FIG. 2. Retardation versus  $E^2$ .

are not perfectly aligned and one sees brighter regions which are slightly biaxial. Under the influence of the electric field, they first become uniaxial and then, at higher field strengths, again biaxial.

The induced birefringence in well aligned films was measured with a Brace-Kohler compensator for small values and by the Senarmont compensation method for larger retardations. The retardation is plotted versus  $E^2$  in Fig. 2. The refractive-index changes are extremely large compared with the changes normally obtainable with Pockels or Kerr materials where similar retardations are only observed with high fields and long light paths.

The role of the polyamide additive is not clear. However, it does not appear unreasonable to speculate that the surfactant properties of the

resin molecules help to foster an alignment in which the elongated axis is normal to the substrate. In some cases especially with very thin evaporated electrodes we obtained small homoeotropic areas with pure ABUTA and the electro-optic effect observed was empirically identical. This indicates that the dopant is not germane to the electro-optic effect but performs a very valuable function by fostering "thick" homoeotropic textures which can be easily measured. Spontaneous homoeotropic alignments have also been described earlier by Chatelain for *p*-azoxyanisole;<sup>9</sup> that author used special chemical or physical cleaning procedures for the substrate.

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## Self-Diffusion and Molecular Order in Lyotropic Liquid Crystals

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The translational self-diffusion coefficients of the H<sub>2</sub>O molecules in the water channels of both hexagonal and lamellar lyotropic liquid crystals have been measured by the variable field-gradient proton spin-echo method, and the temperature dependence of the ordering of D<sub>2</sub>O and H<sub>2</sub>O molecules was studied by quadrupole perturbed deuteron NMR and proton spin-lattice relaxation measurements.

Recent x-ray studies have greatly enhanced<sup>1,2</sup> our knowledge of the structure of the two most common phases—neat and middle—of lyotropic liquid crystals. These systems, which are formed by addition of water to various amphiphil-

ic materials, seem to play an important role in many biological systems including cell membranes. The liquid-crystalline phases are limited by an upper temperature at which the transition to the isotropic liquid occurs, and a lower

one at which ejection of water takes place and an amorphous solid or gel is formed. The neat phase is lamellar and smectic: The hydrocarbon chains are arranged in parallel, equidistant double layers which alternate with intervening layers of water. There is relative freedom of movement of the chains in two dimensions. In the hexagonal middle phase, on the other hand, the hydrocarbon molecules form a two-dimensional lattice of parallel cylinders with intervening water channels and freedom of movement in the third dimension, i.e., along the axis of the cylinders. Whereas the long-range arrangement of the backbone molecules is thus fairly well understood, relatively little is known about the flow properties and molecular order of water in these systems. In the present Letter we report what we believe is the first measurement of self-diffusion coefficients of water in lyotropic liquid crystals as well as a study of the temperature dependence of the ordering of these molecules.

The system studied was sodium palmitate (henceforth designated NaPal) with a varying percentage of heavy or normal water, as the case might be. Both the neat and the middle mesophases were investigated.

The self-diffusion coefficients were measured by the variable field-gradient proton spin-echo method<sup>3</sup> and the quadrupole splitting of the D<sub>2</sub>O deuteron NMR spectrum was used as an indicator of the order of the water molecules. Proton spin-lattice ( $T_1$ ) and spin-spin ( $T_2$ ) relaxation measurements were performed as well on both the palmitate and H<sub>2</sub>O molecules. The main result are as follows:

(i) Deuteron quadrupole coupling.—The temperature dependence of the order in the intervening water channels of lyotropic liquid crystals can be best studied by observing the quadrupole splitting of the deuteron magnetic resonance spectra of the D<sub>2</sub>O molecules. At lower temperatures, where a gel or a coagel is formed, there is no quadrupole splitting of the deuteron line, demonstrating a complete averaging out of the electric field gradient tensor due to isotropic reorientations of the D<sub>2</sub>O molecules. On going to the hexagonal "middle" as well as to the lamellar "neat" liquid-crystalline phase, a quadrupole splitting<sup>4,5</sup> of the deuteron line is observed indicating a preferred average orientation of the D<sub>2</sub>O molecules. The spectrum is of the "powder type" as expected for randomly oriented regions of spin-1 nuclei with a zero asymmetry parameter. The interesting thing is that the quadrupole splitting, and hence the order in the water channels, at first increases with increasing temperature (Fig. 1), stays nearly constant, and then disappears on going to the isotropic liquid. Such a behavior was observed in the hexagonal as well as in the lamellar phase. The quadrupole splitting and hence the molecular order resulting from the coupling between the D<sub>2</sub>O and the palmitate framework increases with decreasing concentration of water. In the 30% NaPal-70% D<sub>2</sub>O system the maximum splitting is

$$(\Delta\nu)_{\max} = \frac{3}{4}(e^2qQ/\hbar)(3\cos^2\theta - 1) \\ = \frac{3}{4}(e^2qQ/\hbar)_D \approx 150 \text{ Hz},$$

whereas  $(\Delta\nu)_{\max} \approx 500 \text{ Hz}$  in the 70% NaPal-30%

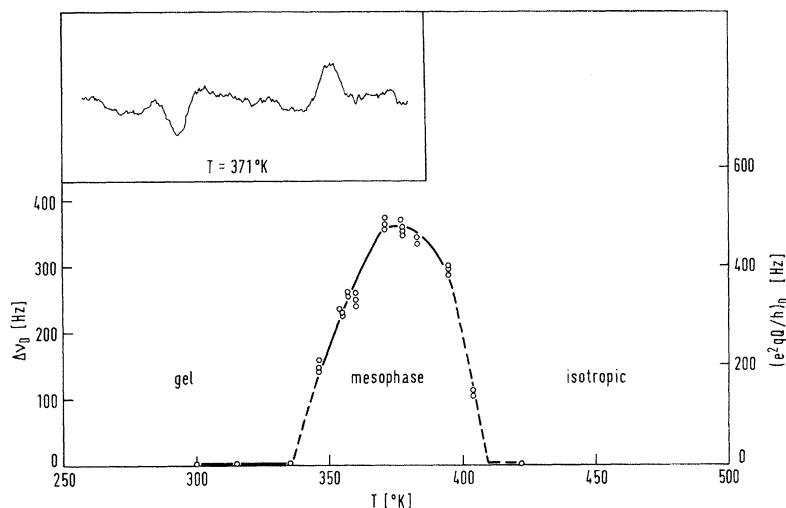


FIG. 1. Temperature dependence of the quadrupole splitting of the D<sub>2</sub>O deuteron magnetic resonance spectrum in the 50% NaPal-50% D<sub>2</sub>O system.

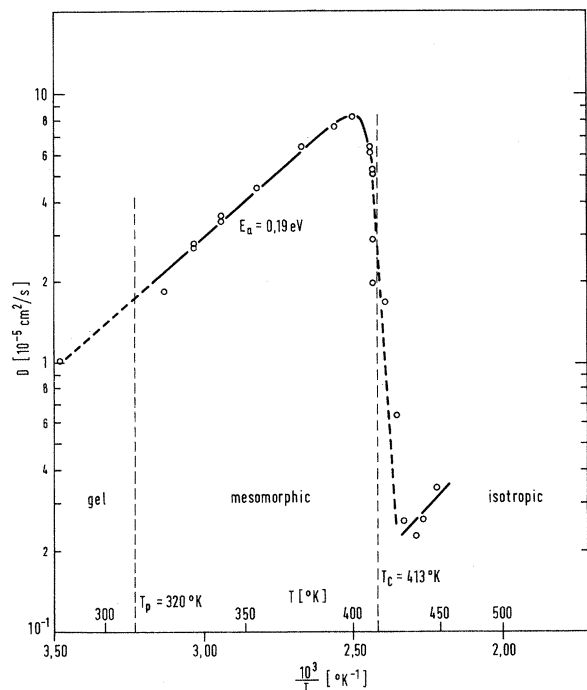


FIG. 2. Temperature dependence of self-diffusion of  $H_2O$  in the 30% NaPal-70%  $H_2O$  system.

$D_2O$  system. Here  $e^2qQ/h$  is the  $D_2O$  deuteron quadrupole coupling constant which is of the order of 200 kHz in ice and  $\theta$  is the angle between the applied magnetic field and the direction of the largest principal axis of the electric field gradient tensor which is a function of time due to molecular motion. The rather small value of  $\langle 3 \cos^2\theta - 1 \rangle$  demonstrates that the anisotropy of  $D_2O$  motion, which makes the time average of  $3 \cos^2\theta - 1$  different from zero, is slight.

At higher temperatures a central component appears in the spectrum indicating the formation of "isotropic" defects and penetration of water into the palmitate framework. The intensity of this component which is absent at lower temperatures greatly increases on approaching the isotropic liquid-phase boundary.

(ii) Self-diffusion of water. — The temperature dependences of the translational  $H_2O$  self-diffusion coefficients  $D$  in the water channels of hexagonal "middle" and lamellar "neat" lyotropic liquid crystals are shown in Figs. 2 and 3, respectively. In both cases the diffusion coefficients exponentially increase with increasing temperature before dropping on going to the isotropic liquid. This is in sharp contrast to the case of nematic para-azoxyanisole where  $D$  was found to be independent of temperature<sup>6</sup> over the whole

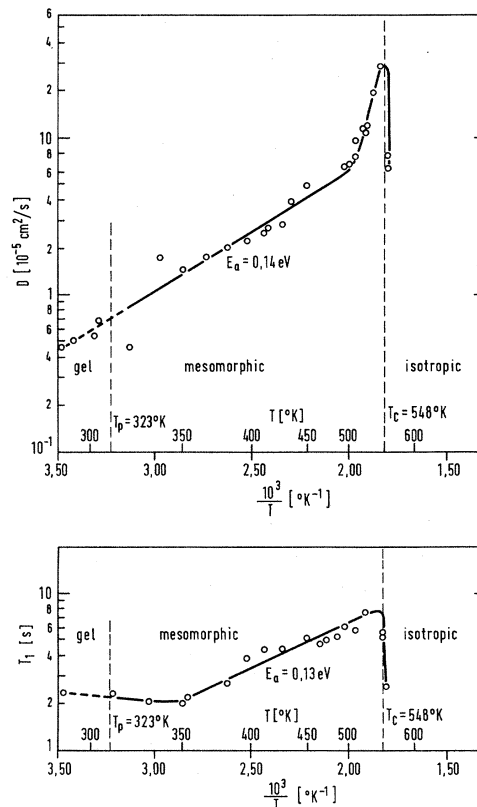


FIG. 3. Temperature dependence of  $H_2O$  self-diffusion  $D$  (upper) and proton spin-lattice relaxation time  $T_1$  (lower) in the 70% NaPal-30%  $H_2O$  system.

liquid-crystal range. The diffusion coefficients are quite large. In the hexagonal 30% NaPal-70%  $H_2O$  system, for instance, at 350°K they are lower only by a factor of 3 than the ones measured in pure  $H_2O$ , and larger by an order of magnitude than the ones found in the zeolites. The magnitude of the diffusion coefficients decreases with decreasing  $H_2O$  content. The diffusion coefficients of the NaPal molecules in the mesophases were too small to be measured with the NMR method.

A tentative explanation of the anomalous drop in the  $H_2O$  self-diffusion coefficient on going from the mesophase to the isotropic liquid is as follows: In the isotropic liquid, an average  $H_2O$  molecule is associated with the NaPal group for a fraction  $p$  of the time of observation in the experiment, so that the self-diffusion coefficient  $D$  can be written as

$$D = D_{NaPal}p + D_{H_2O}(1-p), \quad (1)$$

where  $D_{H_2O}$  represents the self-diffusion coefficient in pure water. As  $p$ —which also represents the average fraction of bound water mole-

cules—is close to 1 in the isotropic liquid, we have  $D \approx D_{\text{NaPal}}$ , i.e., the diffusion rate in the isotropic solution is controlled by the mobility of the NaPal groups. This conclusion has been directly verified by a measurement of the self-diffusion coefficient of the NaPal molecules in a 30% NaPal–70% D<sub>2</sub>O system, where we found exactly the same  $D$  values as in a 30% NaPal–70% H<sub>2</sub>O solution at the same temperature in the isotropic phase.

In the mesophase, on the other hand, the translational mobility of the NaPal groups is much lower than in the isotropic liquid, so that  $D_{\text{NaPal}} \ll D_{\text{H}_2\text{O}}$  and  $D \approx (1-p)D_{\text{H}_2\text{O}}$ . The abrupt decrease in  $D$  on going from the mesophase to the isotropic liquid thus seems to reflect a change in  $p$ .

The proton spin-lattice relaxation time  $T_1$  of the H<sub>2</sub>O molecules in the mesophases is diffusion controlled (Fig. 3). The water molecule spin-spin relaxation time  $T_2$  exhibits an identical temperature dependence to that of  $T_1$ . Its value increases for the 30% NaPal–70% H<sub>2</sub>O system from 1.6 sec at 320°K to 5.6 sec at 410°K. It abruptly decreases to about 0.5 sec on going to the isotropic-liquid phase. The  $T_2$  measurements were made by a Carr-Purcell sequence and the re-

sults were extrapolated to zero pulse spacing.<sup>7</sup> The fact that  $(T_2)_{\text{H}_2\text{O}}$  differs from  $(T_1)_{\text{H}_2\text{O}}$  in the liquid-crystalline state ( $T_1/T_2 = 2$  in the above system) demonstrates a preferred average orientation of the H<sub>2</sub>O molecules in the water channels similarly as this was found for the D<sub>2</sub>O molecules.

For the NaPal protons, on the other hand,  $T_1/T_2 = 10^2$ – $10^4$  in the liquid crystalline state, demonstrating the much smaller freedom of motion of the backbone molecules as compared with the relatively free H<sub>2</sub>O molecules.

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## Inverse Faraday Effect in a Plasma

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We have shown experimentally that a magnetic field is created by the electrons of a plasma subjected to high-power pulses of circularly polarized microwaves. The experimental results confirm the predictions concerning this phenomenon, known as the inverse Faraday effect.

The existence in solids of an inverse Faraday effect (IFE) (excitation of a magnetic field by a circularly polarized wave) has been theoretically predicted<sup>1</sup> and experimentally demonstrated.<sup>2</sup> We have studied the same effect in a plasma.

Under the influence of the electric field  $E_0$  of a circularly polarized wave with angular frequency  $\omega$ , the electrons of a plasma describe circular orbits with frequency  $\omega/2\pi$ ; each electron thus has a magnetic moment and the sum of these electrons creates an induced magnetic field<sup>3</sup> whose value per unit volume is

$$B = (e/2mc^2)(\omega_p^2/\omega^2)E_0^2 = \alpha E_0^2, \quad (1)$$

where  $e$  and  $m$  are, respectively, the electronic

charge and mass;  $c$ , the speed of light in vacuum;  $\omega_p$ , the electronic angular plasma frequency ( $\omega_p^2 = n_e e^2/m\epsilon_0$ ); and  $n_e$ , the electronic plasma density. This shows that  $\partial B/\partial t$  results from the sum of the electronic density variation and the variation of the electric field inside the plasma.

In (1) the effects of the polarization of the plasma have been neglected; when such effects are taken into account one finds<sup>3</sup> that in the limit of small magnetic fields,  $B$  is given by

$$B = (\alpha/N)E_0^2, \quad (2)$$

where  $N^2 = 1 - \omega_p^2/\omega^2$  is the refractive index of the medium.

Note that for  $\omega \approx \omega_p$ ,  $N$  goes to zero (neglecting