Ultrasonic Relaxation and Fast Chemical Kinetics of Some Carbohydrate Aqueous Solutions

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Abstract: Molecular relaxation properties of the monosaccharides (a) D-glucose, (b) methyl β-D-glucopyranoside, (c) methyl α-D-mannopyranoside, (d) D-xylose, (e) D-arabinose, (f) methyl β-D-xylopyranoside, (g) methyl β-D-arabinopyranoside, (h) methyl α-L-(6-deoxy)mannopyranoside, and (i) 1,6-anhydro-β-D-glucopyranoside, all in aqueous solution, have been studied using broad band ultrasonic spectrometry in the frequency range 0.2−2000 MHz. Ultrasonic excess absorption with relaxation characteristics near 80 MHz was found for glucose and the methyl glucosides of D-glucose and D-mannose, but no relaxation process was detected for the other monosaccharides in the same frequency range. From structural aspects it is deduced that the most likely process causing the observed relaxation is the rotation of the exocyclic $-CH_2OH$ group, placing rotational isomerization on the nanosecond time scale. Relaxation parameters for D-glucose and methyl β-D-glucopyranoside solutions were further investigated as a function of concentration and temperature, in order to confirm the assignment of the relaxation process, and to determine some of its thermodynamic and kinetic parameters.

Introduction

Carbohydrates play diverse roles in biology as metabolic intermediates, as important components of nucleic acids, glycoproteins, and glycolipids, and as prime polymeric contributors to the structure and function of the extracellular matrix. It is therefore desirable to understand the solution conformation and structural dynamics of carbohydrates in some detail.

Compositional and conformational equilibria for monosaccharides in aqueous solution have been investigated by a number of methods, including complex formation, optical rotation/circular dichroism, and (most usefully) NMR spectroscopy.[1,2] Preferred ring conformations and ring sizes (furanose vs pyranose) have been identified. Dynamic processes have been much less well characterized. Interconversion of anomers and of pyranose/furanose forms are slow processes (seconds or longer) requiring bond breakage, so that separate resonances are visible in standard NMR spectra. Fast processes, such as molecular reorientation, with correlation times of approximately 10^{-11} to 10^{-10} s can also be monitored by NMR, using relaxation methods. Certain other processes are predicted by molecular dynamics simulations to occur on the 10^{-10} to 10^{-3} s time scale,[3,4] but have not yet been experimentally characterized. These include changes in orientation of the bulky hydroxymethyl group and interconversion of ring conformations.

One technique which can provide direct monitoring of dynamic processes occurring in the time range 10^{-10} to 10^{-6} s is ultrasonic relaxation spectroscopy. Previous reports of ultrasonic studies of D-glucose in water have demonstrated the existence of at least one relaxation process occurring in the nanosecond time range.[5−7] This relaxation has been attributed to hydroxymethyl group rotation,[7] but the authors have previously pointed out that a ring conformational interconversion could also be the source of the relaxation.

In the present study, we have repeated the ultrasonic relaxation analysis of glucose in aqueous solution, using instrumentation which spans the broad frequency range 0.2−2000 MHz, and have extended our study to include a number of different monosaccharides (Figure 1). On the basis of the structural dependence of the relaxation, the process in the nanosecond region is attributed to rotation of the hydroxymethyl group.

Experimental Section

Materials. D-Glucose, 1,6-anhydroglucopyranoside, and methyl β-D-glucopyranoside have been supplied by Fluka. The D-arabinose, D-xylose, methyl β-D-arabinopyranoside, methyl α-D-mannopyranoside, methyl α-L-(6-deoxy)mannopyranoside (methyl α-L-rhamnopyranoside), and methyl β-D-xylopyranoside were Sigma products. After being dried in vacuo (∼1 Torr) at room temperature and checked for additional weight loss, all saccharides were dissolved as received. Solutions have been prepared in volumetric flasks by weighing the carbohydrate and adding distilled, deionized water up to the flask fiduciary mark. For ultrasonic measurements no solution was used later than 3 days after the time of preparation.

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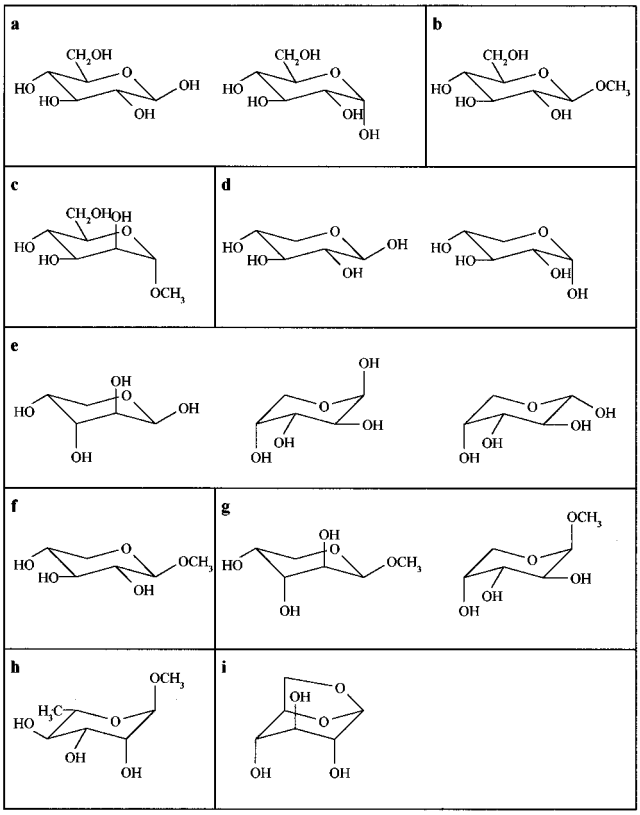

Figure 1. Structures of monosaccharides used in this study. For reducing sugars, both anomers are shown. Where more than one chair conformation is present to an appreciable extent, both $^4C_1$ and $^1C_4$ conformations are depicted. (a) D-Glucose: left, β anomer; right, α anomer. (b) Methyl β-D-glucopyranoside. (c) Methyl α-D-mannopyranoside, (d) D-Xylose: left, β anomer; right, α anomer. (e) D-Arabinose: left, β anomer, $^4C_1$ chair; middle, β anomer, $^1C_4$ chair; right, α anomer. (f) Methyl β-D-xylopyranoside. (g) Methyl β-D-arabinopyranoside: left, $^4C_1$ chair; right, $^1C_4$ chair. (h) Methyl α-L-(6-deoxy)-mannopyranoside. (i) 1,6-Anhydro-β-D-glucose.

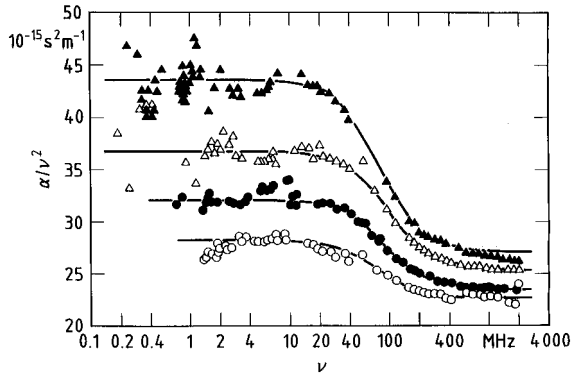

Figure 2. Ultrasonic absorption spectra α/ν^2 for aqueous D-glucose solutions (25 °C) at four concentrations: (○) 0.3 M, (●) 0.5 M, (△) 0.8 M, (▲) 1 M.

Measurements. The sound absorption coefficient α of a solution has been measured as a function of frequency ν between 200 kHz and 2 GHz. As illustrated by the α/ν^2 spectra in Figure 2, the frequency-normalized ultrasonic excess absorption $(\alpha/\nu^2)_{exc}$ may be small in the total frequency range (if there is any excess contribution α_{exc} at all). This excess term can be described as

$$(\alpha/\nu^2)_{exc} = \alpha_{exc}/\nu^2 = \alpha/\nu^2 - B' \qquad (1)$$

with the measured absorption coefficient α and the "classical" term B' from internal viscous friction and thermal conductivity.[8] In order to obtain small $(\alpha/\nu^2)_{exc}$ values accurately, different techniques and several ultrasonic cells, each one matched to the frequency range, had to be employed. Some spectra have been measured independently in two laboratories—Polytechnic University (PU) and Göttingen University (GU)—and compared to assure that small differences in $\alpha/\nu^2 - B'$ are not affected by systematic errors. Data from both laboratories demonstrate that systematic deviations between different sets of apparatus do not exceed the experimental statistical errors.

Because of the general trend in the absorption coefficient, increasing nearly as $\alpha = B'\nu^2$ (B' constant), two different methods had to be applied for all spectra. At "low" frequencies ($\nu < 15$ MHz) and small α ($\alpha x < 0.1$; x = sonic path length) multiple reflections within the sample increase the sensitivity substantially; therefore, a resonator technique has been employed, using cylindrical cavities (circular shape), completely filled with the liquid. At higher frequencies ($\nu > 10$ MHz) a pulse-modulated traveling wave transmission method was employed. A defined variation of path length x permits absolute α measurements.

At PU a resonator (1−8 MHz) with planar transducers (∅ = 25 mm) and a traveling wave cell (10−630 MHz) with variable transducer spacing have been used.[9] At GU we have measured with three resonator cells and three traveling wave cells. At low frequencies cells with plano-concave transducers (0.2−1.5 MHz, ∅ = 80 mm and 1.5−3.8 MHz, ∅ = 60 mm) have reduced diffraction loss.[10] A biplanar cavity cell (∅ = 16 mm) covered the range from 5 to 12 MHz.[11] Two traveling wave transmission cells (15−100 MHz, ∅ = 40 mm and 70−460 MHz, ∅ = 14 mm) were operated at the odd overtones of the transducers (fundamental frequencies 1 and 10 MHz).[12,13] The third cell (0.5−2 GHz) has been described recently;[14] it incorporates (circular) cylindrical lithium niobate transducer rods, employing surface excitation as it has been described by Bömmel and Dransfeld.[15]

The experimental errors of the absorption data depend on frequency: The PU values are $\Delta\alpha/\alpha \approx 0.15$ for $\nu < 15$ MHz and $\Delta\alpha/\alpha \approx 0.03$ for $\nu > 15$ MHz. At GU these values (for small α) are approximately those shown below:

ν (MHz)	0.2−1	1−5	5−20	20−50	50−400	400−700	700−1200	1200−2000
$\Delta\alpha/\alpha$	0.1	0.05	0.04	0.02	0.005	0.2	0.01	0.02

The sound velocity c_S of the sample has been derived from subsequent plane wave resonance frequencies $\nu_n(x)$ and the sonic path length x. These results have been confirmed by the data from the traveling wave transmission method at small transducer separation, resulting in a characteristic waviness of the output signals due to the reflections. The relative errors of velocity are $\Delta c_S/c_S \leq 10^{-4}$.

Results and Data Treatment

In Figure 2 α/ν^2 spectra for D-glucose solutions at four concentrations (25 °C) are shown. Near 80 MHz all spectra exhibit relaxational behavior. The step value $A = \alpha/\nu^2|_{\nu\to 0} - B'$ increases with solute concentration c, whereas the relaxation frequency appears to be almost independent of c. Similar spectra have been obtained for methyl β-D-glucopyranoside and methyl α-D-mannopyranoside. All other carbohydrates in our study showed the absence of detectable relaxational behavior in the same frequency range. Representative data for the latter are given in Figure 3 for 1,6-anhydro-β-D-glucopyranoside.

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Table 1. Parameters of the Relaxational Spectral Function (Defined by Eq 2): Maximum Sound Excess Absorption per Wavelength μ_m (Eq 12) and Sound Velocity c_S for Aqueous Solutions of D-Glucose at Different Temperatures and Concentrations

T °C	c, mol/L	τ, ns	A,10^{-15} s^2/m	$10^{-3}\mu_m$	B', 10^{-15} s^2/m	c_S, m/s
25	0.3	1.94 ± 0.2	5.23 ± 0.8	0.32 ± 0.05	22.6 ± 0.2	1516 ± 3
25	0.5	1.80 ± 0.1	8.65 ± 0.6	0.59 ± 0.04	23.5 ± 0.1	1529 ± 3
25	0.7	1.99 ± 0.2	12.8 ± 3	0.80 ± 0.2	24.7 ± 1	1550 ± 15
25	0.8	1.66 ± 0.1	12.15 ± 0.5	0.90 ± 0.04	25.4 ± 0.6	1545 ± 3
25	0.9	1.68 ± 0.2	15.0 ± 1.5	1.10 ± 0.1	25.3 ± 0.5	1558 ± 15
25	1.0	1.87 ± 0.1	16.8 ± 0.6	1.12 ± 0.04	26.8 ± 0.2	1563 ± 3
25	1.1	1.94 ± 0.2	15.4 ± 5	1.0 ± 0.3	28.8 ± 1.3	1582 ± 15
15	0.9	2.80 ± 0.5	22.5 ± 4	0.99 ± 0.2	36.6 ± 0.6	1540 ± 15
35	0.9	1.07 ± 0.2	9.4 ± 1	1.11 ± 0.1	18.5 ± 0.4	1574 ± 15
45	0.9	0.99 ± 0.1	7.0 ± 0.8	0.89 ± 0.2	15.0 ± 0.4	1591 ± 15

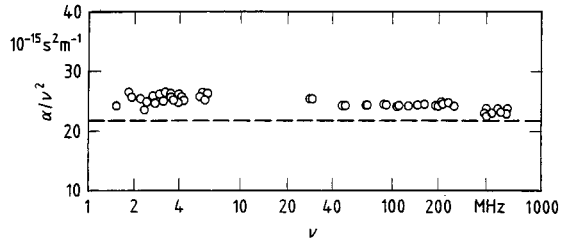

Figure 3. Ultrasonic absorption spectrum α/ν^2 for 1 M 1,6-anhydro-β-D-glucopyranoside aqueous solution and α/ν^2 for water (- - -) at 25 °C.

Table 2. Ultrasonic Parameters as in Table 1, but for Aqueous Solutions of Methyl β-D-Glucopyranoside

T, °C	c, mol/L	τ, ns	A, 10^{-15} s^2/m	$10^{-3}\mu_m$	B', 10^{-15} s^2/m	c_S, m/s
25	0.5	1.2 ± 0.1	11.9 ± 2	1.2 ± 0.2	21.6 ± 0.6	1522 ± 15
25	1	1.7 ± 0.2	20.3 ± 3	1.5 ± 0.2	25.9 ± 0.6	1580 ± 16
25	1.5	1.3 ± 0.2	26.1 ± 3	2.6 ± 0.3	30.3 ± 0.4	1529 ± 16
25	2	1.8 ± 0.2	38.0 ± 4	2.8 ± 0.3	39.0 ± 1	1668 ± 17
9	1	2.6 ± 0.2	44.4 ± 6	2.1 ± 0.5	45.0 ± 0.5	1546 ± 15
15	1	1.8 ± 0.2	33.4 ± 3	2.3 ± 0.2	35.7 ± 0.5	1558 ± 16
35	1	1.3 ± 0.15	14.4 ± 2	1.4 ± 0.2	19.1 ± 0.3	1584 ± 16

Relaxation behavior near 80 MHz was detected only for monosaccharides possessing an exocyclic hydroxymethyl group.

In order to represent measured spectra analytically, several relaxational spectral functions have been fitted to our data, among those the Debye-type function

$$\frac{\alpha(\nu)}{\nu^2} = \frac{A}{1 + (2\pi\nu\tau)^2} + B' \qquad (2)$$

with the (discrete) relaxation time τ. The numerical values of the parameters of this function are collected in Table 1 for aqueous solutions of D-glucose and in Table 2 for methyl β-D-glucopyranoside. These values have been obtained from nonlinear (least-squares) fitting procedures, minimizing the reduced variance

$$X^2 = \frac{1}{N - 1 - P}\sum_{n=1}^{N} \frac{1}{\nu_n{}^4 W^2(\nu_n)}\{\alpha_{meas}(\nu_n) - \alpha_{theor}(\nu_n)\}^2 \qquad (3)$$

Herein the ν_n ($n = 1, 2, ..., N$) are the measurement frequencies, α_{meas} is the measured value, α_{theor} corresponds to the theoretical model, P is the number of adjustable parameters in that model, and w is a weighing factor, assumed to be inversely proportional to the relative error $\Delta\alpha/\alpha$. Also included in w is a factor considering the density of measured data per interval $\Delta \log(\nu/\text{Hz})$ in order to give almost equal weight to the different regions of a spectrum.

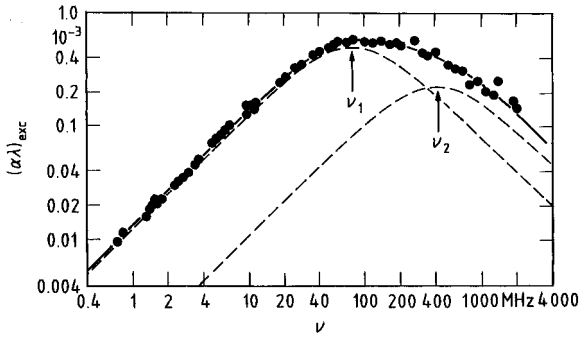

Figure 4. Ultrasonic excess absorption per wavelength $\mu = (\alpha\lambda)_{exc}$ vs frequency ν for 0.5 M aqueous D-glucose solution: (- -) Debye relaxation terms, (—) sum of two Debye terms (eq 5).

The errors in the parameter values (given in Tables 1 and 2) result from additional runs with the model relaxation function fitted to sets of pseudodata $\tilde{\alpha}$. Those sets have been generated by multiplying, within the limits of experimental error, the measured attenuation exponents $\alpha(\nu)$ with a randomized factor

$$\tilde{\alpha}(\nu_n) = \alpha(\nu_n)[1 + r_n\Delta\alpha(\nu_n)/\alpha(\nu_n)] \qquad (4)$$

where r_n $\{-1 \le r_n \le +1\}$ denotes random numbers. We also have tested relaxation spectral functions based on the assumption of a continuous relaxation time distribution, e.g., the Havriliak–Negami function[16] and the Hill function.[17] Additional parameters in such semiempirical functions permit a better description of measured spectra than eq 2, particularly above 400 MHz. The differences between these models and the Debye-type relaxation model as in eq 2, however, are below the experimental errors. A similar result is obtained with a two-step model described by

$$\frac{\alpha}{\nu^2} = \frac{A_1}{1 + (2\pi\nu\tau_1)^2} + \frac{A_2}{1 + (2\pi\nu\tau_2)^2} + B' \qquad (5)$$

The separation of an $(\alpha\lambda)_{exc}$ spectrum of a 0.5 M D-glucose aqueous solution is shown in Figure 4 as an example. The excess absorption per wavelength

$$\mu(\nu) = (\alpha\lambda)_{exc} = c_S\nu(\alpha/\nu^2)_{exc} = \alpha\lambda - c_S B'\nu \qquad (6)$$

is displayed in that diagram in order to accentuate the high-frequency region of the spectrum. Indeed the two-step model yields a superior description of data at high frequencies. Notice, however, that for the second process ($\nu_2 \sim 400$ MHz) it is true that $A_2/A_1 < 0.09$ with $A_i = (4\pi\tau_i/c_S)\mu_{m,i}$ and $\mu_{m,i} = \mu(1/\langle 2\pi\tau_i\rangle)$ ($i = 1, 2$). Hence, the values for A_1 and ν_1 are less affected by

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the assumption of a second relaxation at higher frequencies. Since the existence of this second relaxation is not unequivocal, we will focus on the dominant relaxation near 80 MHz. Therefore, we consider only the case $i = 1$ and omit this index now. In the following analysis of this relaxation it is tacitly assumed that its underlying chemical equilibrium is not coupled to the process which contributes to the excess absorption at higher frequencies.

Discussion

Different Carbohydrates. The similarity of the relaxation times and amplitudes for both D-glucose and methyl β-D-glucopyranoside suggests that the pyranoside form of the glucose, but not the extremely small fraction present in the furanoside form, is responsible for the observed relaxation process. Further progress can be made by an examination of the α/ν^2 spectrum of an aqueous solution of 1,6-anhydro-β-D-glucopyranoside (Figure 3). This diagram, in comparison to Figures 2 and 4, shows the absence of relaxational absorption. Since for 1,6-anhydro-β-D-glucopyranoside both the rotation of the $-CH_2OH$ group and the $^1C_4 \rightleftharpoons {}^4C_4$ ring inversion are impossible, the absence of a relaxation process for 1,6-anhydro-β-D-glucopyranoside suggests that the type of relaxation process for D-glucose is either a rotation of the $-CH_2OH$ group or the inversion of the pyranoside ring, or both. All other processes, potentially responsible for relaxation, are then excluded. These points are further substantiated by examining the $\alpha(\nu)/\nu^2$ relation for a pentose in the pyranoside form, namely, methyl β-D-xylopyranoside, which has been investigated at concentration $c = 0.50$ M in water. No relaxational ultrasonic absorption around 80 MHz, as in D-glucose, was detected. The α/ν^2 data only show a trend upward at the lower end of the spectrum. Similar results (without any trends) have been obtained for 0.50 M methyl β-D-arabinopyranoside, for 0.52 M D-xylose, and for 0.52 M D-arabinose aqueous solutions at 25 °C.

Since for these pentoses (in the pyranoside ring form) no $-CH_2OH$ is present and (at least in the frequency range shown) relaxational absorption is not detected, we must conclude that the observed relaxation for D-glucose and methyl β-D-glucopyranoside originates from a rotation of the $-CH_2OH$ group between two positions, differing by a finite isentropic molar volume change[9]

$$\Delta V_S = \Delta V_T - \frac{\theta}{\rho c_p}\Delta H_0 \qquad (7)$$

ΔV_T = isothermal volume change, ΔH_0 = enthalpy change, $\theta = (\partial V/\partial T)/V$, coefficient of thermal expansion, ρ = density, and c_p = specific heat at constant pressure.

Our conclusion is supported by the fact that no relaxational ultrasonic absorption has been found for aqueous 0.51 M solutions of methyl α-L-(6-deoxy)mannopyranoside at 25 °C in the frequency range 6−400 MHz. A $-CH_3$ group instead of the $-CH_2OH$ group in position 6 of the saccharide eliminates the observed relaxation in the frequency range mentioned before.

Concentration and Temperature. The observed constancy—within the limits of experimental error—of the relaxation time at 25 °C at different concentrations of D-glucose (Table 1) and methyl β-D-glucopyranoside (Table 2) and an approximate linearity of the amplitudes A with saccharide concentration (Figure 5) suggest a chemical equilibrium of the type $Y \rightleftharpoons Y^*$. This mechanism is compatible with the conclusions reached above, favoring a $-CH_2OH$ rotation between two positions, associated with an intramolecular rearrangement. For a process

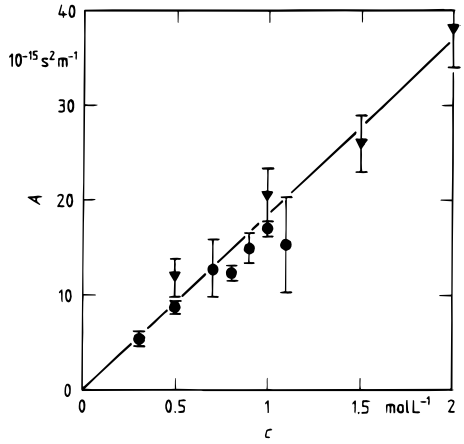

Figure 5. Relaxation amplitude A (eq 2) vs concentration c for aqueous solutions of D-glucose (●) and methyl β-D-glucopyranoside (▼) at 25 °C.

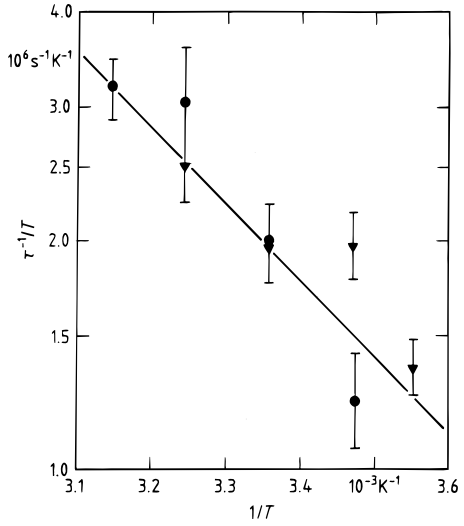

Figure 6. Dependence of τ^{-1}/T vs $1/T$ for aqueous solutions of D-glucose (●, 0.9 M) and methyl β-D-glucopyranoside (▼ 1 M).

of this type the relaxation rate, i.e., the inverse of the relaxation time τ, is related to the forward and reverse rate constants, k_1 and k_{-1}, respectively, by the simple relation

$$\tau^{-1} = k_1 + k_{-1} \qquad (8)$$

The equilibrium constant $K_1 = k_1/k_{-1}$ and the Eyring theory expression

$$k_{-1} = \frac{kT}{h}\exp\left(\frac{\Delta S^{\ddagger}_{-1}}{R}\right)\exp\left(\frac{-\Delta H^{\ddagger}_{-1}}{RT}\right) \qquad (9)$$

lead to

$$\tau^{-1} = k_{-1}(1 + K_1) = \frac{kT}{h}(1 + K_1)\exp\left(\frac{\Delta S^{\ddagger}_{-1}}{R}\right)\exp\left(\frac{-\Delta H^{\ddagger}_{-1}}{RT}\right) \qquad (10)$$

with the usual meaning of the symbols. It follows that a plot of $\ln(h\tau^{-1}/kT)$ vs $1/T$ is linear, having the intercept $\ln(h\tau^{-1}/kT)|_{T\to\infty} = \Delta S^{\ddagger}_{-1}/R$. The slope of this plot is

$$\frac{\mathrm{d}\ln\left(\frac{h\tau^{-1}}{kT}\right)}{\mathrm{d}(1/T)} = -\frac{\Delta H^{\ddagger}_{-1}}{R} + \frac{\mathrm{d}\ln(1+K_1)}{\mathrm{d}(1+K_1)}\frac{\mathrm{d}K_1}{\mathrm{d}(1/T)} = -\frac{\Delta H^{\ddagger}_{-1}}{R} - \frac{K_1}{1+K_1}\frac{\Delta H_0}{R} \quad (11)$$

ΔH_0 is the enthalpy change related to the process. In Figure 6 τ^{-1}/T is plotted vs $1/T$ for 0.9 M D-glucose and 1 M methyl β-D-glucopyranoside aqueous solutions; the intercept of the regression line (—) yields $\Delta S^{\ddagger}_{-1}/R = 1.6$; the slope is 2.3×10^3 K^{-1}.

The maximum of the excess absorption per wavelength μ_m is related to the relaxation amplitude $A = 4\pi\tau\mu_m/c_S$, because a process of type Y $\rightleftharpoons$ Y* depends on K_1 and on the isentropic molar volume change ΔV_S[9]

$$\mu_m = \frac{\pi}{2\beta_S}\frac{\Delta V_S{}^2}{RT}\frac{K_1}{(1+K_1)^2}c \quad (12)$$

with the isentropic compressibility $\beta_S = (\rho c_S{}^2)^{-1}$. Equation 12 yields

$$\ln\left(\mu_m\beta_S RT\frac{\mathrm{mol}}{\mathrm{m}^3}\right) = \ln\left(\frac{\pi}{2}\Delta V_S{}^2 c\frac{\mathrm{mol}}{\mathrm{m}^3}\right) + \ln\left(\frac{K_1}{(1+K_1)^2}\right) \quad (13)$$

using the MKS dimensional system, and

$$\frac{\mathrm{d}\ln(\mu_m\beta_S RT(\mathrm{mol\cdot mol}^{-3}))}{\mathrm{d}(1/T)} = \frac{\mathrm{d}\ln K_1}{\mathrm{d}(1/T)} - 2\frac{\mathrm{d}\ln(1+K_1)}{\mathrm{d}(1+K_1)}\frac{\mathrm{d}K_1}{\mathrm{d}(1/T)} \quad (14)$$

resulting in

$$\frac{\mathrm{d}\ln(\mu_m\beta_S RT(\mathrm{mol\cdot m}^{-3}))}{\mathrm{d}(1/T)} = -\frac{\Delta H_0}{R} + \frac{2K_1}{1+K_1}\frac{\Delta H_0}{R} = \frac{\Delta H_0}{R}\frac{K_1-1}{K_1+1} \quad (15)$$

At present the accuracy of the $\mu_m(T)$ data for a solution with very small excess absorption is not sufficient for an adequate evaluation of the $\mu_m\beta_S T$ vs $1/T$ plots. Nevertheless, these data indicate that it is unlikely to find the ring inversion $^1C_4 \rightleftharpoons {}^4C_1$ as the origin of the observed relaxational ultrasonic absorption. Stoddard[18] has reported calculations of the free energy for the $^4C_1$ and $^1C_4$ conformations for both β-glucose and α-glucose (which eventually appears in aqueous solution, given by the equilibrium between both forms). If the free energy change

$$\Delta G_0 = -RT\ln K_1 \quad (16)$$

as predicted by Stoddard is assumed, the excess absorption data measured cannot be evaluated consistently in the framework of eqs 10, 11, and 15. This result makes it unrealistic to assign our observed process to a $^1C_4 \rightleftharpoons {}^4C_1$ conformational equilibrium, in agreement with the conclusions from a ^{1}H NMR experiment,[18] predicting the $^4C_1$ to be the only stable conformation.

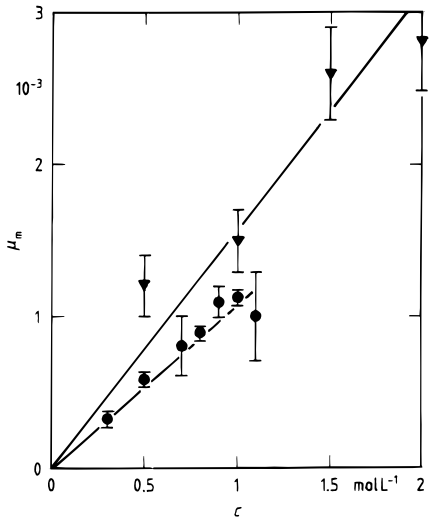

Figure 7. Maximum excess absorption per wavelength μ_m vs concentration c for aqueous solutions of D-glucose (●) and methyl β-D-glucopyranoside (▼) at 25 °C.

Let us finally consider the isentropic molar change in volume ΔV_S. Figure 7 shows a plot of μ_m vs c for the glucose solutions and the methyl β-D-glucopyranoside solutions. Nishida *et al.*[19] determined experimentally (by ^{1}H NMR studies) that for β-D-glucopyranoside the GL and GR rotamers in D_2O were 53% and 45% with $T = 0$%. Similarly they found GL and GR rotamers equal to 57% and 38% for methyl α-D-glucopyranoside in D_2O with $T = 5$%. Using $K_1 = 53/45 \approx 1.2$ and $K_1 = 57/38 \approx 1.5$, respectively—resulting from those data—the slope $\mathrm{d}\mu_m/\mathrm{d}c$ in the linear regression (Figure 7) yields tentative values $\Delta V_S \approx 2$ cm^3/mol for the former and $\Delta V_S \approx 2.4$ cm^3/mol for the latter carbohydrate. This seems to be a realistic figure for the isentropic reaction volume of a rotational conformational change of the $-CH_2OH$ groups. The assumed value for the equilibrium constant K_1 is consistent with our results (instead of Stoddard's value for the $^4C_1 \rightleftharpoons {}^1C_4$ transition). The similarity of the two sets of results for aqueous solutions of D-glucose and of methyl β-D-glucopyranoside (Tables 1 and 2) further supports the hypothesis that for both carbohydrates the same phenomenon, most likely a rotational isomerization of the $-CH_2OH$ group, is responsible for the observed ultrasonic excess absorption in the frequency region around 80 MHz.

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