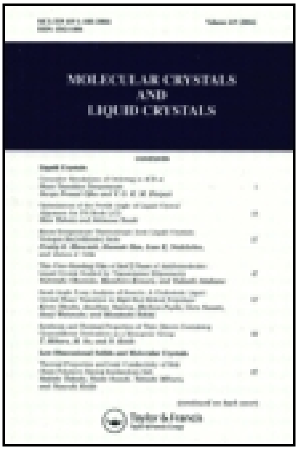

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NMR STUDIES OF SELF-DIFFUSION IN SOME HOMOLOGOUS NEMATIC LIQUID CRYSTALS

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Abstract After briefly reviewing the alternatives to measure diffusion in liquid crystals the paper sketches the principles and some recent refinements of the NMR field gradient (FG) technique, which allows to study mass transport very directly without the necessity to use tracer or dye molecules. In NMR FG experiments on mesophases difficulties arise from the fact that for anisotropic liquids the dipolar nuclear interaction is much less averaged than in isotropic liquids, so that the standard method is generally not applicable. As an alternative to external multi-pulse averaging we have developed a fast field cycling procedure that considerably reduces the effective dipolar coupling by a magic-angle orientation of the magnetic field relative to the director axis of the sample material. Combined with familiar pulsed field gradient (PFG) sequences this cycling made possible extensive measurements of the self-diffusion constants in nematic liquid crystals with values as low as $\sim 10^{-7} cm^2 s^{-1}$. Results are presented for some homologues of the PAA and MBBA series. They show the expected odd-even effects as a function of chain carbon number, whereas most other findings (Arrhenius-type temperature dependence, anomal discontinuity at the nematic-isotropic phase transition, chain length independence of the anisotropy ratio) are not in accordance with existing theories.

1. WHY STUDY MASS TRANSPORT IN LIQUID CRYSTALS?

Diffusion, in particular self-diffusion, belongs to the properties of liquid crystals which are only poorly understood. Of course, there exist numerous experimental methods to study mass transport in mesophases, and also quite a number of experimental results[1]; measurements were made as early as 1917 by Svedberg, i.e. previous to investigations of elastic constants or viscosities. But the consistency of available data and the insight of underlying mechanisms is far from satisfactory. Typically, measured diffusion constants obtained for the same material by different techniques, e.g. by optical detection, neutron scattering or nuclear magnetic resonance, deviate up to more than one order of magnitude from method to method. So far this makes the theoretical discussion impossible or rather meaningless. It is worthwhile to note that de Gennes' book[1] treats diffusion in nematics on less than two pages, with only some lines about the theory. Similarly, Krüger's review on the subject[1], published 1982, essentially concentrates on experimental aspects.

The unsatisfactory situation is primarily due to experimental limitations and related theoretical problems arising from the evaluation of the measurements; but certainly also to the fact that translational molecular motions, described by diffusivities, are not or not directly involved in present-day display technologies. Such applications are more concerned with rotational molecular motions, characterized by viscosities. However, one should realize that the apparently less important diffusion parameters are intimately related to the more spectacular viscous properties by principle - both imply velocity correlations - and therefore the interpretation of both phenomena cannot be completely separated. A more practical viewpoint emphasizing the significance of diffusivities is associated with the resolution of a dot matrix, since with decreasing dot dimensions there necessarily comes a range where diffusional lengths are no longer negligible. Another functional example is already explained in de Gennes' book, namely how diffusion can be used to detect a macroscopic conformational change in a nematic. So there exist good reasons why the understanding of mass transport in liquid crystals should be improved.

2. PROCEDURES TO DETERMINE THE DIFFUSION TENSOR EXPERIMENTALLY

For an anisotropic system like a liquid crystal, the diffusion coefficient introduced by Fick's laws is a second rank tensor $\underline{D}$, the symmetry of which is determined by the symmetry of the mesophase under consideration[1]. This applies to both self- and solute-diffusion. If the symmetry is uniaxial as is the case for nematic, smectic-A or smectic-B phases, it is evident that $\underline{D}$ possesses only two independent components, namely parallel ($\parallel$) and perpendicular ($\perp$) to the director field; they are usually denoted by $D_{\parallel}$ and $D_{\perp}$, respectively. With some restrictions, macroscopically the two component representation also holds for liquid crystals of more complex structure (smectic-C, smectic-G, etc.), since averaging over all domain orientations generally allows to define an average diffusion tensor with no more than two characteristic parameters in a special sample frame; somewhat misleadingly, these tensor elements are also called $D_{\parallel}$ and $D_{\perp}$. Regardless of the mesogenic properties, in the isotropic state of the material, that is above the clearing temperature T_c, any long-range anisotropy disappears and $\underline{D}$ simplifies to a scalar quantity D_{iso}. So diffusion experiments have to deal with the three characteristic parameters $D_{\parallel}$, $D_{\perp}$ and D_{iso}; these diffusivities are accessible indirectly and more or less directly by various techniques[1]. The following text is restricted to self-diffusion in nematogens, apparently the most simple subject; however, actually it has turned out to be the greatest challenge to experimenters.

Self-diffusion in nematogens can be measured rather directly by analysing the mass transport on the basis of Fick's laws, if the system has a well-defined geometry and if one finds a means to label the moving particles suitably. In particular, the second point is hard to materialize. Labelling has been achieved with the help of optical dyes or adequate solutes that allow an optical visualization of the concentration gradient caused by the diffusing molecules; the problem is to get an observable diffusant with a structure almost identical to the studied liquid crystal! As a more reliable alternative, radioactive tracer molecules have been used in combination with counting devices to detect the concentration profile of the tracer. Finally, all nuclear magnetic dipoles, say protons or deuterons, may serve as labels, if one produces a gradient of nuclear magnetization by means of an inhomogeneous magnetic field, and then looks at the subsequent diffusion of magnetization, which is assumed to be identical with the mass self-diffusion. Instead by dye or tracer, in that case the molecules are distinguished on their diffusion path via their changing Larmor frequency at different positions in the inhomogeneous field, making use of standard magnetic resonance.

Indirect measurements of self-diffusion do not need such inconvenient labelling procedures. They attempt to determine the diffusion tensor by considering the effect of mass transport on appropriate spectroscopic phenomena like neutron scattering, light scattering or nuclear magnetic relaxation. Unfortunately, this handling involves rather sophisticated theoretical models to evaluate the desired quantities $D_{\parallel}$, $D_{\perp}$ and D_{iso}. So it is not a surprise that the greatest inconsistencies between published diffusion data stem from this type of studies, a circumstance which nevertheless must not be used to cover the clear discrepancies of direct measurements.

Obviously, both types of approaches have advantages and drawbacks: The direct experiments essentially suffer from technical problems, whereas the indirect ones strongly reflect any weakness of the underlying theoretical formalism. To illustrate this let's shortly refer to some details. For instance, a dye or solute cannot be made completely equivalent to the true liquid crystal molecule, and hence the observed concentration profile does not really disclose self-diffusion, but only the motion of the additive. A radioactive tracer, obtainable by the replacement of protons by tritium or natural carbons by carbon-14 in the mesogen to be studied, substantially improves the conditions, yet the preparation of the tracer is an extremely inconvenient task. Furthermore, there always exist incontrollable isotope effects. The nuclear magnetic resonance field gradient methods avoid such troubles with the sample material. Unfortunately, they entail analogous label problems due to technical limitations in producing well-defined magnetic field gradients of sufficient strength. All that elucidates why the indirect procedures, where the mentioned aspects are irrelevant, have been generally preferred for a long time. However, at a high price! The critical point in this type of experiments is how to separate unambiguously the influence of self-diffusion on scattering or relaxation processes from other potential contributions. In particular, this implies that the anisotropy of diffusion is not easily seen, and it seems questionable if the difficulties can be eliminated satisfactorily in the next future.

At the moment, nuclear magnetic resonance field gradient (NMR FG) techniques offer the most convenient and flexible means to investigate the properties of $\underline{D}$ in nematogens. By various modern refinements they provide a powerful tool to make systematic and not only favourably selected measurements, above all because the sample material does not need a special preparation. We have recently developed a special variant[2] which combines the capabilities of field gradients with those of field cycling, and allowed us to study self-diffusion in all homologues of the PAA- and MBBA-series available to us. Both the experimental principles and the novel results will be describes briefly in the following.

3. THE NUCLEAR MAGNETIC RESONANCE FIELD GRADIENT (NMR FG) TECHNIQUE

Essentially, the NMR FG principle makes possible to work out the components of the diffusion tensor $\underline{D}$ from the observation of a nuclear magnetization decay $\vec{M}(t)$ due to mass transport along the gradient $\vec{G}$ of an inhomogeneous magnetic field $\vec{H}(\vec{r})$ or magnetic induction $\vec{B}(\vec{r})$. As shown in many standard textbooks[3], a Fick's law diffusion ansatz for $\vec{M}(t,\vec{r})$ yields, after some calculations, that for any selected direction but constant strength of $\vec{G}$ the amplitude A of a Hahn spin echo at time $t = 2\tau$ is given by

$$A(2\tau)=A(o)\ \exp[-2\tau/T_2]\ \exp[-\tfrac{2}{3}\ D_G{}^2\gamma^2\ G^2\ \tau^3] \qquad (1)$$

where D_G denotes the diffusion constant parallel to the gradient. As usual, T_2 is the transverse nuclear magnetic relaxation time, γ the magnetogyric ratio of the considered nuclei (generally protons: $\gamma = 2.675\ 10^8\ T^{-1}s^{-1}$), and τ the pulse spacing of the Hahn program. Obviously, adjusting $\vec{G}$ parallel to the director $\vec{n}$ of a liquid crystal reveals $D_{\parallel}$, whereas perpendicular orientation displays $D_{\perp}$, and no special geometry is necessary to measure D_{iso} in the isotropic phase. In practice, it is advantageous to apply the gradient field time dependent to improve the NMR resolution and sensitivity, and such "pulsed field gradients" (PFG) in the form of suitable sequencies give rise to some modifications of the basic equation (1). However, the result remains unchanged in the main: From the echo decay it is easily seen that in order to determine the three diffusivities, the time dependence of the second exponential in Eq.(1) should predominate that of the first one at (small) times τ , where the signal is still sufficiently strong for a reasonable detection. This requirement sets an unpleasant lower limit to the range of accessible diffusion constants, namely

$$D_{min} \gtrsim \frac{12}{T_2{}^3\ \gamma^2\ G^2} \qquad (2)$$

which illuminates why the NMR FG and PFG methods have considerable difficulties with liquid crystalline materials. Realizing that for anisotropic liquids T_2 is typically of the order of 10 ... 100 µs, and that known values of D for nematics range from 10^{-7} ... 10^{-5} $cm^2\ s^{-1}$, extremely large gradient amplitudes of at least several Teslas cm^{-1} are necessary to fulfill condition (2). Therefore, without sophisticated tricks the magnitude of G demanded to intensify the diffusion decay is generally impracticable or completely out of reach for NMR work. Only the isotropic state of mesogens can be and has been handled by the described standard procedure because of the much longer relaxation time T_2 (10^{-2} ... 10 s) occuring in this case[1,4]. In principle, the situation is even worse for the higher-ordered mesophases, where due to the lower temperature the mass transport is slowed down, and on grounds of Eq. (2) one may wonder why nematics have been declared the most critical challenge to exoerimenters (Sect.1). The answer is that refinements to overcome the limitations are experimentally easier for high-viscous materials.

Since the technical problems mainly arise from the fact that in anisotropic liquids the nuclear magnetic (dipolar) interactions are significantly less averaged and entail substantially shorter relaxation times T_2 than in isotropic liquids, one early recognized the possibility to shift the limits by many orders of magnitude with the help of additional, i.e. externally initiated averaging mechanisms. Note that the manipulation of T_2 is clearly more effective than the increase of G because of the higher exponent! One way to lengthen the effective echo decay time, called $T_{2\,eff}$, makes use of radiofrequency irradiation (multipulse averaging[5]), which essentially is a type of magic angle rotation (54.74°) of the magnetic dipoles to reduce the dipolar interaction. We have recently developed an alternative based on the lengthening of $T_{2\ eff}$ by a fast magic angle orientation of the nematic director relative to the magnetic field (field cycling averaging[2]); the rotation must be fast since a non-zero angle between $\vec{n}$ and $\vec{H}$ generates a deviation from equilibrium that must be maintained during the measurement. Our variant seems to us both physically and technically more transparent than the competing procedure. It allowed us to start systematic studies on numerous nematic homologues, including Schiff's bases, which in the light of relation (2) are well-known to belong to the most awkward candidates[1]. Due to the prolongation of $T_{2\ eff}$ up to about 10 ms there was no need of excessively large field gradients; $3\cdot 10^{-2}$ T cm^{-1}, produced by means of a quadrupole coil driven by a 1 kW power supply, proved sufficient to obtain the diffusion regime of the spin echo in any case. Details will be described elsewhere. Our technique also compares well with another elegant extension of the basic PFG experiment, namely the use of multiple quantum echoes[6] instead of the classical (one-quantum) Hahn echo. Such a step increases the effectiveness of the applied gradient proportional to the stimulated order, i.e. G_{eff} □ $m\ G$ with $m = 2 \ldots 6$ having been practiced. But considering Eq.(2) it is unrealistic to believe that manipulations on G become as powerful as those on T_2.

4. NEW RESULTS AND DISCUSSION

To find out the behaviour of the self-diffusion parameters of nematics related to variations of the rigid central core and the flexible end chains, respectively, we performed extensive measurements of $D_{\parallel}$, $D_{\perp}$ and D_{iso}, as a function of temperature, on some alkoxy-azoxy benzenes and Schiff's bases[2]. Seven homologues of the PAA series, the number n of CH_2 groups ranging from 0 to 6 (often abbreviated by PAA, PAP, PrAB, BAB, PAB, HAB, and HpAB), and some MBBA/EBBA mixtures have been investigated up to the present[2]. To our knowledge comparable work on homologous effects does not exist in the literature. As examples, Figs. 1 - 5 illustrate results for PAA (n=o), PAP (n=1), PrAB (n=2), HpAB (n=6), MBBA (n_1=o, n_2=3) and EBBA (n_1=1, n_2=3). Not shown data on the other materials follow the same lines, so that a great number of general features or trends are clearly perceptible:

- The temperature dependence of the three diffusion parameters is within the experimental error limits in any case, both below and above the nematic-to-isotropic (NI) phase transition temperature T_c, strictly Arrhenius-like, i.e. of the form

  $$D_i = D_{oi} \exp(-E_{Di}/RT) \qquad (3)$$

  (i $\hat{=}$ iso, $\parallel$ or $\perp$; D_o = preexponential factor, E_D= activation energy per mol, R = gas constant, T = absolute temperature). Since for PAB, HAB and MBBA/EBBA mixtures the mesophase range is rather broad, significant deviations would have been verified easily. In particular, one should note that the practised temperature resolution of 0.2°C does not evidence pretransitional phenomena. The parameters evaluated for the PAA series are listed in Table 1.

- The discontinuity of the diffusivity at the NI phase transition has always the astonishing form $D_{iso} < D_{\perp} < D_{\parallel}$.

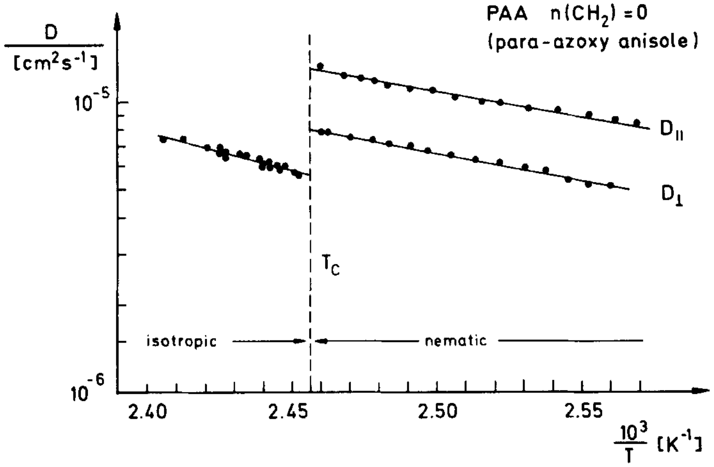

FIGURE 1. Temperature dependence of diffusivity coefficients in the nematic and isotropic phase of para-azoxy anisole (PAA).

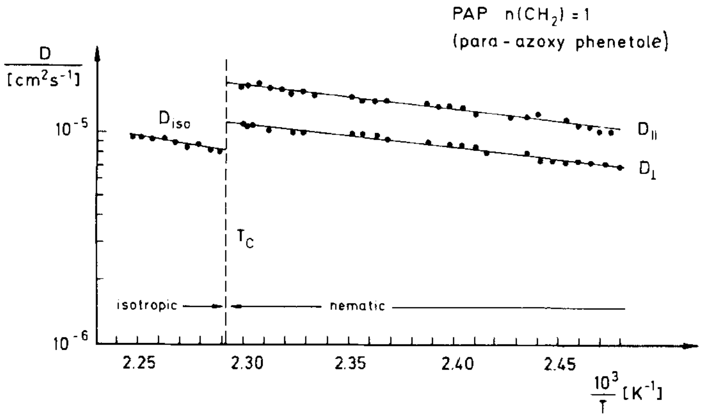

FIGURE 2. Temperature dependence of diffusivity coefficients in the nematic and isotropic phase of para-azoxy phenetole (PAP).

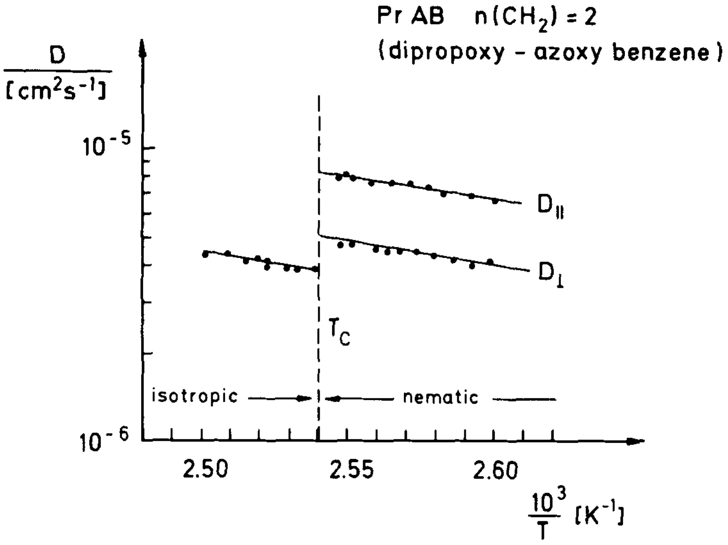

FIGURE 3. Temperature dependence of diffusivity coefficients in the nematic and isotropic phase of p,p'-di-propyloxy-azoxy benzene (PrAB).

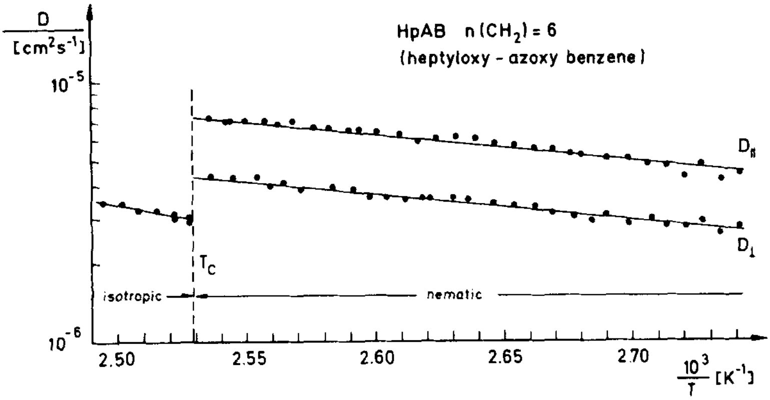

FIGURE 4. Temperature dependence of diffusivity coefficients in the nematic and isotropic physe of p,p'-di-heptyloxy-azoxy benzene (HpAB).

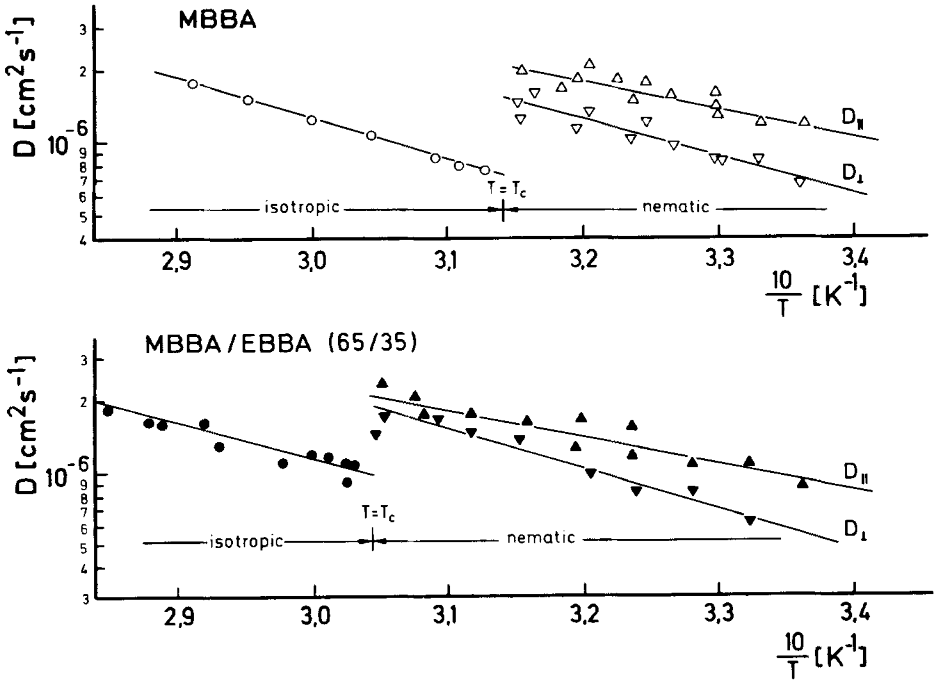

FIGURE 5. Temperature dependence of diffusivity coefficients in nematic and isotropic p-methoxybenzylidene-p'-butylaniline (MBBA), and in a mixture with 35 weight percentage p-ethoxybenzylidene-p'-butylaniline (EBBA).

- All three diffusion coefficients show a characteristic alternation as a function of the number of chain segments, i.e. the well-known odd-even effect, if compared at the same relative temperature $T - T_c \equiv \Delta T$ (Fig. 6a). The alternation largely parallels the changes of T_c itself (Fig. 6b)! Drawn at constant absolute temperature T, the odd-even effect disappears, but the diffusivities show a weak tendency to diminish with increasing molecular length.

- Evidently, the anisotropy ratio $D_{\parallel} / D_{\perp}$ is relatively small and alternates only slightly between the extremes 1.50 (PAP) and 1.68 (HpAB). Fig. 7 elucidates that, overlooking the weak odd-even characteristic, there is essentially no dependence on the chain length.

- The activation energies of self-diffusion in both the isotropic and nematic state, $E_{D\mathrm{iso}}$, $E_{D\parallel}$ and $E_{D\perp}$, respectively, vary rather strangely as a function of n, i.e. do not reveal the familiar odd-even effect (Fig. 8). Surprisingly, one finds in all studied systems $E_{D\mathrm{iso}} > E_{D\parallel}$, the PAA series even manifests $E_{D\mathrm{iso}} > E_{D\perp}$.

- All observed variations due to different chain groups are relatively small. E.g. $D_{\parallel}$ (PAA) $\approx$ $D_{\parallel}$ (PAP) at constant T (extrapolated) or $D_{\parallel}$ (PAA) $\lesssim$ $D_{\perp}$ (PAP) at constant ΔT, and the same holds when comparing MBBA with EBBA. This finding must be contrasted with the considerable shifts due to different cores of the molecules. E.g. $D_{\parallel}$ (PAA) $\gtrsim$ $D_{\parallel}$ (MBBA) at constant T (extrapolated) or $D_{\parallel}$ (PAA)>>

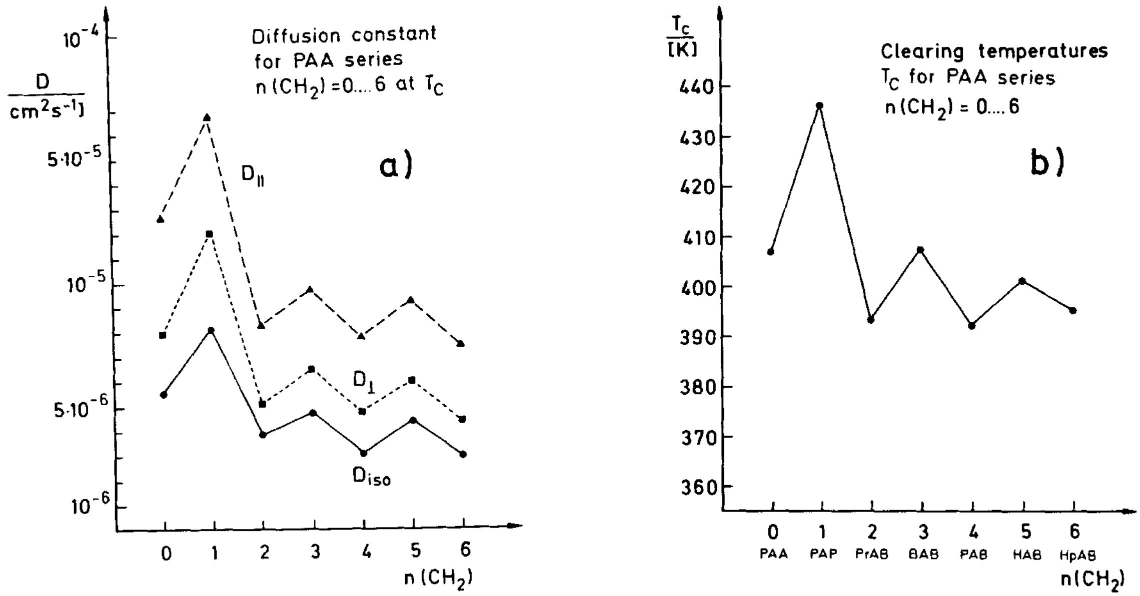

FIGURE 6. Left: Diffusivity coefficients $D_{\parallel}$, $D_{\perp}$ and D_{iso} for the PAA series, n = o ... 6, at the clearing temperatures T_c; right: pertinent values of T_c.

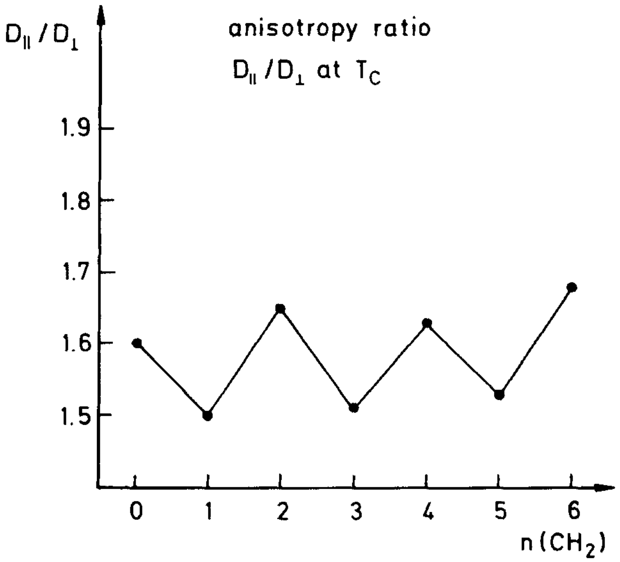

FIGURE 7. Anisotropy ratio $D_\parallel / D_\perp$ for the PAA series, n □ o ... 6, at T_c.

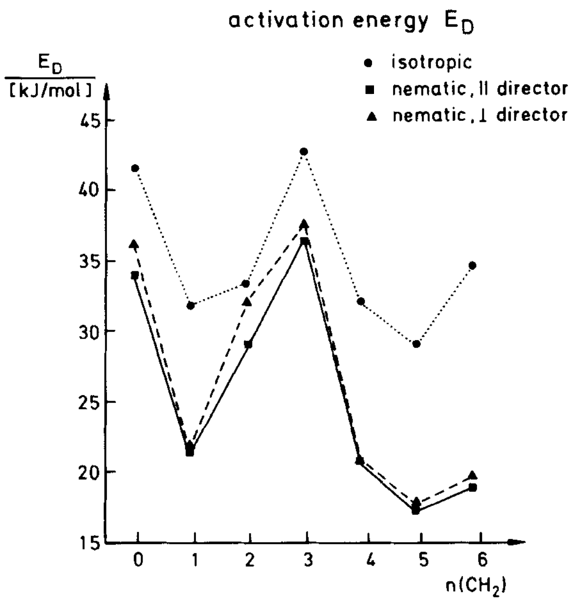

FIGURE 8. Activation energies of self-diffusion, E_{Diso}, $E_{D\parallel}$ and $E_{D\perp}$, for the PAA series, n = o ... 6.

$D_{\parallel}$ (MBBA) at constant ΔT. Note that the molecular weights of PAA and MBBA are about the same, namely 258.3 and 267.4, respectively.

Both PAA and MBBA, have been studied previously many times by the methods sketched at the beginning[1]; systematic measurements on the homologues are rare[1,4,7] and acceptable only for the isotropic phase[4]. As illustrated by Figs. 9 - 10 with reference to some selected works on PAA and MBBA, the experimental results of the diverse research groups and techniques scatter significantly, above all in the nematic state. An interesting point is that even the direct treatments disagree by about one order of magnitude, which nevertheless is not really surprising in view of the commented methodical problems. Our new data are situated in the middle and upper part of the covered ranges. The deviations not only involve the absolute values of the diffusivities, but also the activation energies, the form of the discontinuity at T_c and the anisotropy ratio. Without knowing the exact origin of these discrepancies, it seems ill-timed to go into quantitative details; but irrespective of the reservations on the quality of existing measurements, the extensive new diffusion diagrams lay open some clear limitations or inadequacies of available theoretical estimates[8].

* Obviously, the influence of the central rigid core of the mesogens to the diffusivities is more pronounced than that of the aliphatic end chains. This observation parallels recent reports on the thermal conductivity for the PAA series[9], which discloses similar properties. However, it fundamentally disagrees with predictions of the theory developed by Chu and Moroi[8] (autocorrelation func-

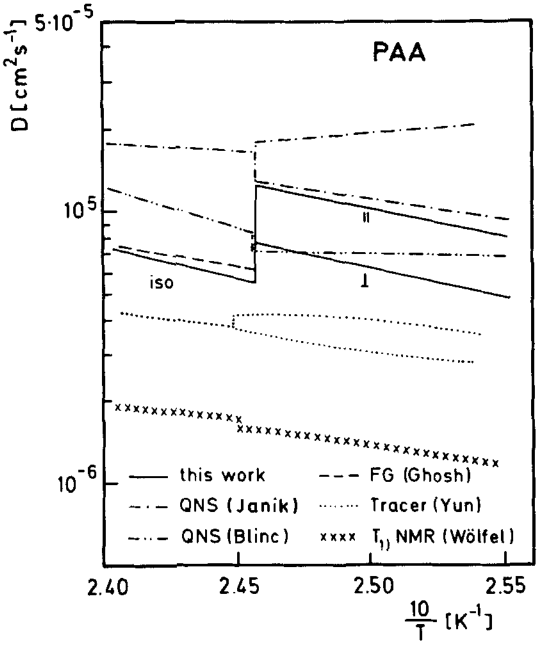

FIGURE 9. Selected literature data on self-diffusion in PAA:

——— this work;

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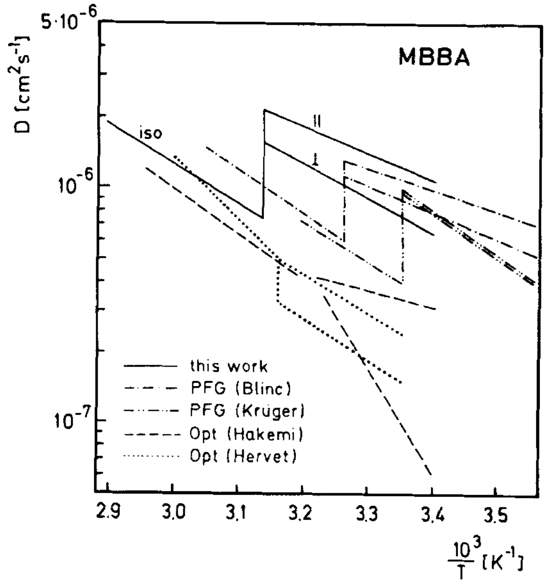

FIGURE 10. Selected literature data on self-diffusion in MBBA:

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tion approach) that require a distinct dependence of the diffusion parameters on the length-to-width ratio of the molecules.

- The simple, Arrhenius-type variation of the diffusivities is indeed astonishing if one recalls the rather complicated temperature dependences of the viscosities in nematic phases[10]. According to the Franklin theory[8] (Kirkwood approach), $D_{\parallel}$ and $D_{\perp}$ should be strongly related to the Leslie viscosities and to the order parameter, and hence reflect the pertinent impact of temperature; such a behaviour is not seen experimentally.
- The unexpected form of the discontinuity at the NI phase transition, now established in quite a number of nematics, emphasizes another problem of the theory, namely the statement $D_{\perp} < D_{iso} < D_{\parallel}$[8]. Since the present studies were performed on pure liquid crystals and not with the help of added solutes, the strange transition can no longer be attributed solely to solute effects as suggested in the literature[1,11]. Impurities are known to reduce the anisotropy, i.e. lessen $D_{\parallel}/D_{\perp}$, and nearly always entail $D_{iso} < D_{\perp}$[1].

These three remarks underline that self-diffusion in liquid crystals is only poorly understood until now. Nonetheless, not least due to some novel NMR procedures, the experimental side of the subject begins to improve.

Acknowledgements The author sincerely thanks Dipl.Phys. D. Leiningen, Dipl.Phys. G. Rollmann and Dr. W. Wölfel for the manifold contributions to this work.

TABLE I Diffusion parameters according to Eq. (3) (activation energy E_D, preexponential factor D_o) for the n = o ... 6 homologues of the PAA series.

sample	E_{Diso} (kJ/mol)	D_{Diso} (cm²/s)	$E_{D\parallel}$ (kJ/mol)	$D_{0\parallel}$ (cm²/s)	$E_{D\perp}$ (kJ/mol)	$D_{0\perp}$ (cm²/s)
PAA (n=0)	41,5	$1{,}2 \cdot 10^{0}$	33,9	$2{,}85 \cdot 10^{-1}$	36,2	$3{,}6 \cdot 10^{-1}$
PAP (n=1)	31,8	$5{,}3 \cdot 10^{-2}$	21,3	$6{,}05 \cdot 10^{-3}$	21,5	$4{,}35 \cdot 10^{-3}$
PrAB (n=2)	33,4	$1{,}02 \cdot 10^{-1}$	29,0	$5{,}33 \cdot 10^{-2}$	32,0	$8{,}89 \cdot 10^{-2}$
BAB (n=3)	42,8	$1{,}49 \cdot 10^{0}$	36,5	$4{,}7 \cdot 10^{-1}$	37,8	$4{,}45 \cdot 10^{-1}$
PAB (n=4)	32,1	$5{,}8 \cdot 10^{-2}$	20,6	$4{,}2 \cdot 10^{-3}$	20,5	$2{,}6 \cdot 10^{-3}$
HAB (n=5)	29,1	$1{,}4 \cdot 10^{-2}$	17,3	$2{,}3 \cdot 10^{-3}$	17,9	$1{,}25 \cdot 10^{-3}$
HpAB (n=6)	34,8	$1{,}1 \cdot 10^{-1}$	19,0	$2{,}4 \cdot 10^{-3}$	19,8	$1{,}35 \cdot 10^{-3}$

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