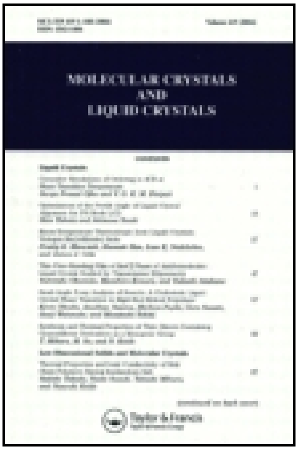

Molecular Crystals and Liquid Crystals

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

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Version of record first published: 20 Apr 2011.

To cite this article: M. E. Moseley , R. Poupko & Z. Luz (1983): Translational Diffusion of CH_4 and CH_2Cl_2 Dissolved in Cholesteric Liquid Crystals, Molecular Crystals and Liquid Crystals, 95:3-4, 279-285

To link to this article: http://dx.doi.org/10.1080/00268948308072468

Mol. Cryst. Liq. Cryst., 1983, Vol. 95, pp. 279–285
0026-8941/83/9504–0279/$18.50/0

Translational Diffusion of CH_4 and CH_2Cl_2 Dissolved in Cholesteric Liquid Crystals

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(Received December 21, 1982)

Translational diffusion coefficients of CH_4 and CH_2Cl_2 dissolved in five cholesteric mixtures of alkylcyanobicyclohexane-cholesterylchloride were measured in the temperature range 25°C to 75°C, using the NMR pulse gradient spin echo method. The pitch of the solvents studied depends on the cholesterylchloride concentration and ranged between ∞ and 2.2μ. The results indicate a slight difference in the diffusion constant parallel ($D_\parallel$) and perpendicular ($_\perp$) to the cholesteric pitch axis, with $D_\perp/D_\parallel \simeq 1.1$. The Arrhenius activation energies for the diffusion constants are about 6 to 7 kcal/mole for both probes. No dependence of the diffusion coefficients on the cholesterylchloride concentration and thus on the pitch was observed.

INTRODUCTION

In the present paper we present results of measurements of the translational diffusion of small solute molecules (CH_4, CH_2Cl_2) dissolved in a series of cholesteric liquid crystals. This work complements previous studies on the diffusion of similar probes in polymorphic liquid crystals containing nematic and smectic phase.[1] For the cholesteric mesophase one expects the diffusion coefficient along the pitch ($D_\parallel$) to be different from that along the perpendicular direction ($D_\perp$). Moreover recent NMR studies[2–4] in neat cholesterics suggested that $D_\parallel$ is proportional to the square of the pitch, i.e. $D_\parallel \propto P^2$. More recently this relation was derived from a simple random walk model of the cholesterics.[5] Our measurements were performed in mixtures of a nematic liquid crystal (Merck ZLI1167) and cholesterylchloride

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(C.C.). The mixtures contained up to 20% C. C. in which the pitch at room temperature is as short as 2.2μ. Although we find a small but systematic difference between $D_{\parallel}$ and $D_{\perp}(D_{\perp}/D_{\parallel} \simeq 1.1)$, within our experimental accuracy, no dependence of D on the pitch is observed.

MATERIAL AND EXPERIMENTAL PROCEDURES

The cholesteric liquid crystalline solvents used were mixtures of the nematic ZLI1167 (from E. Merck, Darmstadt) and cholesterylchloride. The ZLI1167 is reported[6] to consist of a eutectic ternary mixture of propyl-, pentyl- and heptyl-4′-cyanobicyclohexane. Its clearing temperature is 83°C and it transforms into a smectic phase at 32°C. Five different solvents were used, containing 0, 1, 5, 10 and 20 wt. % cholesterylchloride in ZLI1167. The introduction of C. C. reduced the phase transition temperature to the smectic phase, but affected very little the clearing temperature.

The rotary viscosities of some of the mixtures were determined at room temperature (25°C) using a Gebrüder Haake Rotovisco type PK-I viscometer. The results are shown in Table I. They indicate a slight increase in viscosity with C. C. concentration.

The cholesteric pitch of these mixtures was determined using two optical microscopy methods; in one the pitch was determined from the fingerprint structures while in the other, the Cano wedge method was employed. The results for room temperature are indicated in Table I and in the insert in Figure 2. It may be seen that $1/P$ is very nearly linear with C. C. concen-

TABLE I

Rotational viscosity coefficients (η) and pitch (P) for the ZLI-1167-cholesterylchloride mixtures used in the present work (t = 25°C).

C.C. wt.%	η (cp)	P (μ)
20.1	90	2.2
10.4	80	4.4
4.9	70	8.8
1.0	—[a]	44.4[a,b]
0	—[a]	∞

[a] For 0 and 1.0 wt.% C.C. the mixture at 25°C is smectic and therefore no experimental data are given.

[b] Extrapolated from a linear plot of 1/P vs. wt.% C.C.

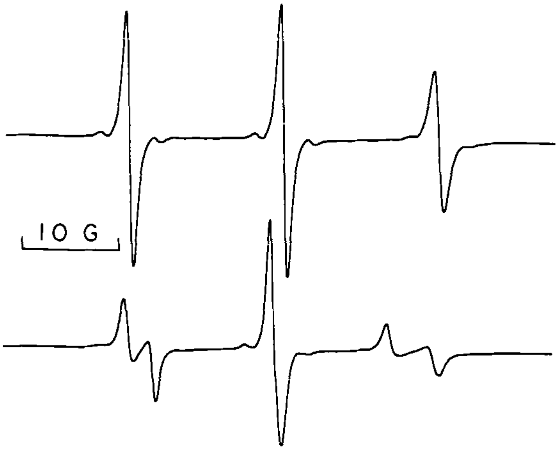

FIGURE 1 ESR (X-band) spectra of a dilute solution of TEMPO in a ZLI1167-C.C. mixture containing 5 wt.% cholesterylchloride. The upper trace is for an aligned sample in which the pitch axis is parallel to the magnetic field. The lower trace was obtained after rotating the sample by 90° about an axis perpendicular to the magnetic field.

tration. Changing the temperature in the range 25°C to 50°C had almost no effect on *P*.

The experiments were made on two probe molecules, i.e. CH_2Cl_2 and CH_4 dissolved in the five mixtures described above. The concentration of the methylene chloride was 5.2 wt.% in all solvents. The methane probe was introduced under pressure (8 at.) into a 3.4 mm inner diameter pyrex glass sample tubes, as described in Ref. 1. The introduction of the probe molecules, particularly the methylene chloride, reduced both the clearing temperature and the transition temperature to the smectic phase.

The diffusion measurements were performed using the pulse field gradient spin echo technique[7] on the proton signal of the CH_2Cl_2 and CH_4 molecules. The spectrometer was a Bruker WH-90, and the experimental setup for the diffusion experiments was as described in Ref. 1.

RESULTS AND DISCUSSION

The magnetic susceptibilities of the cyanobicyclohexane derivatives and of C. C. are such that the solvent liquid crystal molecules prefer to align with their long axes perpendicular to the external magnetic field. Consequently in sufficiently strong fields the solvents will align with their cholesteric axes parallel to the external field. In such samples there is no distortions of the helical structure by the magnetic field. This makes it particularly easy

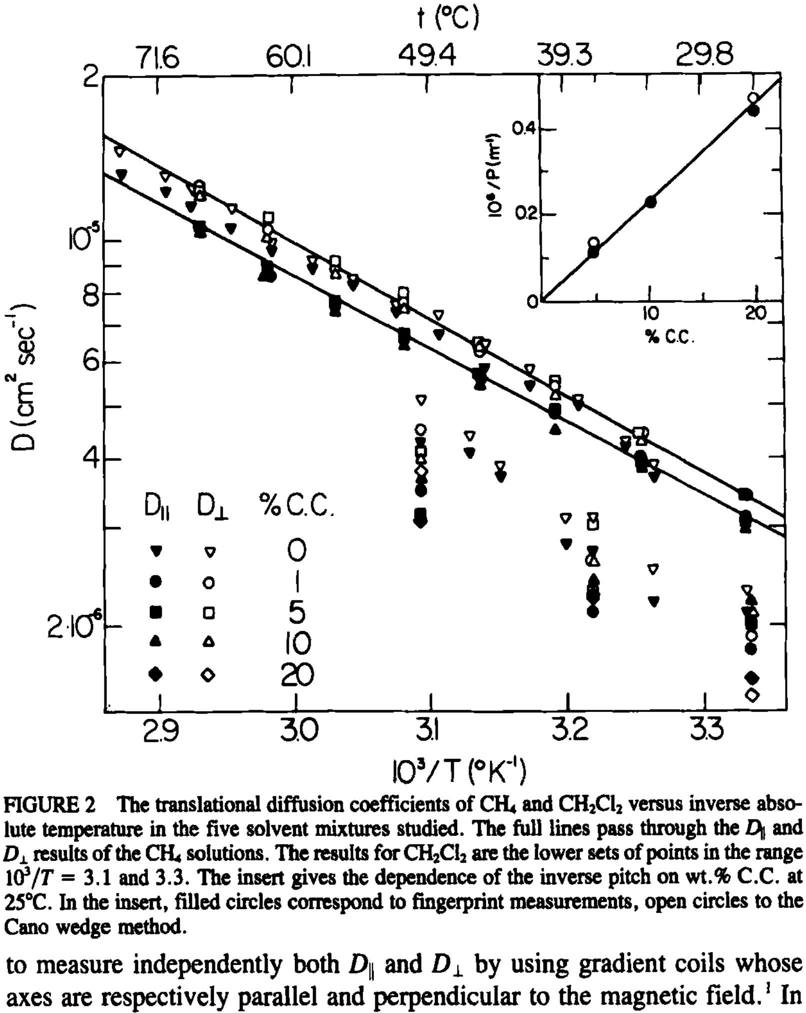

FIGURE 2 The translational diffusion coefficients of CH_4 and CH_2Cl_2 versus inverse absolute temperature in the five solvent mixtures studied. The full lines pass through the $D_\parallel$ and $D_\perp$ results of the CH_4 solutions. The results for CH_2Cl_2 are the lower sets of points in the range $10^3/T = 3.1$ and 3.3. The insert gives the dependence of the inverse pitch on wt.% C.C. at 25°C. In the insert, filled circles correspond to fingerprint measurements, open circles to the Cano wedge method.

to measure independently both $D_\parallel$ and $D_\perp$ by using gradient coils whose axes are respectively parallel and perpendicular to the magnetic field.[1] In this respect the present method is superior to the NMR lineshape method[8,9] in which an average diffusion rate is obtained from an analysis of the deuterium NMR spectra of deuterated probe molecules.

The aligned samples were prepared by slowly cooling the solutions from the isotropic liquid down to the cholesteric phase while placed in the magnetic field. To check that indeed this procedure yields single domains we investigated the ESR spectrum of a paramagnetic probe (TEMPO) dissolved in a solvent mixture containing 5 wt.% C. C. The sample was first oriented as described above in a magnetic field of 20 KGauss. The field was then reduced to 3.2 KGauss for performing the ESR experiment, without changing the orientation of the sample. At this orientation the ESR spectrum shown in the upper trace of Figure 1 was observed. Upon rotation of the sample by 90° about an axis perpendicular to the field direction the spectrum shown by the lower trace was obtained. The behavior of the spectra is typical of a two-dimensional distribution of the director field as is indeed expected for an aligned cholesteric sample.[10] (We used ESR spectroscopy for this experiment because the magnetic field in this case will not reorient the pitch axes).

As indicated above the translational diffusion of CH_2Cl_2 and CH_4 was measured in different solvent mixtures with cholesterylchloride concentration ranging from 0 to 20 wt.%, for CH_2Cl_2 and 0 to 10 wt.% for CH_4. Since the addition of methylene chloride reduced the clearing temperature quite drastically, much more than in the case of the methane solutions, the results for the latter probe cover a much wider temperature range and are more significant. The discussion below refers therefore mainly to the methane data. The results for $D_\parallel$ and $D_\perp$ for the two probes in the various solvent mixtures are given in Tables II and III and are plotted versus the reciprocal absolute temperature in Fig. 2.

The main features of the results may be summarized by the following points:

(a) At each temperature there is a small but systematic difference between $D_\parallel$ and $D_\perp$, the ratio between the two being $D_\perp/D_\parallel \simeq 1.1$.

(b) There is a monotonic increase of D with temperature which for CH_4 is characterized by an Arrhenius activation energy of 6.4 kcal/mole for $D_\perp$ and 6.1 kcal/mole for $D_\parallel$.

(c) Within our experimental accuracy there does not appear to be any dependence of the D's on the C.C. concentration.

The activation energies for the translational diffusion of the CH_4 probe are very similar to those determined previously in other nematics and the slight anisotropy ($D_\perp/D_\parallel \simeq 1.1$) is also consistent with previous results.[1]

TABLE II

Diffusion coefficients of CH_4 in ZLI-1167-C.C. mixtures.[a]

	$D_\parallel \times 10^5 (cm^2 sec^{-1})$				$D_\perp \times 10^5 (cm^2 sec^{-1})$			
t°C	0	1	5	10	0	1	5	10
27.0	–[b]	0.31	0.31	0.31	–[b]	0.34	0.34	0.33
33.7	0.39	0.40	0.40	0.40	0.40	0.44	0.44	0.43
45.5	0.63	0.57	0.56	0.55	0.66	0.65	0.65	0.64
52.0	0.72	0.65	0.67	0.64	0.76	0.77	0.80	0.75
62.1	0.94	0.86	0.86	0.89	0.99	1.05	1.08	1.09
68.0	1.13	1.05	1.03	1.05	1.21	1.25	1.21	1.24

[a] The columns headings give the wt.% cholesterylchloride in the mixtures.

[b] At this temperature (27°C) the sample is smectic and therefore no data are given.

TABLE III

Diffusion coefficients of CH_2Cl_2 in ZLI-1167-C.C. mixtures.[a]

	$D_\parallel \times 10^5(cm^2sec^{-1})$					$D_\perp \times 10^5(cm^2sec^{-1})$				
t°C	0	1	5	10	20	0	1	5	10	20
26.7	0.21	0.18	0.20	0.22	0.16	0.23	0.19	0.20	0.21	0.15
37.4	0.26	0.21	0.23	0.24	0.22	0.30	0.26	0.30	0.26	0.22
50.0	0.43	0.35	0.31	0.37	0.31	0.51	0.45	0.41	0.40	0.38

[a] The columns headings give the wt.% cholesterylchloride in the mixtures.

For comparison with diffusion in the nematic phase, $D_\parallel$ of the cholesteric must be identified with diffusion perpendicular to the nematic director, $d_\perp$, and $D_\perp$ with the average of the perpendicular and parallel diffusion coefficients in nematics $\frac{1}{2}(d_\parallel + d_\perp)$. Thus $D_\perp/D_\parallel \simeq 1.1$ corresponds to $d_\parallel/d_\perp \simeq 1.2$, which is indeed the ratio observed for small probes in nematics.[1]

The results fail to indicate any effect of added C.C. on $D_\parallel$ (or $D_\perp$) despite the small increase in viscosity and the fact that over the C.C. concentration range studied the pitch varied from ∞ to 2.2μ. This observation differs from that of Doane and coworkers[2-4] who found that the parallel self-diffusion ($D_\parallel$) coefficient of mesogen molecules in cholesterics is proportional to the square of the pitch. If this relation would hold for the probe molecules the $D_\parallel$'s in the 10 wt.% C.C. mixtures should have been hundred-fold smaller than in the 1 wt.% mixture (and infinitely smaller than in the nematic 0 wt.% solvent) (cf. Table I). In this connection it is worth mentioning that in a recent study[11] of a lyotropic cholesteric system there was also no effect of the diffusion coefficients of the constituent molecules on the pitch. If the $D_\parallel \propto P^2$ relation indeed exists it may perhaps apply to the mesogen only. This would mean that the mechanism for diffusion of small probe molecules is different from that of large mesogen molecules.

Acknowledgments

This work was supported in part by the U.S.-Israel Binational Science Foundation, Jerusalem. We are grateful to Professors Loewenstein and Labes for their help and advise in preparing the samples and in performing the pitch measurements.

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