**Liquid Crystals**
Publication details, including instructions for authors and subscription information:
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**To cite this Article** Sinha, G. , Oka, A. , Glorieux, C. and Thoen Corresponding author, J.(2004) 'Weakly polar liquid crystal dispersed with hydrophobic and hydrophilic aerosils: a broadband dielectric study', Liquid Crystals, 31: 8, 1123 — 1129
**To link to this Article: DOI:** 10.1080/02678290410001720894
**URL:** http://dx.doi.org/10.1080/02678290410001720894

LIQUID CRYSTALS, VOL. 31, NO. 8, AUGUST 2004, 1123–1129

# Weakly polar liquid crystal dispersed with hydrophobic and hydrophilic aerosils: a broadband dielectric study

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(*Received 8 December 2003; in final form 9 March 2004; accepted 26 March 2004*)

Complex dielectric permittivities for parallel orientations of the director **n**, with the probing electric field **E** (**E** ∥ **n**), of the weakly polar liquid crystal (LC) 4,4′-di-*n*-hexylazoxybenzene (D6AOB) dispersed with hydrophobic and hydrophilic aerosils, have been measured in the frequency range 20 Hz to 30 MHz. In the nematic phase of D6AOB dispersed with hydrophobic and hydrophilic aerosils, significant changes in the dielectric properties are observed. An additional slow process due to the restricted motion of the molecules in surface layers is observed for hydrophilic samples. The slow process is absent in the hydrophobic samples suggesting that in the LC–hydrophilic aerosils a surface layer is formed at the aerosil interface. The process does not depend on temperature and has a wide distribution of relaxation times. The bulk-like rotation around the short axis for D6AOB dispersed with hydrophilic aerosils has been modified significantly. It seems that this could be due to an overlap between the main bulk-like process and a hindered rotation of molecules around their long axes for molecules that are oriented perpendicular to the probing electric field.

## 1. Introduction

The study of confined liquids and liquid crystals (LCs) has been a topic of great interest in recent years [1–6]. From a theoretical point of view the quenched disorder posed by the confining system has attracted the attention of various scientists seeking to probe the nature of phase transition in such systems [6–8]. On the other hand various experiments have been devoted to confined systems which often exploit the presence of a large interfacial area [8–18]. These studies have primarily investigated structure and phase and glass transitions, as well as the dynamics of molecular motion of isotropic liquids and liquid crystals in confining geometries. The types of confinement used were mainly external physical restrictions on the liquids and liquid crystals. More recently, an internal restriction imposed on the liquid crystals by introducing nano-sized silica particles into the phase has been a field of active research [19–26].

In one of the first detailed studies of LC–aerosil systems, two distinct regimes of $\rho_s$ (silica density) – dependent behaviours were observed with a crossover between them at $\rho_s \approx 0.1\,\mathrm{g\,cm^{-3}}$ [25]. The low density regime was termed as 'soft gel' for which sharp second order *Cp* peaks were observed at the N–SmA transitions. In the high density 'stiff gel' regime single rounded *Cp* peaks were observed at the N–I and N–SmA transitions that were due to the quenched elastic strain smearing effects. In another study of an LC–aerosil system by deuteron NMR similar behaviour was observed [23]. Below the crossover regime a bulk-like orientational order was seen, whereas in the stiff regime a rigid isotropic network of voids leading to a broadening of phase transitions was observed. In a pyroelectric study of the system in the 'soft gel' regime, different thermal conductivity values were obtained on cooling and heating [26]. The effect was explained by the difference in the orientational order in the system, lower order in cooling and higher order in heating, for the different runs.

Dielectric measurements can be very informative for studying relaxation processes near the LC–substrate interface for substances that have a very large surface area, such as porous media. In the case of polar LCs filled with aerosils, the polar ordered layer at the interface will have a different molecular mobility due to molecule–surface interactions, resulting in slower dynamics for molecules at the interface. In some of the dielectric studies performed on 4-alkylcyanobiphenyls filled with high concentrations of hydrophilic aerosils, an additional process was observed that was

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*Liquid Crystals* ISSN 0267-8292 print/ISSN 1366-5855 online © 2004 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290410001720894

attributed to the hindered rotation of molecules located in the surface layers formed at the aerosil surface [19, 21]. In another dielectric study of the Goldstone and soft modes in the soft regime of the filled LC, it was observed that the main contribution to the dielectric permittivity came from bulk-like domains in the sample in which pinning of fluctuations by hydrophilic aerosils was negligible [18].

It is known that LCs with a strong dipole moment such as 4-*n*′-pentyl-cyanobiphenyl (5CB), when dispersed with aerosils show a surface-related process. The hydrophilic aerosils have several hydroxyl groups at their surface. LC molecules with a strong dipole moment at one end of the molecules can attach to the hydroxyl groups via hydrogen bonds. In such cases a polar ordering may also arise in the surface layers around the aerosils. Most of the dielectric studies on LC–aerosil systems have involved molecules having a strong dipole moment [19, 20, 27–31]. However, studies on LC–aerosil systems with the LC having a weak dipole moment may provide some additional information on the nature of the interaction between the LC molecules and the surface of the aerosils. In this investigation we are interested in probing the effect of dispersing hydrophobic and hydrophilic aerosils in LCs with weaker dipole moments.

## 2. Experimental

Our study concerns the weakly polar liquid crystal 4,4′-di-*n*-hexylazoxybenzene (D6AOB) which was used as obtained from Sigma-Aldrich. The alkyl chains on each side of the molecule provide the added advantage that the deviation of the molecular long axis from the direction of the orienting magnetic field is minimal. D6AOB has the sequence of phase transitions: Cr 23°C N 53.1°C I. The dipole moment in D6AOB has an angle of 64.9° from the molecular axis and a magnitude of 1.70 D [32, 33].

For the experiment, hydrophilic aerosils (type 300) with diameter around 70 Å and surface area $300\,\mathrm{m^2\,g^{-1}}$, and hydrophobic aerosils of type R972 with diameter around 160 Å and surface area $110\,\mathrm{m^2\,g^{-1}}$ were used. The filled LCs were prepared in the following way. The aerosils, both hydrophilic and hydrophobic, were dried under vacuum at 200°C for around 15 h. The required amounts of these fine particles were added to a D6AOB–acetone mixture so that there was around 0.02 g of aerosils per $\mathrm{cm^3}$ of LC. The whole mixture was then sonicated for about 1 h to obtain a good dispersion of the aerosils in the medium. Acetone was then allowed to evaporate slowly while keeping the temperature of the mixture above 55°C. The remaining sample was then kept overnight in vacuum, to ensure complete evaporation of acetone, with the vacuum jar placed in an oven at 55°C. We prepared two different concentrations of hydrophobic aerosils with $\rho_s$ 0.117 and $0.164\,\mathrm{g\,cm^{-3}}$, and one concentration of hydrophilic aerosils with $\rho_s$ as $0.191\,\mathrm{g\,cm^{-3}}$, where $\rho_s = (m_s/m_{LC})\,\rho_{LC}$, and $m_s$ and $m_{LC}$ are the masses of the aerosils and LCs used, respectively, in the mixture preparation. We can approximate the concentration as $\approx (m_s/m_{LC})\,(1\,\mathrm{g\,cm^{-3}})$.

Real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of the complex dielectric permittivity ($\varepsilon^*$) were measured in the frequency range 20 Hz to 30 MHz. D6AOB was measured between 30 and 67°C. In the frequency range 20 Hz to 1 MHz, a Hewlett-Packard HP 4284A precision LCR meter was used for measurement. In the frequency range 75 kHz to 30 MHz, a Hewlett-Packard HP 4285A precision LCR meter was used. The sample cell was in the form of a parallel plate capacitor, with a guard ring that eliminated the stray capacitance caused by the edge effect. The cell was housed in an oven that could be placed between magnets with parallel or perpendicular field orientations. For the aerosil-dispersed samples the available magnetic field, which was around 0.4 T, was not enough. To obtain a good orientation of the director parallel to the probing field, an a.c. electric field at 1000 Hz with a magnitude of $35\,\mathrm{kV\,cm^{-1}}$ was applied to the sample. However, using such a procedure a perpendicular orientation of the director cannot be achieved for a positive anisotropy liquid crystal such as D6AOB. The high electric field was needed for orienting the LC molecules under the influence of a high density of aerosil particles. The samples were cooled from the isotropic phase to the lowest temperature with the electric field on. The field was then removed and the orientation was maintained due to the memory effect of the sample. The measurements were then performed during a heating run. The distance between the two electrodes was about 200 μm. Temperatures were controlled using an oven designed to accommodate the cell [19]; accuracy and stability were better than 0.01 K. The data from the low frequency LCR meter was adjusted to the high frequency meter for the high concentration hydrophobic and hydrophilic samples where there was always an uncertainty in the thickness of the sample between the capacitor plates. The absolute values of the data in the low frequency range were adjusted according to the values around 75 kHz obtained by the high frequency LCR meter.

## 3. Results and discussion

The static dielectric permittivities $\varepsilon'$ of the bulk and aerosil-dispersed hexylazoxybenzene, measured at 100 kHz as function of temperature for $\mathbf{E} \parallel \mathbf{n}$ and $\mathbf{E} \perp \mathbf{n}$ orientations, are shown in figure 1. The values $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$

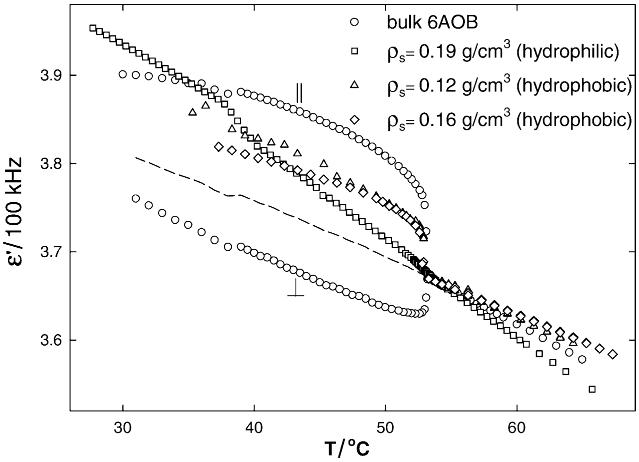

Figure 1. Temperature dependence of the static dielectric permittivity $\varepsilon'$ (measured at 100 kHz): bulk D6AOB (○) with parallel (∥) and perpendicular (⊥) orientations; 0.117 g hydrophobic aerosils cm$^{-3}$ of D6AOB (△); 0.164 g hydrophobic aerosils cm$^{-3}$ of D6AOB (◇); and 0.191 g hydrophilic aerosils cm$^{-3}$ of D6AOB (□) in the nematic phase and isotropic phases. The dashed line represents $(\varepsilon'_{\parallel}+2\varepsilon'_{\perp})/3$ for bulk D6AOB.

represent the dielectric constants for the applied electric field **E** parallel or perpendicular to the macroscopic molecular orientation **n**, respectively. It is seen that $\varepsilon_{\parallel}$ increases with decreasing temperature for all samples, which is due to the increasing nematic order. A small step in $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ for bulk D6AOB is seen around 39°C because the data were taken from two different measurements performed above and below this temperature. The values of the dielectric permittivity $\varepsilon_{\parallel}$ for the aerosil-dispersed samples were adjusted to the bulk values by using a scaling factor determined from values of $\varepsilon'$ for bulk and dispersed samples at around 53.3°C. A better method for comparing the values would have been by using models for computing the dielectric permittivity for concentrated disperse systems of spherical particles, as for example given by Hanai [34]. However, such a comparison is difficult because the absolute values for dispersed samples could not be obtained for the high concentration samples as it was difficult to obtain a precise value of the sample thickness. Shifts in the transition temperatures were also observed. The trend of the shifts was not clear and hence in the figure the temperatures of the dispersed samples were shifted by matching the transition temperatures with respect to the bulk value. On increasing the aerosil concentration the effect of the aerosils increases, as is evident from the difficulty in obtaining a parallel oriented sample. In the 0.191 g cm$^{-3}$ sample the effect of aerosils was strong enough to induce disorder in the phase, which prevented the alignment of the director in the field direction. Hence in this case the value of $\varepsilon_{\parallel}$ obtained is close to the average value $(\varepsilon_{\parallel}+2\varepsilon\perp)/3$ as molecules would be oriented in all directions around the aerosil particles. Although 100 kHz is not low enough to reach a static value of the real part of the dielectric permittivity for D6AOB with hydrophilic aerosils, we have chosen this frequency for comparison with the other samples. A small increase in the value below 40°C could be due to the influence of the relaxation processes in the neighbourhood of the chosen frequency.

In order to study the influence of the aerosils on rotational motions of the molecules, dielectric relaxation spectra were obtained at various temperatures for all concentrations. The frequency dependences of the dielectric permittivities for aerosil-dispersed D6AOB in the nematic phase for parallel alignment are shown in figure 2, which gives typical relaxation spectra observed in the nematic phases with parallel alignment. For comparison a spectrum for bulk D6AOB obtained at the same temperature is also shown in the figure (for details see [35]). As reported in our previous work, D6AOB has two clear molecular relaxation processes in the nematic phase for a probing field parallel to the director. In the case where the director is perpendicular to the probing field, a major process due to the rotation of the molecules around the long axis is observed in the GHz region. The spectra measured for bulk and dispersed D6AOB were analysed by fitting them to the empirical Havriliak–Negami formula [36] given by:

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

where $\varepsilon_\infty$ is the high frequency limit of the permittivity, $\Delta\varepsilon_j$ the dielectric strength, $\tau_j$ the mean relaxation time, and $j$ the number of the relaxation process. The exponents $\alpha_j$ and $\beta_j$ describe the symmetric and asymmetric distribution of relaxation times. The term $i(\sigma/2\pi\varepsilon_0 f^n)$ accounts for the contribution of conductivity $\sigma$, with $n$ as a fitting parameter. In the figure the solid lines represent the fitting of such curves to the data. The dashed lines represent the resolution into two molecular relaxation processes. The values of the fitting parameters are listed in the table. The first process in bulk D6AOB with parallel alignment has a characteristic frequency of 2 MHz while the second process has a characteristic frequency of 0.5 GHz. The slow process is attributed to the molecular rotation around the short axes and is of Debye type whereas the GHz process is of non-Debye type. The temperature dependence of the relaxation times in the nematic and isotropic phase of bulk D6AOB are of Arrhenius type.

For D6AOB dispersed with hydrophobic aerosils little influence on the relaxation processes was

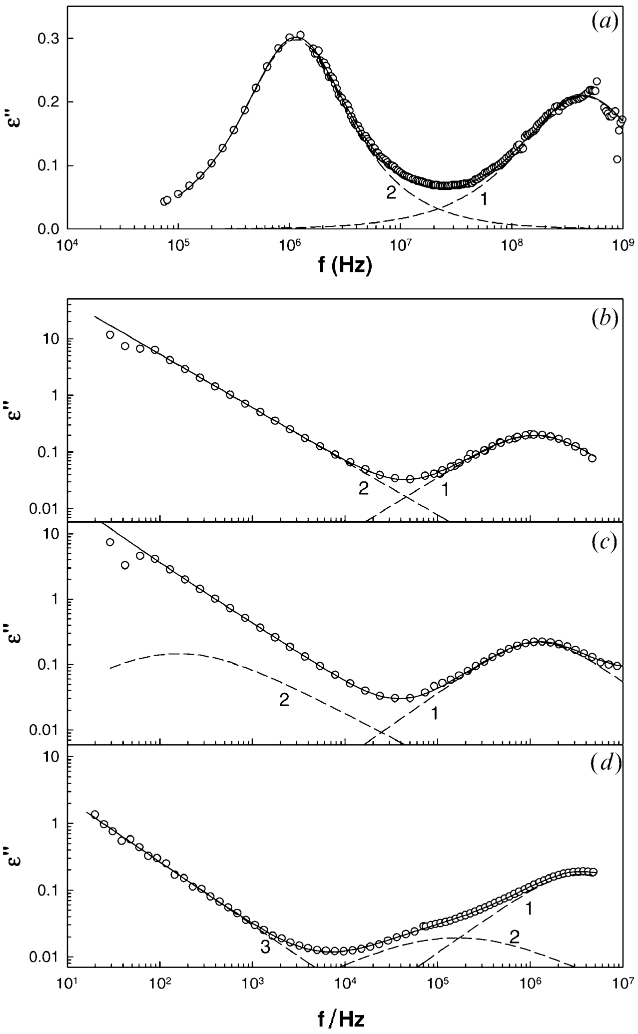

Figure 2. The frequency dependence of the imaginary parts of the dielectric permittivity of: (*a*) bulk nematic D6AOB at $T = 35.5°\mathrm{C}$; (*b*) D6AOB dispersed with $0.117\,\mathrm{g\,cm^{-3}}$ of hydrophobic aerosils at 36°C; (*c*) D6AOB dispersed with $0.164\,\mathrm{g\,cm^{-3}}$ of hydrophobic aerosils at 36.0°C; and (*d*) D6AOB dispersed with $0.191\,\mathrm{g\,cm^{-3}}$ of hydrophilic aerosils, measured for **E** ∥ **n** at $T = 36.0°\mathrm{C}$. Solid lines are fits to equation (1). Dashed lines represent deconvolution into elementary contributions.

observed. However, in the case of the high concentration sample a very slow process seemed to have emerged with a maximum around 1 Hz. In figure 2 (*c*) we show one such typical process, represented by a dashed curve (2), that was obtained for $0.164\,\mathrm{g\,cm^{-3}}$ at $T = 36°\mathrm{C}$. We note that the whole spectrum below 10 kHz for this sample could also be fitted without considering the extra process but taking only conductivity into account. However, in such a case the value of the fitting parameter $n$ was around 0.85 at most of the temperatures, whereas this parameter in the bulk and for low concentrated hydrophobic sample was above 0.95. On including a slow relaxation process such as the one shown in the figure the value of $n$ was close to 1. The relaxation time of the process is similar to that observed for 5CB filled with 2.3% (by volume) of hydrophilic and hydrophobic aerosils [27, 28]. The origin of this process could be similar to that described in these references. Even though there could exist a slow collective relaxation process due to the orientation of permanent dipoles at the aerosil–liquid crystal interface, it is difficult to exclude the possibility that the process could instead be due to a Maxwell–Wagner effect resulting from free ions and the network. The relaxation times of the bulk-like process due to rotation around the short axis for the $0.164\,\mathrm{g\,cm^{-3}}$ sample was, however, slightly smaller than for the bulk and $0.117\,\mathrm{g\,cm^{-3}}$ samples. The increase in the speed can also be seen from the plot of the relaxation times vs. frequency shown later.

Table. Parameters obtained from the fitting of the imaginary part of the dielectric permittivity of bulk D6AOB and D6AOB dispersed with aerosils measured for **E** ∥ **n**.

| Process | $\sigma/\mathrm{S\,cm^{-1}}$ | $n$ | $\Delta\varepsilon_i$ | $\tau_i/\mathrm{s}$ | $\alpha_i$ | $\beta_i$ |
|---|---|---|---|---|---|---|
| *D6AOB (bulk)* | | | | | | |
| $\varepsilon^{\parallel}(\omega, T = 35.5°\mathrm{C})$ | | | | | | |
| 1 | — | — | 0.60 | $1.40\times10^{-7}$ | 0 | 0.99 |
| 2 | — | — | 0.49 | $3.58\times10^{-10}$ | 0.89 | 1.00 |
| *$0.117\,\mathrm{g\,cm^{-3}}$ hydrophobic sample* | | | | | | |
| $\varepsilon^{\parallel}(\omega, T = 36.0°\mathrm{C})$ | | | | | | |
| | $3.26\times10^{-10}$ | 0.94 | — | — | — | — |
| 1 | — | — | 0.40 | $1.43\times10^{-7}$ | 0 | 1.0 |
| *$0.164\,\mathrm{g\,cm^{-3}}$ hydrophobic sample* | | | | | | |
| $\varepsilon^{\parallel}(\omega, T = 36.0°\mathrm{C})$ | | | | | | |
| | $1.94\times10^{-10}$ | 1.0 | — | — | — | — |
| 1 | — | — | 0.44 | $1.00\times10^{-3}$ | 0.75 | 1.0 |
| 2 | — | — | 0.44 | $1.29\times10^{-7}$ | 0.99 | 1.0 |
| *$0.191\,\mathrm{g\,cm^{-3}}$ hydrophilic sample* | | | | | | |
| $\varepsilon^{\parallel}(\omega, T = 36.0°\mathrm{C})$ | | | | | | |
| | $1.35\times10^{-11}$ | 0.94 | — | — | — | — |
| 1 | — | — | 0.07 | $9.88\times10^{-7}$ | 0.67 | 1.0 |
| 2 | — | — | 0.36 | $4.61\times10^{-8}$ | 0.97 | 1.0 |

In the case of the hydrophilic sample, an additional slow process comparable in frequency to the surface process observed for 7CB dispersed with hydrophilic aerosils [19], was observed. The process seems to be of similar origin as [19], and due to the hindered rotation of molecules around their short axes in surface layers. In the case of D6AOB dispersed with hydrophilic aerosils, the surface area of the aerosils is close to three times greater than that of the hydrophobic aerosils. Additionally, the concentration of the aerosils in the hydrophilic sample is higher. However, in the case of hydrophobic aerosils there is no evidence for a slow process with similar characteristic relaxational frequencies. This suggests that there could be some affinity for the LC molecules at the hydrophilic aerosil surface that is not present with the hydrophobic aerosils. In the case of 7CB dispersed with aerosils the hindrance in rotation around the short axis is due to the higher viscosity in the surface layers which is greater than the bulk viscosity [19]. The cause of the higher viscosity may be the preference of the dipole moment that is at the end of the molecule to hydrogen bond with the silanol group ($C{\equiv}N \cdots H\text{–}O$) present at the surface of the aerosils [37]. Recently, an investigation by FTIR spectroscopy on 8CB–aerosil systems showed IR spectra due to hydrogen bonds between the CN groups of 8CB and OH groups on the surface of aerosil particles [38]. In fact hydrogen bonds can exist to a varying degree between electronegative atoms such as 'N' and 'H' atoms covalently bound to similar electronegative atoms such as 'O'. Thus a preferential polar ordering can also exist at the surface with the polar cyano group pointing towards the aerosil surface [39]. The strength of hydrogen bonds lies between 10 and 40 kJ mol$^{-1}$, which is stronger than a typical van der Waals bond ($\sim$1 kJ mol$^{-1}$) but weaker than a covalent bond ($\sim$500 kJ mol$^{-1}$) [37]. The bonding may be dynamic, leading to a considerable slowing of the rotation of the molecules. In the case of D6AOB the dipole moment is much weaker than in 7CB (around one-third) and secondly the dipolar part of the molecule is situated closer to its centre, with the molecule being nearly symmetric in structure. The dipole moment is at an angle around 64.9° from the long axis of the molecule. It is possible that the hydrogen bonding between the 'O' and the silanol groups on aerosils causes a planar alignment of the molecules with a pretilt at the surface. Comparing the bulk-like processes in hydrophilic aerosils with that in the bulk D6AOB and D6AOB dispersed with hydrophobic aerosils, may further support this conclusion.

The main bulk-like process due to the rotation around the short axis is strongly influenced by the presence of hydrophilic aerosils. The characteristic relaxation frequency of the process is three to four times higher than the bulk values. In figure 3 we present the relaxation times of the process due to rotation around the short axis for D6AOB dispersed with hydrophobic and hydrophilic aerosil samples in the nematic phase. The bulk relaxation times are also shown in the nematic and isotropic phase for comparison. The relaxation times for the low concentration hydrophobic aerosil samples are close to the bulk values. In the higher concentration of hydrophobic aerosil samples the process is slightly faster. However, in the case of the hydrophilic samples the process seems to be much faster than that observed in the bulk. In the case of D6AOB the bulk sample has a fast relaxation process due to rotation around the long axis, for the probing field perpendicular to the director. For a sample with a high concentration of hydrophilic aerosils there is strong disorder present in the phase, causing an isotropic-like orientation of molecules around the probing field direction, at least for molecules close to the aerosils. In such a case, a large number of molecules would also be present that are oriented perpendicular to the probing field. Thus for the molecules close to the surface there could be a hindered rotation around the long axis that has a characteristic frequency overlapping with the bulk-like process. However, a simple speeding-up of the molecular rotation in the inner pore space, where the molecules behave more 'freely' than LCs physisorbed at the surface, cannot be ruled out. The latter scenario may then be compared with LCs in cylindrical nanopores where the bulk-like rotations around short axes are faster than in the bulk [15].

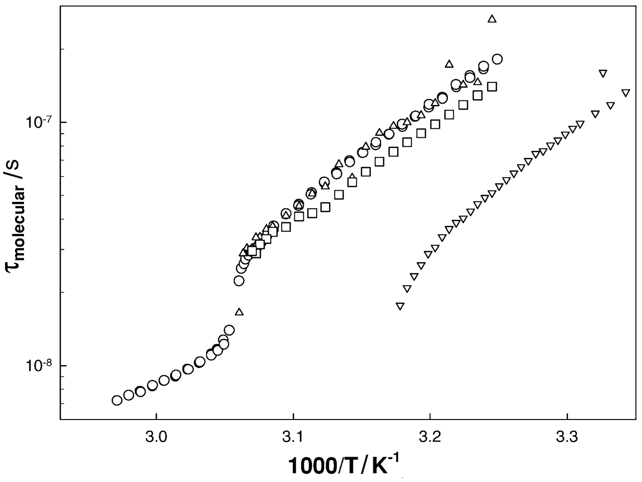

Figure 3. Temperature dependence of the relaxation times of processes with MHz frequency range for bulk and dispersed D6AOB in the nematic phase for parallel alignment: bulk D6AOB (○); D6AOB with 0.191 g cm$^{-3}$ of hydrophilic aerosils (▽); D6AOB with 0.117 g cm$^{-3}$ of hydrophobic aerosils (△); and D6AOB with 0.164 g cm$^{-3}$ of hydrophobic aerosils (□).

In figure 4 we show the plot of the relaxation time vs. temperature for the slow processes. In addition the relaxation times observed for the slow process for hydrophobic aerosils with characteristic frequency around 1 Hz has also been shown. The slow process observed in the hydrophobic sample has a slight dependence on temperature where the dielectric strength increases strongly with the increase in temperature. The relaxation times for the surface process observed in the hydrophilic sample are very weakly dependent on temperature. This suggests a

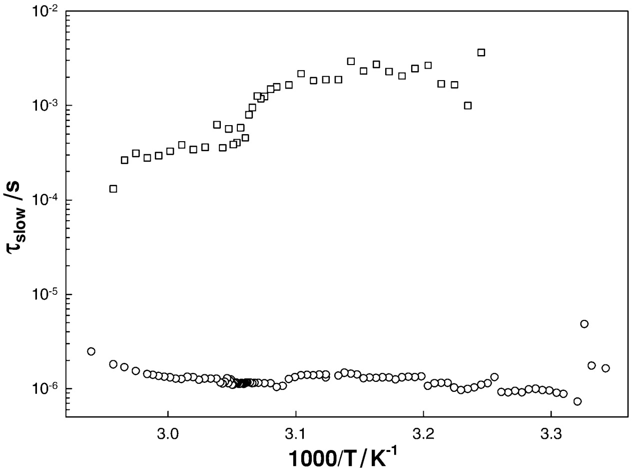

Figure 4. Temperature dependence of the relaxation times of the slow processes for dispersed D6AOB in the nematic phase for parallel alignment: D6AOB with 0.191 g cm$^{-3}$ of hydrophilic aerosils (○); and D6AOB with 0.164 g cm$^{-3}$ of hydrophobic aerosils (□).

constant orientational order parameter in the surface layers that is not influenced significantly by changes in temperature. The surface relaxation process is also very broad with fitting parameter $\alpha$ close to 0.7 throughout the measured temperature range.

## 4. Conclusion

Weakly polar liquid crystal D6AOB dispersed with hydrophobic and hydrophilic aerosils have been studied by dielectric spectroscopy. For bulk D6AOB three main dipolar relaxation processes are observed in the nematic phase—two for parallel alignment and one for perpendicular alignment [35]. In the case of parallel alignment the processes have characteristic frequencies around 2 MHz that are due to rotation around their short axes, and 1 GHz that are due to the molecular rotation on the cone around the director. In the case of perpendicular alignment, the relaxation processes have similar characteristic frequencies to the fast process. The GHz process in the perpendicular alignment is due to the rotation of molecules around their long axes.

In the case of D6AOB dispersed with hydrophobic and hydrophilic aerosils, significant changes in the dielectric properties are observed. An additional process due to the restricted motion of the molecules in surface layers is observed for hydrophilic samples. Such a process is absent in the hydrophobic samples suggesting an affinity of the hydrophilic aerosils for the LC molecules. The process does not depend on temperature and has a wide distribution of relaxation times.

The bulk-like rotation around the short axis for D6AOB dispersed with hydrophilic aerosils has been modified significantly. It is suggested that this could be due to an overlap between the main bulk-like process and a hindered rotation of molecules around their long axes for molecules that are oriented perpendicular to the probing electric field.

This work was supported by the National Science Fund, Flanders (FWO-V), Belgium (project nr.: G.0246.02) and by the Research Council of K. U. Leuven (project GOA-4, 2002).

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