

From Fig. A7 the temperature dependence of the photoconductance at constant spin number has been derived and reproduced in Fig. 7 (of the main part). In the range above T_u the activation energy of the conductance amounts to $\Delta E_1 \approx 0.25$ eV. In the range below T_u ΔE_2 is lying between 0.06 and 0.09 eV,

depending on the spin number N . The low temperature parts of the curves may also be traced by generating a certain spin number at a low temperature by illumination (say $N = 10^{16}$) and heating up slowly (curve h).

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Anisotropy of the Diffusion Coefficient in Nematic Liquid Solutions Measured by NMR Techniques

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A gradient coil has been constructed for exact relative measurements of the longitudinal (D_L) and transverse (D_T) diffusion coefficients of nematic liquid crystals and of small molecules dissolved therein.

Some small molecules dissolved in the nematic phase of Licristal IV showed a D_L/D_T ratio varying from about 1.1 to 1.25, depending on the concentration. In contrast, tetramethylsilane dissolved in p-methoxy-benzylidene-p'-n-butyl-aniline showed no anisotropy in the nematic phase.

1. Introduction

Measurements of self diffusion coefficients in nematic liquid solutions have been reported in an earlier paper¹. It was not possible, however, to substantiate the anisotropy of diffusion in a magnetic field. From the estimated accuracy of measurement it was concluded that the anisotropy could not be more than 30%. A similar measurement has been published by Murphy and Doane², who, however, revoked their results in a later communication³. To make an absolute measurement of two diffusion coefficients which differ by only 30% or even less is

rather difficult. A new measuring arrangement has therefore been constructed which allows rather accurate relative measurements in the longitudinal and transverse directions with respect to the magnetic field.

2. Apparatus and Measurements

The measurements were done by pulsed NMR techniques with pulsed field gradients at 48 MHz using the $90^\circ - 180^\circ$ spin echo^{4,5}. The amplitude M of the nuclear spin echo in the presence of large gradient pulses is given by⁵:

$$M = M_0 \exp \left\{ -\gamma^2 D \delta^2 \left(\Delta - \frac{1}{3} \delta \right) G^2 \right\} \quad (1)$$

where M_0 is the echo amplitude without gradient pulses, γ gyromagnetic ratio of the nuclei, D their

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diffusion coefficient, δ width and Δ spacing of the gradient pulses of magnitude G . In order to measure accurately the longitudinal and transverse diffusion coefficients it is necessary to apply precisely known field gradients in these two directions. For this purpose a rectangular gradient coil was constructed, with square symmetry, which can be rotated by 45° about its longest dimension. Figure 1 shows the coil

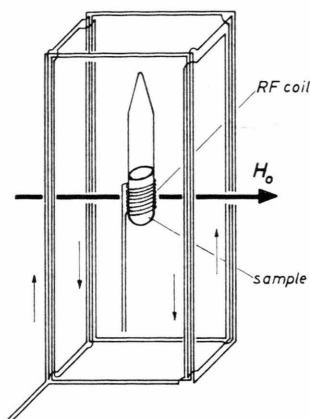


Fig. 1. Coil arrangement, the current direction is indicated by arrows.

schematically together with sample and RF coil in the magnetic field H_0 . In the position shown the coil produces a gradient which is longitudinal with respect to H_0 . If it is turned by 45° the gradient is transverse to H_0 . This is due to the fact that any transverse magnetic field components of the gradient coil do not contribute to the gradient, but simply change the direction of the strong magnetic field slightly. If the coil is exactly quadratic the magnitude of the field gradients in both positions should be exactly the same, provided the current in the coil is the same. The magnetic field gradients of our coil measured by use of the Bessel function A_0 in the free induction decay of a cylindrical sample were, to within 1%, equal in both directions. Some test measurements with liquids of known diffusion coefficient agreed very well with former measurements⁶. If the whole pulse programme and the current in the coil is kept constant, the ratio of the longitudinal diffusion coefficient D_L to the transverse diffusion coefficient D_T is given by:

$$D_L/D_T = \ln(M_0/M)_L / \ln(M_0/M)_T. \quad (2)$$

Since M_0/M is obtained directly from the photograph of the oscilloscope screen, there are no cali-

bration errors. The measurements with isotropic liquids gave the result

$$(D_L/D_T)_{\text{isotropic}} = 0.99 \pm 0.02.$$

This is so close to unity that it does not seem reasonable to correct the D_L/D_T ratio obtained in nematic solutions for the anisotropy of the coil. We account for this small error in the final result by adding a systematic error of $\pm 3\%$ which also covers the nonlinearity errors of oscilloscope and camera used for the measurements.

3. Measurements and Results

As samples, we used solutions of tetramethylsilane (TMS), 1,1-dichloro-2,2-difluoro ethylene (DDE) and 1,1,1-trichloro-2,2,2-trifluoro ethane (TTE) in Licristal IV⁷. A small amount of the organic free radical DPPH was added in order to shorten the spin lattice relaxation time T_1 . In addition, some samples of TMS in p-methoxy-benzylidene-p'-n-butyl-aniline (MBBA)⁸ without DPPH were used for comparison with the results of Murphy and Doane^{2,3}. The concentrations were determined approximately only from a comparison of the signal amplitudes of solute and solvent. Some preliminary measurements using a $90^\circ - 45^\circ$ pulse sequence for the echo¹ were done with the neat nematic phase of Licristal IV.

The measurements in the nematic phase were carried out with the proton signal of TMS and with the ^{19}F signal of DDE and TTE. In the isotropic phase the ^{19}F signal of DDE and TTE and the proton signal of the solutions were used. The latter therefore gives the diffusion coefficient of the solvent rather than that of the dissolved molecules. The gradient was varied from 90 to 250 Oe/cm. The sample temperature was controlled by a heated or cooled air stream and was reproducible to $\pm 1^\circ\text{C}$ measured by a thermocouple attached to the outside of the sample tube. Once thermal equilibrium was reached a set of measurements was carried out rotating the gradient coil forwards and backwards. The temperature, though not known absolutely, was exactly the same for both directions of the field gradient as were all the other parameters. Thus, the only parameter varied was the direction of the field gradient and Eq. (2) could be applied. At the same time Eq. (1) was used to obtain the values for the diffusion coefficients.

A) Licristal IV Samples

Table 1 gives the ratios D_L/D_T together with their errors. The values of the diffusion coefficients of the various samples are shown in Fig. 2 to 5. $D_{F,L}$ and $D_{F,T}$ are the longitudinal and transverse diffusion coefficients of ^{19}F , $D_{p,L}$ and $D_{p,T}$ those of the protons, and $D_{F,is}$ and $D_{p,is}$ are the isotropic diffusion coefficients of ^{19}F and protons respectively. Figure 6 shows the preliminary results obtained with neat Licristal IV. The absolute accuracy is not better than $\pm 15\%$ ($\pm 30\%$ in the case of Figure 6).

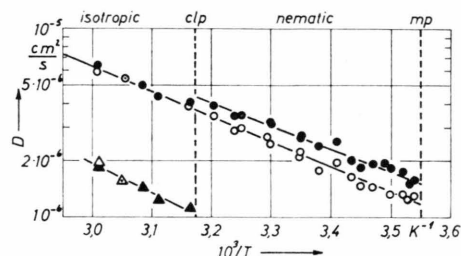


Fig. 2. Diffusion coefficients of a ca. 2% solution of DDE in Licristal IV vs. reciprocal temperature: ● $D_{F,L}$, ○ $D_{F,T}$, ⊙ $D_{F,L} = D_{F,T}$ of ^{19}F in nematic and isotropic phase*; ▲ $D_{p,L}$, △ $D_{p,T}$, △ $D_{p,L} = D_{p,T}$ of the solvent protons in isotropic phase*; clp clearing point, mp melting point.

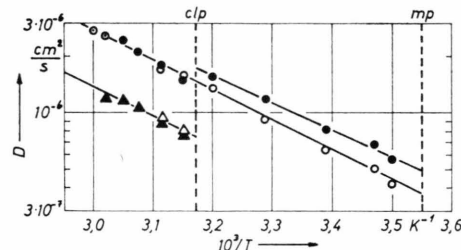


Fig. 3. Same as Fig. 2 for a ca. 2% solution of TTE in Licristal IV.

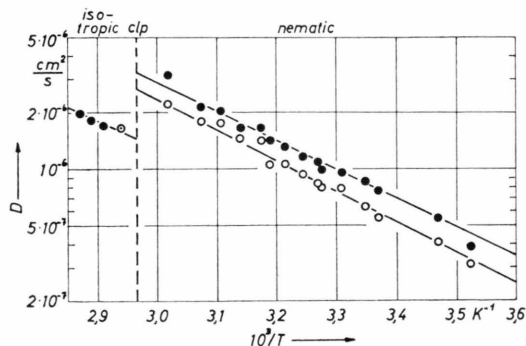


Fig. 4. Diffusion coefficients of a ca. 2% solution of TMS in Licristal IV vs. reciprocal temperature: ● D_L , ○ D_T , ⊙ $D_L = D_T$ of the protons*; clp clearing point, mp melting point. In nematic phase the diffusion coefficients are those of TMS, in isotropic phase those of the whole solution.

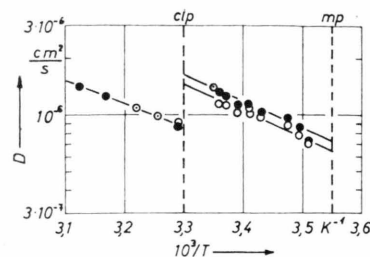


Fig. 5. Same as Fig. 4 for a ca. 10% solution of TMS in Licristal IV.

In general, our measurements show that the dissolved molecules move faster than the liquid crystal solvent in both the nematic and the isotropic phase. All diffusion coefficients increase with increasing concentration of the solute. Furthermore, the ^{19}F diffusion coefficients indicate that $D_{F,T} \approx D_{F,is}$ at the clearing point, whereas $D_{F,L} > D_{F,T}$ at any temperature in the nematic phase (Figures 2 and 3). The same behaviour is shown by the diffusion coefficients of the neat phase (Figure 6). It seems, therefore, that the transverse diffusion coefficient corresponds to the isotropic one, having also the same temperature dependence. The longitudinal diffusion coefficient is, however, larger up to the clearing point and drops when the temperature is raised into the isotropic range. A similar result was obtained by Blinc in neat MBBA⁹.

The activation energies of the different diffusion coefficients are also listed in Table 1. The indexes are those of the diffusion coefficients. The solid lines in the figures have been drawn with these values. The small changes from sample to sample are probably due to the different solutes and concentrations. It seems that the activation energies of the longitudinal diffusion coefficients are systematically smaller than those of the transverse ones. The

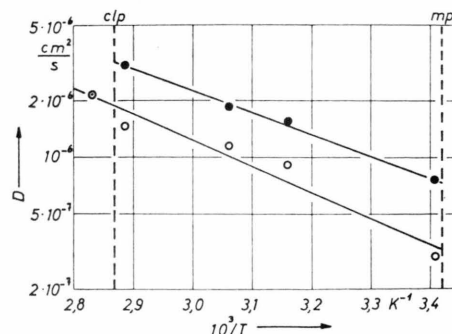


Fig. 6. Self diffusion coefficients of Licristal IV: ● D_L , ○ D_T , ⊙ $D_L = D_T$; clp clearing point, mp melting point*.

Table 1. Ratio D_L/D_T and activation energies (in kcal/mole) of Licristal IV samples. The indexes are those of the diffusion coefficients (see text).

Solute		D_L/D_T	$E_{F,L}$	$E_{F,T}$	$E_{F,is}$	$E_{p,L}$	$E_{p,T}$	$E_{p,is}$
TMS 2%		1.26 ± 0.05				7.0	7.4	6.6
TMS 10%		1.07 ± 0.05				6.6	6.6	5.7
DDE 2%		1.25 ± 0.05	5.5	6.0	6.0			7.1
TTE 2%		1.27 ± 0.06	6.7	7.2	7.2			7.1
neat sample		2.0 ± 0.3				5.3	6.4	

measurement accuracy, however, is not sufficient for this small difference to be significant. The values D_L/D_T given in Table 1 have, therefore, been averaged over all temperatures. The errors given are composed of the mean square errors and the systematic error of 3% mentioned in Section 2. It can be seen that the anisotropy of the diffusion coefficient of the dissolved molecules is smaller than that of the nematic phase itself and that it becomes smaller with increasing concentration of the solute.

B) MBBA Samples

The diffusion coefficients of TMS dissolved in MBBA in different concentrations are shown in Figure 7. Table 2 gives the activation energies. In these measurements it was not possible to distinguish between D_L and D_T in the nematic phase. This does not agree at all with the original results of Murphy and Doane² and is further proof that these must be disregarded completely.

Table 2. Activation energies (in kcal/mole) of the diffusion coefficients of MBBA samples containing TMS. All measurements were made on protons.

Conc. of TMS	$E_L = D_T$	E_{is}
2%	8.2	7.2
4%	8.5	7.8
8%	8.6	8.2

* The measurements in the isotropic phase were carried out using longitudinal and transverse field gradients to show their coincidence.

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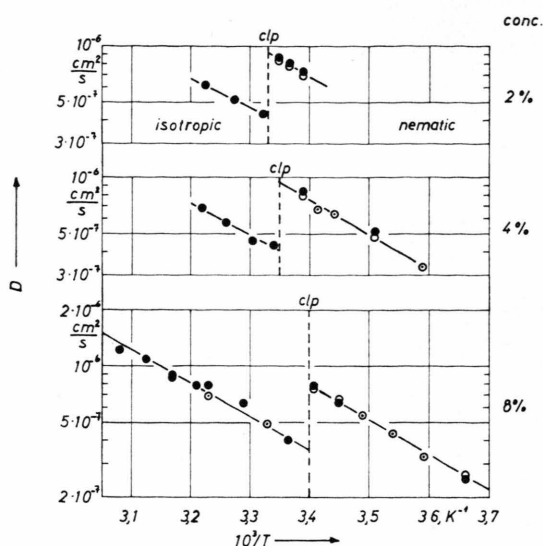


Fig. 7. Diffusion coefficients of different solutions of TMS in MBBA: ● D_L , ○ D_T , ◐ $D_L = D_T$. The diffusion coefficients in the nematic phase are those of TMS, in the isotropic those of the whole solution*.

4. Conclusion

In conclusion we state that the anisotropy of diffusion of TMS dissolved in MBBA is very small compared with that of some small molecules dissolved in Licristal IV. If there is anisotropy, however, we find that the transverse diffusion coefficient equals the isotropic one at the clearing point whereas the longitudinal one is larger.

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