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c,T-Dependence of the viscosity and the self-diffusion coefficients in some aqueous carbohydrate solutions

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Abstract

Self-diffusion coefficients for both components are reported for the highly concentrated aqueous solutions of some disaccharides and fructose as a function of temperature and concentration. These data are complemented by viscosity measurements. The disaccharides studied are sucrose, α,α-trehalose, allosucrose, and leucrose. Up to a sugar concentration of ≈30% w/w the viscosity and the self diffusion coefficients of the four disaccharides are identical within experimental error for a given concentration and temperature. Water diffusion shows no differences in the four systems studied under these conditions. At higher concentrations significant differences are observed that become more pronounced with increasing temperature. Analysis of the data by the VTF equation yields the result that at a given concentration the self diffusion coefficients of the sugar D_c and the viscosity η are described by identical ideal glass transition temperatures T_0, while the diffusion of the water D_W molecule decouples from these properties. T_0^W is always lower than $T_0^{c,\eta}$. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Disaccharides; Fructose; Water, self-diffusion, viscosity

1. Introduction

The aqueous solutions of simple carbohydrates are of importance for a multitude of biological processes. Organisms accumulate a wide variety of this class of compounds under cold and heat stress to protect their cells from damage [1,2]. Also, many industrial and technological processes ranging from food preparations to cryostorage of biological specimens deal with aqueous carbohydrate solutions. A very interesting class of applications is the dry storage of biotechnologically produced proteins. In order to obtain a sufficient shelf life at ambient temperatures, proteins have to be stored in their freeze dried state. To prevent denaturation and loss of activity during freeze drying, a huge surplus of mixtures of various carbohydrates is added to these solutions. The exact composition of these additions can be established empirically only, and is found in tedious experimental trials. It is possible that the extent of these experimentations in this and other applications could be reduced if the physical properties of the binary aqueous carbohydrate solutions were better known.

The fundamental knowledge of the macroscopic and molecular behaviour of concentrated aqueous carbohydrate solutions is also the basis for the understanding of the process of crystallisation. The nucleation, growth kinetics, and the extent of oversaturation are

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influenced by the liquid film surrounding the crystals [3].

Our group has studied the self diffusion coefficients and the rotational molecular mobility for some binary aqueous carbohydrate solutions [4–8]. The data presented in the following extend and systematise older studies by including shear viscosity measurements. In contrast to our previous studies, the self-diffusion coefficients D_c of the carbohydrates were measured by ^{13}C NMR. This experiment is more time consuming than the ^{1}H NMR technique applied before, but has the great advantage that it avoids the use of heavy water. Thus, it eliminates the need for considering the dynamic isotope effect in the calculation of the properties of light water as a solvent and, furthermore, it permits the self-diffusion coefficient of the water D_W to be determined in a much wider range of temperature and concentration.

The sugars investigated in this study were chosen with respect to chemical structure and industrial interest. α,α-Trehalose (α-D-glucopyranosyl-α-D-gluco-pyranoside) is a disaccharide frequently used in nature and technology because of its high potential to prevent freeze and anhydrobiosis damage resulting from its pronounced ability to form stable hydrogen bonded networks [1,2]. Not to mention the great importance of sucrose, fructose is the second important bulk sugar in food industry [9]. Fructose is strongly soluble in water (79% w/w at 20 °C), and the industrial crystallisation from aqueous solution has to cope with high viscosities [10]. Successful crystallisation can only be achieved by a defined process control. Such a control may be improved by modelling based not only on viscosity data but also on the diffusion coefficients of water and the different tautomers of this sugar. Leucrose (5-*O*-α-D-glucopyranosyl-β-D-fructopyranose) is produced by enzymatic isomerization of sucrose (2-*O*-α-D-glucopyranosyl-β-D-fructofuranose) [11], while allosucrose (2-*O*-α-D-allopyranosyl-β-D-fructofuranose), a sugar not found in nature, stems from microbial oxidation of the 3-position in the glucose moiety, followed by a reduction with hydrogen [12]. The latter compounds have been developed as non-cariogenic and low-calorie bulk sweeteners. A special feature of allosucrose is its extraordinary high solubility (82% w/w at 20 °C) compared with other disaccharides, which enables an unusual insight into highly concentrated thermodynamically stable sugar solutions.

2. Experimental

Substances.—Fructose, sucrose, and α,α-trehalose of the highest purity available were purchased from E. Merck (Darmstadt, BRD) and leucrose from Fluka Chemie (Buchs, Switzerland). Allosucrose was a preparation from the Institut für Technologie der Kohlenhydrate e.V., Braunschweig, BRD [11]. All compounds were dissolved without further purification in ultrapure water drawn freshly from a Mill-Q-Unit (Millipore, Eschborn, BRD). Highly concentrated oversaturated solutions were prepared by water removal in a rotary evaporator at temperatures between 25 and 35 °C. The concentration of the sugars was determined by Karl–Fischer titration and refractometry.

Methods.—Viscosities were measured in a rotational viscosimeter model Rotovisco RV2 (Haake, Karlsruhe, BRD), which was thermostated to ± 0.2 K. By controlling the sugar concentration before and after the measurement, the viscosities obtained are judged reliably to be ± 0.5%.

The self-diffusion coefficients D_i were taken in a Bruker MSL-300 spectrometer by the NMR-PGSE (pulsed field gradient spin echo) technique [13]. For this pulse sequence the amplitude of the echo A after a waiting period τ between the 90 and 180° pulse is given by:

$$A(2\tau) = A(0)\exp(-2\tau/T_2) \times \exp[-\gamma^2\delta^2 g^2 D(\Delta - \delta/3)] \qquad (1)$$

T_2 is the spin-relaxation time of the nucleus under study, and γ it the magnetogyric ratio, and 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 components were determined from the amplitude of the signals of the Fourier transformed second half of the spin echoes. The self-diffusion coefficients of the carbohydrates D_c were obtained from the decoupled ^{13}C NMR spectra. This required the accumulation of up to 4000 free induction decays. The self-diffusion coefficient of water D_W was measured by proton NMR. 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 [14], the calibration being controlled with a second substance. Cyclooctane was usually used for these control experiments [15].

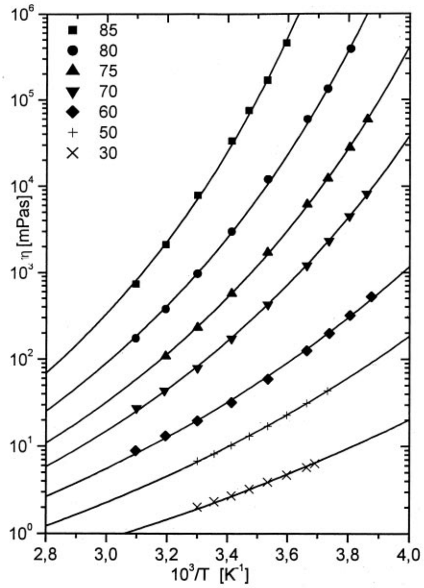


Fig. 1. Viscosity of fructose/water solutions. Numbers behind the symbols are % w/w of fructose.

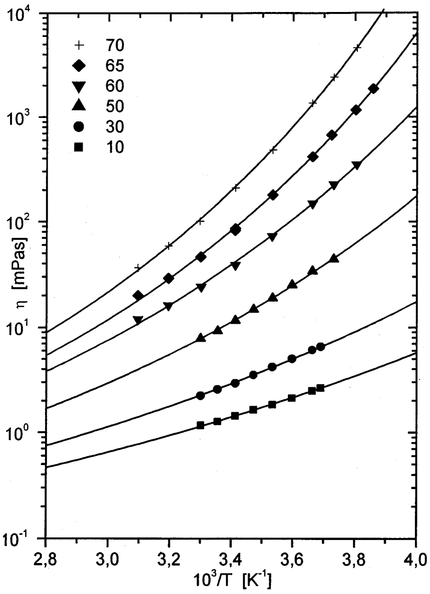


Fig. 2. Viscosity of leucrose/water solutions. Numbers behind the symbols are % w/w of leucrose.

In the cold concentrated aqueous carbohydrate solutions the self-diffusion coefficients of both water and sugar become very small, and thus an actively shielded set of gradient coils had to be used in order to eliminate interferences from image currents. The temperatures were controlled by a metal sheathed chromel/alumel thermocouple to ± 1 K. The D_W and D_c are judged reliable to ± 5%, they were reproducible to ± 2%.

3. Results and discussion

Disaccharides.—Figs. 1–4 present viscosity data and the self-diffusion coefficients for the carbohydrates and water for some of the systems studied. The complete set of data for all systems is given in Tables 1–3.

Since trehalose, sucrose and allosucrose are non-reducing disaccharides, tautomerisation is not possible, and each molecule exists in a defined configuration. Leucrose can occur in the acyclic keto form and the α- or β-fructopyranose form, while the existence of a fructofuranose moiety is forbidden due to its inherent (1–5) glycosidic bond. Previous NMR measurements of an aqueous 20% w/w solution have revealed the fraction of the α form to be only 1 (1 °C) and 8% (70 °C), the acyclic form being below the detection limit [16]. In this study NMR signals of the α-species were also found to be lower than 10% at the higher concentrations. Not to mention that the difference at the diffusivity between the α and the β form is expected to be very small [8], the measured diffusion coefficients of leucrose are solely attributed to the 5-*O*-α-D-glucopyranosyl-β-D-fructopyranose anomer.

Viscosity and self-diffusion values of trehalose extend known data [17,18] to a broader range of temperature and concentration, while all data referring to leucrose and allosucrose are reported here for the first time. Viscosity

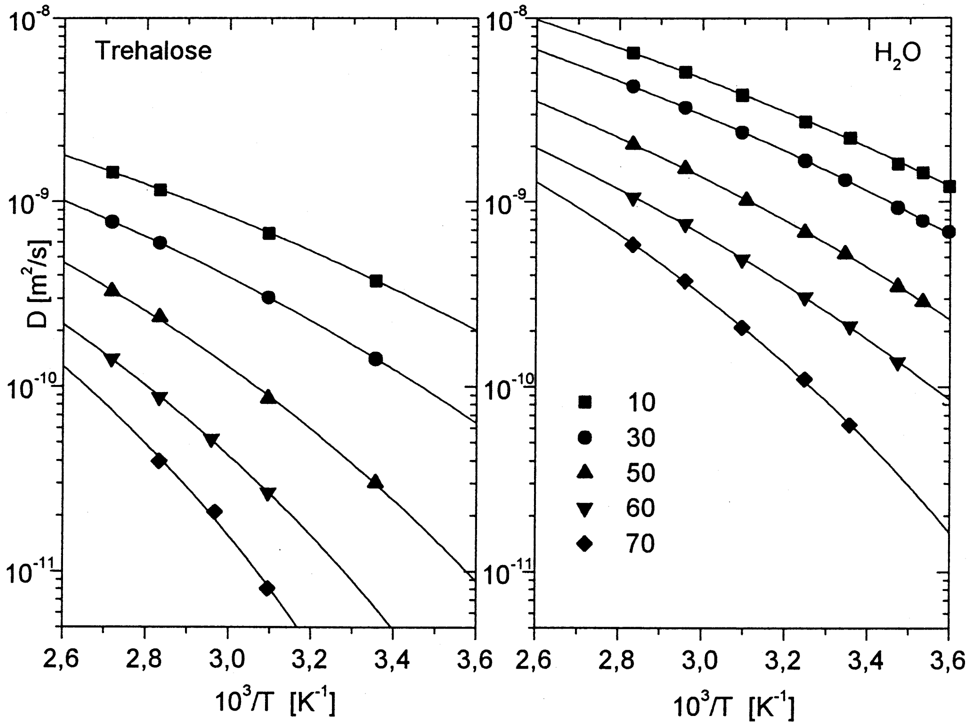


Fig. 3. Diffusion coefficient of trehalose and water in trehalose/water solutions. Numbers behind the symbols given in % w/w of trehalose.

of sucrose refers to a refined set of data discussed in another publication of the authors [19].

In the more dilute solutions, the viscosities and self-diffusion coefficients of the four disaccharide systems studied here are rather similar. With concentration $c > 30\%$ w/w differences become measurable, the viscosities in the trehalose solutions always being higher than in the three other mixtures. Also, the self-diffusion coefficients of both compounds in the aqueous trehalose solutions are, at high concentrations, slower. Differences between the systems do become more pronounced with falling temperature. It appears interesting to note that differences in all dynamic properties become measurable only at concentrations where direct contact between the sugar molecules become probable. For $c > 50\%$, the amount of water does not suffice to form complete and extended solvation layers around the carbohydrate molecules. (A 50% w/w solution corresponds to 19 water molecules per disaccharide.) As a consequence, hydrogen bonds between the carbohydrate molecules must form and the sterical restriction imposed by the rather rigid carbon skeleton of the disaccharides start to influence the dynamics. The structures of the four dihexoses are given below for a qualitative impression of the differences. The finding that differences only become measurable at high concentrations points to the fact that the dynamic properties are not very sensitive to the overall molecular dimensions of the disaccharides, but that the sterical restraints imposed by the sugar hydroxyl groups upon the forma-

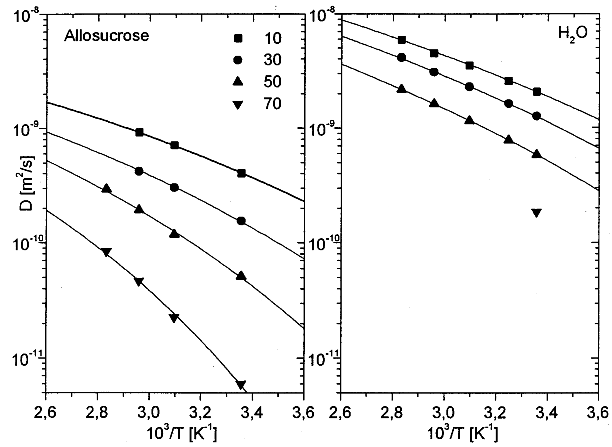
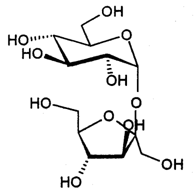


Fig. 4. Diffusion coefficient of allosucrose and water in allosucrose/water solutions. Numbers behind the symbols given in % w/w of allosucrose.

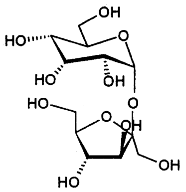
Table 1
Dynamic viscosities η (in mPas) of aqueous carbohydrate solutions

T (K)	258	263	268	273	283	293	303	313	323
c % w/w	*Fructose/water*								
30				5.7	3.87	2.71	2.02		
50				31.35	17.2	10.3	6.77		
60	522	318	198	125.8	59.2	32.2	19.8	13.2	8.9
70	8140	4480	2320	1200	424	173.5	79.5	43.7	27.5
75	59,200	28,000	12,300	6130	1710	568	232	109	
80		38,8000	134,000	59,300	11,900	2980	972	377	174
85					168,000	33,300	7820	2110	735
	Allosucrose/water								
40			20.9	14.9	9.46	6.57	4.87		2.96
50		86.9		44.9	25.5	15.3	10.2		5.46
60	1210	702		272	123	63.1	37.2	24.2	16.1
76			143,000	61,400	14,600	3970	1340	559	257
	Leucrose/water								
10				2.48	1.84	1.44	1.17		
30				6.09	4.18	2.87	2.24		
50			43.4	33.9	18.9	12.1	7.85		
60		351	226	149	72.9	38.8	24.2	16.2	11.9
65	2420	1160	671	416	180	85.7	46.2	29.1	20.0
70		4620	2410	1360	483	210	101	58.9	36.6
	Trehalose/water								
10				2.49	1.84	1.48	1.15		
30				7.34	5.06	3.54	2.67		
50				50.1	28.2	17.3	11.2	7.90	5.64

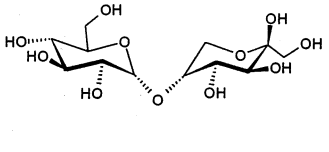
tion of the hydrogen bonded network are important since these define and limit the extent of sugar–sugar and sugar–water hydrogen bonds and thus also the local geometry of the possible water–water bonds.



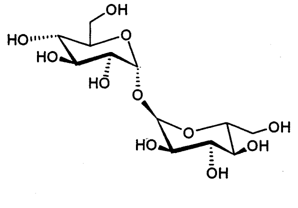
2-O-α-D-Glucopyranosyl-β-D-fructofuranoside (*Sucrose*)



2-O-α-D-allopyranosyl-β-D-Fructofuranoside (*Allosucrose*)



5-O-α-D-Glucopyranosyl-β-D-fructopyranose (*Leucrose*)



l-O-α-D-Glucopyranosyl α-D-glucopyranoside (*Trehalose*)

The fact that these influences become pronounced only at $c \approx 50\%$ w/w of sugar clearly show that these sterical restraint are short ranged and cannot have any measurable influence beyond the first water layer around any given carbohydrate molecule.

The plots log *D* versus the reciprocal temperature of Figs. 1–4 all show a distinct curvature, the slope increasing with falling temperature. This is typical for the dynamic properties of the aqueous solutions of carbohydrates and also for many other liquids and solutions. This behaviour has been empirically described by the Vogel–Tammann–Fulcher (VTF) equation [20–22]

$$D = D_0 e^{\left(-\frac{B}{T - T_0}\right)} \qquad (2)$$

which implies that the molecular mobility of the supercooled liquid is completely stopped at the ideal glass transition temperature T_0. Angell replaced B by the product $B = CT_0$ [23,24] with C the fragility parameter that classifies the fluids through their T-dependence of the dynamic properties in the approach to T_0. The Adam–Gibbs theory [25,26] provides the theoretical background for this type of analysis.

All viscosities and self-diffusion data collected in Tables 1–3 were fitted to the VTF equation, which contains three free parameters. All of the data end at least 100 K above the T_0 derived from the fits. It is obvious that the precise fit parameters are best obtained from experimental results in the close vicinity of T_0. This analysis thus contains a certain ambiguity. In previous studies [27], it was found for several monohydric alcohols that the preexponential factor (η_0 resp. D_0) of (A) Eq. (1) is rather constant in similar systems. Thus all fits given here were started with the restriction that this preexponential factor for all binary mixtures of one carbohydrate is independent of concentration. Only in cases where this led to physically unacceptable parameters was this restriction relaxed.

Tables 4 and 5 give the parameter derived. Some interesting general conclusions can be drawn from these results: (i) within the limits of the precision of this analysis, the T_0 derived for the viscosity and the carbohydrate self-diffusion in every mixture ($T_0^{\eta} \equiv T_0^{c}$) are identical; (ii) T_0^{W} obtained for the water self-diffusion data in all mixtures is smaller than T_0^{c}; (iii) for concentrations up to about 50% w/w, T_0^{W} is almost independent of concentration and equal to the T_0^{W} derived for neat water [28].

This divergence between T_0^{c} and T_0^{W} has been observed previously in other aqueous carbohydrate systems [4] and could be taken as evidence for a supercooled state in the T range between $T_0^{c} \equiv T_0^{\eta}$ and T_0^{W} in which the carbohydrates form, via their hydrogen bonds, a rigid amorphous network while the water molecules retain a ‘liquid-like’ translational and rotational diffusivisity [7].

The concentration dependence of T_0 in the four disaccharide systems is collected in Fig. 5. Among the compounds studied, trehalose has the strongest increase of T_0 with concentration, while in leucrose this increase is least pronounced. These differences are assumed to

Table 2
Intradiffusion coefficients D_c (10^{-10} m/s^2) of the carbohydrates in aqueous solution

T (K)	277	283	288	298	308	323	338	353	368
c % w/w	*Trehalose*								
10				3.73		6.69		11.5	14.4
30				1.41		3.04		5.90	7.73
50				0.30		0.86		2.35	3.27
60						0.27	0.52	0.87	1.41
70						0.08	0.21	0.39	
	Allosucrose								
10				4.03		7.06	9.12		
30				1.55		3.01	4.18		
50				0.51		1.18	1.92	2.89	
70				0.06		0.23	0.46	0.84	
	Leucrose								
30				1.53	2.14	3.39	4.77	6.41	
50				0.49	0.73	1.35	1.93	2.79	
70					0.13	0.27	0.45	0.72	
	Fructose, β-furanose								
30	0.95		1.48	2.22	2.94	4.56	6.48		
50		0.30		0.67	1.05	1.75			
70					0.13	0.33	0.58	1.18	
	Fructose, β-pyranose								
30	0.92		1.39	2.1	2.91	4.42	6.22		
50		0.28		0.65	0.95	1.66			
70					0.14	0.31	0.56	1.13	

Table 3
Intradiffusion coefficients D_W of the water molecules in aqueous carbohydrate solution

T (K)	273	278	283	288	298	308	323	338	353
c % w/w	*Sucrose*								
10					2.15	2.75	3.70	4.78	6.27
30					1.37	1.77	2.46	3.33	4.23
50					0.51	0.70	1.04	1.46	1.94
70						0.12	0.28	0.39	0.59
	Trehalose								
10	1.04	1.21	1.43	1.60	2.21	2.71	3.78	5.05	6.45
30		0.68	0.79	0.92	1.31	1.66	2.37	3.24	4.23
50			0.29	0.35	0.52	0.68	1.02	1.50	2.05
60				0.14	0.21	0.31	0.49	0.75	1.05
70					0.06	0.11	0.21	0.37	0.58
	Allosucrose								
10					2.06	2.55	3.48	4.52	5.92
30					1.26	1.62	2.28	3.08	4.12
50					0.58	0.78	1.15	1.62	2.16
70					0.19				
	Leucrose								
30					1.40	1.82	2.54	3.38	4.25
50					0.66	0.87	1.23	1.70	2.24
70						0.19	0.33	0.50	0.69
	Fructose								
30					1.57	2.03	2.86	3.77	4.62
50					0.65	0.85	1.24	1.81	2.31
70					0.22	0.30	0.49	0.70	0.96

correlate with the ability to form mixed hydrogen bonded networks incorporating water and carbohydrate molecules. This may be correlated to physical parameters such as the partial molar volume or heat of solution [1,2,17]. A real understanding of the influence of the molecular structure on the macroscopic properties should be provided by molecular modelling. However, up to now, calculations of hydrated sugar molecules are restricted to dilute solutions and only available for trehalose [29,30] and sucrose [31,32].

The fragility parameter C obtained from the analysis of the data (Table 4) vary between 5 and 9 in an unsystematic fashion. Thus all mixtures studied here belong to the extremely fragile class.

The VTF analysis of our data presented above is of limited precision, since it proved impossible to follow the self-diffusion and the viscosity into the deeply supercooled range. It has however the advantage that the individual behaviour of the two components becomes obvious and thus permits a better understanding of the dynamics in these complex liquids.

In the following, we will try to use established correlations between η and D to learn more about the behaviour of the saccharide solution in the extreme ranges of supercooling, not reached by the experiments given here. In typical simple liquids, the Stokes–Einstein relation [32]

$$D = \frac{kT}{6\pi\eta R} \tag{3}$$

yields a quantitative correlation between the viscosity and the diffusion coefficients. Here, k characterises the friction between the spherical molecule with radius R and its surrounding liquid [33]. Debenedetti [34] states that this correlation breaks down in the deeply supercooled state, the viscosity changing some orders of magnitude faster than the self-diffusion coefficients. Simple arithmetic shows that for a given binary mixture, the ratio of the self-diffusion coefficients of the two compounds as a function of temperature should be constant. This is in fact found for simple unpolar mixtures [35,36]. In Fig. 6, the product $D_W \eta T^{-1}$ is given for the systems sucrose/water and trehalose/water. They are typical for all other mixtures. The plots $D_c \eta T^{-1}$ for the carbohydrate self-diffusion coefficients D_c are qualitatively the same, with the exception of the 70% sucrose solution [7]. The most likely explanation for this are systematic errors in the older diffusion data.

Finally, in Fig. 7 the ratio D_W/D_c is plotted for the four disaccharides.

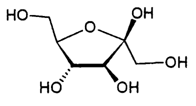
In all solutions with $c \geq 50\%$ w/w, this ratio increases with falling temperature. This effect being most pronounced in the 70% w/w trehalose solution, where this ratio has increased by a factor of 10 at 300 K. This temperature is more than 100 K above the T_0^c and already at this temperature indicates the strong decoupling between the mobility of the sugar and the water molecules.

Table 4
VTF parameters extrapolated from viscosity data

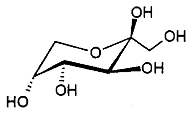
c (%)	η_0 (mPas)	C	T_0 (K)
	Fructose		
30	8.67×10^{-3}	7.71	124
50	8.67×10^{-3}	7.29	144
60	8.67×10^{-3}	7.95	149
70	8.67×10^{-3}	7.10	171
75	8.67×10^{-3}	7.21	178
80	8.67×10^{-3}	7.41	185
85	8.67×10^{-3}	7.20	198
	Sucrose		
10	2.63×10^{-2}	4.85	130
20	2.63×10^{-2}	4.77	135
30	2.63×10^{-2}	5.33	139
40	2.63×10^{-2}	5.74	143
50	2.63×10^{-2}	5.95	152
60	2.63×10^{-2}	6.23	162
70	2.63×10^{-2}	6.44	177
	Allosucrose		
40	3.44×10^{-2}	5.47	144
50	3.44×10^{-2}	5.57	154
60	3.44×10^{-2}	5.72	167
76	3.44×10^{-2}	6.31	190
	Leucrose		
10	2.22×10^{-2}	6.01	120
30	2.22×10^{-2}	6.16	130
50	2.22×10^{-2}	5.98	150
60	2.22×10^{-2}	6.71	155
65	2.22×10^{-2}	6.29	165
70	2.22×10^{-2}	6.43	172
	Trehalose		
10	2.29×10^{-2}	4.95	130
30	2.29×10^{-2}	5.35	138
50	2.29×10^{-2}	5.23	162

The fructose/water solutions.—Viscosity of aqueous fructose solutions can be found in standard reference books for sugar technology [37]. However, the data available do not cover the low temperature region. Results of our own measurements are compiled in Table 1. They allow the extrapolation of the ideal glass transition temperature T_0 and the fragility parameter (Table 4).

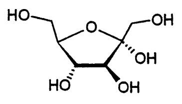
In contrast to the disaccharides discussed before, fructose, dissolved in water, has to be considered as a mixture of five tautomers, in principle. At room temperature, the composition of a 10% w/w solution is 2.3% α-, 72.0% β-pyranose, 5.2% α- and 20.0% β-furanose, the acyclic keto form being in the range of 0.5% [17,38]. The distribution is about the same at a concentration of 75% w/w [39]. However, it is known that the β-pyranose:β-furanose ratio increases with increasing temperature (0 → 60 °C) [38,39]. Within our own experiments, all cyclic tautomers could be identified in the NMR spectrum at 75 MHz over a broad range of temperature and concentration.



β-D-Fructofuranose



β-D-Fructopyranose



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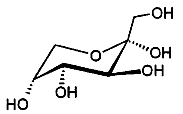

α-D-Fructopyranose

Only the two β forms occur at sufficiently high concentrations to permit the determination of their self-diffusion coefficients by ^{13}C NMR in acceptable instrument times. In Fig. 8, self-diffusion coefficients of the fructose/water system are compiled. For the β-fructopyranose, they are systematically lower than those for the β-fructofuranose form. It must be

Table 5
VTF parameters extrapolated from the self-diffusion of water (w) and the sugar (c)

c (%)	D_0 (m^2/s)	*C*	T_0 (K)	D_0 (m^2/s)	*C*	T_0 (K)
	Sucrose c			*Sucrose w*		
0				2.58×10^{-8}	729	118
10	2.28×10^{-8}	5.37	125	1.85×10^{-7}	6.79	118
20	2.40×10^{-8}	5.90	127			
30	3.28×10^{-8}	6.78	129	1.69×10^{-7}	7.24	119
40	4.34×10^{-8}	7.15	136			
50	3.55×10^{-8}	6.65	146	1.17×10^{-7}	6.80	132
60	2.46×10^{-8}	5.80	164			
70	8.22×10^{-8}	6.05	186	1.17×10^{-7}	6.55	158
	Trehalose c			*Trehalose w*		
10	3.95×10^{-8}	6.38	126	2.24×10^{-7}	7.08	118
30	3.95×10^{-8}	6.72	136	1.81×10^{-7}	6.86	121
50	3.95×10^{-8}	6.34	158	1.72×10^{-7}	8.08	125
60	3.95×10^{-8}	6.57	170	1.39×10^{-7}	8.08	133
70	3.95×10^{-8}	5.60	195	1.34×10^{-7}	6.27	164
	Allosucrose c			*Allosucrose w*		
10	2.81×10^{-8}	5.63	126	1.86×10^{-7}	6.98	118
30	2.81×10^{-8}	6.31	135	1.86×10^{-7}	7.57	119
50	2.81×10^{-8}	6.17	151	1.37×10^{-7}	7.53	125
70	2.81×10^{-8}	5.99	175	6.35×10^{-8}	5.26	155
	Leucrose c			*Leucrose w*		
30	5.12×10^{-8}	7.51	130	1.60×10^{-7}	7.08	119
50	5.12×10^{-8}	8.53	134	1.35×10^{-7}	8.02	119
70	5.12×10^{-8}	9.77	142	6.02×10^{-8}	5.82	153

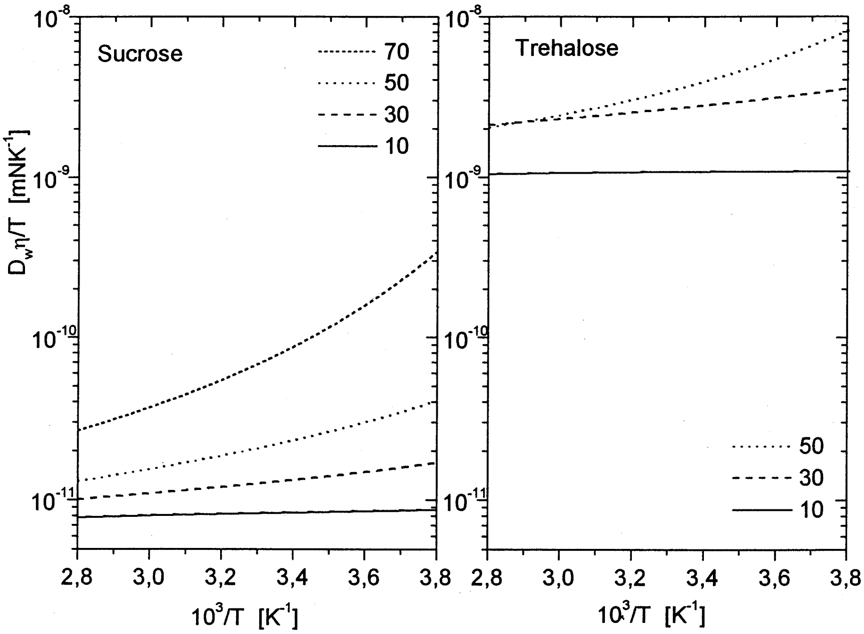

Fig. 5. *c*-Dependence of T_0 for the viscosity, saccharide, and water self-diffusion.

mentioned that these two sets of data were collected simultaneously from one set of spectra. The uncertainty of the temperature measurements has no influence upon the ratio D_{fur}/D_{pyr}. Thus the small effects consistently observed should be real and are an indication of the effects that could occur in more complex aqueous carbohydrate mixtures.

In such multicomponent systems widely found in nature and also used in many technical applications, it appears possible that not only the water mobility decouples from the saccharide mobility, but also that the different carbohydrates possess significantly different local mobilities and thus could act as plasticizers in the hydrogen bonded networks of the sugar moieties [40].

The ratios for the $D_{\mathrm{W}}:D_{\beta-\mathrm{pyr}}$ and $D_{\mathrm{W}}:D_{\beta-\mathrm{fur}}$ are given in Fig. 9. Comparison with the data in Fig. 8 shows that these ratios increase with concentration and falling temperature even faster than observed for the trehalose solution. Inspection of the structures given above shows that this is most likely caused by the geometry of the hydroxylgroups of the monosaccharides, which allow more extended and less ordered sugar networks to be formed.

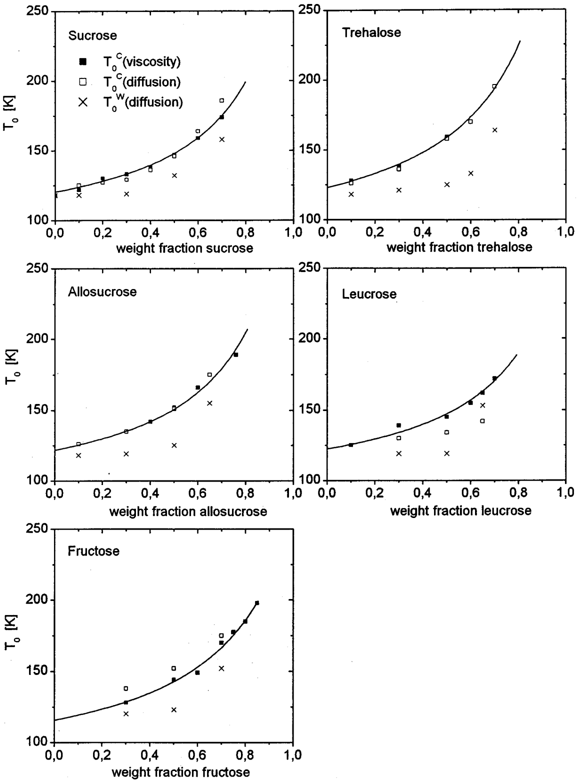

Fig. 6. Stokes–Einstein ratio of water in solutions of sucrose and trehalose.

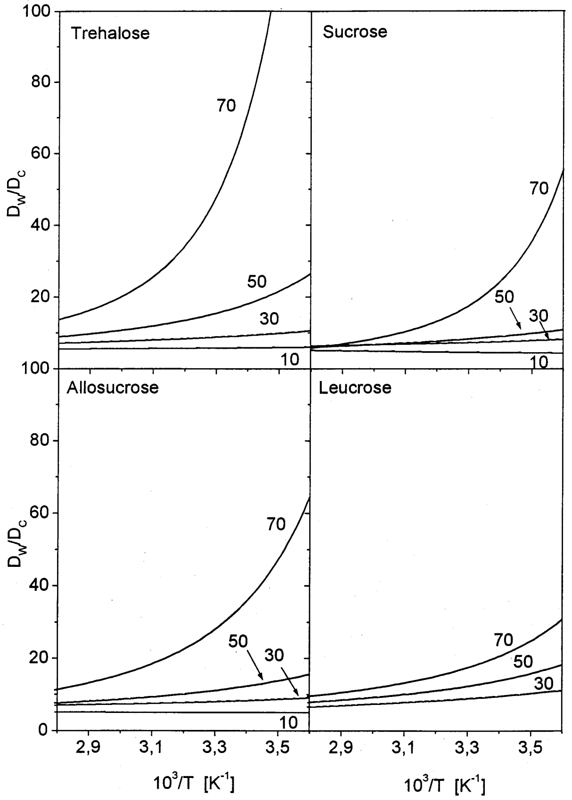

Fig. 7. Ratio of water to carbohydrate diffusion of various carbohydrate/water solutions. Numbers given in the graph are % w/w of the saccharide.

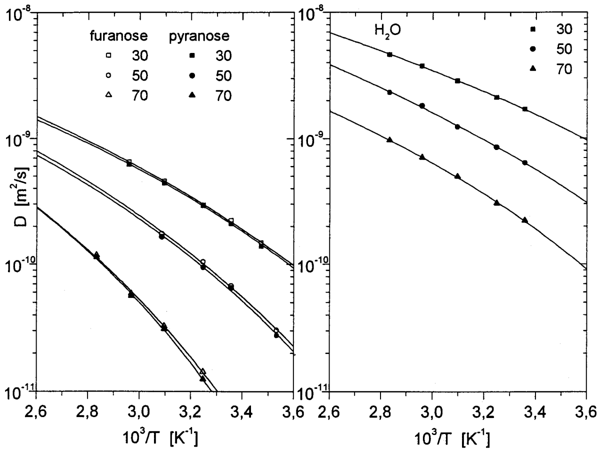

Fig. 8. Diffusion coefficient of fructose and water in fructose/water solutions. Numbers behind the symbols given in % w/w of fructose.

4. Conclusions

The measurements of the self-diffusion coefficients of the four aqueous disaccharide systems present for the first time a more detailed picture of the translational mobility in highly concentrated carbohydrate solutions.

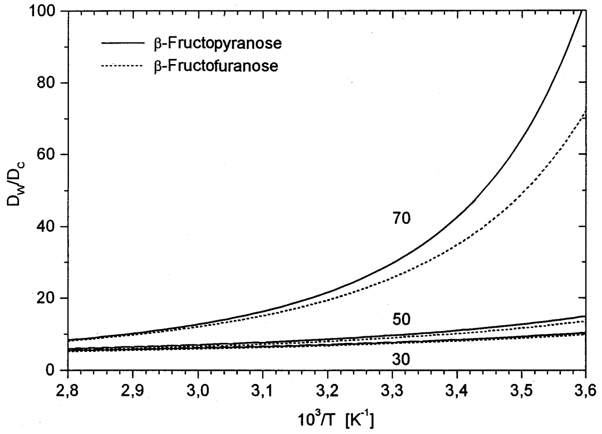

Fig. 9. Ratio of water to carbohydrate diffusion for fructose/water solutions. Numbers at the lines given in % w/w of fructose.

The general conclusion being that at lower concentrations ($c < 50\%$ w/w) all four carbohydrates have at equal concentration and temperature nearly the same D_c. This also holds for water diffusion. Only at higher concentrations, where the carbohydrate molecules must come into direct contact with each other, significant differences are observed.

For $c > 50\%$ w/w and temperatures $T \geq 300$ K the Stokes–Einstein equation shows a decoupling of D_c and D_W from the viscosity η, the latter increasing with falling temperature much faster than D_c and D_W. Also, the ratio D_W:D_c increases dramatically in the low temperature range. Description of the T-dependence of D_c, D_W, and η by the VTF equation yields significant differences in the ideal glass transition temperatures derived for the diffusion coefficients of the water molecules and the carbohydrates. One might speculate that in the deeply supercooled solution the carbohydrates form an open rigid three-dimensional hydrogen bonded network through which the water molecules can still diffuse.

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