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The reversal of the diamagnetic anisotropy in amphiphilic nematic liquid crystals using the aromatic counterions phenyl sulphonate and benzoate

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Proton N.M.R. is used to investigate the inclusion of the phenylsulphonate and the benzoate ion as counterions in samples of amphiphilic nematic liquid crystals. When these aromatic counterions are substituted in sufficient amounts the sign of the diamagnetic anisotropy is reversed. The orientation parameters are also shown to be dependent upon the micelle shape, as well as the sign of the diamagnetic anisotropy.

1. Introduction

Counterion binding studies in the electrical double layer of surfactant micelles are of considerable importance in the chemistry, physics and biochemistry of colloidal and interface science. N.M.R. has been used almost exclusively to study alkali metal and halide ions [1, 2] and to a lesser extent various tetrahedral ions [3] and organic ions [4]. Aqueous surfactant solutions can give rise to several amphiphilic nematic liquid crystals, which are considered to be orientationally ordered aqueous micelle solutions. There are two thermodynamically distinct uniaxial amphiphilic nematic liquid crystals, whose micelle shapes are closely related to the dimensionally ordered lyotropic liquid crystals i.e. N_C cylinder/hexagonal and N_D disk/lamellar respectively [5, 6]. When there is a thermodynamic change $N_C \rightarrow N_D$ and visa versa the sign of the diamagnetic anisotropy is reversed. These amphiphilic nematic liquid crystals are ideal orientation matrices for the proton N.M.R. studies of small solute molecules and ions such as the organic counterions [4]. In a similar fashion to thermotropic nematic liquid crystals, these amphiphilic nematic liquid crystals spontaneously align in magnetic fields and give rise to high resolution N.M.R. spectra.

An important type of organic ion is the aromatic counterions such as the phenyl sulphonate and the benzoate ion. They have a special property in that when they are present in sufficient quantities they reverse the sign of the diamagnetic anisotropy [7]. The sign of the diamagnetic anisotropy can be reversed by the inclusion of aromatic species in amphiphilic nematic liquid crystal samples [8, 9, 10] as well as in thermotropic nematic liquid crystal samples [11–14]. The sign of the degree of orientation S_{ZZ} is determined by the sign of the diamagnetic anisotropy as well as the structure of the micelle. The sign of the S_{ZZ} could also be influenced by multisite counterion binding but is usually unimportant when aromatic counterions are involved. The ^{1}H N.M.R. spectrum of a phenyl aromatic ion seems very complex but is easily analysed using a computer program.

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The dipolar couplings D_{ij} for a molecule with D_{2h} symmetry are related to the principal components of the ordering matrix by

$$\tilde{D}_{ij} = -\gamma_i\gamma_j h[S_{zz}\langle(3\cos^2\theta_{ij} - 1)R_{ij}^{-3}\rangle + (S_{xx} - S_{yy})\langle(\cos^2\theta_{ijx} - \cos^2\theta_{ijy})R_{ij}^{-3}\rangle],$$

where γ_i and γ_j are the gyromagnetic ratios of the interacting nuclei, R_{ij} is the distance between nuclei i and j and θ_{ijy} is the angle R_{ij} makes with the x principal axis of S. The principal axis coincides with the C_2 axis of the phenyl aromatic ion. The angular brackets denote averaging over the vibrational modes of the molecule [15]. Proton N.M.R. studies give rise to precise information concerning the sign and magnitude of the dipolar coupling and the degree of orientation S_{ZZ} if the sign of the indirect J coupling is known. Structural information can also be derived. The phenylsulphonate ion has been studied before some years ago and the ion was shown to induce a reversal in the sign of the diamagnetic anisotropy when the ion was present in sufficient quantities in an amphiphilic nematic liquid crystal [7]. It was later shown by one of the present authors (KR) that these transitions in the sign of the diamagnetic anisotropy could be investigated using S_{ZZ} measurements obtained from the high resolution proton N.M.R. spectra (16 (*a*), (*b*)) of the methyl phosphonate ion and the phenyl sulphonate ion. Other authors [8] have extended this work using high resolution proton N.M.R. to investigate the phenylsulphonate ion in amphiphilic nematic liquid crystals derived from various cationic and anionic detergents. They found the changes in the relative order parameters S_{XX}/S_{ZZ} of the phenylsulphonate ion interacting in the electrical double layer (edl) of the surface of the micelles derived from the various cationic and anionic detergents could be both theoretically and experimentally related to the zero diamagnetic anisotropy composition. The present investigation is restricted to one type of detergent tetradecyltrimethylammonium bromide, which involves the proton determination of the orientation parameters of the phenylsulphonate and the benzoate ions in both N_C and N_D amphiphilic nematic liquid crystals and its implication to ion binding and diamagnetic anisotropy. As far as the authors know the benzoate ion has not been investigated in a amphiphilic nematic liquid crystal sample before.

2. Experimental

The amphiphilic nematic liquid crystals were derived from three detergents tetradecyltrimethylammonium bromide, phenyl sulphonate and benzoate, which were prepared as previously described [16]. The samples of the mesophases with various micelle shapes and diamagnetic anisotropies were weighed out into test tubes and heat sealed. The composition of the samples are presented in tables 1, 2, 3 and 4. Double distilled D_2O and specially purified *n*-decanol were used throughout. The samples were homogeneously mixed by repeated heating and centrifuging. The samples were placed in 5 mm N.M.R. tubes and these tubes were heat sealed.

The micelle shape of the phase in each sample was determined as previously described [17]. Small quantities were sucked into a CAMLAB microslide. Samples with disc shaped micelles give rise to polar micrographs with pseudo isotropic textures while samples with cylindrical shaped micelles give rise to polar micrographs with planar textures. The structure can also be inferred from the concentration gradients where when the samples begin to dry out a dimensionally ordered phase of known structure appears next to the nematic phase. The ^{2}D N.M.R. of D_2O was used to determine the diamagnetic anisotropy of each sample. Initially when placed in the magnetic field the ^{2}D N.M.R. is a powder pattern. The line shapes evolve with time.

Table 1. Mesophase composition and measured N.M.R. parameters of the phenyl sulphonate ion for the molar substitution of the phenyl sulphonate ions for bromide ions in cylindrical type phases.

	Composition Mg			N.M.R. parameter Hz					
% PS	TDTABr†	TDTAPS†	D_2O	$\Delta\nu$ D-2	S_{ZZ}	S_{XX}	S_{YY}	$S_{XX} - S_{YY}$	$\frac{S_{XX} - S_{YY}}{S_{ZZ}}$
5·4	342	20	638	52·0	−0·1062	−0·0029	0·1120	−0·1149	1·082
10·8	324	40	636	40·0	−0·1084	−0·0039	0·1123	−0·1162	1·072
11·4	320	44	636	34·9	−0·1072	−0·0027	0·1099	−0·1126	1·050
12·5	317	48	639	32·7	−0·1079	−0·0027	0·1106	−0·1133	1·050
13·5	314	52	639	14·5	0·0543	0·0013	−0·0556	0·0569	1·048
14·5	310	56	634	14·0	0·0545	0·0012	−0·0557	0·0569	1·044
15·6	306	60	634	12·9	0·0549	0·0014	−0·0562	0·0576	1·048
20·8	288	80	632	11·0	0·0544	0·0007	−0·0551	0·0558	1·026
25·9	270	100	630	1·0	0·0541	0·0009	−0·0550	0·0559	1·033
31·1	252	120	628	5·0	0·0557	0·0007	−0·0564	0·0571	1·025

† Tetradecyltrimethylammonium bromide TDTABr and tetradecyltrimethyl-ammonium phenyl sulphonate; mole fraction TDTABr in total detergent.

Table 2. Mesophase composition and measured N.M.R. parameters of the benzoate ion for the molar substitution of the benzoate ions for bromide ions in cylindrical type phases.

Composition Mg				N.M.R. parameter Hz					
% Bz	TDTABr†	TDTABz†	D_2O	$\Delta\nu$ D-2	S_{ZZ}	S_{XX}	S_{YY}	$S_{XX} - S_{YY}$	$\frac{S_{XX} - S_{YY}}{S_{ZZ}}$
1·98	353	8	640	58·4	−0·1604	0·0297	0·1307	−0·1010	0·630
3·96	345	16	639	56·2	−0·1638	0·0309	0·1329	−0·1020	0·623
5·95	338	24	638	51·0	−0·1667	0·0317	0·1350	−0·1033	0·620
7·93	331	32	637	50·3	−0·1629	0·0318	0·1311	−0·0993	0·610
8·91	327	36	637	23·0	0·08500‡	−0·0160‡	−0·0690‡	0·0520‡	0·610‡
9·91	324	40	636	23·2	0·08524	−0·0165	−0·0687	0·0522	0·612
14·88	306	60	634	19·4	0·08594	−0·0167	−0·0692	0·0525	0·611
19·84	288	80	632	16·4	0·08813	−0·0176	−0·0705	0·0529	0·601

† Tetradecyltrimethylammonium TDTABr and tetradecyltrimethylammonium benzoate TDTABz; mole fraction TDTABr in total detergent.

‡ The sample was poorly aligned, estimated values.

Table 3. Mesophase composition and measured parameter N.M.R. of the phenyl sulphate ion for the molar substitution of the phenyl sulphate ions for the bromide ion in samples of disk type phases.

Composition Mg				N.M.R. parameter Hz					
% PS	TDTABr†	TDTAPS†	Decanol	$\Delta\nu$ D-2	S_{ZZ}	S_{XX}	S_{YY}	$S_{XX} - S_{YY}$	$\frac{S_{XX} - S_{YY}}{S_{ZZ}}$
5	320	21	60	19·2	−0·0825	0·0125	0·0700	−0·0576	0·678
10	303	42	60	24·7	−0·0838	0·0129	0·0709	−0·0580	0·692
15	286	63	55	23·0	−0·0753	0·0113	0·0641	−0·0528	0·701
20	270	83	55	28·7	−0·0772	0·0118	0·0654	−0·0537	0·695
25	254	104	55	33·0	−0·0770	0·0118	0·0652	−0·0534	0·694
26	250	108	55	32·0	−0·0746	0·0114	0·0632	−0·0518	0·694
27	246	112	55	31·4	−0·0738	0·0112	0·0626	−0·0515	0·697
28	243	116	50	55·0	0·133	−0·0190	−0·1140	0·0950	0·714
29	239	121	50	54·0	0·131	−0·0193	−0·1120	0·0924	0·705
30	236	125	50	55·2	0·128	−0·0192	−0·1088	0·0896	0·700
35	219	146	50	64·0	0·128	−0·0192	−0·1088	0·0896	0·700
40	202	112	50	70·3	0·125	−0·0189	−0·1061	0·0872	0·698

† As table 1†.

‡ Each sample was prepared with 900 mg of D_2O containing 2 per cent NaBr by weight.

Table 4. Mesophase composition and measured parameters of the benzoate ion for the molar substitution of the benzoate ions for bromide ions in samples of disk type phases.

Composition Mg				N.M.R. parameter Hz					
% Bz	TDTABr†	TDTABz†	Decanol	$\Delta\nu$ D-2	S_{ZZ}	S_{XX}	S_{YY}	$S_{XX} - S_{YY}$	$\dfrac{S_{XX} - S_{YY}}{S_{ZZ}}$
5	320	19	60	17·0	−0·1100	0·0365	0·0735	−0·0370	0·336
10	303	38	60	21·0	−0·1107	0·0370	0·0737	−0·0367	0·332
15	286	57	60	20·0	−0·1064	0·0359	0·0705	−0·0346	0·325
20	270	75	60	23·0	−0·1034	0·0339	0·0695	−0·0356	0·344
25	253	94	60	25·0	−0·1051	0·0366	0·0685	−0·0319	0·304
26	250	98	60	25·0	−0·1052	0·0362	0·0686	−0·0324	0·308
27	246	102	60	49·0	0·2088	−0·0709	−0·1379	0·0670	0·321
28	243	106	60	53·0	0·2134	−0·0728	−0·1406	0·0678	0·318
29	239	110	60	50·0	0·2071	−0·0705	−0·1366	0·0661	0·319
30	236	113	60	53·0	0·2090	−0·0713	−0·1377	0·0664	0·317
35	219	131	60	51·0	0·1910	−0·0654	−0·1256	0·0602	0·315
40	202	151	60	51·0	0·1972	−0·0676	−0·1206	0·0620	0·314

† As table 2†.

‡ Each sample was prepared with 900 mg of D_2O containing 2 percent NaBr by weight.

If a nematic phase sample has positive diamagnetic anisotropy a sharp doublet evolves from the wings where as with negative diamagnetic anisotropy a sharp doublet evolves from the centre.

N.M.R. spectra were obtained at 22°C using a Brucker 400 MHz and 100 MHz N.M.R. spectrometers. The 400 MHz spectrometer was used mainly for slow orienting samples. In the superconductivity magnets of WP spectrometer, the sample spinning axis corresponds to the magnetic field direction. In such N.M.R. spectrometers nematic samples can be routinely spun without regard to the sign of the diamagnetic anisotropy to produce high resolution N.M.R. spectra. The spectra were analysed using a suitable computer program and the results are presented in tables 1, 2, 3 and 4. The anisotropic part of J coupling was assumed to be zero where $J(1, 2) = 7{\cdot}86$ Hz; $J(1, 3) = 1{\cdot}17$ Hz; $J(1, 4) = 0{\cdot}58$ Hz; $J(1, 5) = 1{\cdot}86$ Hz; $J(2, 3) = 7{\cdot}51$ Hz and $J(2, 4) = 1{\cdot}37$ Hz (8). The degrees of orientation were calculated from the dipole couplings assuming an inter proton distance of 2·477 Å found for benzene [18].

3. Results and discussion

The degree of order S_{ZZ} for both the phenyl sulphonate and the benzoate ion, which were determined using proton N.M.R. spectra in the samples of amphiphilic nematic liquid crystal, are plotted as a function of the molar substitution of the bromide ion in the original sample. The samples of amphiphilic nematic liquid crystals prepared without decanol were inferred to have cylindrical shaped micelle structure using a polarizing microscope while amphiphilic nematic liquid crystals prepared with decanol were inferred to have disc shaped micelle structure. (See figures 1 and 2). In all four cases at a given, but different in each case, concentration the S_{ZZ} changed abruptly. In the N_D nematic phases samples the S_{ZZ} was increased by a factor of -2 and in the N_C nematic phase samples the S_{ZZ} was decreased by a factor of $-\frac{1}{2}$. When the nematic phase samples were investigated using the ^{2}D N.M.R. of D_2O it was found in the samples of amphiphilic nematic liquid crystal, with a low concentration of aromatic ion substitution, behind the change in S_{ZZ}, that the N_C phase samples had positive diamagnetic anisotropy and the N_D phase samples had negative diamagnetic anisotropy. In front of the change in S_{ZZ} the diamagnetism is reversed to give phase samples of negative—cylinders and positive—discs. The S_{ZZ} would be expected to change by a factor of -2 when the sign of diamagnetic anisotropy changes from negative to positive and a corresponding change in S_{ZZ} in a reversed situation in the absence of a micelle shape transition, which is what was observed in the experiments. In figure 1 and 2 it can be seen the values of S_{ZZ} in nematic samples with positive diamagnetic anisotropy next to the nematic sample with zero diamagnetism composition are: phenylsulphonate cylinders $-0{\cdot}1079$; phenylsulphonate discs 0·133; benzoate cylinders $-0{\cdot}1629$; and benzoate discs 0·2088. The corresponding values for S_{ZZ} in nematic samples with negative diamagnetism are: 0·0543; $-0{\cdot}0738$; 0·085; and $-0{\cdot}1052$ respectively. Similar results have been found in the N.M.R. spectra of solute molecules dissolved in thermotropic nematic liquid crystals at the zero diamagnetism composition (11–14). When a transition involves a change in the micelle shape the S_{ZZ} changes by a factor of $-\frac{1}{2}$ for the disc → cylinder transition with a corresponding change in the sign of the diamagnetism. Hence there is no change in the sign of S_{ZZ} for the $N_C \rightarrow N_D$ transition and visa versa. If infinite cylinders and infinite discs (lamellar) were involved in the transition, the magnitude of S_{ZZ} would not change for

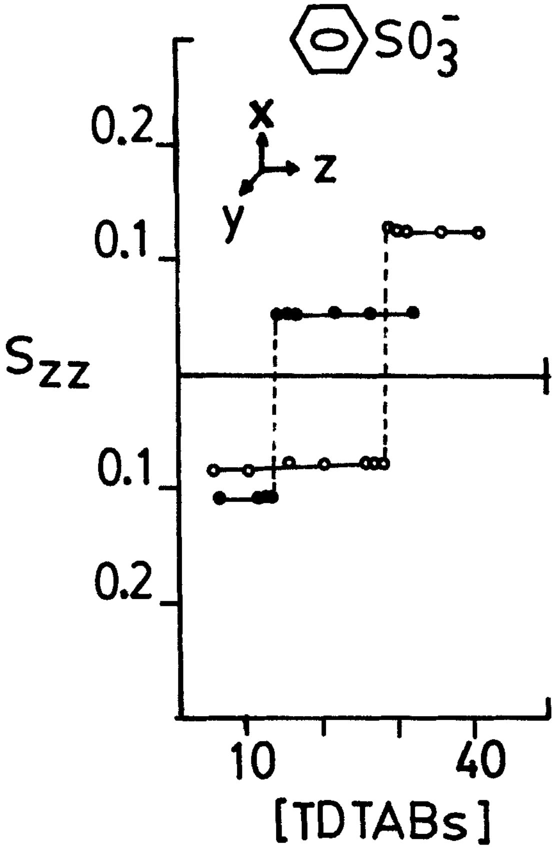

Figure 1. The order parameter S_{ZZ}, determined using the proton N.M.R. of the phenyl sulphonate ion in an amphiphilic nematic liquid crystal where TDTAPS is substituted for TDTABr, as a function of the mol % of TDTAPS to the total detergent. Open circles ○ represent samples of disk type phases and closed circles ● represent samples cylindrical type phases.

the $N_C^+ \rightarrow N_D^-$ transition whereas for the $N_D^+ \rightarrow N_C^-$ transition the magnitude of S_{ZZ} would decrease by a factor of $\frac{1}{4}$. In practice in amphiphilic nematic liquid crystals the micelles have shapes which are finite cylinders and finite discs. In the experiments it was observed the S_{ZZ} sign changes were consistent with micelle shapes and the diamagnetism transitions but the magnitude of S_{ZZ} change lay well inside the limits of $\frac{1}{4}$ to 1. The finite cylinders and finite discs in these phases have both a flat and a curve surface where the aromatic ions interact with the edl made up of the detergent head groups. These aromatic ions probably do not have the same distribution density in the curved surface as in the flat surface. The S_{ZZ} for the aromatic ions oriented in the curved surface will have a negative sign while the S_{ZZ} for the aromatic ions in the flat surface will have a positive sign. With cylindrical shaped micelles the curved surface dominates so S_{ZZ} is always negative and with disc shaped micelles the flat surface always dominates so S_{ZZ} is always positive. This discussion of S_{ZZ} sign changes due to micelle shape do not take into account S_{ZZ} sign changes due to form diamagnetic anisotropy. In the simple flat versus curved surface micelle model (as developed qualitatively in the previous four sentences) when the flat and the curved surface areas

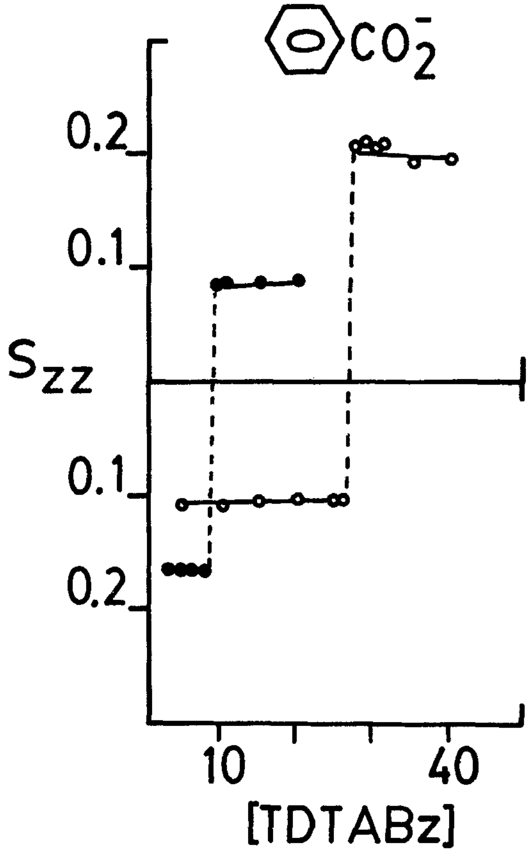

Figure 2. The order parameter S_{ZZ}, determined by using the proton N.M.R. of the benzoate ion is an amphiphilic nematic liquid crystal where TDTABz is substituted for TDTABr, as a function of the mol % of TDTABz to the total detergent. Open circles ○ represent samples of disk type phases and closed circles ● represent samples of cylindrical type phase.

are equal the micelles are still disc shaped. This model although useful is too simple because real micelles are ellipsoids with smooth curved edges. This simple model also assumes at the $N_C \rightarrow N_D$ transition the micelle shape is a sphere but in practice the transition can involve a biaxial phase where probably the ellipsoidal micelles have unequal axes. It has already been stated that changes in S_{ZZ} corresponding to changes in micelle shape were not at the limits 1 and $\frac{1}{4}$.

The bulk magnetism in all materials is usually classically interpreted in terms of the intensity of the magnetic field generated by the electric currents due to the angular momentum of unpaired electrons in atomic orbitals. The atoms of the ferromagnetic and the paramagnetic materials have unpaired electrons and these materials give rise to permanent magnetism. Most materials contain atomic orbits with paired electrons whose individual angular momentum is equal and opposite which in the absence of a magnetic field does not give rise to magnetism. If electron pairs in the same orbit are placed in a magnetic field one electron is said to be slowed down and the other speeded-up resulting in a induced magnetic field described by the term diamagnetism. These paired electrons occur mainly in three type of orbitals. The first type of paired electrons are in the fully filled atom shells closely bound to the atoms and non bonding. These paired electrons result in induced magnetism which is small compared to type two and three and is usually negligible. The two other types of paired electrons involve molecular orbitals i.e. π and σ bonds. σ bonds are the fundamental bonding orbitals and in long hydrocarbon chains set up diamagnetic anisotropy which is negative in respect to the long molecular axis. On the other hand π bonds which are involved in double bonds set up corresponding diamagnetism which is positive in respect to the long molecular axis. In any case the magnitude of the diamagnetism derived from the loosely bound π bond is much bigger than that derived from the tightly bound σ bond. In the case of aromatic rings with 3π bonds, i.e. 3 electron pairs, the six electrons hydbridize; the diamagnetic anisotropy is reinforced. The magnitude of the diamagnetism due to an aromatic ring could be at least one order of magnitude greater than the equivalent σ bonds. It has already been stated the sign of the diamagnetic anisotropy for hydrocarbon chains is negative whereas for aromatic rings it is positive. If the diamagnetism of the constituent molecules dominates the diamagnetic anisotropy of the amphiphilic nematic liquid crystals and not the inherent shape diamagnetism of the micelles, increasing amounts of the aromatic ion will make the diamagnetic anisotropy move through zero and eventually reverse the original sign as was observed [19].

It has already been mentioned the changes in S_{ZZ} for the $N_C \rightarrow N_D$ transition and vice versa do not give whole numbers. The corresponding S_{ZZ} values for the phenyl sulphonate and the benzoate are not the same, S_{ZZ} in the phenyl sulphonate is smaller than in the benzoate. S_{ZZ} is proportional to p the number of aromatic ions interacting in the micelle surface. If there were a smaller number of aromatic ions oriented in the micelle surface in the first case than the second case it would be expected the amount of aromatic ion needed to induce the zero in diamagnetic anisotropy to be greater in the first case than in the second case. This is born out in the case of the phenyl sulphonate and the benzoate ion. The corresponding S_{ZZ} and the zero diamagnetic anisotropy composition are 0·11–13 per cent and 0·16–8 per cent for the cylindrical shaped micelles; and 0·07–27·5 per cent and 0·11–26·5 per cent for the disc shaped micelles. This does not explain adequately why the zero diamagnetic anisotropy composition differ. The large differences and the variation of the ratio of the order parameter are probably due to the difference in the intermolecular interactions which impose the orientation on the aromatic ion. These intermolecular interactions will involve the interaction of the head group of the aromatic ion with the edl of the micelle surface. The apparent biaxiality of the aromatic ions means the orientation can be expressed by two independent order parameters S_{ZZ} and $S_{XX} - S_{YY}$ with the ratio $(S_{XX} - S_{YY})/S_{ZZ}$. When $S_{XX} - S_{YY} = 0$ there is no biaxiality in the orientation and the ionic orientation approaches the limit corresponding to cylindrical symmetry. On the other hand when $S_{XX} = 0$ while $S_{ZZ} \neq 0$ indicates that there is no preferential orientation of the ionic major axis. This seems to be the case for the phenyl sulphonate ion oriented in a N_C phase sample, see table 1 and figure 1. The figure 3 shows $(S_{XX} - S_{YY})/S_{ZZ}$ plotted as a function of molar substitution of the aromatic ion for all four systems. For all four plots $(S_{XX} - S_{YY})/S_{ZZ}$ is constant but different individually as it moves through the sign change of the diamagnetic anisotropy. Each plot shows small deviation from constancy over all the concentration ranges indicating each ion reacts somewhat differently with each of the surfaces. The interaction of the aromatic ions with e.d.l. of the micelle surface can be monitored using the ^{2}D N.M.R. of D_2O in the samples. The inference of the results is that the benzoate ion interacts

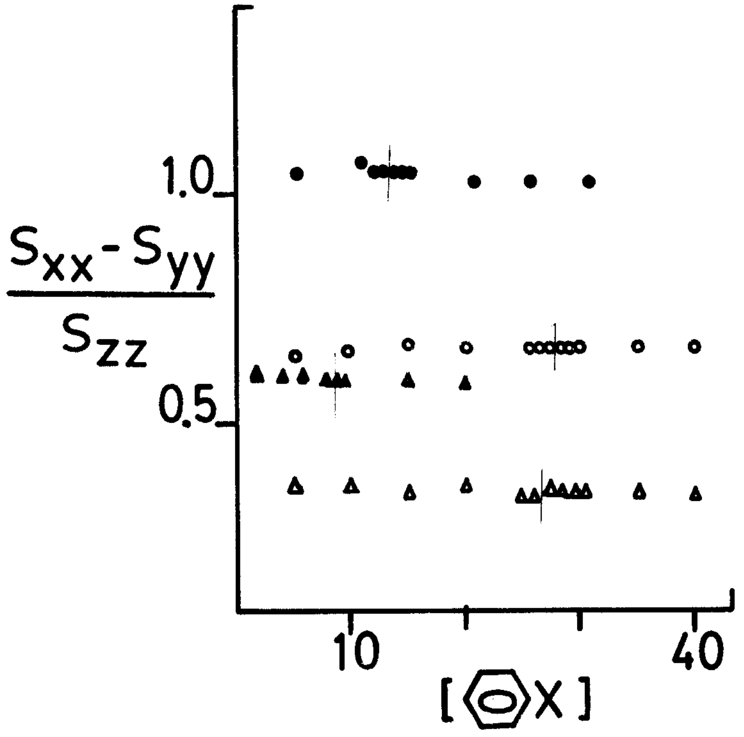

Figure 3. The relative order parameters $(S_{XX} - S_{YY})/S_{ZZ}$, determined using the proton N.M.R. of the phenyl sulphonate ion and the benzoate ion in samples of amphiphilic nematic liquid crystals as in figure 1 and figure 2, as a function of the mol % of TDTAPS and TDTABz respectively to the total detergent. Open characters represent samples of disc type phases and closed character represent samples of cylindrical type phases. △ represents benzoate ion and ○ represents phenyl sulphonate ion data.

much stronger with the surface than the phenyl sulphonate because the ^{2}D N.M.R. quadrupolar splitting are smaller in the benzoate ion than in the phenyl sulphonate ion samples. This seems to be born out in terms of the amount of decanol needed to maintain the nematic phase samples. The phenyl sulphonate ion displaces about 10 per cent of the decanol compared to the benzoate ion which displaces only small amounts. The ratio $(S_{XX} - S_{YY})/S_{ZZ}$ in each of the four systems are different as is the aromatic ion molar substitution concentration at zero diamagnetic anisotropy. In the present study there is not sufficient data to make a quantitative study. It can be said the degree of orientation of the axis perpendicular to the aromatic ring is qualitatively limited to the aromatic ion concentration at zero diamagnetic anisotropy. This effect is more pronounced in the two cylinder systems than in the two disc systems.

Benzene has recently been studied in various amphiphic nematic liquid crystals with various micelle structure and various signs of diamagnetic anisotropy using high resolution proton N.M.R. They found the signs of the S_{ZZ} order parameter were consistent with the micelle structure and the signs of the diamagnetic anisotropy [20]. Other authors found the S_{ZZ} and S_{XX}/S_{ZZ} were very much dependent upon the various cationic and anionic detergents in the micelle surface [8]. One of the present authors (AST) found while investigating monohalegonbenzene solutes in amphiphilic nematic liquid crystals the order parameters and relative order parameters were very much dependent upon the halogon substituted on the benzene. The authors recently have had two papers accepted for publication which involved N.M.R. investigations of the ability of the aromatic ions analinium, trimethylanalinium and benzene phosphonate to induce the reversal in the sign of the diamagnetic anisotropy [23, 24]. Ion binding via relative molecular orientation seems to be less important in these three cases. The solubility of the aromatic ion in the aqueous region which influences the distribution of the ion between the aqueous region and the interior of the micelle seems to be much more important. The benzene phosphonate ion which is quite soluble in water, within the bounds of the experiments does not induce a reversal in the sign of the diamagnetic anisotropy. Preliminary studies on benzene arsenoate seem to suggest this ion follows these tendencies even more [24].

4. Conclusion

It has been demonstrated that the aromatic counterions phenyl sulphonate and benzoate when introduced into amphiphilic nematic liquid crystals in sufficient quantities reverse the sign of the diamagnetic anisotropy. The ability of individual counterions to induce such changes depends on the individual orientation parameters. The relative orientational parameter $(S_{XX} - S_{YY})/S_{YY}$ is dependent upon the individual aromatic counterion as well as the micelle shape. The ionbinding of the aromatic counterion ions in amphiphilic nematic liquid crystal is much more complex than the ionbinding of the small alkali metal ion. The dominant factors with the alkali metal ions are distortion while with the organic ions orientation is the main mechanism.

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