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

Self-diffusion in Liquid Crystals

R. Blinc [a] , V. Dimic [a] , J. Pirš [a] , M. Vilfan [a] & I. Zupanšiš [a]
[a] University of Ljubljana Institute "J. Stefan", Ljubljana, Yugoslavia

Version of record first published: 28 Mar 2007.

To cite this article: R. Blinc , V. Dimic , J. Pirš , M. Vilfan & I. Zupanšiš (1971): Self-diffusion in Liquid Crystals, Molecular Crystals and Liquid Crystals, 14:1-2, 97-113

To link to this article: http://dx.doi.org/10.1080/15421407108083560

Molecular Crystals and Liquid Crystals. 1971. Vol. 14, pp. 97–113

Printed in Great Britain.

Self-diffusion in Liquid Crystals†

R. BLINC, V. DIMIC, J. PIRŠ, M. VILFAN and I. ZUPANČIČ

University of Ljubljana
Institute "J. Stefan"
Ljubljana, Yugoslavia

Received November, 16, 1970; *in revised form December* 28, 1970

Abstract—The temperature dependence of the diffusion coefficients in PAA, anisalazine, 4,4'-diheptyloxy-azoxybenzene, anhidrous Na-palmitate and Na-palmitate-water mixtures has been studied by quasi-elastic scattering of cold neutrons and by the variable gradient proton spin echo method.

Introduction

The most basic property of liquid crystals is that they flow while sustaining an ordered structure. Very little however is known on the nature of this process on a molecular basis, and only recently the first attempts have been made to measure diffusion coefficients in nematic systems.(1,2)

To throw some additional light on this problem we decided to measure the temperature dependence of the diffusion coefficients in some thermotropic and lyotropic liquid crystals. Systems exhibiting nematic as well as smectic ordering were included in our study.

The methods used were quasi-elastic incoherent cold neutron scattering and variable field gradient proton spin echo measurements. It should be stressed that whereas in the spin echo method the true translational self-diffusion coefficient is measured, quasi-elastic cold neutron scattering is sensitive to both translational and rotational motions of the molecules.(3) Whereas the measuring period in NMR diffusion measurements is typically $10^{-3} - 10^{-2}$ sec, neutron scattering detects diffusive motions which occur in a time of about 10^{-11} sec.

The cross section for quasi-elastic cold neutron scattering may be approximated by a Lorentzian line with a half-width that depends on the true self-diffusion coefficient describing the translational motion

---

† Presented at the Third International Liquid Crystal Conference in Berlin, August 24–28, 1970.

of the molecular center of gravity, and on another coefficient describing the proton motion relative to the center of gravity. This relative motion can be rotation or rotational diffusion, which may occur in small steps or in large jumps. It is expected that in systems of low viscosity the translational term is dominant whereas in high viscosity systems the width of the quasi-elastic peak will be determined by rotational diffusion. Following Larsson,$^{(4)}$ the asymptotic quasi-elastic line width is in the limit $K^2 \rightarrow \infty$ given by

$$(\Delta\omega)_{K^2\rightarrow\infty} = 2\left(\frac{1}{\tau_0} + \frac{2}{3}D_pK^2\right) \tag{1}$$

whereas it is in the limit $K^2 \rightarrow 0$ given by:

$$(\Delta\omega)_{K^2\rightarrow 0} = 2 \cdot \text{``}D\text{''} \cdot K^2. \tag{2}$$

Here $\hbar K$ is the momentum transfer in the scattering process, τ_0 is the time the molecule spends in a quasi-stable position before jumping to a new state or site, D_p is the coefficient describing the protonic rotational diffusion on the surface of a sphere around the molecular center of gravity, and

$$\text{``}D\text{''} = D + D_{\text{rel}} + D_{\text{mix}} \tag{3}$$

is an apparent diffusion coefficient which is a sum of the true self-diffusion coefficient D, a fictitious coefficient $D_{\text{rel}} \geqslant D_p$ describing the motion of the average proton relative to its molecular center of gravity and a small mixture term, D_{mix}, between the relative motion and the center of gravity motion.

The NMR spin echo method$^{(5)}$ for the determination of the diffusion coefficient, on the other hand, is based on the observation of an extra damping of the transverse nuclear magnetization due to a change in the Larmor frequency as a result of translational diffusion of the molecule across the inhomogeneous applied magnetic field. Rotational diffusion does not result in a significant change in the proton Larmor frequency during the time of the experiment and is therefore not observable.

The spatial dependence of the applied magnetic field across the sample can be described as

$$H_z = H_0 + (\mathbf{G} \cdot \mathbf{r}) \tag{4}$$

where $\mathbf{G}$ can be assumed to be a constant. The equation of motion$^{(6)}$

of the transverse magnetization $m = M_x + iM_y$ precessing in the $x-y$ plane after a 90° pulse is

$$\frac{\delta m}{\delta t} = i\omega_0 m - \frac{m}{T_2} - i\gamma(\mathbf{G}\cdot\mathbf{r})m + \nabla\cdot D\cdot\nabla m \tag{5}$$

where $\omega_0 = \gamma H_0$ is the unperturbed Larmor frequency, T_2 is the spin-spin relaxation time, and D is the self-diffusion constant tensor. The solution of this equation is particularly simple for a time independent field gradient $\mathbf{G}$. After a refocusing 180° pulse applied at a time τ after the 90° pulse, we obtain:

$$m(t) = m_0 \exp\left[i\omega_0 t + i\gamma(\mathbf{G}\cdot\mathbf{r})(t-2\tau) - \left(\frac{\gamma^2\mathbf{G}\cdot D\cdot\mathbf{G}t^3}{12} + \frac{t}{T_2}\right)\right] \tag{6}$$

Expression (6) predicts the formation of a spin echo at a time $t = 2\tau$ the amplitude of which depends on the applied field gradient and the self-diffusion constant D. By measuring the amplitude of the echo as a function of the applied field gradient or by varying t at fixed G we thus obtain D.

All molecular displacements between the 90° and 180° pulse contribute to the attenuation of the echo in the above method. In order to limit the diffusion time as well as to be able to use larger field gradients, it is often useful(6) to apply the gradient in the form of two very short pulses of width δ the first of which is applied after the 90° and the second after the 180° pulse. We thus have a procedure to detect motion in the interval Δ between the two pulses. The additional attenuation of the echo due to molecular diffusion in this interval Δ is easily obtained from Eq. (5) and is given by

$$m(\Delta) = m_0 \exp\left[-\gamma^2\delta^2\mathbf{G}\cdot D\cdot\mathbf{G}\Delta\right]. \tag{7}$$

Equation (7) reduces in the case of isotropic diffusion to the well-known expression:

$$m(\Delta) = m_0 \exp\left[-\gamma^2\delta^2 G^2 D\Delta\right]. \tag{8}$$

Experimental Procedure

The quasi-elastic broadening of the Be-filtered neutron beam has been measured with the time of flight spectrometer on line with a CDC 1700 computer at the Triga Mark II reactor in Ljubljana at the angles $\delta = 24°, 51°, 76°$ and $110°$. The corresponding momentum transfer in the scattering process is $K = 4\pi/\lambda_0 \sin \delta/2$ where $\lambda_0 = 3.96$ Å. A liquid methane cold neutron source in the tangential channel has been used. The samples were placed into a cylindrical container. The thickness of the samples was such that the transmission was about 90%. The temperature was measured with three copper-constantan thermocouples to ± 1 °C. No attempt was made to orient the samples so that only the average of the diffusion constant tensor was obtained in neutron scattering.

The NMR diffusion measurements were performed on a home built pulsed spectrometer operating at 37 MHz. A constant as well as a pulsed field gradient was used. Unless otherwise stated the component of the D tensor parallel to the magnetic field, $D_{\parallel}$, was measured.

Results

(1) P-azoxyanisole (PAA): A typical dependence of the broadening of the quasi-elastic neutron peak on the square of the momentum transfer for nematic PAA is shown on Fig. 1a. The results shown on this figure were obtained after the inelastic background—centered at 12 cm^{-1} and probably representing —CH_3 rotation—was subtracted. It can be clearly seen that no horizontal saturation value is approached. The slope of the tangent to the curve at high momentum transfers gives the rotational contribution, $4/3\ D_p$, and the intersection of the tangent with the $\Delta\omega$ axis gives $2/\tau_0$. The slope of the line width curves near the origin ($K^2 \rightarrow 0$) on the other hand gives the apparent diffusion coefficient 2 "D". At 120 °C we thus obtain $\tau_0 = 2.5 \times 10^{-12}$ sec, $D_p = 1.6 \times 10^{-6}$ cm²/sec and "D" $= (0.75 \pm 0.5) \times 10^{-5}$ cm²/sec. The pure rotational contribution thus seems to represent only a small part of "D".

The temperature dependence of the quasi-elastic broadening is quite puzzling.

In the solid phase from room temperature up to 112 °C no quasi-elastic broadening could be observed demonstrating that "D" is lower than 10^{-6} cm²/sec.

In the nematic phase, on the other hand, there is a very distinct broadening. Contrary to expectations, however, the momentum transfer dependence of the broadening was found to be identical at

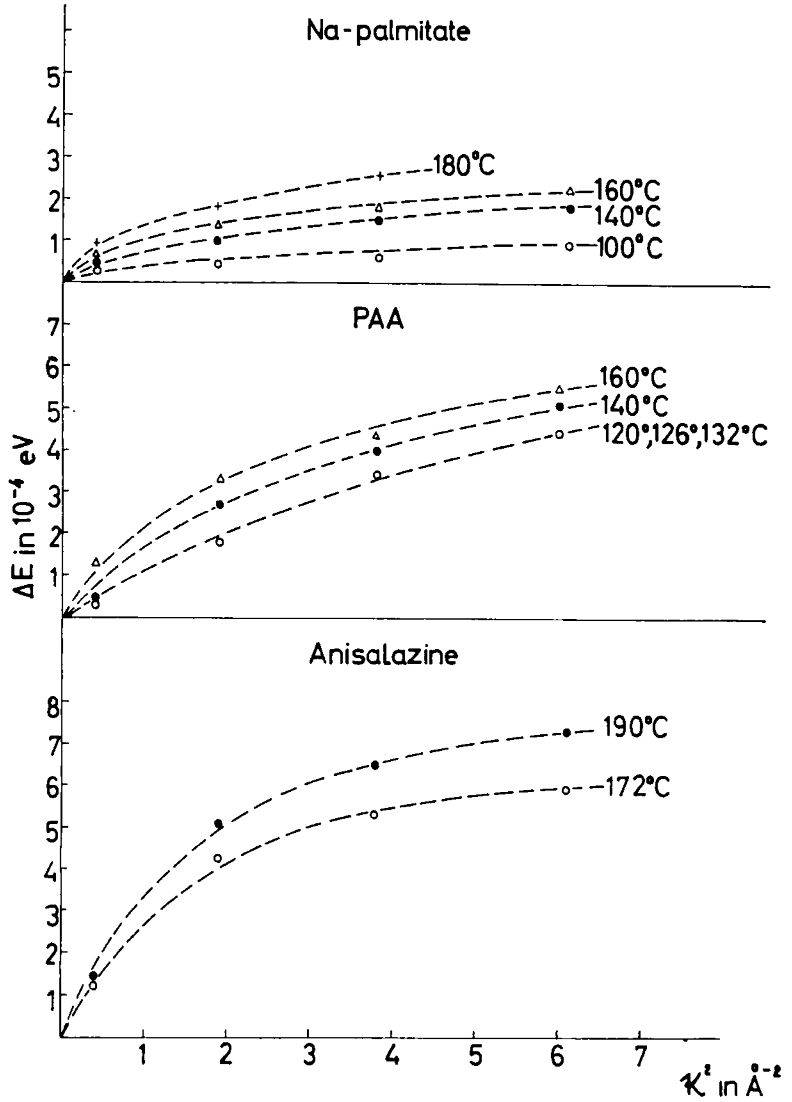


Figure 1. Quasi-elastic broadening of the incoherently scattered cold neutron line in (a) Na-palmitate, (b) PAA and (c) anisalazine as a function of the square of the momentum transfer.

120 °C, 126 °C and 132 °C. The apparent diffusion coefficient "D" thus does not seem to depend on temperature in nematic PAA (Fig. 2).

In the isotropic liquid phase the diffusion coefficient "D" exponentially increases with increasing temperature. Both the value and the activation energy $E = 8$ kcal/mol are rather close to the ones obtained by the proton spin echo method.(1) This means that in liquid PAA, "D" is determined by the translational contribution. The value of $D_{\parallel}$ measured by the proton spin echo method in the liquid-like region right below the nematic-liquid transition is somewhat higher than "D" obtained from the neutron scattering data. This might be due to the anisotropy of the diffusion constant tensor. Preliminary measurements in nematic PAA have namely shown that $D_{\parallel} > D_{\perp}$.

It should be mentioned that the value of the translational self-diffusion coefficient D obtained from the Einstein equation

$$D = \frac{kT}{6\pi r\eta} \tag{9}$$

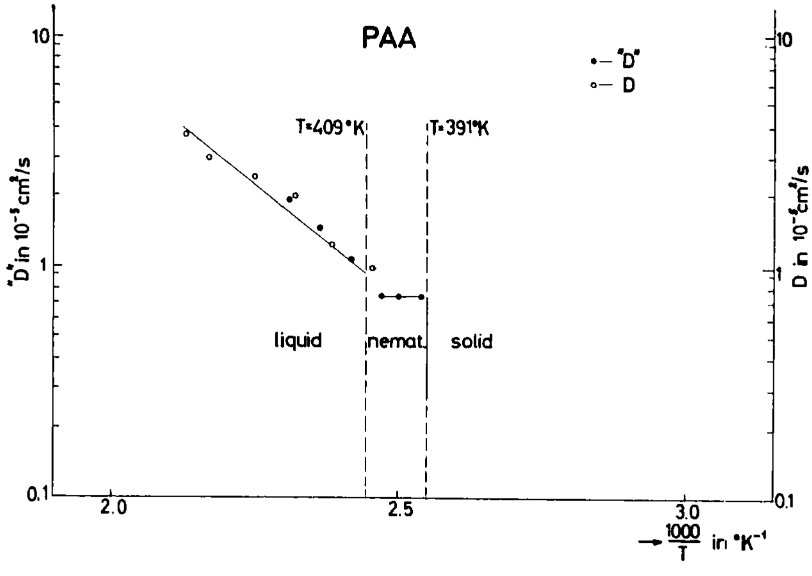


Figure 2. Temperature dependence of the diffusion coefficients in PAA. "D" is the apparent diffusion coefficient obtained from the neutron scattering data as $K \to 0$, and D is the self-diffusion coefficient determined by NMR.

is by a factor of ten smaller than "D" or D as determined by neutron scattering respectively NMR measurements. As PAA is far from being a spherical molecule for which Eq. (9) is valid, this discrepancy is not too serious.

One way to explain the temperature independence of "D" in the nematic phase would be to assign "D" as being due to rotation of the PAA molecules around their principal symmetry axes. Such motion is known to occur in nematic PAA. Within this model it is however hard to understand the relatively good agreement between the NMR and neutron scattering data.

Alternatively one could explain the temperature independence of "D" by the fact that the components of the D tensor have opposite temperature dependences as is this indeed the case for the viscosity coefficients.(7)

A definite explanation of the above results and in particular of the puzzling temperature independence of "D" in the nematic phase has to be postponed until the temperature behavior of all the elements of the diffusion constant tensor is known. Work along these lines is in progress.

(2) Anisalazine: The neutron scattering results for this compound which exhibits a nematic phase between 168 °C and 182 °C are rather similar to the ones obtained for PAA. The value of "D" does not depend on temperature in the nematic phase and equals to "D" = 1.3×10^{-5} cm²/sec. The value of D_p at 172 °C is 2.4×10^{-6} cm²/sec. In the liquid region a normal thermally activated diffusion rate is observed (Fig. 3). The NMR results seem to agree with the neutron data in the isotropic liquid just above the nematic region.

(3) 4,4'-Diheptyloxy-azoxybenzene (PAH): This compound which is a higher homologue of PAA, exhibits a smectic mesophase between 65° and 89 °C and a nematic one between 89 °C and 118 °C. The neutron scattering results are again very puzzling: "D" is temperature independent *throughout* the smectic and the nematic phase (Fig. 4). Its value is "D" $= (0.5 \pm 0.05) \times 10^{-5}$ cm²/sec. D_p, on the other hand, equals 3×10^{-6} cm²/sec in the smectic phase and significantly changes on going to the nematic region. In the liquid phase above 118 °C we again find a normal, thermally activated temperature dependence of "D". The self-diffusion coefficients D, determined by NMR, agree rather well with the neutron data.

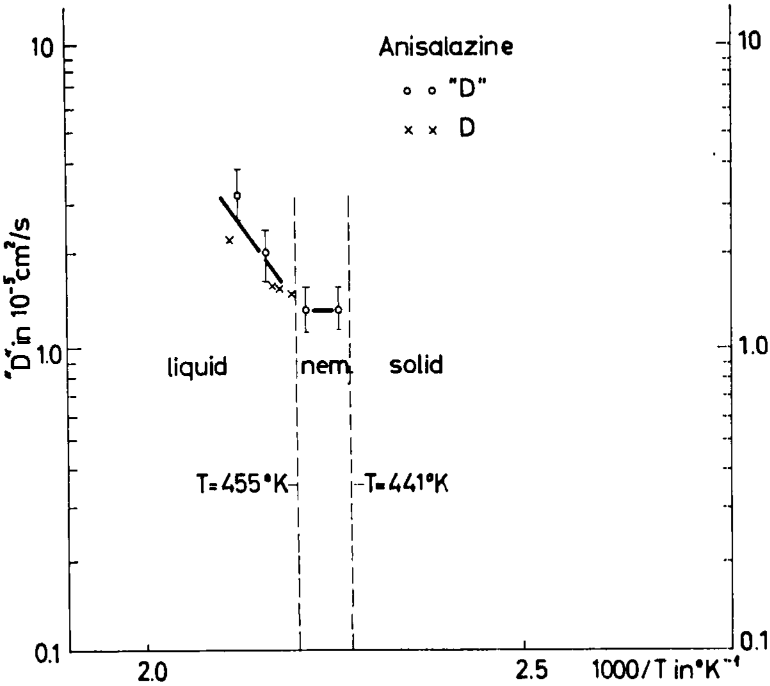


Figure 3. Temperature dependence of the diffusion coefficients in anisalazine.

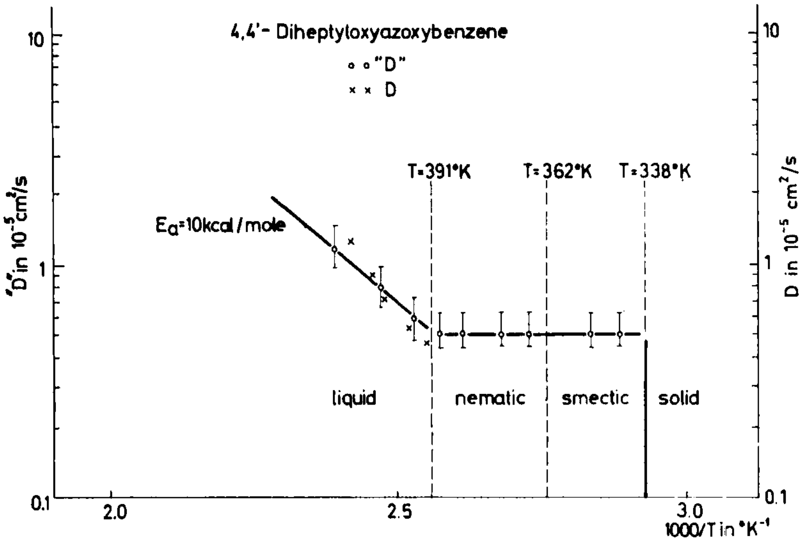


Figure 4. Temperature dependence of the diffusion coefficients in 4,4'-diheptyloxy-azoxybenzene (PAH).

To throw some additional light on these surprising results we measured the Zeeman and the dipolar (Fig. 5) proton spin-lattice relaxation times as a function of temperature. The Zeeman relaxation time measured at $\omega_0/2\pi = 37$ MHz is rather long in the solid phase and drops abruptly on going to the smectic phase, where it continues to increase with increasing temperature throughout the smectic and nematic phase until leveling off just before the nematic-liquid transition. On going to the liquid phase, there is again a discontinuous drop in T_1, followed by an exponential increase with increasing temperature in the liquid phase.

The dipolar proton spin-lattice relaxation time T_{1D}, on the other hand, shows a different behavior. It decreases with increasing temperature in the solid and discontinuously increases on going to the smectic mesophase, where it exponentially increases with increasing temperature. This means that the characteristic time τ for diffusion—which, however can be of rotational or translational origin—is longer than 10^{-4} sec in the solid and shorter than that in the smectic mesophase, where it behaves like $\tau = \tau_0 \exp(E/kT)$. In the nematic mesophase, on the other hand, T_{1D} is practically temperature independent, and by a factor of 4 shorter than T_1. Whether T_{1D} is in the nematic phase dominated by order fluctuations or by diffusion is still an open question. Here as well as in PAA, measurements of the anisotropy of the diffusion constant tensor might help to solve this problem.

(4) Anhidrous Na-palmitate (NaP): To see whether the surprising temperature independence of "D" is limited to homologues of PAA or whether it is a more general characteristic of liquid crystals we decided to investigate anhidrous NaP which is known to undergo five different smectic liquid crystal transitions(8) before melting.

In contrast to the previous cases "D" was found to be exponentially dependent on temperature (Fig. 6), and varied between 10^{-6} cm^2/sec in the "subcurd" and 10^{-5} cm^2/sec in the "superwaxy" phase. Because of the too large broadening of the quasi-elastic peak, "D" could not be measured at higher temperatures. An estimate of D_v and of the mean square displacements obtained from the Debye-Waller factor shows that the translational contribution to "D" is very small.

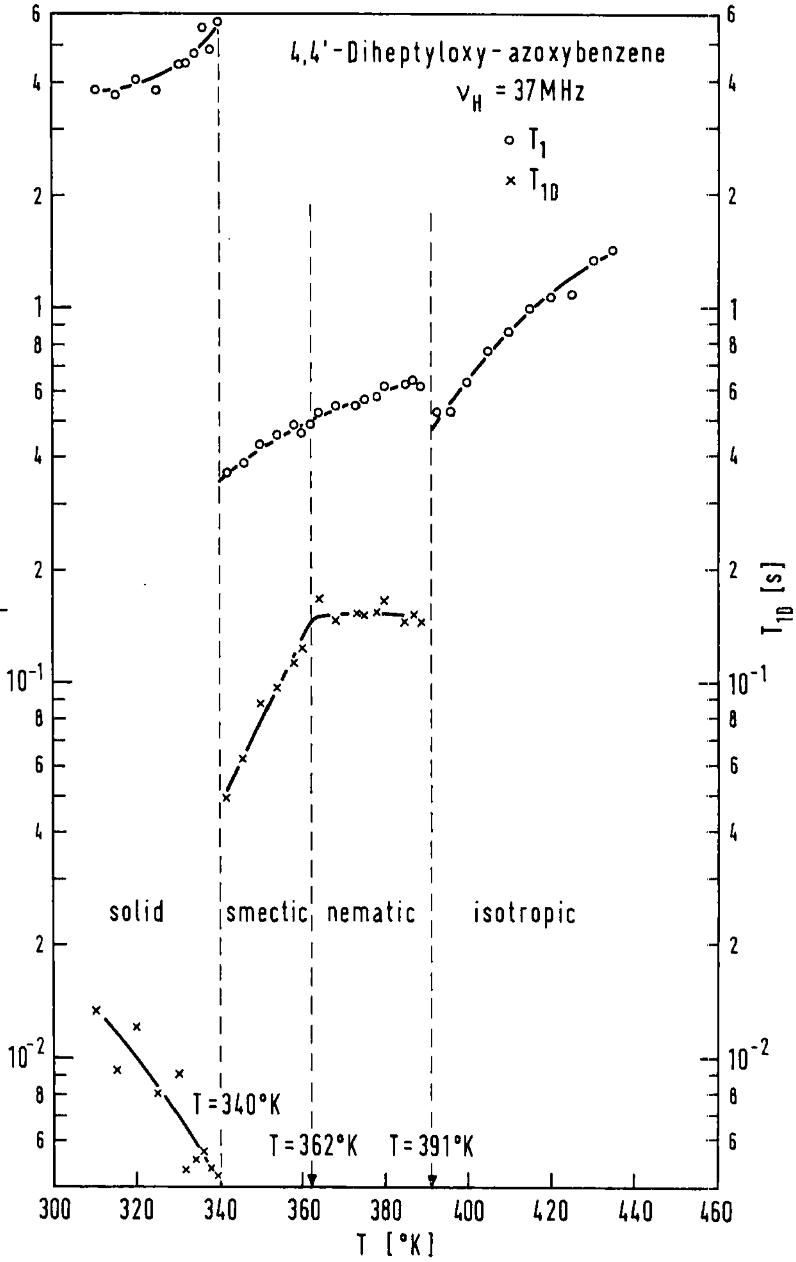


Figure 5. Temperature dependences of the Zeeman and dipolar proton spin-lattice relaxation times in PAH.

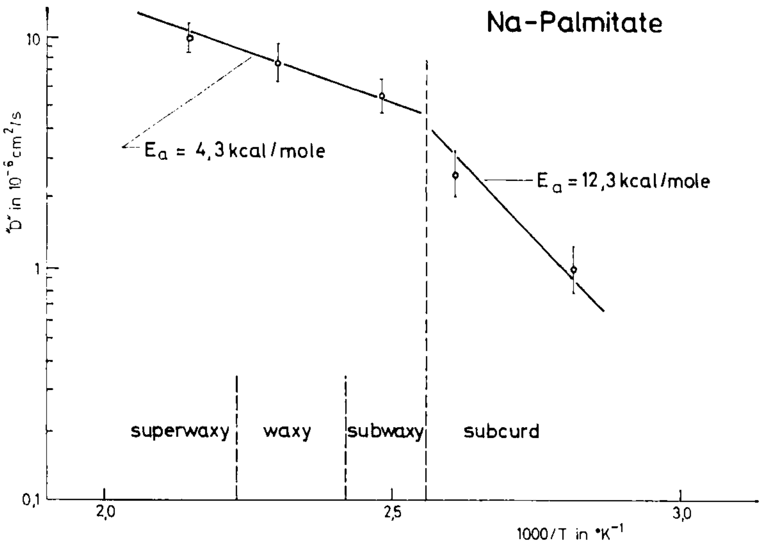


Figure 6. Temperature dependence of the apparent diffusion coefficient " D " in anhidrous Na-palmitate (NaP).

This conclusion is confirmed by a direct measurement of the translational self-diffusion coefficient D by the proton spin echo method. The NMR method could be used only above 525 °K where the proton line becomes sufficiently narrow to allow the observation of spin echoes. The self-diffusion coefficients D (Fig. 7) are of the order of 6×10^{-6} cm^2/sec in the subneat and neat (smectic B) mesomorphic phase, whereas an extrapolation of the neutron scattering results yields "D" $= 2 \times 10^{-5}$ cm^2/sec in this temperature region. The translational contribution to "D" in NaP is thus small indeed.

The most surprising result is however the fact that the translational self-diffusion coefficients D in contrast to " D " do not seem to depend on temperature in the mesomorphic phase. In the isotropic liquid phase, on the other hand, a normal, thermally activated temperature dependence of D is found. The self-diffusion behavior of smectic NaP is thus analogous to the one found in PAA.

(5) Na-palmitate-water mixtures (NaP-H_2O): Lyotropic liquid crystals which are formed by the addition of water to various amphiphilic 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

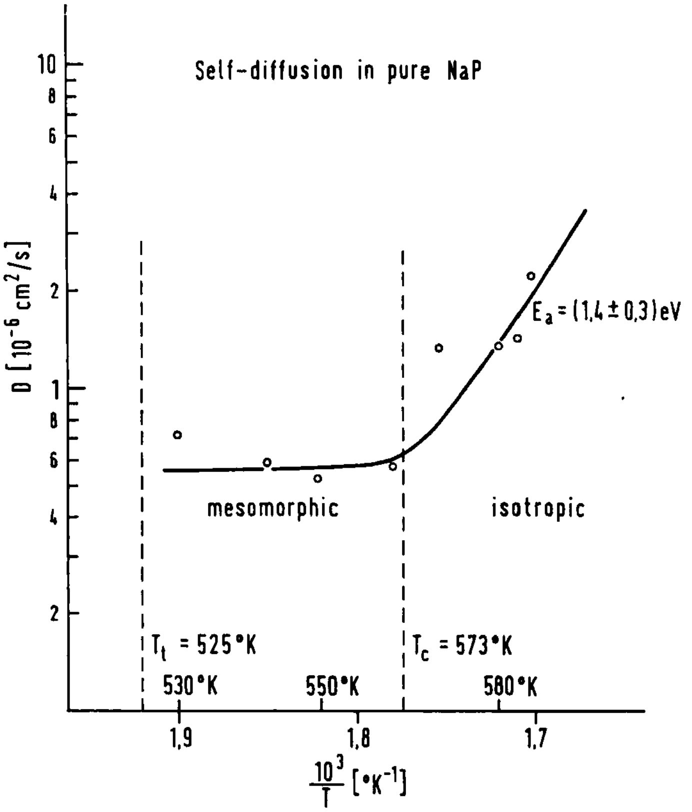
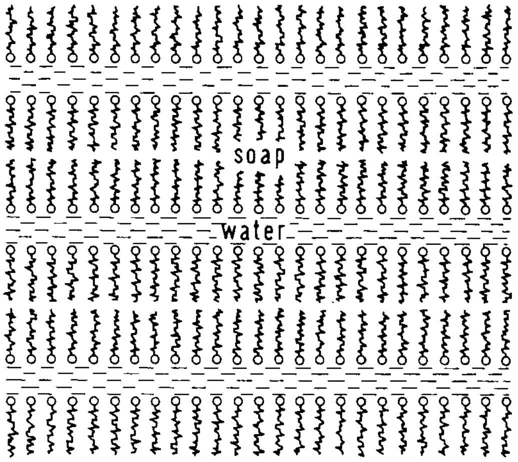


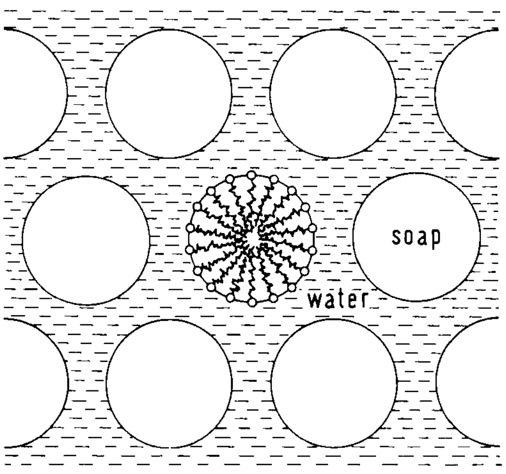
Figure 7. Temperature dependence of the self-diffusion coefficient D in NaP as determined by NMR.

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 (Fig. 8) is lamellar and smectic: the hydrocarbon chains are arranged in parallel equidistant double layers which alternate with intervening layers of water. In the hexagonal *middle* phase, on the other hand, the hydrocarbon molecules form a two dimensional lattice of parallel cylinders with intervening water channels (Fig. 8). It was the purpose of our study to investigate the diffusion properties of the H_2O molecules in these channels.

Deuteron resonance measurements(9) have shown that the motion of the D_2O molecules in such systems is not completely isotropic and that there is on the time average a small amount of preferential ordering of the D_2O molecules. The temperature dependence of the quadrupole splitting of the D_2O NMR spectrum for a 30% NaP-70% D_2O mixture is shown in Fig. 9. The spectra are of the " powder " type as expected for randomly oriented regions of spin 1 nuclei with a zero asymmetry parameter. The splitting first increases with



lamellar mesophase



hexagonal mesophase

Figure 8. Structures of the " neat " lamellar and the " middle " hexagonal mesophases of NaP-H_2O systems.

increasing T, stays nearly constant and then disappears on going to the isotropic liquid. It should be mentioned that a similar behavior was observed in the lamellar as well as in the hexagonal phase. In view of the fact that the maximum splitting increases with decreasing D_2O content it is tempting to explain the observed D_2O splitting as a result of " fast " exchange between " free " D_2O molecules within the channel and " bound " D_2O molecules at the polar ends of the hydrocarbon chains. This model also explains the fact that a single deuteron line is observed except very close to the temperature of the transition to the isotropic liquid. The deuteron spins thus see a time averaged electric field gradient

$$\bar{q} = q_{\text{bound}}\, p + q_{\text{free D}_2\text{O}}\,(1-p) \tag{10}$$

where p is the fraction of the time the D_2O molecule spends in a " bound " state and q_{bound} and q_{free} are the maximum components of the electric field gradient tensor in the " bound " respectively the " free " state. In case of an axially symmetric field gradient ($\eta = 0$) q is related to the quadrupole splitting of the deuteron NMR line by $\Delta\nu = \frac{3}{4} e^2 qQ/h$, where Q is the quadrupole moment of the deuteron. As the electric field gradient tensor of a free D_2O molecule in water

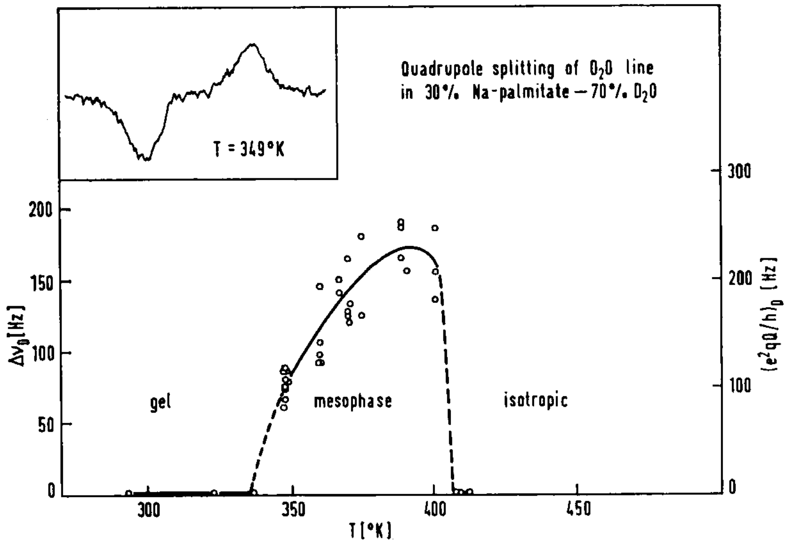


Figure 9. Temperature dependence of the quadrupole splitting of the deuteron D_2O NMR spectrum in a 70% D_2O–30% NaP system.

is averaged out by molecular motion, one may assume that $q \xrightarrow[\text{free } D_2O]{} 0$, and that

$$\bar{q} = q_{\text{bound}}\, p. \qquad (11)$$

If this model is correct one can immediately obtain the temperature dependence of the self-diffusion coefficients of the H_2O molecules as:

$$D_{\parallel} = D_{\text{NaP}} \cdot p + D_{H_2O} \cdot (1-p) \qquad (12)$$

where D_{NaP} is the self-diffusion coefficient of those H_2O molecules which are rigidly bound to the NaP groups and D_{H_2O} is the self-diffusion coefficient of the free H_2O molecules. As $D_{\text{NaP}} \ll D_{H_2O}$, in the liquid crystalline state, we have

$$D_{\parallel} \approx D_{H_2O}(1-p), \quad T < T_{l.c. \to i.l.} \qquad (13)$$

The experimental results are shown in Fig. 10 for both the hexagonal and the lamellar phase of the NaP-H_2O system. In both cases the diffusion coefficients exponentially increase with increasing temperature before *dropping* on going to the isotropic liquid.

The self-diffusion coefficients in the water channels are quite large and are at 350 °K in the 30% NaP-70% H_2O system only by a factor of 3 lower than the ones measured in pure H_2O at the same temperature and with the same spacing (40–100 msec) between the 90° and the 180° pulses. The values of $D_{\parallel}$ increase with increasing H_2O content.

It should be also mentioned that in the isotropic liquid state the self-diffusion coefficients for a 30% NaP-70% H_2O and a 30% NaP-70% D_2O mixtures are identical and are of the order of 3.10^{-6} cm^2/sec. This means that in the isotropic liquid in contrast to Eq. (13).

$$D \approx D_{\text{NaP}}, \quad T > T_{l.c. \to i.l.} \qquad (14)$$

i.e., $p \approx 1$, what can be understood only if a significant change in p accompanies the liquid crystal→ isotropic fluid transition.

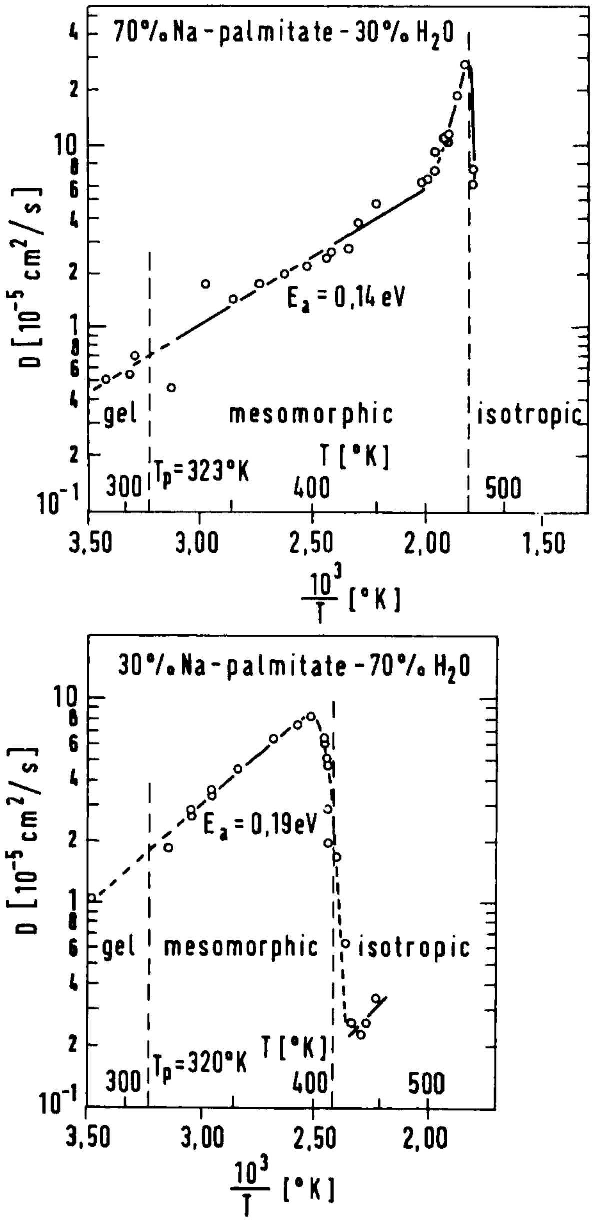


Figure 10. Temperature dependences of the self-diffusion coefficients D of the H_2O molecules in both lamellar and hexagonal NaP-H_2O systems.

REFERENCES

1. Blinc, R., Hogenboom, D. L., O' Reilly, D. E. and Peterson, E. M., *Phys. Rev. Letters* **23**, 969 (1969).
2. Blinc, R. and Dimic, V., *Phys. Letters* **31A**, 10 (1970). Janik, J. A., Janik, J. M., Otnes, K. and Riste, T., paper presented at the III. Liquid Crystal Conference, Berlin, (1970).
3. Singwi, K. S. and Sjolander, A., *Phys. Rev.* **119**, 863 (1960).
4. Larsson, K. E., *Phys. Rev.* **67**, 171 (1968).
5. Abragam, A., *The Principles of Nuclear Magnetism*, (Oxford University Press, 1961).
6. Stejskal, E. O., *J. Chem. Phys.* **43**, 3597 (1965).
7. Miesowizc, M., *Nature* **136**, 261 (1935); **158**, 27 (1946).
8. Powel, B. D. and Puddington, I. E., *Can. J. Chem.* **31**, 828 (1953). Nordsieck, H., Rosevear, F. B. and Ferguson. R. H., *J. Chem. Phys.* **16**, 175 (1948).
9. Lawson, K. D. and Flaut, T. J., *J. Phys. Chem.* **72**, 2066 (1968). Charvolin, J. and Rigny, P., *J. de Phys.* **30**, C4—76 (1969).