Molecular Crystals and Liquid Crystals

Anisotropic Mass Diffusion in Liquid Crystals

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Anisotropic Mass Diffusion in Liquid Crystals†

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Abstract—Self and binary mass diffusion in smectic, nematic and cholesteric liquid crystals was studied experimentally. The diffusing molecules were tagged with C-14 radioactive isotopes and the time course of their distribution in a modified Loschmidt cell was determined by liquid scintillation counting. Diffusion coefficients were obtained as functions of temperature and the strength of an applied magnetic field, which increased (when parallel to mass flux) or decreased (when perpendicular) the diffusion rate in nematic *p*-azoxyanisole. Application of a static electric field resulted in chaotic convection. The experimental results indicate that a mass of about 5×10^{-11} g (a swarm) is the unit of cooperative orientation in nematic *p*-azoxyanisole and that the microscopic fluctuations in the concentration gradient are independent of the fluctuations in the orientation of swarms.

Introduction

An externally applied electromagnetic field can induce anistropy in many of the physical properties of liquids. Anisotropy may exist (and in the case of liquid crystals usually does exist) even in the absence of applied fields. It is generally agreed that induced anisotropies are due to the field-induced orientation of the particles comprising the system. In isotropic liquids, in which a molecule is the unit of orientation, the effect of thermal agitation is so great that field-induced anisotropy is not detectable. But in liquid crystals, in particular in nematic liquid crystals, in which a large number of molecules is the unit of orientation, the thermal agitation is far less effective so that even a field of moderate strength may cause considerable orientation and thus induce detectible anisotropies in their properties. The mass diffusion coefficient is one of many such properties.

Because of thermal agitation, the molecules of a liquid are always translating and rotating in a random fashion, such motion appearing as a self-diffusion process.   In liquid crystals, the rotational motions of individual molecules are partly suppressed by the orientation-dependent potential energy barriers among them, but the molecules are still more or less free to translate in space.   Thus it has been postulated that measurements of the rate of the self-diffusion process in an oriented liquid crystal might give useful information on its structure.

The only previous study of the mass diffusion in liquid crystals appears to be that of Svedberg[6] who measured the diffusion coefficients of m-nitrophenol in an equimolar mixture of nematic p-azoxyanisole and p-azoxyphenetole.   He found that the diffusion coefficients increased when a strong magnetic field was applied in the direction of the mass flux and decreased when it was applied in a perpendicular direction to the flux.   His observations were mostly qualitative.

In the present work, the self and binary mass diffusion coefficients of several liquid crystals were measured as a function of temperature and of the strength of an applied magnetic field.   The size of the diffusion cell used was relatively large (about 1 cm³) such that interfacial effects were believed to be very small.   The experimental results confirm Svedberg's observations and, furthermore, they are in a good agreement with our postulates concerning transport processes in such anisotropic liquids (under preparation for publication).

Experiments

Self-diffusion coefficients of nematic p-azoxyanisole (PAA), smectic and cholesteric cholesteryl myristate (ChMy), and isotropic liquids of both PAA and ChMy and binary diffusion coefficients of a trace of p-nitrophenol (PNP) in nematic PAA were measured as a function of temperature and applied magnetic field strength.

For calibration, diffusion coefficients of cholesterol in toluene and PAA in benzene were measured.

The sheared boundary method, with a modified Loschmidt cell, was employed.

MATERIALS

The molecules of the diffusing solutes were tagged with carbon-14 radioactive isotopes. Cholesterol-4-C^{14} was purchased from Volk Radiochem. Co. (Burbank, Calif.) and PNP-2, 6-C^{14} from Tracer Lab (Waltham, Mass.). The tagged PAA was synthesized by starting from a mixture of ordinary PNP and PNP-2, 6-C^{14}. Likewise, the tagged ChMy was synthesized from cholesterol-4-C^{14}. The details of the syntheses are described elsewhere.[9] Untagged PAA was purchased from City Chemical Corp. (New York). Both PAA and ChMy were recrystallized from boiling ethanol at least three times before use. Phase transition temperatures were determined with a heating stage placed on a polarizing microscope. The samples used had the following transition temperatures, where C, S, N, and I are crystalline, smectic, nematic, and isotropic liquid phases, respectively.

$$\text{PAA} \qquad C \xleftrightarrow{\;119\,°C\;} N \xleftrightarrow{\;135.5\,°C\;} I$$

$$\text{ChMy} \qquad C \xleftrightarrow{\;71\,°C\;} S \xleftrightarrow{\;77\,°C\;} Ch \xleftrightarrow{\;83\,°C\;} I$$
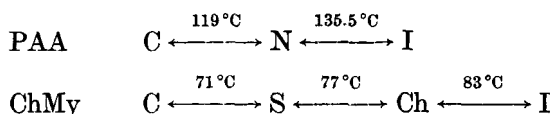
APPARATUS

The diffusion cell was composed of two identical half-cells, each of which measured $\frac{3}{8}'' \times \frac{3}{8}''$ (square cross-section) $\times \frac{3}{16}''$ (depth). Each half-cell was a square hole in a circular ceramic disk. Two additional disks were needed to provide the walls of the cell, making the total number of disks four (called A, B, C and D from the top to the bottom) as shown in Fig. 1. Samples were fed into the half-cells with the help of gravity and the diffusion flux was always in the vertical direction. The disks were placed in a brass housing unit as shown in Fig. 2 and operated from outside through a ceramic rod, which fitted into the triangular holes at the centers of the disks. To ensure perfect contacts between any two disks, the surfaces of the disks were polished until the thickness variation was less than 0.2 mil and the disks in the housing were pressed down by a strong spring. The liquids used in the diffusion experiment were themselves the lubricant on the contact surfaces of the disks.

The housing unit was placed in a thermal bath made of brass; this could be reached from the outside of the bath with a ceramic knob as shown in Fig. 2 so that one could either rotate, lift up or push down

the operating rod without opening the lid of the bath. When the knob was not in use, its hole was plugged with a cork and the housing unit was practically under thermal isolation from the outside. The cross-section of the front end of the thermal bath, where the housing unit sat, was smaller than a $4'' \times 4''$ square. A pumping unit agitated the bath fluid and circulated a part of it to the front end. Molten wax was used as the bath fluid for operations above 70 °C and water was used for operations below 70 °C. A heater combined with a controlling circuit kept the amplitude of the temperature fluctuation below 0.02 °C and at about 1 cycle per 1.5 minute. For room-
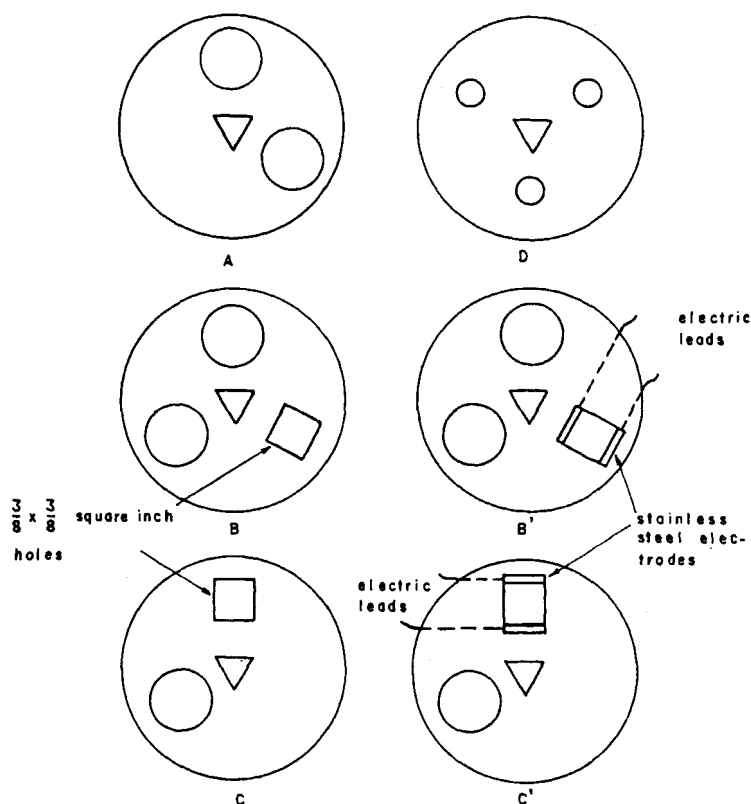
Figure 1.   Disks used in the diffusion apparatus. All of the above disks are made of ceramic material and $\frac{3}{16}$ inch thick. $A_{\frac{1}{4}}$ and $A'_{\frac{1}{4}}$ are identical to A; and $D_{\frac{1}{4}}$ and $D'_{\frac{1}{4}}$ are identical to D except for the thicknesses and materials. $A_{\frac{1}{4}}$ and $D_{\frac{1}{4}}$ are ceramic and $\frac{1}{8}$ inch thick; and $A'_{\frac{1}{4}}$ and $D'_{\frac{1}{4}}$ are brass and $\frac{1}{16}$ inch thick.

Figure 2. Diffusion cell—housing unit. All materials are brass unless labeled otherwise. *A–D* are four ceramic disks with triangular holes at the center. *E* is a knob for the operation of the rod; the part between the dotted lines is cylindrical and ot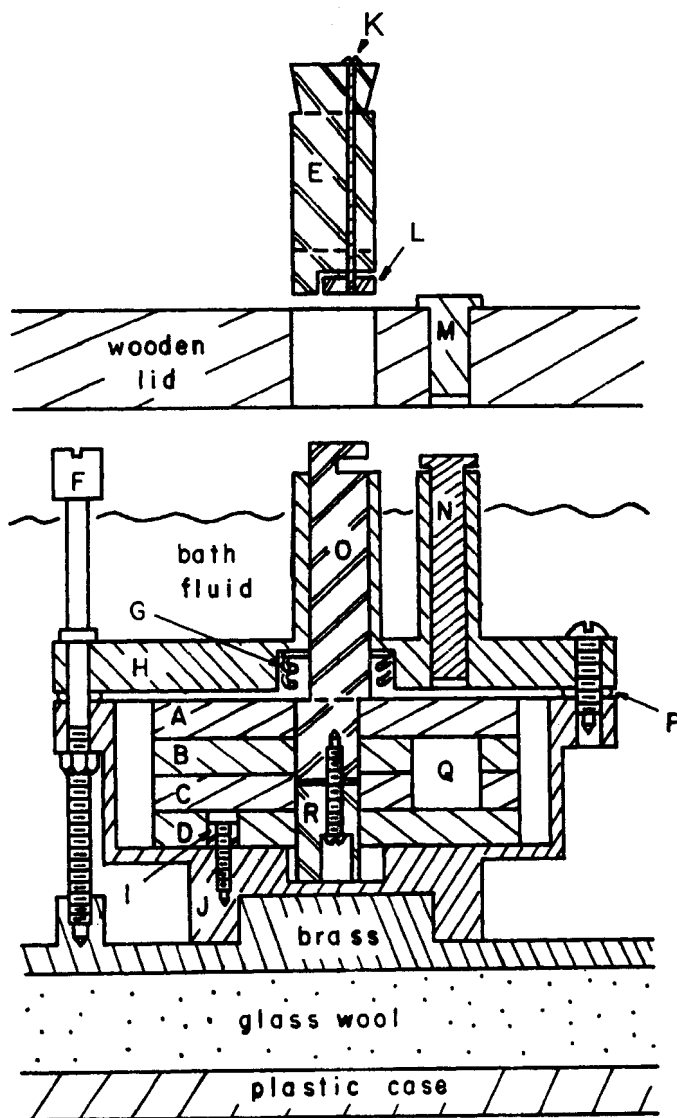her parts are flat; ceramic. *F* is a pin screwed to the bottom of the bath to prevent up-and-down motions and rotations of the housing unit. *G* is a spring and its holder which presses the disks down. *H* is the housing lid. *I* are three equally spaced small ceramic rods screwed on the housing to fix the disk *D*. *J* is the housing. *K* is a screw for the operation of the flap, to which its end is fixed. *L* is the flap that engages the knob to the rod; ceramic. *M* are three cork plugs equally spaced. *N* are three brass plugs equally spaced; used when no electric field is applied. *O* is the ceramic rod with which one may rotate the disks; cylindrical above and triangular below the dotted line. *P* is a teflon gasket; *Q* is the sample in the diffusion cell. *R* is the lower part of the rod; may rotate independently of the upper part; ceramic.

temperature runs, a cooling water coil (tap water) was combined with the heater.

For the application of magnetic fields, the front end of the thermal bath was placed between the pole faces of a water-cooled electro-magnet, Alpha Scientific Model 7600, combined with a current-regulated power supply, Alpha Scientific Model 45–30. The gap-width used was 3.5–4.0 inches, in which range this magnet gives fields from − 80 to 3,500 gauss with the line drift less than 100 ppm in 8 hours. The field strength was determined and the magnet calibrated with a Dyna-Empire Model D855 gaussmeter and a 1,000 Gauss standard magnet. The gradient of the field strength in the space between the pole faces was less than 1% /cm. The magnet could be rotated to change the direction of the field with respect to the direction of mass flux.

For the application of electric fields, 6 additional disks, $A_{\frac{1}{4}}$, $A'_{\frac{1}{4}}$, B', C', $D_{\frac{1}{4}}$, $D'_{\frac{1}{4}}$ were used. These are shown in Fig. 1. To have the field in the direction of the mass flux, a combination $A_{\frac{1}{4}} - A'_{\frac{1}{4}} - B - C - D'_{\frac{1}{4}} - D_{\frac{1}{4}}$ was used and the brass disks $A'_{\frac{1}{4}}$ and $D'_{\frac{1}{4}}$ worked as the electrodes. To have the field in a direction perpendicular to the mass flux, a combination $A - B' - C' - D$ was used. A series of dry cells that could provide up to about 400 volts was the source of the static field.

The housing unit and the operating rod were designed such that the disks C and D were always locked to the housing and either the disk A or both the disks A and B could be rotated from outside.

PROCEDURE

The operation of the disks is shown in Fig. 3. During the feed period, samples were fed into the half-cells; solvent in the top cell (in disk B) and solution in the bottom cell (in disk C). When the sample was crystalline at room temperature, the housing unit was heated on a heater until the crystals melted. The cells were filled to about 50% excess. After the sample feed, the samples were crystallized again, the whole unit was assembled and placed in the thermal bath, thermal equilibrium was attained (4–8 hours), and then disk A was rotated clockwise to start the draining period, during which time the excess amount of the top sample in disk A was drained into the circular hole in disk C. This period was followed
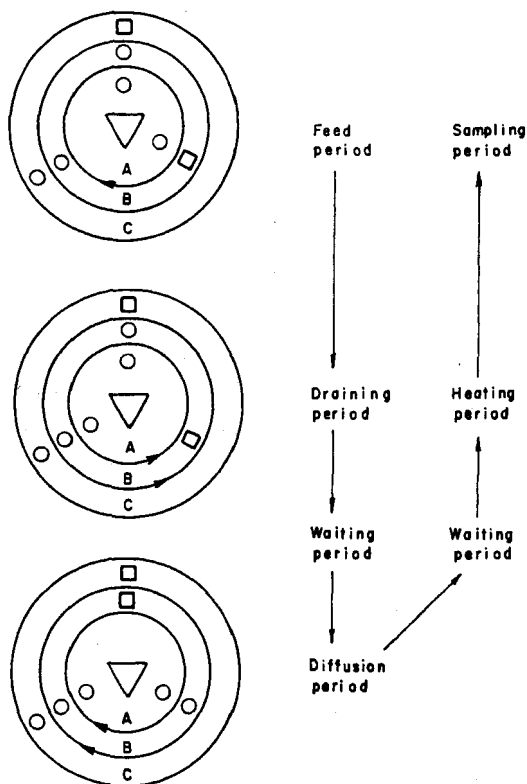
Figure 3. Operation of the diffusion apparatus. The relative orientation of the disks is shown by drawing them as concentric circles. The arrows show the direction of the rotation (120°) of the specified disks to obtain the next configuration. The arrows should be reversed for the last two steps. The waiting periods are obtained by rotating only a half-way (60°).

by a rotation of disks *A* and *B* by a half-way (60°) anticlockwise turn, starting the waiting period, during which time both half-cells were completely surrounded by the solid walls. The electric or the magnetic field was applied at this point, if they were to be employed. The waiting period was usually overnight. By completing the remaining half of the rotation, the excess amount of the bottom sample in disk *B* was drained into the circular hole in disk *C* and diffusion was started. A digital timer was used for the measurement of the diffusion time. When the set diffusion time was over, the whole operation was reversed as shown in Fig. 3 and the samples were collected.

The distribution of the tagged molecules was determined with the help of a three channel liquid scintillation counter, Ansitron-II of Picker Nuclear. The level of total radioactivity for each run was 10^4–10^5 dpm. The scintillation liquid was composed of toluene (reagent grade from J. T. Baker Chem. Co., Phillipsburg, N.J.), 2, 5-diphenyloxazole (PPO; scintillation grade from Aldrich Chem. Co., Inc., Milwaukee, Wis.), and 1, 4-bis (2-(4-methyl-5-phenyl-oxazolyl) benzene (DMPOPOP; scintillation grade from Amersham/Searle, Des Plaines, Ill.). In the case of calibration runs, the concentration of the diffusing solutes was so small that the counting efficiency (counting rate/disintegration rate) was higher than 95% when 16 cc scintillation liquid (approximately 1g DMPOPOP and 4g PPO in 1 liter toluene) was used for each sample. The background counting rate was 33 cpm. In case of the runs with either PAA or ChMy as the solvent for the diffusion, the quenching effect was so great that the collected samples had to be further split and the composition of the scintillation liquid optimized. By placing 0.0500 g of the sample in each scintillation vial (glass, 22 cc) and adding 16 cc scintillation liquid (PPO 6.25 g and DMPOPOP 1.4 g in 1 liter toluene), a counting efficiency of about 40% was obtained. The background counting rate was 30 cpm and the counting efficiency was found to be independent of the radioactivity level of the sample in the range of 10^2–10^6 cpm. At least 3 samples (0.05 g each) were counted for each collected solution to determine the average concentration of radioactivity in a half-cell and each vial was counted at least for 100 minutes.

Diffusion coefficients were determined as follows: This one-dimensional diffusion process may be described by the conservation law of mass;

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2},$$

$$c = \begin{cases} c_0, & -L < z < 0, \\ 0, & 0 < z < L, \end{cases} \quad \text{for} \quad t \leqslant 0, \qquad (1)$$

and

$$\frac{\partial c}{\partial z} = 0, \quad z = \pm L,$$

where c is the concentration of the diffusing molecules, c_0 is the initial concentration of the bottom sample, L is the depth of a half-cell

($L = 0.4623$ cm in this case), and D is the diffusion coefficient. The solution of the above equation is well-known;

$$\frac{c_B - c_T}{c_B + c_T} = \sum_{k=1}^{\infty} \frac{2}{(k - \frac{1}{2})^2 \pi^2} \exp\left(-(k - \frac{1}{2})^2 \pi^2 \frac{Dt}{L^2}\right),\qquad(2)$$

where c_B and c_T are the average concentrations in the bottom and in the top half-cells at time t respectively. When $Dt/L^2 > 0.1$, the above solution may be written as

$$D \doteq \frac{4L^2}{\pi^2 t} \ln\left(\frac{8}{\pi^2} \frac{c_B + c_T}{c_B - c_T}\right).\qquad(3)$$

Since the concentration of the tagged molecules is proportional to the net counting rate of the sample and the counting efficiency is independent of the level of radioactivity, one may write

$$\frac{c_B - c_T}{c_B + c_T} = \frac{R_B - R_T}{R_B + R_T - 2R_0},\qquad(4)$$

where R_B and R_T are the counting rate of equal amounts of the bottom and the top samples respectively and where R_0 is the background counting rate.

CALIBRATION

The results of the calibration runs are shown in Fig. 4. The experimental points agree with Eq. (3). From the slopes of the empirical straight lines in the figure, it was determined that $D = 1.20 \times 10^{-5}$ cm²/sec for the diffusion of cholesterol (1.6×10^{-7} g/cm³) in toluene at 20 °C and $D = 1.34 \times 10^{-5}$ cm²/sec for the diffusion of PAA (0.005 g/cm³) in benzene at 22 °C. The reproducibility was about $\pm 4\%$. The latter value of D agrees with Tsvetkov's[7] $D = (1.31 \pm 0.07) \times 10^{-5}$ cm²/sec obtained under identical thermal conditions but different concentration of PAA molecules (0.06%).

RESULTS

The experimental data are plotted in Figs. 5–8. The dots denote the average values and the arrows denote the range of reproducibility.

The self-diffusion coefficient (D_0) of liquid PAA (Fig. 5) shows a more or less linear dependence on the temperature. It changes

continuously across the nematic-isotropic transition.   The principal diffusion coefficients of the nematic liquid, as measured by applying a magnetic field of 3,500 Gauss in a direction either parallel (D_s^a) or perpendicular (D_s^t) to the mass flux are also shown.   The field had no effect on self-diffusion in the isotropic liquids.

Values of the self-diffusion coefficients of nematic PAA at $125\,°C$ $(D^{\shortparallel}$ when the magnetic field is parallel to the mass flux and $D^{\perp}$ when the field is perpendicular to the flux) are shown in Fig. 6 as a function of the field strength. $(D^{\shortparallel} - D_0)/D_0$ was about 16% and $(D_0 - D^{\perp})/D_0$
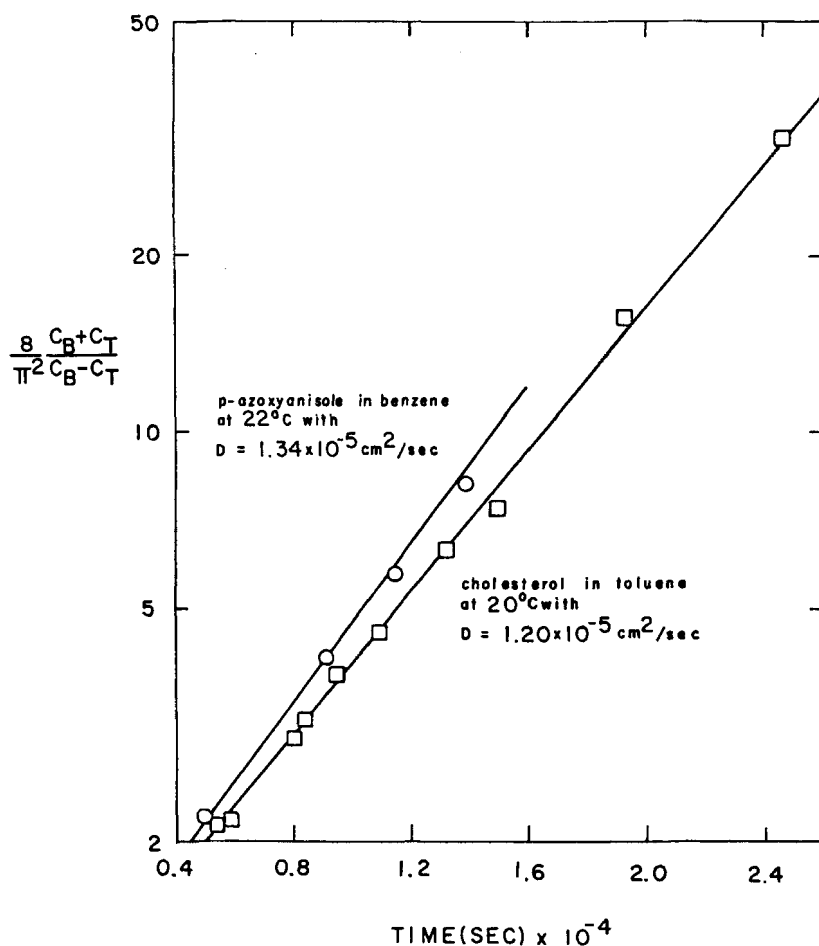

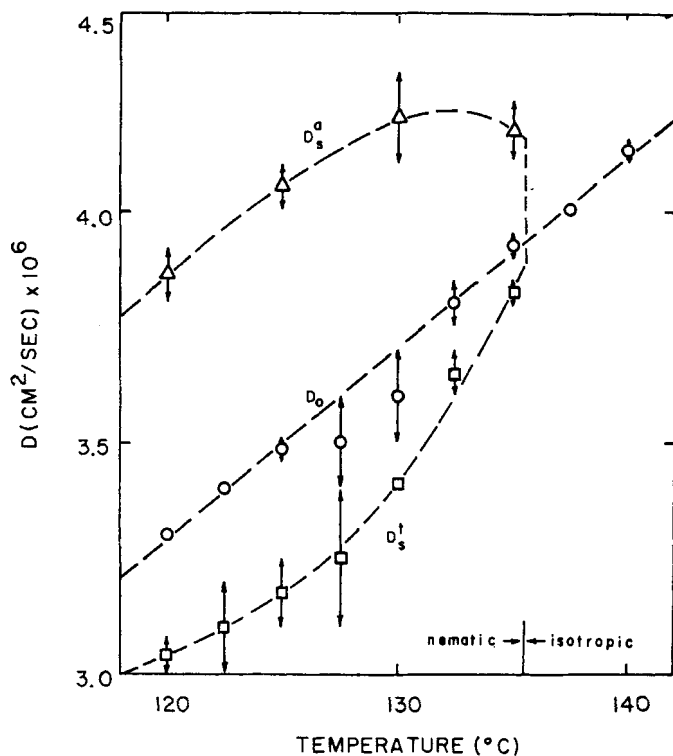Figure 4.   Calibration runs for diffusion cell.

Figure 5. Self-diffusion coefficients of p-azoxyanisole. D_0 is the value of a disoriented liquid; D_s^a and D_s^t were determined by applying a magnetic field of 3,500 Gauss in the directions parallel and perpendicular to the mass flux, respectively.

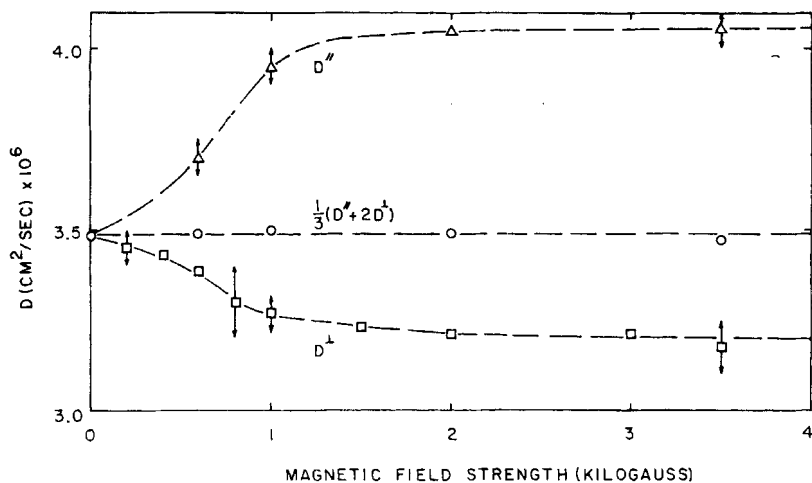Figure 6. Self-diffusion coefficients of p-azoxyanisole at 125 °C in a magnetic field. The values of $D^{\parallel}$ and $D^{\perp}$ were determined by applying the field in the directions parallel and perpendicular to the mass flux respectively.
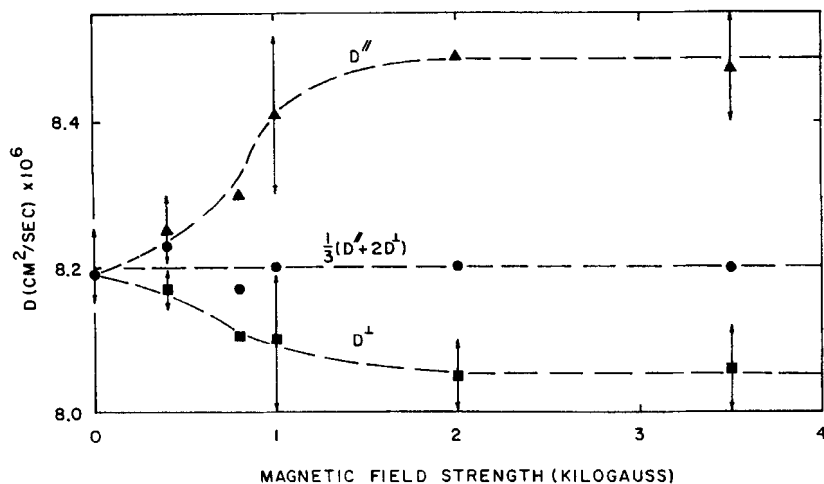
MAGNETIC FIELD STRENGTH (KILOGAUSS)

Figure 7. Binary diffusion coefficients of a trace of p-nitrophenol in nematic p-azoxyanisole at $125\,°\mathrm{C}$ in a magnetic field. The values of $D^{\|}$ and $D^{\perp}$ were determined in the same way as for Fig. 6.
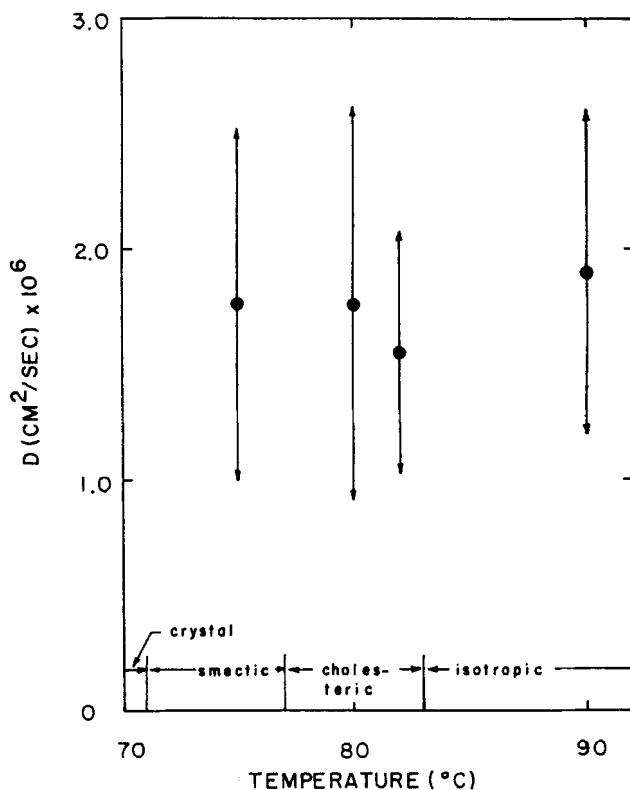

Figure 8. Self-diffusion coefficients of cholesteryl myristate.

was about 8% at saturation. It was noted that the values of $\frac{1}{3}(D^{\shortparallel} + 2D^{\perp})$ remained unchanged for all field strengths.

The binary diffusion coefficients of PNP (concentration $\sim 5 \times 10^{-7}$ g/cm³) in nematic PAA at 125 °C showed a similar dependence on the strength of the applied magnetic field (Fig. 7). In this case, $(D^{\shortparallel} - D_0)/D_0 \doteq 3.5\%$ and $(D_0 - D^{\perp})/D_0 \doteq 1.8\%$ at saturation.

Application of a static electric field as small as about 150 volts/cm to nematic PAA seemed to give a chaotic convection. The mixing was so complete that it was not possible to determine the diffusion coefficients.

The measurements of the self-diffusion coefficients of smectic, cholesteric, and isotropic liquids of ChMy gave no reproducible data and the approximate range of the scattering of data is shown in Fig. 8. Since all ChMy samples were synthesized from cholesterol and myristoyl chloride, the presence of the reactants in the final product was suspected, but further purification of the sample gave no better results.

The primary cause of the errors in the measurements seemed to be mechanical shocks to the apparatus, particularly the vibration due to the agitator of the bath fluid. The effect of the initial shearing on the experimental results appeared to be smaller than expected because the time path of diffusion would not follow Eq. (2) otherwise. The diffusion times varied from 3 to 10 hours, depending on the magnitude of D. The error was smaller for the runs with shorter diffusion time. The reproducibilities of the measurements were: $\pm 5\%$ for the self-diffusion coefficients of PAA and $\pm 1.5\%$ for the binary diffusion coefficients of PNP in nematic PAA.

Discussion of Results

When a nematic liquid is subjected to a magnetic field $\mathbf{H}$, the system is transversely isotropic about the direction of the field designated by a unit vector $\hat{\mathbf{H}}$ such that the diffusion coefficient dyadic may be written as

$$\mathbf{D} = D^{\perp}\boldsymbol{\delta} + (D^{\shortparallel} - D^{\perp})\hat{\mathbf{H}}\hat{\mathbf{H}}, \tag{5}$$

where $\boldsymbol{\delta}$ is the unit tensor. Our postulates on the transport process

in nematic liquids,[9] which will eventually be presented elsewhere, give the relations

$$D^{\parallel} = D_0 + (D_s^a - D_s^t)\left(\frac{\partial}{\partial\alpha}\ln G - \tfrac{1}{3}\right) \tag{6}$$

and

$$D^{\perp} = D_0 - \tfrac{1}{2}(D_s^a - D_s^t)\left(\frac{\partial}{\partial\alpha}\ln G - \tfrac{1}{3}\right) \tag{7}$$

for the dependence of $D^{\parallel}$ and $D^{\perp}$ on field strength. In these equations, D_s^a and D_s^t are the principal diffusion coefficients of a perfectly oriented nematic liquid in the direction of $\mathbf{H}$ and in the transverse direction, respectively, and D_0 is the diffusion coefficient of a dis-oriented liquid. The dimensionless field strength α and the normalizing constant G are defined by

$$\alpha = \frac{\Delta\chi_s H^2}{2kT} \tag{8}$$

and

$$G = \int_{-1}^{+1} e^{\alpha x^2}\, dx, \tag{9}$$

where $\Delta\chi_s$ is the anisotropy in the principal magnetic polarizabilities of the unit particle of orientation.

Eqs. (6–9) may be converted to the relation

$$\alpha = \alpha(D^{\parallel} \text{ or } D^{\perp}, D_0, D_s^a - D_s^t). \tag{10}$$

Because of Eq. (8), a plot of the values of α obtained from the above relation against the corresponding field strength H on a log–log scale is expected to give a straight line of slope 2. Since we have the experimental values of $D^{\parallel}$, $D^{\perp}$, D_0, and $D_s^a - D_s^t$ (values at $H = 3{,}500$ Gauss) for self and binary (of PNP) diffusion in PAA at 125 °C, we may calculate the corresponding value of α for each field strength used. Figure 9 shows such a plot. The experimental points clearly form a straight line of slope 2 as we have predicted and from its position the value of α/H^2 is obtained as

$$\alpha/H^2 = \Delta\chi_s/2kT = 6.5 \times 10^{-6} \text{ Gauss}^{-2}, \tag{11}$$

which agrees fairly well with the value 6.27×10^{-6} Gauss^{-2} we obtained[8] from the measurements of the temperature rise in nematic p-azoxyanisole at 123.5 °C. Since the anisotropy in the principal

polarizabilities of a unit particle (or swarm) $\Delta\chi_s$ is related to the corresponding anisotropy of a molecule $\Delta\chi$ (per unit mass) by

$$\Delta\chi_s = S_m M_s \Delta\chi, \qquad (12)$$

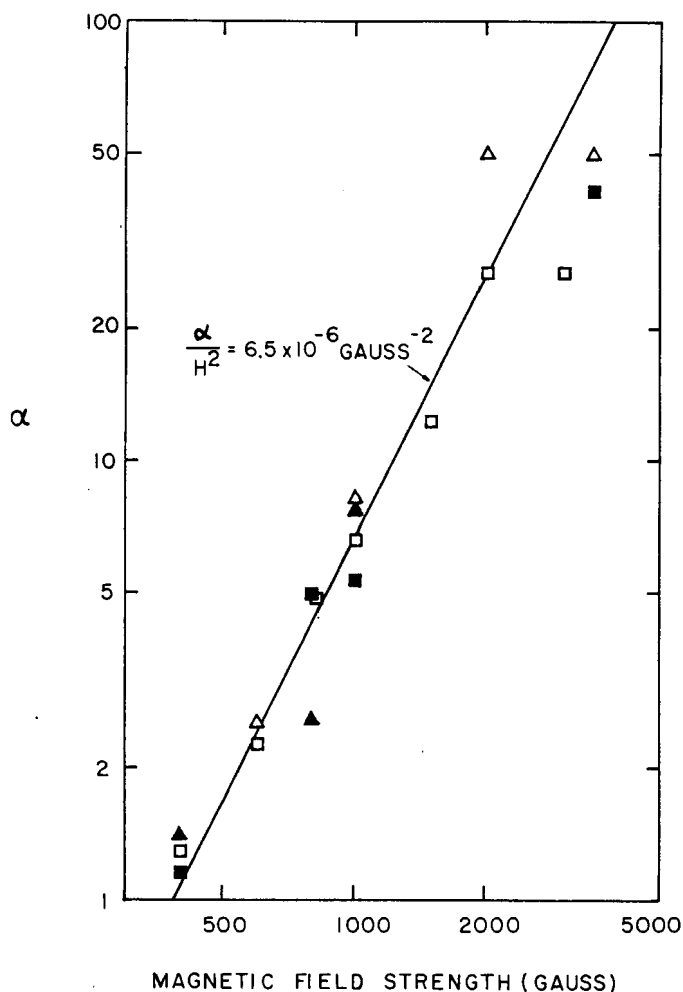where S_m is the degree of orientation,[4] one may calculate the mass

Figure 9. Experimental values of the dimensionless field strength against the actual strength of the magnetic field used. Determined from the diffusion coefficient measurements in nematic p-azoxyanisole at 125 °C. The experimental points are shown as triangles ($\triangle$ for self and $\blacktriangle$ for binary diffusion) for $D^{\parallel}$ and squares ($\square$ for self and $\blacksquare$ for binary diffusions) for $D^{\perp}$.

M_s of such a particle with the values $S_m = 0.556$ (Maier and Saupe[4] and Yun[9]) and $\varDelta\chi = 2.42 \times 10^{-7}$ cgs/g (Föex[2]);

$$M_s = 5.3 \times 10^{-12} \text{ g.} \tag{13}$$

In our postulates mentioned above, it was also proposed that, if the fluctuations in particle orientations are independent of the fluctuations in the driving force (concentration gradient), then one may write

$$D_0 = \tfrac{1}{3}(D_s^a + 2D_s^t) \tag{14}$$

and

$$D^\shortparallel - D_0 = 2(D_0 - D^\perp). \tag{15}$$

A plot of the experimental values of D_0 against those of $\tfrac{1}{3}(D_s^a + 2D_s^t)$ for self-diffusion in nematic PAA is presented in Fig. 10 and a plot of $D^\shortparallel - D_0$ against $2(D_0 - D^\perp)$ for self and binary diffusions in nematic PAA is presented in Fig. 11. Both figures show that the experimental results are in good agreement with the above prediction and thus support our postulates.
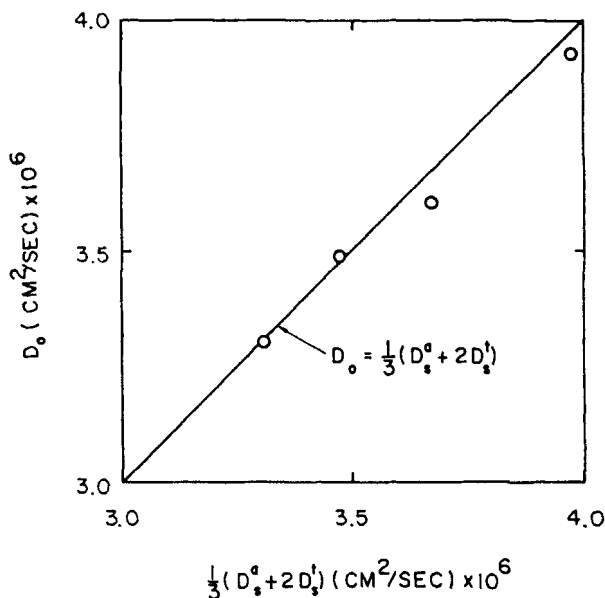

Figure 10.   Experimental verification of Eq. (14).   Experimental points were taken from Fig. 5 for nematic p-azoxyanisole.
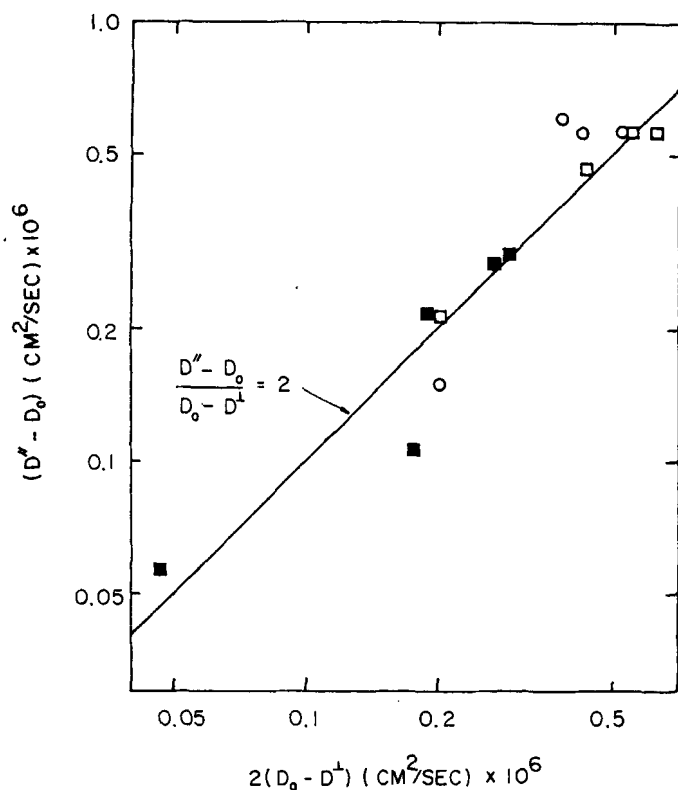
Figure 11. Experimentl verification of Eq. (15). Experimental points were taken from Figs. 5(○), 6(□) and 7(■) for nematic p-azoxyanisole.

Conclusions

This experiment confirms that the mass diffusion rate in a nematic liquid is larger in the direction of the applied magnetic field than in a transverse direction. Since the molecules of all known nematic liquids appear to be oriented with their longer axes in the direction of the applied magnetic field, it is expected that this experimental result with p-azoxyanisole sufficiently represents the behavior of nematic liquids in this respect.

According to the Einstein relation $\mathbf{D} = \alpha kT$, where α is the translational mobility dyadic of a molecule, the diffusion coefficient is inversely proportional to the viscosity of the surroundings. In this

light, our observation of the continuous change of self-diffusion coefficient of the disoriented liquid across the nematic-isotropic transition appears to indicate that the viscosity also changes continuously across the transition in contradiction with the observed discontinuity[5] in the viscosity values determined with macroscopic flows.   The discrepancy is believed to be due to the fact that the nematic liquid behaves as a structured fluid when it flows such that the mechanism of momentum transport is quite different from that of the viscous resistance of the surroundings to the motion of a molecule.   This view is supported by the value of the rotational diffusion coefficient of the unit particle of nematic PAA, $D_R = 0.075$ sec^{-1}, obtained by Fisher and Fredrickson,[1] which is 10^9–10^{10} times smaller than the value for an isotropic liquid.   Since the value of D_R is inversely proportional to the volume of the rotating particle, this value indicates that the unit particle of shear-induced orientation is 10^9–10^{10} times larger than a molecule.   This happens to correspond to the mass of the unit particle of magnetic field-induced orientation given by Eq. (13).   These observations on transport phenomena suggest, even if they do not prove, that the orientable unit in nematic liquid crystals is much larger than a molecule.   Furthermore, thermodynamic considerations[9,10] suggest that a system composed of molecular aggregates or swarms in which the molecules tend to be aligned in the same direction, but which direction can vary from aggregate to aggregate, is usually more stable than a system in which all of the molecules tend to align in the same direction.   These considerations taken together are, in our view, good reason for retaining the swarm model of the nematic mesophase.

The chaotic convection in an electric field observed during this work is not a new fact, but the field was quite homogeneous when the disks $A'_{\frac{1}{4}}$ and $D'_{\frac{1}{4}}$ were used as the electrodes in this work while the fields employed in many optical observations[3] are usually inhomogeneous.   This observation is also in agreement with Fisher and Fredrickson's[1] finding that the thermal conductivity increases rapidly as the strength of the applied electric field (60 Hz) is increased above 200–400 volts/cm.

An important result of this work is the experimental verification of Eqs. (14) and (15).   This establishes the notion that the fluctuations in swarm orientations are independent of the fluctuations in the

driving force of the diffusion process in a nematic liquid. We see no reason why this would not be applicable to other similar physical processes, the driving forces of which do not affect swarm orientations. Thermal conductivities, dielectric constants, and relative magnetic permeabilities of nematic liquids are likely to satisfy Eqs. (14) and (15) as long as the driving forces are very small.

It is unfortunate that we could not obtain any reproducible data on the self-diffusion in liquid ChMy. Such data would give an important clue to the structures of smectic and cholesteric liquids; that is, how free a molecule in either a smectic or a cholesteric layer is.

REFERENCES

1. Fisher, J. and Fredrickson, A. G., " Transport processes in anisotropic fluids. II. Coupling of momentum and energy transport in a nematic mesophase ", *Mole. Cryst. and Liq. Cryst.* 6, 255–271 (1969).
2. Föex, G., " Magnetic properties of mesomorphic substances. Analogies with ferromagnetics ", *Trans. Farad. Soc.* 29, 958–972 (1933).
3. Frèedricksz, V. and Zolina, V., " Forces causing the orientation of an anisotropic liquid ", *Trans. Farad. Soc.* 29, 919–930 (1933).
4. Maier, W. and Saupe, A., " Eine einfache molekular-statistische Theorie der nematischen kristallinflüssigen Phase. Teil II ", *Z. Naturforsch.* 15a, 287–292 (1960).
5. Porter, R. S. and Johnson, J. F., " The rheology of liquid crystals ", Chap. 5, pp. 317–345 in " Rheology ", Vol. 4, ed. by F. R. Eirich (New York: Academic Press, 1967).
6. Svedberg, T., " Diffusion in anisotropen Flüssigkeiten ", *Kolloid Z.*, 22, 68–71 (1918).
7. Tsvetkov, V. N., " Polarization-interferometer study of diffusion in liquids ", *Zhur. Eksptl. Teoret. Fiz.* 21, 701–710 (1951).
8. Yun, C. K. and Fredrickson, A. G., " Heat generation in nematic mesophases subjected to magnetic fields ", pp. 239–258 in " Liquid crystals and ordered fluids ", ed. by J. F. Johnson and R. S. Porter (New York: Plenum Press, 1970).
9. Yun, C. K., " Transport phenomena in anisotropic liquids—liquid crystals ", Ph.D. Thesis, University of Minnesota, 1970.
10. Yun, C. K. and Fredrickson, A. G., " Formation of Liquid Crystals " (manuscript in preparation).