

Diffusion studies in confined nematic liquid crystals by MAS PFG NMR

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ABSTRACT

Pulsed field gradient (PFG) NMR and magic-angle spinning (MAS) NMR have been combined in order to measure the diffusion coefficients of liquid crystals in confined geometry. Combination of MAS NMR with PFG NMR has a higher spectroscopic resolution in comparison with conventional PFG NMR and improves the application of NMR diffusometry to liquid crystals. It is found that the confinement of the liquid crystal 5CB in porous glasses with mean pore diameters of 30 and 200 nm does not notably change its diffusion behavior in comparison with the bulk state.

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1. Introduction

Liquid crystals (LC) in confined geometries attracted much attention of scientists due to their application in electro-optical devices and sensors [1–3]. In contact with solid surfaces, the LCs gained a significant importance also in biomedical applications [4]. A rapidly growing interest in these systems during the last decade was caused by their exploitation in synthesis of novel nanostructured materials using a procedure called “liquid crystal templating” [5–7]. Fabrication of these materials with tailored functionalities is based on the use of ordering properties of the LCs which serve as the self-organized templates for a specific alignment of the material particles.

Molecular dynamical and transport properties of the LCs and their interactions with solid interfaces play an important role for final material properties both in electro-optics and in guided synthesis. However, whereas re-orientational dynamics of the confined LCs was extensively probed by various NMR techniques [8–10], their self-diffusion remains very poorly investigated. One of the main difficulties of performing diffusion experiments is due to the relatively strong residual dipolar interactions remaining in these systems. The general problem is that although the internal molecular dynamics is fast, anisotropic orientation of molecules along the local symmetry axis prevents a complete averaging of

dipolar couplings on the time scale of the NMR experiments [11]. This in turn leads to fast attenuation of the transverse magnetization which hinders an application of the conventional diffusion techniques, such as Pulsed Field Gradient (PFG) NMR [12–14]. The latter technique relies on the implementation of the field gradient pulses between the r.f. pulses which should have a time separation of at least a few milliseconds [15]. If transverse relaxation time is below this limit, as it is typically the case in many LCs, measuring diffusion with the help of pulsed field gradients becomes difficult and demands implementation of sophisticated line-narrowing techniques [16,17]. The application of the alternative NMR diffusometry technique employing the fringe magnetic field gradient [18] and allowing for short r.f. pulse separations is hindered by the so-called Dipolar Correlation Effect [19,20] which becomes the dominating mechanism of echo attenuation and masks any effect caused by translational diffusion.

Several modifications of the PFG NMR method including nematic and solid echoes [15,21], dipolar decoupling [15,21,22], magic-angle sample orientation [15,23], and a combination of multipulse dipolar decoupling in addition to the stimulated echo [17,24] were suggested to overcome the above-mentioned difficulties. The most accurate value of the diffusion coefficient in liquid crystals was obtained by using a gradient slice selection, stimulated echoes and a multipulse homonuclear decoupling [16,17,25].

An alternative novel technique, usually abbreviated as MAS PFG NMR, combines magic-angle spinning (MAS) with the pulsed field gradients [26–31]. MAS implies the orientation of the axis of a fast spinning sample in an angle of $\theta_m \approx 54.7^\circ$ with respect to the external magnetic field. This has two advantages. First, the

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increased resolution in the ppm-scale permits one to observe separately each individual group with identical electronic surroundings. Second, the enhanced transverse relaxation time under MAS conditions allows for a sufficient time for the implementation of the pulsed magnetic field gradients. The application to liquid systems should be performed carefully since the measured self-diffusion coefficient tends to deviate from its intrinsic value at higher MAS frequencies [32].

In this work we apply the MAS PFG NMR technique to a confined liquid crystal 4'-pentyl-4-cyanobiphenyl (5CB). This nematic LC has been most extensively studied in the literature and established itself as the classical model system for investigation by NMR. Dynamic properties of the confined nematic liquid crystal 5CB has been studied by several NMR techniques, including NMR deuterium spectrometry and relaxometry [8,33], the Dipolar Correlation Effect [20] and Field Cycling Relaxometry [34–36]. However, no NMR diffusion measurements were performed so far rather than that above the isotropization temperature [37] where the relaxation times become long again. The primary aim of the current study is an extension of the novel MAS PFG NMR method to the class of systems with short relaxation times where conventional pulsed field gradient diffusometry would fail. This application is exemplified for the confined nematic 5CB which exhibits particularly short relaxation times, of the order of a few hundreds of microseconds [35].

2. Experimental

NMR measurements were performed on a Bruker AVANCE spectrometer operating at 750 MHz with a wide-bore magnet and a 4-mm-MAS-probe with pulsed field gradient capabilities. The MAS frequency was $\nu_{\text{rot}} = 10$ kHz and the nutation frequency of the radio frequency (r.f.) power was $\nu_{\text{r.f.}} = 100$ kHz. The maximum gradient strength in this system is 0.54 T m^{-1} . Diffusion measurements were performed using the stimulated-echo sequence with bipolar sin-gradient pulses and eddy current delay before detec-

tion, see Fig. 1. The signal attenuation for single-component isotropic diffusion is given by [38]

$$S = S_0 \exp \left[-D \left(\frac{4\delta g \gamma}{\pi} \right)^2 \left(\Delta - \frac{\tau}{2} - \frac{2\delta}{3} - p_\pi \right) \right] = S_0 \exp(-Dk)$$

where D denotes self-diffusion coefficient, γ the gyromagnetic ratio, δ the gradient pulse width, Δ the observation time, τ the inter-gradient delay, and p_π the duration of the π -pulse. The factor k is defined by the equation above. The delay between gradient pulse and subsequent r.f. pulse was $500 \mu\text{s}$. The durations of the dephasing and rephasing periods and the spacings between alternating pulses are multiples of the rotor period. Sine-shaped gradients with 2 ms duration were applied.

Diffusion experiments were carried out by varying the strength of the gradient pulses in the linear range between 10% and 90% of their maximum value (0.54 T m^{-1}).

The MAS-induced temperature gradient was determined by means of a ^{207}Pb NMR thermometer [39]. Fig. 2 shows two signals measured at $T = 300$ K. The dashed spectrum in Fig. 2 corresponds to a 4-mm-rotor filled with a 1.5 mm thick layer of $\text{Pb}(\text{NO}_3)_2$ in the middle and ^{207}Pb NMR insensitive material (zeolite powder) above and below. The solid spectrum corresponds to a fused glass sample, which was filled with $\text{Pb}(\text{NO}_3)_2$ in a length of 8 mm. A temperature gradient of about 5 K over a length of 8 mm is obtained from the shift/temperature equation $0.775 \pm 0.007 \text{ ppm K}^{-1}$ [40]. Therefore, our measurements of samples in fused glass ampoules were performed with a large temperature gradient. The consequence is that, as a matter of principle, a sharp jump of the NMR parameter (at the phase transition temperature) cannot be observed by MAS NMR of larger samples. Therefore, we focus our studies to temperatures, which are about 10 K above or below the well-known phase transition temperature. Some measurements of the bulk material were performed with 5CB in a half full 12 μL -rotor. The temperature gradient is less than ± 0.5 K for the volume in this rotor, which is small compared to the volume of about 35 μL in the fused glass ampoules with an outer diameter of 3 mm, and a length of 10 mm.

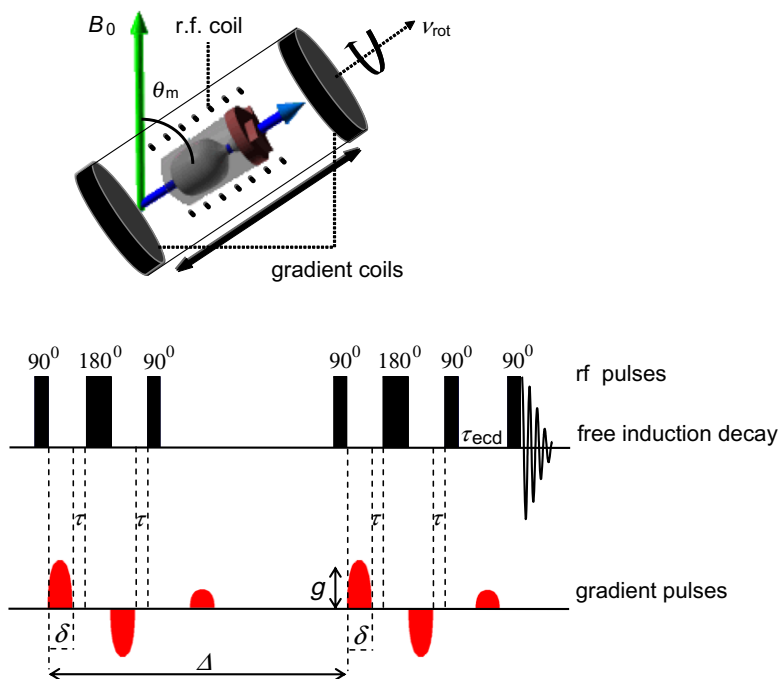


Fig. 1. The MAS design combined with two coils for the pulsed field gradients in a high-resolution MAS NMR probe (top). Radio frequency (r.f.) and gradient pulse scheme of the MAS PFG NMR experiment is shown below. The parameters are diffusion time Δ , gradient pulse width δ , gradient pulse strength g , eddy current delay τ_{ecd} , inter-gradient delay τ . Two weak sine-shaped spoiler gradients (about 0.15 T m^{-1}) average undesirable coherences.

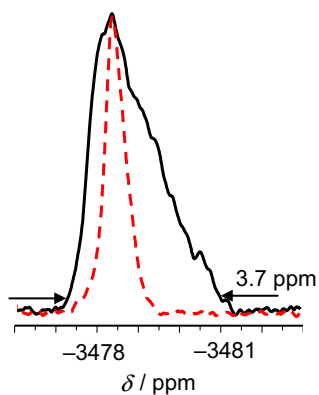


Fig. 2. ^{207}Pb MAS NMR signals of the $\text{Pb}(\text{NO}_3)_2$ powder in a 4-mm-rotor spinning at 10 kHz. The dashed spectrum corresponds to a 4-mm-rotor filled with a 1.5 mm thick layer in the middle and zeolite powder above and below. The solid spectrum corresponds to a fused glass sample, which was filled in a length of 8 mm.

MAS NMR measurements need a special temperature calibration, since the temperature unit measures the temperature in the stator. The temperature in the rotor was determined by means of the ^{207}Pb NMR thermometer using the chemical shift of -3490.4 ppm at 295 K [41] and the slope of 0.775 ppm K^{-1} [40]. Two effects cause a significant temperature difference between stator and rotor. The minor one is the Joule–Thompson effect that causes a linear decrease of the temperature of the rotor with increasing pressure of the bearing air. A value of $\Delta T = -1.2$ K per 1 bar was obtained [39] for a constant rotation frequency of 6 kHz in a 4-mm-rotor. The major effect is the friction of the rotor in the air, which causes a temperature increase proportional to the square of the rotation frequency [39]. For our probe we observed a temperature increase by 9 K going from 1 to 10 kHz rotation frequency, even though the bearing pressure is increased from 0.5 to 2.7 bar.

The nematic liquid crystal 5CB (4'-pentyl-4-cyanobiphenyl) was purchased from Merck Ltd, Poole, England. The transition temperature between the solid and the nematic phases is 297.2 K. The isotropization temperature is $T_c = 308.5$ K. Bioran porous glasses with mean pore diameters of $d = 30$ nm and 200 nm and narrow pore size distributions (90% within $\pm 5\%$) were purchased from Schott Glaswerke, Mainz, Germany. The porosity is in the range 0.67–0.69 for all glasses. The glasses were filled with 5CB using the bulk-to-bulk method [9].

3. Results and discussion

The temperature dependence of the full-width-at-half-maximum (*fwhm*) of 5CB signals confined in 30-nm and 200-nm-Bioran-glasses, see Fig. 3, is shown in Fig. 4. We have a significant line broadening with decreasing temperature from about 30 Hz in the isotropic phase to about 250 Hz in the nematic phase. It should be noted that Fig. 4 shows the width of only one signal with the highest chemical shift in the isotropic phase, and the unresolved signal in the nematic phase corresponds to three signals with a shift difference of 100 Hz. Fig. 4 demonstrates that the isotropic–nematic phase transition at 308.5 K can be observed by MAS experiments. Spinning liquid crystal samples may have an impact on the local ordering, as the viscous and the magnetic torque compete [42]. The effect should disappear for the magic-angle, see p. 151 in [42].

Fig. 4 shows that the nematic–crystalline phase transition does not occur in our samples at 297.2 K due to undercooling. It seems that 5CB is in the nematic state in the temperature range below 308.5 K down to 294 K.

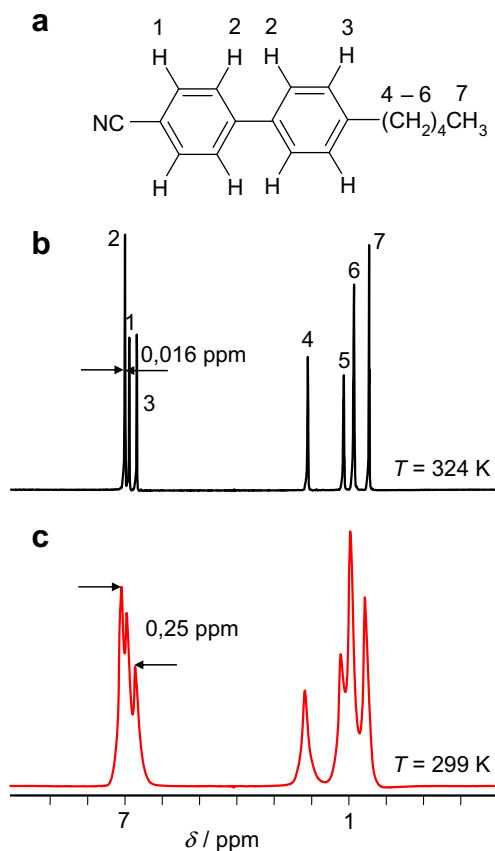


Fig. 3. The chemical structure of 5CB (a). ^1H MAS NMR spectra of 5CB confined in Bioran glasses with a pore diameter of 200 nm above (b) and below (c) the isotropization temperature T_c .

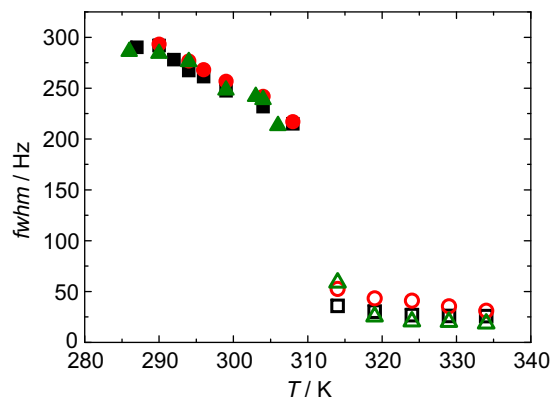


Fig. 4. Temperature dependence of the ^1H NMR linewidth for bulk 5CB (\blacktriangle) and for 5CB confined in Bioran glasses with a pore diameter of 30 nm (\bullet) and 200 nm (\blacksquare). Empty symbols correspond to the isotropic phase and full symbols correspond to the crystalline phase.

Fig. 3 shows the ^1H MAS NMR spectra of 5CB confined in 200-nm-Bioran-glass in the isotropic phase at 324 K and in the nematic phase at 299 K. Similar ^1H MAS NMR spectra were acquired for 5CB confined in 30-nm-Bioran-glass. Signals at ca. 1 ppm and 7 ppm correspond to aliphatic and biphenyl fragments, respectively. In the isotropic phase, the *fwhm* was equal to 0.016 ppm. In contrast, the nematic phase is characterized by two broadened lines, with *fwhm* of the biphenyl group and aliphatic fragment of 0.17 and 0.31 ppm, respectively.

Fig. 5 shows the typical PFG NMR spin-echo decays of 5CB confined in 30-nm and 200-nm-Bioran-glasses above ($T = 334$ K) and below ($T = 299$ K) the phase transition. The experiments were performed with an observation time of $\Delta = 400$ ms and a gradient pulse length of $\delta = 2$ ms. Attenuation curves were fitted by a single-exponential decay which permits to determine the diffusion coefficient D .

The temperature dependence of the diffusion coefficients of 5CB in 200-nm and 30-nm-Bioran glasses is shown in Fig. 6. Opposite to [32], we could not find a significant influence of the rotation frequency in our experiments. Fig. 6 shows two additional values for the lower frequency of 5 kHz and one value without rotation. These values agree with the values for $\nu_{\text{rot}} = 10$ kHz. The diffusion coefficient in the isotropic phase can be described by $D = D_0 \exp(-E/kT)$ with an apparent activation energy of $E_a^{\text{iso}} = (27 \pm 5)$ kJ mol $^{-1}$. Diffusion behavior in the nematic phase can also be approximated by an Arrhenius relationship with an activation energy $E_a^{\text{nematic}} = (38 \pm 6)$ kJ mol $^{-1}$, which is about the same for 30-nm and 200-nm-Bioran glasses. Dvinskikh et al. [17] observed in both phases (geometric average for the nematic phase) an activation energy of (32.8 ± 0.5) kJ mol $^{-1}$. We may state that in the temperature range from 294 to 334 K our diffusivity data for confined 5CB are in the range 1.5 – 4.8×10^{-11} m 2 s $^{-1}$. In the bulk material Dvinskikh et al. [17] found isotropic values of the self-

diffusion coefficient in the range 2.8 – 8.0×10^{-11} m 2 s $^{-1}$, going from 295 to 323 K. Fig. 6 shows our values 2.5 – 5.5×10^{-11} m 2 s $^{-1}$ for the bulk material in the temperature range 294–334 K. From Fig. 6 one may conclude that between bulk, 30-nm-Bioran and 200-nm-Bioran the 5CB diffusivities differ by a factor of about 1.5 or less.

4. Conclusions

For the first time, PFG NMR and MAS NMR have been combined in order to measure the diffusion coefficients of liquid crystals in confined geometry. It could be demonstrated that one of the limitations of the application of PFG NMR to liquid crystals, the line broadening due to dipole–dipole interactions and the limited time interval for the application of the magnetic field gradient pulses, may be overcome. With our present experimental set up we are able to measure diffusion coefficients of confined nematic LCs in the range of 10^{-10} – 10^{-11} m 2 s $^{-1}$ in less than 30 min of experimental time.

Acknowledgments

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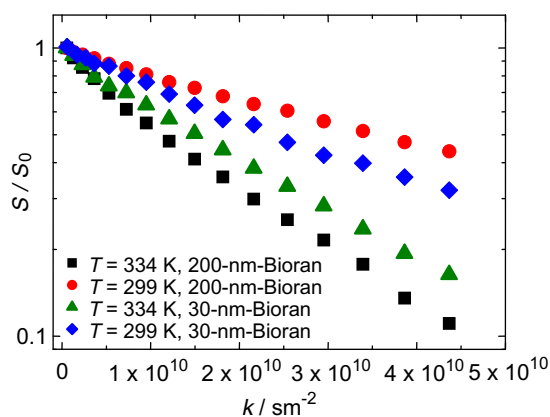


Fig. 5. ^1H MAS PFG NMR spin echo attenuation S/S_0 of the 5CB confined in Bioran glasses with a pore diameter of 30 and 200 nm.

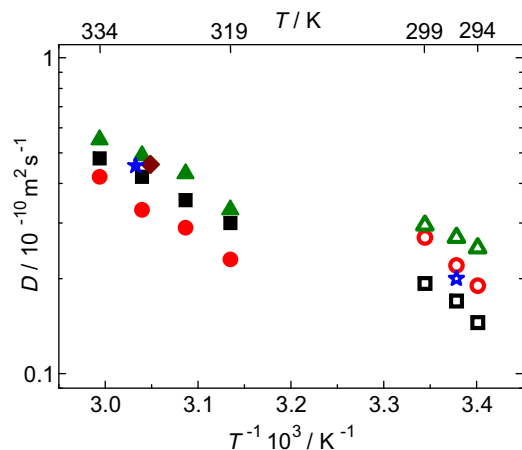


Fig. 6. Temperature dependence of the diffusion coefficient D of bulk 5CB (\blacktriangle) and of 5CB confined in Bioran glasses with pore diameter of 30 nm (\bullet) and 200 nm (\blacksquare). The diffusivities were measured at 10 kHz rotation frequency, except three values for 200-nm-Bioran glass, which were measured at 5 kHz (\star) and without rotation (\diamond). Empty symbols correspond to the isotropic phase and full symbols correspond to the crystalline phase.

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