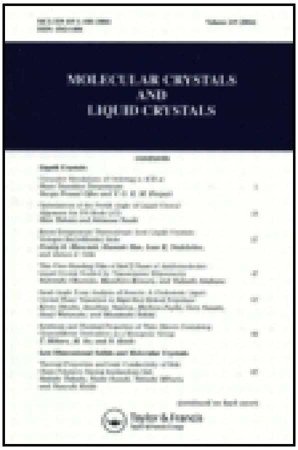

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Interface Anchoring of p-alkyl Phenols in Disc-micelles of Mesophases

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Interface Anchoring of *p*-alkyl Phenols in Disc-micelles of Mesophases

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Five para-alkyl substituted phenols have been studied as solutes in two chemically different type II DM mesophases. The degrees of order for the aromatic ring, are not significantly affected by the different short alkyl chains, showing that the anchoring of the —OH group at the aqueous interface is the dominant determinant of local motion. The principal change in the diagonal degrees of order between the chemically different mesophases resides in the change in size of disc micelles with consequent changes in their motional freedom. The anchoring of the phenol —OH at the aqueous interface shows little or no perturbation from the chemical variation of neighboring amphiphiles in the micelle bilayer.

The location and degrees of order of solute molecules or ions in lyomesophases of the aqueous type based on finite micelles[1] has relevance in the field of solubilization and the data is also useful in the study of other related solute species by the techniques developed using nuclear magnetic resonance (NMR) for structural information.[2] The study of simple amphiphilic ions and molecules as dilute solutes is especially interesting because the polar or ionic moiety is known to reside in the interface and

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the hydrophobic part of the species inserts into the micelle bilayer, if the stereochemical situation is favorable.[1] With this local arrangement assured, the variation of order at the solute site with systematic changes in its chemical structure, can furnish considerable insight into the factors, which determine the nature of hydrophobic/hydrophilic-interfaces. The degree of order of the αCD_2 segment of a carboxylic acid or carboxylate amphiphile with an unbranched chain, inserted as a dilute solute into a micelle bilayer increases linearly with the length of the chain.[3] The alignment of lyotropic liquid crystals with finite disc micelles in magnetic fields is a well studied phenomenon[4,5] and it brings special advantages to bear on the resultant NMR spectra. At the same time the degrees of order measured using deuterium NMR spectra[6] carry information about the motion of the micelle as a whole, which is not relevant to the local structure at micelle interfaces.[1] It is possible to separate the contributions of micelle motion by a procedure where the ratios of degrees of order effect a cancellation of the micelle motion effect, enabling degrees of order within the same *micelle* to be compared for both the same and different species.[7] Such a procedure would not be required in lamellar lyotropic liquid crystals, where the micelles have essentially infinite size. On the other hand the fact that these phases do not align in the magnetic field makes the resultant NMR spectra more difficult to interpret[7] and obtain.

The present study is directed toward the determination of approximate order matrices[2] for the aromatic ring in a series of short chain para-alkyl phenols in two different bilayer micelles.

EXPERIMENTAL

Alkyl phenols were deuterated as previously described,[8] and recrystallized in ethanol-water solvent mixture (50% v/v) or distilled under reduced pressure.

Proton NMR spectrometry was used to check the percent deuteration as 80–90% in the ortho position. The anionic mesophases were made from sodium decylsulphate (SDS), *n*-decanol, sodium sulphate and water. The cationic phases were composed of decylammonium chloride (DACl), ammonium chloride and acidified water (pH = 2/HCl). The composition of the mesophases made in the present study are listed in Table I.

The deuterium NMR spectra of the oriented phenols in the type II (DM) mesophase were recorded on a Bruker WP-80 spectrometer at a

TABLE I

Composition of the type II DM mesophases used in this study.

	moles		moles
SDS	0.960	DACl	0.960
SDSαd_2	0.040	DAClαd_2	0.040
Na_2SO_4	0.241	NH_4Cl	0.260
n-decanol	0.220	H_2O**	16.23
H_2O*	19.36	phenol	0.054
phenol	0.055		

* H_2O (0.1% D_2O)
** H_2O (0.1% D_2O; pH = 2/HCl)

probe temperature of 25°C. The deuterium labelled α—CD_2 position of the detergents were also recorded. The α-deuteriated detergents were obtained from a previously prepared stock in the Waterloo laboratory.

RESULTS

The deuterium NMR spectrum of the ortho-deuteriated 4-*n*-propyl phenol in DACl mesophases is reproduced as Figure 1. It is typical of all five phenols studied. The α—CD_2— position of the detergent was also deuteriated as was a small percentage of the water. The peaks can easily be assigned to the respective deuterium sites in the mesophase molecules. The deuterium spectrum of the ortho position on the phenol ring is a quadrupole doublet split further by dipole–dipole coupling to the protons in the meta-position. The determination of the degrees of order for the aromatic ring is made in the approximation that rotation about the C—C bond to the *p*-alkyl chain is rapid, rendering the ring an effective plane of symmetry for the substituted phenol. A determination of the order matrix for the ring under these circumstances, is taken to be a representation of the motional freedom and inclination to the hydrophobic interface of this part of the molecule.

Normally the order matrix is measured using the proton–proton dipole-dipole couplings[2] but the alkyl chains complicate the spectra a great deal because of the large number of dipole–dipole interactions. The simple modification of deuteriating the ortho-positions allows the observation of the residual quadrupole splitting and the deuterium-proton dipole–dipole coupling in the deuterium NMR spectra. The quadrupole splittings have been used previously for determination of the degrees of order along the —C—D bonds in aromatic rings[9] and the

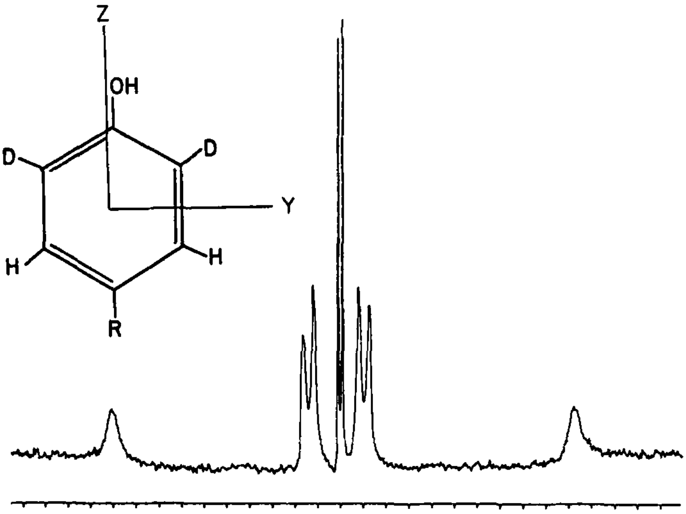

FIGURE 1 Deuterium NMR spectrum of *p*-*n*-propyl phenol in the decylammonium chloride mesophase. The HDO splitting is the centre pair of peaks, the next doubletted splitting corresponds to the ortho C—D position of the phenol and the outer splitting is the —αCD_2— group of the decylammonium chloride detergent. The markers in the base are separated by 1000 Hz. The spectrum was recorded on a Bruker WH-400 spectrometer operating at 61.43 MHz.

procedure used here is exactly that of this prior study. It is usual to assure that the assymmetry parameter of the deuterium quadrupole coupling in the aromatic ring is ~0.05 and this is the value used here. The principal value of the quadrupole coupling at the deuterium in the ring is assumed to be 188.3 KHz.[9]

The table II lists the derived order parameters along the diagonal order matrix[2] for all phenols in both mesophase studied. This table also gives the quadrupole splittings of the —αCD_2— position in the detergent.

DISCUSSION

The degree of order "S_{C-D}" along —C—D axis in a detergent chain is given by;

$$S_{C-D} = S_{MO} \cdot S_{CO} \cdot S_{diff} \cdot S_{k/j} \times 1/2(3\cos^2\Omega - 1) \qquad (1)$$

for a disc-micelle type II DM nematic mesophase.

$S_{MO} \cdot S_{CO}$ is the inseparable degree of order product arising from oscillation of pseudo-extended chains about the director of the mesophase.[1]

The first motion S_{MO} corresponds to cooperative oscillation of all chains i.e. micelle oscillation, and the second S_{CO} corresponds to independent oscillations of each chain, which will depend on the chemical identity of the amphiphile and perhaps the composition of the micelle. S_{diff} is usually taken to be unity because the micelles are large and the only diffusive motion leaves the angle between the pseudo-extended chain and the magnetic field unchanged.[7] Diffusion out of the disc-micelle is considered to be extremely slow. $S_{k/j}$ is the intramolecular contribution of kinks and jogs which has been shown to be a separable effect.[7] At the αCD_2 position of a detergent chain, where direct bonding to the polar or ionic head group occurs, the value of $S_{k/j}$ can be taken to be unity. The angle Ω is the angle between the director of the mesophase and the magnetic field, which by definition of a type II system is $\pi/2$, giving a value $-1/2$ to the last term.[7]

Under the conditions that we shall use Eq. (1), it simplifies to;

$$S_{C-D} = -1/2 S_{MO} \cdot S_{CO} \qquad (2)$$

The principal change in S_{C-D} among mesophases of the same amphiphile arises because the micelles are different in size and the term S_{MO} changes. The mesophases of decylsulphate/decanol do show very small changes in S_{C-D} which can arise because of the small concentration of different phenols. The large change between mesophases of decylsulphate/decanol and those formed from decylammonium ions arises (Table II) because the micelles in the two mesophase systems have in general a large difference in size.[1,10] There is of course, an intrinsically different anchoring of the respective amphiphiles in their respective micelles in the two systems but we suggest that this is a small term compared to the variation in the value of S_{MO} as will be shown.[7]

Supposing S_{C-D} for the αCD_2 groups to be determined by S_{MO} in all the systems studied, it is possible to normalize the quadrupole splittings (proportional directly to S_{C-D}) by multiplying by a simple factor, so as to render all the order parameters of all the α—CD_2— groups in all the mesophases the same. All degrees of order have therefore been reduced to an —αCD_2— splitting of 17.560 KHz. This procedure neglects any changes in S_{CO}, (between different chemical species) which have been previously shown to be rather small in the region of ±10%. For the purposes of this study, this effect will be assumed constant. The normalizing factor to reduce all —αCD_2— degrees of order to a common value must also be used for any other α group such as the aromatic ring of the phenols in order to correct these experimental values for the effect of micelle size and this has been listed in Table III.

TABLE II

Diagonal order parameters derived from experimental spectra for the phenol ring in mesophases of SDS and DACl. Quadrupole splittings of the —α CD_2— groups of the detergent are also listed in the last column of data. The axes of the order matrix correspond to those shown on the figure. The sign assignments of the order parameters correspond to phenol rings inserted in a disc-bilayer which lies in the plane of the magnetic field. The axis Z of the molecule is along the director of the mesophase.

			SDS			DACl		
	S_{zz}	S_{yy}	S_{xx}	$\Delta\nu\alpha CD_2$ (Hz)	S_{zz}	S_{yy}	S_{xx}	$\Delta\nu\alpha CD_2$ (Hz)
4 ethylϕ	+0.1125	−0.0368	−0.0757	12412	+0.1719	−0.0400	−0.1320	21477
4 *n*-propylϕ	+0.1642	−0.0490	−0.1159	13729	+0.1910	−0.0580	−0.1330	20271
4 tertbutylϕ	+0.1160	−0.0337	−0.0823	13525	+0.1881	−0.0463	−0.1418	22125
4 tertamyl	+0.1183	−0.0286	−0.0896	13614	+0.1831	−0.0507	−0.1324	23362
4 sec butylϕ	+0.1164	−0.0275	−0.0889	12651	+0.1959	−0.0602	−0.1358	21889

TABLE III

Normalized diagonal order parameter for phenol aromatic rings taken for an —α CD_2—deuterium quadrupole splitting of 17,560 Hz.

		SDS			DACl	
	S_{zz}	S_{yy}	S_{xx}	S_{zz}	S_{yy}	S_{xx}
4 ethylϕ	+0.159	−0.052	−0.107	+0.140	−0.033	−0.108
4 *n*-propylϕ	+0.210	−0.062	−0.148	+0.165	−0.050	−0.115
4 Tertbutylϕ	+0.150	−0.044	−0.107	+0.150	−0.037	−0.112
4 Tertamyl ϕ	+0.150	−0.037	−0.116	+0.138	−0.038	−0.099
4 sec butylϕ	+0.160	−0.038	−0.123	+0.157	−0.048	−0.109

The diagonal order parameters for the aromatic ring of phenols vary somewhat among the mesophases of the same type but are profoundly changed between the decylsulphate/decanol and decylammonium systems. The variations from phenol derivative to phenol derivative are not large, showing that the relatively short alkyl chains, even though some are branched do not affect the inclination or degrees of order (motional averages) of the aromatic ring significantly. The anchoring of the phenol ring by the —OH group at the interface is by far the dominant force determining the motion of the ring therefore. Such a result is rather similar to the behavior of linear alkyl chains, whose order profiles in the first segments are not affected by chain length, beyond the half bilayer length.[3]

Dealing at this point with the second tabulation of normalized phenol order parameters, it is evident that the relatively crude correction for micelle size and its consequent effect on the magnitude of the motions is sufficient to render all parameters for the phenol rings the same within reasonable limits. Often the agreement is much better than expected and this must be considered fortuitous. The normalized value of S_{ZZ} for *p-n*-propyl phenol is a little higher than expected in the decylsulphate/decanol mesophase, perhaps because *n*-propyl is the longest linear chain substituted. The values of S_{yy} in the second table as for those of S_{xx}, are also remarkably similar. The value of S_{xx} for *n*-propyl phenol is again a little high in the decylsulphate/decanol mesophase and this reinforces the suggestion that the somewhat longer *n*-propyl chain has some minor effect in restricting motion of the aromatic ring. The overall conclusion that correction of degrees of order can be made for micelle motion according to the first section of this discussion, is justified by the results. The reality of disc micelles has been established[11] and this work emphasizes that their freedom of motion in the mesophases is the principal factor in determining the degrees of order of moieties which are α substituted with respect to the head groups

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