



Sugar, water and free volume networks in concentrated sucrose solutions

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Abstract

We used molecular dynamics simulations to determine the sucrose hydrogen bond network (HBN) in amorphous sucrose with 0–50% w/w water. We find that the onset of a percolated sugar HBN network (between 33% and 40%) coincides with the experimental observation of the decoupling of viscosity and probe diffusion for these mixtures. The analysis of the free volume (FV) in these mixtures shows a non-monotonic behavior with water content which is consistent with experimental observations of hydrogen bond compaction and negative apparent partial volume of dilution, but in disagreement with the FV theory model of plasticization by water.

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1. Introduction

Water–sucrose solutions are of utmost relevance in food science [1], where concentrated carbohydrate–water mixtures behave as polymers in their viscoelastic response [2]. This behavior has been attributed to the existence of a supramolecular hydrogen bonded network (HBN) [3]. Indeed MD simulations on sugar found a HBN in 15% w/w water glucose solutions [4], but no studies have been reported on the threshold concentration at which the HBN is formed. It is reasonable to assume that the formation of an extended sugar

network will affect the dynamical response of the mixture for long wavelength deformations, decoupling the viscosity of the solution from the diffusion of non-HB molecules, and the ratio between water and sugar diffusion. These two decoupling effects has been reported for water–sucrose solutions: the activation energy for viscous flow is increasingly higher than that for diffusion of a non-HB probe (fluorescein) when water concentration is lower than $38 \pm 4\%$ w/w [5] while the diffusion of water and sucrose decouples for water contents below $\sim 50\%$ w/w [6]. Water diffusion increases with water content and decreases with temperature, but – interestingly – it is *not* arrested below the glass transition [7]. It has been suggested [7] that water may still undergo rapid translational and rotational motion within the pores formed by

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the rotationally frozen sugar matrix. The distribution of FV shapes and size of the voids and width of the percolating channels cannot be inferred from the existing experiments on water–carbohydrate solutions. In this Letter, we compute the FV and sucrose and water connectivity in concentrated sucrose solutions and discuss their influence in plasticization, water mobility and onset of the ‘polymeric’ behavior in these mixtures.

2. Models and methods

Atomistic molecular dynamics NPT [8] simulations were performed using Cerius2[®] [9]. We used the DREIDING force field [10], except that we use explicitly off-diagonal van der Waals interactions between any carbohydrate oxygen (O_c) and a H_{OH} of sugar or water, with the parameters $D = 0.03783$ kcal/mol, $R = 2.4$ Å and $\xi = 12.76$ based on fitting crystal structure and amorphous data. The hydrogen bond parameters [10] were taken as $D_{OO} = 2.5$ kcal/mol and $R_{OO} = 3.2$ Å. The partial charges on water atoms were obtained by LMP2-QM calculations: $qO = -0.7287$ and $qH = 0.3643$ e.u. Partial charges on carbohydrate atoms were obtained by charge equilibration [11] of the saccharide molecule, averaged over an NVT simulation in water box at 300 K and density 1 g/cm³. Long-range interactions were evaluated with Ewald sums as implemented in [12].

The enthalpy of fusion of sucrose was computed as the potential energy difference between an

average over 30 ps of NPT for amorphous sucrose at 470 K and 30 ps NPT dynamics of crystalline sucrose at 450 K. The experimental melting temperature is 461 K [1]. Crystal simulations were started from the X-ray structure [13].

We studied amorphous sucrose solutions with 0–50% w/w water at 60 °C. These systems have relaxation times for the order of a nanosecond and above [14]. For the sake of structural analysis, sampling multiple relevant configurations is more efficient than long-time simulations. Hence, three samples were prepared for each composition using a thorough procedure [15] to construct equilibrated amorphous systems via a series of annealing steps. Table 1 lists the composition, temperature and density for each system.

3. Results and discussion

The predicted densities for crystalline and amorphous sucrose and its aqueous mixtures are within 2% of the experimental value [13,16,17] over the full concentration range (Table 1). The enthalpy of fusion of sucrose (8.8 ± 3 kcal/mol) compares very well with the experimental value of 8.4 kcal/mol [17]. The heat of vaporization (E_{vap}) of amorphous sucrose is calculated to be 81.7 ± 1.1 kcal/mol at 294 K, but there is no experimental data for comparison. A second way to estimate E_{vap} of amorphous sucrose at 298 K is to scale E_{vap} of glucose [18] by the ratio of free OH groups in both molecules. This leads to a heat of vaporization

Table 1
Densities (ρ) and percolation probabilities (PP) of sucrose solutions

Water (% w/w)	W	S	ρ (g cm ⁻³)	ρ_{exp} (g cm ⁻³)	PPS	PPW
0	0	32	1.46 ± 0.01	1.43	1	N/A
10	100	32	1.41 ± 0.02	–	1	0
18	84	20	1.39 ± 0.01	1.40	1	1
33	278	30	1.31 ± 0.02	1.31	1	1
40	190	15	1.24 ± 0.01	1.26	0	1
45	233	15	1.24 ± 0.01	1.24	0	1
50	285	15	1.22 ± 0.01	1.21	0	1
Crystal 298 K		32	1.594 ± 0.002	1.59	1	N/A

W and S are the number of water and sucrose molecules. PPS and PPW denote PP of sucrose and water, respectively. Experimental densities are from [13,16,17].

for sucrose of 83.5 ± 2.0 kcal/mol, in excellent agreement. These results validate the force field.

3.1. Sucrose network

The HB connectivity of sucrose molecules was defined using a geometric criterion. We consider that a HB has formed if the donor hydrogen and acceptor oxygen distance is less than 2.4 Å and the OHO angle is within $180^\circ \pm 20^\circ$ [19]. If at least one HB exists between two sucrose molecules we consider that they belong to the same cluster. A cluster is percolated if it is connected with its periodic images in the three directions. We define the percolation probability for each composition as the fraction of samples in which sucrose percolates. The results (Table 1) locate the percolation threshold for sucrose HBN between 33% and 40% w/w water. Although sucrose HBN is percolated at 33% w/w water, 5 out of 30 molecules do not belong to the percolated cluster. For lower water content, all sucrose molecules are involved in the percolated HBN. For the 50% w/w solution, we found an average of 2.5 sucroses per cluster, although we detected clusters containing as much as 10 molecules.

The percolated HBN is a possible explanation of the experimental observation of a relative increase of the activation energy of viscous flow with respect to the diffusion of a probe molecule at water content below $38 \pm 4\%$ w/w. We believe that both the resistance to shear deformation and mechanical stability of the mixture would increase upon formation of the sucrose network. Hence, the HBN percolation should increase the activation energy for collective motion. The dynamics and mechanical behavior of the sucrose matrix, thus, would become similar to that of a cross-linked polymer matrix, as observed in the experiments [5]. The clustering observed at 50% w/w is also consistent with the observed [6] decoupling of the diffusion of water and the sterically restrained sucrose.

3.2. Free volume

We computed the free volume (FV) for the sucrose-percolated mixtures. The FV is defined as

the volume fraction of the total volume available for the probe. FV accessible to a probe of radius R_p was calculated over a 3D grid of size 0.1 Å, and measuring the space occupied by spheres of radius $R_a + R_p$, where R_a is the contact radius (1.2, 1.52 and 1.70 Å for H, O and C, respectively). The void percolation radius R_{pc} is defined as the largest probe that senses accessible FV channels percolated in all directions. Fig. 1 displays FV vs R_p for amorphous sucrose. Fig. 2 shows FV of representative conformation of sucrose mixtures for $R_p = 0.7$ and 0.9 Å. The key features of the void distributions are:

1. FV changes non-monotonously with water content; the higher FV corresponds to 0% w/w, drops about 1% with 10% w/w water and then increase slightly with water content (Fig. 2, inset). These results are consistent with the decrease in the partial apparent volume per sucrose molecule with increasing dilution, obtained through density measurements [16]. FTIR experiments of malto-oligosaccharides–water mixtures [20] also support an increase in the HB packing with water content.
2. The voids are compact for $R_p < 0.9$ Å. For $R_p < 0.7$ Å the voids are connected through channels (Fig. 2), that percolate at $R_{pc} \sim 0.4$ –0.5 Å. The percolating radius is smaller

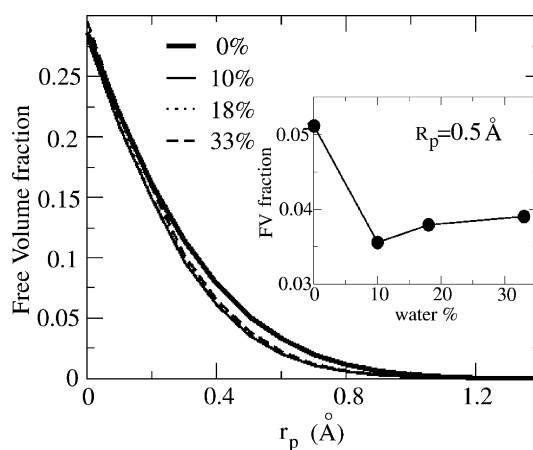


Fig. 1. FV fraction as a function of probe radius, for sucrose–water solutions. The inset shows the non-monotonous FV dependence with concentration, for a probe size close to the percolating FV radius, 0.5 Å.

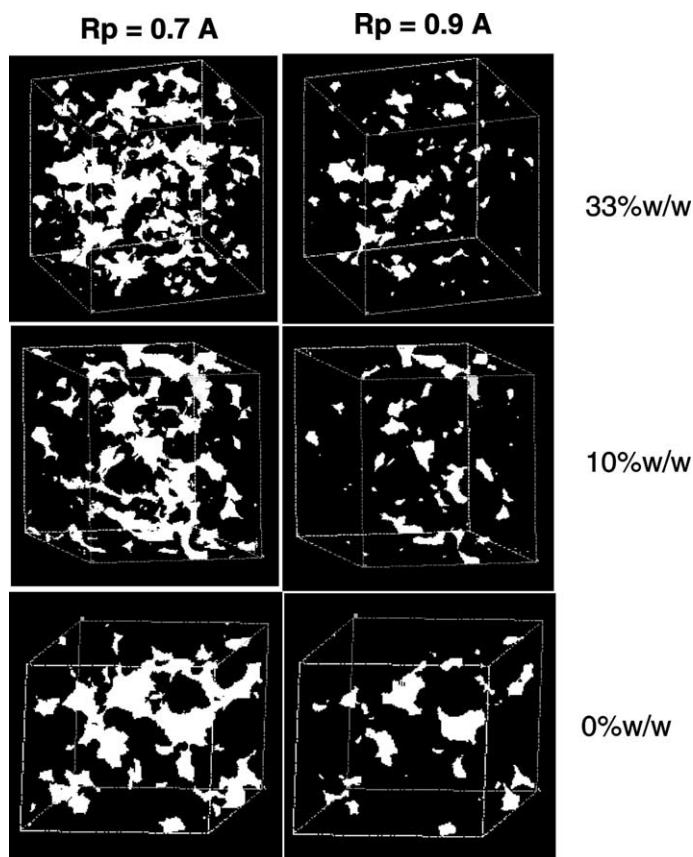


Fig. 2. Free volume accessible to a probe with radius 0.7 (left) and 0.9 Å (right) for amorphous sucrose with 0%, 10% and 33% w/w water. The cell lengths are ~ 20 , 25 and 27 Å, respectively.

than any species in the system; it is close to the 0.55 Å obtained for a glass of random closed packed spheres and well below the 0.9–1.1 Å observed for polymers as polypropylene [14,21].

3. The absence of holes of the size of water or larger. The FV accessible to $R_p = 1.4$ Å was less than 0.01% of the total for all the systems.
4. The free volume fractions for $R_p = 0.45$ Å $\cong R_{pc}$ are in the range 4.8–5.2% for the aqueous mixtures and 6.4% for anhydrous sucrose. These values agree (within the uncertainties of the method) with the 5.5% percolating FV found for model polymers [22].

In summary, our results indicate that although concentrated sucrose solutions behave in their viscoelastic response as polymers, due to the sucrose HBN, they present different FV distribution

than macromolecules: smaller and more spherical voids, not constrained by the connectivity of polymer segments. The low value of the percolating radius discards the possibility of water diffusion through FV channels and stresses the importance of sucrose dynamics for water diffusion.

The addition of water produces a decrease in the friction and glass transition temperature (T_g) known as plasticization [1]. The decrease of T_g with the addition of small molecules can be due to an increase in FV fraction and/or a modification of the mechanism of escape from the topological constraint [2]. Our results indicate that the plasticizer effect of water on sucrose cannot be explained solely on the basis of the total FV fraction, which *decreases* from 0% to 10% water and is rather

insensitive to water content in the range 10–33% w/w (Fig. 2, inset). The decrease of friction with water content may be related, thus, with the facilitation of relaxation routes. Some authors [20] have suggested that water in carbohydrate mixtures increase in mobility due to the replacement of sugar–sugar and water–sugar HB by shorter-lived water–water HB. Next section addresses this issue, through the analysis of water–water connectivity.

3.3. Water connectivity

Two water molecules are considered as connected if they are at a distance shorter than the first minimum of their radial distribution function (*rdf*) in the *actual* mixture. This differs from the criteria of basing the connectivity on the pure water HB distance as used by earlier studies of water clustering in carbohydrate solutions [4,19]. Our results indicate that the first minimum of the *rdf* moves to higher distances, 4 Å for low water content mixtures, as observed in MD for sucrose [23] and monosaccharides [19]. The most remarkable aspect of water distribution is that it is heterogeneous in the scale of a few angstroms (Fig. 3). Water does not form ‘pockets’ but instead forms scattered clusters with chain-like and star-like portions (Fig. 3) that grow with water content. Considering a clustering distance of 4 Å, we find the percolation threshold for water to be between 10% and 18% w/w water (Table 1). The average connectivity increases with water content: 2.0, 2.7 and 4.5 at 10%, 18% and 33% w/w water, respectively.

To interpret water diffusion below water percolation threshold, we propose that water diffusion in rubbery and glassy carbohydrate matrices can be mapped into a dynamic bond percolation problem [24] with two time constants: one associated with the breathing modes of the matrix, that contribute to open and close water-size gates, and another time for the probability of a water molecule to jump either into a water-occupied site – exchange or into a dynamic void. If the probability of the exchange process is higher than the void driven one – as expected in these low FV mixtures – an increase in the coordination between water molecules would enhance diffusion.

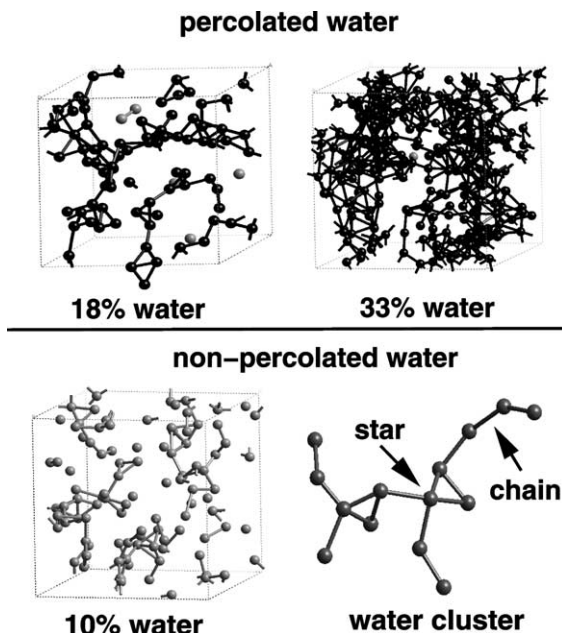


Fig. 3. Water clusters in sucrose solutions. The threshold distance for clustering is 4 Å. Water molecules belonging to a percolated cluster are shown in black, others in gray. Bonds are drawn to show coordination. Left-hand side of lower panel shows a water cluster from a 10% w/w water mixture.

4. Conclusions

We have studied the incremental formation of sugar–sugar HB that gives concentrated sugar solutions their characteristic ‘polymeric’ properties. We computed the sucrose–HBN percolation concentration and found that it coincides with the decoupling of viscosity and diffusion in water–sucrose mixtures [5]. Extended sucrose clusters were found for water contents as high as 50% w/w. We interpret the HBN-percolation to be intrinsically related to the decoupling of viscosity and guest diffusion, and the formation of sucrose HB-restrained clusters to be origin of the decoupling of water and sucrose diffusion.

The explanation of the plasticizer effect usually relies on a simplified theory that assumes a linear increase of free volume of the mixture with water content [2]. We provide the first microscopic study of the FV in water–sucrose mixtures, and show that FV fraction does *not* correlate with the

plasticizer effect, in disagreement with the usual assumption.

We found the width of the free volume channels in concentrated sucrose solutions to be far smaller than water radius, thus stressing the role of matrix dynamics on water diffusion. If the time constant of water–water exchange is faster than those of matrix librations – as expected in the deep supercooled and glassy state – the percolation of the water network (between 10% and 18% w/w water) may have implications for phenomena limited by water transport, as is the case of water crystallization. Interestingly, water–carbohydrate mixtures form ice while cooled only for water content above 20% w/w [1].

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References

- [1] L. Slade, H. Levine, *Crit. Rev. Food Sci.* 30 (1991) 115.
- [2] J.D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1980.
- [3] F. Franks, J.R. Grigera, *Solution Properties of Low Molecular Weight Polyhydroxy Compounds*, Cambridge University Press, Cambridge, 1985.
- [4] E.R. Caffarena, J.R. Grigera, *Carboh. Res.* 315 (1999) 63.
- [5] D. Champion, H. Hervet, G. Blond, M. LeMeste, D. Simatos, *J. Phys. Chem. B* 101 (1997) 10674.
- [6] M. Rampp, C. Buttersack, H.D. Ludemann, *Carboh. Res.* 328 (2000) 561.
- [7] B.P. Hills, Y.L. Wang, H.R. Tang, *Mol. Phys.* 99 (2001) 1679.
- [8] M.P. Allen, D.J. Tildesley, *Computer Simulation of Liquids*, Clarendon Press, Oxford University Press, Oxford, New York, 1989.
- [9] MSI – Accelrys, *Cerius2*, San Diego, 1999.
- [10] S.L. Mayo, B.D. Olafson, W.A. Goddard, *J. Phys. Chem.* 94 (1990) 8897.
- [11] A.K. Rappe, W.A. Goddard, *J. Phys. Chem.* 95 (1991) 3358.
- [12] N. Karasawa, W.A. Goddard, *J. Phys. Chem.* 93 (1989) 7320.
- [13] J.C. Hanson, L.C. Sieker, L.H. Jensen, *Acta Cryst. B* 29 (1973) 797.
- [14] D. Girlich, H.D. Ludemann, *Z. Naturforsch. C* 49 (1994) 250.
- [15] W.A. Goddard, T. Cagin, M. Blanco, N. Vaidehi, S. Dasgupta, W. Floriano, M. Belmares, J. Kua, G. Zamanakos, S. Kashiara, M. Iotov, G.H. Gao, *Comp. Theor. Polymer Sci.* 11 (2001) 329.
- [16] P. Reiser, G.G. Birch, M. Mathlouthi, in: Mathlouthi M. (Ed.), *Sucrose: Properties and Applications*, Blackie Academic and Professional, Glasgow, 1995, p. 186.
- [17] S.L. Shamblin, X.L. Tang, L.Q. Chang, B.C. Hancock, M.J. Pikal, *J. Phys. Chem. B* 103 (1999) 4113.
- [18] V. Oja, E.M. Suuberg, *J. Chem. Eng. Data* 44 (1999) 26.
- [19] C.J. Roberts, P.G. Debenedetti, *J. Phys. Chem. B* 103 (1999) 7308.
- [20] I.J. van den Dries, D. van Dusschoten, M.A. Hemminga, E. van der Linden, *J. Phys. Chem. B* 104 (2000) 10126.
- [21] M.L. Greenfield, D.N. Theodorou, *Macromolecule* 26 (1993) 5461.
- [22] H. Takeuchi, K. Okazaki, *Makromolekul. Chem.* (1993) 81.
- [23] N.C. Ekdawi-Sever, P.B. Conrad, J.J. de Pablo, *J. Phys. Chem. A* 105 (2001) 734.
- [24] A. Nitzan, M.A. Ratner, *J. Phys. Chem.* 98 (1994) 1765.