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# ANISOTROPY OF RADIOTRACER DIFFUSION IN SOME NEMATIC LIQUID CRYSTALS

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Abstract The radiotracer impurity diffusion coefficients $D_{11} = D_{22}$ and $D_{33}$ in 4-n-pentyl-4-cyanobiphenyl (5CB), 4-n-octyl-4-cyanobiphenyl (8CB), 4-n-pentyloxy-4-cyanobiphenyl (5OCB), and 4-n-octyloxy-4-cyanobiphenyl (8OCB) have been determined over their nematic phase. An electromagnet was used for the particles orientation and diffusion of impurity which was water solution of natrium pertechnate ($NaTcO_4$), traced with Tc - 99m was investigated.
Using literature data for the temperature dependence of the order parameter S, given for 5CB and 8CB, a relation between the anisotropy of diffusion coefficients and order parameter S is discussed. The linear dependence obtained between the diffusion coefficients and the order parameter S is analogous to the equations obtained by author for the anisotropy of other transport properties, i.e. viscosity and heat conduction coefficients, for the same liquid crystals.

*Keywords: nematic liquid crystals, cyanobiphenyls, radiotracer, anisotropy of diffusion*

## INTRODUCTION

The first observations concerning the anisotropy of diffusion in nematic liquid crystals were made by Svedberg in 1918 (1). However, these were rather qualitative observations. For a long time, the research on the phenomenon had not been conducted till the 70ties (2), when the interest in the subject grew rapidly.
The overview is presented in a monography published by Kruger (3).
The experimental work can be divided into two groups, namely the work in which self-diffusion coefficients were determined and the experiments in which diffusion of the impurities was investigated.
The equation of diffusion for an anisotropic system in which the main directions of diffusion are along the coordinate axes(in arrangement given by the symmetry axis of a

medium) can be written in the following form:

$$c = D_{11}\frac{\partial}{\partial x_1}(c,_1) + D_{22}\frac{\partial}{\partial x_2}(c,_2) + D_{33}\frac{\partial}{\partial x_3}(c,_3) \qquad (1)$$

The symmetry of a nematic liquid crystal (Fig. 1) is analogous to the symmetry of a cylinder.

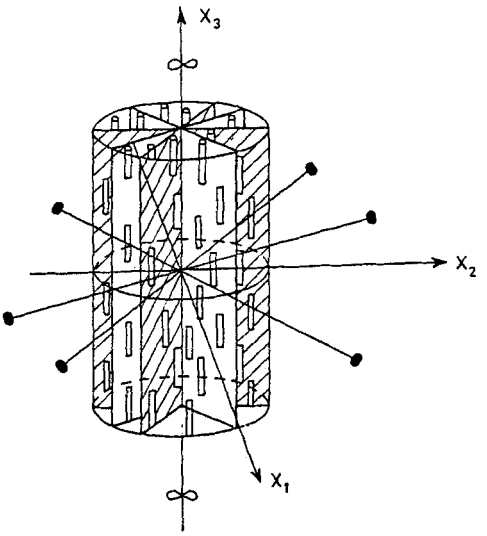



FIG.1: Symmetry of nematic liquid crystal

According to the international rotation, which gives only the symmetry generators, the symmetry in this case is described by the symbol $\infty$ /mm. The basic law which links the symmetry of physical phenomena with the symmetry of the medium is the Neuman's law. On the other hand the P.Curie's principle assumes as a characteristic symmetry of the phenomenon the highest symmetry of the medium in which it can be observed. For diffusion, that is of course an isotropic medium. The form of diffusion tensor is then obtained by superposition of symmetry group $\infty\infty$ m (isotropic medium, sphere) with symmetry group characteristic for nematic liquid crystals $\infty$ /mm (cylinder) in the way that $\infty$ axis should recline along coordinate axis $x_3$. The highest common subgroup is $\infty$ /mm.
The geometric visualisation of such symmetry is rotary ellipsoid which reflects the symmetry of diffusion tensor in nematic liquid crystals:

$$D_{ij} = \begin{bmatrix} D_{11} & 0 & 0 \\ 0 & D_{22} & 0 \\ 0 & 0 & D_{33} \end{bmatrix} \qquad (2)$$

That means that the values of diffusion coefficients along the axis $x_1$ and $x_2$ are equal and different from the coefficients of diffusion along the $x_3$ axis. To determine the values of the diffusion coefficients it is necessary to make two independent experiments. One for the case in which diffusion takes place along the director and the second when diffusion direction is perpendicular to the director.

EXPERIMENTAL

The investigations have been carried out for four substances of the cyanobiphenyl homologues. The temperature range examined corresponds to the nematic phase temperature. The following compounds and temperatures have been examined;
4-n-pentyl-4-cyanobiphenyl (5CB), S(22°C) N(34°C) IL;
4-n-octyl-4-cyanobiphenyl (8 CB), S(21°C) SM(32.5°C) N(40°C)JL;
4-n-pentyloxy-4-cyanobiphenyl (5 OCB), S(47°C) N(66.3°C)JL;
4-n-octyloxy-4-cyanobiphenyl (8 OCB), S(54°C)SM (66.5°C) N(79.8°C)JL. The compounds used were synthesized at the Institute of Organic Chemistry and Technology, Warsaw Technical University. For determining the two diffusion coefficients a Loschmidt diffusiometer was used (4). The complete device is shown in Figure 2.

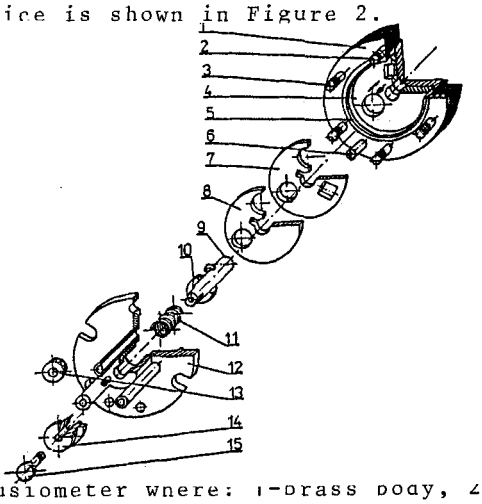



FIG.2: The diffusiometer where: 1-brass body, 2,3(etc.)-screw plugs, 4,7,8 -rotatory discs, 5-sealing, 6-plug, 9-roller, 10-teflon gasket, 11-spring, 12-brass cover, 13-nut, 14-knob, 15-screw

The volume of a single compartment is ca 0.5 $cm^3$. The path of diffusion is equal to 0.5 cm. The whole apparatus is shown in Figure 3.

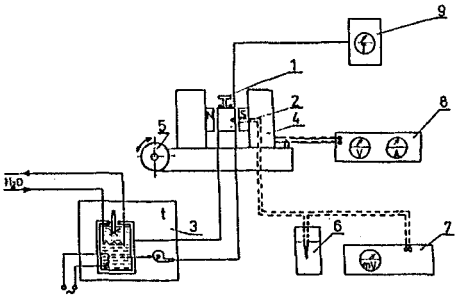



FIG.3: The stand for measuring the diffusion coefficients, 1-diffusiometer, 2-thermostatic vessel, 3-thermostat, 4-electromagnet, 5-electromagnetrotation device, 6-Dewar flask, 7-milivoltometer connected with thermocouple, 8-power supply for electromagnet, 9-teslometer

The diffusiometer was calibrated measuring the diffusion coefficients of methanol in benzene. The estimated accuracy is 10%.
The radiotracer Tc-99m (T1/2=6h, $\gamma$ quantum energy 140 keV) in the form of $NaTcO_4$ in water solution was used. Final concentration of impurity in liquid crystal was equal to 1% by volume. The concentration (activity) changes in the compartments were established by sampling method using scintillation counter with the NaJ(TL) crystal connected with an electronic scaler.
The measurements of the diffusion coefficients were carried out for two positions of the electromagnet with respect to the direction of diffusion (director parallel and perpendicular to this direction). The magnetic field intensity was 0.4T. The measurements for unoriented samples were made as well.

RESULTS

To calculate the diffusion coefficients $D_{11}$ and $D_{33}$ it is necessary to solve the diffusion equation for one-dimensional case:

$$c_i = D_{ij} \frac{\partial}{\partial x_i} (c_i, _j) \qquad (i=1, 3) \qquad (3)$$

with the boundary conditions imposed by the system geometry:

$$c=\begin{cases} c_o & -L < x_i < 0 \\ 0 & 0 < x_i < L \end{cases} \qquad \text{for } \tau \leq 0 \qquad (4)$$

$$c_{i,j}=0 \qquad x_i = 2L$$

The solution of the equation (3) with assumption that $\frac{D\tau}{L^2} > 0.1$ gives the expression for the diffusion coefficient:

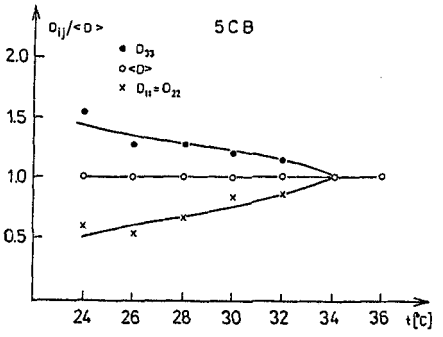
$$D= \frac{4L^2}{\pi^2 \tau} \ln \frac{8}{\pi^2} \frac{c_u + c_b}{c_b - c_u} \qquad (5)$$

where: L - path of diffusion (m)
$\tau$ - time (s)
$c_u$ - concentration in upper compartment (cpm)
$c_b$ - concentration in lower compartment (cpm)

The coefficient $D_{33}$ was obtained for the case when the path of diffusion $(-L, +L)$ lays along the $X_3$ axis.
For the case when sample (director) is oriented in the plane $X_1$ $X_2$, due to the properties of cylindrical symmetry, along $X_1$ or $X_2$ the remaining diffusion coefficients, $D_{11} = D_{22}$ were obtained. For unoriented sample the diffusion coefficient $< D >$ was measured. The results given as $D_{11} / < D >$ and $D_{33} / < D >$ ratios are presented in Figures 4, 5, 6, and 7. They are also presented in the diagram on a semilong scale. The diagram shows the dependence of the above given ratios of diffusion coefficients plotted against the dimensionless temperature parameter, Figures 8 and 9.

## THEORETICAL MODELS

There exists a number of theoretical models describing the diffusion in nematic liquid crystals. One of them, proposed by Franklin (5, 6), is a modification of Kirkwood's theory which describes movement of macromolecules in a solvent (7). The solution of the problem is complicated and Kirkwood and his coworkers have published a number of papers in which they make an attempt to simplify the theory (8).
Franklin using Kirkwood's theory and applying the hydrodynamic theory of nematics given by Leslie (9, 10, 11), and



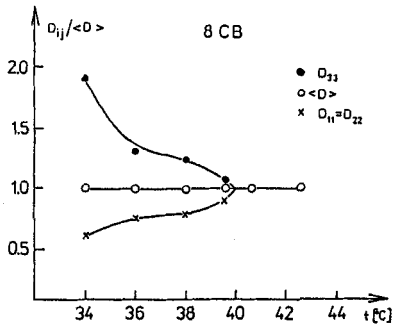
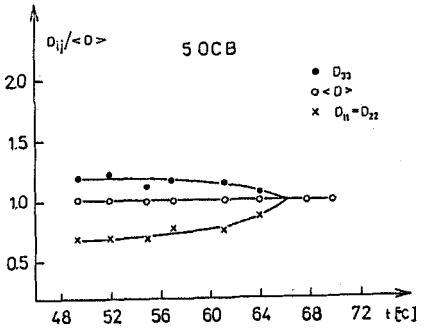




FIG.4: Anisotropy of radiotracer diffusion in 5 CB
FIG.5: Anisotropy of radiotracer diffusion in 8 CB

Ericsen (12, 13) has presented an equation for $D_{11}$ and $D_{33}$ calculations. Unfortunately, lack of parameters describing the molecular structure of investigated substances does not allow to verify the theory.
The other presentation of the problem was given by Chu and Mori (14). They used a momentum autocorrelation function for definition of the mean self-diffusion coefficient.



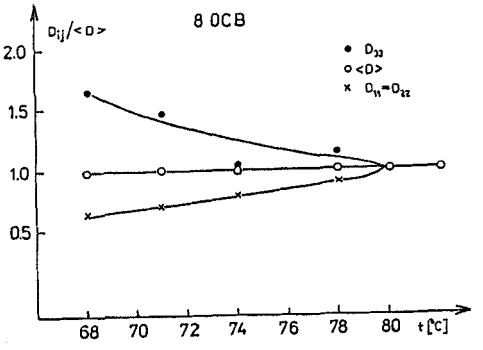
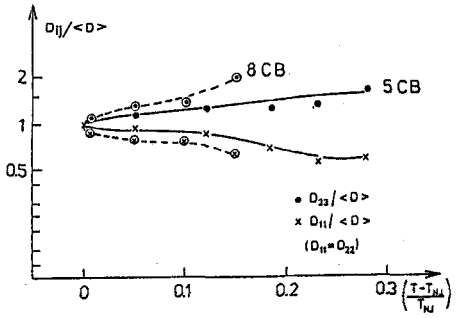




FIG.6: Anisotropy of radiotracer diffusion in 5 OCB
FIG.7: Anisotropy of radiotracer diffusion in 8 OCB



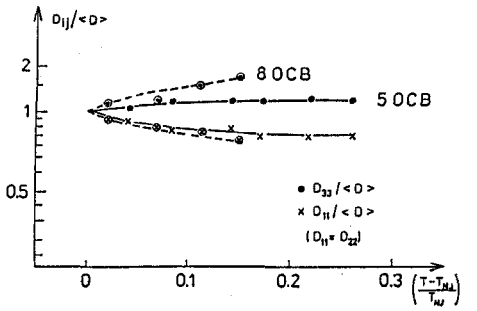




FIG.8: Comparison of anisotropy of radiotracer diffusion in 5 CB and 8 CB
FIG.9: Comparison of anisotropy of radiotracer diffusion in 5 OCB and 8 OCB

In the paper they also proposed another approach to the problem which can be interesting from the point of view of this work. The authors considered diffusion in the perfectly ordered medium, in which the order parameter S is equal to 1. Such conditions exist in a solid or in a single nematic lc domain. In such medium two planes, one parallel and second perpendicular to the main molecule axis, can be imagined. The projections of cylinder intersections on these planes form the areas $A=d\,l$ and $A=\frac{\pi d^2}{4}$ respectively (where d -molecule diameter and l-its length).
Because, according to the theory of interspatial diffusion, the coefficients are proportional to the free area, the ratio of coefficients is given by the equation:

$$\frac{D^s_{11}}{D^s_{33}} = \frac{A_\perp}{A_{||}} = \frac{\pi d}{4l} \qquad (6)$$

This of course is a simplification of the phenomenon.
The structure of the molecule is in most cases more complicated and its fragments can perform motions.
From the literature data (15, 16) it is known that the lenght of the 5CB molecule is about 18 Å, and that of 8CB - 23 Å.
The diameter of the 5CB molecule is equal to 6.5 Å and one can assume that the same value can be adopted for 8CB.

That means that diffusion coefficients anisotropy $D_{11}/D_{33}$ should be higher for 8CB than for 5CB, and this is illustrated by the curves given in Fig. 8. This is also the case when oxygenic compounds are considered.

## APPLICATION OF THE PHENOMENOLOGICAL ANALOGIES FOR CORRELATING THE D AND S COEFFICIENT

In the previous paper (17) the linear dependence between viscosity coefficients and order parameter S was presented. Some phenomenological theories of diffusion in liquids and crystals are based on the free volume concept. This type of theory is represented by the previously mentioned Chu and Mori model. The ordering of mesogen molecules in relation to the direction of diffusion will have an impact on the velocity of movement of the tracer.

The degree of ordering is given by the order parameter S. This has the same meaning if we consider the structure of LC as being composed of many perfectly ordered domains. The Roentgenographic studies prove the existence of such domains (15, 16), in the case of 5CB they consist of approximately 100 molecules, each (16). Domains are arranged different angles in relation to the director.

Let us consider two coordinate system, one $x_1, x_2, x_3$ in which the $x_3$ axis lies along director $n_i$ (in our experiments along magnetic field direction); the other coordinate system $x'_1, x'_2, x'_3$ is selected in such a way that $x_1 = x'_1$ and $x'_3$ is given along the molecule long axis in domain tilted by an angle $\alpha$. The sample and domain are characterized by diagonal matrixs $D_{ij}$ and $D^s_{ij}$ respectively. We can find the relationships between the diffusion coefficients for both systems:

$$D_{33} = c_{31}c_{32}D^s_{11} + c_{32}c_{32}D^s_{22} + c_{33}c_{33}D^s_{33} = D^s_{11}\sin^2\alpha + D^s_{33}\cos^2\alpha \quad (7)$$

where $c_{ij}$ are direction cosines.

The mean diffusion coefficient is equal to one third of the diffusion tensor trace:

$$\langle D \rangle = \frac{1}{3}(2D_{11} + D_{33}) \quad (8)$$

$$\langle D \rangle = \frac{1}{3}(2D^s_{11} + D^s_{33}) \quad (9)$$

Because:

$$S = \frac{1}{2} \langle (3\cos^2\theta - 1) \rangle = \int f(\theta)\frac{1}{2}(3\cos^2\theta - 1)\sin\theta \, d\theta \quad (10)$$

where $f(\theta)$ is the orientational distribution.
Thus:

$$D_{33} = \langle D \rangle (1-S) + SD^{s}_{33} \quad (11)$$

$$D_{11} = \langle D \rangle (1-S) + SD^{s}_{11} \quad (12)$$

and after substraction we obtain

$$S = \frac{D_{33} - D_{11}}{D^{s}_{33} - D^{s}_{11}} \quad (13)$$

The value given in denominator is constant and we can write:

$$D_{33} - D_{11} = AS \quad (14)$$

Analytical forms of the straight lines representing the relationships for 5 CB and 8 CB, i.e. compounds for which the S coefficients values have been found in literature (18) are given in Table I. The calculations were made without taking into account the values obtained for temperature close to smectic-nematic and solid-nematic transition point where anomalies are observed.

## CONCLUSIONS

The observed anisotropy of diffusion for some nematic liquid crystals is greater for the nematogens with longer molecule chains.
The anisotropy of diffusion coefficients ($\Delta D$) can be correlated with the alignment parameter S, analogously to the anisotropy of other physical properties.

TABLE 1

STRAIGHT - LINE EQUATIONS FOR THE FUNCTION $\Delta D = f(S)$

| Compound | Straight-line equation $D[m^2/s\ 10^{10}]$ | Intersection point $\Delta D\ 10^{10}$ $S = 0$ | Correlation Coeff. |
|---|---|---|---|
| 5 CB | $\Delta D = 0{,}627S$ | -0.004 | 0.996 |
| 8 CB | $\Delta D = 0{,}619S$ | -0.012 | 0,954 |

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