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Natural-Abundance Oxygen-17 Magnetic Relaxation in Aqueous Solutions of Carbohydrates

Hisashi UEDAIRA,*,† Mitsuhiko IKURA,† and Hatsuho UEDAIRA††
†Department of Polymer Science, Faculty of Science, Hokkaido University, Sapporo 060
††Research Institute for Polymers and Textiles, Tsukuba, Ibaraki Pref. 305

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The spin-lattice relaxation times, T_1, of $H_2{}^{17}O$ have been measured for aqueous solutions of several pentoses, hexoses, di-, and trisaccharides as a function of the concentration at 25 °C. The coordination numbers, n_h, and the rotational correlation times, τ_c^h, of water molecules around the sugars were estimated and compared with that of pure water, τ_c°. The value of $\tau_c^h/\tau_c^\circ=4.10$ for glucose is largest, while that of $\tau_c^h/\tau_c^\circ=2.82$ for ribose is the smallest, among these sugars. The value of n_h $(\tau_c^h/\tau_c^\circ-1)$ was defined as the dynamic hydration number. The dynamic hydration numbers showed a good correlation with the mean number of the equatorial OH groups and the limiting diffusion coefficients.

Several attempts have been made to elucidate the relation between the hydration and the conformation of carbohydrates in aqueous solutions,[1] since Kabayama and Patterson[2] proposed a model that the conformation of β-D-glucose well matches the tridymite structure in water. Special attention has been paid to the fact that the sugar hydration is affected by the mean value of the number of equatorial OH groups, $n(e\text{-OH})$, existing in the various conformers of sugar ususally found in solutions.[3,4]

Recently, we reported that the values of partial molar heat capacities at infinite dilution,[5] the relative increments in the ultrasonic velocity,[6] and the limiting diffusion coefficients[7] of many pentose, hexose, and oligomers in aqueous solutions correlate well with $n(e\text{-OH})$. It was found that the denaturation temperatures of lysozyme and ovalbumin increase almost linearly with the $n(e\text{-OH})$ of the added sugars.[8,9] The permeable velocity of some hexose through the red cell membrane is inversely proportional to their values.[4] These results show that *e*-OH groups play an important role in the equilibrium, transport, and biochemical properties of aqueous solutions of sugars.

To prove the effect of $n(e\text{-OH})$ on the hydration of sugars, the magnetic relaxation method of oxygen-17 is extremely powerful, since the sugars possess exchangeable protons. As far as we know, Tait et al.[3] have measured only the linewidth of the NMR spectra of ^{17}O-enriched water in concentrated solutions of several monosaccharides. In this work, we report the spin-lattice relaxation times of the natural abundance ^{17}O of water for aqueous solutions of pentose, hexose, and oligosaccharides as a function of the concentration at 25 °C. The concentration dependence of the water-^{17}O relaxation rates is interpreted in terms of the effect of the *e*-OH groups on the sugar hydration. Then we discuss the relation between the diffusion coefficients and the dynamic hydration numbers of sugars.

Experimental

All of the sugars studied were of G. R. (Tokyo Kasei Co.) and has been purified by the method which has been reported previously.[8,10]

Distilled and deionized water was used.

All natural-abundance oxygen-17 NMR experiments were performed using a JEOL GX-500 spectrometer operating at 6.7 MHz. The oxygen-17 T_1 was measured by using the inversion recovery sequence (180°∼τ∼90°). For the oxygen-17 relaxation in neutral water, $T_2<T_1$ is observed in consequence of ^{17}O–^{1}H spin–spin coupling.[11] Therefore, the water and all the solutions were maintained at pH 3.5 by adding *p*-hydroxybenzoic acid,[3] since at this pH value the proton exchange becomes sufficiently fast, making $T_2=T_1$ in pure water.

The temperature was maintained at 25±0.3 °C by means of gas-thermostating.

Results and Discussion

The value of the oxygen-17 T_1 of water was 7.3 ms at 25 °C, in agreement with the data reported by Hindman et al. (6.8 ms).[12] In Figs. 1—3, the values of T_1°/T_1 for $H_2{}^{17}O$ in aqueous solutions of sugars are plotted against their concentrations, where T_1° and T_1 are the spin-lattice relaxation times of ^{17}O in pure water and

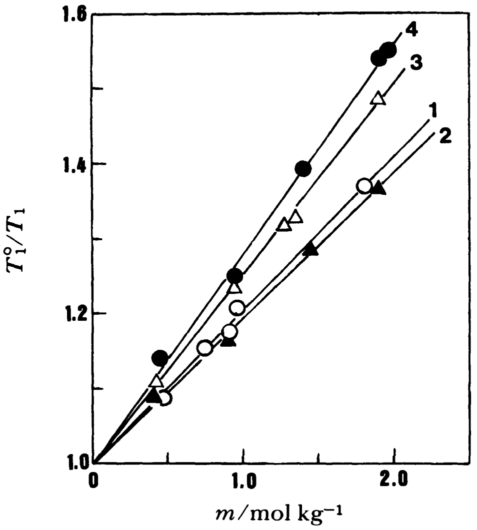

Fig. 1. T_1°/T_1 of $H_2{}^{17}O$ in solutions of monosaccharides as a function of the molality.
1 -○- deoxyribose; 2 -▲- ribose; 3 -△- arabinose; 4 -●- xylose.

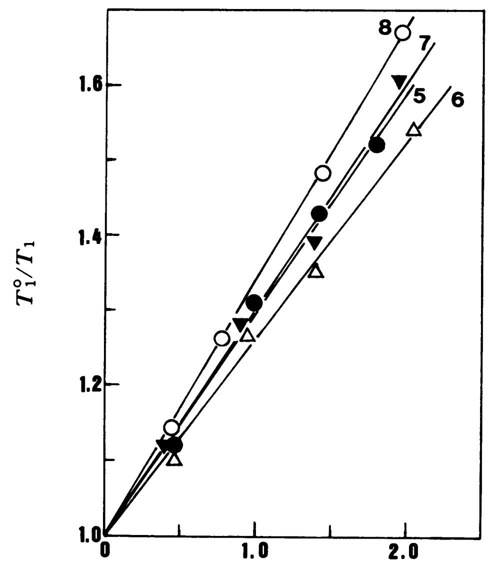

Fig. 2. T_1°/T_1 of $H_2{}^{17}O$ in solutions of monosaccharides as a function of the molality.
5 -●- fructose; 6 -△- mannose; 7 -▼- galactose; 8 -○- glucose.

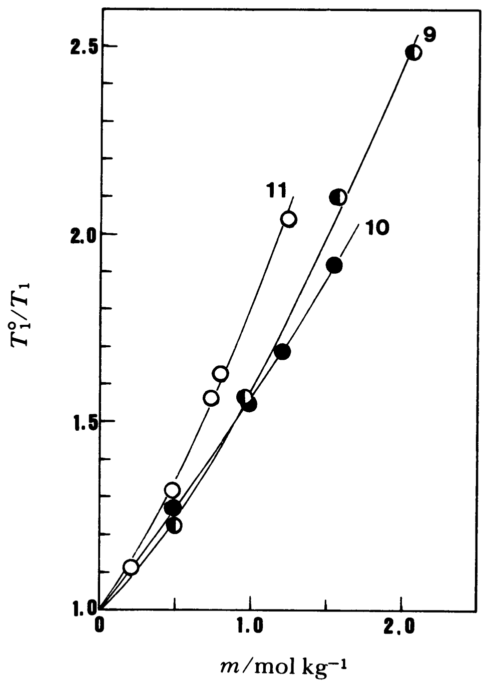

Fig. 3. T_1°/T_1 of $H_2{}^{17}O$ in solutions of oligosaccharides as a function of the molality.
9 -◐- sucrose; 10 -●- maltose; 11 -○- raffinose.

solutions respectively.

The values of T_1°/T_1 for sugar solutions are adequately represented by the empirical equation of this form:

$$T_1^\circ/T_1 = 1 + Bm + Cm^2 \tag{1}$$

where m is the molality of the sugar. Especially, the values of T_1°/T_1 for monosaccharide solutions are well represented by the linear equation of molality, as is shown in Figs. 1 and 2. The solid line in these figures are those calculated by the least-squares method. The correlation coefficients were in the range of 0.997—0.990. The values of $55.5B$ (see Eq. 6) for sugars are given in the third colum in the table. The numbers on the lines and curves in all the figures denote the same sugars as in the table.

In the extreme motional narrowing condition, we obtain for the oxygen-17 relaxation rate:[13]

$$\frac{1}{T_1} = \frac{3}{125}\left(1 + \frac{\eta^2}{3}\right)\left(\frac{e^2qQ}{\hbar}\right)^2 \tau_c \tag{2}$$

where η is an assymmetric parameter of the electrical field gradient, e^2qQ/h is the quadrupole coupling constant, and τ_c is the correlation time of molecular reorientation. The contribution of η will be omitted in the following discussion, since this value is usually small.[14] As the value of e^2qQ/h for pure water is 7.7 MHz,[3] we obtain $\tau_c^\circ = 2.4$ ps from the value of T_1°; this is good agreement with the value (2.5 ps) which Hertz[14] obtained from the relaxation rate of the water protons.

In aqueous sugar solutions, the ^{17}O nuclei are distributed between two motional states with different intrinsic relaxation rates. If the exchange of water molecules between hydration water (mole fraction x_h) and bulk water is fast, the following relation is obtained;[15]

$$1/T_1 = (1 - x_h)/T_1^\circ + x_h/T_{1h} \tag{3}$$

which, by the use of Eq. 2, can be rewritten as:[3,15]

$$\frac{T_1^\circ}{T_1} = 1 + n_h\left(K\frac{\tau_c^h}{\tau_c^\circ} - 1\right)\frac{m}{55.5} \tag{4}$$

$$K \equiv (e^2qQ_h/\hbar)^2/(e^2qQ_0/\hbar)^2 \tag{5}$$

where the subscripts h and zero refer to the water of the hydration sphere (cosphere) and bulk water respectively and n_h is the coordination number.[15] From a comparison of Eqs. 1 and 4, we obtain this relation;

$$55.5B = n_h\left(K\frac{\tau_c^h}{\tau_c^\circ} - 1\right) \tag{6}$$

Then, if the value of n_h is known, we can estimate the value of τ_c^h/τ_c°. Since n_h is the number of the water molecule close to that of sugar, we supposed 6, 10, and 14 for mono-, di-, and trisaccharides respectively, according to Kabayama and Patterson's model.[2] Regarding the quadrupole coupling constant of hydration water, there are two viewpoints. It is usually assumed that e^2qQ/h is equal to that of pure water or ice. Generally, the former assumption is adopted in the case of electrolytes and nonelectro-

Table 1. Hydration Characteristics and Diffusion Coefficients of Sugars in Aqueous Solutions at 25 °C

No.	Sugar	$n(e\text{-OH})$ a)	$55.5B$	n_h	τ_c^h/τ_c^o b)	τ_c^h/τ_c^o c)	$D_0 \times 10^{10}$ d) $\mathrm{m^2\,s^{-1}}$
1	Deoxyribose	1.4	11.4	6	2.90		8.150
2	Ribose	2.1	10.9	6	2.82		7.795
3	Arabinose	2.6	14.0	6	3.32	4.38	
4	Xylose	3.5	15.5	6	3.58	4.72	7.495
5	Fructose	3	16.5	6	3.75	4.90	7.002
6	Mannose	3.3	14.7	6	3.45	4.55	
7	Galctose	3.6	16.6	6	3.76	4.96	
8	Glucose	4.6	18.6	6	4.10	5.41	6.75
9	Sucrose	6.3	25.2	10	3.52	4.64	5.223
10	Maltose	7.2	27.2	10	3.72	4.91	5.201
11	Raffinose	8.3	30.7	14	3.19	4.21	4.359

a) Refs. 5 and 7. b) $K=1$. c) $K=0.76$. d) Ref. 7.

lytes.14,15) On the other hand, Tait et al.3) took the e^2qQ/h value of ice as that of glucose and ribose solutions. According to these two assumptions for the value of e^2qQ/h, the values of K in Eq. 5 were calculated to be 1 and 0.76 respectively.

We show in the table the values of $n(e\text{-OH})$, n_h, and τ_c^h/τ_c^o for each sugar. For monosaccharides, a sugar with more e-OH groups shows the larger value of τ_c^h/τ_c^o. This means that the thermal motion of water molecules around sugar is more restricted than in bulk water and that the degree of restriction depends on $n(e\text{-OH})$. Glucose has the largest stabilization effect on the water structure. It is worthy of notice that the values of τ_c^h/τ_c^o for deoxyribose and ribose with smaller $n(e\text{-OH})$ values than those of other sugars are smaller; that is to say, water molecules around both sugars are more mobile. This means that the assumption that the e^2qQ/h value of water in the hydration sphere equals that of ice is not appropriate in the case of these sugars. Accordingly, we did not use this assumption in calculating the values of τ_c^h/τ_c^o for ribose and deoxyribose.

As is shown in the table, the values of τ_c^h/τ_c^o for di- and trisaccharides are nearly equal to those of the constituted monosaccharides. Suggett and Clark16) measured the dielectric relaxation of the concentrated sugar solutions and obtained the values of the dielectric relaxation, τ_r of water molecules in the hydration sphere. The values for glucose, mannose, maltose, and sucrose were 22.0, 21.0, 21.6, and 21.6 ps respectively,17) which agree with the results of τ_c^h/τ_c^o reported in this study. Recently, we also obtained the same τ_c^h/τ_c^o value for the monomers and dimers of sulfonate ions.18)

Previously, we calculated the translational frictional coefficients of oligomers in aqueous solutions and pointed out that the microviscosity around the oligomer is almost the same as that around the monomer.19) Since the microviscosity around a solute molecule is closely related to the rotational correlation time of the solvent in the cosphere, the above results strongly support our idea. Thus, there is little correlation between $n(e\text{-OH})$ and τ_c^h/τ_c^o for oligosaccharides.

The values of $n_h(\tau_c^h/\tau_c^o-1)$,which is equal to $55.5B$, is considered to signify the dynamic state of the water molecule in the cosphere relative to the bulk water formed by the same number of water molecules as the cosphere, as is clear from Eqs. 3 and 6. In this context, $n_h(\tau_c^h/\tau_c^o-1)$ is defined as the dynamic hydration number. The dynamic state of water molecules in the cosphere of sugar molecule depends on the interaction between water and sugar molecules, which is itself affected by $n(e\text{-OH})$. The number of water molecules in the cosphere is in proportion to the number of OH groups in the sugar molecule, as has been mentioned above. The e-OH groups are able to interact with water in a manner which forms a long-lived hydration structure, since e-OH groups on pyranose sugars match the unperturbed water lattice.2) We proposed that the sugar molecule, which has a larger number of e-OH groups in a molecule, has a stronger stabilizing effect on the water structure.4) It is reasonable, therefore, to express the stabilizing effect in the dynamic hydration number. The relation of the dynamic hydration number to $n(e\text{-OH})$ is shown in Fig. 4. This good correlation clearly indicates that the hydration of sugar is essentially determined by the $n(e\text{-OH})$ value.

Recently, we found that the limiting diffusion coefficients, D_0, of sugars in water serve as a linear function of $n(e\text{-OH})$. Therefore, it is of interest to examine the correlation between the dynamic hydration number and the value of D_0. The straight line shown in Fig. 5 is expressed in the following equation by the least-square method:

$$10^{10}D_0 = 10.15 - 0.1872(55.5B)\ (\mathrm{m^2\,s^{-1}}) \qquad (7)$$

The first term on the right-hand side of Eq. 7 indicates the diffusion coefficient of a hypothetical molecule, which has the same interaction as a water–water one. If this hypothetical molecule is a ring formed by

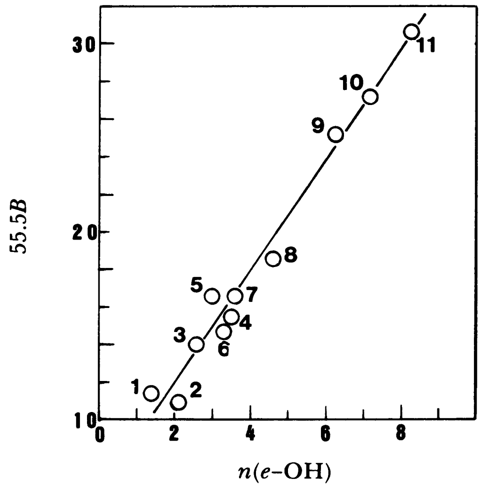

Fig. 4. The relation between 55.5B and $n(e\text{-OH})$. The numbers in figure denote the same sugar as in Table 1.

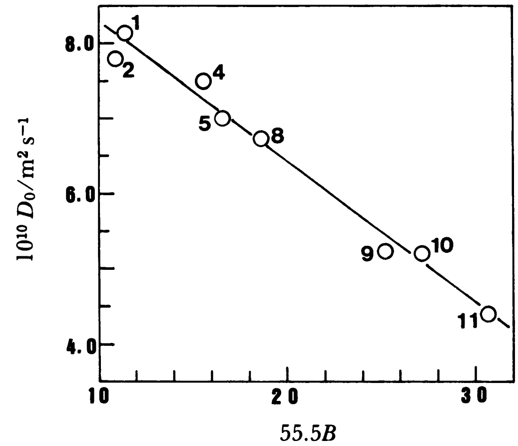

Fig. 5. The relation between D_0 and 55.5B. The numbers in figure denote the same sugar as in Table 1.

several water molecules, we can calculate the D_0 value of the molecule by the use of the following equation:[19,20]

$$D_0 = D_w[11 \ln(L/r)/(6L/r)] \qquad (8)$$

where D_w is the self-diffusion coefficient of pure water (2.3×10^{-9} m^{2}s^{-1} at 25 °C[21]). r is the radius of the water molecule, and L, the length of the ring. We obtain $D_0=10.4\times10^{-10}$ m^{2}s^{-1} for the ring consisting of four water molecules and $D_0=9.34\times10^{-10}$ m^{2}s^{-1} for the ring consisting of five such molecules. These results are reasonable in view of the model in which a molecule of monosaccharide is surrounded by six water molecules. Any other properties which depend on the sugar hydration may be consistently explained by the dynamic hydration number.

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17) The relation between τ_c and τ_r is expressed as follows:[15]

$$1.5\tau_c < \tau_r < 3\tau_c$$

For example, the value of τ_c^h for glucose is 9.84 ps, satisfying this relation.

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