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Deuterium NMR studies of *n*-octyl-, *n*-nonyl-, *n*-decyl- β -D-glucopyranoside liquid crystalline systems

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We report measurements of the deuterium NMR spectra of the lyotropic systems *n*-octyl-, *n*-nonyl- and *n*-decyl- β -D-glucopyranosides with D₂O and C₆D₆. From these spectra the phase diagrams are constructed and include lamellar, hexagonal and isotropic (presumably cubic) phases. The details of the phase diagrams depend upon the sugar homologue and the solvent. The results can be understood qualitatively by considering some of the factors which determine the nature of the phases in these systems. The deuterium spectra belonging to the OD groups in the polar heads of *n*-octyl- α -D-glucopyranoside dissolved in C₆H₆ were measured and compared with analogous spectra, which were reported previously, of the same compound in D₂O.

1. Introduction

Previous deuterium NMR studies of *n*-alkyl- α - and - β -D- glucopyranosides with polar, apolar and mixed solvents have shown that they form ordered phases as a function of the concentration and temperature [1-3]. These studies also dealt with the order profile of the alkyl chains and the orientation of the polar head group in some particular compounds. There exist related X-ray studies which were performed on the pure *n*-octyl- α -D-glucopyranoside (α OG) [4] and on mixtures of *n*-octyl- β -D-glucopyranoside (β OG), *n*-nonyl- β -D-glucopyranoside (β NG) and *n*-decyl- β -D-glucopyranoside (β DG) with water [5]. These X-ray measurements are intrinsically more definitive about the nature of the observed phases. They were however, performed by such a procedure which did not allow precise determination of the concentrations and temperatures at which they were taken.

This work extends our previous deuterium NMR studies. We report here the phase diagrams for β OG, β NG and β DG in water and benzene. We found significant variations in the phase diagrams of the three homologues in water or in benzene. We also compare the behaviour of the hydroxyl deuterons of the polar head in the α OG-benzene system with the respective previous measurements for the α OG-water system. Here too, a difference which reflects the behaviour in polar and apolar media was noted.

As described earlier [3], the deuterium NMR spectra of deuteriated solvents in these systems exhibit characteristic spectra which can be attributed to four different phases: (i) The isotropic phase; a micellar solution above the cmc, is characterized by a single deuterium resonance. (ii) The lamellar phase (uniaxial, $\Delta\chi < 0$) is characterized by a relatively narrow doublet, the spacing between its components being proportional to

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the order parameter of the measured deuterium. (iii) The hexagonal phase (uniaxial, $\Delta\chi > 0$) is characterized by a spectrum which resembles a powder pattern and is composed of two doublets with a spacing ratio of exactly 1/2 between the parallel and perpendicular (inner and outer) components. The relative intensities and widths of the inner and outer doublets can vary and depend upon the distribution of the ordered micro-domains in the sample. The latter is a function of the way the sample is prepared (efficiency of mixing, surface anchoring and its thermal history in the magnet). Different forms of deuterium spectra in an hexagonal phase belonging to a related system are presented in the earlier work of Gutman *et al.* [6]. (iv) An 'NMR isotropic' phase, most likely cubic [5], which is characterized by a single resonance. The latter phase sometimes exists between the lamellar and hexagonal phases in the phase diagram. Typical spectra of all four phases in our systems were presented in [3]. We have also performed some X-ray measurements which confirm the nature of the lamellar and hexagonal phases and are in accord with the X-ray work of Jeffrey *et al.* [5]. We have not performed X-ray measurements on the presumed cubic phase.

2. Experimental

The alkylated sugars were obtained from Sigma and were purified and dried by passing a methanolic solution through a column containing Amberlite MB-1A above Amberlite XAD-2. The methanol was distilled and the material dried under high vacuum for several days. Samples were prepared by weighing and mixing the components in 5 mm NMR tubes which were sealed and heated for equilibration. All measurements were taken during slow cooling ($1 \text{ K } 120 \text{ s}^{-1}$) in the magnetic field. The measurements were performed using a Bruker AM400WB NMR spectrometer operating at a frequency of 61.4 MHz for deuterium. The temperature was adjusted by a flow of heated air or cooled nitrogen over the sample. Temperature precision and stability are estimated as $\pm 2 \text{ K}$ at the highest and lowest temperatures and as $\pm 0.5 \text{ K}$ near room temperature. Samples were not spun in the magnetic field.

3. Results and discussion

3.1. Phase diagrams

A schematic drawing of a representative molecule, the OG, with the numbering system for the atoms is shown in figure 1. Before describing the phase diagrams it might be useful to present some general considerations of factors which govern the nature of the phases formed in these systems. It is important to keep in mind that the alkylated glucopyranosides are thermotropic liquid crystals (of the S_A type), but also form lyotropic systems with polar, apolar or mixed solvents. The energy terms in such systems can be described approximately by the interactions of the core (sugar polar heads in our case), X_s , and of the chains, X_c , with a mean field [7]. The estimated value of X_s/X_c for β OG was found to be about 5 [2]. Similarly, the values of X_s/X_c for some nematics [7] and discotics [8] are > 3 and about 8, respectively. Also, as for any lyotropics, the nature of the solvent plays an important role in the organization of the system. We assume that, at high surfactant concentrations, water, which is located in the polar head region, increases the rigidity and the effective volume of the polar heads. This is achieved through the formation of an intermolecular hydrogen-bonded network which promotes the binding between the polar heads. Benzene, which dissolves in the alkyl chain region, weakens the binding interaction between the chains. For large water concentrations, the binding effect decreases till eventually the transition to micelles occurs. In benzene, it is expected that the transition to a micellar

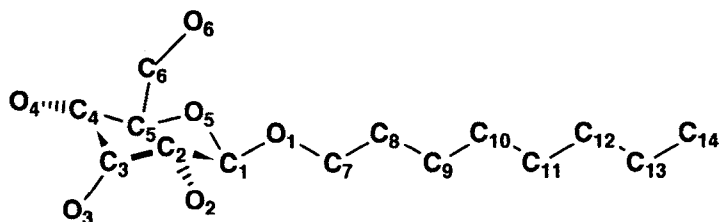


Figure 1. A schematic drawing of the OG molecule with the numbering system for the atoms. The hydrogen atoms are not shown.

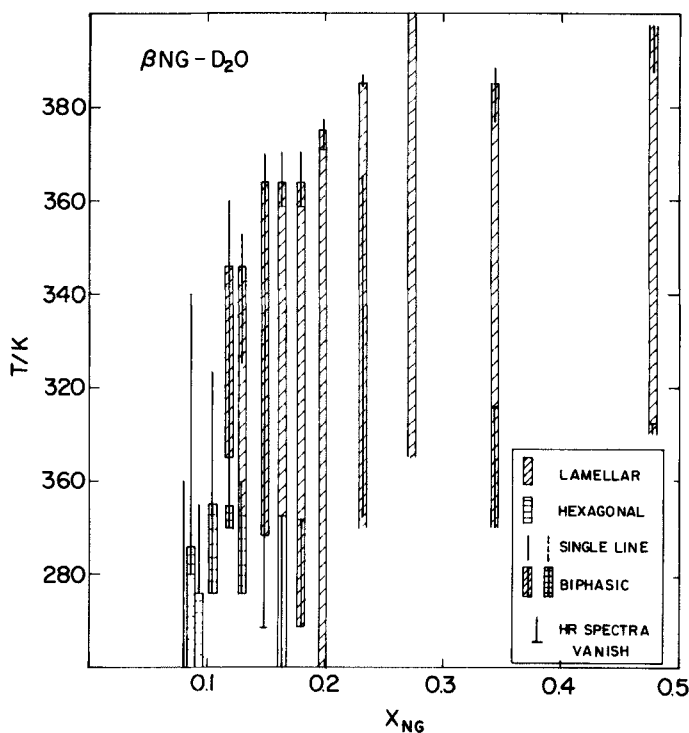


Figure 2. Schematic phase diagram for βNG in water. The notation is explained in the insert to the figure.

solution will occur at higher surfactant concentrations than for water. The experimental results, presented henceforth, concerning the concentrations at which the phase transitions occur and the temperature dependence of the order are in accord with these considerations. We may add that evidence was recently presented [9], that hydrogen bonds play a minor role in the interactions between sugar molecules in dilute solutions.

The phase diagrams for βNG and βDG with water are shown schematically in figures 2 and 3. The phase diagrams are given in a form which presents the actual results of the NMR measurements, at several concentrations, as a function of the temperature and not in the conventional form showing the phase boundaries. The reason for this choice is that the boundaries between phases were not determined precisely because of supercooling effects. A close inspection of the diagrams demonstrates this problem. Consequently the diagrams are denoted as schematic and only rough phase boundaries can be inferred. These diagrams ought to be compared with figure 2 of [3] which shows

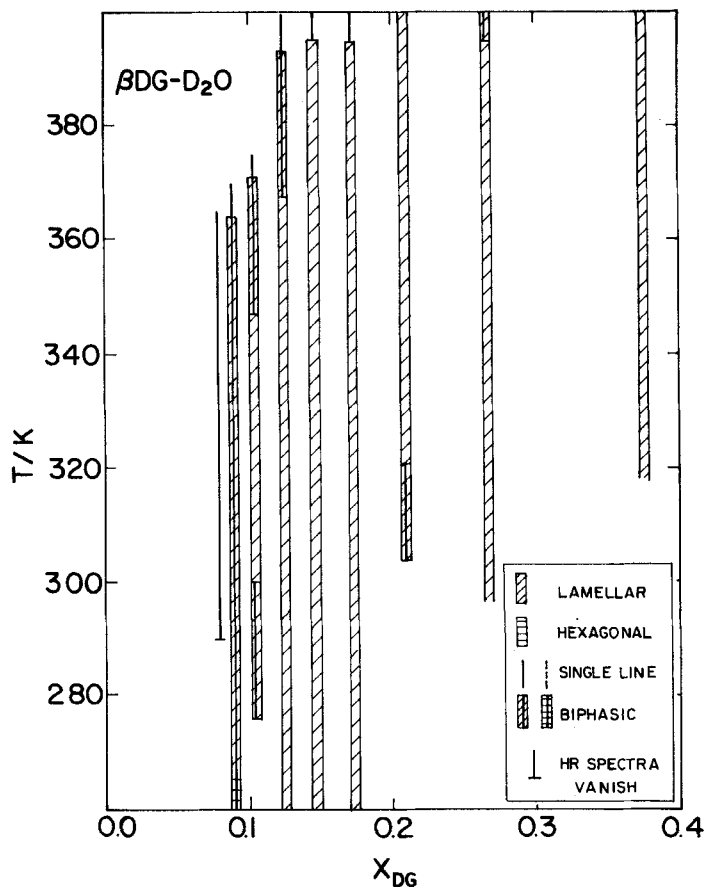


Figure 3. Schematic phase diagram for β DG in water. The notation is explained in the insert to the figure.

the schematic phase diagram for β OG and water. A point to note is that the hexagonal phase in β NG appears at a lower concentration than for β OG ($x_{\beta OG} = 0.16$, $x_{\beta NG} = 0.12$), while in β DG it is very doubtful whether the hexagonal phase appears at all (a very small region may exist around $x_{\beta DG} \cong 0.095$ and at low temperatures). Thus, the addition of one or two methylene units to the octyl chain strongly inhibits the formation of the hexagonal phase. The same effect is noticed for the cubic phases which exist in β OG and β NG solutions, but not in β DG solutions. These results mean that the cylinders, in the hexagonal phase, with outer hydrated glucopyranoside polar heads, do not form with carbohydrate chains longer than nine units. We conclude that a minor change in the length of the alkyl chain has a significant effect on the nature of the phases which are formed with water. Other differences between the phase diagrams within the series β OG, β NG and β DG, are the increasing transition temperatures to the isotropic phases and the extended temperature ranges for which supercooled lamellar phases exist.

Figures 4, 5 and 6 show the schematic phase diagrams of β OG, β NG and β DG with benzene. In the range of high surfactant concentrations the ordered phases are lamellar. The transition to hexagonal phases occurs at considerably higher surfactant concentrations than for the corresponding compounds with water, being approximately $x = 0.56$, 0.47 and 0.42 for β OG, β NG and β DG, respectively. It should be noted that in

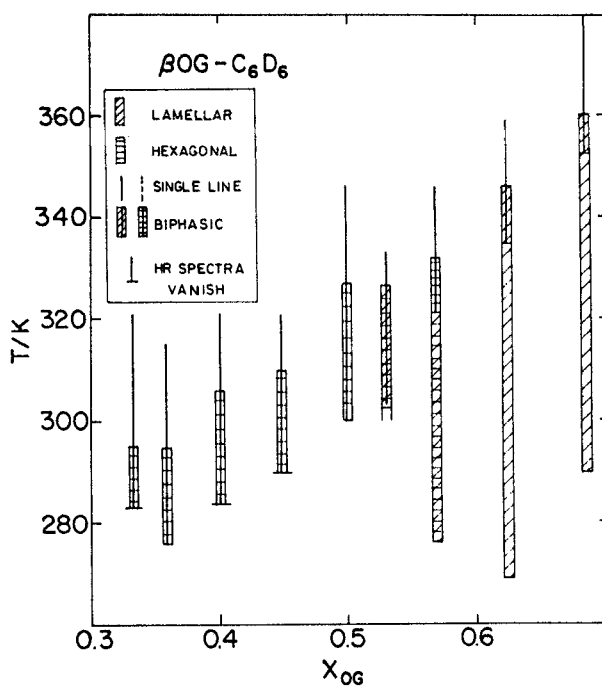


Figure 4. Schematic phase diagram for βOG in benzene. The notation is explained in the inset to the figure.

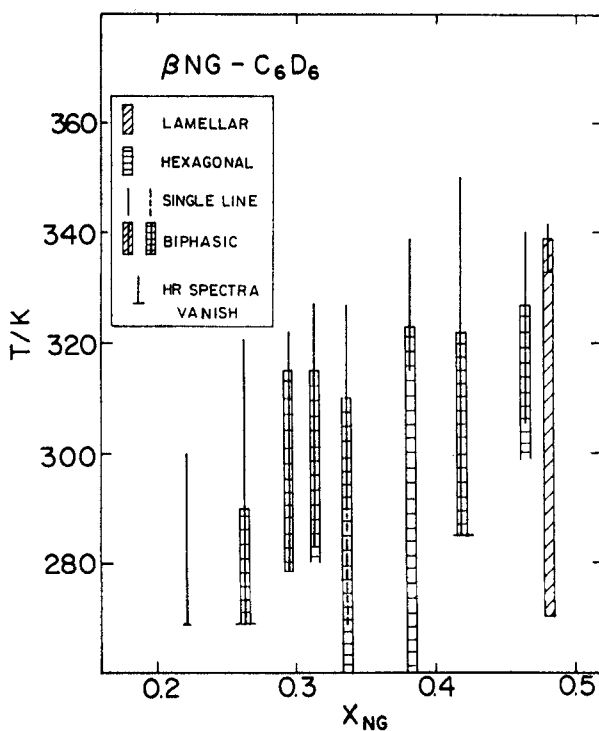


Figure 5. Schematic phase diagram for βNG in benzene. The notation is explained in the inset to the figure.

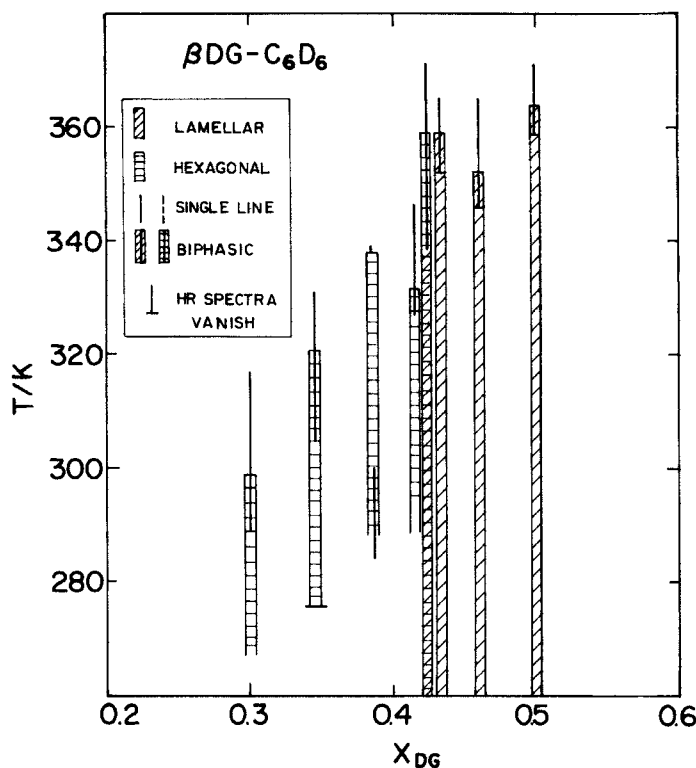


Figure 6. Schematic phase diagram for βDG in benzene. The notation is explained in the insert to the figure.

the transition region we were able to observe (in βOG and βDG), the coexistence of lamellar and hexagonal phases. The transition temperatures to the isotropic phases are considerable lower than for the corresponding aqueous systems. Also, the surfactant concentrations at which the ordered phases cease to exist and micellar solutions are formed, are significantly higher in benzene than for the corresponding aqueous solutions. We conclude that water is better than benzene, as a solvent, for the formation of lyotropic phases in our systems. In benzene, however, the hexagonal phase is preferred over the lamellar phase. We found no indication for the existence of cubic phases in any system with benzene.

The temperature dependence of the quadrupolar splittings of D_2O and C_6D_6 in the lamellar phases of βOG , βNG and βDG is shown in figures 7 and 8. It should be noted that, in solutions of the glucopyranosides in D_2O , when the exchange between the deuterons is slow, the spectra consist of five doublets (four belonging to OD groups in the polar head and the fifth to D_2O). A single doublet is observed when exchange between all deuterons is fast. Intermediate situations also occur when deuterium exchange rates are comparable to the inverse quadrupolar interactions. The deuterium exchange rates depend on temperature and concentration in a complex manner. The data presented in Figure 7 were taken from spectra under the conditions of slow exchange.

Figures 7 and 8 show that the temperature dependence of the quadrupolar splittings is considerably stronger for benzene than for water solutions. Actually, the splittings in D_2O are almost temperature independent and in some cases may even

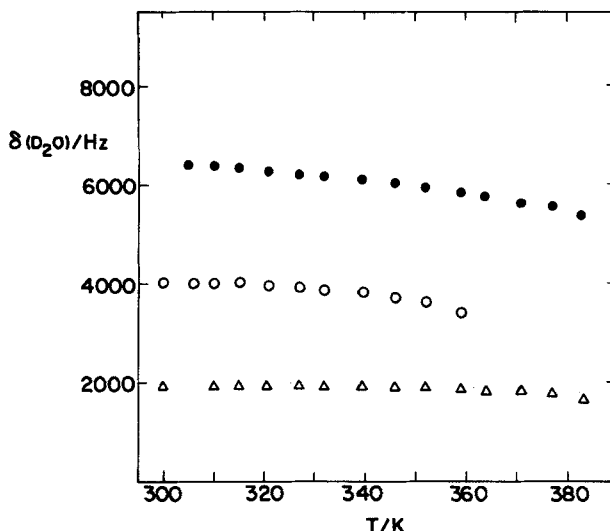


Figure 7. Typical temperature dependence of the deuterium quadrupolar splittings of D₂O in some βOG-, βNG- and βDG-D₂O mixtures. ○, βOG/D₂O, x_{OG}=0.22; ●, βNG/D₂O, x_{NG}=0.27; △, βDG/D₂O, x_{DG}=0.14.

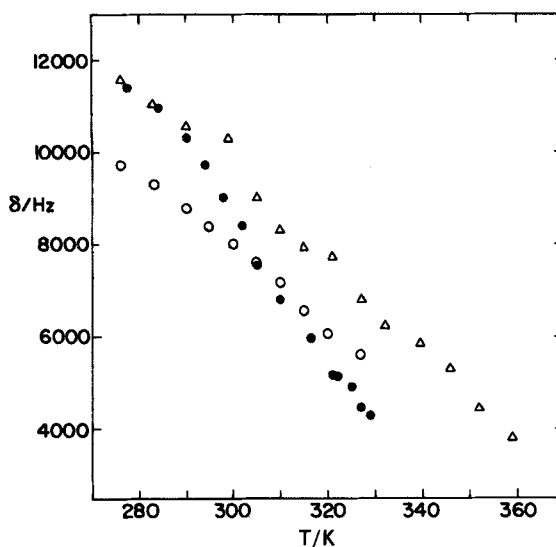


Figure 8. Typical temperature dependence of the deuterium quadrupolar splittings of C₆D₆ in some βOG-, βNG- and βDG-C₆D₆ mixtures. ○, βOG/C₆D₆, x_{OG}=0.62; ●, βNG/C₆D₆, x_{NG}=0.48; △, βDG/C₆D₆, x_{DG}=0.50.

decrease with decreasing temperature which is contrary to the usual behaviour. The temperature dependence is again consistent with the assumption that water interferes little with the order (or may even promote it), while benzene, which penetrates the alkyl chain region, acts to disrupt it. This order disruption effect is expected to be strongly dependent upon the temperature due to enhanced thermal motion at high temperatures.

3.2. Polar head groups

The hydroxyl protons of the glucopyranoside ring can be easily substituted with deuterium by dissolving the material in an excess of D_2O and drying. We applied this procedure to αOG dissolved in C_6H_6 and measured the spectra of the hydroxyl deuterons. The spectra are similar to those reported previously (see figure 5 in [3]) for the hydroxyl deuterons of αOG dissolved in D_2O . The resonances belonging to the outer doublets clearly exhibit a small additional splitting into two lines. Similar, but less pronounced, splittings were also observed in the $\alpha OG/D_2O$ spectra. These splittings may be attributed to the dipolar interaction of one of the OD groups with its neighbouring CH group.

For spectra measured for the lamellar phase we used the model suggested by Tyrell and Prestegard [10] which assumes that the sugar ring is a rigid entity which undergoes fast reorientational diffusion around a single axis. For each quadrupolar doublet belonging to a particular OD, the quadrupolar splitting, δ_i is given by

$$\delta_i = 3/2(QCC)S\langle(3 \cos^2 \alpha_i - 1)/2\rangle,$$

where S is an order parameter for the rotation axis and is assumed to be the same for all the hydroxyl groups, α_i is the angle between the CO bond and the axis of rotation and QCC is the average quadrupole coupling constant for the OD bond and was taken as 200 kHz. We assume that each OD group rotates freely around the CO bond to which it belongs. In our application the α_i s are known functions of the polar angles, ϕ and θ , which determine the axis of rotation of the sugar group in the cartesian system based on the crystal coordinates which are defined in [5]. The average results which were obtained are: $\theta = 60^\circ$ and $\phi = 180^\circ$ which should be compared with the corresponding values of $\theta = 49^\circ$ and $\phi = 174^\circ$ obtained in the $\alpha OG/H_2O$ system. This result means that the axes of rotation of αOG are similar in benzene and water and are approximately parallel to the C_4C_8 axis (cf. figure 1 of this work and figure 7 of [3]).

We attempted to assign the quadrupolar splittings, belonging to particular OD groups, taking into consideration the dipolar splitting observed for one OD group. The analysis, has not yielded unequivocal results, but strongly indicated that the outer quadrupolar doublet (with the largest splitting) belongs to the O_4D group. This result follows from the calculations (for benzene solutions) of γ , which is the angle between the line connecting the mean position of a deuterium atom belonging to a particular OD group and its nearest H atom, with the axis of rotation. The values of γ are 49° and 45° for HC_2O_2D and HC_3O_3D , respectively and 81° for HC_4O_4D . This means that the term $(3 \cos^2 \gamma^{-1})$ is small for O_2D and O_3D but large for O_4D . The smallest quadrupolar splitting belongs, as also reported previously [3], to the O_6D group.

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