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SELF DIFFUSION COEFFICIENTS OF TBBA

G. J. KRÜGER and R. WEISS

Magnetic Resonance Laboratory, Physics Division, Euratom CCR, 21020 Ispra, Italy

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Résumé. — Les coefficients de diffusion $D_{\parallel}$ et $D_{\perp}$ ont été mesurés par la méthode de l'écho RMN avec deux impulsions HF et un gradient orientable du champ magnétique dans le régime nématique du TBBA. Dans cette phase on trouve $D_{\parallel}/D_{\perp} \approx 3$. Le processus de diffusion dans les phases nématique et smectique A est brièvement discuté.

Abstract. — The diffusion coefficients $D_{\parallel}$ and $D_{\perp}$ have been measured by a two pulse NMR spin echo with rotatable pulsed field gradient in the nematic regime of TBBA. In this range we find $D_{\parallel}/D_{\perp} \approx 3$. The diffusion process in both the nematic and the smectic A phases is discussed briefly.

In a former paper [1] we published values of the self diffusion coefficients in the smectic A and C phases of terephthal-*bis* (-p-butylaniline) (TBBA). The diffusion coefficients $D_{\parallel}$ parallel and $D_{\perp}$ perpendicular to the average orientation of the molecular director had been measured using a two pulse NMR spin echo with the sample oriented at the magic angle in combination with a rotatable pulsed magnetic field gradient [1, 2].

Now it has been possible to measure both $D_{\parallel}$ and $D_{\perp}$ in the nematic regime of TBBA at 48 MHz using a 90°-τ-β pulse sequence with $\beta < 90^{\circ}$ [3, 4]. The echo created at time 2τ by this sequence has a rather long decay time, much longer than the 90°-τ-90° solid echo [5, 6]. At the optimum value β_{opt} for the largest echo amplitude and at large pulse spacing τ, the amplitude of this *nematic echo* [7] does not depend on the phase difference between the two RF pulses. As already stated in a recent paper [7] the nematic echo has a phase difference of 180° as compared to the free induction decay (f.i.d.) following the first 90° pulse, if both RF pulses have the same phase. Boden *et al.* have calculated the nematic echo for the simpler case of pairs of two spins [5]. They obtained $\beta_{opt} = 54.7^{\circ}$. In all cases observed by us we found $\beta_{opt} \leqslant 45^{\circ}$ [3, 4, 7]. In the case of TBBA we have $\beta_{opt} \approx 29^{\circ}$.

Since it seems to be quite complicated to calculate the nematic echo in a multiple spin system in a general way, we argued in ref. [7] as follows : in our measurements the spacing of the two RF pulses was in the order of ms. In the case of the nematic regime of TBBA the echo occurs about 3.5 ms after the 90° pulse. This time is much longer than the f.i.d. The nematic echo is formed by a fraction of the transverse components of the nuclear magnetization created by the first 90° pulse and has 180° phase shift with respect to the f.i.d. A strong gradient pulse, applied between the two RF pulses, has an additional dephasing effect on the transverse magnetization components. This additional effect is compensated for by a second gradient pulse, between the second RF pulse and the echo, as in the case of a two pulse echo in a liquid [8]. If diffusion occurs, the echo amplitude in the presence of the gradient pulse pair becomes smaller. The ratio of the echo amplitudes, A, with and, A_0, without gradient pulses then allows the determination of the diffusion coefficient in the same way as in a liquid, provided the spacing and the lengths of the RF pulses remain the same with and without gradient pulses [7]. This is different from the cases of multipulse echoes in nematics [9] and smectics [10] because, there, the time intervals between the RF pulses are much shorter than the f.i.d.

In the case of nematics we apply the two field gradient pulses either parallel or perpendicular to the magnetic measuring field H_0 of about 11.3 kG, which at the same time is used to orient the nematic sample. Thus the diffusion coefficients parallel and perpendicular to the field direction, which corresponds to the average orientation of the molecular director, can be measured. The results for TBBA are shown in figure 1. Though the measuring accuracy is low, due to the bad signal to noise ratio of the nematic echo, it can clearly be seen that $D_{\parallel} > D_{\perp}$ over the whole nematic regime. Together with the measuring accuracy of $\pm$ 30 % the data are compatible with the assumption that both $D_{\parallel}$ and $D_{\perp}$ have about the same activation energy in the nematic range. This has also been observed in other nematics

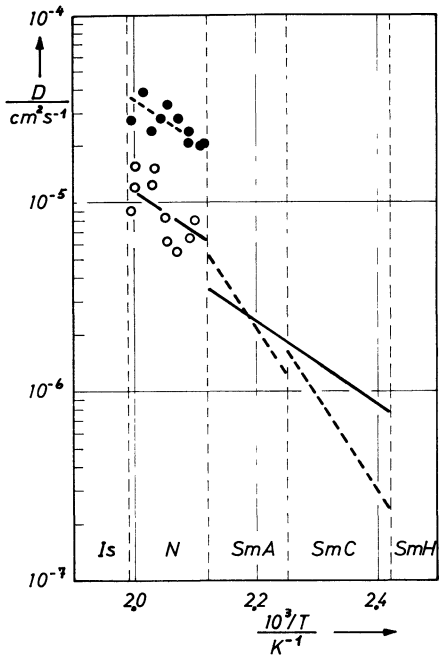

FIG. 1. — Self diffusion coefficients of TBBA vs. reciprocal temperature. O $D_\perp$, ● $D_\parallel$ in the nematic regime, ——— $D_\perp$, - - - - - $D_\parallel$ mean values in the smectic A and C ranges [1], ... extrapolation of $D_\perp$ of the smectic A and C regimes into the nematic and isotropic ranges. Phase transition temperatures are indicated by broken lines.

[4, 9]. Moreover, the activation energy is about the same as that of $D_\perp$ in the smectic A and C phases. This behaviour was also shown by p-hexanoylbenzylidene-p'-aminoazobenzene (C_6-AA) [7]. For comparison, the mean values of our former results for $D_\parallel$ and $D_\perp$ in the smectic A and C phases of TBBA [1] have been included in figure 1, as broken and solid lines respectively.

Both $D_\parallel$ and $D_\perp$ show discontinuities at the liquid to nematic and at the nematic to smectic A phase transitions. This is in contrast to the continuous liquid to nematic transition of $D_\perp$ in Licristal IV [4], and corresponds to the behaviour of MBBA [9]. The ratio of $D_\parallel/D_\perp$, which is about 3 (Fig. 1), compares well with that of other nematics : Licristal IV showed 2.0 [4], MBBA 1.5 [9], C_6-AA 2.6, C_9-AA 1.8 and C_{10}-AA 1.6 [7]. Leadbetter *et al.* [11] have made a neutron scattering measurement and obtained a value for $D_\parallel/D_\perp$ of 2.1 for D-MBCA and 1.3 for 5CB. Unfortunately they measured at only one temperature in each substance, but their absolute values of $D_\parallel$ and $D_\perp$ lie in the same order of magnitude as all the other substances measured by magnetic resonance [4, 7, 9]. Since their magnetic field was only 2.6 kG [11], one might have some doubts as to whether their samples were really oriented as much as possible. Therefore, the ratios of $D_\parallel/D_\perp$ obtained by them could be too small compared with the NMR data.

There has been some comment on the crossover of $D_\parallel$ and $D_\perp$ in the smectic A range at $10^3/T = 2.19\ K^{-1}$ [12]. It has been argued that, if $D_\parallel > D_\perp$ in a smectic, the smectic layers would be destroyed by the diffusion. We do not think that this would be the case, however, because, as pointed out in ref. [1], we must assume that diffusion perpendicular to the molecular director, i.e. inside the smectic A planes, is liquid like, with very small diffusion jumps compared to the molecular diameter. Parallel to the molecular director, on the other hand, we have a jump process, as in a crystalline lattice, with the plane spacing as a jump distance of about the length of one molecule. Therefore, even if $D_\parallel > D_\perp$, jumps parallel to the molecular director always occur with this well defined distance from plane to plane and the smectic A planes remain stable. The diffusion is in that respect similar to permeation [13]. Our argument for the diffusion process being like this in the smectic A phase was based on the different activation energies of $D_\parallel$ and $D_\perp$ in that regime [1]. In the nematic phase, however, with about the same activation energy for both diffusion coefficients, this argument does not hold. The diffusion is probably liquid like in both directions in the sense that in any direction there exists only a mean square displacement and no defined jump distance, as in a lattice. This is another reason for the nonexistence of layers in nematics. Of course it does not exclude the existence of small cybotactic groups near the phase transition.

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References

[1] KRÜGER, G. J., SPIESECKE, H. and VAN STEENWINKEL, R., *J. Physique Colloq.* **37** (1976) C 3-123.
[2] KRÜGER, G. J., SPIESECKE, H. and WEISS, R., *Phys. Lett.* **51A** (1975) 295.
[3] KRÜGER, G. J. and SPIESECKE, H., *Ber. Bunsenges.* **75** (1971) 272.
[4] KRÜGER, G. J. and SPIESECKE, H., *Z. Naturforsch.* **28 A** (1973) 964.
[5] BODEN, N., LEVINE, Y. K., LIGHTOWLERS, D. and SQUIRES, R. T., *Chem. Phys. Lett.* **31** (1975) 511.
[6] BODEN, N., LEVINE, Y. K., LIGHTOWLERS, D. and SQUIRES, R. T., *Chem. Phys. Lett.* **34** (1975) 63.
[7] KRÜGER, G. J., VAN STEENWINKEL, R., SPIESECKE, H. and NOACK, F., Sixth International Liquid Crystal Conference, Kent, August 23-27 (1976) to be published in *Mol. Cryst. Liq. Cryst.*
[8] STEJSKAL, E. O. and TANNER, J. E., *J. Chem. Phys.* **42** (1965) 288.
[9] ZUPANČIČ, I., PIRŠ, J., LUZAR, M., BLINC, R. and DOANE, J. W., *Solid State Commun.* **15** (1974) 227.
[10] BLINC, R., BURGAR, M., LUZAR, M., PIRŠ, J., ZUPANČIČ, I. and ŽUMER, S., *Phys. Rev. Lett.* **33** (1974) 1192.
[11] LEADBETTER, A. J., TEMME, F. P., HEIDEMANN, A. and HOWELLS, W. S., *Chem. Phys. Lett.* **34** (1975) 363.
[12] Private discussions at the MECO seminar on phase transitions in solids and liquids, Bled, Yugoslavia, April 28-30 (1976).
[13] HELFRICH, W., *Phys. Rev. Lett.* **23** (1969) 372.