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Order parameters of dye molecules in lyotropic nematic mesophases

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The alignment in a magnetic field of two similar azo dyes in binary nematic lyotropic phases ($C_7F_{15}CO_2NH_4$ and $C_8F_{17}CO_2NH_4$ in D_2O) has been studied. The order S parameter for the dyes was determined by measuring quadrupolar splittings (deuterium N.M.R.), the anisotropy of the electric conductivity and dichroism. The order parameter of the dye fixed in the disc-like perfluoro micelle with positive diamagnetic anisotropy was determined as a function of magnetic field strength, surfactant concentration, temperature and chain length. In addition the time constants for orientation and disorientation were determined.

1. Introduction

Guest molecules in thermotropic nematic phases can be aligned with the liquid-crystalline matrix by using external fields [1]. Systems in which the dissolved molecule is a chromophore have potential for application as guest–host displays [2]. In such liquid crystal devices the order parameter of the chromophore is essential for good colour contrast. The chromophore and the molecules of the liquid crystal matrix are usually of different geometry, and the order parameter of the guest and host can therefore vary considerably and may have to be determined separately [3].

Dye molecules can also be solubilized in lyotropic nematics. Their order parameter can be measured with respect to the director of the phase or the direction of an external field. The order parameters for the individual CF_2 groups of surfactant in liquid-crystalline mesophases have been determined as a function of their position, but there have been relatively few studies of the order parameter of chromophores in surfactant or liquid mesophases [4]. Some measurements were carried out on mechanically aligned thin layers of lipid membranes [5]. Recently, Johansson *et al.* have used nematic lyotropic phases to align solubilized chromophores in a magnetic field so as to determine the order parameter of the chromophore [6]. In their studies they used ternary surfactant systems with a nematic phase. In such systems it is very time-consuming to determine the whole phase diagram as a function of temperature, and the phase diagram is usually known only for room temperature. As a consequence, very few measurements of the order parameter as a function of temperature and composition have been made. However, Reizlein and Hoffmann have recently observed nematic phases in binary perfluoro–surfactant systems [7]. These and similar systems have also been studied by Photinos and Saupe [8] and by Boden and Holmes [9].

We have continued the work on these nematics, using them for the solubilization of various chromophores; some of the results obtained are reported here.

2. Thermal considerations

It is known from previous measurements [10] that the perfluoro surfactants studied form disc-like micelles in isotropic solution. On lowering the temperature, these micelles grow; this trend continues below the phase transition temperature T_{NI}, in the nematic phase.

It is noteworthy that the nematic–isotropic transition is first order, and that there is a narrow two-phase temperature region around the transition temperature, a region which is sometimes as narrow as a few tenths of a degree. This also means that the two phases, which are in equilibrium around the phase transition temperature, are very close to each other in composition, and that the density differences are very small. Therefore, the macroscopic separation of the two phases takes a long time, and we did not study in detail these effects in the present investigation. However, it is possible to observe macroscopic phase separations at the transition temperature. From experimental evidence it seems that the two-phase region becomes wider with increasing chain length of the surfactants.

On applying a magnetic field to the nematic phase, the disc-like micelles tend align parallel to the field as a result of the positive anisotropy of the diamagnetic susceptibility [11]. All the surfactant molecules therefore align themselves in the same direction. Of interest in this investigation is the behaviour of solubilized dye molecules in the applied magnetic field. The order parameter of the dye, S_{D}, depends on the order parameter S_{P} of the individual micelles in the field, and on the order parameter S_{M} of the dye molecules inside the micelle. S_{P} is determined mainly by the phase behaviour of the liquid crystalline matrix; S_{M} depends on the interaction of the dye with the surfactant molecules. It is likely that the location of the dye molecules inside the micelle does not change at the nematic–isotropic transition, and that the orientation of the whole micelles in a magnetic field occurs only below the phase transition. If the dyes are of cylindrical symmetry with the electrical transition moment parallel to the axis of the cylinder, and if the dyes are fixed with their cylinder axis parallel to the optical axis of the disc-like micelles, S_{M} would be equal to 1.

The dyes used in our systems do not have complete cylindrical symmetry, and the electrical transition moment is not completely parallel to the cylinder axis. Nevertheless, high order parameters of about 0·9 were found. Therefore, in the analysis below the dye molecules are assumed to be of cylindrical symmetry with their electrical transition moment parallel to the axis. The measured order parameter S is a product of S_{M} and S_{P}, and the order parameter S_{D} for a cylindrically symmetric dye molecule may be expressed as [12]

$$S_{\mathrm{D}} = (R - 1)/(R + 2). \tag{1}$$

The dichroic ratio R is given by the ratio of the absorbance of light which polarized parallel and perpendicular to the magnetic field.

Of practical interest in guest–host devices, besides the structure factor, is the dynamic behaviour of the system. The time constant for the orientation depends on the anisotropy of the diamagnetic susceptibility $\Delta\chi$, the magnetic field, B, and the rotational viscosity γ according to [13]

$$\tau_{\mathrm{eff}} = \gamma/\Delta\chi B^2. \tag{2}$$

The rotational viscosity γ can be expressed as the product of a modulus G^0 and a time constant τ^0 [14]. When the magnetic field is switched off the oriented sample loses its alignment with the time constant τ^0. The driving force for equilibration under these conditions is the thermal energy. The term $\Delta\chi B^2$, the energy per unit volume, is even for modest fields much larger than the thermal energy of the micellar structures, and τ_{eff} is much shorter than τ^0.

For a given magnetic field, γ varies strongly with temperature, and therefore so does the effective time constant for the alignment. Diogo and Martins have shown that the data [15] may be fitted with the expression

$$\gamma(T) = g_1 S^2 \exp[\Theta S^2/(T - T_0)], \tag{3}$$

where g_1 is proportional to the probability that the energy of a particle is sufficiently high to overcome the energy barriers in the nematic phase, and the exponential expression is proportional to the probability that the particle finds a volume large enough for reorientation to occur. T_0 is the temperature at which this free volume approaches zero. If the temperature becomes equal to T_0 the exponential expression —and hence the rotational viscosity—would go to infinity, and the director of the nematic phase would then be frozen if no phase transition had taken place previously.

3. Experimental part

3.1. *Preparation of the surfactants* [16]

Excess ammonia was added to a solution of the perfluorocarboxylic acids in ether. The ether was evaporated, and the product was washed several times with a mixture of equal volumes of diethylether and acetone. The purity was checked by I.R. spectroscopy.

3.2. *Construction of the phase diagrams* [16]

In order to determine the sequence of the liquid-crystalline phases, samples of known concentration were kept at different temperatures for several days and checked for birefringence. The liquid-crystalline structures were determined by polarizing microscopy. For these studies a standard Zeiss 18 Pol microscope equipped with a Mettler FP 82 hot stage was used.

3.3. *Solubilized azo dyes*

The following two azo dyes, shown in figures 1 (*a*) and 1 (*b*), were used as guest molecules in the liquid crystal phases of the ammonium salts of the perfluorocarboxylic acids. The dyes were donated by Hoechst AG, Frankfurt. Both dyes are insoluble in water. Their purity was checked by thin layer chromatography.

About 5 mg dye were solubilized in 1 g of liquid crystal phase. Unsolubilized, excess dye was eliminated by filtration of the isotropic solution. The final concentration of the dye was determined with a Zeiss spectrophotometer.

3.4. *Determination of the order parameter S*

In order to determine the absorption of the oriented liquid crystal phase in the magnetic field, the optical set-up shown in figure 1 (*c*) was used. The set-up is constructed along the lines of a simple beam spectrophotometer. Monochromatic light of wavelength $\lambda_{\max}$ of the dye used was linearly polarized parallel or perpendicular to the direction of the magnetic field. The intensity of the light was measured with the photomultiplier tube, and the absorbance E was determined as

$$E_{\|,\perp} = \log(I_{0,\|,\perp}/I_{\|,\perp}), \tag{4}$$

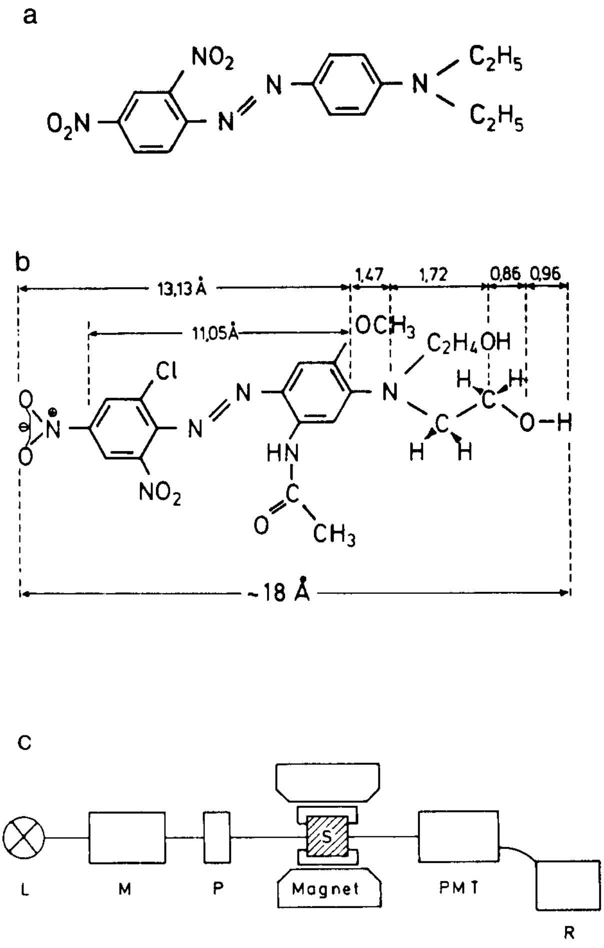

Figure 1. (*a*) Dye **1**, $\lambda_{max} = 530\,nm$ (in $C_nF_{2n+1}CO_2NH_4$, $n = 7, 8, 9$). (*b*) Dye **2**, $\lambda_{max} = 582\,nm$ (in $C_nF_{2n+1}CO_2NH_4$, $n = 7, 8, 9$). (*c*) Schematic drawing of the experimental set-up (L, Xenon XBO 75 arc lamp; M, monochromator; P, polarizer: S, sample; PMT, photomultiplier tube; R, recorder.)

where $I_{0,\parallel\perp}$ is the intensity of the light polarized parallel or perpendicular to the field passing through a sample without dye, and $I_{\parallel,\perp}$ is the intensity of the light passing through the sample with dye.

As figure 1 (*c*) shows, the liquid-crystalline sample was positioned between the pole pieces of the electromagnet. The samples were carefully thermostated. Magnetic fields of up to about 21 kG could be applied. The order parameter S was determined either as a function of the magnetic field at constant temperature, or vice versa. In order to measure the time constant τ, the variation of the light intensity with time t was measured continuously with a recorder.

3.5. *Conductivity measurements*

In order to determine the anisotropy of the electric conductivity and the time constants of the orientation, an electrode was placed in the liquid-crystalline phase.

The sample was positioned in the magnetic field and thermostated. The electrode was connected to a Wayne-Kerr bridge; the cell constant of the electrode was 0·335 cm^{-1}.

4. Results and discussion

4.1. *Phase diagrams*

The phase diagrams of the ammonium salts of the perfluorocarboxylates are shown in figure 2 for different chain lengths. All systems show the same characteristic features. They have a nematic phase, the region of which shifts with increasing concentration to higher temperatures. The phase boundaries for the nematic phase increase more or less linearly with concentration and are almost parallel, but the absolute values of the phase boundaries shift to higher concentrations with decreasing the chain length. As a consequence, the system with the largest chain length begins to form liquid crystals at the smallest concentration. In the $C_9F_{19}CO_2NH_4$ system, a solution containing 10 wt % surfactant is already in the single-phase liquid crystal regions. This shows that the spacings between the micellar layers must be very large, in this case at least ten times the width of the lamellar layer. These large spacings between the lamellar layers obviously result from long-range electrostatic repulsive interactions between the charged micellar layers. The two important parameters for double-layer interactions are the surface charge density of the layers and the ionic strength of the solution. It is likely that for the systems the charge density on the micellar interface is independent of chain length, and that the differences therefore arise from the different ionic strengths of the solution. The ionic strength of the bulk

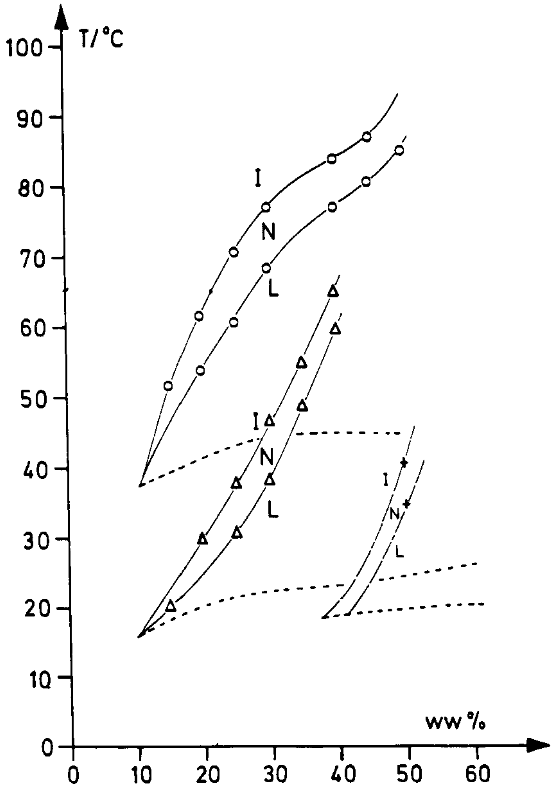

Figure 2. Phase diagrams of the perfluoro surfactants: I, isotropic, $C_9F_{19}CO_2NH_4$; N, nematic, $C_8F_{17}CO_2NH_4$; L, lamellar, $C_7F_{15}CO_2NH_4$.

solution is determined mainly by the critical micelle concentrations, which differ by about a factor three for one CH_2 group in the chain. Since the thickness of the electric double layer varies with the square root of ionic strength, it is likely that the phase boundary for the C_9 system begins at a concentration which is about a factor of four lower than for the C_7 system.

In this model the slope of the initial phase boundary in the temperature–concentration plot could possibly result from a change of the degree of dissociation of the micelles with increasing temperature. The degree of dissociation can decrease or increase for a surfactant system, depending on the type of binding of the counterions at the micellar interface. Usually the degree of dissociation increases somewhat with temperature, so the charge density should increase. This, however, also has an effect on the size of the micelles: they become smaller with increasing temperature, and this would destabilize the liquid-crystalline order of the system [17]. These various energy contributions to the total system make quantitative calculation of the phase boundaries very complex. However, a quantitative description of phase boundaries in model binary systems has been proposed [18].

4.2. *The order parameter as a function of magnetic field*

All the nematic phases of the ammonium salts of the perfluorocarboxylic acids that were examined orient easily in a magnetic field of modest strength. The order parameter S_D for several samples is plotted against field strength in figure 3. The systems are saturated for magnetic fields as low as 3 kG. The saturation depends somewhat on the distance from the nematic–isotropic phase transition.

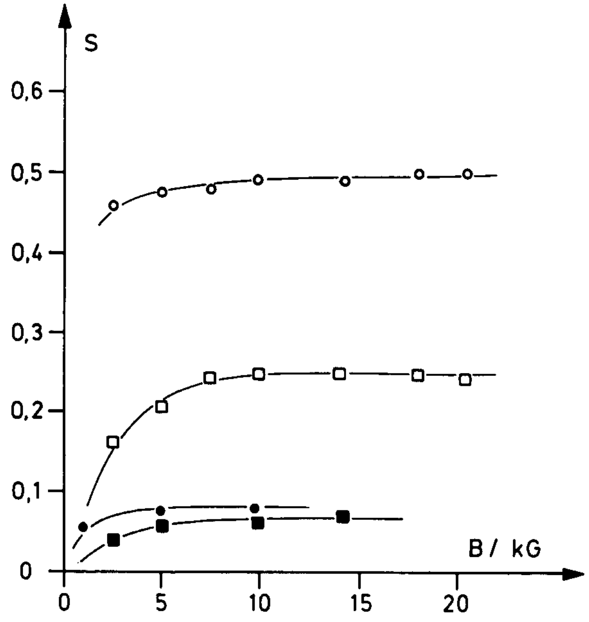

Figure 3. Plot of the order parameter S against magnetic field for different systems: ○, $C_7F_{15}CO_2NH_4$, 42·5 wt % D_2O, dye **2**, T = 24°C; ●, $C_7F_{15}CO_2NH_4$, 20 wt% D_2O, dye **1**, T = 24°C; □, $C_8F_{17}CO_2NH_4$, 20 wt% D_2O, dye **2**, T = 29°C; ■, $C_8F_{17}CO_2NH_4$, 20 wt% D_2O, dye **1**, T = 29°C.

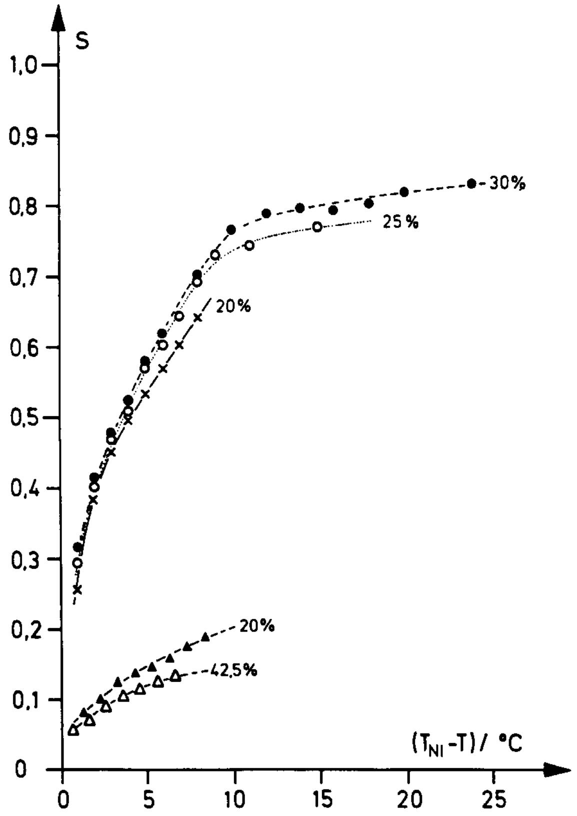

Figure 4. Plot of the order parameter S against the temperature difference between the sample and the nematic–isotropic phase transition for different surfactants, surfactant concentrations and dyes: ●, $C_8F_{17}CO_2NH_4$, 30 wt% D_2O, dye **2**, T_{NI} = 27·7°C; ○, $C_8F_{17}CO_2NH_4$, 25 wt% D_2O, dye **2**, T_{NI} = 27·7°C; ×, $C_8F_{17}CO_2NH_4$, 20 wt% D_2O, dye **2**, T_{NI} = 30·5°C; ▲, $C_8F_{17}CO_2NH_4$, 20 wt% D_2O, dye **1**, T_{NI} = 30·5°C; △, $C_7F_{15}CO_2NH_4$, 42·5 wt% D_2O, dye **1**, T_{NI} = 27·7°C.

4.3. *The order parameter as a function of temperature*

Figure 4 shows a plot of the order parameter S for dye molecules **1** and **2** against temperature. For both systems the order parameter increases steadily from the nematic–isotropic transition with decreasing temperature. In the experiments the temperature was reduced to the Krafft temperature where the surfactant crystallized out. It is therefore likely that the order parameter would even increase if the Krafft temperature of the systems could be lowered without affecting the temperature of the nematic–isotropic phase transition. This could possibly be achieved by the use of surfactant mixtures. The surfactants could vary in their counter-ion, head groups or chain length. The decrease in such mixtures would be the strongest for different surfactants which do not form mixed crystals.

To obtain the results shown in figure 4, the temperature was lowered through the nematic–lamellar phase transition. It is remarkable that no jump of the order parameter was noticed at the transitions. In this respect the data are quite similar to the results which were obtained from the conductivity anisotropy (see figure 5) and from the quadrupolar splittings (see figure 6). Both parameters also varied smoothly when

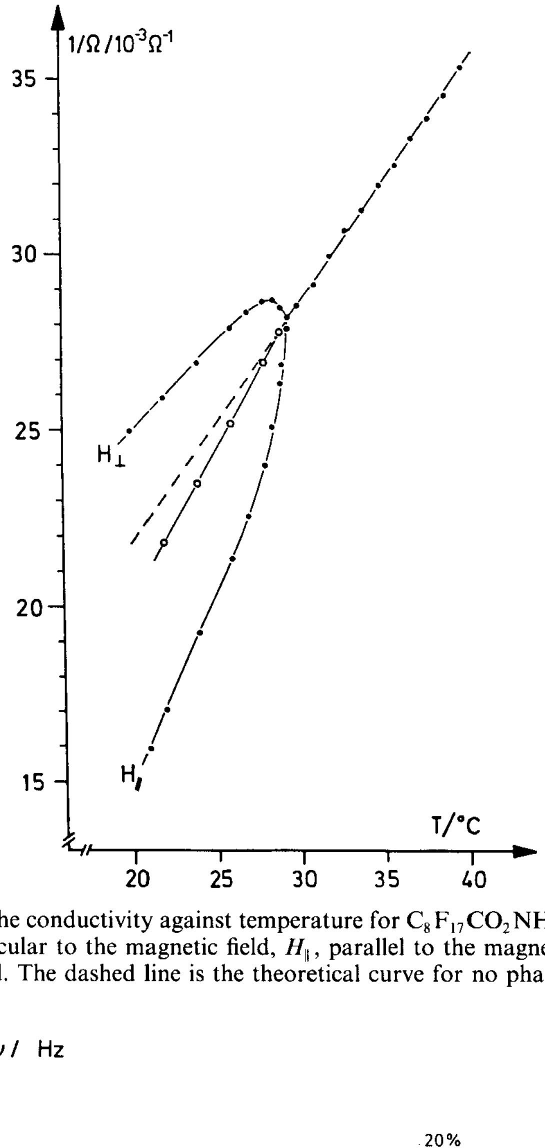

Figure 5. Plot of the conductivity against temperature for $C_8F_{17}CO_2NH_4$ with 20 wt% D_2O: $H_\perp$, perpendicular to the magnetic field, $H_\parallel$, parallel to the magnetic field, o, without magnetic field. The dashed line is the theoretical curve for no phase transition.

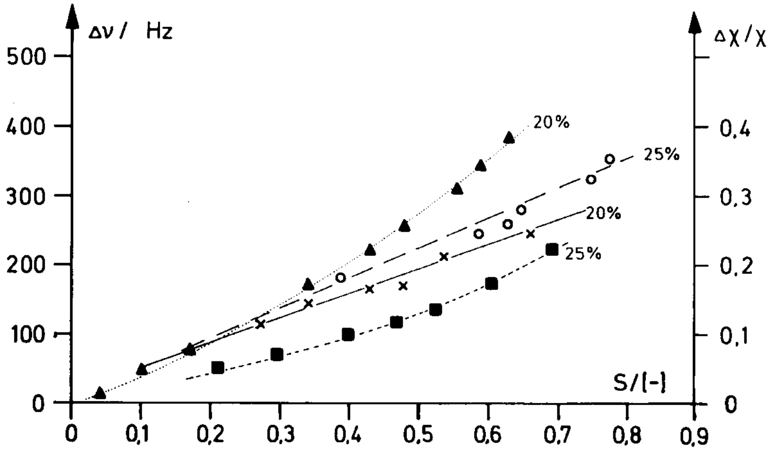

Figure 6. Comparison between the order parameter S, the quadrupolar splittings and the anisotropy of the electric conductivity for the $C_8F_{17}CO_2NH_4/D_2O$ system; ▲, ■, conductivity anisotropy; x, o, quadrupolar splittings.

the temperature was varied through this phase transition. The results indicate that the microscopic structures in the solution obviously do not change at this transition [19, 20].

The experimentally determined order parameter S_D contains information about the orientation of the micelles in the magnetic field and about the order of the dye molecules in the micelles. At least in the nematic phase, both order parameters S_P and S_M have values below 1 and it is difficult to separate the measured value S into its two components. However, Herbst *et al.* recently showed [10] by SANS measurements that S_P is very close to 1 at the lamellar–nematic phase transition. For lower temperatures, S_D is then the complement of S_M. Therefore even the packing of the surfactant molecules in the lamellar phase changes considerably as a function of temperature. There is other information which also shows this. It is known for instance, from accurate SANS and SAXS measurements that the spacing between the lamellar layers in the mesophase increases with decreasing temperature. This is possible only if some layers disappear in the mesophase and the remaining ones are packed more densely. As a consequence, the headgroups of the surfactant molecules moved closer together with decreasing temperature [21].

4.4. *The order parameter as a function of surfactant concentration in the nematic phase*

Figure 4 shows the order parameter for different concentrations of the same surfactant system in a plot of S against $T_{NI} - T$. The absolute sample temperatures are different because the nematic phase region shifts with increasing concentration to higher temperatures. The plot shows clearly that the absolute temperature or concentration does not strongly affect the order parameter. To a first approximation, the order parameter of the dye molecules in the lyotropic phase is determined mainly by how close the sample temperature is to the nematic–isotropic transition temperature. In the temperature range of the nematic phase the influence of concentration is, however, noticeable. For the same temperature difference between the sample and the transition temperature, the order parameter increases somewhat with increasing surfactant concentration. It is likely that this increase comes partly from the packing inside the micelle and partly from the incomplete mutual alignment of the disc-like micelles themselves. It is likely that both order parameters depend on each other in the nematic phase. The structural alignment is controlled by the repulsive interactions between the micelles; with increasing concentration and packing the orientational correlation becomes larger. The repulsive interaction between the micelles exerts, however, also a pressure on the micelles and causes a reduction of the numbers of kinks in the perfluoro chains of the surfactant. In the crystalline state a surfactant chain is in the all-trans configuration, but in the liquid-crystalline state this is no longer the case and there are kinks in each chain. On a statistical level, for a hydrocarbon chain every fourth CH_2 group is in a gauge configuration. Perfluoro chains are probably more ordered, but there are still kinks available. With decreasing temperature or increasing packing it is likely that the number of kinks decreases and the chains become more ordered. Consequently the dye molecules are fixed more rigidly in the micelles, and thus the order parameter S_D is increased.

4.5. *Different dye molecules*

Figure 7 shows the order parameter S_D of dyes **1** and **2** as a function of magnetic field strength. The order parameter of dye **2** is, under comparable conditions, considerably larger than for dye **1**. In view of the similar size and structure of the two

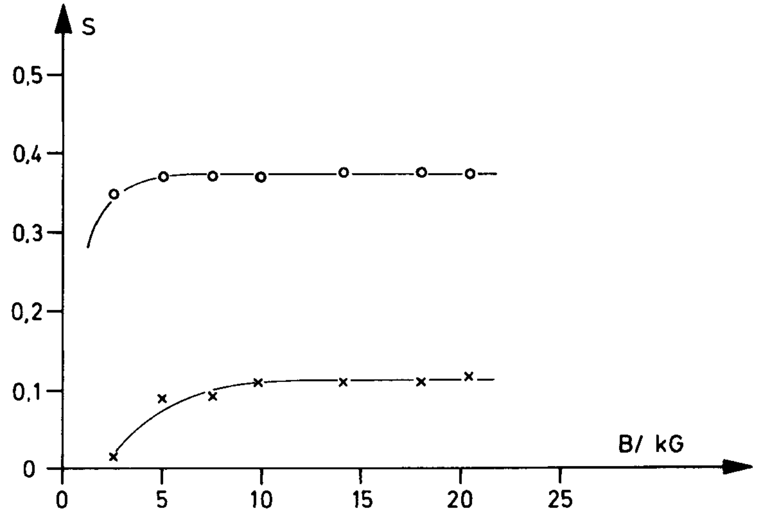

Figure 7. Plot of the order parameter S against the magnetic field for (x) dye **1** and (o) dye **2** in $C_8F_{17}CO_2NH_4$ with 20 wt% H_2O at T = 21°C.

molecules, this is somewhat surprising. It is likely that the difference between the measured order parameters reflects the differing polarities of the extreme positions in the molecules. In the molecule of dye **2** both the NO_2 and the C_2H_4OH groups are sufficiently polar for anchoring to occur at both sides of the double layer. The C_2H_5 groups in the dye **1** molecule are hydrophobic, and cannot be fixed between the hydrophilic head groups of the micelles. Consequently the order of the dye **1** molecule in the micelle is lower than that of the dye **2** molecule.

The order parameter of the CH_2 groups in the micelles has been determined from the α to the ω position by N.M.R. measurements [3]. The average over all carbon atoms is usually quite low, approximately 0·1; this corresponds to the value for the dye **1** molecule. From figure 1 it is also evident that for a given dye molecule the order parameter should have an optimum for a particular chain length of the surfactant. This optimum chain length seems to be around 7 for the dye **2** molecule. The dye molecule is then about twice as long as the surfactant molecule; that is, just about as long as the width of the membrane.

At present we do not have many data for which the conditions were the same, with the exception of the chain length. The available data clearly point to the order parameter for the dye **2** molecule being larger for the C_7 surfactant than for either the C_8 or the C_9 perfluoro chain (see figure 8).

4.6. *The orientation of the nematic phase*

The orientation of the nematic phase in a magnetic field can be followed by measuring the conductivity anisotropy, the quadrupolar splitting or the dichroism as a function of time, when a nematic sample is placed in a magentic field. The build-up and the relaxation of the conductivity anisotropy with time is shown in figure 9. When the magnetic field is switched off the oriented sample disorients again, and the anisotropy is lost. The disorientation time constant is much longer than the time constant for orientation in the field.

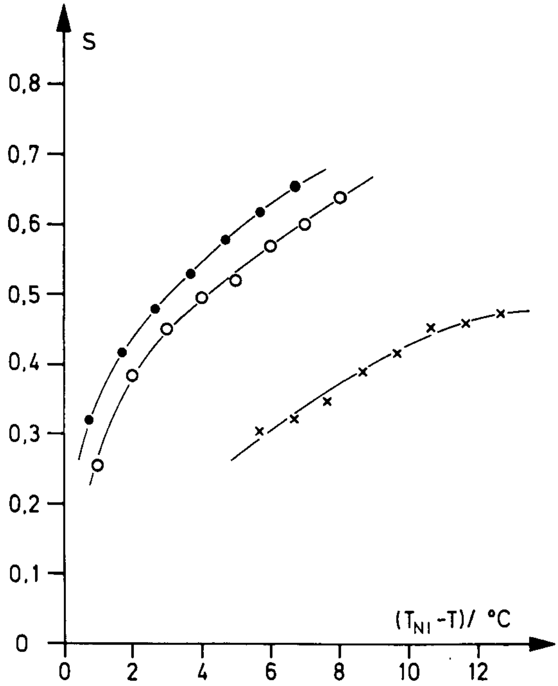

Figure 8. Plot of the order parameter S against the temperature difference between the sample and the nematic–isotropic phase transition for different surfactants: ●, $C_7F_{15}CO_2NH_4$, 42·5 wt% D_2O; o, $C_8F_{17}CO_2NH_4$, 20 wt% D_2O; x, $C_9F_{19}CO_2NH_4$, 21·5 wt% D_2O.

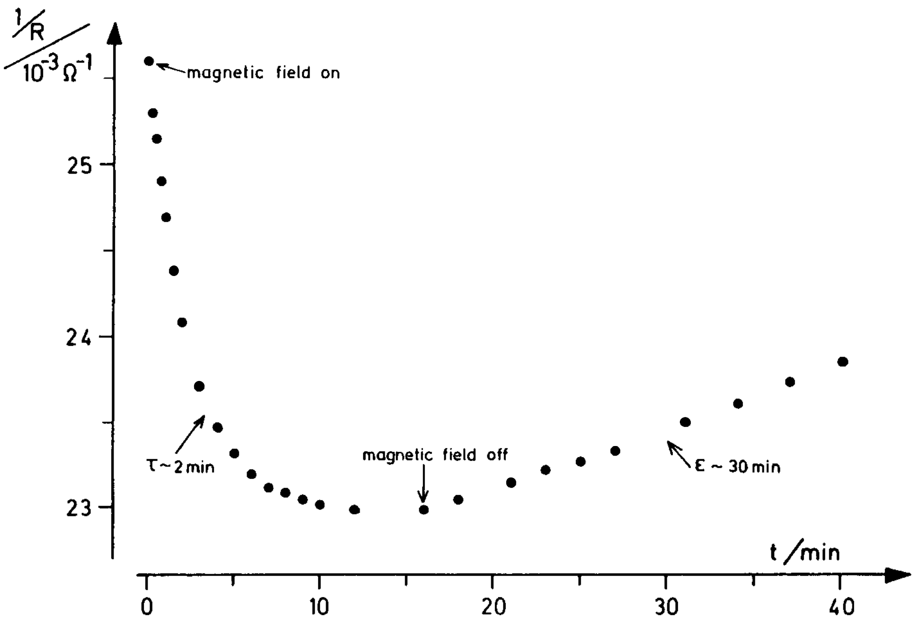

Figure 9. Creation and relaxation of the conductivity anisotropy with time for $C_8F_{17}CO_2NH_4$ with 20 wt% D_2O; T = 29°C, B = 10 kG.

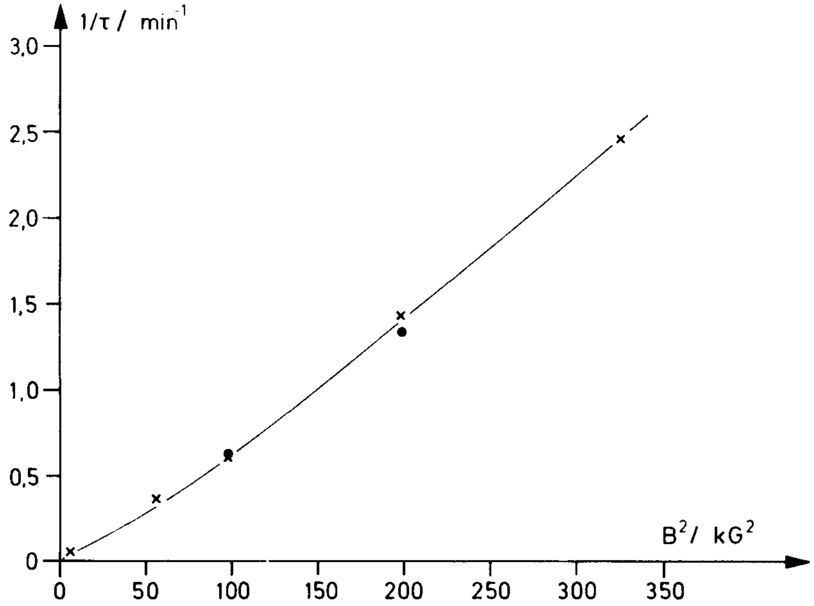

Figure 10. Plot of the reciprocal of the rotational time constant against the square of the magnetic field for different temperatures: ■, $C_8F_{17}CO_2NH_4$, 20 wt% D_2O, $T = 29$°C; x, $C_8F_{17}CO_2NH_4$, 20 wt% D_2O, $T = 21$°C.

The time constants τ determined by one of the methods described are strongly dependent on the strength of the magnetic field and become shorter with increasing field strength. According to equation (2) the reciprocal of the rotational time constant should increase linearly with the square of the magnetic field, and this is shown clearly in figure 10.

4.7. *Comparison between different results*

A number of physicochemical properties investigated for the nematic phase are known and can be compared with the order parameter of the dye molecules. We have reported before [17] for the same system the conductivity anisotropy and the quadrupolar splittings. Furthermore, we have determined by SANS measurements the position and the width of the correlation peak.

In the conductivity plot we chose as a scale for the normalized anisotropy the quantity $\Delta\kappa/\kappa$, where κ is the calculated conductivity of the unaligned nematic or lamellar phase.

For the quadrupolar splittings we used the value $\Delta\nu(T)/\Delta\nu(T_K)$, in which $\Delta\nu(T)$ is the splitting at the Krafft temperature, which was the lowest temperature at which the measurement could be made before the sample crystallized. All the curves look qualitatively very similar; this shows that the various properties which are plotted are correlated with each other. These correlations are independent of the absolute temperature of the sample and the difference between the sample and Krafft temperatures. This is somewhat surprising because it is likely that the number of kinks or the degree of disorder in the lamellar layers should reflect this temperature difference. A comparison between the order parameter, the quadrupolar splittings and the anisotropy of the electrical conductivity is shown in figure 6. The plot is nearly but not completely linear.

5. Conclusions

The alignment in a magnetic field of dichroic azo dyes in nematic lyotropic phases, consisting of ammonium salts of perfluorocarboxylic acids, has been studied. The order parameter of the dye was determined as a function of the magnetic field strength, the temperature, the concentration and the chain length of the surfactant. The director for the micelles and thus also for the chromophores aligned parallel to the applied magnetic field. The most important factors governing the order parameter are the structure of the dye molecule and the difference between the actual temperature in the sample and the nematic–isotropic transition temperature, T_{NI}. The order parameter increased continuously with this temperature difference from values of about 0·2 close to T_{NI} up to 0·85 for $T \geqslant 10°\mathrm{C}$. The absolute temperature, the concentration and the chain length of the surfactant had little effect on S_{D}.

The azo dyes studied both had about the same structure and length. They differed, however, in the polar groups at their ends. It was observed that the dye molecule with two polar end-groups had considerably higher order parameters than the other. This, together with the fact that the dye molecule is about twice as long as a surfactant molecule, implies that the dye is anchored with both polar end-groups in the micelle.

At the lamellar–nematic phase transition no abrupt change of the order parameter occurred. This is further evidence that the microscopic structures in the sample do not change at this transition.

The studies of the dynamic behaviour of the nematic phase showed the expected linear dependence between the reciprocal time constant, $1/\tau$, and the square of the magnetic field strength. The time constants for the orientation were much smaller than the constants for the relaxation caused by thermal motion, even for low field strengths.

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References

[1] Matsumoto, S., Mizunoya, K., Hatou, H., and Tomii, H., 1985, *Molec. Crystals liq. Crystals*, **122**, 285.

[2] Uchida T., and Wada, M., 1981, *Molec. Crystals liq. Crystals*, **63**, 19.

[3] Diehl, P., Fluck, E., and Kosfeld, R. 1975, *NMR Basic Principles and Progress* (Springer-Verlag).

[4] Cognard, I., and Hien Phan, T., 1981, *Molec. Crystals liq. Crystals*, **68**, 207.

[5] Norden, B., Lindblom, G., and Jonas, I., 1977, *J. phys. Chem.*, **81**, 2086.

[6] Johansson, L. B., Söderman, O., Fontell, K., and Lindblom, G., 1981, *J. phys. Chem.*, **85**, 3694.

[7] Reizlein, K.. and Hoffmann, H., 1984, *Prog. Colloid. Polym. Sci.*, **69**, 83.

[8] Photinos, P. J., and Saupe, A., 1986, *J. chem. Phys.*, **84**, 517.

[9] Boden, N., and Holmes, M. C., 1984, *Chem. Phys. Lett.*, **109**, 76.

[10] Herbst, L., Hoffmann, H., Kalus, J., Reizlein, K., and Schmelzer, U., 1985, *Ber. Bunsenges. phys. Chem.*, **89**, 1050.

[11] Hardouin, F., Achard, M. F., Sigand, G., and Gasparoux, G., 1984, *J. Phys. Lett. Paris*, **45**, L143.

[12] Korte, E. H., 1983, *Molec. Crystals liq. Crystals*, **100**, 127.

[13] Boden, N., and McMullen, K., 1980, *J. Colloid Interface Sci.*, p. 667.

[14] Heppke, G., and Schneider, F., 1972, *Z. Naturf.* (9), **27**, 976.

[15] Diogo, A. C., and Martins, A. F., 1981, *Molec. Crystals liq. Crystals*, **66**, 133.

[16] Reizlein, K., 1983, Thesis, Bayreuth. K. Reizlein and H. Hoffmann, 1981, *Prog. Colloid Polym. Sci.*, **69**, 83. B. Schwandner, 1986, Thesis, Bayreuth.

[17] Angel, M., Hoffmann, H., Schwandner, B., and Weber, R., 1985, *Proceedings of the Liquid Crystal Conference*, Halle, Herausg. H. Sackmann, WB 1986/52 (N17), S. 120–155.

[18] Jönsson, B., and Wennerström, H., 1981, *J. Colloid Interface Sci.*, **80**, 482.

[19] Charvolin, J., 1983, *J. Chim. phys.*, **80**, 15.

[20] Photinos, P., Melnik, G., and Saupe, A., 1986, *J. chem. Phys.*, **84**, 6928.

[21] Fontell, K., and Lindmann, B., 1983, *J. phys. Chem.*, **87**, 3289.