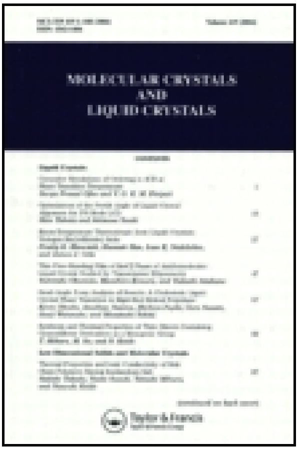

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An ESR Investigation of a New Lyotropic Lamellar Phase from an Amphiphile with a Cationic Head Group

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An ESR Investigation of a New Lyotropic Lamellar Phase from an Amphiphile with a Cationic Head Group

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A new lamellar lyotropic phase with a positively charged polar interface has been obtained by mixing water and decanol with n-decyl isonicotinate hydrochloride in appropriate concentration.

The order parameters of several spin probes incorporated in this mesophase have been determined by electron spin resonance spectroscopy. A comparison is made with the results for the same probes in the lamellar phase of water, decanol, and sodium decanoate, having an anionic interface.

The experimental findings are rationalized in terms of selective interactions of the probes with specific regions of the bilayers.

1 INTRODUCTION

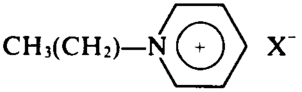
Ionic amphiphiles may produce liquid crystalline phases when mixed with water and/or other suitable solvents, e.g. long chain alcohols, in appropriate concentration.[1,2] These lyotropic liquid crystalline phases may posses a variety of arrangements of the constituent amphiphilic units. For example the most common phases, the so called lamellar and hexagonal, are characterized by a plate-like and thread-like arrangement respectively. A feature shared by the various lyotropic structures is, however, a water layer separated from the hydrophobic region by an interface including the amphiphile polar head groups.

Certain mesomorphous lyotropic phases can be useful as anisotropic solvents for studying spectroscopic properties of incorporated probes and have been used for this purpose[3,4] although perhaps not yet as widely as thermotropic mesophases. For spectroscopic applications the lamellar phases are probably the most useful.

They can, in fact, be easily aligned between suitably treated glass plates, thus allowing selective determinations of the various partially averaged components of the observed tensor property.[4]

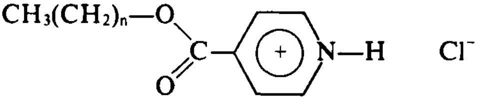
Another reason for the importance of lamellar phases is their similarity to membrane systems and in this connection the possibility of being able to change the interface polarity by varying the nature of the polar head groups is important.

These groups may be dipoles or positively (cationic) or negatively (anionic) charged or mixed. Whilst a number of examples of the anionic type has been described, cationic constituents are rather scarcer and often belong to the same family, i.e., alkylammonium salts,[2] an exception being represented by alkylpyridinium halides (I).[5]



(I)

In the present study we have searched for other amphiphiles with cationic head groups and a structure that makes them potential constituents of lyotropic liquid crystals. We have concentrated our attention on the family of pyridinium alkyl ester salts and in particular on the decyl (II) and octadecyl (III) derivatives.



(II); $n = 9$

(III); $n = 17$

We have found that (II) does indeed produce a lyotropic mesophase in admixture with water and 1-decanol, while similar attempts using (III) have not been successful.

In summary the plan of the present work is as follows. In Section 2 we describe the experimental details of the synthesis of compounds (II) and (III) and the attempts to prepare mesomorphous mixtures using water and aliphatic alcohols as solvents. In Section 3 we illustrate the characterization of the lyotropic liquid crystal resulting from (II) as a lamellar phase by using the electron spin resonance (esr) technique, employing various paramagnetic probes. Finally we discuss the order parameters and the dynamics of the probe reorientation.

2 EXPERIMENTAL

n-Decyl isonicotinate. Thionyl chloride (90 g, 0.76 mol) was added slowly to isonicotinic acid (20.5 g, 0.167 mol) while cooling and stirring. The mixture was heated for two hours and then the excess of thionyl chloride was distilled under reduced pressure. Anhydrous benzene (70 ml) was added to the residue followed by a dropwise addition of 1-decanol (25 g, 0.167 mol). After heating for two hours the reaction mixture was cooled and pyridine (26 ml) and water (200 ml) containing 20% of sodium carbonate were added. The solution was stirred for an additional half an hour, and the organic and water phase were separated. The water layer was shaken with ether. After drying the benzene and ether solutions with sodium sulphate, the solvent was removed by distillation. Yield 63%; b.p. 160 (2.0 mm Hg); n_D^{20} 1.4995.

n-Octadecyl isonicotinate. The same procedure described for n-decyl isonicotinate was employed but extending the reaction time between the acyl chloride and 1-octadecanol up to a week. Yield 57%; b.p. 270° (2.0 mm Hg); m.p. 50–55°.

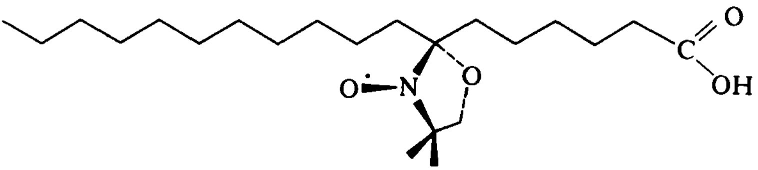
Hydrochlorides (II) and (III). The n-decyl isonicotinate and n-octadecyl isonicotinate were added to an excess of concentrated hydrochloric acid. The resulting mixture was evaporated under vacuum and the residue collected. The m.p. of (II) was 98–100°; the hydrochloride (III) showed a softening point at 62°, while the change to the amorphous liquid occurred gradually between 190° and 210°.

Mesophase mixtures. The pyridinium chloride (II) can be dissolved easily in a solution of 1-decanol and water. However, separation of two phases is normally observed for a variety of compositions of the mixture. In principle it is desirable to construct the complete ternary diagram for the system. However, our aim here is only to demonstrate the ability of this salt to give a lamellar phase, and so we shall confine ourselves to describing how such a phase can be produced. We started by mixing equal amounts by weight of the pyridinium chloride (II) and water and warming until the salt was completely dissolved. Then decanol was added to the mixture in a percent (by weight) ranging from 4% to 14%. A homogeneous and birefringent phase with a waxy consistency immediately formed. Heating produced a "melting" of the phase to an optically isotropic solution. The "melting" point decreases with increasing percent of decanol. With slightly above 14% of the latter component, the liquid crystalline phase can be obtained only by lowering the temperature below 20°C. Further addition of decanol results in phase separation.

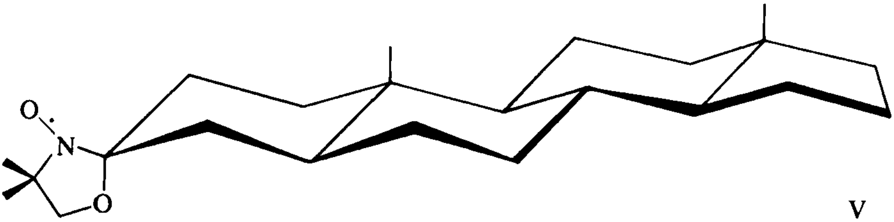
Attempts to prepare a lamellar lyotropic liquid crystal from the octadecyl salt (III) in the temperature range 20–90°C were, on the other hand, completely unsuccessful since this compound is hardly miscible with decanol and water. Even by using octadecanol, instead of decanol, no appreciable mixing of the three components could be achieved.

RESULTS AND DISCUSSION

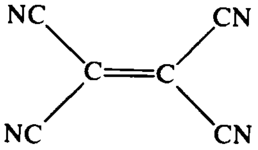
Esr spectra. It is known that esr spectra of spin probes may give information on the surrounding environment and thus on the phase in which they are dissolved. Amongst the information on static properties provided by this technique are the degree of order of the probe and the director distribution of the phase with respect to the magnetic field direction. We chose as spin labels for the present investigation two nitroxides i.e. (5-spiro-(2′-oxyl-3′,3′-dimethyl-oxazolidine))-stearic acid (IV (12,3))† and (3-spiro-(2′-oxyl-3′,3′-dimethyl-oxazolidine))-5α-androstane (V), as well as the polar probe tetracyanoethylene (TCNE) radical anion (VI). In a previous article[6] we have shown that the latter radical is particularly useful for studying the polar interface region of lyotropic liquid crystals.



IV(12,3)



V



VI

The esr spectra of all these radicals incorporated in the lyotropic mixture of the hydrochloride (II) (44%), decanol (12%) and water (44%) contained in a sample tube with a diameter of 4 mm, resemble three dimensional powder spectra of radicals with cylindrically symmetric magnetic interactions. As an example the esr spectrum of IV (12,3) is shown in Figure 1. However, the difference between the parallel and perpendicular components of the hyperfine

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†Where 12,3 defines the population of methylene groups on each side of the oxazolidine ring.

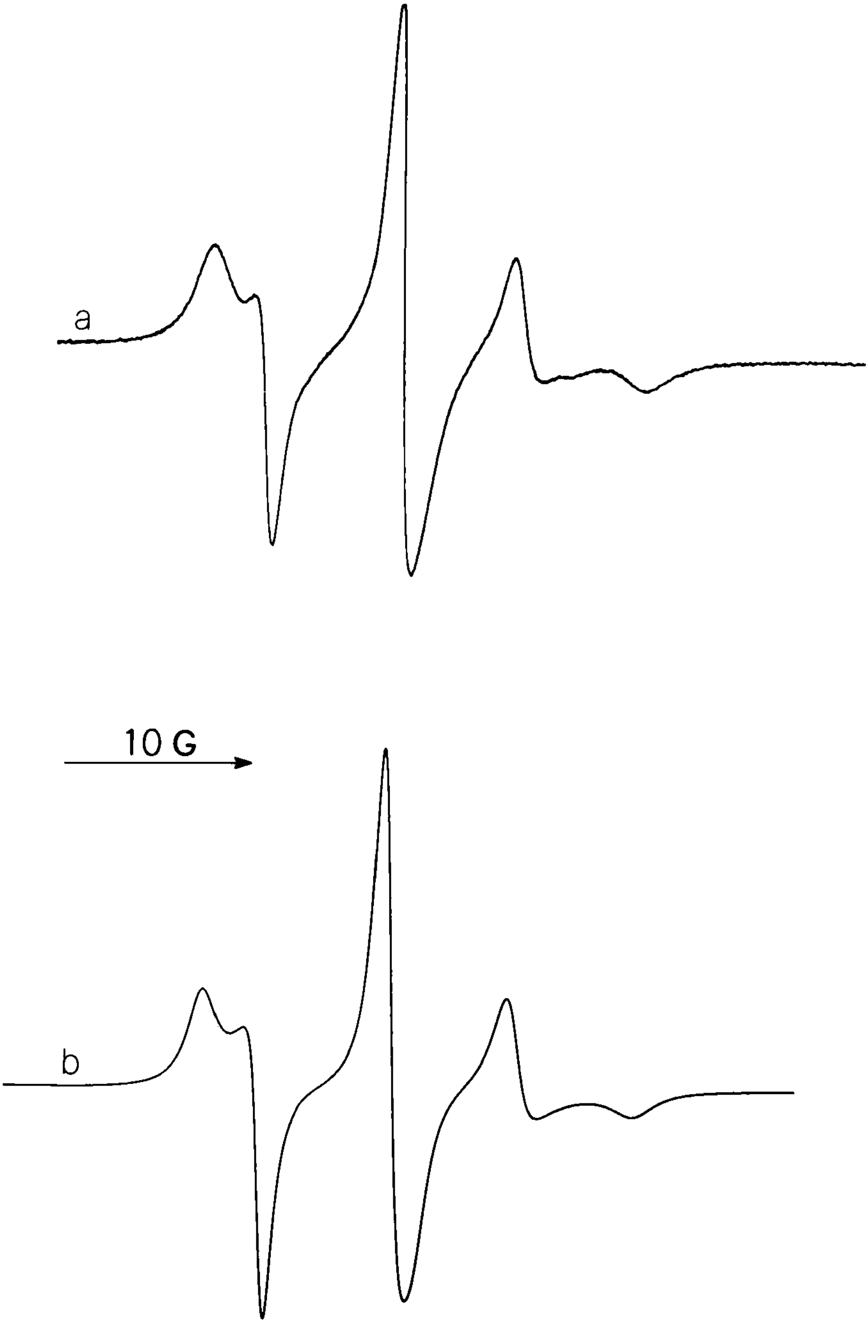

FIGURE 1 Experimental (a) and simulated (b) esr spectrum of the stearic nitroxide IV(12,3) dissolved in the macroscopically disordered cationic phase C. The parameters used for the simulations are : $\bar{P}_2 = 0.32$, $\bar{P}_4 = -0.05$, $\tau_0 = 1 \times 10^{-9}$ s rad^{-1}, $X_0 = 1.0$ G, and $X_2 = 0.4$ G.

tensor determined from these spectra is lower than the value obtained from true polycrystalline samples. This suggests that we are dealing with polyliquid crystalline spectra, involving a situation where the spin label reorients rapidly in a local anisotropic environment, while the directors of each domain are isotropically distributed in space.[4,7] This demonstrates unequivocally that the mixture under investigation is some kind of liquid crystalline phase. The degree of order of the spin probe may be obtained from a knowledge of the principal values $A_\parallel$ and $A_\perp$ of the hyperfine tensor and the partially averaged components of the same tensor $\tilde{A}_\parallel$ and $\tilde{A}_\perp$ determined from the spectra, through the relation (1)

$$\bar{P}_2 = \overline{D^2_{0,0}} = (\tilde{A}_\parallel - \tilde{A}_\perp)/(A_\parallel - A_\perp). \tag{1}$$

The order parameter obtained in this way is referred to the symmetry axis of the hyperfine tensor which is assumed to be uniaxial. This assumption is correct with good approximation both for the nitroxide and the TCNE$^{\overline{\cdot}}$ spin probes considered here.

The polyliquid crystalline spectra do not indicate the kind of lyotropic liquid crystal we are dealing with, apart from suggesting that the phase is uniaxial. A clear distinction between lamellar phases and any other lyotropic phase can be achieved by recording the spectra of thin samples sandwiched between two glass plates.[3,4] It is known that appropriate treatment of the glass surface can induce a macroscopic orientation of lamellar phases, with the elongated amphiphilic molecules, on average, being perpendicular to the glass plates. In these conditions we expect to observe monodomain esr spectra showing an hyperfine splitting constant depending on the relative orientation of the glass plates and the spectrometer's magnetic field. The form of this dependence is given by,[8]

$$a(\gamma) = \frac{(\tilde{g}_\parallel^2 \tilde{A}_\parallel^2 \cos^2\gamma + \tilde{g}_\perp^2 \tilde{A}_\perp^2 \sin^2\gamma)^{1/2}}{(\tilde{g}_\parallel^2 \cos^2\gamma + \tilde{g}_\perp^2 \sin^2\gamma)^{1/2}}, \tag{2}$$

where γ is the angle between the director of the mesophase and the field direction. By contrast, globular and hexagonal phases are not oriented by surface forces and this will be reflected in the esr spectra which will retain a polydomain appearance.

In the present case uniform alignment was achieved by the following method. The cover glasses used for the experiment were first washed with a soap solution, then rinsed with water and acetone and finally dried carefully. A small amount of the liquid crystal containing the spin probe in a concentration of *ca.* 10^{-3}–10^{-4} M was placed between the two glasses and gently squeezed without using spacers. When using TCNE, the procedure described in a previous paper[6] was adopted.

In these conditions, monodomain spectra are actually obtained, showing symmetric lines with a separation depending on the orientation of the glass

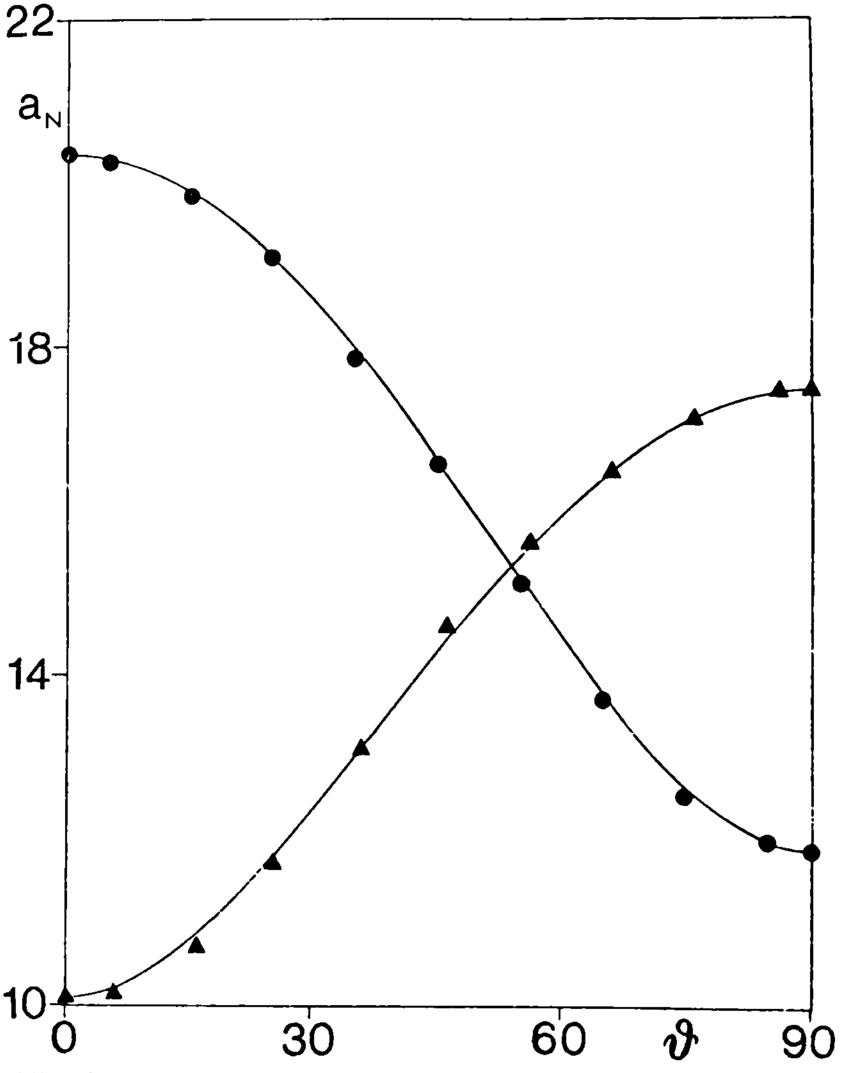

FIGURE 2 Dependence of the nitrogen coupling constant on the angle ϑ between glass normal and magnetic field for the nitroxide spin probes IV(12,3) (full circles) and V (full triangles). The continuous curve is the fit to equation (2).

slides with respect to the magnetic field. When the normal to the glass plates is parallel to the field, the measured hyperfine splitting is coincident with $\tilde{A}_{\parallel}$ determined from the polyliquid crystalline spectrum, while by a rotation of 90° a separation corresponding to $\tilde{A}_{\perp}$ is observed. Between these two limiting orientations, the dependence of the coupling constant on the angle ϑ between glass normal and field, shown in Figures 2 and 3, was measured. The curves obtained by substituting, in Eq. (2), the partially averaged components of the

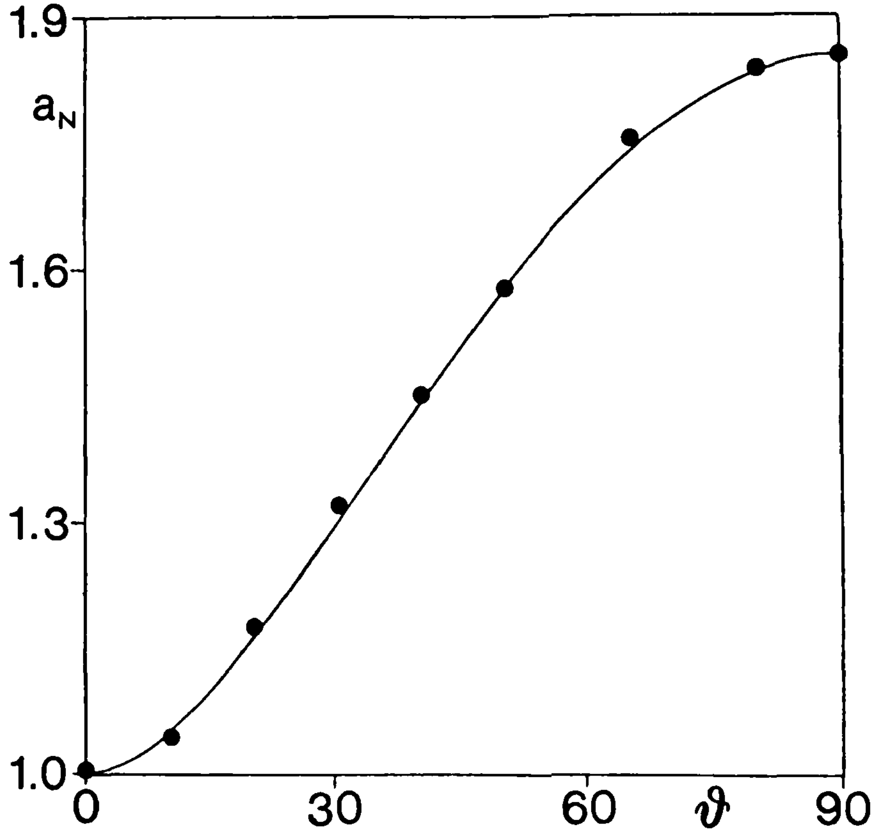

FIGURE 3 Dependence of a_N on the angle ϑ between glass normal and field for the TCNE(VI) anion radical incorporated in phase C. The continuous curve is the fit to a modified form of equation (2) (see Ref. 9, 10).

hyperfine tensors and assuming a simple isotropic $\tilde{g}$, shown as continuous lines in the same figure, fit neatly the experimental points.[9] Since in equation (2), γ is the angle between the director of the mesophase and the magnetic field direction, we conclude that the glass normal and director are parallel. This provides evidence that the phase is lamellar and uniaxial, i.e., to the resolution of our experiment, non-tilted.

Order parameters. The order parameters $\bar{P}_2$ for the three spin probes employed in the present investigation have been determined, using equation (1), from the experimental values of $\tilde{A}_{\parallel}$ and $\tilde{A}_{\perp}$ reported in Table I and the principal components of the hyperfine tensors given in Table II.

It is of interest to compare the order parameters obtained with the present lamellar phase with cationic head groups (liquid crystal C) with those deter-

TABLE I

Hyperfine splitting constants and order parameters of various spin probes, measured at room temperature in the lyotropic mixture of the pyridinium salt (II), decanol and water (phase C) and in a 28:42:30 mixture of sodium-1-decanoate, decanol and water (phase A).

Spin probe	Phase	$\bar{A}_{\parallel}/G$	$\bar{A}_{\perp}/G$	a/G	$\bar{P}_2$	$\bar{P}_4$	Ref.
Stearic	C	20.35	11.9	14.7	0.32	−0.05	—
IV(12,3)	A	25.45	9.63	14.9	0.60	0.11	7
Stearic IV(9,6)	A	20.1	11.9	14.6	0.32	—	11
Stearic IV(5,10)	A	18.25	12.13	14.17	0.23	−0.09	12
Androstane	C	10.12	17.47	15.02	−0.28	—	—
V	A	9.8	17.2	14.7	−0.28	—	11
TCNE$^{\overline{\cdot}}$	C	1.00	1.86	1.57	−0.14	—	—
VI	A	1.18	1.83	1.61	−0.10	—	6

mined in a similar phase resulting from the anionic amphiphile sodium-l-decanoate (liquid crystal A of Table I). For both phases esr measurements were made at room temperature.

An examination of the $\bar{P}_2$ values shows that the degree of order of the stearic spin probe IV(12,3) in the cationic phase C is practically one half of that in the anionic phase A. For the androstane probe V, on the other hand, the degree of order is independent of the nature of the liquid crystal in which it is dissolved. Finally the radical anion of TCNE is more aligned in the cationic phase C.

Even though it is not strictly permissible to make a comparison without knowing the phase diagram of our liquid crystal, since the comparison should be made at the same reduced conditions, some indication on the ordering of the two phases can be gained by concentrating on the androstane label V. Since this probe has a rigid structure and lacks charged or readily ionizable groups which may strongly interact with the two interfaces of opposite polarity, the invariance of $\bar{P}_2$ in the two mesophases can be taken as an indication that the intrinsic ordering of the two phases is not very different. As a consequence the very large variations of the order parameters for the other two probes can be attributed to the existence of specific interactions with the constituents of the bilayers.

TABLE II

Principal values of the hyperfine tensor for radicals IV–VI.

Spin probe	A_{zz}/G	$A_{xx} = A_{yy}/G$	Ref.
IV(12,3)	32.4	6.1	12
V	32.1	6.1	11
VI	5.67	−0.47	13

In the stearic probe IV(12,3), one of the extremities is a carboxylic function which, if it is located in the polar interface region, will dissociate easily thus retaining a negative charge as the amphiphile of the liquid crystalline phase A, i.e., the decanoate ions. In the latter phase the sodium counterions will be shared by amphiphile and guest probe which will as a result be strongly anchored to the interface and therefore highly aligned. By contrast, in liquid crystal C, where the counterions are chloride anions, a specific interaction with the polar heads of the probe will be lacking. Moreover, we expect the negative carboxyl group to interact with the pyridinium cation, with the effect of pushing the probe inside the layer and reducing the degree of order. Supporting this hypothesis is the nitrogen isotropic coupling constant.

In a nitroxide probe the nitrogen splitting decreases with decreasing polarity of the surroundings.[14] Therefore, the smaller value of a_N observed in phase C suggests that the oxazolidine ring of IV(12,3) penetrates more deeply in the hydrophobic region than in phase A.

The same conclusion follows from an inspection of the degree of order $\bar{P}_2$, measured in the anionic mesophase A, for other stearic probes where the nitroxide ring is located at a larger distance from the carboxylic function anchored to the polar interface. Table I shows that the value of $\bar{P}_2$ for the probe IV(9,6) in liquid crystal A is practically the same as that of IV(12,3) in liquid crystal C. If we consider the spin probe as a sort of molecular ruler we infer that the two probes report on regions of comparable ordering, i.e., that in the cationic phase C the distance of the oxazolidine ring from the water layer is larger by *ca.* three methylene units than in the anionic mesophase A. This distance corresponds roughly to the size of the pyridinium ring.

To look for further confirmation of this similarity we have also simulated the polyliquid crystalline spectrum of IV(12,3) reported in Figure 1, to derive the fourth rank order parameter $\bar{P}_4$ and the rotational mobility of the long axis. The theory behind the simulation has been described in detail elsewhere.[7] Here we shall only recall the main points. A spectrum like that in Figure 1 can be considered as a superposition of spectra coming from regions where the spin probe reorients rapidly (in the sense of Redfield theory) in an anisotropic environment. However the local directors are not uniformly oriented but have a distribution $P(\Omega)$ with respect to the magnetic field on a macroscopic scale. Given the local axial symmetry of the mesophase we need only to consider the angle γ between director and field. Thus, the spectrum $S(B)$ at a given value of the field B is

$$S(B) = \sum_{m=0,\pm1} \int \mathscr{L}' \left[B, B_m(\gamma),\, W_m(\gamma)\right] P(\gamma) d\gamma, \qquad (3)$$

where $\mathscr{L}'[B, B_m(\gamma), W_m(\gamma)]$ is the first derivative of a Lorentzian line shape related with the transition labelled by the nuclear spin quantum number m, centered at field $B_m(\gamma)$. The angular dependent linewidth is taken to be

$$W_m(\gamma) = \{[T_2^{-1}(\gamma)]^2 + X^2(\gamma)\}^{1/2}, \tag{4}$$

where

$$T_2^{-1}(\gamma) = A(\gamma) + B(\gamma)m + C(\gamma)m^2 \tag{5}$$

is the rotational relaxation contribution calculated using the theory developed in Ref. 7.

A residual angular linewidth $X(\gamma)$ is added to take into account the unresolved proton hyperfine structure, as

$$X(\gamma) = X_0 + X_2 \cos^2 \gamma \tag{6}$$

The best simulation, shown in Figure 1, is obtained with $\bar{P}_4 = -0.05$ and $\tau_0 = 1 \times 10^{-9}$ s rad^{-1}. This compares with values for the same probe in the anionic phase A of $\bar{P}_4 = 0.11$, $\tau_0 = 1.35 \times 10^{-9}$ s rad^{-1}. We notice incidentally that the values of τ_0 obtained confirm that we are in the fast motion region. The negative value of $\bar{P}_4$ indicates that on average the z axis of the nitroxide ring is not parallel to the director but somewhat tilted. Similar results have been obtained for the stearic spin probe IV(5,10) in the anionic phase A. This further substantiates the conclusion that in the cationic phase the stearic probe IV(12,3) reports on the more inner regions of the bilayer than in the anionic.

Finally the TCNE$^{\bar{\cdot}}$(VI) radical anion is found to be more aligned in the cationic phase C. Given its negative charge this probe may be expected, on the basis of chemical intuition, to sit on the polar interface region rather than in the inner part of the bilayer. This was confirmed by adding to the mixture a small amount of $NiSO_4$ ($\sim 10^{-2}$ M). The strong broadening of the esr lines showed that the paramagentic ions Ni^{2+} dissolved in the water layer, can interact effectively with the radical probe, thus providing an extra relaxation mechanism for the electron spin of TCNE$^{\bar{\cdot}}$. A similar situation is found for the same probe dissolved in the anionic phase A. The finding that the degree of order is higher in the cationic phase is reasonable in view of the opposite sign of the interface charge. In fact this radical anion is expected to interact more strongly with the positive pyridinium ions than with the negative head groups of the decanoate units, with consequent greater alignment.

Acknowledgments

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