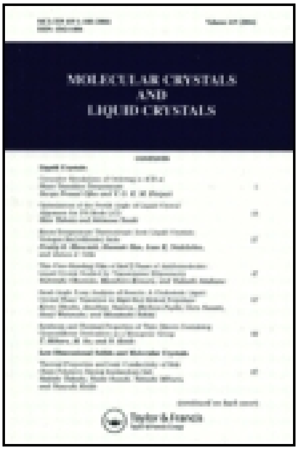

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A Proton NMR Study of Partially Oriented Phenylsulphonate in Various Amphiphilic Nematic Liquid Crystals

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A Proton NMR Study of Partially Oriented Phenylsulphonate in Various Amphiphilic Nematic Liquid Crystals

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Preliminary proton nmr studies have been made on the partially oriented phenylsulphonate ion (present as the counterion) in various amphiphilic nematic phases. The changes in the sign of the degree of orientation of the phenylsulphonate ion are consistent with the micelle structure and the sign of the diamagnetic anisotropy of the various phases.

Keywords: nmr, phenylsulphonate, amphiphilic, nematic

INTRODUCTION

Amphiphilic nematic liquid crystals may be considered to be orientationally-ordered aqueous micellar solutions.[1] There are two distinct mesophase structures depending on the micelle shape[2,3] with disk shaped or cylindrical micelles. These phases are closely related to the dimensionally-ordered lyotropic liquid crystals; ie. the lamellar and the hexagonal phases.[4,5] When the micelle shape changes from disk to cylinder it is accompanied by a change in the sign of the diamagnetism.[6] The sign can also be changed in the absence of a thermodynamic change by the inclusion of fluorocarbons or aromatic

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molecules or ions into the micelle molecular structure.[7,8] It can be considered that there are four types of micellar nematic phase, N_D^+, N_D^-, N_C^+ and N_C^-, where D and C signify micelle shape and the ± symbol indicates the sign of the diamagnetic anisotropy.[9] The director of a nematic phase with positive diamagnetic anisotropy aligns parallel to the magnetic field and in the converse situation of a phase with negative diamagnetic anisotropy, the nematic director aligns perpendicular to the magnetic field.

Amphiphilic nematic liquid crystals are ideal matrices for the proton nmr studies of small solute molecules and ions such as the counterion, phenylsulphonate. Like thermotropic nematic liquid crystals, they spontaneously align in magnetic fields and give rise to high resolution nmr spectra. For the phenylsulphonate ion, the proton nmr spectrum appears complex but can be readily analysed using a computer program.[10] The program used is part of the software of the Aspect 2000 microcomputer which controls the Brüker spectrometers.

If nuclei i and j belong to the same rigid part of the molecule and the director of the nematic phase is parallel to the magnetic field, the dipolar coupling D_{ij} is given by the equation

$$Dij = -\frac{h\gamma_i\gamma_j}{4\pi^2 r^3_{ij}} \cdot S_{ij}$$

where S_{ij} is the degree of orientation of the axis passing through i and j, assuming the distance between nuclei i and j, r_{ij}, is constant neglecting the influence of vibrational motion and γ is the magnetogyric ratio. From such a study, precise information may be derived concerning the sign and the magnitude of the dipolar coupling and the degree of orientation S_{zz} if the indirect J couplings are known. To a lesser extent, some structural information is also given. The sign of the degree of orientation of small ions embedded in the electrical double layer of the micelle surface depends on micelle shape, diamagnetism and ion binding.[11,12]

EXPERIMENTAL RESULTS

In this communication, results from a proton nmr study of the aromatic ion, phenylsulphonate, present as the counterion in an amphiphilic nematic liquid crystal, are reported. The amphiphilic nematogens were derived from the detergents, tetradecyltrimethylammonium bromide and phenylsulphonate (TDTABr and TDTAPS, respectively), which were prepared as previously described.[4] The samples of the mesophases having various micelle shapes and diamagnetic anisotropies were weighted out and mixed as previously described[4] and their compositions are presented in Table I. The micelle shape of the phase in each sample and its diamagnetic anisotropy were determined using polarising microscopy and nmr as previously described.[13]

The proton spectra were recorded using a WP 100 MHz Brüker spectrometer for the disk-shaped micellar solutions and using a WP 400 MHz Brüker spectrometer for the cylindrical micelles. These WP spectrometers have superconducting magnets where the spinning axis of the sample corresponds to the direction of the magnetic field. In such an nmr spectrometer nematic samples can be routinely spun without (regard to) the sign of the diamagnetism to produce high resolution nmr spectra. The proton nmr spectrum of partially oriented phenylsulphonate in an N_C^+ amphiphilic nematic crystal at 20°C is illustrated in Figure 1. The spectra were recorded at 20°C, except for the N_C^- sample where the temperature was 32°C. The spectra were analysed using a computer program and the results are presented in Table II. The anisotropic part of the J coupling was assumed to be zero, where $J(1,2) = J(2,3) = J(3,4) = J(4,5) = \pm 8.0$ Hz; $J(1,3) = J(2,4) = +1.0$ Hz; $J(1,4) = J(2,5) = \pm 0.4$ Hz; $J(1,5) - J(2,4) = +1.0$ Hz.

DISCUSSION

It was assumed that the long z axis of the phenylsulphonate ion lies in a direction more or less parallel to the surface normal of the micelle

TABLE I

Mesophase composition (in mg) with phase type and the predicted sign of the degree of orientation S_{zz}

Mol %	TDTABr	TDTAPS	Decanol	D_2O	Type	Sign of S_{zz}[a]
55.0	151	228	55	550[b]	N_D^+	+
10.0	303	42	60	550[b]	N_D^-	−
10.2	640	80	−	1260	N_C^+	−
100.0	−	800	−	1200	N_C^-	+

[a] S calculated taking micelle shape and diamagnetic anisotropy into consideration.
[b] D_2O containing 2% Cs_2CO_3; 0.4% $CH_3PO(OH)_2$.

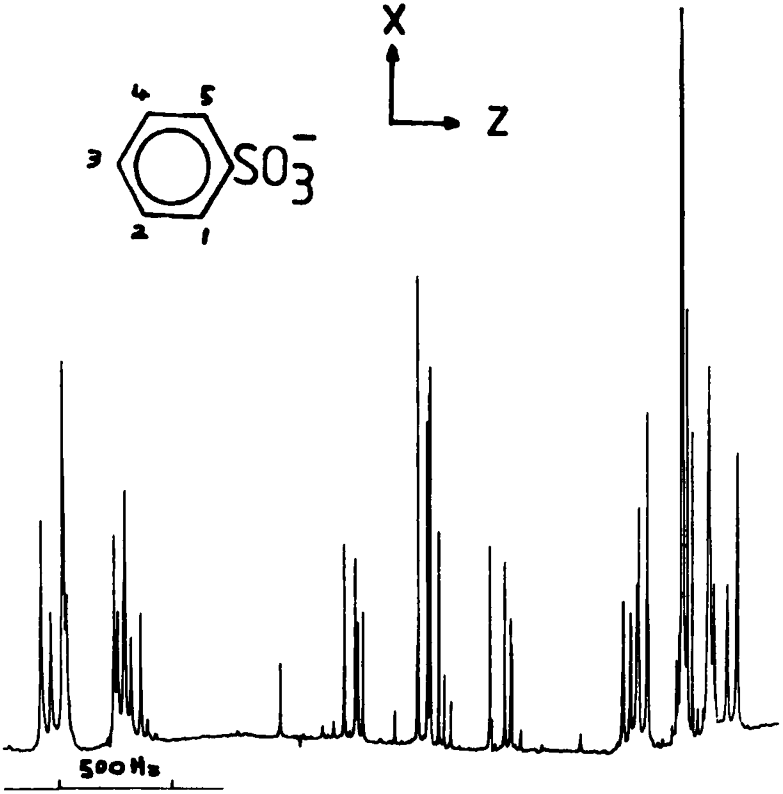

FIGURE 1 The proton nmr spectrum of partially oriented phenylsulphonate in a N_C^+ amphiphilic nematic liquid crystal at 20°C.

surface and that the ion binding does not affect the sign of the degree of orientation S_{zz}. The experimentally determined signs of S_{zz} of the ion are the same as those expected on the basis of micelle shape and the changes in the diamagnetic anisotropy (see Table II). For a change of micelle shape from disk to cylinder (assuming infinitely long rods and infinite bilayers) the S_{zz} of a small ion embedded in the surface would be expected to change by a factor of $-1/2$. When the sign of the diamagnetic anisotropy changes from positive to negative, the S_{zz} is also expected to change by a factor of $-1/2$ and for the appropriate change the factor is -2. A thermodynamic transition, ie. the change of micelle shape from disk to cylinder, is accompanied by a change in the sign of the diamagnetic anisotropy and the predicted result is therefore that there should be no change in the sign of the S_{zz}. Hence, a change in the sign of the diamagnetic anisotropy only causes a

TABLE II

Computer calculated nmr parameters, Hz, for the phenylsulphonate ion in various assigned mesophase types

	N_D^+	N_D^-	N_C^+	N_C^-
Chemical Shift W				
$W(1) = W(5)$	+18.8	−63.7	−289.0	−174.4
$W(2) = W(4)$	−21.9	−35.2	−120.2	−0.6
$W(3) =$	0.9	0.4	0.0	0.0
Dipolar Coupling Constant D				
$D(1,2) = D(4,5)$	−2270.7	+1345.7	+1675.1	−736.5
$D(1,3) = D(3,5)$	−312.0	+188.6	+244.9	−104.1
$D(1,4) = D(2,5)$	−39.2	+23.9	+57.2	−19.0
$D(1,5) = D(2,4)$	+67.3	−38.4	+8.6	+9.8
$D(2,3) = D(3,4)$	−303.4	+180.3	+445.3	−145.1
Degree of Orientation S				
S_{xx}	−0.0223	+0.0127	−0.0029	−0.0032
S_{zz}	+0.145	−0.0856	−0.107	+0.0469
S_{yy}	−0.1227	0.0629	+0.1099	−0.0437
S_{xx}/S_{zz}	−0.15	−0.15	+0.027	−0.070

change of sign of S_{zz} when there is no accompanying thermodynamic transition. The diamagnetic anisotropy for hydrocarbon chains is negative, whereas for aromatic rings it is positive.[14] If the diamagnetism of the constituent molecules, and not the inherent shape diamagnetism of the micelle, dominates the diamagnetic properties of the N_D phase, increasing amounts of the phenylsulphonate ion will cause the diamagnetic anisotropy to move from a negative value through zero to become positive. For the N_C phase the converse will occur. These sequence changes were observed.

The ratio S_{xx}/S_{zz} is small and moves close to zero for the transition from disk to cylinder-shaped micelles. This ratio is less affected by changes in the sign of the diamagnetic anisotropy which are not accompanied by micelle shape transitions. If the factor of $-1/2$ is taken into account for micelle shape and the sign of the diamagnetic anisotropy, the S_{zz} values for the various phase types lie between 0.15 and 0.20. These values are of the same order of magnitude as the degree of orientation of hydrocarbon chains measured using ^{2}D nmr (for example Reference 14).

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