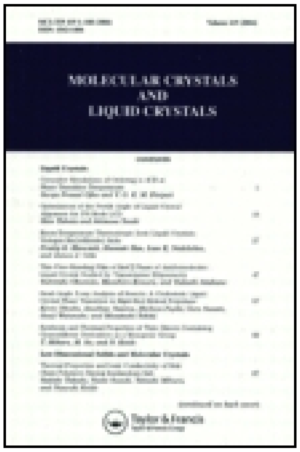

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Reversal of the Sign of the Diamagnetic Anisotropy of Lyotropic Nematic Mesophases Induced by an Aromatic Solute

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In four lyotropic nematic mesophase systems the sign of the anisotropy of the diamagnetic susceptibility was observed to change with the addition of sufficient amounts of benzenesulfonate. Four series of mesophases were examined, two with initially positive diamagnetic anisotropies and two with initially negative anisotropies prepared using alkyltrimethylammonium, decylammonium and dodecanoate surfactants. The sign of the diamagnetic anisotropy and the order parameters of the benzenesulfonate ion were determined from the proton NMR spectra. The concentration of benzenesulfonate ion necessary to form a mesophase with zero diamagnetic anisotropy can be explained in terms of the relative contributions to the macroscopic diamagnetic susceptibility of the aromatic rings and the hydrocarbon chains.

Keywords: lyotropic mesophases, nematic mesophases, diamagnetic anisotropy, NMR

INTRODUCTION

One of the characteristic and useful properties of uniaxial nematic lyotropic mesophases is their ability to align spontaneously in magnetic fields.[1] The homogeneous alignment of these mesophases results in high resolution nuclear magnetic resonance (NMR) spectra and the full potential of the anisotropic NMR parameters can therefore be exploited.[2] In the presence of a magnetic field, anisotropic substances experience a magnetic torque due to the anisotropy of the diamagnetic susceptibility. This torque is normally sufficient to overcome the internal viscous forces of nematic mesophases and the unique axis (director or optic axis) aligns parallel or perpendicular to the applied field direction, when the diamagnetic anisotropy ($\Delta\chi = \chi_{\parallel} - \chi_{\perp}$) is respectively, positive or negative.

X-ray diffraction studies[3-7] have shown that nematic lyotropic mesophases are composed of non-spherical finite micelles with long-range orientational order but without the additional translational order of the more common hexagonal and lamellar lyotropic mesophases. From these studies it was concluded that the nematic mesophases with a positive diamagnetic anisotropy (called type I *CM* or N_C mesophases) are composed of cylindrical or prolate spheroidal micelles, whilst those with a negative diamagnetic anisotropy (called type II *DM* or N_D mesophases) are made up of lamellar disklike or oblate spheroidal micelles. It has been recently suggested that in the uniaxial nematic mesophases the micelles are similar in form to those of the biaxial nematic mesophase and that the only change at the uniaxial-biaxial transitions is in the long-range order.[8]

The diamagnetic anisotropy of lyotropic mesophases arises predominantly from the molecular diamagnetic anisotropy of the hydrocarbon chains of the surfactants[9] (which are on the average oriented perpendicular to the micellar surface). The molecular diamagnetic anisotropy of the hydrocarbon chains together with the shape and orientation of the micelles normally determine the sign of the macroscopic diamagnetic anisotropy. However, if other components with a large molecular diamagnetic anisotropy are present they can have a dominant contribution. Reeves and co-workers[10,11] have shown that the addition of potassium heptyloxybenzoate to nematic lyotropic mesophases can invert the sign of the diamagnetic anisotropy without causing a change in the basic structure of the mesophase. The same effect has been observed in mesophases containing benzenesulfonate[12] and anilinium[13] ions, although in the latter case, this effect was not recognized at the time because the structure of these mesophases had not been clearly established. Aromatic groups present in these mesophases however, do not always produce a contribution opposite in sign to that of the hydrocarbon chains. For example nematic mesophases prepared using hexadecylpyridinium chloride have a "normal" diamagnetic anisotropy.[14,15]

To investigate the molecular contributions to the diamagnetic anisotropy of lyotropic mesophases, the order parameters for the benzenesulfonate ion were obtained from their proton NMR spectra and the concentration of the aromatic ion necessary to invert the sign of the diamagnetic anisotropy was determined. Four series of mesophases were examined; two with cylindrical micelles and two with disklike micelles.

EXPERIMENTAL

All surfactants used were recrystalized two to three times and carefully dried. The tetradecyltrimethylammonium bromide was purchased from Baker Chemical Co. as technical grade hexadecyltrimethylammonium bromide. However the ^1H and ^{13}C NMR spectra together with gas chromatographic analyses of the alkenes, formed by the Hoffmann degradation of the corresponding hydroxide, showed that the product was actually 99.5% tetradecyltrimethylammonium bromide, the main impurity being the hexadecyl homolog. The only impurity detected in the hexadecyltrimethylammonium bromide from Carlo Erba was *ca.* 0.5% of the tetradecyl homolog. Decyltrimethylammonium iodide was prepared by exhaustive methylation. The alkyltrimethylammonium benzenesulfonates were prepared by neutralizing the hydroxide generated by a ion-exchange column.

Four series of mesophases were studied in which it was possible to increase the concentration of the benzenesulfonate ion sufficiently to reverse the sign of the diamagnetic anisotropy.

(A) The mixture, tetradecyltrimethylammonium bromide 3.55%, sodium sulfate 0.75% and water 95.70 mol %, forms a N_C mesophase.[12] In this mesophase the bromide ion could be replaced by the benzenesulfonate ion on a mole for mole basis in all proportions.

(B) The mixture, tetradecyltrimethylammonium bromide 3.36%, decanol 1.01%, sodium sulfate 0.57% and water 95.06%, forms a N_D mesophase.[12] In this case 50% of the bromide ion could be replaced by benzenesulfonate ion without destroying the nematic mesophase.

(C) For the N_D mesophases prepared using decylammonium chloride, decyltrimethylammonium benzenesulfonate, sodium chloride and water (pH ~ 2) with composition 6.86, 2.62 and 90.52 mol %, total surfactant, sodium chloride and water, respectively, nematic mesophases could be prepared with benzenesulfonate ion concentrations up to 30 mol % of the total surfactant.

(D) Nematic mesophases were prepared by the addition of hexadecyltrimethylammonium benzenesulfonate (up to 60 mol % of the total surfactant) to the N_C mesophase pre-

> pared from potassium dodecanoate, potassium chloride and water.[16] However, in this case the mole ratio of surfactant/electrolyte/water could not be maintained constant. Slightly more water was needed to maintain the nematic mesophase with the substitution of potassium dodecanoate.

The sign of the diamagnetic anisotropy of the mesophases was readily determined by observing their angular dependence and the effect of sample spinning[1] on the NMR spectrum.

The proton NMR spectra of partially oriented benzenesulfonate ions were recorded at 32°C on a Varian XL-100 spectrometer using an external fluorine lock signal. Whenever possible, spectra were obtained by the Fourier transform technique using the partially relaxed inversion-recovery method to suppress the water signal. A modified UEA computer program[17] was used for the spectral analyses. The scalar spin-spin couplings of the benzenesulfonate ion, determined in aqueous solution, were assumed to be unchanged in the mesophases. The values, in Hz, obtained were $J(1,2) = 7.86 \pm 0.03$, $J(1,3) = 1.17 \pm 0.03$, $J(1,4) = 0.58 \pm 0.02$, $J(1,5) = 1.86 \pm 0.03$, $J(2,3) = 7.51 \pm 0.03$ and $J(2,4) = 1.37 \pm 0.03$ with a rms deviation of 0.049 Hz for the 44 transitions used in the least-squares analysis.

The signs of the dipolar couplings were determined, assuming that all the scalar couplings are positive.[18] Since the scalar couplings are very small in comparison with the dipolar couplings, the rms deviations of the least-squares fit are not very sensitive to their relative signs. However, in all cases it was possible to determine the signs of the dipolar couplings relative to the scalar couplings. In this respect, the intensities and positions of poorly resolved peaks, which were not used in the iterative calculations, proved to be very useful. Structural and orientational parameters were calculated using the program SHAPE[19] without vibrational corrections. An interproton distance of 2.477 Å, found for benzene,[20] was assumed when calculating the order parameters.

RESULTS

The direct dipole-dipole coupling between a pair of nuclear spins in a rigid molecule, partially oriented in an uniaxial medium, may be expressed as:

$$D_{ij} = -\frac{h\,\gamma_i\,\gamma_j}{4\pi^2 r_{ij}^3} \sum_{\alpha,\beta}^{x,y,z} \cos\mu_\alpha \cos\mu_\beta\, S_{\alpha\beta}\,(3\cos^2\Omega - 1)/2$$

where γ_i and γ_j are the magnetogyric ratios of the nuclei, r_{ij} their internuclear distance, μ_α the angle between the internuclear vector and the axis of the Cartesian coordinates fixed in the molecule and Ω the angle between the director and the magnetic field direction. The orientation of the Cartesian molecular axes system with respect to the director is described by a set of orientation parameters[21] $S_{\alpha\beta}$,

$$S_{\alpha\beta} = \frac{1}{2} \langle 3 \cos \theta_\alpha \cos \theta_\beta - \delta_{\alpha\beta} \rangle$$

where θ_α is the angle between the director and the molecular axis α, $\delta_{\alpha\beta}$ the Kronecker delta and the angular brackets denote an average over the orientations of the molecule in the anisotropic medium.

The numbering of the nuclei and the coordinate system used for the benzenesulfonate ion are presented in Figure 1. For a molecule with C_{2v} symmetry only two independent order parameters are needed to describe the degree of orientation. From an analysis of the proton NMR spectrum of the partially oriented ion, six dipolar couplings can be obtained. The ratios of the interproton distances determined showed no significant deviations from a regular hexagonal geometry.

On increasing the concentration of the benzenesulfonate ion, a reversal of the sign of the diamagnetic anisotropy was observed for

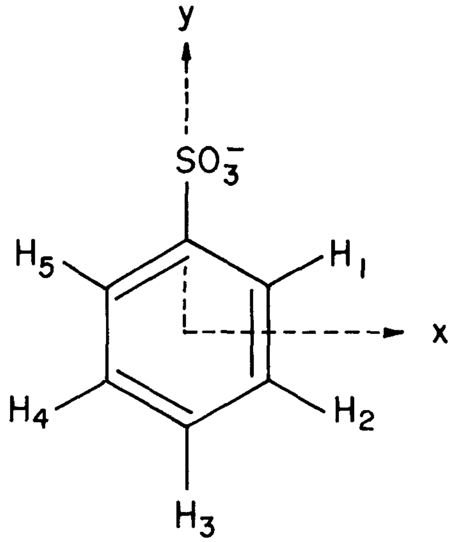

FIGURE 1 The numbering of the nuclei and the coordinate frame used for the order parameter tensor of the benzenesulfonate ion.

each of the four mesophases. No discontinuous change in the order parameters was observed with the change in the sign of the diamagnetic anisotropy. Since the order parameters describe the degree of orientation of the solute with respect to the director, the 90° reorientation of the director in the magnetic field is not accompanied by a change in the basic structure of the mesophases. The variation of the order parameters with the concentration of the benzenesulfonate ion is shown in Figure 2 and the compositions of the mesophases with

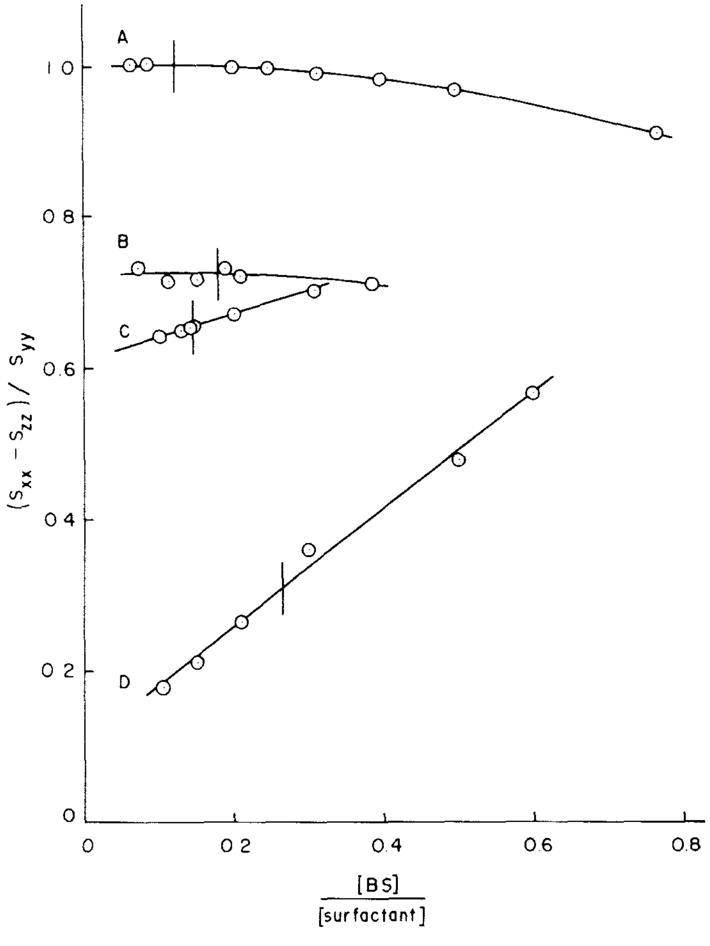

FIGURE 2 Variation of the ratio of the order parameters of the benzenesulfonate ion with the composition of the mesophase. The vertical line indicates the division between mesophases with opposite signs of the diamagnetic anisotropy. The mesophases are described in the experimental section.

TABLE I

The concentration of the benzenesulfonate ion (BS) and order parameters in mesophases with a zero diamagnetic anisotropy

Mesophase[a]	$\frac{[\text{BS}]}{[\text{surfactant}]}$[b]	$\langle n \rangle$[c]	S_{yy}	$\frac{S_{xx} - S_{zz}}{S_{yy}}$
A	0.124 ± 0.005	13.0	−0.103	1.00
B	0.180 ± 0.008	12.1	+0.124	0.722
C	0.1471 ± 0.0004	9.0	+0.180	0.656
D	0.265 ± 0.005	11.3	−0.090	0.310

[a] See experimental section for compositions.

[b] Decanol when present is included in the surfactant concentration.

[c] Average number of methylene groups per surfactant molecule.

isotropic diamagnetic susceptibility are given in Table I. Near the transition the mesophases did not present well resolved spectra, due to a lack of a homogeneous alignment, after remaining overnight in the magnetic field. Although these spectra could not be analyzed, the sign of the diamagnetic anisotropy could be determined. It was found that samples of mesophase C, with extremely small diamagnetic anisotropies could be aligned in magnetic fields—probably because of the low viscosity of these particular mesophases.

Table I also presents the order parameters of the benzenesulfonate ion for mesophases with a zero diamagnetic anisotropy (obtained by interpolation). Except for mesophase C, the order parameter for the C_2 axis, S_{yy}, showed little or no significant dependence on the concentration of the benzenesulfonate ion. For series C, where decylammonium chloride was substituted by tetradecyltrimethylammonium benzenesulfonate, S_{yy} decreased from 0.20 to 0.14 for the mesophases studied.

DISCUSSION

The sign of S_{yy} indicate that the C_2 axis of the benzenesulfonate ion is, on average, oriented perpendicular to the micelle interface in all four mesophases. This axis is the most highly oriented and S_{yy} is the same order of magnitude as the degrees of order observed for the initial segments of the hydrocarbon chains in similar mesophases. In a previous study, the degree of order of the anilinium ion and the initial methylene segments of sodium decylsulfate were found to be almost identical.[13] Also S_{yy} for the benzenesulfonate ion in mesophase D was observed to be independent of the proportion of the two surfactants which have ionic headgroups of opposite charge. This supports the conclusion that the benzenesulfonate ion is effectively incorporated into the micellar structure.

The large differences and variations of the ratio of the order parameters, shown in Figure 2, must be due to the differences in the intermolecular interactions which impose the orientation on the solute. It is not always easy to visualize the orientation of the solute since the three order parameters are not independent. In mesophase A, the null value of S_{xx} indicates that there is no preferred orientation of this axis, while in mesophase D, the solute is approaching the limit for a cylindrical symmetry ($S_{xx} = S_{zz} = -1/2\ S_{yy}$) which represents a free rotational diffusion about the C_2 axis.

The concentration of the benzenesulfonate ion necessary to reverse the sign of the diamagnetic anisotropy should depend on the degree of order of the axis perpendicular to the aromatic ring which has the abnormally large (in magnitude) diamagnetic susceptibility. The basic source of the diamagnetic anisotropy of lyotropic mesophases must be the surfactant molecules since the water molecules have both a very low order and a low molecular diamagnetic anisotropy.

The contribution of a molecule to the diamagnetic susceptibility parallel to the director is given by,

$$\chi_{\parallel} = \bar{\chi} + \frac{2}{3} \sum_{\alpha,\beta} S_{\alpha\beta}\, \chi_{\alpha\beta}$$

where $\bar{\chi}$ is the average molecular susceptibility. Therefore the contribution of the benzenesulfonate ion to the susceptibility parallel to the director can be written,

$$\chi_{\parallel}^{BS} = \bar{\chi}^{BS} + \frac{2}{3} S_{zz}\, \Delta\chi^{BS} + \frac{1}{3}(S_{xx} - S_{yy})(\chi_{xx} - \chi_{yy})$$

where

$$\Delta\chi^{BS} = \chi_{zz} - \frac{1}{2}(\chi_{xx} + \chi_{yy}).$$

Assuming that the methylene groups have effectively a cylindrical symmetry because of rapid rotation about the extended chain axis, the orientation of a methylene group can be described by a single order parameter S_{ch}, the degree of order of the axis perpendicular to the CH_2 plane. The molecular contribution of a methylene group therefore is,

$$\chi_{\parallel}^{CH_2} = \bar{\chi}^{CH_2} + \frac{2}{3} S_{ch}\, \Delta\chi^{CH_2}$$

where

$$\Delta\chi^{CH_2} = \chi_{zz} - \frac{1}{2}(\chi_{xx} + \chi_{yy})$$

with the z-axis perpendicular to the CH_2 plane.

In all four mesophases the sign of S_{zz} indicates that the axis perpendicular to the aromatic plane is on average, oriented, perpendicular to the average direction of the extended chain axis. Therefore S_{zz} and S_{ch} have opposite signs. Since both molecular diamagnetic anisotropies as defined here have the same sign, the benzenesulfonate ion and the hydrocarbon chains of the surfactant molecules have opposite contributions to the bulk diamagnetic anisotropy. A relationship between the concentration and the order parameters at the point where these two contributions cancel can be derived using some simplifying assumptions. Since the degree of order profiles of the hydrocarbon chains were not determined, it is convenient to express the total contribution of the methylene groups to the volume diamagnetic susceptibility in terms of the total surfactant concentration, the average number of methylene groups per surfactant, $\langle n \rangle$, and an average degree of order, $\langle S_{ch} \rangle$. If one assumes that these are the only important contributions to the diamagnetic anisotropy and that the two components of the susceptibility in the aromatic plane are equal, the following relationship can be obtained for mesophases with an isotropic diamagnetic susceptibility:

$$\frac{S_{yy}}{S_{zz}} = -\frac{\Delta\chi^{BS}}{\Delta\chi^{CH_2}} \frac{S_{yy}}{\langle S_{ch} \rangle} \frac{[BS]}{\langle n \rangle [\text{surfactant}]}$$

The variation of the ratio of the order parameters of the benzenesulfonate ion with the composition of the mesophase is presented in Figure 3. The curve clearly does not extrapolate to the origin as predicted by the above equation. This is not surprising since the approximation $\chi_{xx} = \chi_{yy}$ may not be valid and the contributions of the terminal methyl and head groups, as well as that of the water,

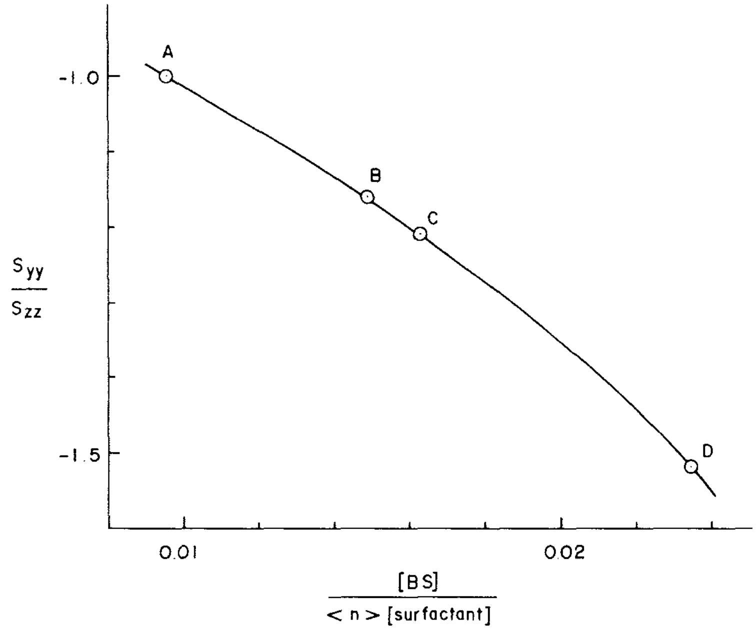

FIGURE 3 Correlation between the ratio of the order parameters and the relative proportions of the benzenesulfonate ion and methylene groups of mesophases with zero diamagnetic anisotropy.

which compose roughly half of the volume, were neglected. The relationship is however approximately linear which indicates that the ratio of the degree of order of the C_2 axis and the average degree of order of the hydrocarbon chain is relatively constant in these mesophases. Also the observed slope of -38, obtained assuming a linear relationship, is reasonable. The anisotropy of a CH_2 group was estimated[22] to be *ca.* -1.6 while the anisotropy of mono-substituted benzenes[23] is in the range -45 to -60 (in units of 10^{-6} erg gaus^{-2} mol^{-1}). Thus the observed slope is consistent with a ratio $S_{yy}/\langle S_{ch}\rangle$ close to unity.

The predominant contribution to the diamagnetic anisotropy of lyotropic mesophases is normally that of the hydrocarbon chains and is a function of the concentration, length and degrees of order of the segments. Nevertheless, the presence of components with a large molecular diamagnetic anisotropy, such as aromatic compounds, can have a dominant effect. The more than two-fold variation in the concentrations of benzenesulfonate ion needed to reverse the sign of the diamagnetic anisotropy in the mesophases studied, reflects the large differences in the degree of order of the axis perpendicular to the aromatic ring. Whilst the degree of order of the C_2 axis is apparently proportional to those of the initial segments of the hydrocarbon chains, the overall degree of orientation of the benzenesulfonate ion in the interfacial region of the micelle is very dependent on the nature of the surfactant headgroups.

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