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c,T-Dependence of the self-diffusion in concentrated aqueous solutions of methyl α- and β-D-glucopyranosides

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Abstract

The self-diffusion coefficients D for methyl α- and β-D-glucopyranosides in aqueous solutions have been measured in the concentration range between 10% and 70% (w/w) glucoside in a wide temperature range. At higher concentrations ($c \geq 40\%$) the mobility of the water and the glucoside molecules is significantly lower in the α-D-glucoside solutions than in the corresponding mixtures containing the β-anomer. © 1996 Elsevier Science Ltd.

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1. Introduction

Concentrated aqueous solutions of carbohydrates occur in several technological processes and are encountered in many biological fluids. For example, the theoretical description of the crystallisation process of glucose requires correct knowledge of the diffusion coefficients of all anomers in supersaturated solutions [1]. It is widely accepted that solvation effects contribute to the anomeric equilibrium and the respective thermodynamic free energies [2]. Therefore, it is reasonable to expect that small differences in the stereochemistry could account for different diffusion coefficients for each anomeric species. In the aqueous solutions of the unmodified hexoses the anomeric equilibria as well as the equilibria between furanoside and pyranoside forms depend on concentration

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and temperature [3]. These equilibria are suppressed in the glycosides and it seemed reasonable to study the well-characterised pair of methyl α- and β-D-glucopyranosides to demonstrate the influence of the anomeric configuration upon self-diffusion.

Another important property of concentrated carbohydrate solutions is their stabilizing property in biology and food technology. A high concentration of carbohydrates in the cytosol can protect cells from the damage done by freezing water [4] and also permit the cells to survive in the quiescent state of anhydrobiosis in extremely dry habitats [5]. For safe storage of deep frozen foodstuff [6] it appears to be important to transfer the complete sample without crystallisation and concomitant phase separation of the water into the glassy state; the presence of high concentrations of carbohydrates is essential for this process. Also the possibility of dry storage of biotechnologically produced peptides and proteins in their pharmacologically active form can, for most compounds, only be achieved when high concentrations of carbohydrates are added to the solutions prior to freeze-drying.

The various mono- and oligo-saccharides show very significant differences in their ability to protect biomaterial against the denaturing effect of drying and/or freezing [4,7–9]. Large differences in the dynamical properties for the aqueous solutions of the disaccharides sucrose and trehalose were also derived from the determination of the rotational and translational mobility of both compounds of these binary solutions by pulsed nuclear magnetic resonance methods [10–13]. These effects obviously result from the stereochemical differences of these sugars, which influence their interaction with the hydrogen-bond network of liquid water.

The disaccharides sucrose and trehalose showed fairly complicated differences in stereochemistry, and thus it seemed desirable to study a pair of stereoisomers where the stereochemistry is different only at one of the stereogenic centres. The aqueous solutions of methyl α- and β-D-glucopyranosides were an obvious choice. In the following, self-diffusion data for both glucosides and the water molecules in a wide range of temperatures and concentrations will be presented.

2. Experimental

Methyl α- and β-D-glucopyranosides ($> 99\%$) were purchased from Fluka (Buchs, Switzerland) and used without further purification. The aqueous solutions were prepared by weighing and degassed by freeze–pump–thaw cycles.

The self-diffusion coefficients were obtained on a Bruker MSL 300 spectrometer operating at 7.05 T at a proton frequency of 300.13 MHz in a home-built probe head. The self-diffusion coefficients were determined from the ^{1}H NMR spectra in a Hahn-spin-echo experiment by application of a pulsed field gradient [14]. For this pulse sequence the amplitude of the echo A after a waiting period τ between the 90°- and 180°-pulse is given by:

$$A(2\tau) = A(0)\exp(-2\tau/T_2)\exp\left[-\gamma^2\delta^2 g^2 D(\Delta - \delta/3)\right] \tag{1}$$

with T_2 the spin–spin relaxation time of the nucleus under study, and γ its magnetogyric ratio; δ is the length of the field gradient pulse. Its strength is given by $g = K \cdot I$

with K the coil constant and I the pulse current. D is the self-diffusion coefficient to be studied and Δ the time span between the two gradient pulses. The self-diffusion coefficients of the two compounds were determined from the amplitude of the signals of the Fourier transformed second half of the spin echoes. It proved most reliable to determine D from a series of 10–12 spin echoes at increasing coil currents I, while keeping all other parameters in Eq. (1) constant. The gradient coil constant K was calibrated with water at 293 K [15], the calibration being controlled with a second substance. For these control experiments cyclooctane was usually used [16].

The temperature was controlled with a metal sheathed Chromel/Alumel thermocouple. The temperatures given are considered reliable to ±1 K. They were constant to ±0.5 K. The accuracy of the self-diffusion coefficients is ±5%.

3. Results and discussion

The solubility of the glucosides decreases rapidly with falling temperature. In supersaturated solutions, as obtained by cooling the highly concentrated mixtures, crystallisation of a fraction of the glucosides is fairly rapid. It thus proved impossible to measure the self-diffusion coefficients D in the deeply supercooled range of the phase diagram. The data obtained are compiled in Tables 1–4. Figs. 1 and 2 give Arrhenius plots for two concentrations. As usual for aqueous solutions of carbohydrates, these plots show a distinct curvature, the slope increasing with falling temperature.

Table 1
Self-diffusion coefficients for 10% (w/w) methyl D-glucopyranoside/H_2O solutions

α-Glucoside			β-Glucoside		
T [K]	$D_{glucoside}$ [10^{-10} m^2/s]	D_{H_2O} [10^{-10} m^2/s]	T [K]	$D_{glucoside}$ [10^{-10} m^2/s]	D_{H_2O} [10^{-10} m^2/s]
255.1	0.92	3.70	255.1	1.16	4.50
273.2	2.15	8.30	262.5	1.51	6.00
293.3	4.54	17.0	271.7	2.19	8.80
316.5	7.53	28.2	276.2	2.59	10.4
334.4	12.6	40.5	287.4	3.76	14.1
355.9	17.9	56.0	291.5	4.46	16.3
383.1	28.7	87.1	295.0	4.85	18.7
423.7	–	126	310.6	6.50	24.4
			322.6	9.58	33.0
			330.0	11.5	38.4
			340.1	13.8	47.3
			352.1	18.0	56.2
			366.3	21.4	66.2
			373.1	24.8	75.6
			384.6	29.5	84.6
			395.3	36.0	94.8

Table 2
Self-diffusion coefficients for 40% (w/w) methyl D-glucopyranoside/H_2O solutions

α-Glucoside			β-Glucoside		
T [K]	$D_{\text{glucoside}}$ [10^{-10} m^2/s]	D_{H_2O} [10^{-10} m^2/s]	T [K]	$D_{\text{glucoside}}$ [10^{-10} m^2/s]	D_{H_2O} [10^{-10} m^2/s]
253.2	0.201	1.10	253.8	0.320	1.53
272.5	0.440	2.46	272.5	0.690	3.08
295.9	1.07	5.94	301.2	1.84	8.01
323.6	3.13	13.3	327.9	3.61	14.4
340.0	5.16	19.5	362.3	8.67	33.9
365.0	9.16	32.6	409.8	22.4	63.3
411.5	21.1	66.6			

It is customary to fit this type of isobar in a three-parameter fitting to the VTF equation [10]:

$$D = D_0 \exp\left[B/(T - T_0)\right].$$

Here T_0 is the ideal glass transition temperature and D_0 and B are free parameters of the fit. However, with the limited data available for the more concentrated solutions this analysis did not seem to yield sufficiently precise parameters. A general trend, however, can be derived. In the solutions with 10% and 40% (w/w) of the glucoside, for both compounds of the mixture, T_0 is found to be 125 ± 5 K. It increases to 140 ± 5 K for the 50% (w/w) solutions, and for all 70% (w/w) solutions $T_0 = 170 \pm 10$ K can be detected. This result agrees with the general behaviour of water–carbohydrate mixtures as measured by differential scanning calorimetry [17]. With the limited data for the most concentrated mixtures it was impossible to show reliably whether for each mixture the ideal glass transition temperatures for the water fraction and for the glucoside molecules differ from each other, a phenomenon found in the trehalose–water and sucrose–water

Table 3
Self-diffusion coefficients for 50% (w/w) methyl D-glucopyranoside/H_2O solutions

α-Glucoside			β-Glucoside		
T [K]	$D_{\text{glucoside}}$ [10^{-10} m^2/s]	D_{H_2O} [10^{-10} m^2/s]	T [K]	$D_{\text{glucoside}}$ [10^{-10} m^2/s]	D_{H_2O} [10^{-10} m^2/s]
250.6	0.120	0.550	254.5	0.250	0.810
260.4	0.190	0.840	273.2	0.490	2.17
277.0	0.380	2.09	298.5	1.23	4.25
293.9	0.820	2.87	328.9	3.49	10.5
328.2	2.05	7.45	352.1	6.23	21.9
351.5	4.21	16.3	371.7	9.76	34.1
371.0	6.11	24.1	396.8	13.8	50.9
397.2	11.7	36.2	427.4	26.0	86.3

Table 4
Self-diffusion coefficients for 70% (w/w) methyl D-glucopyranoside/H_2O solutions

α-Glucoside			β-Glucoside		
T [K]	$D_{\text{glucoside}}$ [10^{-10} m^2/s]	D_{H_2O} [10^{-10} m^2/s]	T [K]	$D_{\text{glucoside}}$ [10^{-10} m^2/s]	D_{H_2O} [10^{-10} m^2/s]
325.2	0.860	3.42	294.8	0.380	1.63
351.2	1.76	6.53	324.7	1.19	5.30
369.7	2.94	11.2	343.5	2.08	9.44
397.1	5.61	18.3	374.5	5.23	26.5
425.5	11.8	30.7	420.2	14.5	59.8

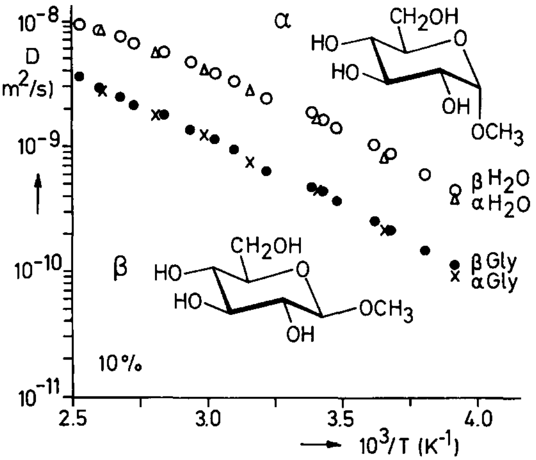

Fig. 1. Self-diffusion coefficients D in 10% (w/w) aqueous solutions of methyl α- and β-D-glucopyranosides as function of temperature.

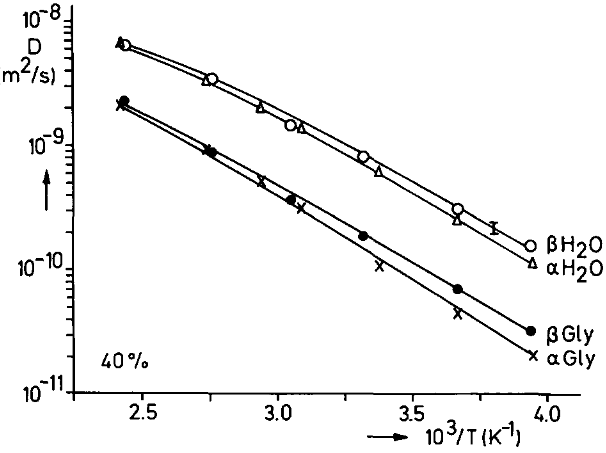

Fig. 2. Self-diffusion coefficients D in 40% (w/w) aqueous solutions of methyl α- and β-D-glucopyranosides as function of temperature.

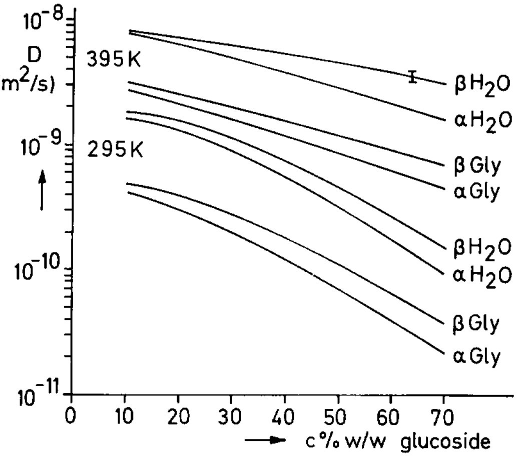

Fig. 3. Two isotherms of the self-diffusion coefficients of water and methyl α-/β-D-glucopyranosides as function of glucoside concentration.

systems [10]. In Fig. 3 two isotherms each of the diffusion coefficient are given for the two mixtures as a function of glucoside concentration.

Fig. 3 shows most clearly the trend of the data. In the 10% (w/w) solution the α- and β-glucosides diffuse with equal rates, and also the water molecules have almost identical diffusion coefficients. This proves that the hydrodynamic properties of the individual glucoside molecules are very similar. A slight trend, well within the limits of accuracy of our measurements, seems to be present: The values of D of both components of the α-glucoside solution appear to drop faster with falling temperature than for the corresponding mixture of the β-glucoside. This trend is obvious in the 40% solutions compared in Fig. 2.

Fig. 3 shows the concentration dependence of D for both systems that support the observation discussed above. Some qualitative conclusions are obvious: At low concentrations, where one expects individual glucoside molecules separated by complete hydration shells, the α- and β-glucosides diffuse at equal speed. At higher concentrations with insufficient water to separate the glucosides completely, contacts between the carbohydrate molecules must occur and consequently a hydrogen-bond network containing glucoside–glucoside as well as glucoside–water and water–water hydrogen bonds must exist. The stereochemistry of α-glucoside molecules is more favourable towards interaction with the solvent resulting in a more intact or rigid network. This idea stems from work by Kabayama and Patterson [18] stating the spatial compatibility of the equatorial hydroxyl groups in pyranoside sugars with the oxygen network of liquid water, and has been generalised and frequently applied by Franks et al. [19,20].

In the low temperature range of the data, the differences in diffusivity between the more viscous α-glucoside solution and the β-glucoside solution of equal concentration amounts to a temperature difference of approximately 10 K.

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