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Deuterium NMR studies of *n*-alkyl-β-D-glucopyranosides liquid-crystalline systems

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Liquid-crystalline systems consisting of *n*-alkyl-β-D-glucopyranosides (heptyl to dodecyl) and solutes (water, *n*-octanol, benzene and methylene dichloride) have been studied by measurement of the deuterium NMR quadrupolar splittings. Particular attention was given to the system of *n*-octyl-β-D-glucopyranoside (OG)–solute for which the OG–water and the OG–benzene phase diagrams were determined. Information about the orientational order of the aliphatic chain was obtained from deuterium NMR measurements of chain deuteriated OG. The order parameter profiles for the chain in this molecule were calculated using a quantitative theoretical model. A qualitative model served to interpret the dependence of the splittings in different solutes upon their concentration. DSC and preliminary X-ray data supplement the NMR measurements

1. Introduction

Recent studies of some alkylated carbohydrates, which are non-ionic amphiphiles, show that they can form thermotropic liquid-crystalline systems [1–12]. These studies were conducted using differential scanning calorimetry [1, 3–6, 9, 12], optical microscopy [1, 6, 8, 10–12] and X-ray diffraction [2–4, 8]. Tentative structure determination for non-aligned samples classifies them as belonging to the smectic A type [6, 7]. The properties of these materials vary as a function of the chemical nature of the polar sugar head group and the length of the alkyl chain attached to it.

Deuterium NMR spectrscopy has been shown to be a very valuable tool in the study of molecular orientational order, phase transitions, chain dynamics and other properties of thermotropic and lyotropic liquid crystals. Measurements are performed on either the mesogenic molecule or on deuteriated solute molecules which are partially aligned through their interaction with the liquid-crystalline solvent [13]. The NMR spectrum of a particular deuterium nucleus in oriented molecules consists of a well-resolved doublet with spacing, $\Delta\tilde{\nu}$, which is a linear function of the components of the deuterium quadrupole tensor and a molecular ordering matrix. In some cases the observed deuterium spectra resemble those obtained for a solid polycrystalline sample which indicates that the system consists of randomly oriented domains of aligned molecules. In a preliminary communication [14] the results of deuterium

NMR studies of deuteriated water, benzene, toluene and acetonitrile dissolved in *n*-octyl-β-D-glucopyranoside (OG), were reported. The main results of that work are as follows:

(1) The quadrupolar splittings of the solute deuterons decrease with increasing temperature without abrupt changes in their slopes. This indicates that only a single liquid-crystalline phase exists.

(2) Water and benzene (or toluene) can be dissolved together, in appreciable quantities, in OG. This indicates that this carbohydrate liquid crystal can accommodate simultaneously both polar and apolar solvents. A similar phenomenon has been claimed for sodium oleate but has not been verified [15].

(3) The spectral linewidths for water are broader than those for benzene; this may be explained by assuming that water, through a hydrogen bonded network with the polar heads, is more tightly bound than benzene.

(4) In the ternary OG–water–benzene system, consisting of protonated and deuteriated solutes, an isotope effect seemed to exist. Measurements described here show that this observation was erroneous.

This communication extends the preliminary report. The phase diagrams for OG–water and OG–benzene are given and more detailed studies of these and other solutes (*n*-octanol and methylene dichloride) are presented. Deuterium NMR measurements of aliphatic chain deuteriated OG, without and with solutes are also given. These measurements yield information on the order parameters of the chain methylene groups, which can be interpreted quantitatively through a theoretical model. The changes in the splittings induced by the addition of solutes are interpreted through a more qualitative model. Further measurements are presented for the deuterium quadrupolar splittings of solutes in the homologous series of *n*-heptyl to *n*-dodecyl-β-D-glucopyranosides. Differential scanning calorimetry (DSC) data and some preliminary X-ray studies complement the NMR measurements.

The quadrupolar splittings are, to a good approximation, directly proportional to the orientational order parameters for the C–D bonds, and provided the director is perpendicular to the magnetic field as found for the OG system,

$$\Delta\tilde{\nu} = -(3/4)q_{\mathrm{CD}}S_{\mathrm{CD}},$$

where q_{CD} is the quadrupolar coupling constant parallel to the C–D bond and is taken to be 170 kHz. The order parameter S_{CD} is defined by

$$S_{\mathrm{CD}} = \overline{P_2(\cos\beta)}.$$

Here $P_2(\cos\beta)$ is the second Legendre polynomial, β is the angle between the C–D bond and the director and the bar indicates an ensemble average over both orientational and conformational fluctuations. The variation of the orientational order parameter, S_{CD}, along the chain in *n*-octyl-β-D-glucopyranoside is somewhat unusual and in an attempt to understand this qualitatively we use the theory developed by Emsley, Luckhurst and Stockley [16] for the ordering of flexible molecules. The theory adopts the Flory rotameric state model which assumes that the molecule can exist only in a discrete number of conformational states so that the conformationally averaged order parameters available from the deuterium NMR experiments are given by

$$S_{\mathrm{CD}} = \sum_n p_n S_{\mathrm{CD}}^n.$$

Here p_n is the statistical weight for the nth conformer for which the order parameter is S^n_{CD}. Such orientational order parameters are determined by the potential of mean torque for the conformer; this is approximated by the second rank expression

$$U_n(\beta, \gamma) = -(X^n_{2,0} d^2_{00}(\beta) + X^n_{2,2} d^2_{02}(\beta) \cos 2\gamma),$$

where $d^2_{0m}(\beta)$ is a reduced Wigner rotation matrix. The spherical polar angles β, γ denote the orientation of the director in the principal axis system of the interaction tensor, $\mathbf{X}^n$, for the conformer. The principal components of the ordering matrix S are obtained from Boltzmann averages, for example,

$$S^n_{\alpha\alpha} = Q_n^{-1} \int \{(3l^2_\alpha - 1)/2\} \exp\{-U_n(\beta, \gamma)/kT\} \sin\beta d\beta\, d\gamma,$$

where the orientational partition function is

$$Q_n = \int \exp\{-U_n(\beta, \gamma)/kT\} \sin\beta d\beta\, d\gamma.$$

The order parameters for the C–D bonds along the chain in a particular conformer are then obtained from these principal components and the conformational geometry. The order parameter for the three equivalent C–D bonds in the methyl group is obtained from that for the terminal carbon–carbon bond, S_{CC}, via

$$S_{CD} = S_{CC} P_2(\cos\omega),$$

where ω is the $\widehat{CCD}$ angle and rotation of the methyl group in a potential with threefold symmetry is assumed. The interaction tensors for the different conformers are constructed by assuming that the rigid sub-units of the flexible molecule each make a contribution which is independent of the conformational state. Finally the statistical weights p_n are determined by the conformational or internal potential $U_{int}(n)$ from

$$p_n = Z^{-1} \exp\{-U_{int}(n)/kT\} Q_n,$$

where the partition function Z is

$$Z = \sum_n \exp\{-U_{int}(n)/kT\} Q_n.$$

The terms involving the orientational partition function for each conformer result from the influence of the potential of mean torque which tends to favour the more elongated conformers. The theory is valid for all uniaxial phases and so applies to smectic A as well as to nematic phases, although for smectic phases the parameters in the potential of mean torque depend on the translational as well as the orientational order.

2. Experimental

2.1. *Materials*

The alkyl-β-glucopyranosides were obtained from Sigma and were used without further purification. The materials were dried under vacuum for several days before the samples were prepared. Deuteriated n-octyl-β-D-glucopyranoside was prepared in two steps using the following procedure.

2.2. *Octyl-d_{17} 2,3,4,6-tetra-O-acetyl-β-glucopyranoside*(*1*)

Compound 1 was prepared according to the method described by Noller and Rockwell [17] starting from *n*-octyl-d_{17} alcohol (4 g), 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl bromide (acetobromoglucose 1·64 g) and silver oxide (1·2 g) in ether (40 ml) in the presence of molecular sieve 4A, (2 g). After 2 h, 2,3,4,6-tetra-O-acety-α-D-glucopyranosyl bromide and silver oxide were added to the reaction mixture and the reaction was continued for a further 2 h. Following filtration and evaporation *in vacuo*, the residue was applied to a silica gel column (Silica Gel 60, 0·063–0·2 mm, Merck; 25 cm long and 2·5 cm in diameter) eluted initially with petroleum ether (300 ml) and followed by ethylacetate–petroleum ether (1 : 3 V/V). Compound 1 emerged after 150 ml of the last solvent mixture (3 g, following evaporation). At this point, the compound contained varying amounts of *n*-octyl-d_{17} alcohol that, following sodium methoxide treatment, also contaminated the resulting compound 2.

Impure compound 1 (1·8 g) was dissolved in pyridine (10 ml), acetic anhydride (8 ml) was added and the mixture was kept overnight at 4°C. Ice (10 g) was added, the mixture was stirred (1 h), evacuated and the residue was applied to a silica gel column (as previously). The column was washed with petroleum ether (150 ml), ethylacetate–petroleum ether (1 : 9, 200 ml) and compound 1 eluted with a mixture of the same solvents (3 : 7, 30 ml). The pure product was available after evaporation (1·5 g) and crystallized from petroleum ether (1·1 g; mp 62–63°C; single spot in TLC, R_r 0·6, on precoated Silica Gel 60 F_{254} sheet, (Merck), eluted with ethylacetate–petroleum ether, 1 : 1, detected by spraying with 10 per cent sulphuric acid in ethanol and heating to 120°C). Proton NMR (400 MHz) confirmed the structure.

2.3. *Octyl-d_{17} β-D-glucopyranoside* (*2*)

Compound 2 was prepared by a modification of the procedure described by Noller and Rockwell [17]. Compound 1 (1·1 g) was dissolved in methanol (5 ml), 0·01 mM sodium methoxide in methanol (5 ml) was added and the reaction mixture was kept overnight at 4°C. The solution was neutralized by stirring with methanol washed Amberlite IR 120 (H^+) filtered and evaporated to yield (0·8 g) TLC-pure compound 2 (R_r 0·5, ethylacetate–methanol, 85 : 15, other details as before). Proton NMR confirmed the structure. All other deuteriated and normal solutes were commercially available.

2.4. *Preparation of samples*

Samples were prepared in 5 mm o.d. NMR sample tubes by weighing the materials, centrifuging, sealing the tubes and mixing through heating to the isotropic solution. The samples were heated in the magnetic field of the spectrometer to beyond the smectic A–isotropic transition temperature at least twice before the measurements were started. The volume of the sealed tubes was about ten times the volume of the material and the entire tube was kept at approximately the same temperature during the measurements. NMR spectra were recorded while cooling the sample, the cooling rate being slower than 0·5 K per min. Some samples, particularly of the *n*-decyl-β-D-glucopyranoside, developed a brownish colour during heating which indicated that some decomposition occurred. We did not observe any special effects (such as changes in the transition temperature) in these samples and so we assume that the degree of decomposition was too small to have a significant effect on the properties of the systems. After the measurements, small quantities of condensed solute were occasionally observed on the walls of the sample. These were estimated to be at most 5 per cent of the total solute volume and this is the upper limit to the error in the composition of the samples.

2.5. *NMR measurements*

NMR measurements were performed on a Bruker AM400WB NMR spectrometer operating at 61·4 MHz for deuterium. The temperature was controlled by heated air flow over the sample. Its precision and stability varied from ±2 K at the highest temperature (*c*. 405 K) to ±0·5 K near room temperature. The samples were not spun in the magnetic field.

2.6. *DSC measurements*

DSC measurements were taken on a Mettler TA 3000 system. For samples containing water or benzene ME 29990 medium pressure crucibles were used. In these crucibles the volume of the material constituted roughly 10 per cent of the total volume, as in the NMR measurements.

3. Results and discussion

3.1. *OG, OG-water and OG-benzene systems*

The phase diagrams of the OG-water and OG-benzene systems, as deduced from measurements of the deuterium NMR spectra of D_2O or C_6D_6 dissolved in OG, are given in figures 1 and 2. The biphasic to isotropic transiton temperature, T_I, was evaluated as the temperature at which the doublet due to the smectic A phase first

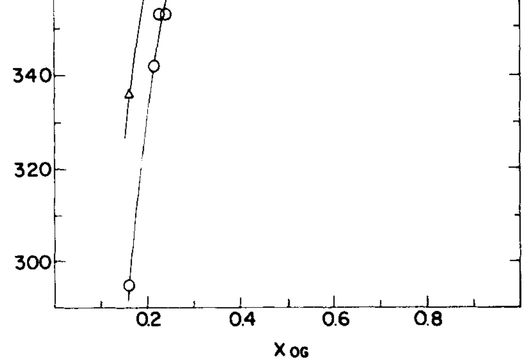

Figure 1. Phase diagram for the OG-water system as determined from the quadrupolar splittings of D_2O. The transition temperature for pure OG (full circle) was taken from DSC measurements. Triangles denote the biphasic to isotropic transition temperatures (T_I) and circles denote the smectic A to biphasic transition temperatures (T_{S_A}). The lines are drawn as guides to the eye and do not necessarily conform to the phase rule.

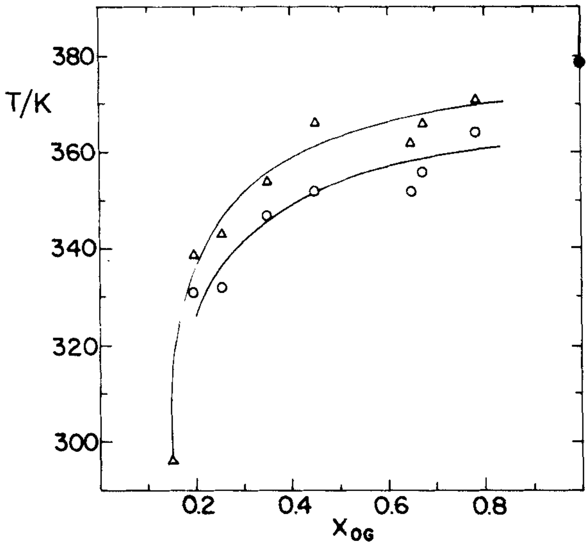

Figure 2. Phase diagram for the OG–benzene system as determined from the quadrupolar splittings for C_6D_6. The transition temperature for pure OG (full circle) was taken from DSC measurements. Triangles denote the biphasic to isotropic transition temperatures (T_I) and circles denote the smectic A to biphasic transition temperatures (T_{S_A}).

appeared. The transition temperature T_{S_A} of the smectic A to biphasic region was evaluated as the temperature where the singlet, due to the isotropic phase, disappeared. As the ability to observe lines depends on several instrumental parameters such as the number of scans, noise filtration etc., an error in the reading of the transition temperature is inevitably introduced. Repeated experiments show that its magnitude is of the order of ±1 K. This error is superimposed on the errors introduced through the temperature instability and precision which have been given. The transition temperature $T_{S_A I}$ for pure OG was determined from DSC measurements. As all of the experiments were performed on cooling, the smectic A phase existed through supercooling, even at low temperatures and the transition to the solid (or lower smectic phases) was never observed. Similar behaviour was observed in DSC measurements. Whereas the phase diagram for OG–benzene (see figure 2) is quite ordinary the OG–water phase diagram has a peculiar feature. There is a maximum in T_I somewhere in the range of x_{OG} between 0·4 and 0·5 (x_{OG} is the mole fraction of OG in the mixtures). This maximum may be understood by the known existence of stable hemi- and mono-hydrates of OG which are observed in the phase diagram. Above the 1 : 1 ratio of OG–water the transition temperatures drop sharply until the composition of about five water molecules per OG molecule is reached, beyond which the liquid-crystalline system transforms, possibly into a gel phase. In dilute aqueous solutions OG forms micelles which were studied recently by dynamic light scattering [18]; this suggests that the liquid-crystalline phases formed by OG with solutes are lyotropic. Such an identification is supported by other studies of the OG–water system by Chung and Jeffrey [19]; using optical microscopy and X-ray diffraction they have reported finding a cubic phase ($x_{OG} \approx 0{\cdot}16$) and a hexagonal phase ($x_{OG} \approx 0{\cdot}10$) in addition to the lamellar phase at room temperature. It should be noted that the D_2O spectral linewidths are invariably broader than those of C_6D_6; this may be explained by the formation of a hydrogen bonded OG–water network

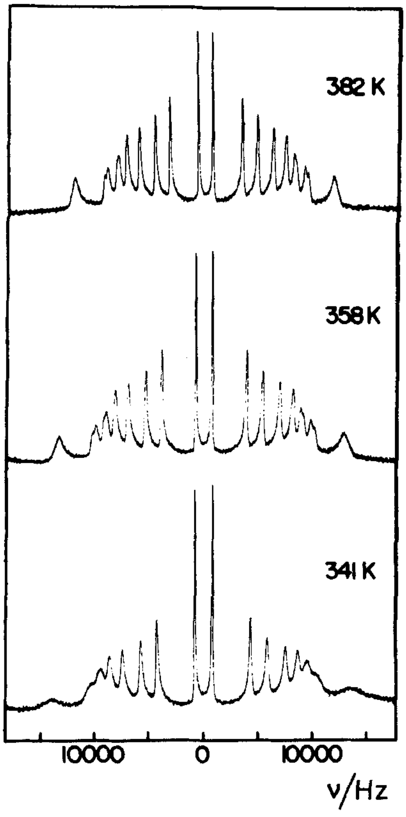

Figure 3. Deuterium NMR spectra of chain deuteriated OG at different temperatures. Number of scans: 120; line broadening: 5 Hz.

which restricts the water mobility. OG has four hydroxyl groups in addition to the ring and esteric oxygens which serve to promote hydrogen bonding [20].

The deuterium NMR spectra of chain deuteriated OG at three different temperatures are shown in figure 3. The spectra show eight distinct quadrupolar doublets which belong to the seven methylene groups and the one methyl group of OG. We use an arbitrary notation for the numbering of the groups as shown in figure 4. Since it

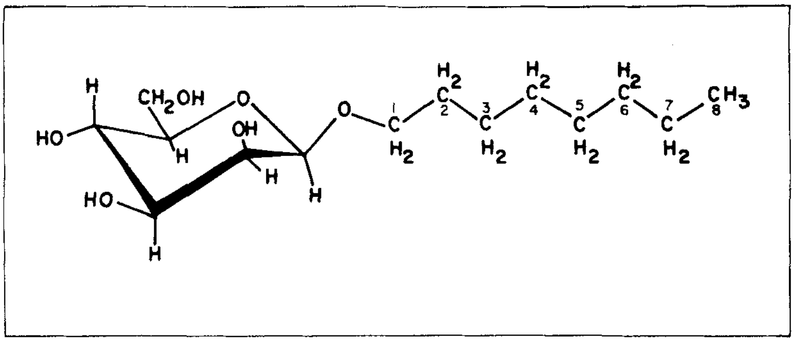

Figure 4. Schematic drawing of the OG molecule with the numbering system for the chain carbon atoms.

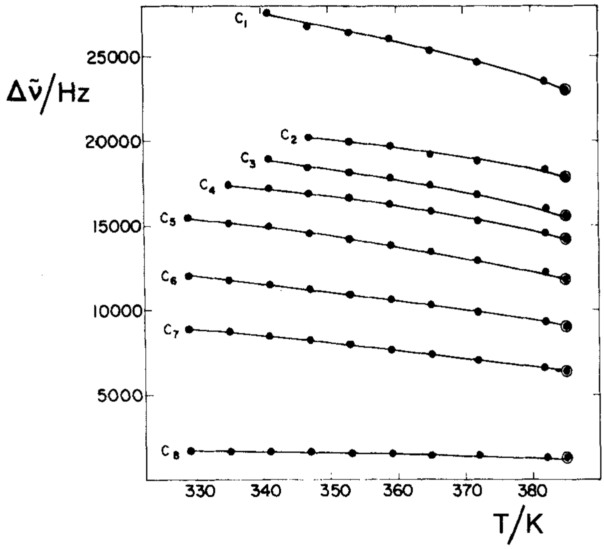

Figure 5. Quadrupolar splittings, $\Delta\tilde{\nu}$, as a function of temperature for deuteriated OG. Those for the C_1 to C_4 methylenes could not be measured at low temperatures because of the broadening and merging of the spectral lines.

is difficult, without using specific labelling, to assign the different resonances unambiguously, we *assume* that the outer doublet belongs to the C_1 methylene and that other doublets follow sequentially along the chain until the innermost methyl (C_8) doublet. This assignment is based on the assumed decreasing order along the chain from the polar head towards the terminal methyl. In some instances, this assumption has been verified experimentally in smectic phases through specific labelling [21]. It should also be noted that dipolar splitting can be noticed in the C_2 and C_3 methylene resonances. The quadrupolar splittings in chain deuteriated OG are shown as a function of temperature in figure 5. Both the quadrupolar splittings, $\Delta\tilde{\nu}$, and the linewidths show a rather weak temperature dependence. This insensitivity of $\Delta\tilde{\nu}$ to temperature is in accord with the predictions of McMillan's molecular field theory of the smectic A phase [22] which shows that the orientational order in the smectic A phase formed directly from the isotropic is both high and weakly temperature dependent.

In applying the model described in the Introduction to understand the order parameter profile for the *n*-octyl chain of OG we have made some rather drastic assumptions in order to avoid the introduction of too many adjustable parameters. We begin by assuming that the molecule is made up of a relatively rigid core composed of the glucopyranoside ring, including an oxygen atom, with a flexible octyl chain attached to it. The basic units of the chain are the C–C bonds but it also includes the O–C bond. These units and that of the core are taken to be cylindrically symmetric in their interactions with the molecular field with strength parameters $X_s(\equiv X_{20}^s)$ and $X_c(\equiv X_{20}^c)$ for the sugar core and chain segments, respectively. To construct the total interaction tensor $\mathbf{X}^n$ for a conformer we also need to know the molecular geometry. We assume that the carbon atoms in the chain have a perfect tetrahedral geometry. Further we take the assumed symmetry axis of the sugar group to lie in the COC_1 plane and make an angle α with the $O–C_1$ bond of the chain. The crystal structure for the α conformer [10] suggests that this angle is about 20° although its value may change in the smectic A phase of the β conformer and so we shall treat it as a variable.

The internal energy associated with the conformation of the alkyl chain is taken to have the simplest form given in the Flory rotameric state model namely

$$U_{\text{int}}(n) = N_g E_{tg},$$

where N_g is the number of gauche links and E_{tg} is the energy difference between a trans and a gauche conformation. This energy difference has been determined although its precise value does vary according to the system and the technique used to determine it. However, for the purpose of our calculations we take it to be 3·18 kJ mol^{-1} such that at the temperature of the NMR measurement of the order parameter profile E_{tg}/RT is 1·0.

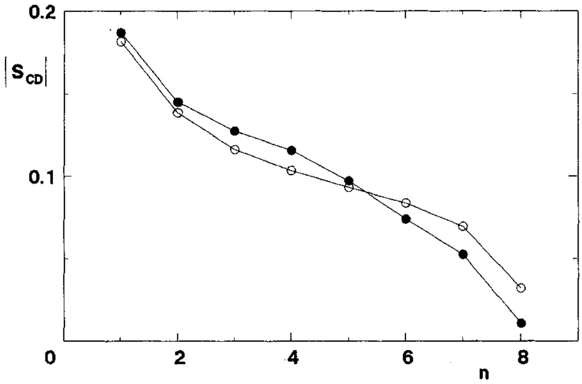

Figure 6. The variation of the order parameter, S_{CD}, along the alkyl chain of *n*-octyl-β-D-glucopyranoside calculated with the angle α between the assumed symmetry axis of the suger core and the O–C_1 bond in the chain to be 30°. The values of X_s/RT and the ratio X_c/X_s used in the calculation were 1·40 and 0·2, respectively. The experimental values, determined at 382 K, are shown as open circles.

The variables in the model are then the angle α and the interaction parameters X_s and X_c, although we expect their ratio X_c/X_s to be less than unity. These have been adjusted to obtain agreement with the order parameter profile of OG determined at 382 K and the best fit is shown in figure 6. The agreement is really quite good given the crude nature of our assumptions, thus the order parameters decrease monotonically along the alkyl chain without the pronounced alternation sometimes shown by normal thermotropic liquid crystals [23]. The optimal values of the parameters appear to be reasonable. Thus the ratio X_c/X_s is 0·2 which is comparable to that found for the 4-*n*-alkyloxy-4′-cyanobiphenyls [24]. This is, perhaps, surprising given the smaller shape anisotropy of the sugar group in comparison with the cyanobiphenyl group; however, it may indicate an enhancement of this anisotropy via hydrogen bonding. The optimum value of the angle α is 30°, although the predicted order parameter profile is relatively sensitive to this. We have repeated the calculations with α set equal to zero, as in a classic mesogen and the results of this calculation are shown in figure 7. Now we see a pronounced alternation in the order parameters which is quite unlike that observed for this sugar smectogen. Strictly, of course, we do not know the assignment of the observed order parameters to particular positions along the octyl chain in OG. However, if we take the calculated order parameters when α is set equal to zero and arrange them in decreasing order of magnitude, then we find a variation which is quite unlike that found experimentally, thus supporting our assignment of

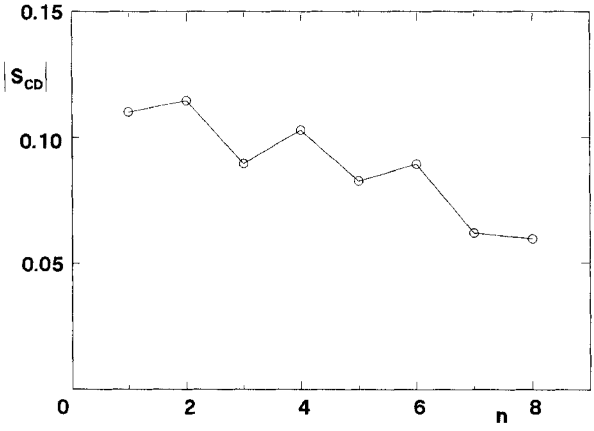

Figure 7. The variation of the order parameter S_{CD} along the alkyl chain in *n*-octyl-β-D-glucopyranoside calculated when the angle α is zero using the parameters $X_s/RT = 1{\cdot}40$ and $X_c/X_s = 0{\cdot}2$.

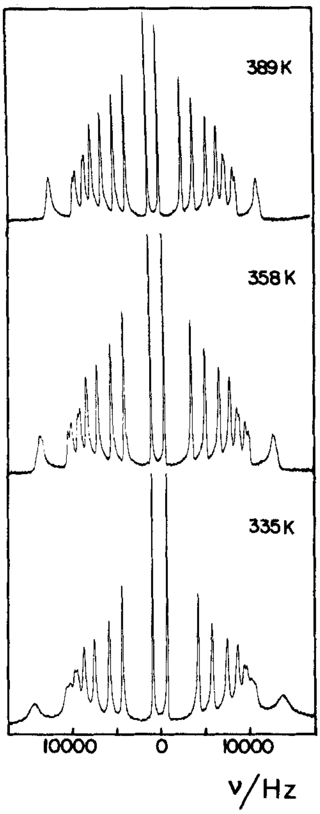

Figure 8. Deuterium NMR spectra of chain deuteriated OG in the OG–water system as a function of temperature. The molar ratio of water/OG, *R*, is 0·32. Number of scans: 120; line broadening: 5 Hz.

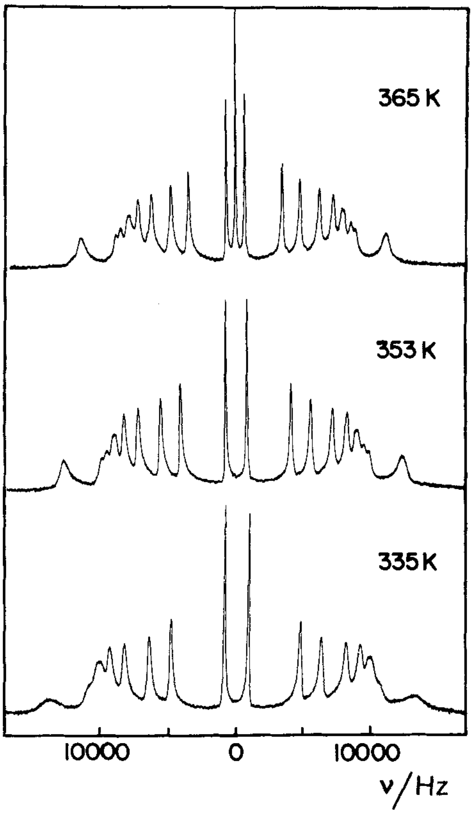

Figure 9. Deuterium NMR spectra of chain deuteriated OG in the OG–benzene system as a function of temperature. The solute to solvent molar ratio, R, is 0·35. The spectrum at T = 365 K also contains a signal from the isotropic solution and corresponds to the smectic A–isotropic biphasic region. Number of scans: 120; line broadening: 5 Hz.

the results. We note that an alternation in the order parameters is also observed if α is increased above 30° but now the larger order parameters are associated with odd rather than even carbon atoms in the chain.

The effect of adding water or benzene on the spectra of chain deuteriated OG is shown in figures 8, 9 and 10. The most pronounced effect is the narrowing of the lines over a larger temperature range, in OG–water mixtures. The OG–benzene spectra are quite similar in appearance to those of pure OG. The comparison of the actual magnitudes of the splittings is made at an arbitrary shifted temperature (T_1–T). At this shifted temperature we have evaluated the percentage changes in the splittings of the methyl and methylene resonances in the OG–water and OG–benzene mixtures as compared to pure OG. The results for different benzene or water concentrations are shown in figure 10 where R is defined as the molar ratio of solute to solvent. It can be noted that upon addition of water (see the upper part of figure 10) the splittings invariably decrease, while for benzene they *increase* at low benzene concentrations and decrease upon further addition of the solute. These results can be interpreted qualitatively in terms of a model which will be described later.

Figure 11 shows the results for the quadrupolar splittings of D_2O and C_6D_6 in the ternary system OG–water–benzene as a function of temperature. In two of the mixtures either the water or the benzene is undeuteriated. These experiments were

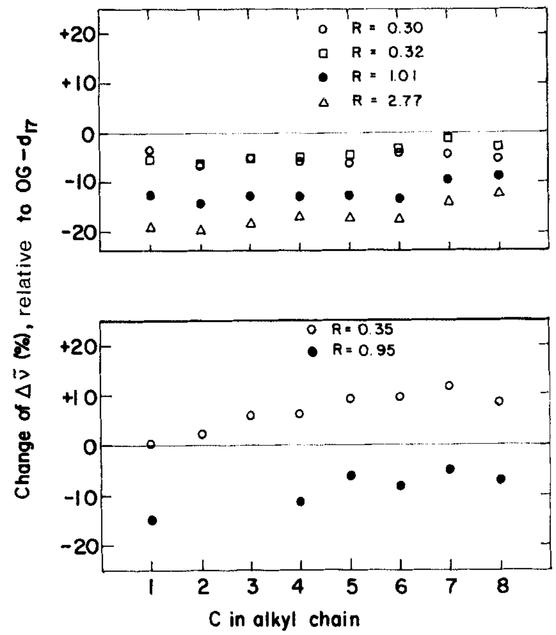

Figure 10. The percentage changes in the quadrupolar splittings of chain deuteriated OG containing water (upper part) or benzene (lower part) as solutes, compared to pure chain deuteriated OG. Data are given for four *R* values of the OG–water system and two *R* values of the OG–benzene system. All measurements are to a constant shifted temperature, T_1-T, of 20 K.

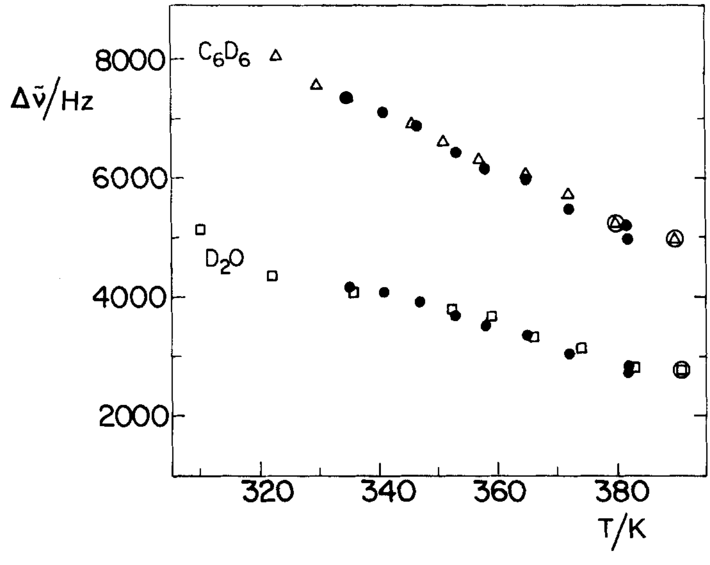

Figure 11. Quadrupolar splittings for C_6D_6 and D_2O in ternary OG–water–benzene mixtures as a function of temperature. The composition of the systems given in mole fractions are as follows: ●, OG 0·26; D_2O 0·65; C_6D_6 0·09. △, OG 0·26; H_2O 0·65; C_6D_6 0·09. □, OG 0·28; D_2O 0·62; C_6H_6 0·10. Encircled markings indicate smectic A–isotropic biphasic regions.

performed in order to reexamine whether the isotope effect which appeared to be present and reported in our preliminary work (cf. figure 6 in [14]) is real. The present measurements were performed with much greater experimental care and do not reproduce our earlier work. We conclude therefore that any possible effect of replacing D_2O by H_2O on the quadrupolar splittings of C_6D_6 in mixtures of OG–benzene–water is small. We suspect that the earlier results are wrong because of incomplete mixing of the ingredients which is the most difficult stage in sample preparation.

3.2. *OG-n-octanol-d_{17} system*

Octanol as a solute is expected to be well accommodated in the ordered phase because of its structural and amphiphilic similarity to OG. Spectra of *n*-octanol-d_{17} dissolved in OG, at different temperatures are shown in figure 12. The most pronounced feature in these spectra, compared with those of chain deuteriated OG, is the coalescence of the C_1 to C_4 methylene resonances. The notation here is analogous to that used for the chain deuteriated OG; the methyl carbon group is C_8. Only in the biphasic region (341 K) can some resolution of the C_1 to C_4 resonances be observed. Some asymmetry is also noticed in this spectrum because of the chemical shift, to lower field, between the C_1 methylene and all other methylene and methyl groups. The

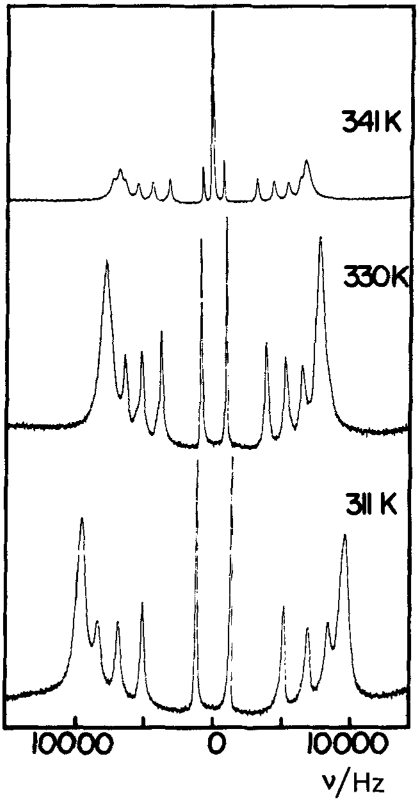

Figure 12. Deuterium NMR spectra of *n*-octanol-d_{17} dissolved in OG at three different temperatures for a molar ratio R of 0·31. At T = 341 K the system is biphasic as evidenced by the characteristic signal from the isotropic phase. Number of scans: 120; line broadening: 5 Hz.

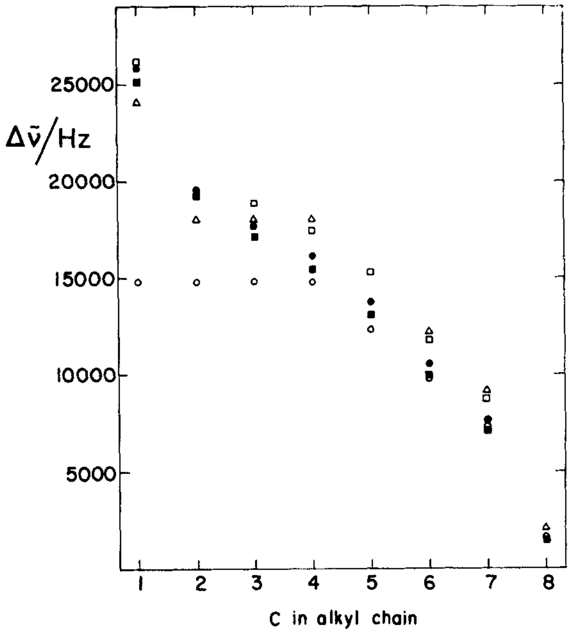

Figure 13. Quadrupolar splittings for chain deuteriated OG and *n*-octanol and in pure OG and solutions at T_I–T of 25 K. ●, OG-d_{17} at 360 K; □, OG-d_{17}/C_6H_6, R = 0·35 at 348 K. ■, OG-d_{17}/H_2O, R = 0·32 at 370 K. △, OG-d_{17}/octanol, R = 0·31 at 333 K. ○, OG/octanol-d_{17}, R = 0·31 at 333 K.

central resonance of the isotropic phase is also split by the chemical shift. The coalescence of the C_1 to C_4 resonances indicates that these groups have the same order parameter, a feature which can be tentatively attributed to a chain fragment in the all-trans conformation [25]. It is interesting to compare these results, at a fixed temperature difference from T_I, with those for chain deuteriated OG–solute systems; this comparison is shown in figure 13. It can be noticed that except for the C_1, C_2 and C_3 methylenes, the behaviour of chain deuteriated OG and *n*-octanol-d_{17} in OG are rather similar. From this we conclude that the influence of the polar head groups in the smectic A phase, in these systems is limited to the first three groups attached to it.

A qualitative model which may account for the experimental observations in the OG–solute systems is as follows. From X-ray measurements and optical microscopy observations we have found that the ordered phase of OG is of the smectic A type consisting of layers with an average thickness of about 2·6 nm. The overall length of the OG molecule, as estimated from X-ray data for the crystal [10], is about 1·3 nm. This indicates that each lamella in the smectic A phase consists of two OG molecules with very little interdigitation. Added water associates mostly with the polar sugar head-group through hydrogen bonding, which increases the layer thickness slightly. This was confirmed by preliminary X-ray measurements which show that the layer thickness increases to 2·7 nm upon the addition of water (x_{OG} ≈ 0·5) [27] in agreement with results obtained by Chung and Jeffrey [19]. Benzene, as solute, behaves quite differently because it is located in the aliphatic chain region and does not seem to affect the layer thickness [27]. Small quantities of benzene promote chain order slightly (especially in the vicinity of the methyl end group) but when its concentration is increased deeper penetration into the aliphatic region disrupts the order (see figure 10). Apart from these small effects the addition of benzene to OG seems to have little influence on the chain dynamics as may be judged from the similar linewidths of the spectra in figures 3 and 9.

3.3. *The homologous series of alkyl-β-D-glucopyranosides*

We have compared the characteristic of the OG mixtures to those of its homologous derivatives (heptyl, nonyl, decyl, undecyl and dodecyl) through DSC and

Differential scanning calorimetry data for *n*-alkyl-β-D-glucopyranosides.

Alkyl chain	Smectic A–isotropic transition temperature T_{S_AI}/K	$\Delta S/R$	Reference
Heptyl	~373	-	[4]
	358	-	This work
Octyl	383	-	[4]
	378	-	[26]
	379	0·531	[6]
	382	0·397	This work
Nonyl	386	-	[4]
	386	-	[6]
	400	0·506	This work
Decyl	406	-	[4]
	406	0·443	[6]
	416	0·623	This work
Undecyl	412	0·452	This work
Dodecyl	415	-	[7]
	416	0·435	[6]
	427	0·435	This work

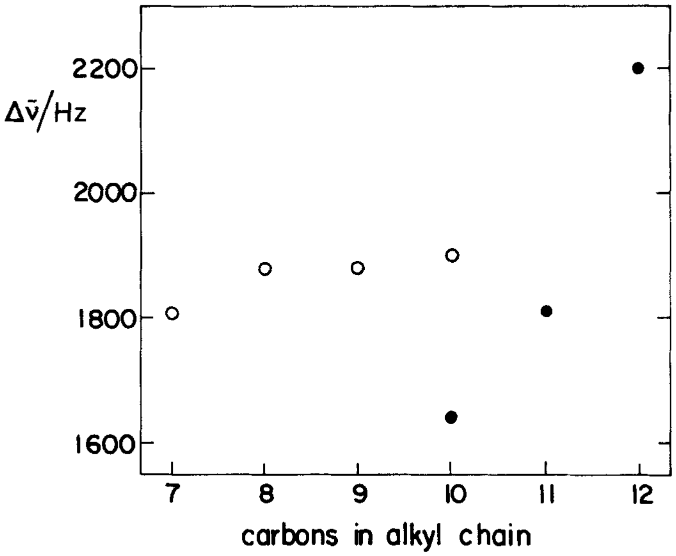

Figure 14. Quadrupolar splittings of CD_2Cl_2 dissolved in 1-*n*-alkyl-β-D-glucopyranosides as a function of the chain length at T_I-T of 25 K and R = 0·67 (○) or 0·85 (●).

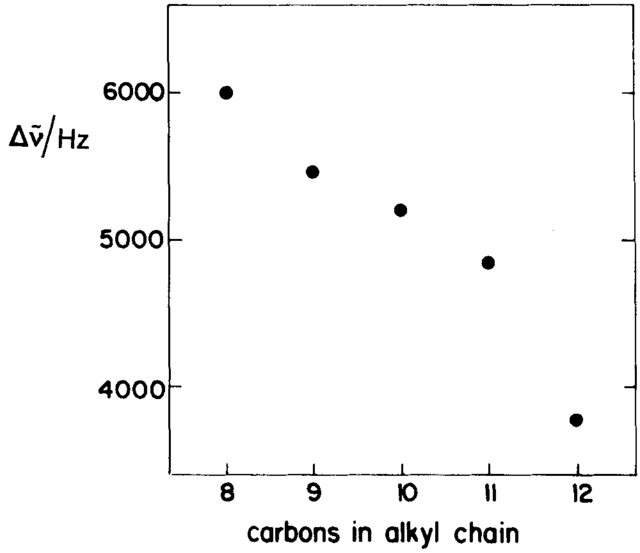

Figure 15. Quadrupolar splittings for C_6D_6 dissolved in 1-*n*-alkyl-β-D-glucopyranosides as a function of the alkyl chain length at $R = 0{\cdot}60$ and $T_I - T$ of 25 K.

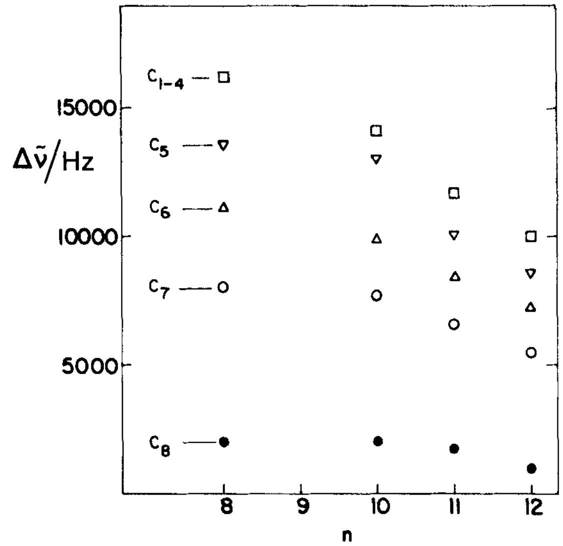

Figure 16. Quadrupolar splittings for chain deuteriated *n*-octanol dissolved in 1-*n*-alkyl-β-D-glucopyranosides as a function of the alkyl chain length at $R = 0{\cdot}29$ and $T_I - T$ of 25 K.

deuterium NMR measurements. The transition temperatures and transition entropies for the series of glucopyranosides are given in the table; most of the data agree fairly well with previous studies. However we should note that the entropies of transition are somewhat lower than those observed for conventional thermotropic liquid crystals exhibiting a smectic A–isotropic transition. Deuterium NMR measurements were performed on three deuteriated solutes, CD_2Cl_2, C_6D_6 and $CD_3(CD_2)_7OH$, dissolved in the homologues C_7, and C_9 and C_{12}. The molar solute/solvent ratio, *R*, was kept constant for each member of the homologous series for the three solutes except for CD_2Cl_2, where two R values were needed to bring the systems into the measureable temperature range. The quadrupolar splittings are compared at a constant shifted temperature ($T_I - T$) of 25 K and the results are shown in figures 14, 15 and 16. For methylene dichloride (see figure 14), the variations in $\Delta\tilde{\nu}$ from the heptyl to the dodecyl derivatives are relatively small while for benzene and *n*-octanol the splittings decrease (see figures 15 and 16) as the aliphatic chain attached to the sugar increases in length. This behaviour contrasts with the expectation that longer chain homologues would serve as better orientating media for host molecules. The orientational order of *n*-octanol is largest in OG, probably because the aliphatic chain lengths of solvent and solute match. This fits with a model which assumes that the hydroxyl group of *n*-octanol is anchored to the polar sugar head group. Benzene and methylene dichloride do not penetrate far into the aliphatic regions of the host molecules and so their order parameters reflect the low order in the vicinity of the methyl end groups, the latter seem to be more disordered in longer chain homologues. This conclusion must still however be confirmed by further studies.

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