c, *T*-Dependence of the Self Diffusion in Concentrated Aqueous Sucrose Solutions

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Z. Naturforsch. **49 c**, 258–264 (1994); received December 2, 1993

Diffusion, Sucrose, Water, Aqueous Solution

The self diffusion coefficients D of the water molecules and of sucrose have been determined by the pulsed field gradient NMR technique over a wide range of temperatures and concentrations ($c_{\max}$: 70% w/w suc.). All temperature dependencies can be fitted to a Vogel-Tammann-Fulcher equation. The isothermic concentration dependence of D for the sucrose is given by a simple exponential concentration dependence.

Introduction

In two previous papers the rotational dynamics of the sucrose [1] and the water molecules [2] in concentrated aqueous solutions of sucrose were studied in order to evaluate the molecular mobility of the individual components of this binary system. The motional models applicable for the description of the two constituents were derived, and it was attempted to characterize the molecular features responsible for the macroscopic behaviour observed in the bulk solutions. In the more concentrated solutions the temperature dependence of the rotational mobility of the water molecules is clearly different from the T-dependence found for the sucrose molecules. The latter being well correlated with the strongly concentration dependent glass transition temperature [3, 4], while in the more concentrated solutions, the rotation of the water molecules is determined by the approach to a concentration independent ideal glass transition temperature T_o of about 120 K.

These studies are complemented here by the determination of the self diffusion coefficients for the two components. This most fundamental characterization of the translational molecular mobility can be determined directly from a pulsed field gradient spin echo experiment [5] without any need to include motional models into the data analysis.

Also in technical applications the self diffusion coefficients are more closely related to the relevant macroscopic phenomena of crystallization and concentration by evaporation.

Previously published results are summarized in [6] and were obtained by tracer diffusion techniques for the sucrose component only. The data presented below include in addition the self diffusion coefficient of the water molecules as determined from the proton signal.

Experimental

Sucrose and heavy water (99.75% deuterated) (E. Merck, Darmstadt, F.R.G.) were used without further purification. The water was taken from a Milli Q unit (Millipore, Eschborn, F.R.G.). The solutions were prepared by weighing and degassed by freeze pump thaw cycles. The self diffusion coefficients D of the sucrose were taken in heavy water solutions. Details of the sample preparation have been given previously [1, 2]. 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 a Hahn-spin-echo experiment by application of a pulsed field gradient [5]. For this pulse sequence the amplitude of the echo A after a waiting period τ between the 90°- and 180°-pulse is given by:

$$A(2\tau) = A(0)\,\exp^{-2\tau}/_{T_2}\,\exp(-\gamma^2\delta^2 g^2 D(\Delta - \delta/3)) \quad (1)$$

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Verlag der Zeitschrift für Naturforschung,
D-72072 Tübingen
0939–5075/94/0300–0258 $ 03.00/0

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 given by $g = K \cdot I$ with the K the coil constant and I the pulse current. D is the self diffusion coefficient to be studied and D 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 to 12 spin echoes at increasing coil currents I, while keeping all other parameters in Eqn. (1) constant. The gradient coil constant K was calibrated with water at 293 K [7]. The calibration being controlled with a second substance. For these control experiments usually cyclooctane was used [8].

The temperature was regulated with the commercial Bruker variable temperature unit. It was controlled with an additional 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 for concentrations $c \leq 50\%$ w/w sucrose is ± 5%. For higher concentrations the reproducibility is lower, because of the steeper temperature dependence of D and because of the low spin-spin relaxation times T_2. In this concentration range the self diffusion coefficients are considered accurate to ± 10%.

The T_2 for the water protons in the 50% and 60% w/w sucrose solutions become probably because of the chemical exchange of the protons between the water molecules and the sugar hydroxyls very short. For these solutions the self diffusion coefficient of the water fraction could not be determined. In the 70% w/w solutions D for the water molecules could be measured reproducibly to ± 20%.

Results and Discussion

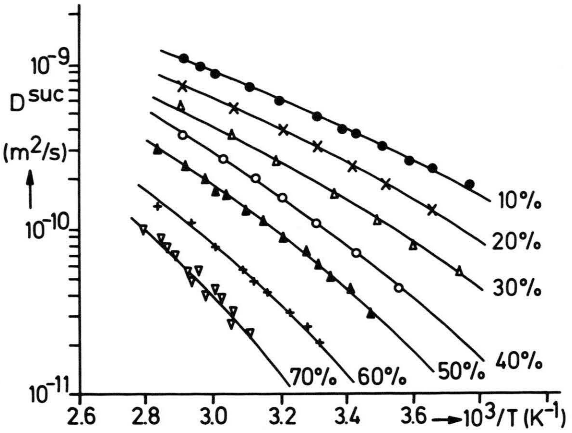

Fig. 1. Arrhenius plots of the self diffusion of the sucrose molecules in aqueous sucrose solution at constant concentrations (in % w/w). The lines drawn through the experimental points result from fitting the data to the VTF equation (Eqn. (2)).

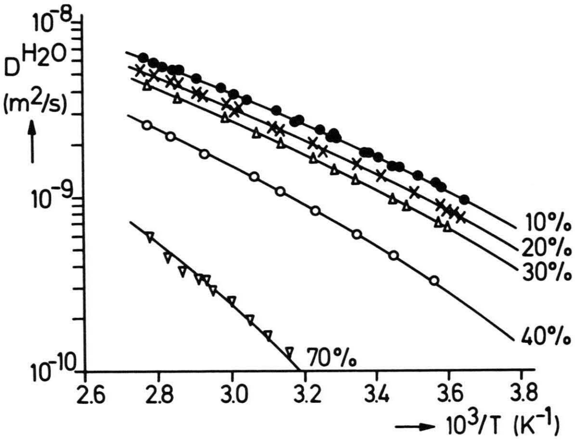

Fig. 2. Arrhenius plots of the self diffusion of the water molecules in aqueous sucrose solution at constant concentrations (in % w/w). The lines drawn through the experimental points result from fitting the data to the VTF equation (Eqn. (2)).

In Fig. 1 and 2 the measured self diffusion coefficients are presented. The strong signal from the water protons renders it impossible, to determine reliably the sucrose D in light water from the proton signals. In our studies therefore the light water was replaced by heavy water. In this exchange all hydroxyl protons of the sugar are replaced by deuterons. Extensive studies of the system investigated here [9] and in neat water [10] and many ionic aqueous solutions [10] proved, that the dynamic isotope effect observed when H_2O is replaced by D_2O is quantitatively equivalent to a reduction of the temperature T_0 by 5 K. The sucrose data of Fig. 1 are thus given with this correction.

Since these data have potential interest in technological applications, the experimental results are also compiled in the Tables I and II. In the region of data overlap the data agree within experimental error with data obtained by tracer diffusion studies [6].

Sucrose mobility

For the limited temperature range studied the sucrose self diffusion in the 10% w/w, 20% w/w and 30% w/w sucrose solutions D^{suc} could be described by one Arrhenian within the limits of experimental error. The energy of activation increasing with concentration (E_A [kJ/mol] 10% = 18.27; 20% = 20.73; 30% = 24.55) [6].

The slopes for the higher concentrated solutions show a definite curvature, that is also observed for the rotational mobilities [1]. In order to remain consistent the temperature dependence of all data characterizing the sugar mobility were thus fitted to the empirical VTF equation [11–14]

$$D = D_o \exp B/T - T_o \qquad (2)$$

with T_o the ideal glass transition temperature. The lines drawn through the experimental points in Fig. 1 and 2 result from these fits. The parameter derived for all dynamic studies are compiled in Tables III and IV. An interesting empirical correlation, that could be of practical use, is presented in Fig. 3. This correlation has been proposed previously in connection with the tracer diffusion data [6, 15]. Here the logarithms of the self diffusion coefficient for sucrose are plotted against the mole fraction of sucrose for three temperatures. These plots are linear within experimental error and described by the following set of exponentials:

$$\begin{aligned} D_{270}\,(\mathrm{m}) &= 2.374 \times 10^{-10}\, \mathrm{e}^{-0.6225 \cdot \mathrm{m}} \\ D_{310}\,(\mathrm{m}) &= 5.191 \times 10^{-10}\, \mathrm{e}^{-0.3463 \cdot \mathrm{m}} \\ D_{350}\,(\mathrm{m}) &= 9.996 \times 10^{-10}\, \mathrm{e}^{-0.2283 \cdot \mathrm{m}}. \end{aligned} \qquad (3)$$

These equations could obviously be applied for the interpolation of the sucrose self diffusion at intermediate concentrations and also for a moderate extrapolation to the more concentrated side of the diagram. As an example, the data have been extrapolated to 80% w/w sucrose. The additional points inserted at this concentration were obtained from a comparison of the rotational correlation times as obtained from the C-13 T_1 studies [1] assuming that the Debye formula given below is applicable to these solutions.

The self diffusion data, the published viscosities [16, 17] and the rotational correlation times as obtained from the C-13 T_1 studies can be correlated with the formalism of the hydrodynamic Stokes-Einstein and the Debye equation [18–21], although the model underlying this description, basically a sphere rotating and translating isotropically in a continuous medium, is at best only partially applicable in the strongly associating aqueous carbohydrate solutions.

Table I. Experimental self diffusion coefficients of sucrose dissolved in heavy water.

Sucrose													
Sucrose concentration													
10% w/w		20% w/w		30% w/w		40% w/w		50% w/w		60% w/w		70% w/w	
T [K]	$D \times 10^{10}$ [m² s⁻¹]	T [K]	$D \times 10^{10}$ [m² s⁻¹]	T [K]	$D \times 10^{10}$ [m² s⁻¹]	T [K]	$D \times 10^{10}$ [m² s⁻¹]	T [K]	$D \times 10^{10}$ [m² s⁻¹]	T [K]	$D \times 10^{10}$ [m² s⁻¹]	T [K]	$D \times 10^{10}$ [m² s⁻¹]
339	10.8	340	7.2	340	5.6	340	3.6	348	3.0	349	1.34	353	9.6
333	9.6	323	5.1	323	3.7	326	2.6	339	2.3	336	1.07	347	8.4
328	8.5	307	3.8	309	2.4	315	2.0	332	2.0	328	0.75	345	7.1
318	7.0	298	3.0	293	1.53	307	1.52	328	1.63	320	0.55	342	6.1
308	5.6	288	2.3	282	1.07	298	1.02	325	1.54	316	0.47	339	4.6
298	4.5	280	1.78	274	0.74	287	0.68	319	1.24	312	0.40	337	5.1
291	3.8	269	1.24	263	0.51	277	0.42	313	1.09	306	0.30	334	5.0
287	3.5	260	0.85	254	0.31	267	0.27	307	0.84	301	0.24	332	3.2
281	3.0							301	0.69	297	0.196	331	3.3
274	2.4							298	0.59	293	0.148	328	3.4
269	2.2							294	0.50			326	2.4
261	1.75							289	0.41			323	2.5
258	1.59							284	0.30			318	1.65
								270	0.143				

Table II. Experimental self diffusion coefficients of the water molecules in aqueous sucrose solutions.

Water									
Sucrose concentration									
10% w/w		20% w/w		30% w/w		40% w/w		70% w/w	
T [K]	$D \times 10^{10}$ [m^2 s^{-1}]	T [K]	$D \times 10^{10}$ [m^2 s^{-1}]	T [K]	$D \times 10^{10}$ [m^2 s^{-1}]	T [K]	$D \times 10^{10}$ [m^2 s^{-1}]	T [K]	$D \times 10^{10}$ [m^2 s^{-1}]
356	6.1	357	5.2	355	4.3	355	2.6	355	5.8
350	5.5	352	4.8	345	3.7	350	2.3	348	4.4
346	5.2	346	4.4	329	2.8	336	1.75	343	3.7
341	4.8	345	4.5	321	2.4	322	1.32	339	3.4
339	4.7	339	3.9	313	2.0	313	1.08	336	3.3
331	4.1	336	3.8	305	1.67	304	0.82	334	2.9
323	3.6	329	3.4	299	1.42	293	0.62	328	2.5
320	3.3	326	3.1	293	1.23	285	0.47	323	1.98
314	3.2	325	3.3	288	1.08	276	0.33	328	1.63
309	2.7	315	2.5	285	0.96	270	0.26	311	1.32
308	2.8	313	2.4	278	0.75			307	0.92
303	2.4	305	2.0	269	0.53				
300	2.2	302	1.82						
299	2.3	293	1.54						
298	2.2	288	1.33						
291	1.91	280	1.04						
290	1.82	274	0.88						
288	1.69	273	0.83						
285	1.49	270	0.78						
283	1.48								
279	1.32								
275	1.18								
274	1.12								
269	0.96								
266	0.88								

The Stokes-Einstein equation [18, 19] correlates

$$D_{tr} = \frac{kT}{6\pi \cdot \eta \cdot R} \qquad (4)$$

the translatoric self diffusion coefficient D_{tr} with the viscosity η and the hydrodynamic radius R. This hydrodynamic radius appears also in the Debye relation [19–21]

$$\tau_2 = \frac{4\pi \cdot R^3 \cdot \eta}{3kT} . \qquad (5)$$

Here τ_2 is the rotational correlation time of the dissolved molecule as for instance obtained from the C-13 spin lattice relaxation times of the sucrose. These formula were used for the calculation of the 80% w/w sucrose data given in Fig. 3.

The graphic representation of the results of this data analysis is given in Fig. 4.

The formalism described above permits in the system studied only a qualitative discussion of the

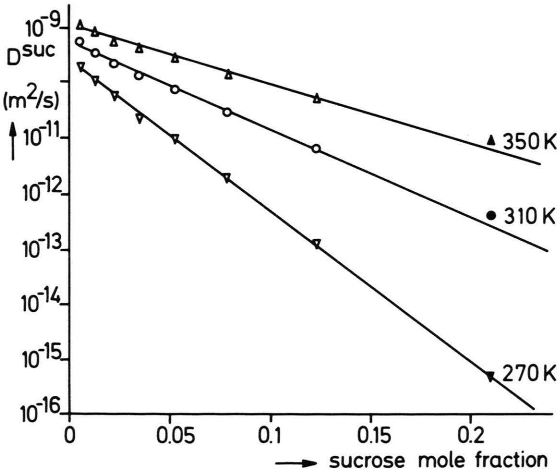

Fig. 3. Isothermal concentration dependence of the self diffusion coefficients of the sucrose molecule. (Open symbols: experimental results; full symbols; results obtained from an application of Eqn. (4) and (5).

Table III. Fit parameter for the dynamic properties of the sucrose molecules in aqueous sucrose solutions. The temperature dependence of all three properties is given by the VTF equation (Eqn. (2)). The correlation times τ_2 for the rotatoric mobility of the sugar molecules have been derived from the C-13 spin lattice relaxation times of the ring carbons [1]. Viscosity data were taken from published values [16, 17].

	Sucrose								
	Translation (D^{suc})			Rotation τ_2^{-1}			Viscosity		
	$D_o \times 10^{-8}$ [m²/s]	B [K]	T_o [K]	$\tau_{20} \times 10^{-13}$ [s]	B [K]	T_o [K]	$\eta_o \times 10^{-5}$ [Pas]	B [K]	T_o [K]
10%	3.24	−750	125	5.6	1060	125	2.52	653	126
20%	3.24	−824	127	5.6	1060	127	2.18	738	128
30%	3.24	−900	129	5.6	1060	129	2.15	816	130
40%	6.05	−1060	136	5.6	1060	136	2.18	882	136
50%	5.05	−1060	146	7.1	1060	146	2.51	924	148
60%	3.96	−1060	164	8.5	1060	164	5.25	946	164
70%	3.96	−1060	186	11.6	1060	186	5.82	945	186
80%	(3.96	−1060 extrapol.	214)	11.6	1060	218	–	–	–

effects of hydration and association upon the self diffusion of the sucrose molecules. For the lower concentrations ($c \leq 40\%$ w/w) and at temperatures larger than 300 K the Stokes-Einstein radius is remarkably constant and with $R \approx 0.5$ nm remarkably similar to the hydrodynamic radii derived by various physical measurements [22, 23].

The increase of R for $c \geq 20\%$ w/w sucrose at the lower temperatures is to be explained either by the stabilization of the hydration shell of the individual sucrose molecule through the removal of thermal energy or by the formation of transient aggregates between the sucrose molecules. The latter explanation is more plausible, because the T-dependence of R becomes stronger with increasing concentration. For $c \geq 50\%$ w/w sucrose R apparently decreases. This could be either explained with the assumption, that these very concentrated solutions contain insufficient water for the formation of complete hydration shells and thus sucrose molecules with a reduced number of water molecules attached to them become the diffusing entities.

It appears however more probable, that the rather strict conditions used for the derivation of the Stokes-Einstein equation are no longer applicable

Table IV. Fit parameter for the dynamic properties of the water molecules in aqueous sucrose solutions. The temperature dependence of the self diffusion is at all concentrations given by the VTF equation (Eqn. (2)), which also characterizes the dependence of the rotatoric mobility as given by τ_2 derived from the deuteron spin lattice relaxation times T_1 [2] for sucrose concentrations $c \leq 50\%$ w/w. For the lower concentrations the T-dependence is given by the dynamic scaling law:

$$\tau_0 = \tau_{20} \left(\frac{T - T_s}{T_s} \right)^{\gamma}. \qquad (2)$$

	H₂O					
	Translation (D)			Rotation (τ_2)		
	$D_o \times 10^{-8}$ [m²/s]	B [K]	T_o [K]	$\tau_{20} \times 10^{-13}$ [s]	T_s [K]	γ
10%	14.4	−750	125	3.75	224	1.92
20%	13.4	−765	127	3.75	221	2.09
30%	12.9	−786	129	3.75	217	2.58
40%	12.1	−860	136	3.75	207	3.06
				τ_{20} [s]	B [K]	T_o [K]
50%	–	–	–	5.2	1060	143
60%	–	–	–	5.2	1060	157
70%	8.4	−860	186	12.8	1320	114
80%	–	–	–	12.8	1320	115

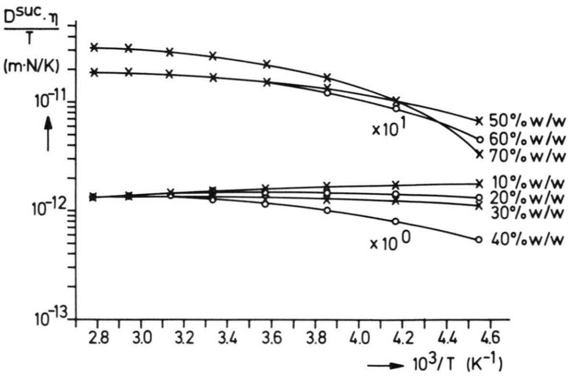

Fig. 4. Temperature dependence of the quotient $D^{suc}\eta/T$ at constant concentration showing the strong deviation from the Stokes-Einstein behaviour at low temperatures and high concentrations.

to these complicated binary hydrogen-bonded liquids. This latter explanation is also supported by a simple numerical calculation. The radius R derived from the rotational correlation time τ_2 as obtained from the C-13 spin lattice relaxation times [1] by insertion of τ_2 and η into Eqn. (5) will reproduce D^{suc} within ±10% for $c \leq 50\%$ w/w. For the solutions with 70% w/w sucrose the deviations increase to ±30%.

Water mobility

In Fig. 2 the self diffusion coefficients for the water molecules are given. Contrary to the drastic effects observed for the rotational dynamics [2], the T-dependence at constant concentration is in the whole range studied describable by a VTF equation. Also the ratio D^{H_2O}/D^{suc} shows a very slight increase with concentration only, which is almost within the limits of experimental error. The most plausible explanation for this being, that the rotational correlation times monitor the short term behaviour of the water molecules only, *i.e.* motions that occur over dimensions of a few molecular diameter, while the measured self diffusion coefficient averages over time ranges of the order of 100 ms. Δ in Eqn. (1) and during this time span the mobile water must come into contact with and be hindered by the less mobile sucrose molecules, that finally at sufficiently high concentrations and for low temperatures form rigid hydrogen-bonded networks that arrest the diffusion of the water molecules over larger distances. If this qualitative explanation holds true, the self diffusion coefficients of the water molecules should increase in hypothetical experiments able to probe the translational mobility over time spans of microseconds or even shorter intervals.

Concluding Remarks

The analysis of the spin lattice relaxation rates [1,2] and the self diffusion coefficients that are compiled with their relevant temperature dependencies in Tables III and IV leads to the following conclusions: At low concentrations the fully hydrated sucrose molecules and the bulk water molecules can be described by models assuming rigid molecules that rotate isotropically with a single correlation time for both, the dissolved sugars and the water molecules. In addition the water molecules can exchange rapidly between the hydration shells and the bulk phase and possess in the hydration shell an extra anisotropic mobility.

With increasing sucrose concentration the water molecules can no longer separate the sugar molecules with complete solvation shells. The sugars start to associate *via* transient hydrogen bonds which either connect directly two sugar molecules or connect *via* an intervening water molecule. These networks become more rigid with lower temperature and higher concentration. At the glass transition temperature T_0^{suc} all observable translational diffusion of the two constituents ceases. Only the rotational motions of the water molecules can be observed at temperatures well below the common T_0^{suc}. This mobility could be responsible for the high configurational entropy of the aqueous sucrose glasses [24]. The rotational dynamic of the water becomes almost concentration independent at $c(\text{suc}) \geq 60\%$ w/w and is characterized by an ideal glass transition temperature $T_0^{H_2O}$ that is within the limits of the precision of the fitting procedure applied identical to the ideal glass transition temperature of neat water [9].

Acknowledgements

Financial support by the Deutsche Forschungsgemeinschaft, BMFT and Verein der Deutschen Zuckerindustrie is gratefully acknowledged.

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