Molecular Mobility of the Water Molecules in Aqueous Sucrose Solutions, Studied by ^{2}H-NMR Relaxation

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Deuteron spin lattice relaxation times T_1 of sucrose/D_2O solutions are given as function of temperature, pressure, frequency and concentration. From the temperature dependence of the ^{2}H-T_1 the rotational dynamics of the hydrated sucrose complex and the water molecules are determined. For high pressure and high concentrations the temperature dependence of the water molecules is described by a Vogel-Tammann-Fulcher equation. The ideal glass transition temperatures $T_o^{H_2O}$ derived for the water molecules are at higher concentrations almost constant and smaller than the T_o^{suc} of the sugar molecules.

Introduction

The rheological properties of aqueous carbohydrate solutions are predominantly determined by the interaction of the dissolved carbohydrate with the water molecules and by the sterical restraints imposed upon these interactions by the rather strict geometrical requirements for the formation of the optimal hydrogen bond network.

For the stable storage of foodstuff [1] and for the stability of organisms against freezing and anhydrobiosis [2] the formation of glassforming solutions is prerequisite.

In the first paper of this series the concentration and temperature dependence of the rotational mobility of sucrose molecules was derived from the analysis of the ^{13}C-spin lattice relaxation rates [3]. These studies are complemented here by deuterium spin lattice relaxation time studies of water molecules, which permit the determination of the rotational mobility of the water molecules. Indirectly these data also permit a critical test of the results obtained from ^{13}C-relaxation, since at least in the more concentrated solutions the dynamics of the deuterons at the hydroxyl positions is clearly separable from the dynamics of the bulk and hydration water.

For many aqueous solutions of electrolytes and nonelectrolytes application of hydrostatic pressure around 200 MPa permits to supercool the solution to much lower temperatures and thus enhances the tendency to form glasses [4], some of the solutions studied here have consequently been investigated at high pressure also.

In this paper the system sucrose/water was studied rather extensively because it is the disaccharide most often encountered in technological processes. Furthermore, it should be possible to apply the methodology presented here and in the first paper [3] for the characterization of other carbohydrates in order to learn about the influence of the sugar stereochemistry upon the solution properties.

Experimental

Sucrose and heavy water (99.75% deuterated) were purchased from E. Merck (Darmstadt, F.R.G.). The spin-lattice-relaxation time (T_1) measurements were performed on Bruker MSL 300 and MSL 100 spectrometer, operating for deuterium at 46.2 MHz respectively 15.4 MHz, with the standard inversion recovery pulse sequence. For very short spin-lattice-relaxation times the RIDE- and inversion recovery pulse sequence was applied in order to suppress acoustic ringing, which becomes very pronounced at the lower temperatures reached in this investigation.

For all solutions the high temperature limit was set by the onset of caramelization of the sucrose, apparent from the brown colour developing in the samples. The low temperature limit is given by the homogeneous nucleation temperature (T_H) of the solutions.

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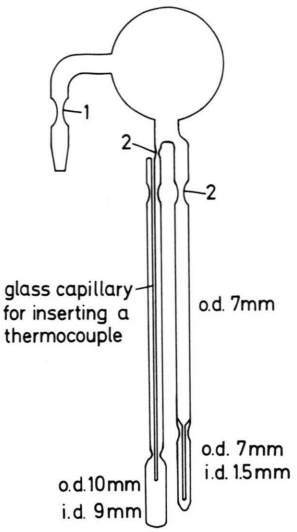

Fig. 1. Glass apparatus for the preparation of oxygen free sucrose solutions. The solutions are degassed in the spherical flask, by freeze-pump-thaw-cycles. The flask is sealed at position 1 and the solution is homogenized again. After that fractions of the solutions are filled into the tubes and the tubes are flame sealed at position 2.

In order to obtain reliably oxygen free solutions, the dissolved air was removed by a series of freeze-pump-thaw-cycles to a final pressure of 1 mPa. During these cycles most of the sucrose crystallized. In order to obtain homogeneous solutions of defined concentration the glass cells shown in Fig. 1 were developed for the degassing procedures.

D_2O and sucrose are weighted directly into the spherical flask and degassed at a high vacuum line. The assembly was flame sealed at position 1. These samples were controlled for weight losses and the solution homogenized by keeping it under frequent shaking at 350 K for 24 h.

Finally adequate amounts of the solution were allowed to run into the two tubings and the tubings were flame sealed at the positions 2.

During the NMR measurements temperature was measured and controlled to an accuracy of ± 0.5 K by a metal sheathed Chromel/Alumel thermocouple, which could be brought into close contact with the liquid samples.

The preparation of the oxygen free emulsion and the filling of these emulsions into the high pressure capillaries has been described elsewhere [5]. The emulsions contained the sugar solutions dispersed in a 1:1 mixture of methylcyclohexane/methylcyclopentane. 2% w/w of sorbitan tristearate emulgator (*Span* 65®, Serva, Heidelberg, F.R.G.) was added to the cycloalkane mixture in order to stabilize the emulsion.

Theory

The deuteron possesses a nuclear spin $I = 1$. Under the conditions of the experiment described here the relaxation of these nuclei is completely dominated by the electric quadrupole interaction. Rotatoric mobility modulates the interaction of the quadrupole with the permanent magnetic field and leads to relaxation. The spin lattice relaxation rate R_1 for the deuteron resp. its reciprocal, the spin lattice relaxation time T_1 is given by [6]:

$$R_1 = T_1^{-1} = \frac{3}{80}\left(\frac{e^2qQ}{\hbar}\right)^2 \{J(\omega_D) + 4J(2\omega_D)\} \qquad (1)$$

with $\frac{e^2qQ}{\hbar}$ the quadrupole coupling constant and $J(\omega_D)$ the spectral density of the rotatoric molecular motion at the resonance frequency of the deuteron ω_D respectively $2\omega_D$:

$$J(a\omega) = \int_0^\infty G(\tau) e^{ia\omega_D\tau} d\tau \qquad (2)$$

The correlation function $G(\tau)$ characterizes the time dependence of the reorientation of the electric field gradient tensor (efg) in the permanent magnetic field. In the case of the deuteron in D_2O this tensor is practically of axial symmetry and coincides almost with the O–D bond.

Assuming isotropic reorientation characterized by a single Debye correlation time τ, the correlation function $G(\tau)$ is given by one exponential, and the spin lattice relaxation rate becomes:

$$R_1 = \frac{3}{4}\left(\frac{e^2qQ}{\hbar}\right)^2 \left\{\frac{\tau}{1+(\omega_D\tau)^2} + \frac{4\tau}{1+(2\omega_D\tau)^2}\right\} \qquad (3)$$

In highly concentrated and thus very viscous liquids it becomes impossible to characterize the spin lattice relaxation rates by a single correlation time. The decay of the magnetization can either be non-exponential or characterized by a distribution of correlation times. Experimental NMR data obtained at a few fixed frequencies cannot distinguish between these two possibilities. In the following the data are described by a distribution of correlation

times first proposed by Cole and Davidson [7]. The correlation function for the Cole-Davidson distribution is given by:

$$g(\tau) = \begin{cases} \frac{\sin(\beta\tau)}{\pi} \left(\frac{\pi}{\tau_o - \tau}\right)^{\beta} & 0 < \tau < \tau_o \\ 0 & \tau > \tau_o \end{cases} \quad (4)$$

with τ_o the long time limit of the correlation time (cut-off time) and $0 \leq \beta \leq 1$ the Cole-Davidson parameter characterizing the width of the distribution. This description yields the spectral density:

$$J(\omega) = \frac{\sin(\beta \arctan(\omega\tau_o))}{\omega(1 + (\omega\tau_o)^2)^{\frac{\beta}{2}}} \quad (5)$$

In the limit $\beta = 1$ the CD treatment becomes identical to the model for isotropic rotation.

Especially the studies on supercooled water have shown, that the rotational motion of the water molecules is isotropic. Dissolved sucrose however orients the hydration water and this leads to an anisotropic mobility of the water of hydration [5]. The deuterium relaxation data for the heavy water molecules in the hydration shell can be described quantitatively by the following model:

1. The individual water molecules perform a thermally activated anisotropic reorientation around an axis formed by hydrogen bonds between the sugar hydroxyls and the water molecules.

2. The complete hydrated sucrose molecules reorient isotropically.

3. Individual water molecules can leave the hydration shell by exchange processes and acquire the dynamic properties of the bulk liquid.

The combination of these modes of mobility yields the relaxation rate [8]:

$$R_1 = \frac{3\pi^2}{10}\left(\frac{e^2qQ}{\hbar}\right)^2 \{A(J(\omega_D\tau_o) + 4J(2\omega_D\tau_o)) + B(J(\omega_D\tau_1) + 4J(2\omega_D\tau_1)) + C(J(\omega_D\tau_2) + 4J(2\omega_D\tau_2))\} \quad (6)$$

$$A = \frac{1}{4}(3\cos^2\vartheta - 1)^2 \qquad B = 3\sin^2\vartheta\cos^2\vartheta \qquad C = \frac{3}{4}\sin^4\vartheta$$

ϑ: Angle between the radial direction of the hydrate complex and the O–D bond of the water molecules.

$$\frac{1}{\tau_o} = \frac{1}{\tau_r} + \frac{1}{\tau_{ex}} \qquad \frac{1}{\tau_1} = \frac{1}{\tau_r} + \frac{1}{\tau_i} \qquad \frac{1}{\tau_2} = \frac{1}{\tau_r} + \frac{4}{\tau_i}$$

τ_r: Correlation time for the reorientation of the complete hydrated complex.

τ_{ex}: Exchange time; characteristic residence time for a water molecule in the hydration shell.

τ_i: Correlation time for the anisotropic reorientation of the individual water molecules. For the description of the temperature dependence of the correlation times of the water molecules in neat water and salt solutions at ambient pressure a dynamic scaling law [9, 10], which predicts a very steep increase of τ_o at the approach of the mechanical stability limit of the supercooled liquid [5]

$$\tau_o = \tau_{oo}\left(\frac{T - T_s}{T_s}\right)^{\gamma} \quad (7)$$

has been used successfully. For the more concentrated solutions and under high pressure the correlation times can be described by the VTF equation:

$$\tau_o = \tau_{oo} e^{\frac{B}{T - T_o}} \quad (8)$$

The T-dependence of the internal anisotropic mobility of the individual water molecules in the hydration shell is characterized by an Arrhenian:

$$\tau_o = \tau_{oo} e^{\frac{E_A}{kT}} \quad (9)$$

The deuteron NMR spectrum of these solutions consists at all concentrations and temperatures of one intense signal only. This signal contains the resonances from the deuterated hydroxyl groups of the sucrose and the deuterons of the D_2O molecules. Small differences in chemical shift, relatively short spin-spin relaxation times and chemical exchange between the two species of hydroxyl groups produce one Lorentzian line. The experimental deuteron R_1 is thus given by [11]:

$$R_1 = (1 - A) \cdot R_1^{suc} + A \cdot R_1^{D_2O} \quad (10)$$

with A the mole fraction of the deuterons in the water molecules and (1-A) the mole fraction bound in the sugar hydroxyls.

$R_1^{D_2O}$ is described in a two state model with R_1^{hyd} characteristic for the water molecules in the hydration shell and R_1^{free} for the solvent molecules in contact only with other water molecules:

$$R_1^{D_2O} = \left(\frac{H}{R} R_1^{hyd} + \frac{R - H}{R} R_1^{free}\right) \quad (11)$$

In Eqn. (11) H is the effective hydration number and R the mole fraction D_2O/sucrose. In the analysis of the experimental results an effective quadru-

pole coupling constant is used, this procedure was previously introduced for supercooled D_2O [12]:

$$\langle QCC \rangle_{\text{eff}} = \chi \left(\frac{e^2 qQ}{\hbar} \right) \tag{12}$$

with χ a motional averaging factor, that characterizes the fast librational oscillations which lead to a reduction of the instantaneous *QCC*.

Results and Discussion

High pressure T_1-measurements

It is obvious from an inspection of the equations presented in the theory section, that thorough checks of the different models presented can only be obtained, in the range were the correlation times become approximately equal to the radiofrequency ω_D *i.e.* in the dispersion region that can only be reached by lowering the temperature under avoidance of crystallization in order to slow down the molecular mobility. The phase diagram for metastable supercooled water [13] shows, that application of pressure suppresses the homogeneous nucleation temperature T_H even more than the melting temperature. At a pressure of 225 MPa the minimum of T_H is reached with $T_H \approx 188$ K. In this area of the phase diagram the deuteron T_1 of neat emulsified D_2O becomes frequency dependent [12] and the study of T_1 as function of the frequency permitted a comprehensive analysis of the spin-lattice relaxation times. In Fig. 2 ^{2}H-T_1 of neat D_2O and 10, 20, 30 and 40% w/w solutions of sucrose in D_2O are given for p = 225 MPa at two magnetic fields. The data given for neat D_2O were taken partly from previous work [12]. The full lines drawn through the experimental points result from a fit of the data to Eqn. (10). All data sets show a minimum in T_1 that is shifted to higher temperatures with increasing sugar concentration and is becoming flatter in the same direction. Also the T_1 value at the minimum is increasing. In the solution with 40% w/w sucrose the data clearly reveal a second dispersion region on the high temperature side of the curves, that is also observable, although less pronounced, in the other three sugar solutions. This extra shoulder is ascribed to the relaxation of the hydroxyl deuterons in the sucrose molecules, and its characterization with the parameters and motional models derived for the sucrose-^{13}C-T_1 data [3] will be discussed together with the ambient pressure data.

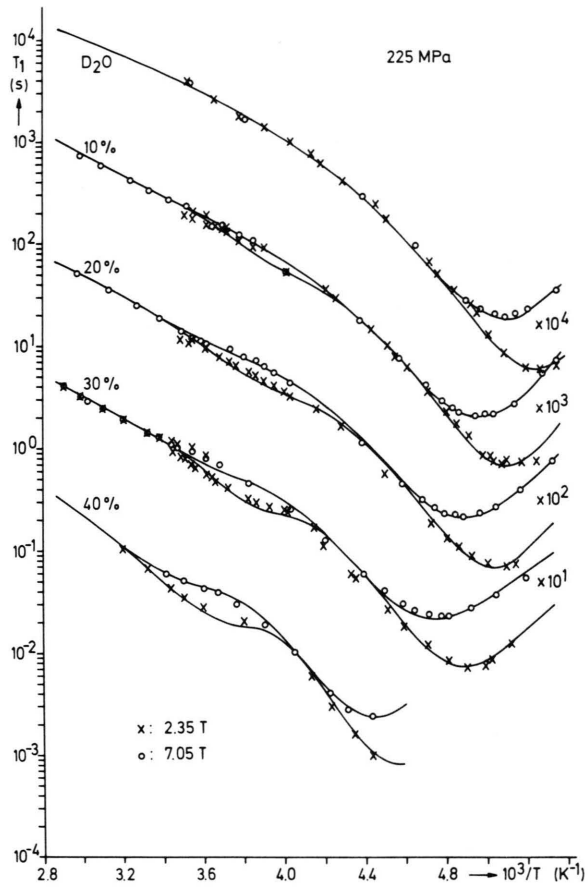

Fig. 2. 225 MPa isobars of the deuteron spin-lattice relaxation time T_1 at two frequencies in several sucrose solutions in D_2O and in neat D_2O. The lines drawn through the experimental points result from the fit of the data to Eqn. (1), (5), (6) and (10).

In the region of the T_1 minimum the relaxation rate of the deuterons is given by Eqn. (1) and (5), and is dominated by the free D_2O molecules. The mobility of the water molecules in the hydrated complex is given by Eqn. (6). In order to limit the number of free parameters in this equation, τ_r, the correlation time describing the mobility of the hydrated sucrose and its temperature dependence were taken from the ^{13}C relaxation data. This procedure leaves four free parameter for the fitting procedure: H the hydration number, T_o, the ideal glass transition temperature, E_A the energy of activation for the anisotropic mobility of the individual water molecule which is described by an Arrhenian and β, the Cole-Davidson parameter (Eqn. (4) and (5)).

The parameter obtained from the fits are given in Table I, together with the constant factors needed for the evaluation.

For the 50% w/w sucrose solution no effect of pressure upon the supercooling behaviour and the deuteron T_1 could be found in the p-range studied (0.1 MPa $\leq p \leq$ 225 MPa). All higher concentrated sucrose solutions can be studied at ambient pressure well into the dispersion region. The low temperature limit being set by the shortening of the spin-spin relaxation time T_2 and not by the limit of supercooling.

Ambient pressure ^{2}H-T_1 measurements

In Fig. 3 the ambient pressure T_1 measurements for neat D_2O and the sucrose solutions with 10 to 40% w/w are given. At ambient pressure the homogeneous nucleation sets in at temperatures around 240 K, and thus it becomes impossible to reach the dispersion region ($\omega_D \approx \tau_o^{-1}$). The significant difference between these data sets and the results given in Fig. 3 is the much steeper temperature dependence of T_1. It has been argued previously, that the dynamic and thermodynamic properties of neat water at ambient pressure are best described by the approach to a low temperature stability limit characterized by T_S [9, 10]. The temperature dependence of many thermodynamic and kinetic properties of neat water is quantitatively described by the dynamic scaling law given in Eqn. (7). This behaviour was thus also assumed for the free water fraction in the sucrose solution. The T-dependence of the rotatoric diffusion of the complete hydrated sucrose molecules is given by the VTF equation (Eqn. (8)). The fit parameter for this description are taken from the ^{13}C relaxation data. With the limited temperature range accessible to the experiment, it appeared not possible to test the different models for the mobility of the water of hydration. Therefore the model-free description was chosen for this deuteron fraction:

$$R_1^{hyd} = S^2\,(J(\omega\tau) + J(2\,\omega\tau)) + (1 - S^2)(J(\omega\tau_i) + J(2\,\omega\tau_i)) \quad (13)$$

Table I. Fit parameter for the 225 MPa isobars of the deuteron T_1 in sucrose/D_2O solutions. Concentration independent factors are: $\tau_{oi} = 4.7 \times 10^{-14}$ s, QCC_{D_2O} = 214 kHz, QCC_{Hydrat} = 195 kHz, $\vartheta = 71°$.

	D_2O	10%	20%	30%	40%
T_o [K]	132	137	140	146	160
E_A [kcal/mol]	–	2.96	2.98	3.02	3.08
β	0.62	0.62	0.46	0.32	0.30
H	–	12	12	12	10

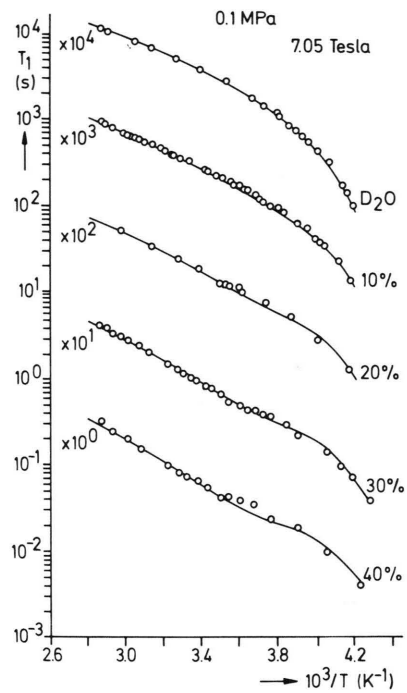

Fig. 3. 0.1 MPa isobars of the deuteron spin-lattice relaxation time T_1 at 46.2 MHz for several sucrose solutions in D_2O and in neat D_2O. The lines drawn through the experimental points result from the fit of the data to Eqn. (1), (10) and (13).

The parameter for the first term in Eqn. (11) are taken from the ^{13}C relaxation data, the hydration number for this treatment is set to $H = 8$. The hydration number derived from an experiment depends to a certain extent upon the physical method and the model used for the data analysis. Recent dielectric [14] and NMR relaxation studies [15, 16] derive for sucrose $6 \leq H \leq 10$.

This data analysis is no longer possible for the sucrose solutions with $c_{suc} \geq 50\%$ w/w, the deuteron T_1 data for these solutions are given in Fig. 4. The temperature dependence of the T_1 data becomes weaker with increasing concentration, as is already apparent from the lowering of T_S to 212 K in the 40% w/w solution. For the more concentrated solutions thus the description of the free and hydration water by the VTF equation had to be assumed.

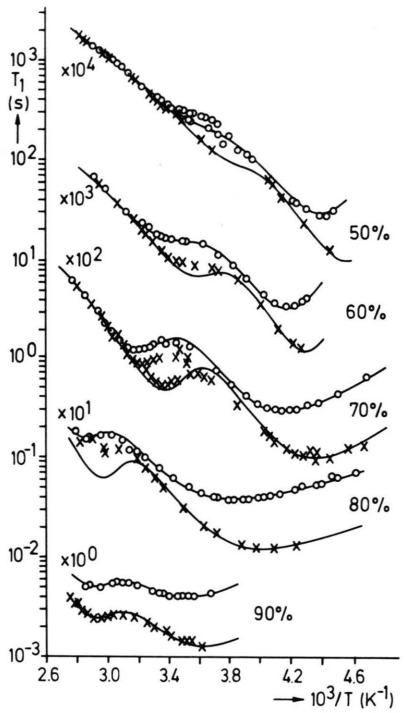

Fig. 4. 0.1 MPa isobars of the deuteron spin-lattice relaxation time T_1 at two frequencies in the most concentrated solutions of sucrose in D_2O. The lines drawn through the experimental points result from the fit of the data to Eqn. (5) and (13).

While for the 50% w/w solution identical glass transition temperatures for the free and bound water are observed, the T_o start to diverge for $c \geq 60\%$ w/w.

At sucrose concentration $c \geq 60\%$ w/w all water is found in direct contact with the sugar if one assumes a hydration number of eight and one would thus expect the isobars of the deuteron T_1 to possess one minimum only. The experimental curves however reveal two distinct minima (*cf.* Fig. 4). The analysis of these curves shows, that the upper minimum can be characterized by the parameter derived from the ^{13}C relaxation data. This minimum should thus be assigned to the hydroxyl deuterons, while all other deuterons show a concentration independent $T_o^{D_2O} \approx 120$ K, which is very close to the glass temperature found for neat D_2O. It is thus plausible to assume, that the sugar molecules form at their glass transition temperature T_o(suc) a gel-like network in which the water molecules retain at least their rotational mobility, which is frozen out only at ~120 K.

In Fig. 5 the relevant transition temperatures for solutions of sucrose in H_2O at ambient pressure are given. At $c \leq 50\%$ w/w the water dynamics are determined by the same dynamic scaling law (Eqn. (7)) that proved to be the most adequate description for the behaviour of low pressure supercooled neat water. Already under these conditions the dynamics of the sucrose molecules are characterized by a VTF temperature dependence. The ideal glass transition temperature T_o^{suc} is in good agreement with the experimental T_G derived from calorimetric studies (T_o is normally found 10–20 K below T_G). T_o and T_G reveal a very strong concentration dependence. The peculiar behaviour observed for the dynamics of the water molecules in the most concentrated solutions *i.e.* the effect, that $T_o(D_2O)$ becomes independent of concentration and very similar to the $T_o(D_2O)$ found for neat D_2O, is rather surprising and appears to be typical for all most concentrated aqueous sugar solutions, although significant quantitative differences exist, when the various disaccharides are compared.

Concluding Remarks

The concentration and temperature dependence of the rotational dynamics of the water molecules reveal a rather complex pattern. It is impossible to describe the experimental deuteron spin-lattice relaxation rates with one simple model. Valuable additional information can be derived from the pressure dependence of R_1. It was attempted to apply the most simple physically acceptable model to the

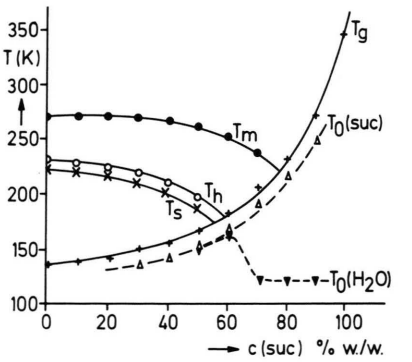

Fig. 5. Part of the phase diagram of sucrose/H_2O solutions. T_m: melting temperature; T_h: homogeneous nucleation temperature; T_o: ideal glass transition temperature; T_g: calorimetric glass transition temperature; T_S: temperature of the mechanical stability limit.

data presented and to minimize the number of free parameter. Wherever possible these parameter where taken from the literature. The actual values used are compiled in Tables II and III. The fit parameter describe the experimental results with ± 2% deviation, which is smaller than experimental error.

Table II. Fit parameter for the 0.1 MPa isobars of the deuteron T_1 in the more dilute sucrose/D_2O solutions. Concentration-independent factors are: τ_{oi} = 4.7×10^{-14} s, $\tau_{ooD_2O} = 5.2 \times 10^{-14}$, $B_{D_2O} = 687$, QCC_{D_2O} = 214 kHz, QCC_{Hydrat} = 194 kHz.

	D_2O	10%	20%	30%	40%
T_o [K]	–	130	132	134	139
E_A [kcal/mol]	–	2.82	2.91	3.05	3.05
H	–	8	8	8	7
S^2	–	0.08	0.09	0.12	0.12
T_s [K]	230	228	226	222	212
$-\gamma$	1.86	1.92	2.09	2.58	3.06

For the lower concentrations ($c_{suc} \leq 40\%$ w/w) the molecular dynamics of the water molecules are pressure-dependent. The ambient pressure dynamics of the water of hydration can be described by the parameter derived from the C-13 relaxation data of the sucrose ring molecules [3]. At these concentration the sugar molecules distort the water hydrogen bond network and increase the rotational mobility of the bulk water, compared to neat D_2O.

The temperature dependence of this bulk mobility is characterized by a dynamic scaling law (Eqn. (7)). At high pressures (225 MPa) the T-dependence is given by the VTF equation (Eqn. (9)), which is also able to describe the water relaxation at the higher concentrations. For $c_{suc} \geq 60\%$ w/w the water dynamics decouple completely from the sucrose mobility. In this concentration range the rotational mobility of the water molecules is given by a VTF dependence with a concentration-independent T_0 of approx. 120 K while for the sucrose molecules a strongly concentration-dependent higher T_0 is derived.

The complex behaviour observed for the sucrose solutions as function of concentration reflects the large structural and dynamic changes occurring in these mixtures.

Acknowledgements

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Table III. Fit parameter for the 0.1 MPa isobars of the deuteron T_1 in the more concentrated sucrose/D_2O solutions. Concentration-independent factors are: τ_{oo}: preexponential factor for the VTF equation, τ_{ooD_2O} = 5.2×10^{-14}, B_{D_2O} =687, β_{D_2O}: Cole-Davidson parameter for the water molecules, β_{suc}: Cole-Davidson parameter for the description of the hydroxyl deuteron dynamics.

	50%	60%		70%	80%	90%
T_o^{sac} [K]	152	169	T_o^{sac} [K]	192	224	246
$T_o^{D_2O}$ [K]	149	161	$T_o^{D_2O}$ [K]	118	120	118
E_A [kcal/mol]	3.04	3.82	QCC [kHz]	206	232	240
H	6	6	β_{D_2O}	0.35	0.16	0.18
$\tau_{oo} \times 10^{-13}$ [s]	7.1	8.2	$\tau_{oo} \times 10^{-13}$ [s]	12.8	28	32
B [K]	1060	1060	β_{suc}	1	0.34	0.42

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