Binary mass diffusion in smectic C and C^A phases as observed by forced Rayleigh scattering

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We have observed the diffusion constants of a dye in several liquid crystals by forced Rayleigh scattering. In a liquid crystal which has a standard phase sequence of N–S_A–S_C, the diffusion anisotropy changes at the N–S_A phase transition and increases with decreasing temperature in S_A and S_C phases. The diffusion constants exhibit a rather smooth decrease with decreasing temperature except an anomaly at the S_A–S_C phase transition. In a liquid crystal which has the antiferroelectric S_{C_A} phase, however, the diffusion constants show discontinuous increase and decrease at the S_A–S_C and the S_C–S_{C_A} phase transition temperatures, respectively: the diffusion constant in S_C is larger than that in the higher temperature S_A phase. Anomalous signal increase and profile were observed at the phase transition temperatures, and were ascribed to the complementary transient grating due to the coexistence of two phases.

1. Introduction

Anisotropic molecular alignment and positional order in liquid crystals are sometimes reflected in their macroscopic properties. Self diffusion and binary mass diffusion in liquid crystals provide information on the anisotropy and molecular orientational structure. It is easily imagined that the diffusion constant parallel to the director is larger than that perpendicular to it in the nematic phase. This is actually the case [1–11]. In the smectic A (S_A) phase, the layer structure is presupposed to suppress the interlayer diffusion. This is experimentally almost the case [1, 10, 12–16]. Theoretical study always predicts that interlayer diffusion is smaller than intralayer [17, 18]. However, the situation is not so simple. In alkylcyanobiphenyls and alkoxycyanobiphenyls, the diffusion anisotropy in the S_A phase is almost the same as that in nematics; namely, even in the S_A phase, interlayer diffusion is larger than the intralayer [9, 11]. Nishikawa *et al.* [19], measured the diffusion anisotropy in mixtures of two liquid crystals which show different anisotropy in the S_A phase and studied the correlation to the layer structure and to the phase appearing below the S_A phase. However, they failed to give the clear correlation.

The purpose of this paper is to examine the difference in diffusion constant and the anisotropy between the S_C and S_{C_A} phases. The S_{C_A} phase has a layer structure in which the molecules tilt with respect to the layer normal and the tilt sense alters from layer to layer [20], while the

tilt sense is unique in the S_C phase. We will show that the diffusion constants in the S_C phase are larger than those in the S_A and the S_{C_A} phases of liquid crystals which show the antiferroelectric phase.

2. Experimental

2.1. Sample preparation

The materials used are listed in the table. MHPOBC [20], TFMHPOBC [21] and MHPOCBC [22] show the antiferroelectric S_{C_A} phase. To avoid the helicoidal structure, racemic mixtures were used. The non-chiral compound (6OBPy8) with the phase sequence of I–N–S_A–S_C was also used for comparison. As a tracer molecule, 4'-N,N-dimethylaminoazobenzene-1-carboxylic acid (methyl red; MR) was lightly doped (about 0·2 mol %) in the host materials.

Homogeneously aligned cells of about 50 μm thick were prepared between two ITO-coated glass plates treated with a surfactant (polyimide, Toray SP-510): one glass plate was rubbed unidirectionally. The material was introduced into the cell at the isotropic phase and cooled slowly.
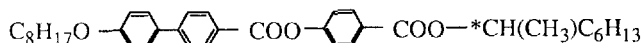
2.2. Experimental set-up

For the diffusion measurements, we adopted the forced Rayleigh scattering method (FRS). FRS is a kind of microscopic tracer method, which probes the diffusion of tracer molecules in host liquid crystals accurately and quickly. We used two laser beams from an Ar^+ laser (NEC
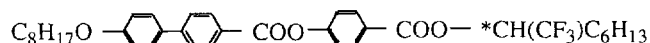
* Author for correspondence.

Structure and transition temperatures (°C) of the liquid crystals
used in this study.

DL-MHPOBC

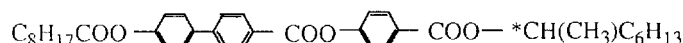$C_8H_{17}O$ —⟨◯⟩—⟨◯⟩— COO—⟨◯⟩— COO—*CH(CH₃)C₆H₁₃

I 146 S_A 120·5 S_C 109·5 S_{C_A}

DL-TFMHPOBC

$C_8H_{17}O$ —⟨◯⟩—⟨◯⟩— COO—⟨◯⟩— COO— *CH(CF₃)C₆H₁₃

I 125 S_A 113 S_C 99·8 S_{C_A}

DL-MHPOCBC

$C_8H_{17}COO$ —⟨◯⟩—⟨◯⟩— COO—⟨◯⟩— COO— *CH(CH₃)C₆H₁₃

I 147 S_A 98·1 S_{C_A}

6OBPy8

$C_6H_{13}O$ —⟨◯⟩—⟨◯N:N⟩—C₈H₁₇
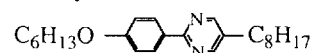
I 65·1 N 57·4 S_A 45·4 S_C

GLG 3250, < 25 mW, 514·5 nm) crossing in a cell. Because of the coherence of the laser light, an interference fringe pattern is produced. Using pulsed writing beams, a kind of holographic grating consisting of *trans-* and *cis*-MR is instantaneously formed and decays according to the diffusion of the dye and the intramolecular relaxation from *cis* to *trans*. Since the lifetime of *cis*-MR is sufficiently long compared with the diffusion process [9], we can determine the diffusion constant of MR by monitoring the disappearance of the diffraction intensity of a probing He–Ne laser (NEC GLG5600, < 12 mW) beam. The optical set-up used was almost the same as the one previously reported [9, 11].

3. Results and discussion

3.1. *Temperature dependence of the diffusion constant*

Figure 1 shows the temperature dependence of the interlayer (parallel to the layer normal, $D_{\parallel}$) and intralayer (perpendicular to the layer normal, $D_{\perp}$) diffusion constants, which are displayed by open and closed symbols, respectively. It should be noted that the diffusion along the director contributes to $D_{\perp}$ as well as $D_{\parallel}$ in the S_C phase. We can see several characteristics: (i) $D_{\perp}$ is larger than $D_{\parallel}$ in all the phases, but the difference is very small particularly in the S_A and S_C phases. (ii) There are discontinuous changes at the phase transition temperature, $T_{S_A-S_C}$ and $T_{S_A-S_{C_A}}$. In particular, the change at $T_{S_A-S_C}$ is very curious.

It has tacitly been believed that the interlayer diffusion is slower than the intralayer diffusion because of the potential barrier due to the smectic layer formation. As

some groups showed recently [9, 11, 19, 23], however, there are the contrary examples, $D_{\parallel} > D_{\perp}$, though the reason is not clear. The anisotropy, $D_{\parallel} > D_{\perp}$ was observed in nCB (alkylcyanobiphenyl) and its mixture with other compounds. In the present case, $D_{\perp} > D_{\parallel}$ was observed and the anisotropy $|D_{\parallel} - D_{\perp}|/(D_{\parallel} + D_{\perp})$ in the S_{C_A} phase is larger than those in the S_A and S_C phases. It is known that the layer structure of nCB is of a sinusoidal density wave [24]. On the other hand, the layer order in MHPOBC is much higher than that in nCB, particularly in S_{C_A}, as reported recently [25]. This fact is consistent with the observed anisotropy.

The surprising experimental fact is that the diffusion constant in the lower temperature phase, S_C, is larger than that in the higher temperature phase, S_A. To show the difference clearly, the decays of the normalized diffraction intensity are plotted in figure 2. All of them exhibit simple decay profiles. The decay in the S_C phase is clearly faster
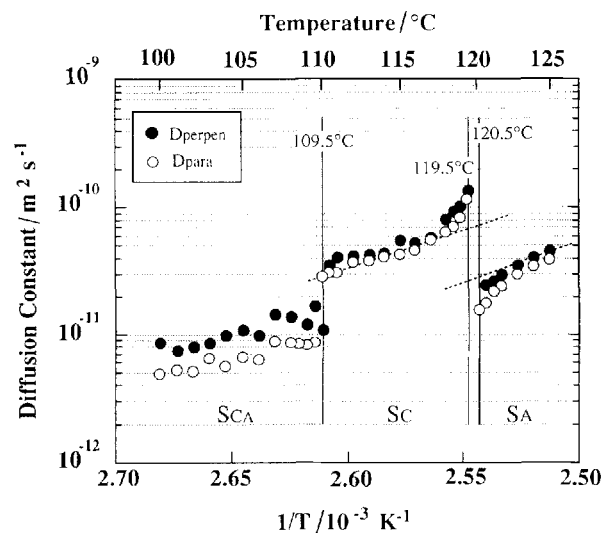

Figure 1.   Temperature dependence of the diffusion constant for MHPOBC.
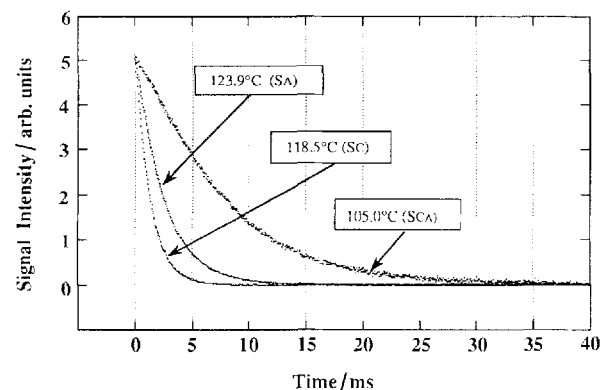

Figure 2.   Typical signal profiles in the S_A, S_C and S_{C_A} phases for MHPOBC.
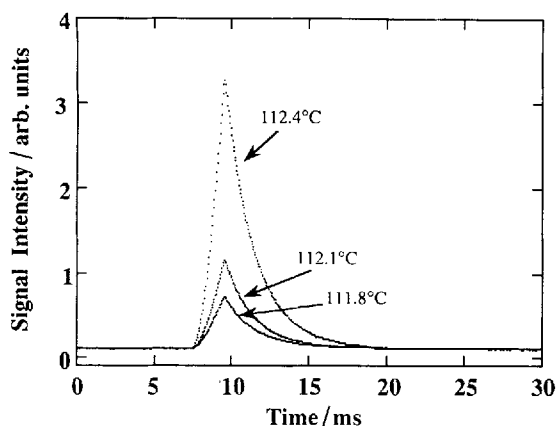
Figure 3. Rapid signal decrease with decreasing temperature in the S_C phase of TFMHPOBC.
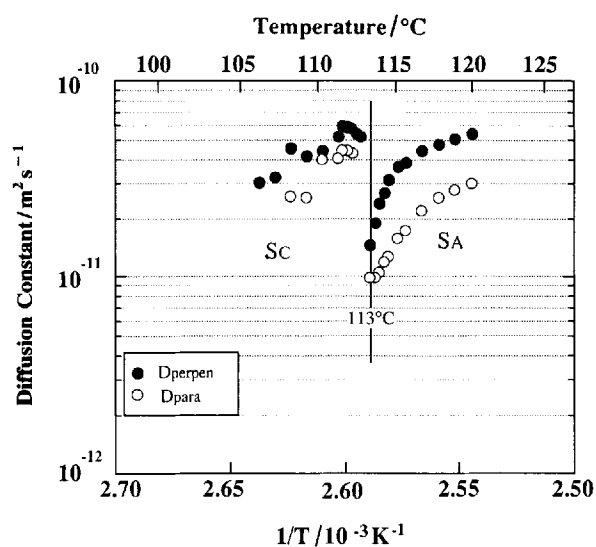

Figure 4. Temperature dependence of the diffusion constant for TFMHPOBC.

than that in the S_A phase. The decay in the S_{C_A} phase is much slower than the other.

The reason why the diffusion constant in the S_C phase is larger than that in the S_A phase is not clear. The fluctuation of the azimuthal angle may promote the diffusion in the tilted S_C phase. The sudden decrease of the diffusion constant at the $T_{S_C-S_{C_A}}$ phase transition is reasonable, since the herringbone molecular orientational structure in the S_{C_A} phase serves as a barrier for the diffusion at least for $D_\parallel$. As for the intralayer diffusion, $D_\perp$'s in the S_C and S_{C_A} phases are expected to be the same. The large difference may be due to the different interlayer correlation in these two phases: the appearance of the S_{C_A} phase has been ascribed to the pairing of molecules in adjacent layers due to dipole interaction [26]. Because of the pairing, the layer tends to be thinner [27], and the

resultant structure suppresses the diffusion of molecules within each layer.

The existence of the temperature range with no data points is due to anomalous signals which will be discussed later. The downward and upward deviations from the Arrhenius type behaviour in the S_A and S_C phases, respectively, may be partly due to the anomalous signals observed in the vicinity of the $T_{S_A-S_C}$ transition temperature. Setting aside the temperature range showing the anomaly, the increase of the diffusion constant in the S_C phase compared with that in the S_A phase is still obvious.

To confirm the anomalous temperature dependence of the diffusion constant in the S_A and S_C phases, the measurements were also carried out in another antiferroelectric liquid crystal, TFMHPOBC. Unfortunately, however, the signal intensity was extremely weak in the lower temperature region, so that the measurements could only be done in the temperatures above the middle of the S_C phase. The signal decrease with decreasing temperature is shown in figure 3.

Figure 4 shows the diffusion constant in the S_A and S_C phases. The downward deviation from the Arrhenius type was observed in S_A in the vicinity of $T_{S_A-S_C}$ transition temperature. In spite of the poor data quality, the upward shift of the overall temperature dependence of the diffusion constant is obvious when the transition takes place from the S_A to the S_C phase. The S_A-S_C phase transition is of the first order in TFMHPOBC, while it is of the second order in MHPOBC. Therefore, the increase of the diffusion constant at $T_{S_A-S_C}$ of antiferroelectric liquid crystals does not depend on the transition order.

The next result is for MHPOCBC, which shows the direct $S_A-S_{C_A}$ transition without passing the S_C phase. Figure 5 shows the temperature dependence of the diffusion constant in MHPOCBC. The temperature dependence is rather smooth and gives no anomaly.

Thus, the anomaly observed in the three antiferroelectric liquid crystals is the unexpectedly large diffusion constant in the S_C phase. We ask if the phenomenon is general for any materials which show a S_A-S_C phase transition or if it is specific in antiferroelectric liquid crystals. To clarify the question, the measurement was also made in the non-chiral 6OBPy8, which shows the N–S_A–S_C phase sequence and has no antiferroelectric phase.

As shown in figure 6, the trend of the temperature dependence of the diffusion constant is smooth, except the behaviour in the phase transition regions. $D_\parallel$ and $D_\perp$ in the nematic (N) phase stand for the diffusion constants parallel and perpendicular to the director, respectively.

The anisotropy, $D_\parallel > D_\perp$, observed in the N phase changes to $D_\parallel < D_\perp$ just below the T_{N-S_A} transition temperature and $|D_\parallel - D_\perp|/(D_\parallel + D_\perp)$ becomes large with decreasing temperature in the S_A phase as is usually the
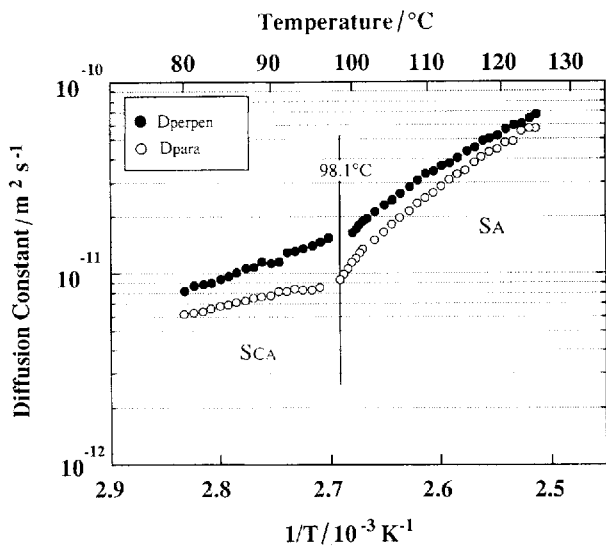
Temperature / °C

Figure 5.   Temperature dependence of the diffusion constant
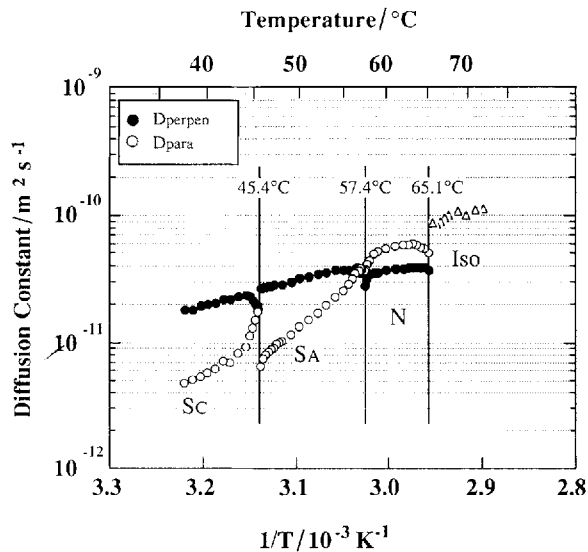for MHPOCBC.

Temperature / °C

Figure 6.   Temperature dependence of the diffusion constant
for 6OBPy8.

case. The tendency continues in the S_C phase except in the
vicinity of the $T_{S_A-S_C}$ transition temperature. Thus, an
abnormal increase in the diffusion constant in the S_C phase
compared with that in the S_A phase was not observed for
the materials which exhibited no antiferroelectric phase.

3.2. *Anomalous signal profiles at the phase transition region*

We observed two anomalies in the vicinity of phase
transition temperatures: the signal intensity becomes large
and sometimes the signal profiles become anomalous
when the transition temperature approaches, though the

signal can otherwise be simulated by a single exponential
curve, as shown in figures 2 and 3. In figure 7, we show
some examples of the anomalous signals observed at
(*a*) $T_{S_A-S_C}$ in MHPOBC, (*b*) $T_{S_A-S_{C_A}}$ in MHPOCBC.

The anomalous signal increase was already seen in the
N phase near the isotropic phase by Hara *et al.* [11], and
was explained by a photostimulated change in the order
parameter, and consequently in the phase transition
temperature. If this change occurs near the phase transition
region where the temperature dependence of the refractive
index is large, the photoinduced modulation of the
refractive index becomes large and gives high diffraction
efficiency.

In the present experimental situation, we produce the
transient grating by the laser irradiation of the crossing
beams. Here, not only the excited stripes but also the
non-excited stripes act as transient gratings, though the
phase is different by 180° to each other. If these two
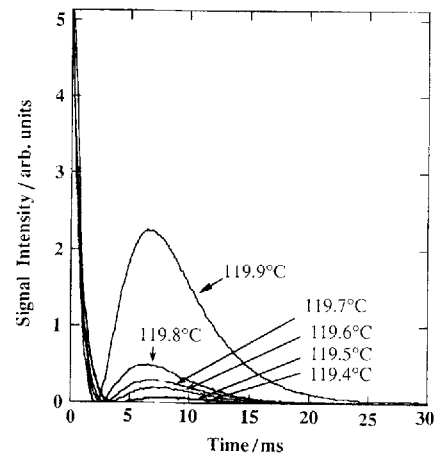
(*a*)
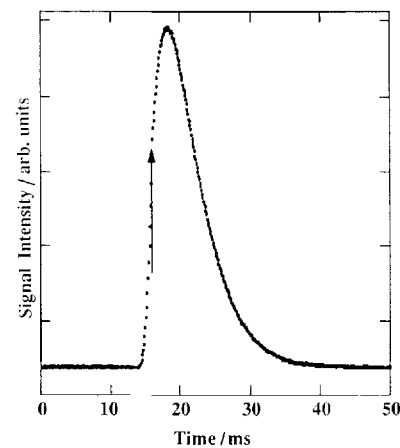
(*b*)

Figure 7.   Anomalous signals observed in the phase transition
region of (*a*) MHPOBC and (*b*) MHPOCBC. The arrow in
(*b*) indicates the time when the light pulse was turned off.

complimentary gratings disappear with the same decay time, we can observe a single exponential decay in the diffraction intensity. However, if the decay times are different, the diffraction intensity is given by

$$I(t) = \left\{ A_1 \exp\left(-\frac{t}{\tau_1} \right) - A_2 \exp\left(-\frac{t}{\tau_2} \right) + B_{coh} \right\}^2 + B_{inc}^2$$

(1)

Here A_i and τ_i ($i = 1$ and 2) are the optical field amplitude and the decay time, respectively, for the two ($i = 1$ and 2) complimentary gratings, and B_{coh} and B_{inc} stand for coherent and incoherent background amplitudes, respectively. Park *et al.* [28], simulated the signal profiles using equation (1), and obtained anomalous signals shown in figure 7: if $A_1 > A_2$, the profiles shown in figure 7 (*a*) are obtained when $\tau_1 < \tau_2$ and that shown in figure 7 (*b*) is obtained when $\tau_1 > \tau_2$.

In our experiments, the anomalous signal rapidly disappears as the temperature moves away from the transition temperature, as shown in figure 7 (*a*). Thus the complimentary grating effect is conspicuous in the vicinity of transition temperatures. This is because the photochemical phase transition takes places in the photo-excited *cis*-rich region, producing a grating of S_A phase in the S_C phase. Since the difference of τs (Ds) in the S_A and S_C phases is very large, as shown in figure 1, we can observe the remarkable complimentary grating effect near the phase transition region.

4. Summary

The diffusion constants were measured in antiferro-electric liquid crystals and a non-chiral smectic liquid crystal. It was found that the diffusion constant in the S_C phase is unexpectedly larger than even that in the S_A phase in antiferroelectric liquid crystals, while the temperature variation is smooth in a non-chiral compound. The discontinuous decrease of the diffusion constant occurs when the transition takes place from the S_C to S_{C_A} phase. The discontinuity in the diffusion constants (of both parallel and perpendicular to the layer normal) was assigned to the molecular rearrangement from the uniformly tilted to the herringbone structure.

Anomalous signal profiles were observed in the phase transition region. They were attributed to the photochemical formation of the complimentary gratings consisting of two phases.

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