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## Liquid Crystals

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## Deuterium N.M.R. of the *n*-octyl- $\beta$ -D-glucopyranoside-solvent liquid-crystalline systems

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Deuterium quadrupolar splittings were measured as a function of concentration and temperature for deuteriated water, benzene- $d_6$ , toluene- $d_8$  and acetonitrile- $d_3$ , dissolved in *n*-octyl- $\beta$ -D-glucopyranoside (OG). The splittings and temperature dependence are larger for the apolar solvents. Water forms rather rigid structures with OG as indicated by its large linewidths. OG can accommodate both water and benzene (or toluene) together and the results for such systems are also reported. Some additional results for the hydroxyl deuteriated OG and for a system containing a lower homologue of OG are reported.

It was recently shown that several alkylated carbohydrates form thermotropic liquid-crystalline systems [1-9]. These studies were conducted using differential scanning calorimetry [1, 3-6, 9], optical microscopy [1, 6, 8] and X-ray diffraction [2-4, 8]. Tentative structure determination of 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 sugar polar head group and the length of the alkyl chain attached to it.

Deuterium N.M.R. has been shown to be very useful in the study of molecular alignment, phase transitions, chain dynamics and other properties of thermotropic and lyotropic liquid crystals. Measurements are performed on either deuteriated mesogen molecules or on deuteriated solute molecules which are partially aligned through their interaction with the liquid crystal solvent [10]. The N.M.R. spectrum of a particular deuterium nucleus in oriented molecules consists of a doublet with spacing  $\Delta q$  which is proportional to the components of the deuterium quadrupolar coupling and of the molecular ordering matrix. In certain cases polycrystalline type deuterium spectra are observed which indicate that the sample consists of randomly oriented domains of aligned molecules.

In this preliminary communication we report results of deuterium N.M.R. studies of deuteriated water, benzene, toluene and acetonitrile dissolved in *n*-octyl- $\beta$ -D-glucopyranoside (OG) [11] (f.w. = 292.38). Deuterium spectra of the deuteriated hydroxyl group in OG are also reported.

All materials are commercially available and were used without further purification. Deuteriated OG was prepared by evaporating excess  $D_2O$  from an OG solution. Samples were prepared by weighing OG and the solvent in a standard 5 mm o.d. N.M.R. tube. The mixing of the components, in closed (often sealed) sample tubes, was achieved by heating to the isotropic phase, centrifugation and shaking. Final equilibration was obtained by heating several times, to the clearing point, in the N.M.R. instrument. Some of the samples become slightly coloured which may be due

to some decomposition of OG. N.M.R. measurements were performed on a Bruker AM 400 WB spectrometer operating at a deuterium frequency of 61.41 MHz. The temperature was controlled by a heated air flow over the sample; its precision and stability varied from  $\pm 5$  K at the highest temperatures (*c.* 393 K) to  $\pm 0.5$  K close to room temperature. The samples were not spun in the magnetic field.

Two typical sets of spectra are shown in figures 1 and 2. Figure 1 shows the spectrum of a sample containing toluene- $d_8$  (41.2 mg  $C_6D_5CD_3$  in 150.8 mg OG) at 311 K. The spectrum consists of three doublets: the inner belongs to the  $CD_3$  deuterons, in the middle is the doublet due to the ortho and meta deuterons of the benzene ring and the outer doublet is due to the para deuterons. The spectrum is similar to that of toluene dissolved in 4,4'-di-*n*-hexyloxyazoxybenzene [12] and can be analysed in terms of its order parameters. Figure 2 shows spectra of a sample containing *both* benzene and water (29.4 mg  $C_6D_6$ , 51 mg  $D_2O$  and 296.6 mg OG). Each solute gives rise to one doublet, the one with the larger splitting is due to benzene. It should be noted that as the temperature is lowered the water resonances broaden significantly more than those of the benzene. A similar effect was observed in solutions containing both toluene and water. In this case, at a certain temperature, only the toluene lines can be observed superimposed on a broad background which is due to the water resonances. The large linewidth for water indicates that it forms rather rigid structures, presumably with the sugar polar head groups or exchanges slowly between different sites. The benzene (or toluene) molecules are less tightly bound to (presumably) the aliphatic tails.

Figures 3–7 show the temperature dependence of the quadrupolar splittings,  $\Delta q$ , as a function of temperature and concentration for various solute–OG systems. Encircled points in the graphs indicate biphasic (liquid crystal–isotropic) regions. In general the effect of benzene (or toluene) on reducing the transition temperature (isotropic–ordered) is significantly greater than that of water.

Figure 3 shows  $\Delta q$  as a function of temperature for OG–water solutions. The isotropic–liquid crystal transition temperature for small  $D_2O$  concentrations is 5 to 10 K higher than that of pure OG (about 385 K). This unusual behaviour was verified by preliminary D.S.C. measurements. Adding more water reduces the transition temperature considerably and also introduces a large biphasic region. When the mole

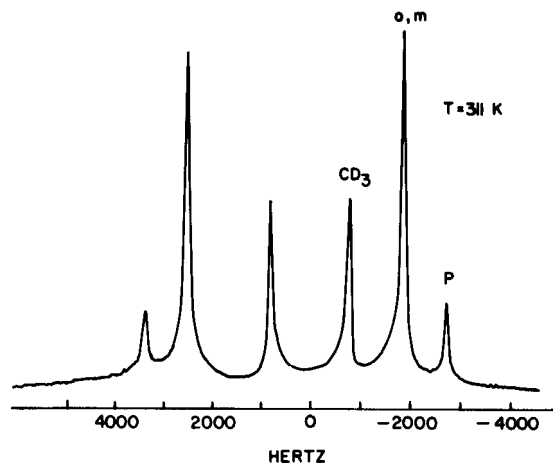


Figure 1. Deuterium N.M.R. spectrum of toluene- $d_8$  dissolved in OG.

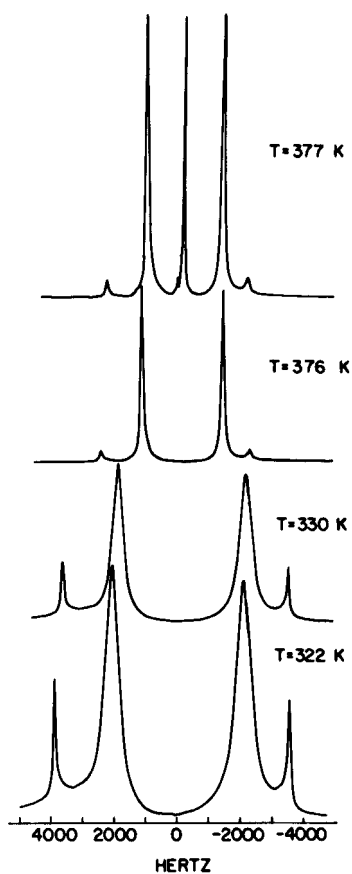


Figure 2. Deuterium N.M.R. spectra of a solution containing both benzene- $d_6$  and  $D_2O$  in OG as a function of temperature.

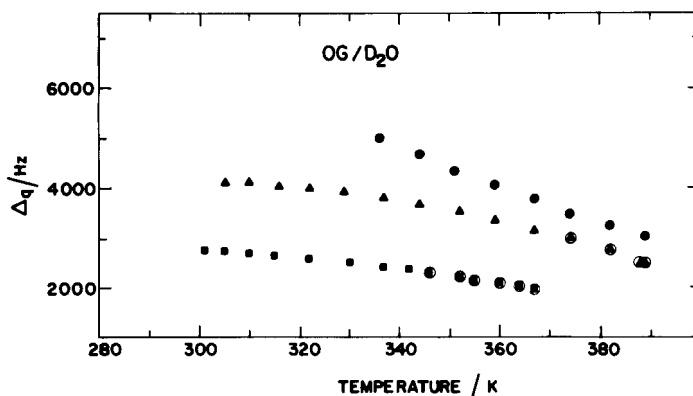


Figure 3. Quadrupolar splittings,  $\Delta q$ , as a function of temperature for  $D_2O$  dissolved in OG; full circles: 152 mg OG, 8.4 mg  $D_2O$  (mole fraction = 0.45); full triangles: 152 mg OG, 25.4 mg  $D_2O$  (mole fraction = 0.71); full squares: 148.7 mg OG, 37 mg  $D_2O$  (mole fraction = 0.78).

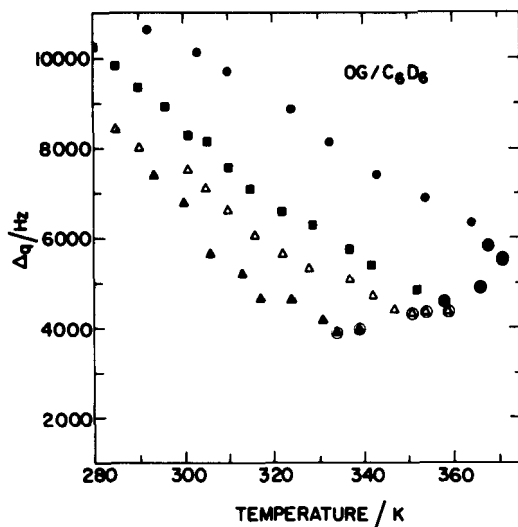


Figure 4. Quadrupolar splittings,  $\Delta q$ , as a function of temperature for  $C_6D_6$  dissolved in OG; full circles: 152 mg OG, 11.8 mg  $C_6D_6$  (mole fraction = 0.21); full squares: 152 mg OG; 53.8 mg  $C_6D_6$  (mole fraction = 0.55); empty triangles: 152 mg OG; 82.2 mg  $C_6D_6$  (mole fraction = 0.65); full triangles: 152 mg OG, 179.2 mg  $C_6D_6$  (mole fraction = 0.80).

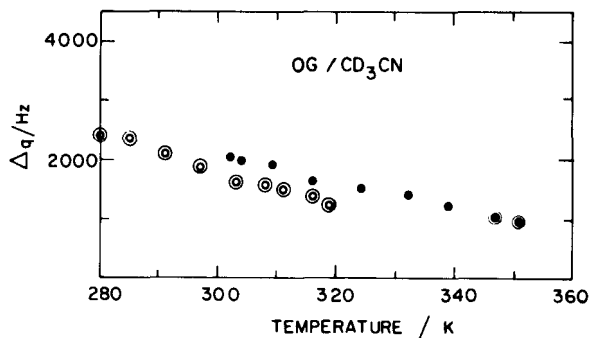


Figure 5. Quadrupolar splittings,  $\Delta q$ , as a function of temperature for  $CD_3CN$  dissolved in OG; full circles: 156 mg OG, 6.6 mg  $CD_3CN$  (mole fraction = 0.22); empty circles: 156 mg OG, 22.4 mg  $CD_3CN$  (mole fraction = 0.49). All spectra show a biphasic system.

fraction of water reaches approximately 0.8, polycrystalline type deuterium spectra including isotropic singlets are observed in the temperature range of 250 to 290 K. At water mole fractions exceeding 0.92 single lines are observed. Figure 4 shows the dependence of  $\Delta q$  on temperature for benzene dissolved in OG. The splittings are larger for benzene than for water and their temperature dependence stronger. The transition temperature is lowered significantly as the concentration of benzene increases. When the benzene mole fraction exceeds *c.* 0.8, the spectra are observed only below room temperature and are of the polycrystalline type together with a superimposed singlet. A similar situation was encountered at high water concentrations. Figure 5 shows the results for acetonitrile in OG. The liquid-crystalline phase is only preserved at very low acetonitrile concentrations which is rather unusual when compared with other solutes. Figure 6 shows the results for solutions containing *both*

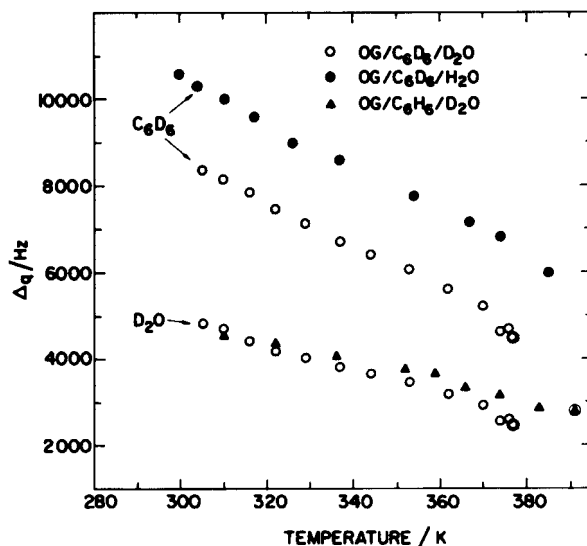


Figure 6. Quadrupolar splittings,  $\Delta q$ , as a function of temperature for solutions containing both benzene and water in OG; empty circles: 296.6 mg OG, 51 mg  $D_2O$ , 29.4 mg  $C_6D_6$ ; full circles: 153.1 mg OG, 23.1 mg  $H_2O$ , 14.6 mg  $C_6D_6$ ; full triangles: 155.2 mg OG, 23.5 mg  $D_2O$ , 15.3 mg  $C_6H_6$ .

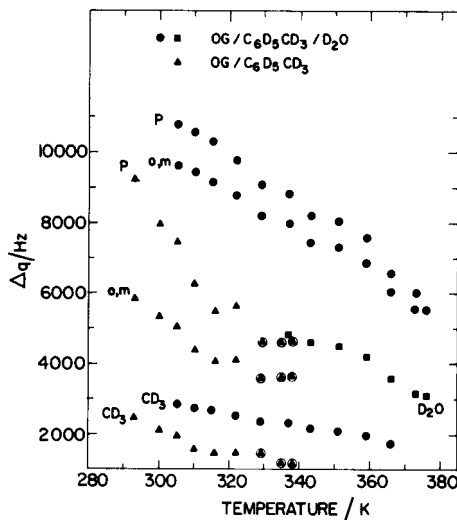


Figure 7. Quadrupolar splittings,  $\Delta q$ , as a function of temperature for solutions containing toluene- $d_8$  or toluene- $d_8$  and water in OG; full triangles: 150.8 mg OG, 41.2 mg  $C_6D_5CD_3$ ; full circles and squares: 152.4 mg OG, 22.4 mg  $C_6D_5CD_3$ , 15 mg  $D_2O$ .

benzene and water. This demonstrates a rather remarkable property of OG being able to accommodate both polar and apolar, small solute molecules [13]. As in the separate OG–water or OG–benzene systems, the water lines are broader and their temperature dependence smaller (cf. figure 2). A rather large difference in the quadrupolar splittings of benzene is noted between samples prepared in  $H_2O$  and  $D_2O$ . Further experiments will be performed to investigate whether this is a true isotope effect or

not. Similar results for the toluene–water–OG system are shown in figure 7 together with results for the toluene–OG system.

Samples of the hydroxyl deuteriated OG show a doublet below 385 K. The lines are very broad and below 360 K the measurement of the quadrupolar splitting becomes impossible. The splitting,  $\Delta q$ , varies from 2900 Hz at the highest temperature to about 3600 Hz.

We have also attempted several experiments with *n*-hexyl- $\beta$ -D-glucopyranoside (HG), which is not a thermotropic liquid crystal. Adding small amounts of D<sub>2</sub>O or C<sub>6</sub>D<sub>6</sub> shows, in addition to a singlet, polycrystalline type of spectra, at temperatures around and below room temperature. From the narrowness of the lines and their small separation we deduce that this system might be capable of forming a lyotropic liquid-crystalline mesophase.

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