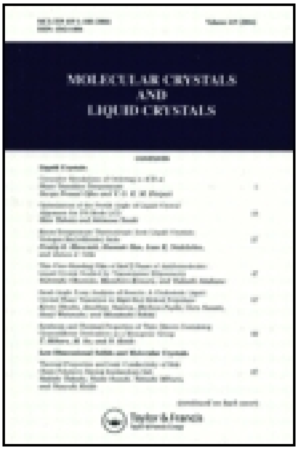

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Anisotropy of Dye Diffusion in Smectic Phases Studied by Forced Rayleigh Scattering

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Version of record first published: 24 Sep 2006.

To cite this article: Takashi Nishikawa , Jiro Minabe , Hideo Takezoe & Atsuo Fukuda (1993): Anisotropy of Dye Diffusion in Smectic Phases Studied by Forced Rayleigh Scattering, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 231:1, 153-161

To link to this article: http://dx.doi.org/10.1080/10587259308032501

Mol. Cryst. Liq. Cryst., 1993, Vol. 231, pp. 153–161
Reprints available directly from the publisher
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Printed in the United States of America

Anisotropy of Dye Diffusion in Smectic Phases Studied by Forced Rayleigh Scattering

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(Received August 7, 1991; in final form October 16, 1992)

We have measured the diffusion constants by means of forced Rayleigh scattering for a variety of mixtures of 4'-*n*-octyloxy-4-cyanobiphenyl (8OCB) and *p*-butoxybenzylidene-*n*-octyl-aniline (4O.8). The anisotropy changes from $D_{\|} > D_{\perp}$ to $D_{\|} < D_{\perp}$, where $D_{\|}$ and $D_{\perp}$ are diffusion constants parallel and perpendicular to the director, respectively, when the ratio, 8OCB:4O.8, changes from 3:5 to 3:17. We cannot find any explicit correlation between the anisotropy change in D and the layer structure; the emergence of the $\mathrm{SmB_{cryst}}$ and the changeover from $\mathrm{SmA_d}$ to $\mathrm{SmA_1}$ occur at a different mixing ratio between 3:1 and 9:11. Thus, the diffusion measurement can tell something in the difference of the smectic layer structure, which cannot be observed by X-ray diffraction.

Keywords: smectic liquid crystal, diffusion constant, anisotropy, forced Rayleigh scattering

1. INTRODUCTION

Since liquid crystals are an anisotropic medium, macroscopic physical quantities exhibit anisotropy. Hence, the study of the anisotropy of these quantities gives information on the degree of orientation, i.e., the orientational order parameter. The nematic phase is symmetric not only for any rotation along the director axis but also for any translation. In contrast, the smectic phase breaks the free translational symmetry and brings about at least one dimensional order, i.e., the smectic layer structure. Therefore, only the information on the degree of orientation is not sufficient to explore the structure of the smectic phase; macroscopic physical quantities which reflect the layer structure must be measured.

Among various physical properties, mass diffusion may be seriously influenced by the formation of layer structure. In the nematic phase, it is well known that a diffusion constant along the director, $D_{\|}$, is larger than that perpendicular to it,

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$D_\perp$.[1-8] In the smectic A phase, we can imagine that $D_\parallel$ tends to be smaller because of the formation of the layer which acts as a potential barrier for mass transport. Consequently, the activation energy for $D_\parallel$ increases and the reversal of the anisotropy, namely $D_\parallel < D_\perp$, is brought about. This is actually the case in many of the smectic A (SmA) phases.[1,9-13] In contrast, however, Takezoe et al.[14] found that $D_\parallel > D_\perp$ even in SmA in 4′-*n*-octyl-4-cyanobiphenyl (8CB) and the activation energies of $D_\parallel$ in SmA and N are almost the same.

In this paper, we report the diffusion constants of a dye molecule in the SmA phases of the mixtures of 4′-*n*-octyloxy-4-cyanobiphenyl (8OCB) and *p*-butoxybenzylidene-*n*-octyl-aniline (4O.8), which show $D_\parallel > D_\perp$ and $D_\parallel < D_\perp$ in each of the SmA phases, respectively. In reference to the X-ray measurements and phase diagram of the mixtures reported,[15] the cause of different anisotropies of the diffusion constants is discussed.

2. EXPERIMENTAL

Among various techniques for measuring the diffusion constant, we adopted the forced Rayleigh scattering (FRS) method. For the measurements, we prepared mixtures of 8OCB and 4O.8 with various mixing ratios containing methyl red (MR) of 0.1 wt%. The materials were sandwiched between two glass plates and aligned homogeneously by the temperature gradient method[16]; a well aligned SmA phase was obtained by decreasing the cell temperature with a gradient parallel to the substrate produced by a local heater. Thus, a single domain SmA larger than 2 × 2 mm was obtained in 25 ~ 100 μm thick cells.

FRS is a kind of microscopic tracer method, which probes diffusion of tracer molecules in host liquid crystals accurately and quickly. Suppose that two laser beams (writing beam) cross 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 life time of cis-MR is sufficiently long compared with the diffusion process,[14] we can determine the diffusion constant of MR by observing the diffraction intensity of a probing laser beam, namely by monitoring the disappearance of the grating.

The experimental setup is almost the same as previously reported.[17] We used an Ar^+ laser (NEC GLG3250, <25 mW, 514.5 nm) as a writing beam and a He-Ne laser (NEC GLG5600, <12 mW, 632.8 nm) as a probing beam. The signal was stored by a transient memory (Kawasaki M-50E) and accumulated and processed by microcomputers (FUJITSU FM7 and EPSON 386S). The signal detected by a photomultiplier tube is described as

$$V(t) = [A \exp(-t/\tau) + B]^2 + C^2 \qquad (1)$$

where B and C stand for the amplitude of the coherent and incoherent scattered field, respectively. It is easy to determine the relaxation time τ by single exponential

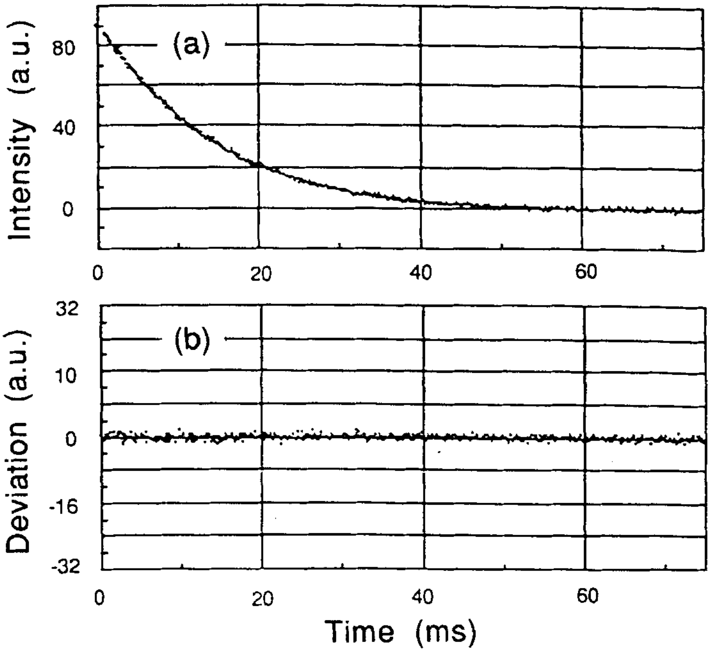


FIGURE 1 Typical signal intensity profile and the deviation between the experimental result and the fitted curve by Eq. (1).

fitting, if either B or C is dominant. Since either of them could not be neglected, four-parameter fitting was performed to determine τ. A typical signal profile and the deviation are plotted in Figure 1, where good four-parameter fitting is shown.

3. RESULTS AND DISCUSSION

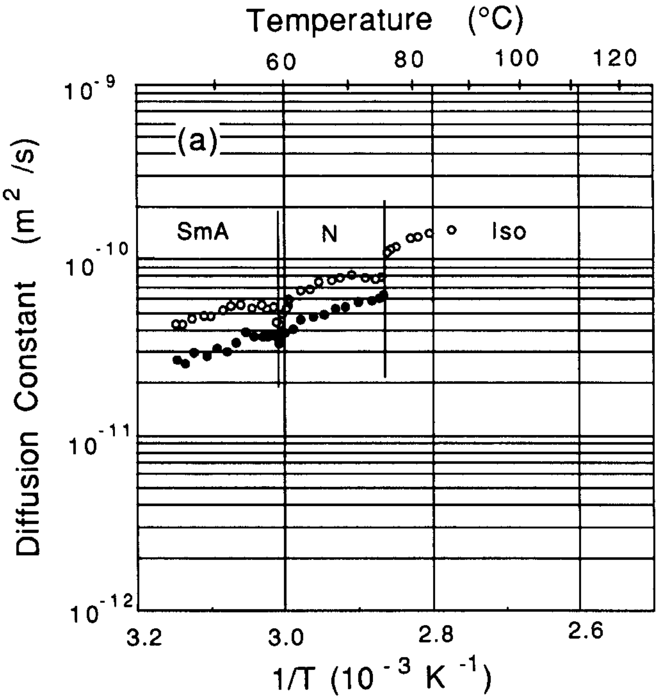
Let us first summarize the characteristics of the base materials, 8OCB and 4O.8. The phase sequences are

8OCB: Cryst – SmA – N – Iso,
4O.8: Cryst – $\mathrm{SmB_{cryst}}$ – SmA – N – Iso.

The main differences are (1) SmA of 8OCB is the bilayer interdigited $\mathrm{SmA_d}$ phase, while that of 4O.8 is the normal monolayer $\mathrm{SmA_1}$ phase, and (2) the $\mathrm{SmB_{cryst}}$ phase exists under the SmA phase in 4O.8, while 8OCB has no other liquid crystalline phases below SmA.

In Reference 18, the different anisotropy of the diffusion constant between nCB and 4O.8 was attributed to either of the above two characteristics, as yet unidentified. The following experimental results will be discussed in relation to the existence of $\mathrm{SmB_{cryst}}$ and the type of SmA phase.

Figure 2 shows the temperature dependence of the diffusion constants, $D_{\parallel}$ and $D_{\perp}$, in various mixtures of 8OCB and 4O.8; (a) 1:0 (8OCB), (b) 7:1, (c) 3:1, (d)



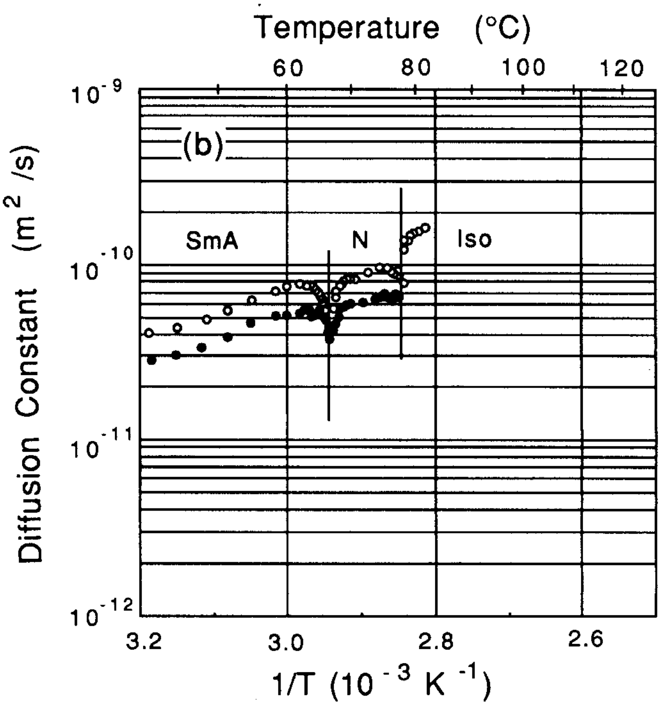


FIGURE 2a and b

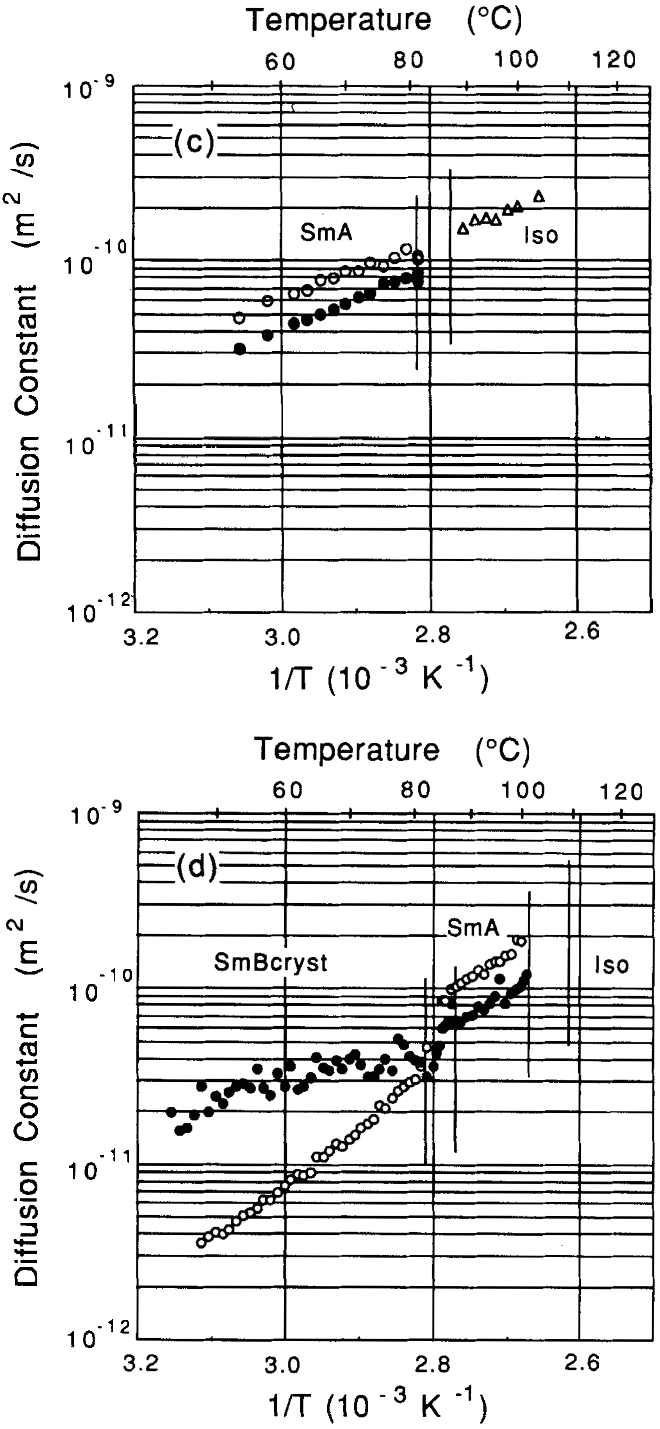
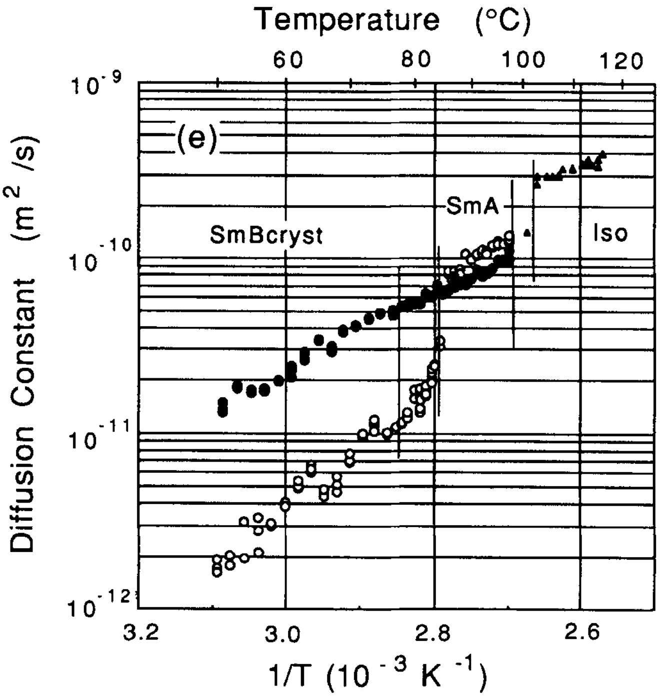


FIGURE 2c and d



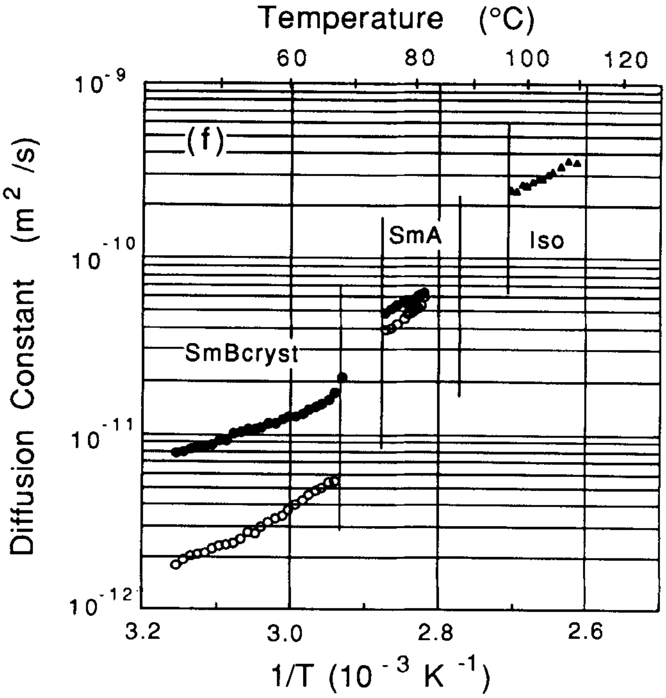


FIGURE 2e and f

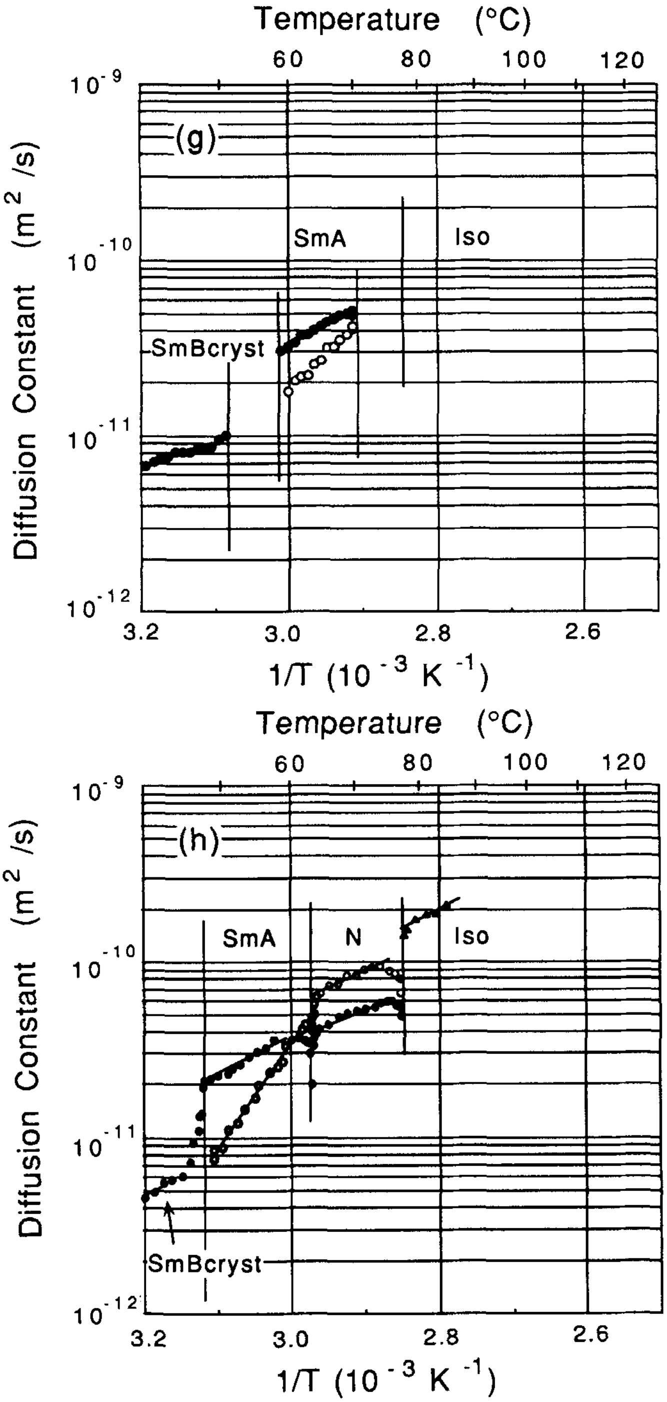


FIGURE 2 Temperature dependence of the diffusion constant for the mixtures of 8OCB and 4O.8, (a) 1:0 (8OCB), (b) 7:1, (c) 3:1, (d) 9:11, (e) 3:5, (f) 3:17, (g) 1:19 and (h) 0:1 (4O.8).

TABLE I

The phase and diffusion characteristics in the mixture of 8OCB and 4O.8

Mixing ratio (8OCB:4O.8)	1:0	7:1	3:1	9:11	3:5	3:17	1:19	0:1
Existence of N	yes	yes	no	no	no	no	no	no
Existence of SmB$_{\text{cryst}}$	no	no	no	yes	yes	yes	yes	yes
Layer struc. of SmA	SmA$_d$	SmA$_d$	SmA$_d$	SmA$_1$	SmA$_1$	SmA$_1$	SmA$_1$	SmA$_1$
$D_{\parallel}/D_{\perp}$ in SmA	1.7	1.5	1.5	1.6	1.3	0.91 ~0.77	0.77 ~0.53	0.77 ~0.36
$E_{\parallel}/E_{\perp}$ in SmA	1.0	1.1	1.0	1.1	1.1	1.3	1.7	3.0

9:11, (e) 3:5, (f) 3:17, (g) 1:19 and (h) 0:1 (4O.8). The result in (b) is essentially the same as that of pure 8OCB in (a); namely $D_{\parallel} > D_{\perp}$ in the SmA phase. The anisotropy in SmA remains the same in (c), where no nematic phase appears. Moreover, the appearance of the SmB phase in (d) does not break the relation $D_{\parallel} > D_{\perp}$ in the SmA phase.

The changeover from $D_{\parallel} > D_{\perp}$ to $D_{\parallel} < D_{\perp}$ occurs between (e) and (f). Two other changes associated with the changeover should be notified. (1) The activation energy for $D_{\parallel}$ becomes larger compared with $D_{\perp}$ as more clearly seen in (g). (2) Not only $D_{\parallel}$ but also $D_{\perp}$ shows a discontinuous change between SmA and SmB$_{\text{cryst}}$. If we take account of in-layer positional order, it is natural that the in-layer diffusion, $D_{\perp}$, shows a discontinuous change at the phase transition point.

In (g) and (h), the anisotropy of the diffusion constants in SmB$_{\text{cryst}}$ becomes so large that we cannot plot the data points of $D_{\parallel}$ in these figures. According to Hara et al.,[18] $D_{\parallel}/D_{\perp}$ in SmB$_{\text{cryst}}$ are 0.028–0.078 depending on temperature, namely $D_{\parallel}$ and $D_{\perp}$ differ by more than one order of magnitude. In this way, the diffusion characteristics are not unique even in the same B_{cryst} phase; the difference can clearly be seen in discontinuity at the phase transition point to SmA and anisotropy.

To exclude a possibility that the SmB$_{\text{hex}}$ phase was misrecognized to be the SmB$_{\text{cryst}}$ phase in (d) and (e), an ordinary wide angle X-ray diffraction measurement, i.e., ($Q_{\parallel}$, 0, 0) scan, using unaligned cells was made. No difference was observed in the X-ray diffraction profiles of all the SmB$_{\text{cryst}}$ phases, supporting the previous phase diagram reported by Cladis.[15] The X-ray diffraction measurement of (1, $Q_{\perp}$, 0) was also made using the similar geometry adopted by Moncton and Pindak[19] to see the interlayer correlation in the SmA phase. No detectable difference was seen except pure 8OCB. Thus, from the viewpoint of the X-ray diffraction study, there are no observable differences in the SmA phases of the various mixtures of 8OCB and 4O.8 nor in their SmB$_{\text{cryst}}$ phases. Nevertheless, the diffusion characteristics change with the mixing ratio.

In Table I are summarized the phase and diffusion characteristics in the mixtures used. It is clear that the two hypotheses previously proposed for the different diffusion anisotropy are not correct; the changeover from bilayer to single layer as well as the appearance of the SmB$_{\text{cryst}}$ occurs between the mixtures of 3:1 and 9:11, although the relation $D_{\parallel} > D_{\perp}$ is preserved there. The correlation is observed between the anisotropy of the diffusion constant, $D_{\|}/D_{\perp}$, and the ratio of the activation energies for $D_{\|}$ and $D_{\perp}$, $E_{\|}/E_{\perp}$. However, it is not clear why the changeovers in $D_{\|}/D_{\perp}$ and $E_{\|}/E_{\perp}$ occur at the same mixing ratio. Anyway, the changeover from $D_{\|} > D_{\perp}$ to $D_{\|} < D_{\perp}$ definitely occurs at a certain mixing ratio. But, we cannot see the explicit correlation to the structure of the smectic layer. In other words, the diffusion measurement can tell something in the difference of the smectic layer structure, which cannot be observed by X-ray diffraction.

4. CONCLUSION

The diffusion constants were measured for a variety of mixtures of 8OCB and 4O.8 by means of forced Rayleigh scattering. The anisotropy of the diffusion constant changes from $D_{\|} > D_{\perp}$ to $D_{\|} < D_{\perp}$ at the mixing ratio (8OCB:4O.8) from 3:5 to 3:17. We cannot see any explicit correlation between the anisotropy change and the layer structure; the emergence of the $\mathrm{SmB_{cryst}}$ and the changeover from $\mathrm{SmA_d}$ to $\mathrm{SmA_1}$ occur at a different mixing ratio between 3:1 and 9:11.

Acknowledgment

This work was partly supported by a Grant in Aid for Scientific Research (#03205045) from the Ministry of Education, Science and Culture. We acknowledge Seiko Epson Corp. for offering us a microcomputer system.

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