Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Time Dependence of Impurity Diffusion in a Nematic Liquid Crystal

H. Hakemi [a]

[a] Department of Chemistry Gross Chemical Laboratory, Duke University, Durham, NC, 27706

Version of record first published: 20 Apr 2011.

To cite this article: H. Hakemi (1982): Time Dependence of Impurity Diffusion in a Nematic Liquid Crystal, Molecular Crystals and Liquid Crystals, 82:9, 303-310

To link to this article: http://dx.doi.org/10.1080/01406568208247022

Mol. Cryst. Liq. Cryst. Vol. 82 (Letters), pp. 303-310
0140-6566/82/8209-0303$06.50/0

TIME DEPENDENCE OF IMPURITY DIFFUSION IN A NEMATIC LIQUID CRYSTAL

H. HAKEMI
Department of Chemistry
Gross Chemical Laboratory
Duke University, Durham NC 27706

(Submitted for publication: September 27, 1982)

ABSTRACT

In the optical method of mass transport in nematic liquid crystals, the diffusion time was employed as a variable experimental parameter. Within the time range where concentration gradient is large, we found that the average diffusion coefficient of the system to increase with time. This is due to an overall material flow coupled with Fickian diffusion at the vicinity of the solute-solvent boundary.

INTRODUCTION

The optical method was originally developed to study diffusion of an optically active impurity into an oriented nematic liquid crystalline thin film. With proper choices of the diffusion boundary conditions and nematic alignments, we have evaluated the temperature dependence of the anisotropy of the Fickian diffusion coefficients in the nematic liquid crystals.(1,2) Depending upon the nature of the diffusing species and the direction of the molecular alignments, the components of parallel and perpendicular average(concentration-independent) coefficients of impurity(1) and self-(2) diffusion have been reported. Correction for mass discrepancies between the solute and solvent species were done by either the relation $\bar{D} \sim (MW)^{-1/2}$ or by allowing a chiral nematic to diffuse into its racemic mixture.

The method of evaluating the diffusion coefficient has been according to the concentration(pitch) -distance analysis of the observable cholesteric pitch gradient of the diffusion profile.

In recent studies,(3,4) we have investigated the concentration(pitch)-dependence of the diffusion coefficient in a cholesteric/nematic system through the dynamic study of the disclination lines in the cholesteric diffusion texture. In a typical experiment, by monitoring the time evolution of the individual disclination line obtained from a homogenuously aligned diffusion texture, we determined a phenomenological relation between concentration and the diffusion coefficient;D_c. The evaluation of the concentration-dependent D_c was done by both concentration(pitch)-distance(3) and distance-time(4) methods.

The resuls of the studies, so far, have indicated that; a)Fick's law is not obeyed within the whole time evolution of the diffusion process, b)one can determine both $\bar{D}$ and D_c in the same experiment and c)the approach to self-diffusion coefficient of the pure nematic can be further refined by extrapolation of D_c to zero concentration(or to infinite pitch).

In the present work, we are investigating the time dependence of the imurity diffusion of cholesteric-oleyl-carbonate (COC) into a homeotropically aligned nematic 4-cyano-4'-pentylbiphenyl (5CB). The dynamic aspect of $\bar{D}$, which is complementary to the diffusion studies, has not been previously reported. Here, the values of $\bar{D}$ are determined at various diffusion time intervals via the textural analysis of the diffusion profile according to the cholesteric pitch-distance analytical method. this method has been mentioned elsewhere.(1) The study is focused at a time range, where a typical $\ln(1/p)$-x^2 exhibits a linear function. This is an assurance that measured values of $\bar{D}$ are not affected by any other factors except the time.

EXPERIMENT

COC and 5CB were obtained from Eastmen Kodak and BDH Chemicals,respectively, and were used as such. We used a 20%(v/v) solution of COC/5CB as the initial concentration of diffusant. Homeotropic alignment of 5CB was acheived by placing the nematic material between two lecithin coated glass plates separated by a 12 μm mylar spacer. The spacer was cut into a rectangular 6.5 by o.5 cm diffusion path.

The diffusion experiment was performed at ambient temperature of 25°C with a semi-infinite boundary condition. The direction of diffusion was perpendicular to both nematic alignment and the average direction of the cholesteric pitch axis.The details of the experimental procedure and mathematical evaluations are mentioned elsewhere.(1,3,4)

RESULTS AND DISCUSSIONS

Figure (1) represents the photomicrograph of the typical diffusion profile of the COC/5CB system with homeotropic orientation. The pitch values reported here are taken at the successive $\tau^{+}\lambda^{-}$ and $\lambda^{+}\tau^{-}$, which are distinguishable in figure (1). Determination of $\bar{D}$ at various time intervals, was done by proper use of the solution to the Fick's second law and necessary substitution for the pitch term. As mentioned elsewhere,(1) the values of the diffusion coefficient were calculated from the linear slope of the following equation;

$$\ln(1/p) = \ln\{M/\gamma(\pi\bar{D}t)^{\frac{1}{2}}\} - x^2/4\bar{D}t \qquad (1)$$

where all terms have been described previously. The experimental plots of equation (1) are shown in figure (2) as a function of diffusion time. The linearity of individual $\ln(1/p)-x^2$ plots indicate that, as long as the pitch gradient is concerned, the diffusion is within the domain of the Fickian diffusion. The slope variations of the data in figure

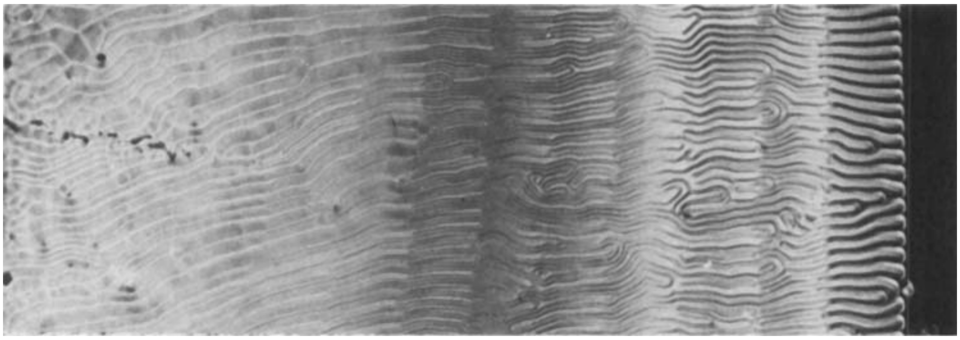
(2) arises from the distributions of the concentrations at the time progression of the diffusion.

In figure(3),the calculated $\bar{D}$ values from the linear slopes of figure(2) are presented. The results indicate the non-linear time dependence of $\bar{D}$. Although, at short time range $\bar{D}$ increases linearly with t (notice that at t=0; $\bar{D}=0$), however at long time limit of the experiment, $\bar{D}$ gradually becomes time independent.

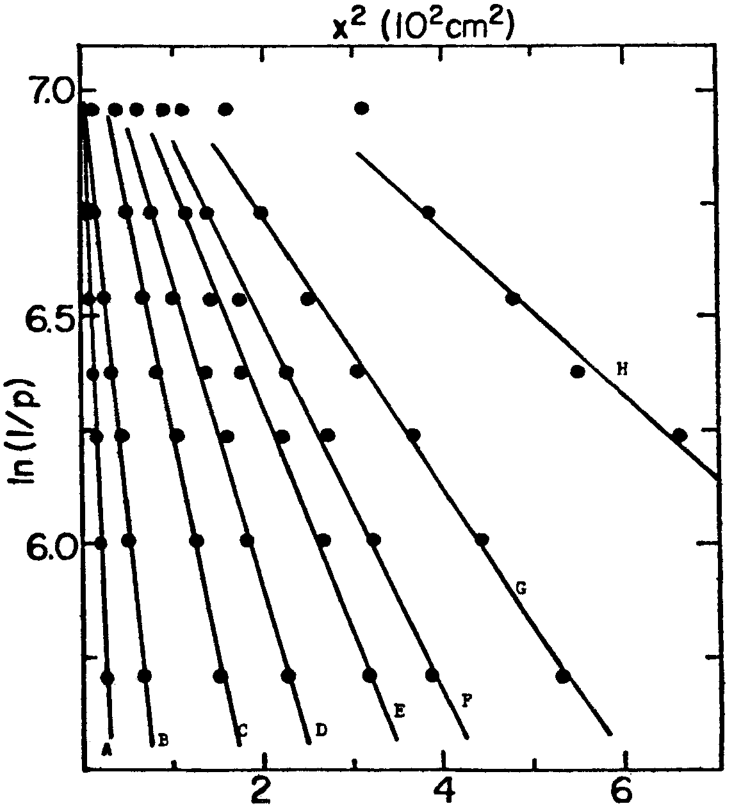
The origin of time dependency of $\bar{D}$ seems to rest on the amount of the diffuant at the diffusion source and the rate of the concentration distribution. The use of relatively large initial concentration of COC/5CB solution would require longer time for the complete relaxation of the Gaussian pitch distribution. The evidence for the beginning of this effect is observed in figure (3), as $\bar{D}$ values levels off at longer time limit. Cosequently, at the shorter times, due to the existance of a large concentration gradient, material flow is a dominant driving force and its coupling with Fickian diffusion would give rise to variable $\bar{D}$ values. At longer time, $\bar{D}$ is expected to reach its Fickian value. In fact, the largest value of diffusion coefficient obtained from figure (3),i.e. $\bar{D}=3.9\times10^{-7}$ cm^2/sec., is in very good agreement with $\langle D\rangle=4.0\times10^{-7}$ cm^2/sec. extracted from ref.(4). <D> is the average value of the concentration-dependent values of D_c obtained by distance-time method at Fickian time range.

Further assertion to the non-Fickian notion of diffusion in the present study lies on the dynamic behavior of the cholesteric disclination lines(or disclination points in this study) of the diffusion profile. In the previous work(4) and recent detailed study,(5) we found that in the early stages of diffusion, the progressive movements of disclinations do not lead to the evaluation of the diffusion coefficients from the Fick's laws. In later stages of diffusion, where the disclinations are well spread and are in the regressive motion twards the diffusion source(i.e., disappearing at $x = 0$),one can successfully apply the Fick's law and obtain D_c values. In this work, we only observed progressive motion of the disclination points. Therefore, the value of $\bar{D}$ at the upper time limit (figure (3)) can be accepted as the value of the average Fickian diffusion coefficient of the present system. It is noteworthy to point out that the discrepancies in D_c values reported in references (3) and (4) for COC/5CB system is due to the above argument, suggesting that the results of the former are obtained at non-Fickian region.

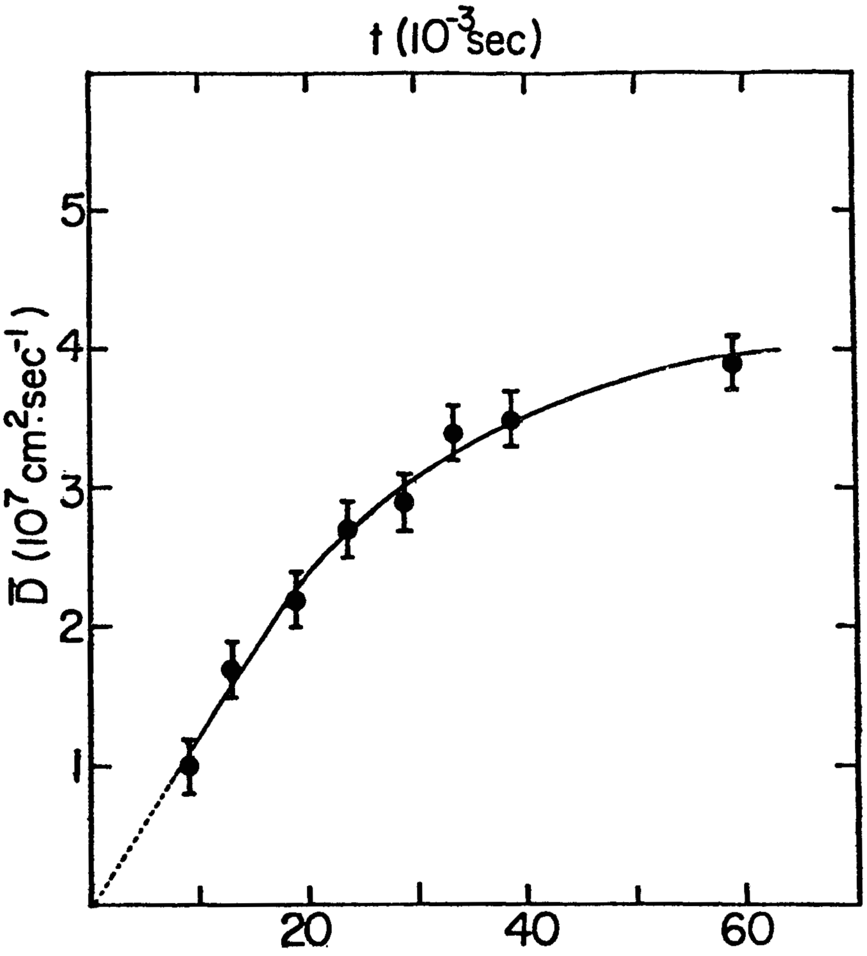
This work will be followed in more details with a recent study at the complete diffusion time range of a chiral nematic/nematic liquid crystal system.



FIGURE(1) Diffusion profile of COC/5CB with homeotropic alignment at 68x crossed-polars. t=33600 sec.



FIGURE(2) Time evolution of equation(1) for COC/5CB system at diffusion times; A:9000, B:13200, C:18900, D:23700, E;28800, F:33600, G:39300 and H:58800 seconds.



FIGURE(3) Time-dependence of $\bar{D}$ from slopes A-H of Figure(2)

REFERENCES

1) H. Hakemi & M. M. Labes, J. Chem. Phys., 61, 4020 (1974).

2) H. Hakemi & M. M. Labes, J. Chem. Phys., 63, 3708 (1975).

3) H. Hakemi, J. Appl. Phys., 53, 5333 (1982).

4) H. Hakemi, J. Chem. Phys., submitted (1982).

5) H. Hakemi, to be published.