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Interaction and orientation of a chiral solute in cholesteric lyotropic mesophases

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Cholesteric lyotropic mesophases are prepared by addition of 2,3:4,6-di-O-isopropylidene-α-L-sorbofuranose or diacetone-sorbose, DAS, to nematic matrices based on several amphiphiles. The orientation of the DAS solute is investigated by deuterium NMR of the labelled DAS-d_6 derivative. This compound was obtained by exchanging one acetone ligand for perdeuteriated acetone. The resulting deuteriated methyl groups are observed as coincident or distinguishable doublets. Quadrupolar splitting values are used for the calculation of parameters of the solute's Saupe ordering matrix, defined in a molecule fixed coordinate system. Decylsulphate lyomesophases containing both caesium and sodium counter-ions are also investigated. For these mesophases, caesium-133 NMR spectra of the counter-ion and deuterium NMR of the residual HDO are also obtained. The present work points out that the DAS ordering in lyomesophases is dependent on the charge and nature of the amphiphile headgroup. The exchange of Na^+ for Cs^+ counter ions in decylsulphate mesophases affects the anisotropic properties of the liquid crystalline medium, changing the ordering of the DAS solute.

1. Introduction

Cholesteric lyotropic mesophases can be obtained by addition of 2,3:4,6-di-O-isopropylidene-α-L-sorbofuranose or diacetone-sorbose, DAS, to a nematic matrix. DAS is obtained by acetonation of L-sorbose being an intermediary in the vitamin C synthesis. It is important to obtain information about its location in the mesophase since it is the inducer of the cholesteric array. As an additional convenience, DAS interchanges one acetone ligand for deuteriated acetone leading to a labelled compound with two CD_3 groups (DAS-d_6), observable by deuterium nuclear magnetic resonance (NMR). Here we report ^{2}H NMR results on the DAS-d_6 orientation added to several nematic matrices, complemented with ^{133}Cs NMR observations of the counter ions.

The quadrupole interaction of a nucleus with spin $I > \frac{1}{2}$ is defined as follows [1,2]

$$\Delta\nu_Q^{(i)} = \frac{3}{2}\frac{1}{I(2I-1)}\frac{e^2Q_iq_i}{h}S_i, \qquad (1)$$

where $(e^2Q_iq_i)/h$ is the static quadrupole coupling constant, $\Delta\nu_Q^{(i)}$ is the observed multiplet quadrupole splitting, $S_i = \frac{1}{2}\langle 3\cos^2\beta - 1\rangle$ (the angular brackets represent time average) and β is the angle between the electrical field gradient direction on the nucleus and the magnetic field. [1–3] This expression holds when the asymmetry parameter (η) is negligible, a condition satisfied by the nuclei here investigated [4]. For HDO and Cs^+ the calculated values for the S_i parameters are weighted by the population of species that are associated to an orientation site on the micellar surface [5]. The degree of order of the OD axis of HDO can be calculated from the experimental NMR splittings using the above relation. The gradient field direction is assumed to be axially symmetric about the O–D bond [2]. The Cs^+ degree of order is calculated from the ^{133}Cs NMR splittings ($\Delta\nu_Q^{Cs^+}$), taking $I = \frac{7}{2}$. In this case, the electric field gradient is supposed to be in the direction of the uniaxial deformation of the ion imposed by the mesophase anisotropy [6,7]. The DAS-d_6 molecule is dissymetric therefore two distinct doublets, assigned to each deuteriated methyl group, are expected in the ^{2}H NMR spectrum. The C–D bond order parameter, S_{CD}, can be calculated from equation (1) set above, assuming that the electrical field gradient is axially symmetric about the C–D bond direction. Since in the acetone ligand there is a free rotation of the CD_3 group about the threefold old symmetry axis (C_3) corresponding to the C–C single bond, the order parameter, S_{C_3}, of this axis can be calculated from [8]

$$S_{C_3} = S_{CD}\tfrac{1}{2}(3\cos^2\Omega - 1), \qquad (2)$$

where Ω is the angle between the CD bond axis and the

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C_3 axis. If tetrahedral angles are assumed, Ω will be equal to 70·53°.

The solute orientation in a mesophase can be analysed from the Saupe ordering matrix [9]. The elements of this matrix are averages over the anisotropic movements of the solute and are referred to a molecule fixed coordinate system [2, 9]. In the present case, the elements of the Saupe ordering matrix (S_{ij}), defined in the molecule-fixed axis system shown in figure 1, were calculated from C_3 axis degrees of order, allowing the comparison of the DAS ordering in different mesophases. For dissymetric molecules, like DAS, the Saupe matrix has five independent elements. The S_{C_3} are related to the S_{ij} by the coordinate transformation [9]

$$S_{C_3} = \sum \cos\theta_i \cos\theta_j S_{ij}, \tag{3}$$

where $i,j = x, y, z$, θ_i and θ_j are the director angles between the C_3 axis and the coordinate axis and S_{ij} are the terms of Saupe matrix [1, 2]. Assuming tetrahedral angles and the molecule-fixed coordinate system described above, the

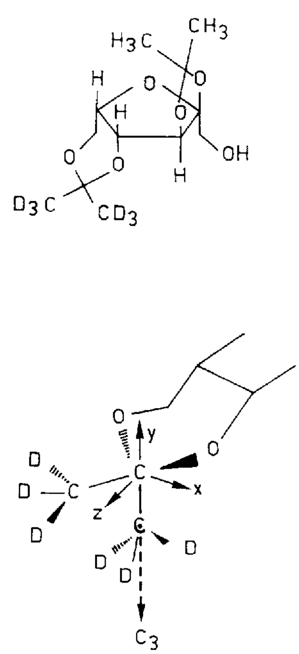

Figure 1. DAS structure and molecule-fixed coordinate system. C_3 is the threefold rotation axis of the CD_3 group.

Table 1. Director angles of the deuteriated methyl groups.

Methyl group 1	Methyl group 2
$\theta_x = 90°$	$\theta_x = 90°$
$\theta_y = 90° - \alpha$	$\theta_y = 90° + \alpha$
$\theta_z = \alpha$	$\theta_z = \alpha$

director angles, with $\alpha = 109{\cdot}47°/2 = 54{\cdot}74°$, are shown in table 1.

The equations corresponding to the degree of order of the C_3 axis take the form

$$S^{(1)}_{C_3} = \cos^2(90 - \alpha)S_{yy} + \cos^2\alpha S_{zz} + 2\cos(90 - \alpha)\cos\alpha S_{yz}, \tag{4 a}$$

and

$$S^{(2)}_{C_3} = \cos^2(90 + \alpha)S_{yy} + \cos^2\alpha S_{zz} + 2\cos(90 + \alpha)\cos\alpha S_{yz}. \tag{4 b}$$

Taking into account the trigonometric reduction formulae and the fact that Saupe matrix is traceless, relations can be rewritten

$$S^{(1)}_{C_3} = \tfrac{1}{2}(3\cos^2\alpha - 1)S_{zz} - \tfrac{1}{2}\sin^2\alpha(S_{xx} - S_{yy}) + 2\sin\alpha\cos\alpha S_{yz}, \tag{5 a}$$

and

$$S^{(2)}_{C_3} = \tfrac{1}{2}(3\cos^2\alpha - 1)S_{zz} - \tfrac{1}{2}\sin^2\alpha(S_{xx} - S_{yy}) - 2\sin\alpha\cos\alpha S_{yz}, \tag{5 b}$$

or

$$S^{(1)}_{C_3} = A + B, \tag{6 a}$$

and

$$S^{(2)}_{C_3} = A - B, \tag{6 b}$$

where

$$A = \tfrac{1}{2}(3\cos^2\alpha - 1)S_{zz} - \tfrac{1}{2}\sin^2\alpha(S_{xx} - S_{yy}), \tag{7}$$

and

$$B = 2\sin\alpha\cos\alpha S_{yz}. \tag{8}$$

Equations (5 (*a*)) and (5 (*b*)) indicate that the $S^{(1)}_{C_3}$ and $S^{(2)}_{C_3}$ values will be different only when $S_{yz} \neq 0$. The orientational distribution described by the S_{yz} term refers to the *yz* plane of the molecule-fixed coordinate system, with a maximum probability of the magnetic field at the bisectrices of the angles formed by the *y* and *z* axes [1, 2, 10]. This means that distinguishable methyl splittings are verified when the solute molecule is arranged, on average, with a component of the magnetic field at 45° to the *y* and *z* axes, in the *yz* plane of the molecule-fixed coordinate. Nevertheless the equation system (5 *a*, *b*) presented here has more unknowns than the data available. Considering the α angle equal to 54·74°, the term $\tfrac{1}{2}(3\cos^2\alpha - 1)$ is equal to $-1{\cdot}1 \times 10^{-4}$, a small value when compared with the other coefficients. Therefore, the S_{zz} contribution can be neglected. With this approximation it is possible to obtain $(S_{xx} - S_{yy})$ and S_{yz} values.

2. Experimental

DAS was prepared from L-sorbose according to the classical Reichstein method for vitamin C synthesis [11]. DAS-d_6 was prepared from DAS by an acid catalysed exchange reaction of the acetone attached to the 4,6-position of the furanosidic ring for perdeuteriated acetone

Table 2. Phase compositions (per cent mol fractions)

Phase	KL	KCl	DeOH	H_2O/D_2O	DAS_{d6}
1	3·25	1·50	0·80	94·18	0·27
2	3·27	1·49	0·82	94·26	0·16
3	3·05	1·44	0·80	94·58	0·13
4	3·08	1·48	0·76	94·54	0·14
5	3·31	1·49	0·80	94·25	0·15
6	3·08	1·47	0·79	94·59	0·12

Phase	DAC	NH_4Cl	H_2O/D_2O	DAS_{d6}
7	6·77	2·04	90·99	0·20
8	6·82	1·94	91·13	0·11
9	6·76	1·82	91·26	0·16
10	6·44	2·15	91·26	0·15
11	6·38	2·16	91·23	0·23
12	6·47	2·12	91·34	0·07

Phase	SDS	CsDS	Na_2SO_4	Cs_2SO_4	DeOH	H_2O/D_2O	DAS_{d6}
13	4·26	—	0·85	—	0·60	94·17	0·12
14	4·38	—	1·00	—	1·08	93·43	0·11
15	3·93	0·45	0·99	—	1·08	93·42	0·13
16	3·22	1·08	0·97	—	1·08	93·52	0·13
17	2·16	2·14	1·00	—	1·07	93·48	0·15
18	1·10	3·20	0·96	—	1·11	93·50	0·13
19	—	4·38	1·00	—	1·10	93·39	0·13
20	—	4·38	0·50	0·50	1·08	93·41	0·13

[12]. The exchange in the 4,6-position occurs in about 30 min, while for the 2,3-position the process takes few days [13]. A small amount of concentrated sulphuric acid was added to a solution of DAS in perdeuteriated acetone. The exchange was monitored by proton NMR, observing the decrease of the peaks assigned to the 4,6-acetone and the corresponding increase of that attributed to the free acetone. After approximately 1 hour, the exchange was completed and the reaction was interrupted by neutralization with solid sodium carbonate. The final product was filtered and recrystallized from petroleum ether (30–60°C fraction).

In the present work several cholesteric lyomesomorphic systems were investigated, based on potassium laurate (KL), decylammonium chloride (DAC), sodium decylsulphate (SDS) and caesium decylsulphate (CsDS) amphiphiles. The mesophases were prepared by weighing, mixing and centrifugation of the components. All mesophases were characterized as Ch_D systems by deuterium NMR and by polarizing microscopy. The compositions (in per cent mol fraction) for the different systems investigated are shown in table 2.

NMR spectra were obtained using a Varian XL-100-12 FT spectrometer operating with the Gyrocode Option in the frequencies 15·3 MHz for deuterium and 13·1 MHz for ^{133}Cs, with fluorine external lock. Values of static quadrupolar coupling constants $(e^2Q_iq_i)/h$ for deuterium and caesium were adopted as shown in table 3 [14–17].

The observed deuterium and caesium quadrupolar splittings are shown in table 4. The values for water and Cs^+ degrees of order calculated directly from equation (1) are weighted by means of different site populations (p_i) and their corresponding degrees of order (S_i) [5]. In the present case the following assumptions have been made:

(*a*) For each lyotropic system, the HDO and Cs^+ species have just one ordering site where $S_i \neq 0$.
(*b*) Since all systems have the same molar fraction composition, the populations of HDO and Cs^+ at the ordering sites are the same for each phase.

According to these suppositions the calculated S values will reflect the overall orientation effects acting on each species.

Table 3. Deuterium and caesium static quadrupolar coupling constants.

i	CD	OD	Cs
$\frac{e^2Q_iq_i}{h}$ kHz	170	216	1240
Reference	14	15	[16, 17]

Table 4. Observed deuterium and caesium quadrupolar splittings.

System	Phase	$\Delta\nu_{HDO}$/Hz	$\Delta\nu_{(CD_3)_1}$/Hz	$\Delta\nu_{(CD_3)_2}$/Hz	$\Delta\nu_{Cs^+}$/Hz
KL	1	130	829	613	—
KL	2	295	2085	1511	—
KL	3	347	2826	2045	—
KL	4	287	2190	1614	—
KL	5	321	2308	1664	—
KL	6	260	1832	1338	—
DAC	7	262	1414	28	—
DAC	8	288	1657	13	—
DAC	9	780	1275	16	—
DAC	10	—	1710	37	—
DAC	11	—	1055	29	—
DAC	12	—	2006	41	—
SDS	13	261	1138	1138	—
SDS	14	257	1147	1147	—
SDS	15	205	880	880	486
SDS/CsDS	16	296	1435	1435	724
SDS/CsDS	17	278	1627	12627	788
SDS/CsDS	18	326	2010	1926	910
SDS/CsDS	19	330	2172	2094	919
SDS/CsDS	20	326	2398	2240	1011

3. Results and discussion

3.1. *Mesophases based on KL, DAC, CsDS and SDS amphiphiles*

Two distinct doublets were verified in the deuterium NMR for the two DAS methyl groups in the mesophases based on KL, DAC and CsDS and coincidents doublets for the mesophases based on SDS. The plot of $\Delta\nu_Q^{(1)}$ (greatest splitting) versus $\Delta\nu_Q^{(2)}$ (smallest splitting) is shown in figure 2. Linear correlations with different angular coefficients, namely 1·0, 0·7 and 0·02, are observed, respectively, for SDS, KL and DAC systems. The inclination difference is an indication that the DAS ordering process in the anisotropic medium depends on the amphiphile nature, head group charge and can be better observed by the examination of figure 3 where a graph of $(S_{xx} - S_{yy})$ versus S_{yz} is presented. The linear correlation for systems based on KL and DAC points out that the ordering and the orientational disposition is unique for each system.

Available data from chain order profiles measured by deuterium NMR of perdeuteriated amphiphiles, indicate that the DAS is located inside the micelle for KL systems and outside the micelle for DAC mesophases [18]. The relevant point is that in spite of such differences on solute location, the correlations above are always of the linear type.

3.2. *Mesophases based on CsDS/SDS mixtures*

Deuterium NMR spectra show a coincident doublet for DAS-d_6 in pure SDS systems and two distinct doublets for pure CsDS mesophases. These results suggest the preparation of mixed counter-ion mesophases, where the Na^+ ion is gradually exchanged for Cs^+ starting from a mesophase based on SDS. In these mesophases, the coincident doublets were observed for pure SDS and in mixed phases where the molar $[Cs^+]/[Na^+]$ ratio is lower than 1. Distinct doublets have appeared only when the molar $[Cs^+]/[Na^+]$ ratio is greater than 1. For a caesium systems ^{133}Cs and ^{2}H NMR spectra were obtained. With these data, several parameters were calculated: the degree of order of the electric field gradient axis of the caesium counter-ions, of the HDO oriented in the micellar surface (both according to the assumptions previously discussed) and of that related to the deuteriated methyl groups. The results are visualized in figure 4 as a plot of degree of order versus molar $[Cs^+]/[Na^+]$ ratio.

It can be seen from figure 4 that the degree of order for the HDO is approximately the same in all mesophases indicating that the micellar order is of the same magnitude for all phases.

If we consider that Cs^+ ion is preferentially attached to charged surfaces [19], it is possible to propose that the Cs^+ ordering is of same magnitude as that of the CD_3 groups of the DAS-d_6. The experimental result represented in figure 4 confirms this proposition and also corroborates the simplying assumptions used for calculations of S_{Cs^+} values.

The plot S_{CD} versus S_{HDO} (see figure 5) shows the existence of a threshold value at which the S_{CD} values increase rapidly, corresponding to the $[Cs^+]/[Na^+]$ molar ratio equal to 1. This behaviour shows that the HDO and DAS-d_6 orientation process are affected differently by the

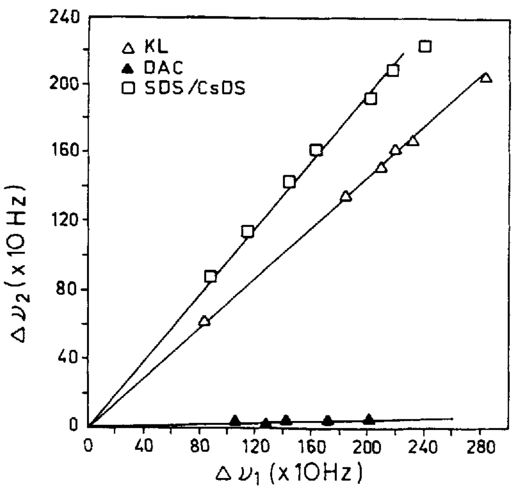

Figure 2. Deuterium NMR splittings for DAS-d_6 labelled methyl groups observed for different systems.

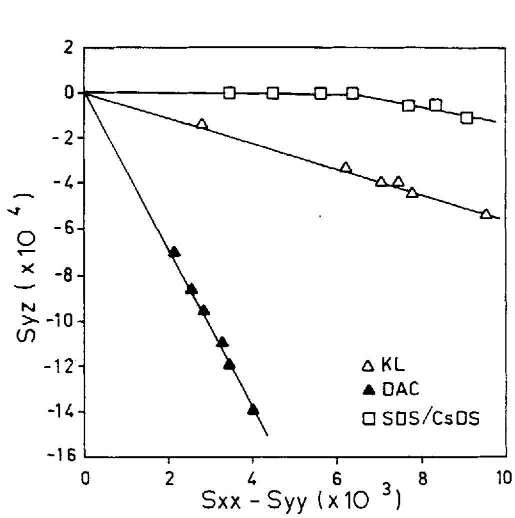

Figure 3. DAS-d_6 orientation parameters calculated for different systems.

electrolyte variation, the solute movements inside micelles contributing more strongly to the solute CD axis ordering.

Although L-sorbose must be hydrophilic solute [20] its acetonated form, DAS, should be hydrophobic and located inside the lyotropic micelle. The results reported here assert that the solute orientation is strongly dependent on the caesium concentration. When the Na^+ concentration predominates over Cs^+ the DAS is oriented aligning the z axis of the molecule-fixed coordinates parallel to the local bilayer normal and perpendicular to the magnetic field. In these conditions $S_{yz}=0$ leads to coincident doublets for the two CD_3 groups in the deuterium NMR spectra.

The ionic radius of the Cs^+ (1·69 Å) is greater than that corresponding to the Na^+ ion (0·95 Å) but the hydrated radii are about the same for both, i.e. 3·6 Å and 3·3 Å for the caesium and sodium ions respectively [21]. Nevertheless, when the counter ion is bound to the micellar surface hydration molecules must be lost, making evident the ionic radius difference [5, 21] Therefore, the counter ions exchange modifies the sulphate head group area. The hydrocarbon chain conformations of the amphiphile must be changed in order to occupy all available space under the increased area [22].

In the present case, the exchange of Na^+ for Cs^+ determines an increase of the area available for each sulphate head group. Therefore, the DAS will rearrange itself in order to place one of its deuteriated methyl groups approximately parallel to the magnetic field. In this

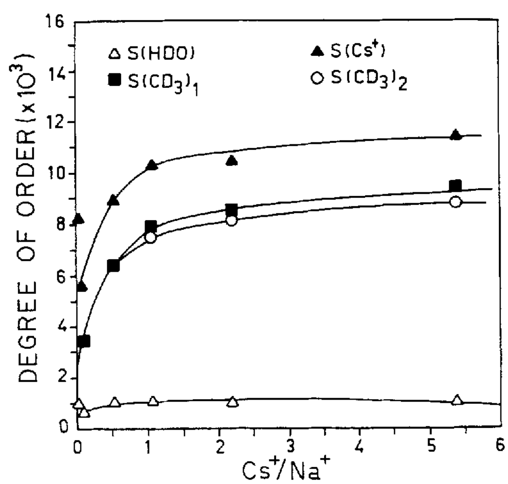

Figure 4. Variation of the degree of order with the $[Cs^+]/[Na^+]$ ratio for SDS/CsDS systems.

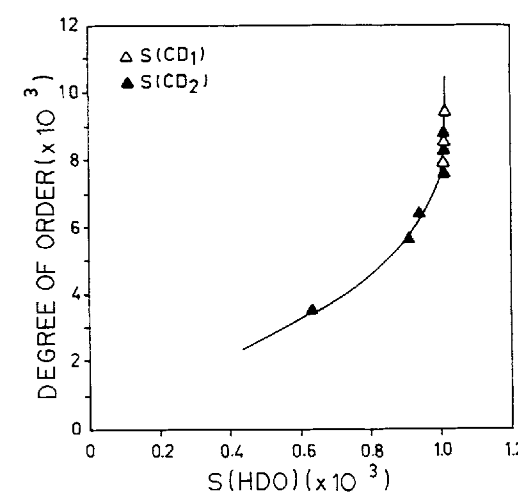

Figure 5. Variation of the CD_3 degree of order with the water degree of order for SDS/CsDS systems.

disposition the associated S_{yz} value will be different from zero, resulting in two different doublets being observed for the labelled methyl groups.

4. Conclusions

The occurrence of distinct doublets in the deuterium NMR spectra for CsDS, KL and DAC systems and coincident doublets for SDS mesophases shows that the DAS ordering in lyomesophases is strongly dependent on the charge and nature of the amphiphile head group. In the present case, it was verified that the solute has greater degrees of order in KL and CsDS than in DAC systems. This can be associated with a stronger solute–micelle interaction in anionic than in cationic mesophases.

From the Saupe ordering matrix treatment, it is seen that the distinguishability of the two CD_3 groups of the DAS-d_6 is determined mainly by the values of the S_{yz} term. In any case two distinct doublets are observed when the magnetic field has a component, on average, at 45° relative to the y and z axes, in the yz plane of the molecule-fixed coordinate. This condition will be almost achieved when one deuteriated methyl group is aligned about perpendicular to the magnetic field while the other is approximately parallel to it. It should be emphasized that such orientation was observed for anionic mesophases where the DAS is located in the hydrocarbon core and even for DAC systems where it is outside the lyotropic micelle.

The exchange of the Na^+ for Cs^+ counter ions, in decylsulphate systems, has affected the micellar surface charge density and consequently the anisotropy of the liquid crystalline medium. This has reflected on the orientation of the DAS solute leading to different NMR spectral patterns. Two hypotheses can be given to explain this ordering process. The first one is related to an alteration in the DAS molecular conformation maintaining the same anchoring at the lyotropic micelle. The second one proposes that the solute ordering is a result from changes of the DAS insertion in the hydrocarbon compartment, without conformational alterations.

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