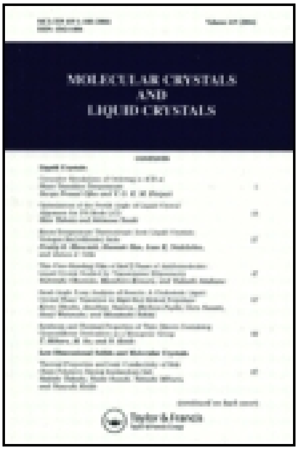

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NMR Spectra of Molecules Oriented in a Lyotropic Mesophase

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Abstract—A lyotropic liquid crystalline phase has been used as an orienting matrix for NMR studies. The solvent and orientation properties of this phase are somewhat different from those of thermotropic nematogens. Spinning samples can be used facilitating the recording of well-resolved spectra suitable for analysis. The spectrum of ethanol has been recorded and analyzed in full by an iterative computer procedure. It is shown that the preferred orientation of ethanol in the mesophase is such that the C—C—O plane is perpendicular to the magnetic field.

Proton and deuteron magnetic resonance rotation studies have also been performed and are discussed in the light of the high resolution results.

Introduction

The discovery by Saupe and Englert[1] that nematic liquid crystalline phases are suitable solvents for NMR studies of dissolved molecules has led to a number of investigations using this technique.[2] These studies have provided information about relative bond distances, bond angles and chemical shift anisotropies of the dissolved molecules as well as solute-solvent interactions within the nematic phase.

In an earlier communication[3] we reported a new kind of nematic phase formed by a mixture of C_8 or C_{10} alkyl sulfates, the corresponding alcohol, sodium sulfate and water (or deuterium oxide) in approximate proportions 40, 5, 5, 50 respectively. In this work we present further results pertinent to the use of this system in orientation studies. The spectrum of dissolved ethanol has been recorded and the orienting effect of the mesophase is compared with that noted earlier for benzene.[4] In addition the results of proton and deuteron magnetic resonance orientation studies of the phase are presented.

Experimental

For most NMR studies the following phase composition (by weight) is used; 36% sodium decyl sulfate (SDS), 7% decyl alcohol ($C_{10}OD$, deuterated by exchange with D_2O for proton NMR purposes), 7% sodium sulfate and 50% deuterium oxide. The phase can be prepared also from the C_8 sulfate and alcohol or the C_8 sulfate and C_{10} alcohol. The above composition appears to fall at about the middle of the nematic range (extending from 30–42% SDS), however this varies somewhat depending on the solute used.

Commercial decyl alcohol, sodium sulfate and deuterium oxide have been used in this work. Sodium decyl sulfate was prepared by the reaction of sulfur trioxide with decyl alcohol in dioxane followed by neutralization with sodium hydroxide.[5] The material so obtained was extracted with petroleum ether to remove excess alcohol and then recrystallized from ethanol, the resultant product was analyzed as 99.4% SDS.‡

The phase can be prepared either by mixing together the various components or the alkyl sulfate can be hydrolyzed with sulfuric acid to give the correct composition. This latter method is not as convenient since it is difficult to stop the hydrolysis at the desired point. In either method the components are weighed into a 15 mm × 125 mm glass tube constricted to 2–4 mm at one point along its length, the tube sealed and the mixture centrifuged back and forth several times at slightly elevated temperatures, ca. 50–70 °C (higher temperatures should be avoided to minimize hydrolysis). The material to be oriented can be added with the phase if it is not heat sensitive.

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‡ Since the publication of the original paper[1] several workers have reported difficulty in preparing this mesophase. We believe this to be due to the use of impure SDS; a commercial sample was purchased and found on analysis to contain 8% unsulfated alcohol.

The presence of the phase can be recognized by its typical nematic " threaded " or " schlieren " microscopic texture (Fig. 1)[6]. When viewed through crossed polaroid plates the phase shows a strong birefringence.

Proton magnetic resonance spectra were recorded on a Varian HA-100 spectrometer. Deuteron magnetic resonance spectra were obtained on a wide line spectrometer operating at 9.2 MHz using " first side band " conditions with a modulation frequency of 2 kHz for detection of the ^{2}H signals.[7]

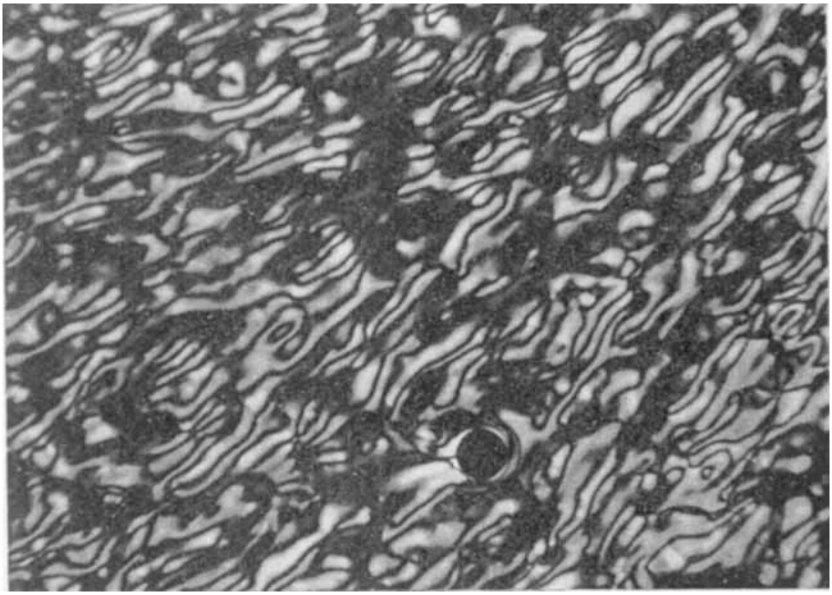

Figure 1. " Threaded " texture in homogenous nematic mesophase viewed through crossed nicols at 100 x magnification.

Mesophase Properties

The proton resonance spectrum of the chain protons of the mesophase is a broad structureless line approximately 4 kHz wide. This presents a broad background against which the sharp lines of the solute spectrum are readily distinguished.

This mesophase offers several advantages over many of the thermotropic nematogens commonly used for orientation studies. Its temperature range (10–75 °C) is such that spectra can be obtained at the probe temperature, removing the need for special gradient-free variable temperature inserts.[8] Because of its composition the phase dissolves both hydrophilic and lipophilic materials. Aromatic substances are of limited solubility ($\frac{1}{2}$–1% by weight), however useable results may be obtained in some cases by accumulation of spectra.[4] This type of mesophase thus complements the usual thermotropic nematogens in which hydrophobic materials are the more soluble. Finally, and most significantly, the orientation of the phase is such that the sample may be spun at 20–30 Hz about an axis perpendicular to the field direction to improve field homogeneity and hence spectral resolution. Using this facility, which is routinely available in normal high resolution NMR spectroscopy, typical linewidths are 1–4 Hz. The degree of orientation is independent of the spinning rate. Thermotropic nematic melts cannot usually be spun in this manner, except perhaps at rather low speeds[9]; their degree of orientation depends on the spinning rate.

The phase is quite viscous and appears to orient relatively slowly in the magnetic field (see below). Reasonable spectra are obtained after a few minutes but best resolution is achieved by allowing the sample to spin in the field for several hours.

Rotation Studies of D_2O and Dissolved Solute

The phase orientation can be monitored by observing the deuteron resonance of the D_2O. Studies on a number of samples of various compositions (both with and without solute) within the nematic range indicate that the precise rate and degree of orientation are quite composition-sensitive. The number of variables involved precludes an exhaustive study of this dependence, however some general observations are possible.

When the sample is first placed in the field the deuteron resonance is the typical "powder-type" pattern (Fig. 2a) ex-

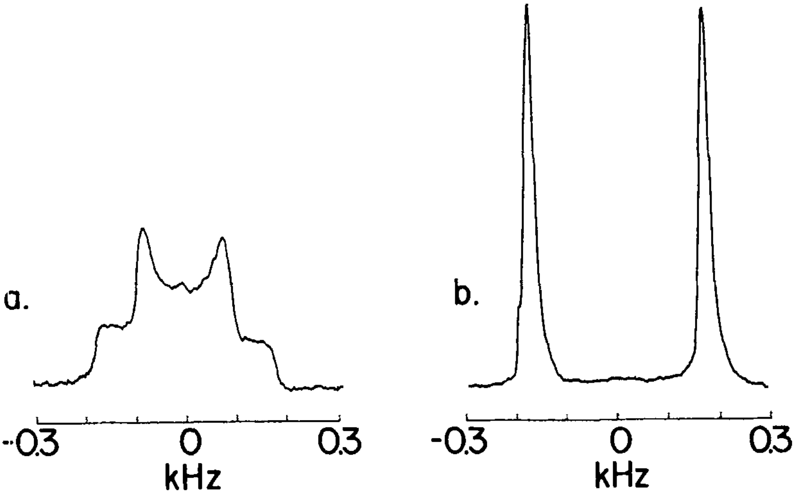

Figure 2. Deuteron spectrum of nematic mesophase (a) immediately after being placed in the magnetic field (b) after being in the magnetic field for several hours.

pected from randomly oriented crystallites or aggregates of $I = 1$ nuclei in which the asymmetry parameter is zero.[10] On standing in the field this spectrum converts to the type expected from a system of $I = 1$ nuclei in which the electric field gradients have a preferred orientation with respect to the magnetic field, i.e. a simple 1 : 1 doublet (Fig. 2b).[11] This conversion typically requires a few minutes for compositions of interest (the presence of solute is an accelerating factor), although samples of composition 42% SDS, 4% $C_{10}OD$, 4% Na_2SO_4 and 50% D_2O require an hour or more to convert. In this latter case the doublet separation shows an $A(3\cos^2\theta - 1)$ angular dependence. Measured quadrupole splittings range from 0.3 to 0.6 kHz. Comparison with the value of 213 kHz found in D_2O ice[12] indicates that most of the quadrupole coupling is averaged by motion. The relatively sharp lines (width ca. 20 Hz) indicate that this motion is rapid compared to the characteristic quadrupole splitting. This splitting then represents the effect of anisotropic rotation of the D_2O molecules conferred by their environment.

The effect of manual rotation on the spectra of solute-containing samples is quite unusual. The rotation of an oriented sample through 180° about an axis perpendicular to the field has no observable effect. Rotation through some other angle (e.g. 45–90°) reinduces a random-type orientation, i.e. a " powder-type " pattern as in Fig. 2a which again, over a period of minutes, recovers to the oriented state. With succeeding rotations however, the reconversion to the random configuration becomes less pronounced. After the sample has been rotated thus through a few revolutions the sharp doublet characteristic of full orientation is maintained regardless of rotation. This rotation-induced orientation is retained for an hour or more after the sample is removed from the magnetic field. A similar phenomenon is noted when the sample is spun at 20–30 Hz about the same axis.

Corresponding proton NMR studies on samples containing 3% glycine yield results consistent with the deuterium studies. Glycine in an anisotropic medium gives a proton spectrum consisting of a simple 1 : 1 doublet of separation 230–300 Hz (depending on mesophase composition) and linewidths of 10 Hz (non-spinning) arising from dipolar interaction between the equivalent methylene protons. On rotating the sample 45–90° the doublet components disappear, presumably to be replaced by an unobservably broad superposition of doublets of varying separations resulting from glycine in the neighborhood of randomly oriented mesophase aggregates. Reorientation takes place over a time similar to that observed with the deuteron spectra, and the doublet recovers to its original intensity, retaining the original spacing throughout. As with the ^{2}H spectra the effect of rotation becomes less pronounced after a few revolutions until eventually the doublet intensity is rotation-independent.

High Resolution Spectra of Dissolved Molecules

As noted above both hydrophilic and lipophilic materials can be oriented in this phase. Substances which have been dissolved include alcohols, amino acids, nitriles, sulfones, organic and inorganic phosphates and phosphonates. The spectrum of ethanol (Fig. 3a) dissolved 3% by weight in the mesophase (36% SDS, 7% $C_{10}OD$, 7% Na_2SO_4, 50% D_2O) is typical; analysis of this spectrum also serves to provide further information about solute-solvent interactions in this system. This spectrum was recorded from a spinning sample contained in a 5 mm tube. The observed linewidths are approximately 2 Hz.

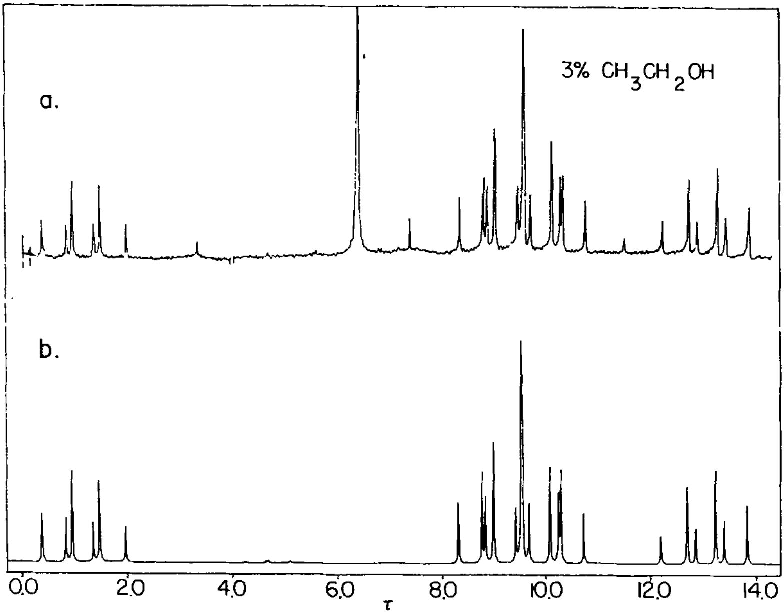

Figure 3. (a) Experimental proton spectrum of ethanol in a lyotropic nematic mesophase; (b) Computer simulation with the parameters given in the text.

The presence of two impurities is noted. A small 1 : 2 : 1 triplet (splitting 410 Hz, centered at $\tau = 7.4$) is due to a trace of methanol. The intense peak at $\tau = 6.4$ is due to HDO resulting from incomplete deuteration of the water and alcohols. The remainder of the spectrum may be analyzed as an A_3B_2 system (the hydroxyl proton exchanges readily in the hydrophilic medium). There are five parameters to be determined, viz., the chemical shift difference $\nu_A - \nu_B$, the indirect spin coupling J_{AB} and the anisotropic couplings D_{AA}, D_{BB}, D_{AB}. Rotation about the C—C bond results in full equivalence[13] within the A and B groups of nuclei, thus the anisotropic phase spectrum will be independent of the indirect spin couplings J_{AA}, J_{BB}.

The major spectral features are readily explained. The two widely spaced groups of six lines at the extremities of the spectrum arise from anisotropic coupling D_{BB} between the two methylene protons, each group is essentially a 1 : 3 : 3 : 1 quartet (with further second-order splitting) due to the interactions D_{AB} and J_{AB} with the three equivalent methyl protons. Likewise the methyl group resonances, centered at $\tau = 9.5$, may be broadly considered as an overlapping 1 : 2 : 1 triplet of 1 : 2 : 1 triplets. Assuming an approximate magnitude of 7 Hz for the indirect coupling $|J_{AB}|$ from the isotropic phase spectrum of ethanol,[14] first-order estimates of the three anisotropic couplings were readily derived.

There are eight possible relative sign combinations of the four couplings, the symmetry of ethanol (C_s) is not sufficient to preclude any of these. Trial spectra calculated with all eight combinations showed that the second-order splitting in the methylene proton resonances can be reproduced only when J_{AB} and D_{AB} are of opposite sign, but did not serve to unequivocally identify as correct any one of the four groups of parameters fulfilling this condition. The iterative computer program LAOCN3[15], modified to take account of anisotropic couplings as well as indirect spin couplings and chemical shifts in the spectral calculation and iterative fitting,[4] was used to select the appropriate sign combination. The iterative refinement was performed for each combination using only such lines as could be unambiguously assigned. The final rms errors after convergence are given in Table 1 (the sign combinations are given with respect to the sign of the indirect coupling J_{AB}). Only combinations with D_{AB}, J_{AB} of opposite sign are considered. It is immediately apparent that the best fit is achieved when the anisotropic couplings D_{AB}, D_{BB}, D_{AB} are all of the same sign and opposite to that of J_{AB}. Reiteration of this case with all assignable lines included gave the final parameters and their probable errors quoted in Table 2; the vicinal coupling J_{AB} has been assumed positive[16] and the D's therefore negative. The rms error in this final fitting increases to 0.399 Hz due to uncertainties in the frequency measurement of overlapping lines, the greatest deviation between calculated and observed line positions is 1.1 Hz. A theoretical simulation of the spectrum assuming a Lorentzian lineshape (linewidth at half-height 2 Hz) is shown in Fig. 3b; this agrees well with the experimental spectrum. Theoretical spectra were also plotted for the other sign combinations. While the parameter set finally chosen on the basis of iterative analysis appears to yield the best visual fit of the experimental line intensities, the differences are relatively slight. This points up the advantage of an iterative refinement in allowing one to choose the appropriate parameter set on a more objective basis and with considerably more confidence than is afforded by a trial-and-error approach coupled with visual simulation. This is particularly so in this case where second-order effects are relatively slight.

TABLE 1 Rms Errors after Iterative Fitting for Different Sign Combinations of Indirect and Direct Couplings of Ethanol Protons

Sign Combination (with respect to J_{AB}) Same Sign	Opposite Sign	Rms Error (Hz)
D_{AA}, D_{BB}	D_{AB}	1.865
D_{AA}	D_{BB}, D_{AB}	1.190
D_{BB}	D_{AA}, D_{AB}	1.080
	D_{AA}, D_{BB}, D_{AB}	0.063

TABLE 2 Final Parameters in Ethanol Analysis (J_{AB} is assumed positive)

Parameter	Value
$\tau_A - \tau_B$	2.462 ± 0.11 ppm.
J_{AB}	+ 7.05 ± 0.07 Hz.
D_{AA}	− 46.38 ± 0.14 Hz.
D_{BB}	− 780.69 ± 0.13 Hz.
D_{AB}	− 62.59 ± 0.11 Hz.

Assuming that the contribution of the anisotropic part of the indirect coupling is small, the couplings D_{ij} may be interpreted in terms of the direct coupling of nuclear magnetic dipoles. Ethanol in its staggered conformation has C_s symmetry. Choice of a molecule-fixed coordinate system such that the z-axis is perpendicular to the molecular plane of symmetry and the x-axis lies along the C—C bond allows the direct dipolar couplings to be written in terms of three motional constants $c_{3z^2-r^2}$, $c_{x^2-y^2}$, c_{xy} defining the anisotropic motion,[17] viz.,

$$D_{ij}{}^{dir} = -\frac{\gamma_i\gamma_j\hbar}{\pi 5^{1/2} r_{ij}{}^{-5}}\left[c_{3z^2-r^2}\langle(\Delta z_{ij})^2 - 1/2(\Delta x_{ij})^2 - 1/2(\Delta y_{ij})^2\rangle\right.$$
$$\left. + c_{x^2-y^2}3^{1/2}\langle 1/2(\Delta x_{ij})^2 - 1/2(\Delta y_{ij})^2\rangle + c_{xy}3^{1/2}\Delta x_{ij}\Delta y_{ij}\right]$$

where r_{ij} is the distance between nuclei i and j, Δx_{ij}, Δy_{ij}, Δz_{ij} are the average differences (taken over molecular vibrations) between the x, y and z coordinates of nuclei i and j and γ_i is the magnetogyric ratio of the ith nucleus.

Calculation of the motional constants from the observed anisotropic couplings has been performed assuming regular tetrahedral geometry for each carbon atom and C—C, C—H bond lengths of 1.55, 1.09 Å respectively. With this geometry the expressions obtained by Woodman[13] for the analogous case of ethyl iodide are applicable and have been used here without change. Insertion of the anisotropic couplings from Table 2 yields the following motional constants:

$$c_{3z^2-r^2} = +0.03988$$

$$c_{x^2-y^2} = +0.01760$$

$$c_{xy} = -0.05981$$

The expansion of $P(\theta, \phi)$, the probability density per unit solid angle that the applied field is θ and ϕ in the coordinate system chosen,[17] is given as

$$P(\theta, \phi) = 0.076029 + 0.010646\cos^2\theta$$
$$+ 0.002712\sin^2\theta\cos 2\phi$$
$$- 0.009216\sin^2\theta\sin 2\phi$$

This function has its maximum value for $\theta = 0°$ regardless of ϕ, i.e. the most probable orientation of the ethanol molecule in the lyotropic mesophase is with the applied field direction perpendicular to the C—C—O plane.

Discussion

We noted previously[4] that the preferred orientation of benzene in the same lyotropic mesophase used here is that in which the molecular plane is perpendicular to the applied field. This is in contrast to the behavior induced by thermotropic nematogens; in *p*, *p'*-di-*n*-hexyloxyazoxybenzene the parallel alignment is preferred.[7,18] This, taken in conjunction with the fact that the sample can be spun in the magnetic field without destroying the field-induced mesophase orientation, led us to conclude that the phase alignment is one in which the long axes of the surfactant molecules are perpendicular to the field, rather than parallel as expected for thermotropic nematogens.

The results obtained for ethanol are analogous to those reported for benzene. The preferred orientation of the molecule can be broadly considered as again perpendicular to the field. Woodman has shown that the related molecule ethyl iodide, when dissolved in a thermotropic nematogen, orients with its C—C—I plane parallel to the applied field.[13]

The deuteron and proton magnetic resonance orientation studies may be considered in the light of the above results. It is not possible on the basis of NMR results alone to deduce the specific mesophase structure in terms of the shape and distribution of surfactant " aggregates ", however the observations can be considered in terms of a simplified model. Without specifically defining the aggregate shape, we consider its overall magnetic anisotropy to be such that the preferred orientation induced by a magnetic field is that with some structural feature (perhaps the long axes of the surfactant molecules) perpendicular to the field (orientation of an aggregate is defined here only in these terms). Such a condition could be fulfilled for example by a lamellar-type aggregate structure oriented such that the preferred field direction is parallel to the plane of the lamellae and perpendicular to the long axes of the component molecules. We further consider that it is interaction with the structural feature which confers anisotropy of motion upon the D_2O and dissolved solute molecules. When a sample is first placed in the field the aggregates are randomly oriented, leading to a powder type deuteron resonance pattern (or an unobservedly broad solute proton resonance pattern). The effect of the field will then be to orient the aggregates in a plane perpendicular to the field, within this plane all orientations are equally probable. Rotation by 180° about an axis perpendicular to the field does not alter this situation. On rotation by say 45–90° some aggregates will remain perpendicular to the field or nearly so, most will be required to reorient. Again this is observed as the conversion from a powder-type pattern to a sharp doublet. If the thermal random motion of the aggregates is low as seems reasonable from consideration of (a) the viscosity of the mesophase, (b) the relatively slow rate of reorientation under high magnetic fields and (c) the retention of rotation history after removal from the field, a relatively few such rotation experiments will suffice to orient all aggregates in the only direction uniformly perpendicular to the field, i.e. along the axis of rotation. At this point further rotation experiments become ineffective. The D_2O quadrupolar splitting is consistent with an anisotropic rotation of D_2O about this (invariant) axis. Rapid spinning of the sample about this axis produces an equivalent result.

Conclusions

Although the structure and behavior of this mesophase are not fully understood, it should prove a versatile and useful addition to the group of solvents suitable for NMR orientation studies of dissolved molecules, the more so as its solvent and orientation properties are quite different from those of the usual thermotropic nematogens. Multicomponent lyotropic mixtures give rise to an extensive variety of mesophases, the existence of other nematic-type mixtures suitable for this type of study would therefore seem quite probable.

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