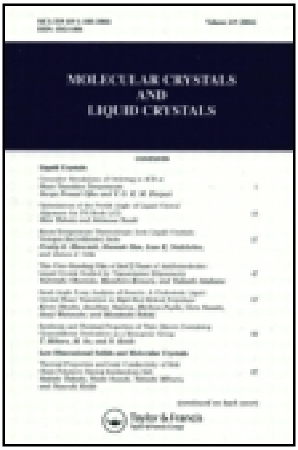

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Self-Diffusion Coefficients of Cholesteric/Nematic Systems with Dynamic Mass Transport Method

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Self-Diffusion Coefficients of Cholesteric/Nematic Systems with Dynamic Mass Transport Method

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Dynamic approach to mass transport study in cholesteric/nematic systems by the optical method provides the evaluation of the self-diffusion coefficients of both solute and solvent. These values are obtained by extrapolating to the $C = 0$ and $C = 1$ limits from the scaling law found between the diffusion coefficient and the concentration gradient. The numerical values of the local concentrations are obtained from the pitch values in both homogeneous and homeotropic boundary conditions.

INTRODUCTION

The self-diffusion coefficient of a system is a parameter of fundamental importance which gives a direct indication of thermally driven translational motion of the constituent molecules. In liquid crystalline systems, this dynamic property has not been studied extensively, considering that the first investigation in nematics was performed as early as 1917 by Svedbert.[1] Due to the scarcity of the experimental data, the available diffusion theories in nematics[2–4] and smectics[4,5] have not been satisfactorily verified. Experimental methods for studying translational diffusion in liquid crystals include the direct mass transport methods as well as NMR (direct spin-echo and indirect relaxation) and quasi-elastic neutron scattering techniques. A general review of these techniques has recently been reported.[6]

Until recently, the study of the translational diffusion in nematic liquid crystals by the direct mass transport methods has not been given much attention. This has been due to the experimental limitations arising mainly from the long diffusion time required for the establishment of the concentration gradient and also due to recent developments in NMR techniques.

In recent investigations we demonstrated that direct mass transport technique via the optical impurity diffusion approach[7] can be dramatically improved by using diffusion time as an independent experimental variable.[8,9] Accordingly, when an optically active impurity is allowed to diffuse under a proper boundary condition into a uniaxial nematic thin film, the development of the concentration gradient—manifested by the observable pitch gradient—can be studied dynamically. Depending upon the proper analytical approach, one can distinguish two types of interdependent translational diffusion coefficients: (a) the "concentration gradient averaged diffusion coefficient," $\overline{D}$, which is determined by the conventional concentration (or pitch)-distance analysis of the diffusion profile at constant time[7] and/or at variable time,[10] and (b) the "concentration-dependent diffusion coefficient," D_c, which is evaluated from distance-time analysis of the individual local concentrations within the diffusion profile.[9] Notice that the establishment of the local concentrations in the diffusion profile, which are manifested by the pitch disclinations, is imposed by the boundary conditions and is independent of the initial concentration, C_o, of the optical impurity.

In addition to the impurity diffusion, the optical method has also been utilized for studying self-diffusion in nematics by allowing a chiral nematic to diffuse into its own racemic mixture and the components of parallel and perpendicular $\overline{D}$ have been evaluated accordingly.[11] In a recent study,[12] we found that the evaluation of the self-diffusion coefficient can be further refined when the effect of the concentration gradient is also considered. Accordingly, the self-diffusion coefficient of the pure nematic was obtained by C = O extrapolation of the empirical relation:

$$D_c = D_0 \exp(-\beta C) \tag{1}$$

where D_0 is the self-diffusion coefficient of the pure nematic (or D_c at infinite dilution), β is the proportionality factor and C is the local concentration. Notice that in Eq. (1) the effect of the anisotropy diffusion is not considered, i.e. D_c or D_o values are averaged over the components of the diffusion anisotropy. Therefore, a more realistic approach to the self-diffusion by mass transport methods is to consider the effect of the concentration gradient, in addition to the use of a chemically equivalent solute (mass effect) at the infinite dilute limit (initial concentration effect).

In the present work, we give the exact quantitative approach for evaluation of the self-diffusion coefficients of the solvent and solute in a cholesteric/nematic diffusion system. The data are based on the previous diffusion studies of a cholesteryl-oleyl-carbonate (COC) impurity, diffusing into thin films of 4-cyano-4′-pentylbiphenyl (5CB) in the nematic phase with both homogeneous[8,9] and homeotropic[10,12] initial alignments. In this study, we calculated the exact values of the local concentrations (C) from their related local pitch values (P_c) according to the theoretical relation of Bak and Labes[13] (this will be mentioned in the following section). The numerical values of D_c as a function of C were subsequently determined from the procedure mentioned previously[9] and the self-diffusion coefficients at the two limits of the solute weight fractions; namely at $C = 0$ and $C = 1$, were obtained by extrapolation of the data on a scaling law, which gives a better linear relation than Eq. (1). From the present diffusion study we also determined the concentration-pitch proportionality constant, the pitch value for pure COC, and provided a new simple method for the cholesteric pitch measurement from the diffusion profile.

EXPERIMENTAL AND RESULTS

1. General

The diffusion profile of the COC/5CB system was established by allowing a depletable amount of COC/5CB solution with initial concentration $C_o = 0.145$ (g/g) to diffuse unidirectionally into 12 μm films of homogeneous and homeotropic nematic 5CB at ambient temperatures of 25°C. Time evolution of the respective diffusion pitch gradients were observed and measured using a Vickers M74 polarizing microscope at crossed polars position. Regardless of the initial direction of the nematic alignment, the direction of the established cholesteric pitch axis is always perpendicular to that of the diffusion.

This is observed in the diffusion profiles shown in Figure 1a and 1b. The direction of helix axis h is also indicated in Figure 1c. The reason for the establishment of the pitch axis perpendicular to the diffusion direction is that both components of the diffusion anisotropy, i.e. $D_{\parallel}$ and $D_{\perp}$ are allowed to contribute to the relaxation of the concentration gradient. These contributions to the average diffusion coefficient of the cholesteric structure can be described by an average diffusion coefficient, $\overline{D} = D_{\parallel} \cos \theta^2 + D_{\perp} \sin \theta^2$, where θ is the angle between molecular axis and diffusion direction. However, the establishment of the pitch axis parallel to the diffusion direction in either geometry would require that only one component of diffusion anisotropy, namely $D_{\perp}$, to contribute to the diffusion process. This is an unfavorable mechanism for concentration gradient relaxation, since in nematic diffusion, $D_{\parallel} > D_{\perp}$.

Consequently, in the present boundary conditions and in the absence of an external force of alignment, the reported diffusion coefficients are

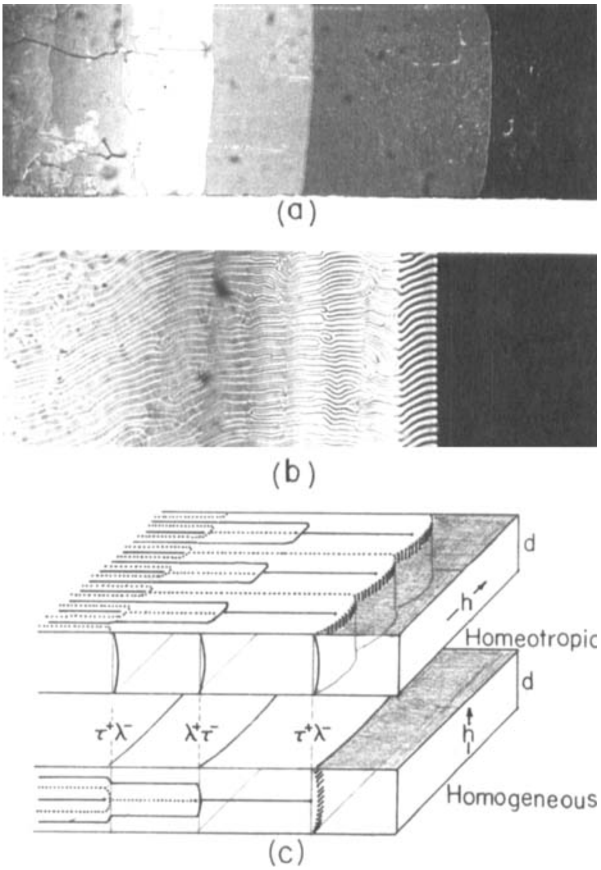

FIGURE 1 Diffusion profiles of the COC/5CB system; (a) with homogeneous alignment at $t = 40.5 \times 10^3$ sec, 68X, (b) with homeotropic alignment at $t = 28.8 \times 10^3$ sec, 68X and (c) diagram of the simplified disclination lines in the two geometries. d is the film thickness and h is the pitch axis.

averaged over the anisotropy contributions. The details of the sample preparations and experimental procedure have been mentioned in the previous works.[7,11] The estimated total experimental error of the present data are within ±10%.

2. Measurement of the diffusion pitch values

In this section we give the experimental procedure for measuring the pitch values in the diffusion concentration gradients at homogeneous and homeotropic boundary conditions. The required corrections in the pitch values in the latter by a correlation factor deduced from their diffusion data, provides a new simple method for evaluating the pitch at the diffusion source (i.e. P_{c_0}).

The diffusion profile of COC/5CB with homogeneous (parallel) orientation consists of a pitch gradient with successive and expanding discontinuities which resemble the Grandjean bands in a wedge-typed cell. The only difference is that while in the former the pitch discontinuities are established by concentration gradient, in the latter they are produced by thickness gradient. Figure 1a shows a photo-micrograph of a typical diffusion profile under homogeneous boundary condition. These pitch discontinuities are in fact a series of alternating $\tau^+\lambda^-$ and $\lambda^+\tau^-$ pairs of singularities (disclination) lines with half-strength (i.e. $s = \pm\frac{1}{2}$). The relation between the value of the undisturbed pitch, P_k, at the mid-distance of each band and sample thickness, d, is given by

$$\frac{1}{2}P_k = d/k \tag{2}$$

where $k = 1, 2, \ldots, n$ is the integer value with increasing trend towards the diffusion source. Notice that each disclination line represents a $P_k^0 \rightarrow P_{k+1}^0$ pitch jump also satisfied by Eq. (2), where P_k^0 and P_{k+1}^0 are the values of the disturbed pitch under compression and expansion, respectively. The schematic diagram of pitch variations and discontinuities is shown in Figure 1c. The values of P_k measured by the above procedure for the present system were extracted from Ref. 9 and are also tabulated in Table I.

Diffusion of the optical impurity COC into the homeotropic film of nematic 5CB, on the other hand, produces a diffusion texture consisting of a continuous pitch gradient which is shown in the photo-micrograph of Figure 1b. The pitch increase is manifested by a monotonous variation of the retardation lines (so-called fingerprint patterns) whose thicknesses are a measure of the half-pitch according to $S = \frac{1}{2}P$. In this boundary condition the singularity points (as indicated in Figure 1c) are again a series of alternating $\tau^+\lambda^-$ and $\lambda^+\tau^-$ disclination lines oriented perpendicularly to the supporting glass boundaries. Since the appearance of the disclinations in a homeotropic diffusion profile are not influenced by the thickness as they are in the homogeneous case [Eq. (2)], their location in the diffusion profile seems to be more influenced by the concentration gradient. Consequently, there is no direct correlation between the pitch values in the two boundary conditions. In fact, we have found that in homeotropic alignment the cholesteric pitch axis at low concentration is subjected to partial tilting. This effect has been noticed from a non-linear behavior of the concentration-pitch relation.[7]

In order to present the diffusion data of the two boundary conditions on the same scale, we found their pitch values relation by comparing their diffusion coefficients from Ref. 9 and 12. Accordingly, for homogeneous boundary the diffusion coefficients D_c = 2.4 and 4.5 $\times$ 10^{-7} cm^2 sec^{-1} are related to P_c = 12 and 24 $\times$ 10^{-4} cm, while in the homeotropic boundary the same D_c values have the pitch values P_c = 19 and 39 $\times$ 10^{-4} cm, respectively. From this comparison we found the following relation:

P_c (homeotropic)/P_c (homogeneous) = 1.60 ± 0.05 (COC/5CB) the relation is also a measure of the tilt of the pitch axis in the homeotropic alignment. The above relation was used to correct all the pitch values in the homeotropic case and the results are tabulated in Table I.

Numerical evaluation of the concentration gradient which will be mentioned in the following section, would require a standard set of concentration-pitch values. In the following we give a method for measuring the pitch value at the diffusion source (i.e. at x = 0), whose concentration is that of the diffusing species, namely C_0 = 0.145 g/g.

As mentioned previously, the diffusion texture with homogeneous alignment consists of a discrete pitch gradient (see Figures 1a and 1c), whose

TABLE I

Concentration and pitch dependence of the COC/5CB diffusion coefficient at 25°C

P_c ($10^4 \cdot$ cm)	C ($10^3 \cdot$ g/g)	D_c ($10^7 \cdot$ cm$^2 \cdot$ sec^{-1})
41.1*	3.80	6.5
30.5*	5.45	5.2
24.3*	6.78	4.5
24.0@	6.80	4.5
21.2*	7.93	3.7
18.1*	9.09	3.3
14.9*	10.9	2.9
12.0@	13.6	2.4
11.8*	13.9	2.4
8.0@	20.4	2.0
6.0@	27.2	1.6
4.8@	34.0	1.3
4.0@	40.8	1.1
1.30	145	0.45
0.25	1000	D_l = 0.061#
∞	0	D_0 = 10.4†

@from homogeneous alignment, *from corrected homeotropic alignment, #self-diffusion coefficient of COC, †self-diffusion coefficient of 5CB.

exact jump values may be determined from Eq. (2) with the knowledge of the values of d and k. The integer values $k = 1, 2, 3 \ldots, n$ are simply the Grandjean band numbers with increasing values as going from the diffusion front towards the source. If $k = n$ is the last Grandjean band to appear in the vicinity of the source, i.e. near $x = 0$, then in first-order approximation, the pitch at the source should lie between $k = n$ and $k = n + 1$. Hence, the most probable value of the pitch at $x = 0$, i.e. the pitch of the diffusing solution P_{c_o}, may be described by:

$$P_{c_o} = (P_n + P_{n+1})/2 = d(2n + 1)/n(n + 1) \qquad (3)$$

where P_n and P_{n+1} are obtained by substitution of $k = n$ and $k = n + 1$ in Eq. (2). Equation (3) provides a general approach to the determination of both the intrinsic and virtual pitch values of optically active cholesteric and non-cholesteric compounds, respectively.

The above method provides a simple alternative for the pitch measurement, whose accuracy depends upon the proper choice of the film thickness as well as the nature of the nematic matrix, the surface treatment, resolution power of the microscope and temperature. In spite of the relatively long time required for the development of the diffusion profile, the method is advantageous for its dependence on just one experimental parameter: namely, the film thickness.

In this work, by using the above approach and Eq. (3), we found that the diffusion of the COC/5CB solution with initial concentration $C_0 = 0.145$ g/g into a 12 μm thick film of homogeneously aligned 5CB provides a diffusion profile with maximum Grandjean bands $n = 18 \pm 1$, whose pitch value is $P_{c_o} = (1.30 \pm 0.07) \times 10^{-4}$ cm (see also Table I). These values of C_0 and P_{c_o} are used to calculate the local concentrations according to the procedure mentioned in the following section.

3. Calculation of the local concentrations

Investigation of the concentration dependency of the diffusion in cholesteric/nematic systems require the knowledge of the numerical values of the local concentrations in the diffusion profile. These can be obtained from a pitch-concentration relation. In a binary cholesteric/nematic mixture it is well known that in the low concentration region, the resultant pitch is inversely proportional to the concentration.[14] However, in total range of concentration, where deviation from the concentration-(pitch)$^{-1}$ linearity is expected, the precise nature of such relationships has been difficult to define. On the basis of the concept of the long range distortions induced by chiral molecules in a nematic matrix, Bak and Labes[13] proposed a theoretical relation providing a linear concentration-(pitch)$^{-1}$ dependency of the quadratic nature. This theory is applicable in all the concentration range of the components. Accordingly, the precise concentration-pitch relation in terms of the weight fraction of the cholesteric component is given by:

$$[M_c + (M_n - M_c)C]/2P_c \cdot \rho \cdot C = [N\beta_c(M_n/M_c) - 2N\beta_{cn}]C + 2N\beta_{cn} \tag{4}$$

where M_c and M_n are the molecular weights of the chiral and nematic components, respectively, C is the concentration of the chiral component in weight fraction with the related pitch P_c, $N\beta_c$ and $N\beta_{cn}$ are the molar twisting powers of the pure chiral and mixed chiral/nematic components. ρ is the density of the mixture described by:

$$\rho = \rho_n[1 + (\rho_n/\rho_c - 1)C]^{-1} \tag{5}$$

where ρ_n and ρ_c are the densities of the nematic and the chiral components, respectively.

In the present study, by utilizing Eqs. (4) and (5) we calculated local C values for the COC/5CB mixture in the diffusion profile from their related P_c values. The results are also tabulated in Table I. The experimental parameters required by Eqs. (4) and (5) for the present calculations are: $M_n = 249$, $M_c = 681$, $\rho_n = 1.02(\text{g/cm}^3)$, $\rho_c = 0.86(\text{g/cm}^3)$, $N\beta_c = 16.0 \times 10^6\ \text{cm}^2$ (obtained from Ref. 13) and $N\beta_{cn} = 10.2 \times 10^6\ \text{cm}^2$ (calculated from Eq. (4) when C_0 and P_{c_0} were used).

Figure 2 presents the relation between the local concentration and the inverse pitch values for the two diffusion boundary conditions (see Table I). The result confirms our previous assumption that the concentration-pitch relation in a diffusion system should satisfy a linear relation given by

$$\mathrm{C} = \gamma(P_c)^{-1} \tag{6}$$

where γ is the proportionality constant. From the data of Figure 2, one can evaluate the value of the slope by a linear regression method. Accordingly, we found that $\gamma(\text{COC/5CB}) = 1.6 \times 10^{-5}$ cm. In order to evaluate the pitch of pure COC (i.e. at C = 1) limit), extrapolation of data according to Eq. (6) would give $P_{c=1} = 1.6 \times 10^{-5}$ cm. However, since in the region of large concentration Eq. (6) is not expected to hold while Eq. (4) would completely satisfy the criterion of the C–P_c linearity,[13] the latter was used to calculate the pitch of pure COC. Accordingly, we found a more reliable result: $P_{c=1} = 2.5 \times 10^{-5}$ cm. This result is also given in table (I).

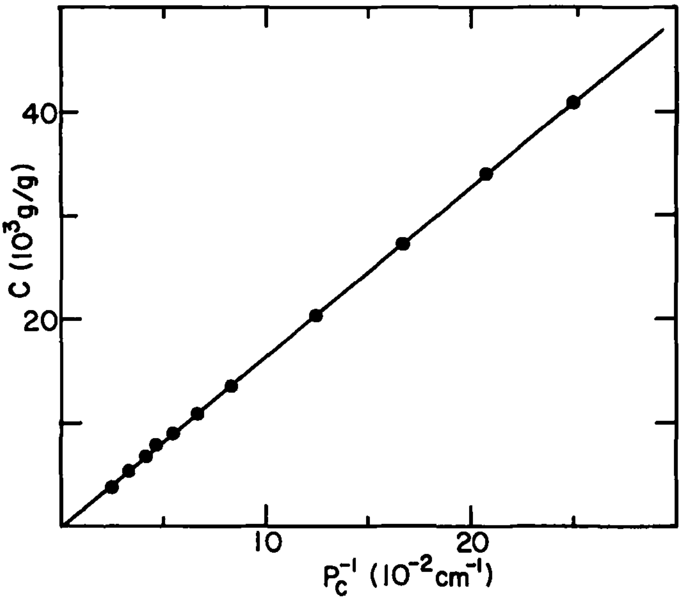

FIGURE 2 Linear C-O_c^{-1} relation for COC/5CB diffusion system according to Eq. (4).

4. Determination of the Diffusion Coefficient

The evaluation procedure of the COC/5CB diffusion coefficient, D_c, as a function of the local concentration of the diffusion concentration gradient is based on the distance-time analysis of the individual pitch values within the diffusion profile. In the homogeneous alignment, the mid-point of the Grandjean bands were subjected to a dynamic study [see Figures 1a and 1c, and Eq. (2)], while in the homeotropic alignment the time-distance analysis of the retardations were done at the singularity points (see Figures 1b and 1c). In either case, the local concentration of the respective pitch value is determined by Eq. (4) (see also Table I).

According to linear diffusion theory with semi-infinite boundary condition, the diffusion coefficient D_c at each concentration is evaluated from[9]

$$x_c^2/t = 2D_c \ln(M^2/\pi D_c \cdot C^2) - 2D_c \cdot \ln(t) \qquad (7)$$

where x_c is the penetration distance of the local concentration C (or local pitch P_c) at variable time t and M is the total amount of solute at the source.

As the first term in the right hand side of Eq. (7) is constant, a plot of x_c^2/t vs $\ln(t)$ should provide a linear curve whose slope, $-2D_c$, gives the diffusion coefficient. The D_c values for the present system which are determined according to Eq. (7),[9,12] are also tabulated in Table I. Notice that all D_c values are corrected for mass discrepancies between COC and 5CB according to the approximation:[14]

$$D_c(5\text{CB})/D_c(\text{COC}) = [MW(\text{COC})/MW(5\text{CB})]^{1/2}$$

where MW represents the molecular weight.

To determine the self-diffusion coefficients of pure components 5CB and COC (i.e. D_0 at $C = 0$ and D_1 at $C = 1$ limits, respectively) we plotted the present diffusion data according to the scaling law. Figure 3 shows the

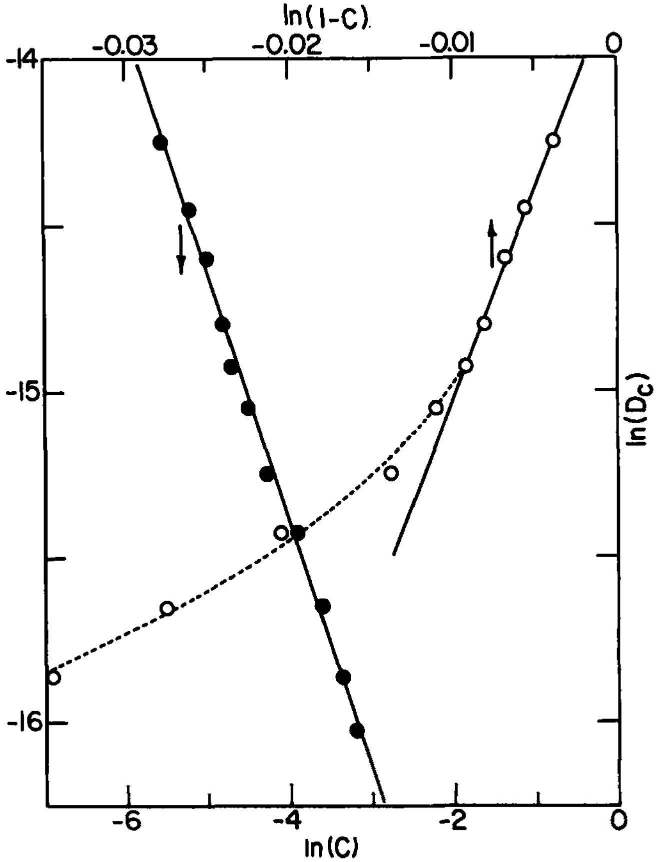

FIGURE 3 Scaling relation of D_c against C and $1-C$ for the COC/5CB diffusion system.

ln–ln plots of D_c as a function of C and $1 - C$. The results on $\ln(D_c) - \ln(C)$ bases indicates a remarkable linearity within the total concentration range of the present diffusion study, which suggests that the D_c values may be scaled with concentration by;

$$D_c = D_1 \cdot C^{\nu} \tag{8}$$

where ν is the scaling exponent and the prefactor D_1 is the value of D_c at the extrapolated $C = 1$ limit (which also represents the self-diffusion coefficient of the pure COC solute). Accordingly, by linear extrapolation of the $\ln(D_c) - \ln(C)$ plot to $C = 1$, we found that:

$$D_1 = 6.1 \times 10^{-9}\ \text{cm}^2 \cdot \text{sec}^{-1} \qquad \text{(mass corrected)}$$

In addition, from the calculation of the slope by the linear regression method we obtained $\nu = -0.75$.

The scaling Eq. (8) would also allow us to determine the diffusion coefficient of the COC/5CB solute at the diffusion source. Namely, by substitution of $C_0 = 0.145$ in Eq. (8), we get

$$D_{c_0} = 4.5 \times 10^{-8}\ \text{cm}^2 \cdot \text{sec}^{-1}$$

The result of the $\ln(D_c) - \ln(1 - C)$ plot in Figure 3 shows a linear behavior at the lower concentration [higher $(1 - C)$] portion of the curve, whose linear relation in this limit may be described by;

$$D_c = D_0 \cdot (1 - C)^{\nu'} \tag{9}$$

where ν' is the scaling exponential and D_0 is the diffusion coefficient at the $C = 0$ limit (or the self-diffusion coefficient of the pure 5CB). From extrapolation procedure we then obtained;

$$D_0 = 10.4 \times 10^{-7}\ \text{cm}^2 \cdot \text{sec}^{-1}$$

and from the slope of $\ln(D_c) - \ln(1 - C)$, the scaling exponential is $\nu' = 1.27 \times 10^{-2}$. The D_0 value obtained from Eq. (9) is in very good agreement with that reported previously according to Eq. (1).[12] The results of the present self-diffusion data are also tabulated in Table I.

CONCLUSION

In the present study, we evaluated the self-diffusion coefficients of a cholesteric/nematic system at two concentration limits of the solution by scaling the impurity diffusion coefficients of the system on the local concentration of the diffusion profile. The empirical scaling relation between D_c and C, described by Eqs. (8) and (9), was obtained according to the dynamical analysis of the diffusion concentration gradient. Numerical values of the local concentrations were determined from the quadratic relation of Eq. (4), where the related pitch values were evaluated according to the geometrical boundary conditions imposed by surface alignments. Evaluation of the diffusion coefficients was based on the use of the proper solution to the Fick's law and the necessary parametric rearrangement [Eq. (7)].

The reported diffusion coefficients: $D(5CB) = 10.4 \times 10^{-7}$ and $D(COC) = 6.1 \times 10^{-9}\ cm^2 \cdot sec^{-1}$, are the values obtained by the extrapolation procedure which represent both mass and concentration gradient corrected self-diffusion coefficients of the nematic solvent and cholesteric solute, respectively.

The overall linear behavior of the present data on a $\ln(D_c) - \ln(C)$ plot is of particular interest (see Figure 3). This is because, it reflects a universality of the relation between the diffusion coefficient and the concentration of the $D_c \sim C^{-0.75}$ type, which is also in qualitative agreement with the scaling theory of de Gennes in polymer solutions.[16] According to this theory, which has been verified experimentally, the predicted scaling exponents for self- and cooperative diffusion in semidilute polymer solutions are -1.75 and 0.75, respectively. Although, further quantitative comparison between the present system and polymer solutions cannot be given here, the scaling properties suggest that diffusion in both cases may be described by a common relation. Further understanding of the relation between diffusion coefficient and concentration gradient with the present mass transport approach requires more systematic studies, which is the subject of current investigations.

Considering the relation between the diffusion coefficient and its related pitch value, Yaniv, Chidichimo, Vaz and Doane[17] proposed a phenomenological relation in which the diffusion along pitch axis is proportional to the square of the pitch according to $D/P^2 \approx 6.2\ sec^{-1}$. Their experimental result for the MBBA/CB15 system with $P \sim 3.0 \times 10^{-4}$ cm, has been $D/P^2 = (0.25 - 1.30)\ sec^{-1}$. Whereas in the present study, within the range of $D_c = (0.61 - 4.5) \times 10^{-8}\ cm^2 \cdot sec^{-1}$ (see Table I), we found that $D_c/P_c^2 = (2.7 - 9.8)\ sec^{-1}$. This result indicates that in the limit of small pitch values, the theory of Yaniv, Chidichimo, Vaz and Doane may have a more general implication in describing the relation between the diffusion coefficient and the pitch. From Eqs. (6) and (8) one can also show that

$$D_c \sim P_c^{\nu''} \tag{10}$$

where ν'' is the scaling exponent. Figure 4 is the plot of the experimental data of Table I according to Eq. (10) with $\nu'' = 0.75$. The differences between the present exponent value and that of Yaniv, *et al.*,[17] ($\nu'' = 2.0$)

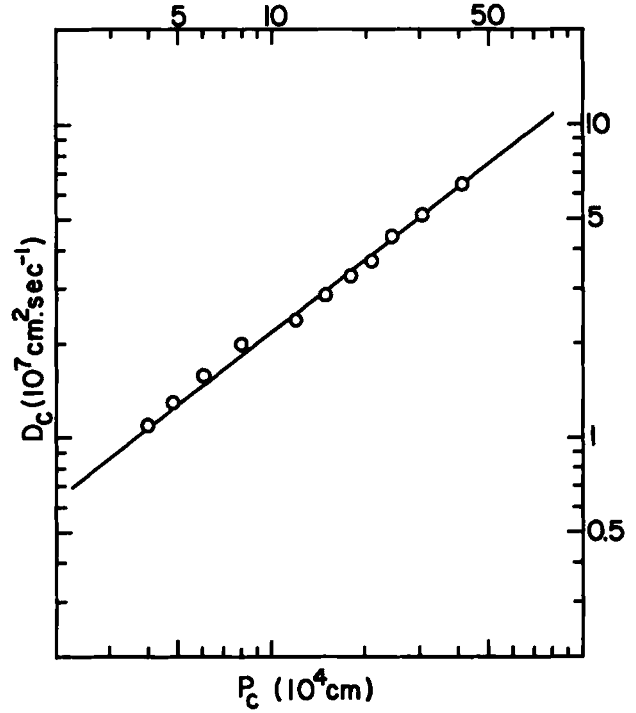

FIGURE 4 Scaling relation of D_c against P_c for the COC/5CB diffusion system.

may reflect a difference in the geometry of the diffusion experiment. Notice that in their experiment, diffusion is along the helix axis and the measured diffusion coefficient is in fact a rotating $D_\perp$ component. In order to verify the generality of Eq. (10), further experimental results are required. Currently, we are conducting a more detailed dynamic diffusion study on the CB15/5CB system and the results will be published shortly.

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