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Binary Mass Diffusion Measurements in Nematic and Smectic Liquid Crystals by Forced Rayleigh Scattering

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Binary Mass Diffusion Measurements in Nematic and Smectic Liquid Crystals by Forced Rayleigh Scattering

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The binary mass diffusion constants of methyl red in 8CB were measured in the smectic A, nematic and isotropic phases by forced Rayleigh scattering (FRS). The diffusion constant parallel to the director orientation, $D_{\parallel}$, is always larger than the perpendicular one, $D_{\perp}$, not only in the nematic but also in the smectic phase. The present result $D_{\parallel} > D_{\perp}$ in the smectic phase conflicts with that of methane diffusion, $D_{\parallel} < D_{\perp}$, obtained by NMR. The difference was ascribed not to the different method employed but to the different tracer molecules used. The temperature dependence shows nearly an Arrhenius type, but has sharp dip at T_{AN}. The anomaly was attributed to the formation of cybotactic clusters of a smectic phase in a nematic medium and of a nematic phase in a smectic medium.

1. INTRODUCTION

A self diffusion constant is one of the important parameters to describe the dynamic properties of liquid crystals. The measurements have been performed by several methods such as NMR, neutron scattering and dye tracer methods. Recent development of an NMR spin echo method raises the reliability, but the accurate determination of the diffusion constant is still difficult by this method.[1] The tracer method is a fairly reliable direct method but has a disadvantage that it takes a long time to obtain the diffusion constant. To overcome these problems we have initiated the diffusion measurement by forced Rayleigh scattering.

The forced Rayleigh scattering was first applied to a liquid crystal by Hervet et al.[2] Let us first outline the principle briefly. Two coherent laser beams intersecting in an absorbing medium interfere with each other and form a holographic grating due to a periodic change of refractive index. When pulsed beams are used, a grating is transiently formed and disappears. The disappearance is affected by the intramolecular relaxation of the photoexcited state with the time constant τ_{life} and the translational diffusion with the diffusion constant D. Thus the number of photoexcited state $N(t)$ decreases with the relaxation time τ;

$$1/\tau = 1/\tau_{life} + (4\pi^2/d^2)D, \tag{1}$$

where the fringe spacing d in a sample is expressed by

$$d = \lambda_0/2\sin(\theta/2), \tag{2}$$

where λ_0 is the wavelength in vacuo of the pulsed laser beam (writing beam) and θ the crossing angle in vacuo. The transient grating can be monitored by a third beam using a diffraction method.

We have already measured the binary mass diffusion constants of methyl red in nematogens, MBBA and 5CB by FRS.[3] The temperature dependences showed almost the Arrhenius type except near the nematic-isotropic phase transition temperature. Comparing the results with the self diffusion measurements by NMR spin echo method, we showed that the binary mass diffusion of methyl red serves as a good measure of self diffusion. In this paper, we extend the technique to a smectic phase for the first time to explore the self diffusion especially the anisotropy in the smectic phase. The new experimental findings are two-fold. The diffusion constant $D_{\parallel}$ is always larger than $D_{\perp}$ even in the smectic A phase. There appears a sharp dip at T_{AN} in the temperature dependence of the diffusion constant. The details will be described in the following.

2. EXPERIMENTAL

A host liquid crystal used was 4'-*n*-octyl-4-cyanobiphenyl (8CB) obtained from the sealed container without further purification. The smectic A to nematic transition temperature, T_{AN}, was 33.5° C and the nematic to isotropic one, T_{NI}, 40.8 °C after adding 0.1 wt% methyl red as a tracer molecule which is nearly identical in shape to the host liquid crystal. The excited cis state of methyl red is attained

by 514.5 nm Ar ion laser. Sample cells consisted of two plane parallel microscope slide glass plates, 20 mm × 10 mm × 1 mm, separated by two 100 μm spacers. Those plates were treated by 0.1 wt% aqueous solution of polyvinyl alcohol and rubbed unidirectionally back and forth. A reasonable size homogeneous monodomain cell of the smectic A phase was prepared by decreasing the sample temperature slowly enough from the nematic phase.

The scattering measurements were performed with two coherent pulsed Ar ion laser beams intersecting in a sample cell and the third He-Ne laser beam for reading the transient holographic grating. Our experimental set up was described in our previous papers in detail.[3,4] The output voltage of a photomultiplier tube is written as

$$V(t) = (A \exp(-t/\tau) + B)^2 + C^2, \tag{3}$$

where B and C are the amplitudes of coherently and incoherently scattered fields, respectively. Since we had confirmed that the contribution of B is negligible in our previous paper,[4] the relaxation time τ was determined by plotting the $\log(V(t) - V(\infty))$ against t and by processing with the linear least squares method.

3. RESULTS AND DISCUSSION

The typical signal is shown in Fig. 1 in a linear and log scales. As expected, the log plot gives straight line over two decades. The inverse of relaxation time $1/\tau$ thus obtained is plotted as a function of

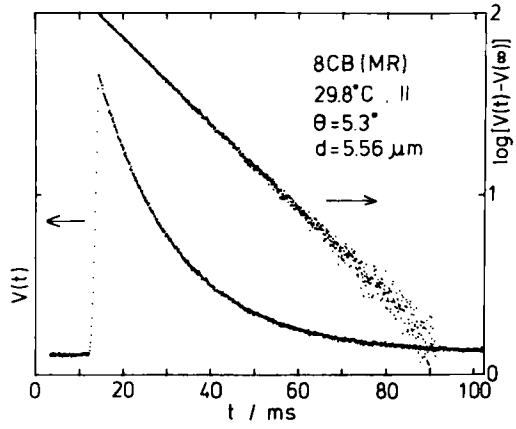

FIGURE 1 Typical signal of the photomultiplier output $V(t)$ in a linear and log scales. Note that $\log(V(t) - V(\infty))$ vs t gives a straight line over two decades.

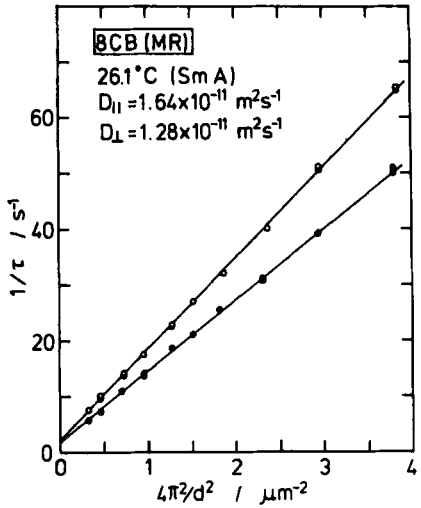

FIGURE 2 Inverse of relaxation time $1/\tau$ vs $4\pi^4/d^2$ in Sm A phase. The slopes give the diffusion constants parallel and perpendicular to the optical axis, showing $D_{\parallel} > D_{\perp}$. The intersections give the lifetime of photoexcited state of methyl red.

$4\pi^2/d^2$ in the smectic A phase in Fig. 2, which certifies the relation given by Eq. (1). The slopes determined by the analysis of the linear least squares fitting give the diffusion constants parallel $D_{\parallel}$ and perpendicular $D_{\perp}$ to the optical axis, respectively. Those straight lines intersect the ordinate at almost the same point which gives $1/\tau_{life}$ for methyl red in 8CB; $\tau_{life} = 0.7 \pm 0.3$ sec.

Two diffusion constants $D_{\parallel}$ and $D_{\perp}$ were thus determined, typically using the results at four crossing angles, as a function of temperature. Temperature dependence of methyl red diffusion in 8CB is given in Fig. 3. It is of the Arrhenius type except near the phase transition temperatures T_{AN} and T_{NI}. The activation energies are listed in Table I. In the figure, two characteristic features should be noticed; sharp dips at T_{AN} and the anisotropy $D_{\parallel}/D_{\perp}$ in the smectic phase. These will be discussed in the following.

As far as we know, it is for the first time that such anomaly is clearly observed in the temperature dependence of the diffusion constant at the transition temperature, although some of the results reported suggest this kind of trend; downward deviation from the Arrhenius type temperature dependence in a nematic phase at T_{NI}[1,5] and even in a smectic phase at T_{AN}.[6] Sharp descent of the present diffusion constant is remarkable in the smectic A and nematic phases near T_{AN} and in the isotropic phase near T_{NI}. In the nematic phase

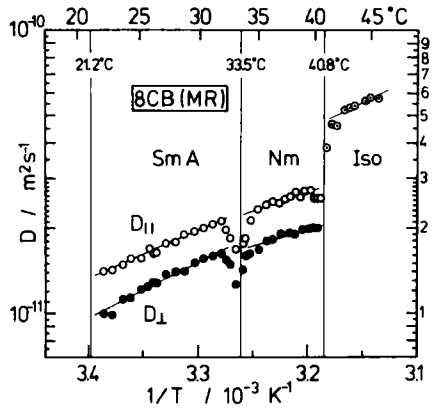

FIGURE 3 Temperature dependence of the diffusion constants of 8CB.

TABLE I

List of activation energies obtained (KJ/mol)

$\Delta E_{\parallel}$(Sm A)	$\Delta E_{\perp}$(Sm A)	$\Delta E_{\parallel}$(Nm)	$\Delta E_{\perp}$(Nm)	ΔE_0(Iso)
33	37	27	23	37

near T_{NI}, only $D_{\parallel}$ exhibits slight downward deviation. These sharp descent in the diffusion constant can be attributed to the formation of cybotactic clusters, i.e., small domains with a local smectic organization in the nematic medium or small local nematic domains in the smectic medium and in the isotropic medium. Such a cybotactic cluster formation was confirmed by several methods: X-ray measurements[7] showed nematics with heavily damped density waves which suggest weak short range smectic-like ordering. Furthermore, many elastic constant measurements[8] in a nematic phase near T_{AN} exhibit a pretransitional effect due to the cybotactic cluster formation. Such cybotactic cluster may appear and disappear occasionally. Then the diffusion may get slower in the environment including the cybotactic clusters. Thus the dip and sharp descent near T_{AN} and T_{NI} may give new evidence for the formation of the cybotactic cluster. The fact in the smectic A phase is specifically worthwhile to notice since this is generally hard to observe.

We now turn to another characteristic observation of the anisotropy in the diffusion constant. In a smectic phase, the diffusion constant $D_{\perp}$ has generally been believed to be larger than $D_{\parallel}$ because of the layered structure. Actually methane diffusion in 8CB obtained

by NMR spin echo method[9] clearly showed $D_{\parallel} < D_{\perp}$ in the smectic A phase. The present result shows $D_{\parallel} > D_{\perp}$ not only in the nematic phase but also in the smectic phase, although the anisotropy $D_{\parallel}/D_{\perp} = 1.3 \sim 1.4$ is smaller in both phases compared with that of MBBA and 5CB which do not have smectic phases below the nematic phases, $D_{\parallel}/D_{\perp} \simeq 1.6$.[3] The fact $D_{\parallel} > D_{\perp}$ in the smectic phase totally conflicts with the methane diffusion. We claim, however, that the difference does not originate from the different method employed but originates from the different tracer molecules used. Actually, according to Krüger et al.,[10,11] the anisotropy of the diffusion constant $D_{\parallel}/D_{\perp}$ seriously changed by the tracer molecules: They showed $D_{\parallel} \ll D_{\perp}$ for a nearly spherical molecule, trichlorotrifluoroethane,[10] while for self diffusion $D_{\parallel} \simeq D_{\perp}$ and even $D_{\parallel} > D_{\perp}$ in high temperature region of the smectic phase.[11] Since methyl red is much more similar in shape and size to a cyanobiphenyl than methane, the diffusion characteristics reflect the self diffusion of a host liquid crystal. Thus the present result $D_{\parallel} > D_{\perp}$ in the smectic phase suggests that the smectic A does not have well defined layered structure but has just a periodic distribution of a density wave of molecules as illustrated by Schaetzing and Litster[12] based on a X-ray analysis. The experiments in well ordered smectic phase such as a smectic B must be interesting and are one of our future problems.

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