NMR Pulsed Field Gradient Study of Self-Diffusion in the Isotropic Phase of the Liquid Crystals MBBA and EBBA

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In refinement of a previous study made by Hayward and Packer, the self-diffusion coefficients D of the nematogen liquid crystals MBBA and EBBA were remeasured in the isotropic phase by means of the NMR pulsed field gradient technique. In particular, the diffusion measurements were made for the first time at different Larmor frequencies. A comparison with results obtained recently on the same samples by NMR T_1 relaxation analysis reveals a severe discrepancy. Since the gradient method gives results in essential agreement with optical spectroscopies, the observed discrepancy must be attributed to shortages of the relaxation analysis (incorrect models, insufficient experimental accuracy). It is also shown that D depends more strongly on the molecular weight m than $m^{-1/2}$.

1. Introduction

To get a better insight into the molecular dynamics of liquid crystals, the self-diffusion coefficient D has recently been studied in quite a number of mesogens in the liquid crystalline and isotropic phases by various methods [1]. By now it is well established that in the liquid crystalline state D is anisotropic, i. e. values observed parallel ($||$) or perpendicular ($\perp$) to the average direction of the molecular director differ substantially, with $D_{||}$ both larger and smaller than $D_{\perp}$. In the isotropic state, there is no long-range order in the direction of the molecules, and diffusion measurements performed so far could be described by one single constant, $D_{\text{iso}} \equiv D$. The dependence of D, $D_{||}$ and $D_{\perp}$ on the temperature ϑ was found to be Arrhenius-like, with $D(\vartheta)$ generally being *not* a continuation of the behaviour of $D_{||}$, $D_{\perp}$ or $\frac{1}{3}(D_{||} + 2D_{\perp})$ of the nematic phase above the nematic-isotropic phase transition point.

A closer look at the experimental findings is less satisfactory. In the following we shall only consider D; new data on $D_{||}$ and $D_{\perp}$ will be given elsewhere. Table 1 summarizes data on D and the related Arrhenius parameters (preexponential factor D_0, activation energy E_D) from the literature [2] for one of the most intensively studied nematogen, MBBA, and the homologous compound EBBA. The table clearly illustrates that the agreement between the results of different experimental methods is far from good with regard to both the absolute D value and the activation energy. In particular, there exists a considerable discrepancy between NMR data obtained with relaxation and field gradient techniques, respectively [2 a – d, 2 e – g]. It was the purpose of this investigation to find out whether the discrepancy could be eliminated or at least reduced by comparing refined measurements, i. e. by applying both NMR methods on the same sample material. Our relaxation study has recently been described elsewhere [3]. This paper presents details of the pulsed field gradient work [4].

2. Experimental Techniques and Results

2.1. Techniques

The majority of our D measurements of the liquid crystals MBBA and EBBA were performed on materials obtained from Riedel-de Haen (clearing points: 46.5 °C and 77.9 °C, respectively). For comparison in some cases additional measurements were made on Eastman-Kodak chemicals. After degassing, samples of $0.5 \ldots 2.5\,\text{cm}^3$ were sealed in evacuated glass tubes, suitable for both relaxation and diffusion measurements. By using an additional, self-built pulsed magnetic field gradient apparatus, our frequency variable pulsed spectrometer described previously [5] allowed us to make D measurements at different proton Larmor frequencies. The standard pulsed field gradient technique [6] involves a $\pi/2$ rf-pulse at time $t = 0$, followed by a field gradient pulse (length δ; amplitude g) at time $t = t_1$, a π rf-pulse at $t = \tau$ and a second field gradient pulse of equal length and amplitude as the first at $t = t_1 + \Delta$. A spin echo occurs at $t = 2\tau$ and the ratio R of the signal heights M of this echo in the pres-

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Table 1. Self-diffusion parameters for MBBA and EBBA from the literature [2 a—m], [3]. SFG: Steady Field Gradient Technique; PFG: Pulsed Field Gradient Technique; NS: Neutron Scattering; *: Data from plots.

Liquid Crystal	Method	References	D_0 [cm²/s]	E_D [kJ/mol]	$D [10^{-6}$ cm²/s]	
					MBBA: 50 °C	EBBA: 89 °C
MBBA	NMR-T_1	2 a (1971)	—	29.3	—	—
	NMR-T_1	2 b (1972)	—	19.3	—	—
	NMR-T_1	2 c (1972)	—	—	0.09	—
	NMR-T_1	2 d (1975)	$(2.5 \pm 0.4 \cdot 10^0) \cdot 10^2$	56.9	0.16 ± 0.02	—
	NMR-T_1	3 (1979)	$6.2 \cdot 10^{-2}$	33.5	0.24	—
	NMR-SFG	2 e (1973	$(1.25 \pm 0.03 \cdot 10^0) \cdot 10^{-2}$	24.95 ± 0.08	1.16 ± 0.06	—
	NMR-PFG	2 f (1973)	$\left(5.2 \begin{smallmatrix} +1.7 \cdot 10^2 \\ -5.0 \cdot 10^0 \end{smallmatrix}\right) \cdot 10^{-1}$ *	35.2 ± 9.2 *	1.07 ± 0.15 *	—
	NMR-PFG	2 g (1974)	$6.7 \cdot 10^{-1}$ *	35.4 *	1.27 *	—
	NS	2 h (1972)	$1.5 \cdot 10^4$ *	57.8	7 *	—
	Optical	2 i, j (1974/75)	$\left(1.7 \begin{smallmatrix} +1.8 \cdot 10^1 \\ -1.5 \cdot 10^0 \end{smallmatrix}\right) \cdot 10^{-1}$ *	33.5 ± 6.7	0.64 *	—
	Optical	2 k (1978)	$\left(4.5 \begin{smallmatrix} +4.3 \cdot 10^1 \\ -4.0 \cdot 10^0 \end{smallmatrix}\right) \cdot 10^0$ *	41.9 ± 6.3	0.77 *	—
EBBA	NMR-PFG	2 f (1973)	$\left(1.3 \begin{smallmatrix} +1.5 \cdot 10^3 \\ -1.3 \cdot 10^0 \end{smallmatrix}\right) \cdot 10^{-2}$ *	24.8 ± 21 *	—	3.4 ± 0.8 *
	NMR-T_1	2 l (1974)	—	36.8 ± 4.2	—	—
	NMR-T_1	2 m, 3 (1976/79)	$2.6 \cdot 10^{-2}$	33.1	—	0.44

ence or absence of the gradient pulses is given by [6]

$$R = \frac{M(2\,\tau, g)}{M(2\,\tau, 0)} = \exp\left[-\gamma^2\,\delta^2\left(\Delta - \frac{1}{3}\,\delta\right) g^2\,D\right] \quad (1)$$

where γ means the magnetogyric ratio of the considered nuclear spin. For the present study the proton resonance was applied ($\gamma = 2.67 \cdot 10^4\ \mathrm{G^{-1}\,s^{-1}}$). D was determined from semi-logarithmic plots of the echo attenuation R against $\gamma^2\,\delta^2\left(\Delta - \frac{1}{3}\,\delta\right) g^2$ with appropriately adjusted values of δ, Δ and g. The adjusted pulse length and pulse separation were measured with a counter. The gradient (33 Gcm^{-1} and 47 Gcm^{-1}) was obtained by fitting Eq. (1) to the echo diffusion decay for a material with a known diffusion constant. We used water where very accurate data are available in the literature, e. g. [7] $D_{\mathrm{H_2O}}(23.5\ °\mathrm{C}) = (2.50 \pm 0.025) \cdot 10^{-5}\ \mathrm{cm^2\,s^{-1}}$.

The stability of the pulsed field gradients proved sufficient for phase sensitive detection and signal averaging. This procedure considerably increased the experimental accuracy and thus made it possible to perform and compare D measurements at proton Larmor frequencies ν differing by more than a factor 10 (2.1 MHz and 23.5 MHz). As estimated from the root mean square deviation the *random error limits* of the data presented below were found to be about 2.5% at 23.5 MHz and 3.5% at 2.1 MHz. These limits are mainly due to uncertainties of the pulsed field gradient g (± 0.4 Gcm^{-1}) and of the sample temperature ϑ (± 1 °C). Additional *systematic errors* originating from the quality of the calibration constant $D_{\mathrm{H_2O}}$ ($\pm 0.025\ \mathrm{cm^2\,s^{-1}}$), the influence of a constant field gradient g_0 superimposed on g ($g_0 \leqq 0.2$ Gcm^{-1}) and the inhomogenity of the pulsed field gradient were found to be in some cases as high as 10%, with the third contribution being the main error source. The pulsed field gradient was produced by Helmholtz-type gradient coils (radius R, distance d) using the Berger-Butterweck condition $R = d/\sqrt{3}$ [8] to make g as homogeneous as possible over the sample volume V. Theoretical estimates [9] showed that for the conditions practicable in this work (at 2.1 MHz: $V \cong 2.2$ cm³, $R = 3.4$ cm; at 23.5 MHz: $V \cong 0.6$ cm³, $R = 2.2$ cm) g could be made constant within ± 2.5% or ± 5%, respectively. To reduce the systematic error due to these inhomogenities we tried very hard to make the measurements under conditions as equivalent as possible. Our studies at different Larmor frequencies illustrate the limits of these efforts (systematic deviation for EBBA $\cong +10$%; for MBBA $\cong 0$%; for the MBBA-EBBA mixture $\cong +6$%; see below). Fortunately the total error bars are much smaller than the discrepancies under consideration.

2.2. *Results*

The diffusion parameters of pure MBBA, pure EBBA and a 1 : 1 mixture of both materials obtained with the technique described above are illustrated in Fig. 1 and Table 2. For comparison Fig. 1 also shows available literature data [2]. We emphasize the following results:

(a) In all cases D as a function of the temperature ϑ can be described by an Arrhenius-law

$$D = D_0 \exp(-E_D/R\,\vartheta) \qquad (2)$$

with appropriate values of D_0 and E_D (R: gas constant). Whereas the preexponential factors differ for the three materials, the activation energies are almost the same. Within the experimental error limits no deviation from Eq. (2) could be observed (e.g. a temperature dependence of E_D) in the considered ϑ range, although it was particularly searched near the phase transition points.

(b) The new D values essentially agree with data obtained previously by NMR techniques using constant or pulsed field gradients [2 e, f, g] and by optical methods [2 i, j, k]. However, there exist considerable discrepancies with respect to the neutron scattering [2 h] and NMR relaxation [2 a – d, 3] studies.

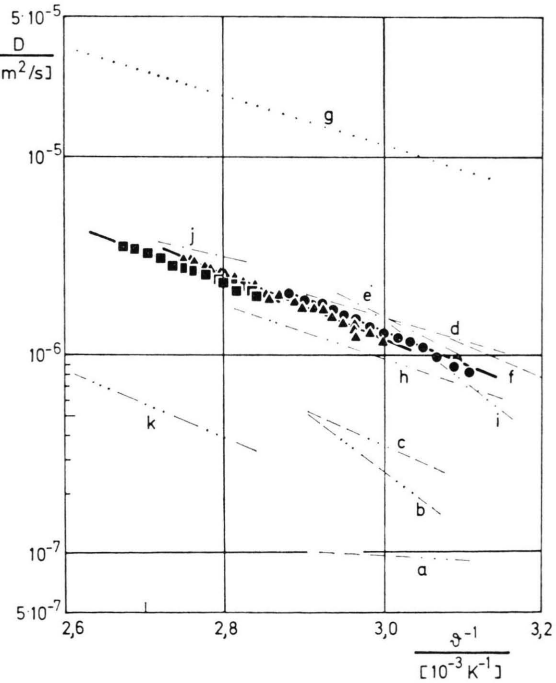

Fig. 1. Self-diffusion coefficient D for MBBA (–●–), EBBA (–■–), and a 1 : 1 MBBA/EBBA mixture (–▲–) obtained in this work at a proton Larmor frequency ν = 23.5 MHz and results from the literature: (a) Dong 1972; (b) Reinhart 1975; (c) Reinhart 1979; (d) Ghosh 1973; (e) Hayward 1973; (f) Zupancic 1974; (g) Dimic 1972; (h) Hakemi 1974, 1975; (i) Hervet 1978; (j) Hayward 1973; (k) Seeliger 1976; Reinhart 1979.

Table 2. Self-diffusion parameters for MBBA, EBBA and a 1 : 1 MBBA/EBBA mixture evaluated from the data points of Figure 1.

Liquid Crystal	D_0 [10^{-2} cm²/s]	E_D [kJ/mol]	D [10^{-6} cm²/s]
MBBA	$11.7\ ^{+10.6}_{-5.2}$	31.7 ± 1.6	0.9 ± 0.03 (50 °C)
EBBA	$3.2\ ^{+2.8}_{-1.7}$	28.5 ± 2.1	2.5 ± 0.18 (89 °C)
Mixture	$7.7\ ^{+7.6}_{-3.4}$	30.7 ± 1.9	1.9 ± 0.04 (75 °C)

(c) As expected, D is found to be independent of the Larmor frequency or the respective magnetic field strength if one takes into account the different error limits of g at 2.1 MHz and 23.5 MHz. The important aspect of this finding is that the pulsed field gradient technique is self-consistent as far as the discrepancy with relaxation spectroscopy results is independent of the experimental Larmor frequency.

(d) The ratio of the diffusion coefficients for MBBA and EBBA extrapolated to the same temperature, or the ratio of the preexponential factors $D_{0\,\mathrm{MBBA}}/D_{0\,\mathrm{EBBA}}$, is different from unity. Making the Arrhenius fits with identical activation energies for both D's (30.1 kJ/mol) we find the ratio 1.19, whereas the slightly better fit with somewhat differing activation energies (MBBA: 31.7 kJ/mol; EBBA: 28.5 kJ/mol) leads to a temperature dependent ratio which varies from 1.15 to 1.30 in the studied temperature range. The data of the 1 : 1 mixture lie between the results of the pure materials. Since in this case the NMR experiment determines the weighted average of D_{MBBA} and D_{EBBA}, this finding confirms that D steadily increases in going from EBBA to MBBA.

Unexpectedly, samples of different quality (Riedel-de Haen, Eastman-Kodak) did not show a different behaviour as long as the material was in the isotropic phase (see Figure 2). Effects such as described by Hayward [2 f] (poor reproducibility near the clearing points, different D values from samples which were heated to the isotropic phase within or outside the magnetic field) could not be observed.

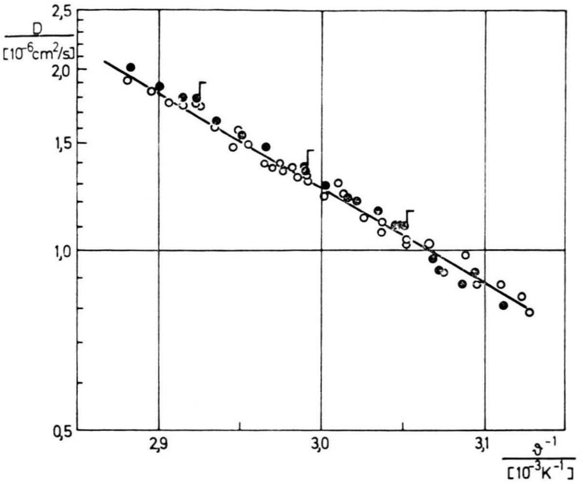

Fig. 2. Self-diffusion coefficient D for MBBA measured at proton Larmor frequencies $\nu = 23.5$ MHz (—●—) and $\nu = 2.1$ MHz (—○—). The marked points (—ʃ—) are additional data at 23.5 MHz for different sample materials (Riedel-de Haen, Eastman-Kodak).

3. Discussion and Conclusions

It has been stated in the literature [2 j] that mass transport measurements by optical or tracer techniques give the only reliable information on self-diffusion in liquid crystals. This statement is incorrect. The present note clearly demonstrates that the NMR pulsed field gradient method is fully consistent with the mass transport studies. Only NMR T_1 relaxation spectroscopy has lead to different results, and this only with regard to values of D_0. The origin of the NMR dilemma, which is known even more drastically for plastic molecular crystals [10], is not quite clear yet; it can originate either from a T_1-analysis based on incorrect or incomplete relaxation models, since the D values obtained from T_1 critically depend on the dynamic model, or from insufficient experimental data, since the model fits critically depend on the experimental error limits. It is interesting to note that the more recent works [3] show smaller inconsistencies than former ones (see Table 1; [2 a – d]). Obviously a similar development emerges from neutron spectroscopy [11], where recent diffusion studies of liquid crystals largely reduced the original discrepancies with respect to the optical data. Unfortunately, D of neither MBBA nor EBBA has been investigated in the isotropic phase by neutron scattering.

Since the molecular theory of translational diffusion in the isotropic phase of liquid crystals has not yet been developed, no theoretical estimates on the values of D_0 and E_D can be given. Nevertheless, the observed ratio $D_{\text{MBBA}}/D_{\text{EBBA}} \cong 1.15 \ldots 1.30$ and the ratios observed for the mixture allow an interesting conclusion. The theoretical weight dependence at constant temperature of D developed for simple liquids, but sometimes also applied [2 i, 12] to liquid crystals, $D \sim \text{m}^{-1/2}$ (m: molecular weight), is not observed in the present case, because according to this relation the ratio should be $(m_{\text{MBBA}}/m_{\text{EBBA}})^{-1/2} = 1.03$. The difference between the experimental and the theoretical ratios is clearly beyond the random experimental error limits. Therefore, the standard evaluation of diffusion parameters by means of dye or label molecules should be revised. By comparing the data at the same temperature similar effects can be found in the literature on D of homologous liquid crystals [13] in some cases where the scatter of the experimental data is not too large. Following the arguments given by Franklin [14] for rotational diffusion mechanisms, the mass dependency stronger than $D \sim \text{m}^{-1/2}$ could be an indication that molecular clusters and not single molecules govern the transport process. The rather large value of the preexponential factor D_0 supports such a conclusion, since it must involve a considerable amount of activation entropy [15].

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