

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relaxation modes for the molecular dipole in an anisotropic environment. Nordio *et al.* [11] have shown that for the rotational diffusion model, $\phi^1_{ij}(t)$ may be written as a sum of exponentials. However, the first term is dominant and the time dependence of each of the four separate contributions to the correlation functions (1 *a*, 1 *b*) can be described by a single characteristic time, τ_k (1 corresponds to 00, 2 to 01, 3 to 10 and 4 to 11). In the frequency domain the four relaxation modes, two for each main component, are described by the Debye function:

$$\Delta\varepsilon_k(\omega) = \frac{\Delta\varepsilon_k}{1 + i\omega\tau_k} \qquad (2)$$

Let us use $\omega_k = 1/\tau_k$, the characteristic frequency of each mode, to label the mode itself. The molecular assignment usually accepted [14] is that ω_1 is due to molecular rotation about the short molecular axis, ω_2 is due to rotation about the long molecular axis, while ω_3 is due to the precessional motion of the molecules around the director, and ω_4 is due to rotation about the long axis of the precessing molecule. The actual frequencies depend on the molecular anisotropy and on the value of the orientational order parameter [14], *S*, with ω_1 decreasing strongly with increasing order, while ω_2 and ω_3 increase with order and ω_4 is approximately independent of order. The relative strengths of the relaxations can be related to the dipole components using the Maier and Meier equations [15]:

$$\varepsilon_{\|} - \varepsilon_{\|\infty} = \frac{NLF^2}{3\varepsilon_0 k_{\mathrm{B}} T}\left\{\left[\mu_{\mathrm{l}}^2(1+2S)\right]_{\omega_1} + \left[\mu_{\mathrm{t}}^2(1-S)\right]_{\omega_2}\right\} \qquad (3a)$$

$$\varepsilon_{\perp} - \varepsilon_{\perp\infty} = \frac{NLF^2}{3\varepsilon_0 k_{\mathrm{B}} T}\left\{\left[\mu_{\mathrm{l}}^2(1-S)\right]_{\omega_3} + \left[\mu_{\mathrm{t}}^2(1+S/2)\right]_{\omega_4}\right\} \qquad (3b)$$

where *N* is the number density, and *L* and *F* are internal field factors [12]. The subscripts ω_k indicate those terms that contribute to the strength of the different relaxation processes. One of the major difficulties in the analysis of the dielectric relaxation spectra of liquid crystals is the fact that the different relaxations do not occur at well separated characteristic frequencies. Moreover, the spectral shape, in general, does not correspond to the pure exponential Debye, and the empirical Havriliak–Negami (H-N) function:

$$\Delta\varepsilon_k(\omega) = \frac{\Delta\varepsilon_k}{\left[1 + (i\omega\tau_k)^{\alpha}\right]^{\beta}} \qquad (4)$$

should be used. The parameters α, β control the shape of the relaxation: $\alpha = \beta = 1$ corresponds to the Debye relaxation, $\alpha = 1$ to the Cole–Davidson relaxation and $\beta = 1$ to the Cole–Cole relaxation.

In this paper a dielectric spectroscopy study in bulk (homeotropic–parallel and planar–perpendicular alignments) and cylindrically confined 8CB (axial and radial) is presented. As for bulk 8CB, considerable effort to separate the different superimposed relaxation modes was made in order to obtain an accurate physical picture of the molecular motions. This point is of extreme importance if one looks forward to interpreting properly the subtle changes of the molecular motions when 8CB is confined to the slightly-restricted geometries of Anopore membranes. Unlike earlier publications [3, 8], we propose how to re-scale the data in confined geometries in order to compare the corresponding dielectric strengths with those of the bulk. Among other facts, these re-scaled dielectric values allow us to estimate the number of molecules near the pore walls that do not contribute to the (orientational) dielectric permittivity; that is to say, the molecules on a boundary layer that are more hindered than in the bulk. This estimation is comparable to that inferred by Iannacchione and Finotello [4] from the specific-heat peak suppression at the N–I transition.

The paper is structured as follows. First we describe the sample preparation and the experimental set-up. In § 3 the experimental results in bulk and confined 8CB are presented; the results are discussed in § 4. Finally, in § 5 our main conclusions are summarized.

2. Experimental

The dielectric permittivity of the materials was measured in the range 10^2–1.8×10^9 Hz using the HP 4192A and the Agilent 4291A impedance analysers. The cell (for the non-confined samples) consisted of two gold plated electrodes of 5 mm diameter separated by 50 μm thick silica spacers, making a parallel plate capacitor located at the end of a coaxial line. A modified HP16091A coaxial test fixture was used as the sample holder. It was held in a cryostat from Novocontrol, which screens the system, and both temperature and dielectric measurements were computer controlled.

8CB, 4-octyl-4′-cyanobiphenyl, was synthesized by Professor Dabrowsky in the Institute of Chemistry, Military University of Technology, Warsaw, Poland. The purity was stated to be higher than 99.9%, and no further purification was made. It has the following sequence of phase transitions (on cooling): I (isotropic) (39.5°C) N (nematic) (32°C) SmA (smectic A); we obtained transition temperatures lower (between 0.5 and 1.5°C) than other authors, see for example [16]. It has an important positive dielectric anisotropy and the parallel configuration was easily obtained by applying a 40 $\mathrm{V_{dc}}$ voltage. We studied the permittivity vs. voltage, controlling that with 40 $\mathrm{V_{dc}}$ it was well saturated. We note that with this method one aligns, essentially, the axis of maximum orientational polarizability of the molecules that coincides with the direction of the resultant dipole moment of the molecule. To obtain the perpendicular configuration, both electrodes were spin-coated with PI2555 polyimide (HD Mycrosystems) following the procedure described by the manufacturer and then rubbed uniaxilly. Although the polyimide layers were very thin, they contribute to the measured capacity, which should be attributed to two series capacitors, the polyimide layers and the liquid crystal sample. We have corrected the results assuming for the polyimide a temperature and frequency-independent capacity and taking into account that in the I phase in both types of cell (treated and non-treated electrodes) the measurements should coincide. It is worth noting that this series capacitor changes not only the absolute value of the 'measured' pemittivity but also the relaxation frequencies.

To confine the liquid crystal we used Anopore™ (Whatman) membranes with cylindrical parallel pores of 200 nm diameter and porosity of 70%. The thickness of the membranes was 60 µm. We used untreated and treated membranes (with HTBA, hexadecyltrimethylammonium bromide). In both cases we controlled the mass before and after filling the pores with the liquid crystal. The filling ratio was about 85% in all cases, similar to that obtained by other authors [4, 17]. As we shall see below and according to the literature [3, 4, 9, 17, 18], with the untreated membranes the liquid crystal molecules align mainly parallel to the pore axis, axial configuration, allowing us to measure $\varepsilon_{\|}$. For the treated membranes, the HTBA aligns the molecules mainly perpendicularly to the pore axis, allowing us to measure $\varepsilon_{\perp}$. When the liquid crystal is confined in the membranes, the measured capacity could be attributed to two parallel capacitors: the alumina matrix and the dispersed liquid crystal. We can deduce an 'apparent complex permittivity': $\varepsilon_{ap}=(C_m-C_{al})/pC_0$, where $C_{al}=(1-p)C_0\varepsilon_{al}$ accounts for the matrix capacity (in this equation ε_{ap} and C_m are complex quantities; in the studied frequency and temperature ranges, the permittivity of the alumina is nearly constant and C_{al} is a real quantity), $p=0.7$ is the porosity and C_0 is the geometrical capacity of the capacitor. From this value we cannot deduce the liquid crystal permittivity because we cannot propose an equivalent circuit for the system pores+liquid crystal due to the possible inhomogeneity of the filling of the cylindrical pores by the liquid crystal. However, in order to compare the dielectric strengths of the different modes in the bulk and in the confined geometries (both axial and radial) the residual high frequency permittivity in the isotropic phase (for the confined case with the above defined apparent quantities) has been compared, obtaining: axial confinement $\varepsilon_{\infty bulk}/\varepsilon_{\infty ap}\cong 1$, radial confinement $\varepsilon_{\infty bulk}/\varepsilon_{\infty ap}\cong 1.17$. Assuming that the physical mechanisms contributing to ε_∞, mainly the induced polarization (for bulk sample we obtain for ε_∞ 2.6 in the I phase, 2.7 in N parallel, and 2.5 in N perpendicular, values very near n^2), should not be greatly affected by the confinement, all the data have been re-scaled according to these values.

3. Results

3.1. *Bulk 8CB*

Figures 1 (*a*) and 1 (*b*) are three-dimensional plots of the losses vs. temperature and frequency for the parallel and perpendicular alignments, respectively, in the

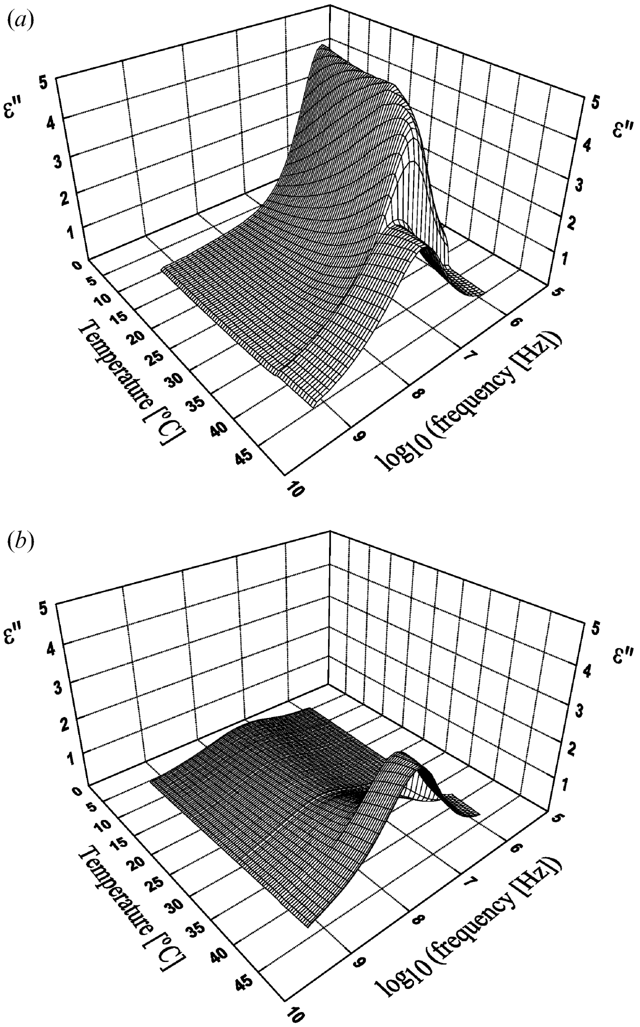

Figure 1. Three-dimensional plot of the dielectric losses vs. temperature and frequency for bulk 8CB: (*a*) parallel (**E**‖**n**) configuration, (*b*) perpendicular (**E**⊥**n**).

10^6–1.8×10^9 Hz frequency range. In figure 1 (*a*), the spectrum is dominated by the mode related to the rotation about the short molecular axis, ω_1, in all phases (I, N and SmA), because the dipole moment is due mainly to the CN group. We note that this dipole is not exactly along the steric main axis, as pointed out by Jadzyn *et al.* [2, 19], and can confirm this from the analysis of our measurements. For the perpendicular alignment, figure 1 (*b*), the spectrum is quite different with respect to the parallel component. At the I–N transition a deep decrease of the dielectric response takes place and the losses appear as a very broad peak. Measurements in the 10^2–10^6 Hz range did not reveal the existence of any additional process.

Let us analyse in detail these results. Figure 2 (*a*) shows both components of the dielectric permittivity in the isotropic phase. The results are fitted to two near-Debye modes; $\alpha=1$ for the high frequency mode and $\alpha=.95$ for the low frequency mode. The high frequency mode may be attributed to rotation around the molecular long axis, and the low frequency mode to rotation around the molecular short axis. We have estimated the angle between the dipole moment and long axis of the molecule from the relative strengths of each mode in the isotropic phase, $\Delta\varepsilon_1\propto\mu_l^2$ and $\Delta\varepsilon_2\propto\mu_t^2$. The value obtained, around 18°, is quite high for an *n*CB compound and it should be taken with care because $\Delta\varepsilon_2$ is very sensitive to the fitting procedure (depending much on α, β and ε_∞). Nevertheless, other authors have estimated values ranging from 13° to 21° for similar compounds [2, 9, 19].

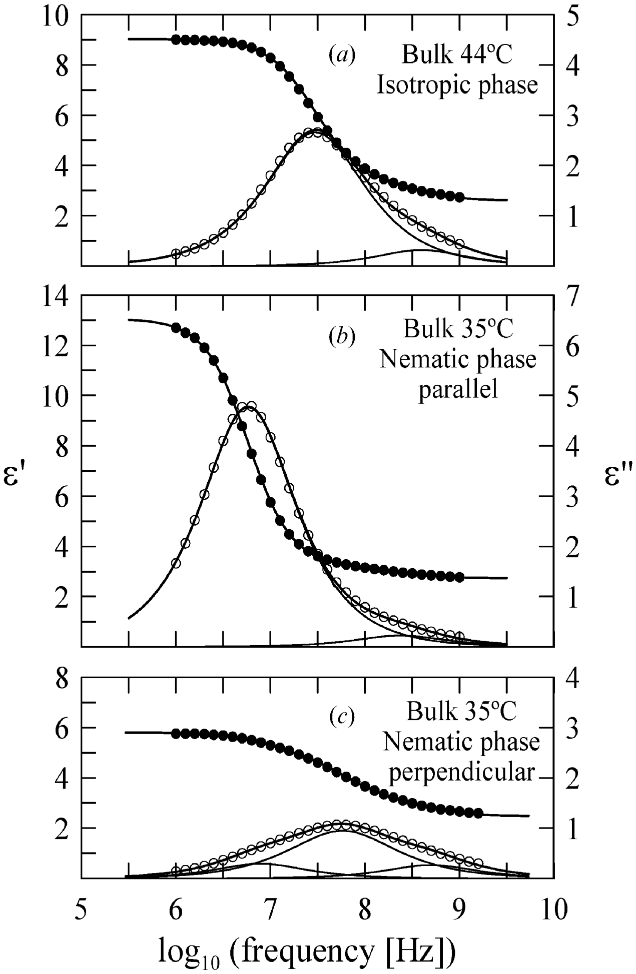

Figure 2. Frequency dependence of both components of the complex dielectric permittivity of bulk 8CB: (*a*) in the isotropic phase, (*b*) in the nematic phase parallel alignment, (*c*) in the nematic phase perpendicular. Solid lines are fit curves.

Figure 2 (*b*) shows, for the parallel alignment, both components of the dielectric permittivity in the N phase, where the results are also fitted to two near-Debye modes; $\alpha=1$, $\beta=1$ (both fixed) for the high frequency mode and $\alpha=.98$ $\beta=1$ for the low frequency mode. Figure 2 (*c*) corresponds to the N phase, but for the perpendicular alignment. According to equation (3 *b*), if the molecules have transverse and longitudinal dipole moments, in the N phase for the perpendicular alignment one needs two relaxations: ω_3, the precessional motion of the long axis around the director, and ω_4, the rotation around the long axis of the precessing molecule. However, to fit our data we need three modes: ω_4 ($\alpha=1$, $\beta=1$, both fixed) at high frequency, ω_3 ($\alpha=.9$, $\beta=1$ fixed) at intermediate frequency and another at low frequency ($\alpha=1$, $\beta=1$, both fixed). Let us call this mode $\omega_{1\perp}$. Figures 3 and 4 show, respectively, the dielectric strengths and characteristic frequencies vs. temperature of all the aforementioned modes.

We simultaneously fit real and imaginary components of the dielectric permittivity. In all cases, the multi-mode loss peaks were fitted to multi-Havriliak–Negami functions, even those modes with very low dielectric strength. Nevertheless, in general when the β-parameter fitting is close to 1, then it is held fixed and the subsequent fittings run over the other parameters. Thus, in the following, when the β-value is unwritten it was held fixed to 1.

3.2. *Confined 8CB*

As mentioned in § 2, the measurements in confinement were re-scaled, after subtraction of the alumina contribution, assuming that the physical mechanisms contributing to ε_∞ in the isotropic phase, mainly the induced polarization, should not be greatly affected by the confinement.

With untreated membranes axial confinement is achieved, as confirmed by the dielectric results. Although the pores are hydrophilic (which would

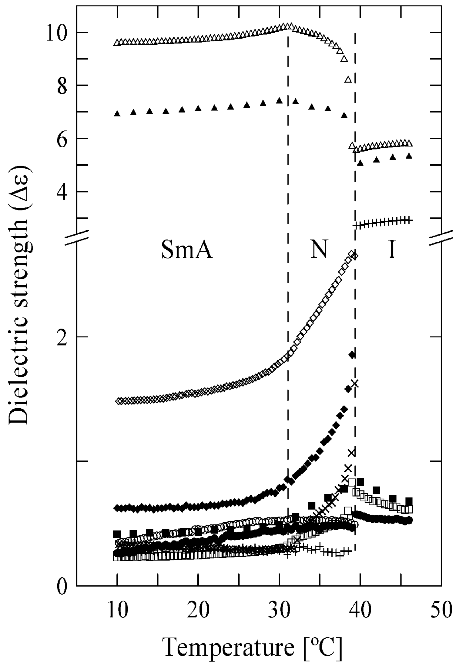

Figure 3. Dielectric strength vs. temperature of the different elementary contributions. Bulk parallel: (△)ω_1 and (□)ω_2; bulk perpendicular: (○)ω_4, (◇) ω_3 and (×) $\omega_{1\perp}$; bulk isotropic phase: (△)ω_1 and (□)ω_2. Axial confinement: (▲)ω_1 and (■)ω_2; isotropic phase: (▲)ω_1 and (■)ω_2. Radial confinement: (●)ω_4, (◆)ω_3 and (+)$\omega_{1\perp}$; isotropic phase: (+)ω_1 and (●)ω_2.

favour the homeotropic alignment because the polar cyano head group attaches to the inner-pore surface), when the membranes are almost filled, the molecules tend to arrange along the pore [20]. The dielectric spectrum is quite similar to that obtained in bulk samples with parallel alignment. Figure 5 (*a*) is a three-dimensional plot of the losses vs. temperature and frequency. The spectrum in all phases is dominated by mode ω_1, which is accompanied by another at higher frequencies, mode ω_2. When the membranes are treated with HTBA, homeotropic boundary conditions with respect to the pore walls are provided, and the perpendicular component of the dielectric permittivity, $\varepsilon_\perp$, can be measured. We will denote this type of alignment as radial [18]. Figure 5 (*b*) is a three-dimensional plot of the losses vs. temperature and frequency. The dielectric spectrum is quite similar to that obtained in bulk samples with perpendicular alignment.

Figures 6 (*a*) and 6 (*b*) show both components of the dielectric permittivity in the N phase for axial and radial

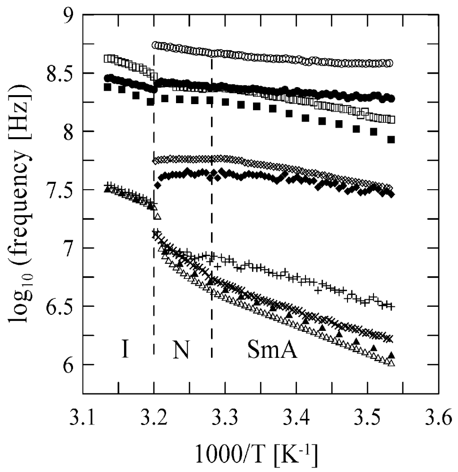

Figure 4. Arrhenius plot of the frequency of the different elementary contributions. Bulk parallel: (△)ω_1 and (□)ω_2; bulk perpendicular: (○)ω_4, (◇)ω_3 and (×) $\omega_{1\perp}$; bulk isotropic phase: (△)ω_1 and (□)ω_2. Axial confinement: (▲)ω_1 and (■)ω_2; isotropic phase: (▲)ω_1 and (■)ω_2. Radial confinement: (●)ω_4, (◆)ω_3 and (+)$\omega_{1\perp}$; isotropic phase: (+)ω_1 and (●)ω_2.

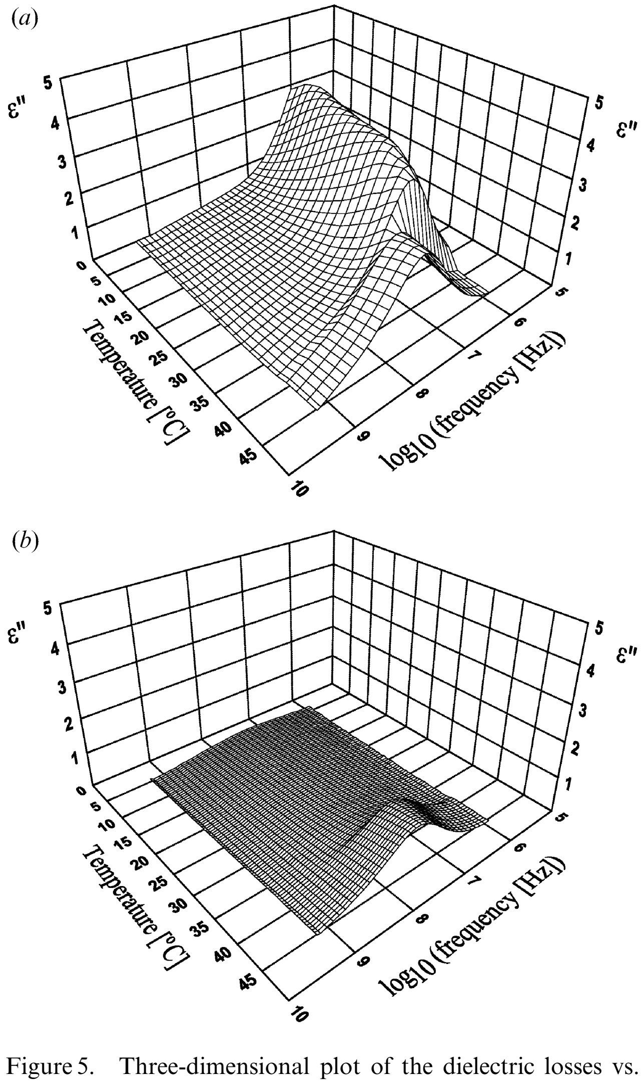

Figure 5. Three-dimensional plot of the dielectric losses vs. temperature and frequency for: (*a*) axially confined 8CB, (*b*) radially confined 8CB.

confinements, respectively. In figure 6 (*a*), the results were fitted to two near-Debye modes (α=1 for the high frequency mode and α=.96 for the low frequency mode), as for parallel alignment in bulk samples. In figure 6 (*b*), the results were fitted to three modes: ω_3 (α=0.9), ω_4 and $\omega_{1\perp}$, as for perpendicular alignment in bulk samples. In figures 3 and 4 we have also represented the dielectric strengths and characteristic frequencies corresponding to the axial and radial confinements. Measurements in the 10^2–10^6 Hz frequency range did not reveal the existence of any additional process to those present in figures 5 (*a*) and 5 (*b*).

4. Discussion

Although *n*-alkylcyanobiphenyls are perhaps the most widely studied liquid crystals from a dielectric point of view [1, 10, 21–23] some aspects of their behaviour are still not clear. For example most authors fit the dielectric data in the I phase to only one broad relaxation [3, 8, 22]. This is also possible with our data. A good fit to only one mode, Cole–Davidson β=0.65, can be achieved. However in the N phase parallel configuration, figure 2 (*b*), the fit to only one mode (Havriliak–Negami with two shape parameters) is roughly achieved. Thus, it seems reasonable to assume that a higher frequency mode should be included in the fit procedure. In ref. [8] a shoulder at high frequency for 10CB was also reported in the N phase (parallel). The authors attempted to explain this shoulder as 'the molecular rotation in a cone around the director'. We feel that this explanation seems not to be feasible because this motion should contribute to the perpendicular permittivity. Thus we will assume that this high frequency mode must be related to a non-vanishing component of the dipole moment perpendicular to the molecular long axis. Then, if it exists in the N phase it should also be present in the I phase whenever the rotational diffusion tensor were anisotropic [13, 14, 24]. See, for example, the results in the isotropic phase for the compound 6BPA(F) for which the transverse component of the dipole moment is larger than the longitudinal component [23]. We will also assume rigid molecules in the explanation of our results.

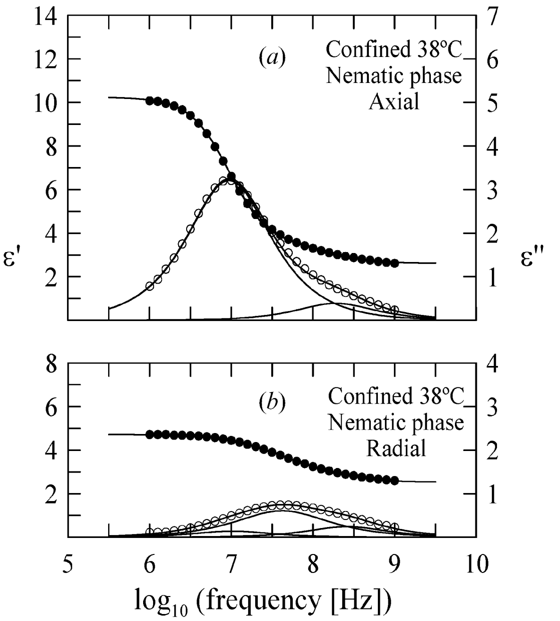

Figure 6. Frequency dependence of both components of the complex dielectric permittivity for confined 8CB: (*a*) axial nematic phase, (*b*) radial nematic phase. Solid lines are fit curves.

For parallel alignment the behaviour of the dielectric strengths is as expected. The dielectric strength of mode ω_1 increases and that of mode ω_2 decreases at the I–N phase transition due to the onset of nematic order. Regarding the characteristic frequencies, ω_1 suffers a jump to lower frequencies at the I–N transition followed by a continuous decrease with temperature. In the N phase this frequency does not follow the Arrhenius law; however, one can determine an activation energy, excluding a small temperature range near the I–N transition temperature of around 75 kJ mol^{-1}. It is worth noting that in the SmA phase this activation energy is much smaller than in the N phase (45 and 75 kJ mol^{-1}, respectively), a fact usually observed and which indicates that in the SmA phase the energy barrier hindering the molecular motions is smaller than in the N phase [21, 23, 25]. The change of ω_2 is smoother across the I–N transition. We have to point out that our fit of this high frequency mode, above all near the phase transition, is not so confident because its frequency is high and its strength very low with respect to that of ω_1. In the N and SmA phases ω_2 depends smoothly on temperature. In the nematic temperature range it is practically constant, and in the SmA range experiments decreases with decreasing temperature.

For the perpendicular alignment, one can observe that in the mesophases the shape of the relaxation is very broad; see the three-dimensional plot of the losses vs. temperature and frequency, figure 1 (*b*). Other authors [3] fit to only one broad mode and obtain a relaxation frequency that in the N phase increases with decreasing temperature, and next, in the SmA, decreases with decreasing temperature. They attribute this mode to the 'librational motion of the molecules'. If we take just the maximum of the losses this is also our case. However, using the same arguments as at the beginning of this section, the dipole moment has longitudinal and transverse components, and then, even with the perpendicular alignment, two modes should also be present in the dielectric spectrum of the mesophases: modes ω_3 (precession of long axis around director) that involves the longitudinal dipole moment, and ω_4 (rotation around long axis of the precessing molecule) that involves the transverse dipole moment. However, in order to fit our data properly we need a third mode in the low frequency side, as can be seen in figure 2 (*c*). This mode was also obtained by other authors for perpendicular alignment in bulk samples [2, 26]. It was attributed to the rotation around the short molecular axis, the same origin as mode ω_1; let us call it mode $\omega_{1\perp}$. Its presence in this alignment is due to imperfect alignment, a fact that nearly always happens because the axis of magnetic or dielectric maximum susceptibility does not coincide with the steric main axis. The same idea is applicable when the director is forced by surface effects that align the molecules.

Looking at the frequencies, see figure 4, mode ω_4 has a larger frequency than mode ω_2, and mode ω_3 has an intermediate frequency between ω_1 and ω_2, as predicted by theory [14] and also obtained by other authors for similar compounds [26]. In the N phase ω_3 is almost constant and in the SmA phase decreases with activation energy around 20 kJ mol^{-1}. The explanation of this may be that in the N phase the effect of the increase of the order parameter dominates and when the temperature is lower the effect of viscosity prevails. Concerning the frequency of mode $\omega_{1\perp}$, the jump at the I–N phase transition is smaller than that corresponding to mode ω_1 (parallel alignment), given its activation energy is also smaller. This result was also obtained by other authors [26]. They argued that the difference is due to the vanishing of the coupling between the dipole moment and the field.

The dielectric behaviour in the axial confinement does not greatly differ from the bulk behaviour, as can be seen in figures 3 and 4. If other physical quantities are taken into account, such as, for example, specific heat [4, 17], axial confinement mimics more or less bulk results. In the I phase the characteristic frequencies of mode ω_1 almost coincide with those of the bulk while in the mesophases they are slightly larger. However, the activation energy in the mesophases of this mode is similar to that corresponding to the bulk-parallel. Its shape is a little broader (α=0.96) than in the bulk sample (α=0.98). Regarding this point, one should take into account that the alignment in both cases may not be exactly the same. For the bulk sample, a bias field was applied to obtain the parallel alignment, and then the axis of larger orientational polarizability should be perpendicular to the electrodes [26]. For the axially confined sample, the alignment agent is just a surface effect. Regarding the strengths, in the I phase for the liquid crystal confined in the untreated membranes, mode ω_1 has a dielectric strength only slightly smaller than for the bulk sample. However, in the mesophases it is much smaller than for the bulk.

All these observations would suggest that the molecular dynamics is not greatly affected by confinement but that a portion of the molecules, those near the pore walls, does not contribute to the (orientational) dielectric permittivity. We could estimate this effect, close to the N–I phase transition, to be about 30%, a value not too different to that obtained by Iannacchione and Finotello [4], from the axial specific heat peak suppression. In recent work regarding 7OCB a similar effect was also observed by means of calorimetric studies [9]. At this point we have to say that our measurements in the 10^2–10^6 Hz frequency range did not reveal additional relaxations to those mentioned above, as similarly reported by Leys *et al.* [8] and even by ourselves [10] when the same kind of confinement was considered. Nevertheless, in addition to the relaxational bulk-like modes, new relaxational modes were found from dielectric measurements, when these liquid crystals and other related materials were confined to strongly restricted random porous media [3, 7, 8, 27].

We now considerer the results for radial confinement. In the I phase mode ω_1 has a dielectric strength much smaller than in the bulk and axial confinement. One could suggest that there is strong anchoring of the molecules perpendicularly to the pore walls. In the mesophases the most important contribution comes from mode ω_3, precessional motion of the long axis around the director, as in the bulk perpendicularly aligned. Although its strength is smaller than in the bulk, the temperature trend is similar with a decrease as temperature decreases, as predicted by equation (3 *b*): it should follow the law (1–*S*). The strength of mode $\omega_{1\perp}$ in the mesophases is very small, similar to the strength for bulk-perpendicular. The possibility of the so-called ‘escaped radial’ and ‘escaped radial with point defects’ configurations [9, 17] should be discarded. According to our line of reasoning, if these configurations exist in radial confinement, the strength data related to $\omega_{1\perp}$ should be of the same order as those for mode ω_1 for axial confinement.

With the purpose of summarizing the most relevant results of the present paper some simple questions may be addressed. What is the effect of confinement to slightly-restricted cylindrical geometries on the dynamics of liquid crystals? How is the molecular mobility of the liquid crystal inside the cylindrical pores modified? How is the nematic order changed? On one hand the dielectric strengths of the relevant modes (ω_1 for parallel and ω_3 for perpendicular configurations) are smaller than in the bulk; while on the other hand, the activation energies are quite similar, indicating that the barriers hindering the processes are also quite similar. Both facts taken together may indicate that some of the molecules inside the pore wall, in fact those near the pore walls, display completely hindered reorientational molecular motions (at least for those with relaxation frequencies in the range 10^2–1.8×10^9 Hz for which dielectric experiments have been conducted). Nevertheless, there exists another ensemble of molecules inside the pores, probably those located at the centre of the cylindrical pore, that performs reorientational molecular motions in a similar way as the bulk, but they are generally faster.

Moreover, the so-called retardation factor ω_1(I–phase)/ω_1(N–phase) is larger for bulk than for axial confinement (see figure 4). Taking into account that it is related to the change of the probability of molecular reorientations around the short axis when the I–N transition takes place [23], the difference would indicate that the N phase, axial confinement, is less ordered than the bulk close to the phase transition. This smaller retardation factor should be the origin of the larger value of the relaxation frequency of mode ω_1 for the axially confined liquid crystal. We think that the same explanation will also account for the behaviour of mode ω_3. For this mode the jump (up) at the phase transition ω_3(N–phase)/ω_1(I–phase) is also smaller for the radial confinement than for the bulk perpendicular, and then the frequency is smaller for the radial confinement than for the bulk perpendicular. Both facts would indicate that the order parameter is smaller in cylindrically confined samples than in bulk samples, at least near the N–I transition temperature. We deduced a similar conclusion in a recent paper devoted to 7OCB from the comparison of calculated average order parameters obtained from specific heat measurements [9].

5. Concluding remarks

Dielectric spectroscopy has been used to analyse the effect of confinement on the dynamics of liquid crystals. Both components of the complex dielectric permittivity of bulk (homeotropic and planar alignments) and cylindrically confined (axial and radial) 8CB have been measured. We propose a method of how to re-scale the data concerning the liquid crystal confined to parallel cylindrical pores, which allows us to compare not only the relaxation frequencies of the different modes, but also the dielectric strengths, with the results corresponding to bulk liquid crystal. Our data treatment allows us a decomposition of the spectrum that includes a high frequency mode related to the transverse dipole moment. This fact has great importance and above all when treating with $\varepsilon_\perp$ (bulk perpendicular and radial confinement) because the temperature dependence of the frequency of the precessional motion of the long molecular axis around the director, when one fits including this high frequency mode, is different (our results against those of ref. [3]). In our case its temperature dependence is smooth in both the N and SmA phase. In [3] upon decreasing the temperature the frequency increases before going down. Recently a paper treating to explain this type of non-monotonic relaxation kinetics has appeared [28]. The model was also applied to explain the behaviour of radially confined 8CB. However, we think that for this case it would not be applicable because this behaviour depends much on the fit procedure.

Our analysis suggests that for the confined liquid crystal, there is a fraction of the molecules, those near the pore walls, whose motion is completely hindered. Moreover, the order parameter is smaller in cylindrically confined samples than in bulk samples, at least near the N–I transition temperature.

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