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Influence of hydrophilic and hydrophobic aerosil particles on the molecular modes in the liquid crystal 4-*n*-pentyl-4′-cyanobiphenyl

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Dielectric spectroscopy in the frequency range 10^6–10^9 Hz was applied to investigate the influence of hydrophilic and hydrophobic aerosil particles on molecular processes in the liquid crystal 4-*n*-pentyl-4′-cyanobiphenyl. The dynamics of the molecular process in the isotropic phase is non-Arrhenius; it weakly depends on the aerosil density and shows critical temperature dependence of the activation energy near the isotropic–nematic phase transition. The relaxation rate of the process related to the hindered rotation of the molecule around its molecular short axis (slower process) follows an Arrhenius law over about thirty degrees in the nematic range (except close to the phase transition) with an activation energy comparable to the bulk and is almost independent of the aerosil density. The relaxation rate of the process originating from the fluctuation of the molecular long axis around the director (librational mode, faster process), however, follows the Vogel–Fulcher–Tammann law. With increasing disorder achieved by increasing the aerosil density, the relative dielectric strength of the librational mode increases in comparison with the bulk. The relaxation frequency of the slower process increases but that of the faster process decreases with increasing aerosil density. Both these effects are less pronounced for hydrophobic than for hydrophilic aerosils.

1. Introduction

The molecular dynamics of nematic liquid crystals confined in porous matrices, or forming dispersions with solid particles, have received considerable attention [1]. The nematogen can be adsorbed in different kinds of macroporous membranes [2–6], glasses [7–10] and molecular sieves [11], dispersed with different types of aerosil particles [12–19] or even aerosil dispersions can be confined in Anopore membranes [20, 21]. In particular, aerosil-dispersed organic composites are very promising from the technological as well as from the scientific point of view, and interest for these types of materials is growing considerably. By changing the aerosil density in the dispersion, controlled disorder can be introduced into soft matter. This possibility opens a new area for the investigation of the influence of structural effects, surface interactions and finite size effects on the molecular dynamics and thermal properties of liquid crystals (LCs). Different experimental methods are used to probe the influence of confinement on the physical properties of LCs [1]. However, broadband dielectric spectroscopy (BDS) is especially useful for the investigation of molecular dynamics of polar molecules under geometrical restrictions. The changes in the relaxation rate, and dielectric strength, and the broadening and/or asymmetry of the relaxation processes, give valuable information about molecular dynamics in confinement. A growing number of dielectric investigations have been performed on the above-mentioned composites during recent years, however some questions still remain open.

LCs belonging to the 4-*n*-alkyl-4′-cyanobiphenyl (*n*CB) homologous series are very often used in dielectric experiments that probe the influence of geometrical restrictions on the molecular dynamics. However, only a few papers deal with the problem of the influence of the different types of confinement on the relaxation rate of the librational process observed in the nematic phase [2, 3, 5, 8, 10, 12]. Particularly extensive studies were devoted to the investigation of molecular dynamics of 4-*n*-pentyl-4′-cyanobiphenyl (5CB) and 4-*n*-octyl-4′-cyanobiphenyl (8CB) in different kinds of confinement such as organic Synpor membranes [2], inorganic Anopore membranes [3–6], porous silica glasses [7], controlled pore glasses (CPG) [8, 9], molecular sieves [11] or aerosil dispersions [12–18,

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20–22]. In these mesogens the strong dipole moment is oriented nearly parallel to the molecular long axis, which greatly simplifies the interpretation of the dielectric spectra. The dielectric measurements in untreated Anopore membranes confirm the planar axial order of the nematic director but in treated membranes with different surfactants (e.g. aliphatic acids, lecithin) a polar–radial or polar–polar orientation has been observed [1, 3–6].

Besides the one relaxation process in the isotropic phase, two relaxation processes are observed in the nematic phase of the bulk materials: the slower one assigned to the hindered rotation of the molecule around their molecular short axis, and a faster second process assigned to the libration of the molecule around the direction of the nematic director (librational mode). In the cylindrical geometry of Anopore filters these two relaxation processes can be separated. The relaxation frequency of the slower process is higher but for the librational mode it is slightly lower in comparison with the bulk. In the nitrocellulose Synpor membrane filters the dielectric data for 5CB reveal that the confinement influences the relative amplitude of the observed molecular relaxation processes [2]. Additionally, the relaxation frequencies of both molecular processes exhibit the same tendency as observed in Anopore membranes when compared with the frequencies of the bulk molecular processes. The temperature dependence of the relaxation rates of these processes is very often fitted, in a limited temperature range, with an Arrhenius law. However, according to [8, 23, 24] and as will be shown later in this paper, the applicability of the Arrhenius law in determining the activation energy has some limitations, and a more precise derivative analysis is needed, especially near the isotropic–nematic (I–N) phase transition for the bulk as well as for the confined systems. Furthermore, in lecithin-treated cylindrical pores of Anopore membranes the relaxation time of the librational mode for 5CB [10] and 8CB [5] shows a well pronounced nonmonotonic behaviour with increasing temperature in the nematic phase towards the N–I phase transition, which was explained by introducing a temperature dependence of the orientational order parameter. An alternative explanation of experimental data was given in the framework of a model based on the free volume concept [25]. It was shown that a single process that is a kind of reorientation or tilt of a molecule in this case gives the librational mode. All observed relaxation processes in geometrical restrictions are of non-Debye type.

For 5CB and 8CB confined in the molecular sieve AlMCM-41 a new, slow relaxation process was detected due to the motions of the molecules restricted in the pores [11]. The relaxation frequency of this process obeys a Vogel–Fulcher–Tammann (VFT) law. In the composites prepared from aerosils and *n*CBs an additional slow relaxation process was detected and assigned to the cyanobiphenyl surface monolayer of LC molecules on the surface of silica particles [13, 16]. The temperature dependence of the relaxation rate of this process also shows VFT behaviour [13, 14].

In the present study dielectric spectroscopy in the frequency range 10^6–10^9 Hz was applied to investigate the influence of the hydrophilic and hydrophobic aerosil density on the molecular processes in the nematic liquid crystal 5CB. Especially interesting is the question of the influence of different types and densities of aerosil on the relaxation rate and dielectric strength of the slow and fast molecular processes present in the nematic phase of 5CB. The influence of the hydrogen-bonded structure and different surface treatment of the aerosil particles on the nematic director field is discussed.

2. Experimental

The liquid crystal 5CB obtained from Merck was used in the dielectric experiment without further purification. 5CB is a well known member of the *n*CB homologous series of liquid crystals that exhibits a nematic phase in the temperature range from 308 K to 295 K and can be easily supercooled to approximately 270 K. The dipole moment (about 4 D) of the 5CB, mainly determined by the cyano group, is oriented nearly parallel to the molecular long axis [26].

Aerosils (Degussa Corp.) with different surface treatment were used to probe the influence of controlled disorder on the molecular processes in 5CB. The hydrophilic aerosil 300 with a diameter of the primary particles of about 7 nm and specific area of 300 $\mathrm{m^2\,g^{-1}}$ was used to prepare 5CB mixtures with a density ρ_S=0.01, 0.05, 0.10 and 0.15 $\mathrm{g\,cm^{-3}}$. The surfaces of the silica particles are covered by hydroxyl groups and in solution can form a hydrogen-bonded network. The hydrophobic aerosil R812 with the same diameter of primary particles but specific area of about 260 $\mathrm{m^2\,g^{-1}}$ was also used to prepare aerosil–5CB composites with a density ρ_S=0.10 and 0.15 $\mathrm{g\,cm^{-3}}$. For this aerosil ≡SiOH groups are replaced at a maximum extent by $SiO–Si(CH_3)_2$ groups which prevents considerably H-bonded agglomeration of the aerosil particles in the mixture. The samples with different density of aerosils were prepared using a solvent method [15, 16]. To the diluted solution of 5CB in acetone (0.02 g of LC per $\mathrm{cm^3}$ of solvent) the required amount of aerosils, dried under vacuum at 473 K for about 15 h, was added. The mixture was then sonicated for 1 h to obtain a homogenous dispersion of the aerosils in the solution.

Finally, the acetone was evaporated slowly while keeping the temperature of the mixture above 323 K. The remaining sample was then held overnight above 323 K in vacuum, to ensure complete evaporation of the solvent.

The complex dielectric function $\varepsilon^*(\omega)=\varepsilon'(\omega)-i\varepsilon''(\omega)$ of bulk 5CB and aerosil–5CB mixtures was measured in the frequency range 10^6–10^9 Hz using the HP4291B RF impedance analyser in combination with a homemade cell [16]. Both electrodes of the measuring capacitor were spin-coated with the polyimide SE1211 (Nissan Chemicals) which promotes homeotropic orientation of the LC molecules with respect to the electrode surface (probing electric field **E** parallel to the director **n**). It was verified that optical cells made from SE1211-coated glass slides resulted in homeotropic alignment for 5CB, before coating on the polished metal electrodes used in the dielectric permittivity measurements. The temperature control for these high frequency measurements was similar to that described in [16].

In the investigated frequency range only one relaxation process is observed in the isotropic phase of 5CB and dielectric spectra were evaluated using the empirical formula given by Havriliak and Negami [27]:

$$\varepsilon^*(\omega, T \geq T_{\mathrm{NI}}) = \varepsilon_\infty + \frac{\Delta\varepsilon_{\mathrm{I}}}{\left[1+(\mathrm{i}\omega\tau_{\mathrm{HN,I}})^{1-\alpha_{\mathrm{I}}}\right]^{\beta_{\mathrm{I}}}}. \quad (1)$$

However, in the nematic phase two relaxation processes appear and the dielectric spectra were fitted with two Havriliak–Negami functions:

$$\varepsilon^*(\omega, T \leq T_{\mathrm{NI}}) = \varepsilon_\infty + \sum_{k=1}^{2} \frac{\Delta\varepsilon_k}{\left[1+(\mathrm{i}\omega\tau_{\mathrm{HN},k})^{1-\alpha_k}\right]^{\beta_k}} \quad (2)$$

where parameters characterizing the relaxation process are the relaxation times τ_{HN} and the relaxation strength $\Delta\varepsilon$. The exponents α and β describe broadening and asymmetry of the relaxation time distribution, respectively. ε_∞ is the high frequency limit of the permittivity.

For the parameters α, β and τ_{HN}, the relaxation time in the maximum of the process, $\tau_{\max}=1/\omega_{\max}$ can be calculated using the equation [28]:

$$\tau_{\max} = \tau_{\mathrm{HN}} \sin^{-1/\alpha}[\alpha\pi/(2+2\beta)]\sin^{1/\alpha}[\alpha\beta\pi/(2+2\beta)]. \quad (3)$$

The temperature dependence of the relaxation frequency of some relaxation processes observed in liquid crystals usually follows the Arrhenius law [28, 29]:

$$f = f_0 \exp\left(-\frac{E_{\mathrm{A}}}{k_{\mathrm{B}}T}\right) \quad (4)$$

where E_{A} is the activation energy, f_0 is the pre-exponential factor, $k_{\mathrm{B}}=1.381\times10^{-23}\,\mathrm{J\,K^{-1}}$ is the Boltzmann constant and T is the temperature. By taking the logarithm of equation (4), the experimental data can easily be fitted with a linear equation.

However, in many cases the Arrhenius law has some limitations and cannot explain the experimentally observed temperature dependence of the relaxation rates. Therefore, especially for amorphous and fragile glass-forming systems the most widely used law is the Vogel–Fulcher–Tammann law [25, 28, 29]:

$$f = f_0 \exp\left(-\frac{A}{T-T_0}\right) \quad (5)$$

where A is a constant and T_0 is the so-called Vogel temperature. Similarly to the Arrhenius law, experimental data can be fitted with a logarithmically linearized equation. The coincidence between experimental data and the VFT law is taken as an indication of cooperative behaviour in disordered and glass-like systems [25].

3. Results and discussion

In the isotropic phase of bulk 5CB one relaxation process is observed and assigned to the random reorientation of the molecules. However, in the nematic phase two processes are observed: the slower one is related to the hindered rotation of the molecules around their molecular short axis, and the faster process is assigned to the reorientation of the long axis of the molecules around the direction of the director (the so-called librational mode). Choosing homeotropic and planar orientations of the liquid crystal molecules in a measuring capacitor, one can separate these processes. With homeotropic orientation (**E** $\parallel$ **n**) the slow process can be detected, and with planar orientation (**E** $\perp$ **n**) the fast process can be determined. These orientations of the molecules can be achieved by treatment of the surfaces with surfactants or by the application of an external magnetic field. However, in a real experiment molecular ordering is never perfect and both processes can be found in the dielectric spectrum.

Figure 1 shows the frequency dependence of the real and imaginary parts of the permittivity at a chosen temperature in the nematic phase with homeotropic alignment in the bulk. The data for the dielectric losses are fitted with two relaxation processes using equation (2), figure 1 (*b*). In particular near the I–N phase transition, difficulties arise in fitting the librational mode because the bump related with this process is located near the border of the frequency window in the gigahertz range. Nevertheless, with decreasing temperature the process shifts to lower frequencies and the separation of both processes is more accurate. The

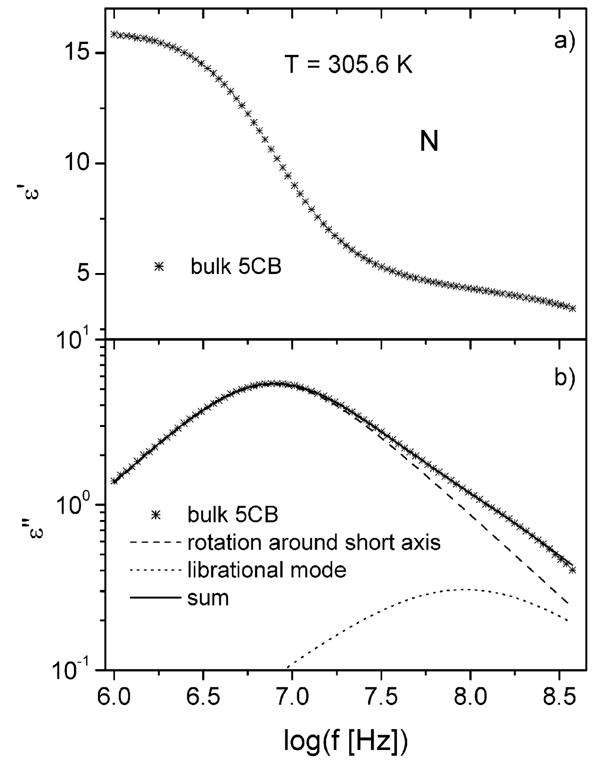

Figure 1. Frequency dependence of the (*a*) real and (*b*) imaginary part of the permittivity for bulk 5CB in the nematic phase for **E**||**n** induced orientation with fits of the main relaxation processes.

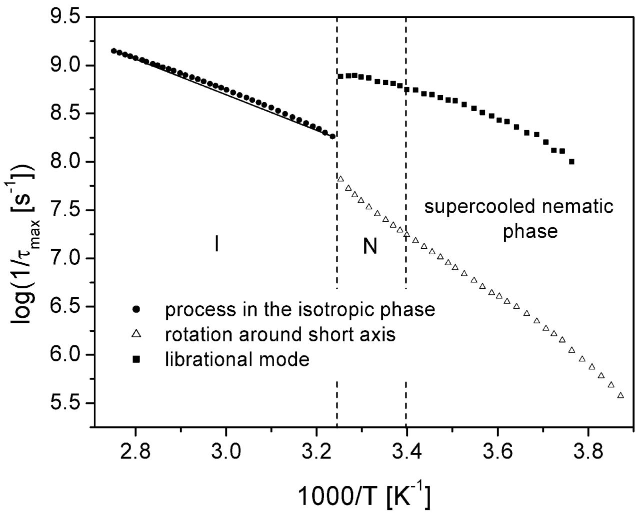

Figure 2. Temperature dependence of the relaxation rates of the processes related to the hindered rotation of the molecules around the molecular short axis and of the librational mode. The straight line in the isotropic phase is shown to visualize the deviation of the data from linear dependence.

results are shown on the activation plot presented in figure 2. At first sight, the temperature dependence of the relaxation rate in the isotropic phase seems to follow the Arrhenius law, equation (4). However, a more precise analysis of the data shows that this dependence is non-linear and cannot be simply fitted by the Arrhenius equation to find the activation energy E_A of the process, especially close to the I–N phase transition [30].

The derivative of the linearized form of equation (4) in the form of $d(\ln f)/d(1/T) = -E_A/k_B$ provides very useful information about the temperature dependence of the activation energy and allows a more adequate analysis of the experimental data. The derivative technique enables the calculation of the activation energy to be made at every temperature and allows the checking of its temperature dependence. In this way calculated activation energies of the process observed in the isotropic phase, indeed, show temperature dependence and change from about 30 kJ mol^{-1} in the high temperature range to about 45 kJ mol^{-1} close to the I–N phase transition (figure 3). The temperature dependence of the activation energy can be fitted with an equation: $E_A = B(T - T^*)^{-\beta}$, where B is constant, T^* denotes a virtual phase transition temperature and β is a critical exponent. The parameters obtained for bulk 5CB are: $B = 70\,\mathrm{kJ\,K^{-1}\,mol^{-1}}$, $T^* = 304\,\mathrm{K}$ and $\beta = 0.21$. The critical increase in the activation energy near the I–N phase transition of 5CB was recently also mentioned in [23, 31]. Figure 3 also presents a critical increase in the activation energies of aerosil–5CB mixtures. The fitting parameters obtained for $\rho_S = 0.01\,\mathrm{g\,cm^{-3}}$ are: $B = 57\,\mathrm{kJ\,K^{-1}\,mol^{-1}}$, $T^* = 307\,\mathrm{K}$ and $\beta = 0.16$. It was also found that the temperature dependence of the relaxation rate of bulk 5CB in the isotropic phase can be

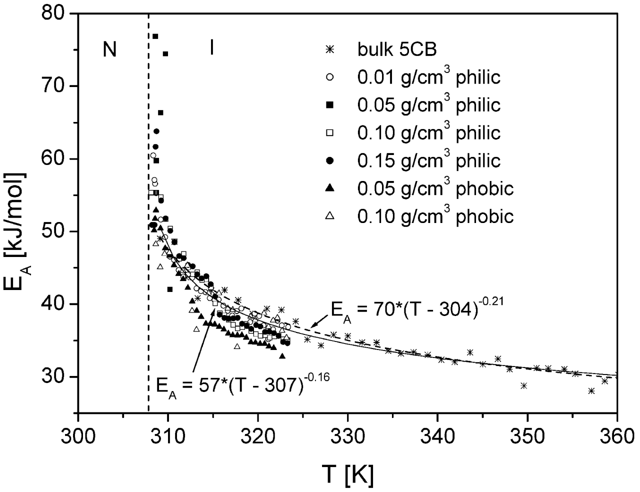

Figure 3. Temperature dependence of the activation energy of the relaxation process in the isotropic phase of bulk 5CB and hydrophilic and hydrophobic aerosil–5CB composites.

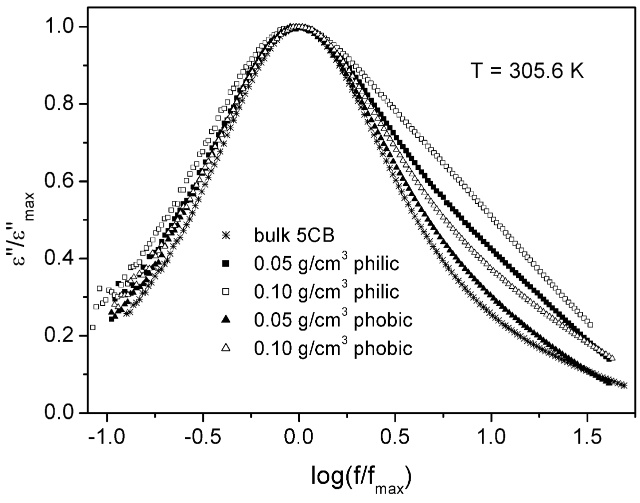

Figure 4. Normalized dielectric losses versus normalized frequency for different hydrophilic and hydrophobic aerosil densities at 305.6 K compared with bulk 5CB.

well fitted by the linearized VFT law with fitting parameters: $\ln(f_0)=25$, $A=718\,\mathrm{K}$ and $T_0=195\,\mathrm{K}$. Additionally, it should be noticed that for a temperature close to the phase transition, the activation energy slightly decreases with increasing aerosil density. This effect can be related to the lowering of the prenematic order in the isotropic phase near the phase transition with increasing aerosil density.

In the activation plot presented in figure 2 four areas can be resolved: (i) close to the I→N phase transition, (ii) close to the N→I phase transition, (iii) the nominal nematic phase in the temperature range from 308 to 295 K, (iv) the supercooled nematic phase. Close to the phase transition from the nematic phase side, the activation energy for the slow process changes non-linearly with increasing temperature. In this region the main temperature effects are related to the change of the order parameter [30]. In the nominal nematic phase the temperature dependence of the relaxation rate roughly follows an Arrhenius law and the activation energy attains a value of about $61\,\mathrm{kJ\,mol^{-1}}$, while in the supercooled nematic phase the activation energy is about $70\,\mathrm{kJ\,mol^{-1}}$. In the broad range of temperatures this dependence can be fitted with average activation energy of about $65\,\mathrm{kJ\,mol^{-1}}$. In the supercooled nematic phase of bulk 5CB, especially at lower temperatures, the data show clear deviations from Arrhenius behaviour. The relaxation rate of the librational mode shows different temperature dependence. Near the nematic–isotropic transition, order parameter-induced curvature can also be observed in the present data [30]. In the nominal nematic phase, the activation energy estimated from the Arrhenius law is about $20\,\mathrm{kJ\,mol^{-1}}$. But in the broad temperature range, where the supercooled nematic phase exists, a non-Arrhenius dependence is observed and the data for bulk 5CB can be fitted more adequately with a linearized form of the VFT law, equation (5), with fitting parameters: $\ln(f_0)=22$, $A=107\,\mathrm{K}$ and $T_0=236\,\mathrm{K}$.

Figure 4 shows a comparison of normalized dielectric losses, $\varepsilon''/\varepsilon''_{\max}$ as a function of the normalized frequency, $f/f_{\max}$ for bulk 5CB and hydrophilic and hydrophobic aerosil–5CB mixtures in the nematic phase at a temperature $T=305.6\,\mathrm{K}$. Table 1 includes fitting parameters of the relaxation processes presented in figure 4. For bulk 5CB the slow relaxation process is not broadened ($\alpha_1=0$) but slightly asymmetrical ($\beta_1=0.98$), while in contrast the fast relaxation process is broadened ($\alpha_2=0.23$) but symmetrical ($\beta_2=1$). The broadening of the fast process is observed for nearly all densities of aerosils but it is symmetrical except for $\rho_s=0.10\,\mathrm{g\,cm^{-3}}$. It should be noted that in bulk 5CB with homeotropic sample orientation this process is very weak and somewhat difficult to extract from the dielectric spectrum. With increasing hydrophilic aerosil density an increase of the broadening of the slow process is observed and the parameter α_1 change from 0 to about 0.08. However, the parameter $\beta_1=1$ for all aerosil densities. Simultaneously, the relative dielectric strength, $\Delta\varepsilon_2/\Delta\varepsilon_1$ of the fast relaxation process increases

Table 1. Parameters in equation (2) characterizing relaxation processes presented in figure 4, observed in the bulk 5CB and in aerosil–5CB mixtures.

Fitting parameters	Bulk 5CB	Density of hydrophilic aerosil $\rho_s/\mathrm{g\,cm^{-3}}$ 0.01	0.05	0.10	0.15	Density of hydrophobic aerosil $\rho_s/\mathrm{g\,cm^{-3}}$ 0.05	0.10
α_1	0	0.02	0.04	0.08	0.08	0.04	0.06
β_1	0.98	1	1	1	1	1	1
α_2	0.23	0.11	0.14	0.13	0.16	0	0.06
β_2	1	1	1	1	1	1	0.84
$\Delta\varepsilon_2/\Delta\varepsilon_1$	0.08	0.14	0.33	0.42	0.47	0.09	0.16

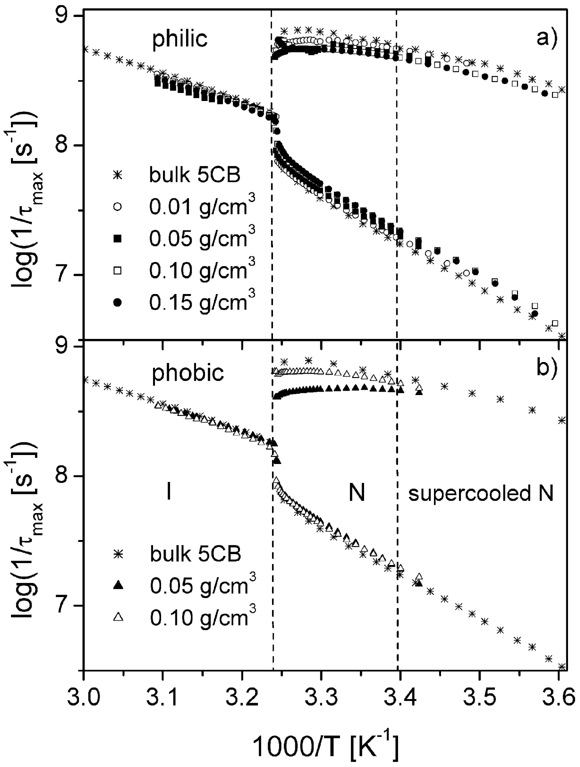

Figure 5. Temperature dependence of the characteristic relaxation frequency for (*a*) hydrophilic aerosil–5CB and (*b*) hydrophobic aerosil–5CB mixtures compared with bulk 5CB.

with increasing hydrophilic aerosil density from about 0.08 in the bulk to about 0.47 for the density $\rho_S=0.15\,\mathrm{g\,cm^{-3}}$. Also with increasing hydrophobic aerosil density the broadening of the slow relaxation process increases. With increasing aerosil density the relaxation processes shows more non-Debye characteristics. However, the relative dielectric strength of the librational mode for the hydrophobic aerosil is much less than for comparable densities of hydrophilic aerosils (figure 4). These findings clearly show a significant difference between the influences of two different types of aerosil on the dielectric properties of composites. The hydrophilic aerosil particles covered by hydroxyl groups causes changes, with increasing density, in the ordering of the liquid crystal through strong hydrogen bonds of the polar molecules to the surface. The increasing disorder manifests itself as an increase of dielectric strength of the librational mode because fewer molecules are oriented perfectly parallel to the measuring electric field. The changes in homeotropic ordering of the nematogen introduced by hydrophobic aerosil are more local and less pronounced in comparison with the hydrophilic aerosil because of much fewer –OH groups present on the aerosil particles surface.

Figure 5 presents a comparison of the temperature dependence of characteristic relaxation frequencies of the relaxation processes observed in the bulk nematogen and in aerosil–5CB mixtures for different hydrophilic and hydrophobic aerosil densities. In the isotropic phase the relaxation frequencies for both composites are slightly lower than in the bulk. Derivative analysis shows (figure 3) that the activation energy depends on the temperature and changes rapidly near the I–N phase transition, as for the bulk 5CB. For the hydrophilic aerosil mixtures the relaxation frequency of the slower process increases with increasing aerosil density but the relaxation frequency of the librational mode decreases, figure 5 (*a*). However, for the hydrophobic mixtures, with increasing aerosil density the relaxation frequency of the slower process only slightly increases in comparison with the bulk relaxation frequency, and seems to be only weakly density dependent, figure 5 (*b*). The librational mode frequency for the hydrophobic aerosil–5CB composite is slightly lowered for $\rho_S=0.10\,\mathrm{g\,cm^{-3}}$ and comparable to the bulk. Surprisingly, however, the relaxation frequency of the librational mode for $\rho_S=0.05\,\mathrm{g\,cm^{-3}}$ is shifted significantly lower. At present we have no explanation for this behavior at $\rho_S=0.05\,\mathrm{g\,cm^{-3}}$.

The temperature dependence of the relaxation frequency of the slower process for the aerosil–5CB mixtures can be fitted, except close to the isotropic–nematic phase transition, using the Arrhenius law, equation (4). Obtained activation energies for different hydrophilic and hydrophobic aerosil concentrations are nearly the same and comparable with the average

Table 2. Parameters obtained from fitting the temperature dependence of rate of the relaxation processes related to rotation around molecular short axis by an Arrhenius law.

		Density of hydrophilic aerosil $\rho_S/\mathrm{g\,cm^{-3}}$				Density of hydrophobic aerosil $\rho_S/\mathrm{g\,cm^{-3}}$	
Fitting parameters	Bulk 5CB	0.01	0.05	0.10	0.15	0.05	0.10
$\ln(f_0/\mathrm{Hz})$	44	43	44	44	44	45	43
$E_A/\mathrm{kJ\,mol^{-1}}$	66	64	67	65	67	69	64

Table 3. Parameters obtained from fitting the temperature dependence of the relaxation rate of the librational mode by a Vogel–Fulcher–Tammann law.

Fitting parameters	Bulk 5CB	Density of hydrophilic aerosil ρ_s/g cm^{-3} 0.01	0.05	0.10	0.15	Density of hydrophobic aerosil ρ_s/g cm^{-3} 0.05	0.10
ln (f_0/Hz)	22	21	21	22	21	20	21
A/K	107	41	28	133	68	6	13
T_0/K	236	256	261	229	245	247	275

activation energy for bulk 5CB (table 2). The activation energy for this process is nearly independent of the aerosil density. However, the temperature dependence of the relaxation frequency of the librational mode is in general non-Arrhenius. The derivative analysis shows that the activation energy is not constant and changes significantly in the investigated range of temperatures. Therefore, to probe this non-Arrhenius behaviour the data for the librational mode were fitted using the VFT law, equation (5). To check the usefulness of the VFT law in this case, the data were analysed using the derivative of its linearized expression in the form $[\mathrm{d}(\ln f)/\mathrm{d}T]^{-1/2}=A^{-1/2}(T-T_0)$. The results obtained by fitting the relaxation frequency of the librational mode to VFT temperature dependence are presented in table 3. The parameter ln (f_0) is nearly constant and independent of the aerosil type and density. The fit parameter A changes irregularly with aerosil density but is much lower for the hydrophobic aerosil–5CB composites. The Vogel temperature T_0 seems to be comparable for all composites and changes little with aerosil density.

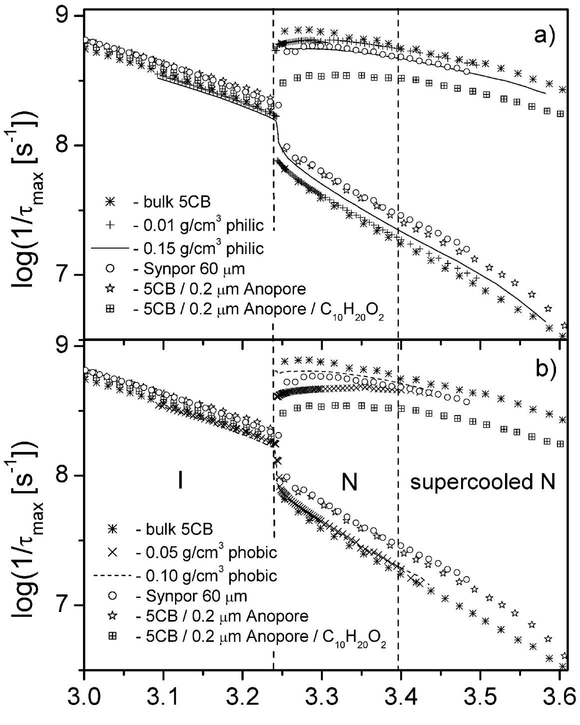

Figure 6. Temperature dependence of the rate of relaxation processes observed in bulk 5CB and under different geometrical restrictions compared with (*a*) hydrophilic aerosil-5CB and (*b*) hydrophobic aerosil–5CB composites.

Figure 6 summarizes the influence of different kinds of confinement on the temperature dependence of the relaxation frequency of the relaxation processes. The observed changes in the relaxation rate of the processes related to rotation of the molecule around the molecular short axis, and of the librational mode with increasing hydrophilic and hydrophobic aerosil density, exhibit the same tendency as for 5CB in Synpor [2] and Anopore [3] membranes. In well ordered untreated cylindrical channels of Anopore membranes the relaxation frequency of the slower process increases as a result of better orientation (axial) of the nematic molecules in the channels (order parameter increases). For aerosil–5CB composites and the fractal-like structure of Synpor membranes the effect is related to increasing disorder resulting in an increasing number of small nematic domains with deviating director orientation, macroscopically resembling a sample in the isotropic phase [20]. The relaxation frequency of the librational mode decreases in aliphatic acid-treated channels of Anopore as a result of a defects-induced decrease of the order parameter of the homeotropically oriented molecules on the walls of the cylindrical channels (measuring electric field parallel to the axis of the channels). Also, introducing aerosil particles in 5CB or filling them in the very complex structure of Synpor membranes causes a multidomain-induced decrease of the order parameter of the overall sample, which results in a decrease of the relaxation frequency of the librational mode. Considering this, it can be concluded that the observed effect arises mainly from surface interactions and disorder introduced in the liquid crystal.

4. Conclusions

The results obtained were analysed using the first derivative method, which allows one more precisely to distinguish any changes in the temperature dependence of the activation energies of the observed relaxation processes. The temperature dependence of the activation energies of the characteristic relaxation frequencies was compared with the Arrhenius and Vogel–Fulcher–Tammann laws. Detailed analysis of the data shows that the Arrhenius law has some limitations. In several cases it should be replaced by a more suitable expression, as for instance the VFT law.

The relaxation frequency in the isotropic phase of 5CB is almost uninfluenced by the aerosils, and only slightly shifted to lower frequencies, and exhibits non-Arrhenius temperature dependence. The observed decrease of the activation energy near the isotropic–nematic phase transition with increasing aerosil density can be related to the influence of the disorder on the formation of the prenematic phase. The relaxation frequencies of the two relaxation processes observed in the nematic phase differ in temperature dependence: the relaxation rate of the slow relaxation process follows the Arrhenius law in the nematic temperature range (except very near T_{NI}), while the relaxation rate of the fast process exhibits VFT dependence. The deviation from Arrhenius dependence increases with increasing aerosils density. The activation energies of the slow process are also independent of the aerosils density and comparable to the activation energy in the nematic phase of the bulk material. However, the changes observed in relaxation rate depend on the type of aerosils. By increasing the hydrophilic aerosil density the relaxation frequency of the slow process increases, but the fast process decreases compared with the bulk. On increasing the hydrophobic aerosil density the frequency of the slow process only slightly increases and the librational mode weakly decreases. These changes are related to the different treatment of the surfaces of these two types of aerosil. With increasing aerosil density the relative dielectric strength of the libration mode increases compared with the bulk. However, the extent of the increase is higher for hydrophilic aerosil, which is related to the creation of a hydrogen-bonded structure and higher disorder in the director field.

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