Relationships between hydration number, water activity and density of aqueous sugar solutions

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Abstract

Hydration numbers (n_h) of simple sugars have been investigated for decades using thermodynamic, spectroscopic as well as molecular modelling techniques. Results were shown to depend on the technique employed. The most reliable values only concern the first hydration shell assuming a maximum oxygen–oxygen distance below 2.8 Å. As concentration increases, sugar–sugar interactions become preponderant and n_h decreases. Assuming that no long range structuring effect is exerted by the solute on water, it is possible to estimate the volume occupied by each of hydration water (with nearly 9% volume contraction) and bulk water from density measurements. Likewise, the volume occupied by non-hydrated sugar molecules in the aqueous medium allows finding for sugar density in the aqueous medium a value comparable to that of solid crystalline form. On the other hand, using the literature values of aqueous sugar solution densities, it was possible to calculate the hydration numbers at different temperatures and concentrations. These values of n_h show a noticeable decrease as temperature is raised and concentration increased. Decrease in n_h can be explained assuming a partial occupation of potential hydration sites (OHs) because of differences in H-bonds lifetimes on the one hand and molecular folding around glycosidic bond on the other.

Calculation of water activity coefficients (f_w) based on n_h values was made for sucrose solutions. Results show the same trend as found previously [Starzak, M., & Mathlouthi, M. (2006). Temperature dependence of water activity in aqueous solutions of sucrose. *Food Chemistry, 96*, 346–370] for sucrose, i.e. a decrease of f_w with increasing molar concentration. Temperature effect on water activity coefficients and hydration numbers is also determined. It shows a decrease in hydration number as temperature is increased.

In this paper, empirical relations are proposed to calculate water activity coefficients and hydration numbers at different concentrations and temperatures by use of accurate density values. These models were first applied to sucrose, the most documented sugar and applied to disaccharides (maltose, trehalose) and monosaccharides (glucose, fructose).
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Keywords: Monosaccharide; Disaccharide; Hydration number; Density; Water activity coefficient

1. Introduction

Aqueous solutions of small carbohydrates present more than an interest in such fields as food science, biology or physical chemistry. Apart from their obvious role in nutrition or biotechnology, they are often taken as standards for the calibration of laboratory refractometry or viscosity devices (sucrose) or as simple molecular models for the simulation of solvent–nonelectrolyte interactions. However, a binary mixture composed of water and small sugar is not as simple as it seems to be when molecular structure is investigated. The sugar molecule, on the one hand, is sensitive to solvent polarity which yields solute conformational changes and the solvent, on the other hand, might exhibit solvation and self association phenomena. As concentration is increased, solute–solvent interactions become more complex and the clustering of solute molecules may occur as well.

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Despite the complexity of such systems, it is worth considering a practical approach for revealing from the abundant previous work on hydration numbers, activity coefficients and solution properties of sugars, a rational way of interpretation of their structure based on easily available data like density and water activity values at different temperatures and concentrations. Among small carbohydrates, the most studied one is sucrose for which the literature is particularly rich in information using all types of experimental techniques as well as molecular modelling. Our purpose is to thoroughly study the relationships between density and water activity in the case of sucrose and then apply the same approach to other sugars. At the origin of the complexity of the structure of water–sucrose binary mixture, are the different species of hydrogen bonds involved.

Water is known as a highly self-associating liquid as well as solvating (hydrating) agent. On the other hand, the sucrose molecule with its eight hydroxyl groups, three hydrophilic oxygen atoms and 14 hydrogen atoms, can readily interact through hydrogen bonding with water as well as other sucrose molecules. Therefore, at least three elementary types of molecular interactions take place in sucrose solutions: water–water, sucrose–water and sucrose–sucrose, all resulting in the formation of intermolecular hydrogen bonds. Likewise, aggregates between already formed sucrose–sucrose or sucrose–water associates are possible as well. Moreover, the possible presence of sucrose conformers due to the formation of intra-molecular hydrogen bonds (Immel & Lichtenthaler, 1995; Mathlouthi, 1981; Mathlouthi, Luu, Meffroy-Biget, & Luu, 1980) would make the overall picture even more complicated.

The first rigorous chemical model of the sucrose–water system was due to Scatchard (1921). The model in its most general form accounts for hydration of sucrose as well as association of water to dimers. The hydration reaction leads directly to an assumed hydrate. Scatchard (1921) postulated the formation of either hexahydrate or heptahydrate. A satisfactory agreement with experimental osmotic coefficient data was obtained at sucrose concentrations not exceeding 50% w/w. The model proposed by Stokes and Robinson (1966) is a natural extension of the Scatchard model. Although this model ignores water association, it introduces the important concept of successive stepwise equilibria for the hydration of sucrose, instead of the rather unrealistic single-step mechanism proposed by Scatchard. In addition, the model assumes that the probability of hydration/dehydration of a sucrose molecule does not depend on the number of water molecules which are already attached to it. According to the Stokes–Robinson model, the maximum number of binding sites available on a single molecule of sucrose is 11. The model fits not only the dilute region data, but also shows a fairly good performance up to 75% w/w sucrose. Unfortunately, the model overestimates the water activity coefficient for more concentrated solutions.

The rare models accounting for sucrose–sucrose interactions were introduced by Starzak and Mathlouthi (2002) and Van Hook (1987). Apart from hexahydrates, it also assumes the formation of hexameric clusters of non-hydrated sucrose. It ignores, however, association of water molecules. Although the concept never reached the form of a rigorous chemical model of water activity, results of computations revealed the key role of the sucrose association mechanism on the water activity behaviour in highly concentrated solutions. The incorporation of this mechanism remarkably improves the model performance beyond 80% w/w sucrose. The water activity coefficient shows a minimum at about 85% w/w sucrose and then starts to increase, rapidly exceeding the value of one. The process has a simple physical interpretation. Sucrose clustering reduces the number of free sucrose molecules in the solution and at the same time lowers the total number of molecules in the system. As a result, at a sufficiently high degree of sucrose clustering (high sucrose concentration), the mole fraction of free water becomes higher than the nominal mole fraction of water resulting from its original quantity used to make up the solution. This is, in fact, what makes the observed water activity coefficient greater than one. One should bear in mind, however, that Van Hook's model gives a very simplistic picture of chemical transformation taking place in the real solution. The incorporation of an extended model of water association, a more realistic model for sucrose hydration (like that of Schönert, 1968) as well as cascading sucrose clustering (association) equilibria, similar to those developed by Stokes and Robinson (1966) for hydration, should produce a powerful model of the sucrose–water system valid in the entire range of sucrose concentrations.

As a general rule, the hydration numbers (n_h) given in literature for sucrose as well as for other saccharides greatly varies with the technique used to determine it. It may range from 1.8 (NMR) to 21 (NIR) as reported by Allen and Wood (1974). From the viscosity results, using Einstein's relation for intrinsic viscosity, it was possible to obtain $n_h = 5.3$ for sucrose (Mathlouthi & Génotelle, 1994). From water activity measurements a hydration number of $5H_2O$/sucrose was proposed (Akhumov, 1981) and ultrasound velocity and density data led to a value of 13.8 (Galema & Høiland, 1991). Apart from the difference in sensitivity of each of the techniques used to weak energy interactions, the scattering of n_h values has also other origins like the difference in reactivity of the eight hydroxyls of the sucrose molecule (Hough & Khan, 1978) or the folding of sucrose molecule and the establishment of sucrose–sucrose interaction when concentration is increased.

The hydration of other sugars than sucrose has been investigated using different experimental techniques as well as molecular modelling. Water vapour pressure above aqueous solutions of glucose, maltose and related oligomers was determined experimentally (Abderafi & Bounahmidi, 1994; Cooke, Jónsdóttir, & Westh, 2002;

Rüegg & Blanc, 1981; Taylor & Rawlinson, 1955). Likewise activity coefficients were predicted for mono- and disaccharides using the modified UNIQUAC model (Larsen, Rasmussen, & Fredenslund, 1987), especially by Catté, Dussap, Achard, and Gros (1994). More recently, Ferreira, Brignole, and Macedo (2003) applied the A-UNIFAC model which incorporates the effect of hydrogen bonding in water–sugar systems to stimulate water activity coefficient.

A particular interest is devoted to the disaccharide trehalose, because of its bioprotective ability and the numerous potential applications it might have in food, pharmaceutical and cosmetic industry (Crowe et al., 2001; Wang, 1999). Water–disaccharide (trehalose, maltose, sucrose) interactions were investigated using molecular dynamics simulation (Lerbret, Bordat, Affouard, Descamps, & Migliardo, 2005). In particular, trehalose was found more hydrated than maltose and sucrose in the conditions of modelling chosen by authors, which covered a concentration range from 4% to 66% at 0 °C and 100 °C. In the same simulation, trehalose was found more flexible than sucrose and maltose at low concentrations and forming larger trehalose–trehalose clusters as concentration is increased from 33% to 66%.

Our aim in this work is to show that the abundant literature on density, water activity and hydration numbers of mono- and disaccharides in aqueous solutions can be used to approach their properties at the molecular level providing some hypothesis. Our approach is first applied to sucrose–water system for which the most reliable and precise data are available and than extended to mono- and disaccharides.

2. Density and hydration in aqueous sucrose solution

2.1. Effect of hydration on sucrose solution density

An attempt is made to find relationships between solution properties and hydration of sucrose. To establish the relationship between water activity and density of a sucrose solution, it was needed to use an approximation relative to free water. For that, we had to hypothesize that the volume occupied by water molecules not bound to sucrose in aqueous solution is not affected by the solute. Therefore, bulk water in the solution has the same density as pure water, i.e. 998.2 kg/m³ at 20 °C. Using this hypothesis and using density tables (Emmerich, 1994) and sucrose hydration numbers from literature (Akhumov, 1975; Bressan & Mathlouthi, 1994; Starzak, Peacock, & Mathlouthi, 2000), we could calculate the volumes of free and bound water as well as the volume of hydrated sucrose (Table 1).

After calculation of bound water mass, we may deduce mass and volume of free water. This allows obtaining the volume occupied by hydrated sucrose. Fig. 1 represents the variation of sucrose molar volume given in Table 1 as a function of hydration number n_h.

From these results it is possible to draw the following conclusions:

- The volume $V_{hS,20}$ occupied by a hydrated sucrose molecule at 20°C varies linearly in function of hydration number n_h

$$V_{hS,20} = 221 + 16.4n_h \qquad (1)$$

- As hydration takes place, bound water augments the volume of hydrated sucrose with an increment of 16.4 ml/mol sucrose, which means that the volume occupied by free water decreases roughly about 1.65 ml/mol sucrose ($18.05 - 16.4 = 1.65$ ml, i.e. 9.2%). It is possible, on the other hand to estimate the reduction of volume of the hydration water molecule assuming an appropriate H-bond length.

2.2. Estimation of volume contraction due to H-bonding

In Fig. 2a the position of water molecule just before establishing a hydrogen bond with an oxygen atom of sucrose hydroxyl, indicates alignment of O–H–O′ and a distance between molecules estimated to 0.30 Å (Fig. 2a). The distance (O···H = 1.8 Å) usually adopted for strong

Table 1
Calculated volumes of free and bound water and hydrated sucrose at 20 °C

	Sucrose concentration (g%g solution)											
	0	10	20	30	40	50	60	70	80	85	90	95
Density (g/ml)[a]	0.9982	1.0382	1.0810	1.1270	1.1765	1.2296	1.2866	1.3475	1.4122	1.4459	1.4805	1.5159
Mass of total water (g)	–	90	80	70	60	50	40	30	20	15	10	5
Hydration number	–	**5**	**4.95**	**4.9**	**4.8**	**4.7**	**4.2**	**3.4**	**2.5**	**2**	**1.53**	**0.85**
Mass of bound water (g)	–	2.632	5.211	7.737	10.11	12.3684	13.26	12.53	10.53	8.947	7.247	4.25
Mass of free water (g)	–	87.37	74.79	62.26	49.89	37.6316	26.74	17.47	9.474	6.053	2.753	0.75
Solution volume (ml)	–	96.32	92.51	88.73	85	81.3273	77.72	74.21	70.81	69.16	67.54	65.97
Free water volume (ml)	–	87.53	74.92	62.38	49.98	37.70	26.79	17.51	9.49	6.06	2.76	0.75
Hydrated sucrose volume (ml/mol)	–	8.79	17.58	26.35	35.01	43.63	50.94	56.71	61.32	63.10	64.79	65.22
Hydrated sucrose molar volume (ml)	–	**301.0**	**301.0**	**300.7**	**299.6**	**298.7**	**290.6**	**277.3**	**262.4**	**254.1**	**246.4**	**235**

[a] Emmerich (1994).

H-bonds (Guinier, 1980), was chosen for the establishing of water–sugar H-bond (Fig. 2b). It is not easy to quantify the volume contraction in solution due to H-bonding. Decrease of volume can be, however, roughly considered as partially composed of H atom overlapping the van der Waals sphere of sucrose oxygen on the one hand and of a fraction of the volume of vacuum separating molecules on the other.

By reference to the hypothesis illustrated in Fig. 2b, the estimation including surrounding vacuum, gives a volume loss (contraction) of 2.6 Å^3 or $2.6/30 \times 100 = 8.7\%$ (which is close to 9.2%, the contraction estimated from density), where 30 represents the volume of a single water molecule in the liquid state (molar volume of water divided by Avogadro number).
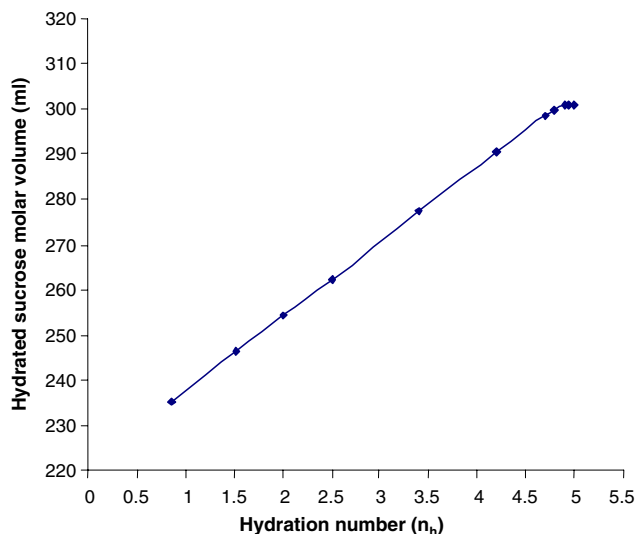
2.3. Consequences on the molar volume of sucrose in aqueous solution

The van der Waals volume of a single sucrose molecule (278 Å^3) represents the sum of atoms volumes taking into account bond lengths. Equivalent sphere has a diameter of 8.1 Å. Its mass is 568.4×10^{-24} g and the specific mass of a sucrose molecule is 2.04 g/ml while crystal density is 1.587 g/ml at 20 °C.

In aqueous solution, the sucrose molecule (considered here as not hydrated) occupies a volume composed of that of the molecule itself plus the interstitial vacuum. It corresponds to the volume of a virtual envelope surrounded with *free* water molecules. From density results, the volume occupied by sucrose molecule is approximately 221 ml/mol (Fig. 1), which corresponds to 367 Å^3 for a non-hydrated molecule. This apparent volume involves 24%

Fig. 1. Hydrated sucrose molar volume of vs. hydration number (n_h).
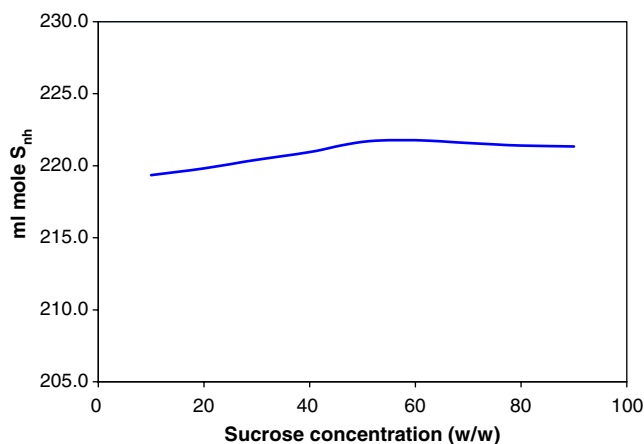

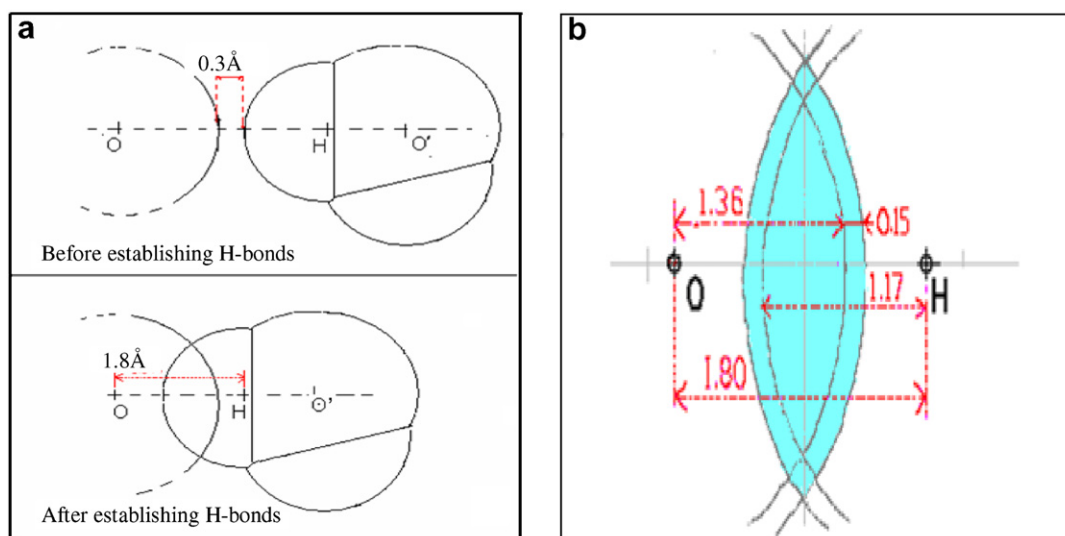Fig. 3. Molar volume (ml/mol) of non-hydrated sucrose vs. sucrose mass concentration.

Fig. 2. Schematic representation of water molecule before and after establishing H-bond with sucrose oxygen (a) and the dimensions of portions of spheres used to calculate volume loss (b) (bond distances from Guinier, 1980).

Table 2
Molar volume (ml/mol) and density of non-hydrated sucrose molecule

	C (g%g solution)								
	10	20	30	40	50	60	70	80	90
n_h	5.00	4.97	4.96	4.82	4.57	4.07	3.38	2.59	1.58
S_h (ml/mol)	301.3	301.0	300.8	299.7	298.7	290.6	277.3	262.4	246.4
S_{nh} (ml/mol)	219.4	219.8	220.4	221.0	221.7	221.8	221.6	221.4	221.3
Non-hydrated Sucrose density (g/ml)	1.5605	1.557	1.5525	1.549	1.546	1.545	1.545	1.545	1.546

of vacuum between atoms represented by their van der Waals spheres. The equivalent sphere diameter is 8.86 Å and the corresponding specific mass is 1.549 g/ml at 20 °C. The specific mass of sucrose is constant in the whole range of concentrations (Fig. 3 and Table 2). Except for high concentrations (>95%) which are extrapolated, all density data are experimental (Emmerich, 1994).

It may also be observed that a slight change in specific mass slope occurs at low concentrations (Fig. 3). The calculated value of sucrose specific mass (1.549) also corresponds to the value of sucrose solution density at 20 °C extrapolated to 100% concentration. This observation was also made at other temperatures.

It can be noticed from Fig. 1 that the variation of volume occupied by 1 mol of hydrated sucrose in function of hydration number n_h shows a slight curvature for n_h approaching 5, namely for dilute solutions. An attempt to explain such a deviation is given in Table 2.

The variation of the molar volume, V_{nh}, of non-hydrated sucrose molecules in function of solution concentration is reported in Fig. 3. A slight decrease of V_{nh} is observed as concentration decreases. It is assigned to the molecular folding around glycosidic bond (Mathlouthi, 1981). As concentration overreaches 40%, V_{nh} is stabilised and the conformation of sucrose becomes comparable to that found in the crystal involving two intra-molecular H-bonds.

Exploitation of density data allows concluding that:

- For $n_h = 0$ (Fig. 1), non-hydrated sucrose molecule occupies in aqueous solution a volume approximately equal to 221 ml, which corresponds to a specific mass equal to 1.549 g/ml, and this value is nearly constant at all concentrations above 40%.
- As n_h becomes higher than 4, a small variation of molar volume slope is observed (Fig. 3). This decrease in sucrose molar volume of about 1%, may be assigned to a change in the sucrose molecule conformation (unfolding) in dilute solution as was shown from Raman and X-ray studies (Mathlouthi, 1981).

3. Density and water activity of sucrose aqueous solutions: effect of temperature

3.1. Effect of temperature on sucrose molar volume

It is well known that increase in temperature provokes an increase of water activity coefficient and a decrease in hydration number. We have shown above the relationships between density and hydration number at 20 °C. Effect of temperature on sucrose molar volume is estimated using the same method as at 20 °C (Table 1). Calculation at 0 and 100 °C was based on density tables (Emmerich, 1994) and hydration numbers from literature (Lerbret et al., 2005). Values other than 0, 20 and 100 °C are interpolated. Results are summarised in Table 3. The molar volume of non-hydrated sucrose shows an expansion as temperature is increased and the specific mass decreases.

3.2. Effect of temperature on hydration number and water activity coefficients

The first step of this determination consists in estimating the effective volume of water in solution (difference between solution volume and volume occupied by non-hydrated sucrose). A variation ΔV between this volume and that of the same mass of water considered as *free* water corresponds to the shrinkage of hydration water molecules. As a first approximation, we consider the loss of volume due to shrinkage equal to 9.2% as was found at 20 °C, although a slight change might occur as temperature is varied. ΔV and hydration number (n_h) are related by the following equation:

$$\Delta V = n_h \times (S/M) \times (18.02/\rho_w) \times 0.092 \qquad (2)$$

where S (% w/w) is the concentration of sucrose in solution; $M = 342.3$, the molar mass of sucrose and ρ_w, the density of pure water.

This equation allows for obtaining n_h and activity coefficients for aqueous sucrose solutions between 0 and 80 °C and in the mass concentration range (10–90%, w/w) (Table 4). Hydration numbers shown in Table 4 are slightly

Table 3
Effect of temperature on non-hydrated sucrose molar volume

	Temperature (°C)					
	0	20	40	60	80	100
Molar volume of non-hydrated sucrose (ml/mol)	219.5	221	222.4	223.9	225.3	227.2
Density of non-hydrated sucrose (g/ml)	1.559	1.549	1.539	1.529	1.519	1.509

Table 4
Hydration numbers of sucrose in solution at temperatures between 0 and 80 °C

Temperature (°C)	Sucrose concentration (% w/w)									
	10	20	30	40	50	60	70	80	85	90
0	7.55	7.06	6.53	5.94	5.26	4.50	3.63	2.64	2.09	1.51
20	5.99	5.65	5.26	4.83	4.32	3.73	3.04	2.25	1.80	1.32
40	5.12	4.86	4.55	4.18	3.76	3.26	2.67	1.98	1.59	1.16
60	4.65	4.40	4.12	3.79	3.40	2.94	2.39	1.75	1.39	0.99
80	4.37	4.12	3.85	3.53	3.16	2.71	2.19	1.56	1.21	0.83
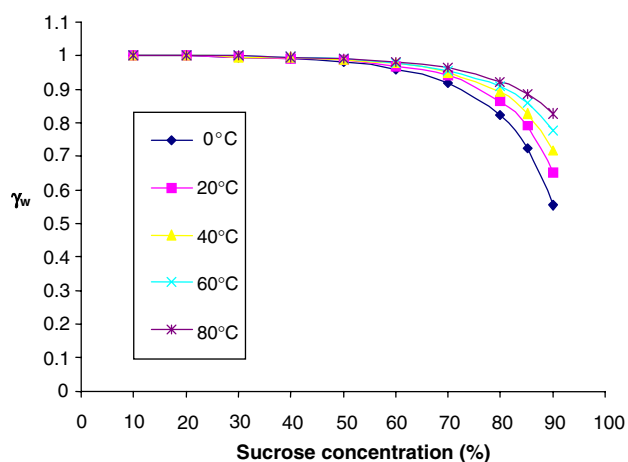
Fig. 4. Water activity coefficients in sucrose solutions at different temperatures and concentrations.

Fig. 5. Variation of molar volume of hydrated sucrose with hydration number at 100 °C.

higher at low concentrations (<30%), around 7H$_2$O/sucrose molecule at 0 °C, 5–6 at 20 °C and 4 at 80 °C. These values nevertheless lie within the most frequently used sucrose hydration numbers reported in literature.

Water activity coefficients γ_w derived from hydration water reported in Table 4 show stronger dependence than that expected from the application of classical thermodynamic approach on concentration and temperature as concentrations are raised above 50% (Fig. 4). Such behaviour was observed and discussed by Starzak and Mathlouthi (2006) and Starzak et al. (2000).

3.3. Effect of temperature on sucrose molar volume

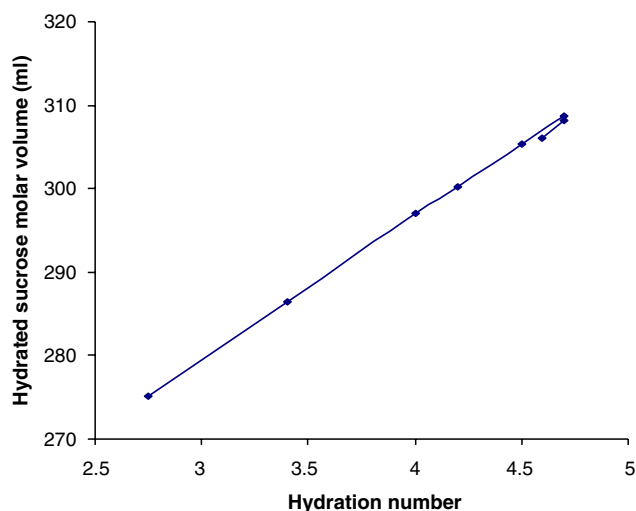*At 100 °C:* Using hydration numbers obtained in Table 4, it is possible to apply the same approach as at 20 °C for the determination of the molar volume of hydrated sucrose as well as specific mass. Results are reported in Table 5 and Fig. 5. From the data in Table 5 it is possible to express molar volume of hydrated sucrose as a function of hydration number

$$V_{hS,100} = 227.2 + 17.2n_h \qquad (3)$$

This yields for hydrated sucrose an apparent density of 1.509 g/ml at 100 °C and a volume of 17.2 ml/mol bound H$_2$O. Apparent density is comparable to the value (1.507) obtained by extrapolation of sucrose solution density at 100 °C. The same agreement between calculated and extrapolated values was observed at 20 °C.

Table 5
Density and molar volume of hydrated sucrose at 100 °C

	Sucrose concentration (% w/w)								
	0	5	10	20	30	40	50	60	70
Volumic mass (g/ml)	0.95834	0.97716	0.99666	1.0379	1.0824	1.13048	1.18243	1.23855	1.29907
Hydration number	–	**4.6**	**4.7**	**4.7**	**4.5**	**4.2**	**4**	**3.4**	**2.75**
Total water mass (g)	–	95	90	80	70	60	50	40	30
Bound water mass (g)	–	1.21053	2.47368	4.94737	7.10526	8.84211	10.5263	10.7368	10.1316
Free water mass (g)	–	93.7895	87.5263	75.0526	62.8947	51.1579	39.4737	29.2632	19.8684
Solution volume (ml)	–	102.337	100.335	96.3484	92.3873	88.458	84.5716	80.7396	76.9781
Free water volume (ml)	–	97.8666	91.3312	78.3152	65.6288	53.3818	41.1896	30.5353	20.7321
Hydrated sucrose molar volume (ml)	–	**306.07**	**308.205**	**308.637**	**305.314**	**300.165**	**296.993**	**286.416**	**275.043**

Table 6
Density and molar volume of hydrated sucrose at 0 °C

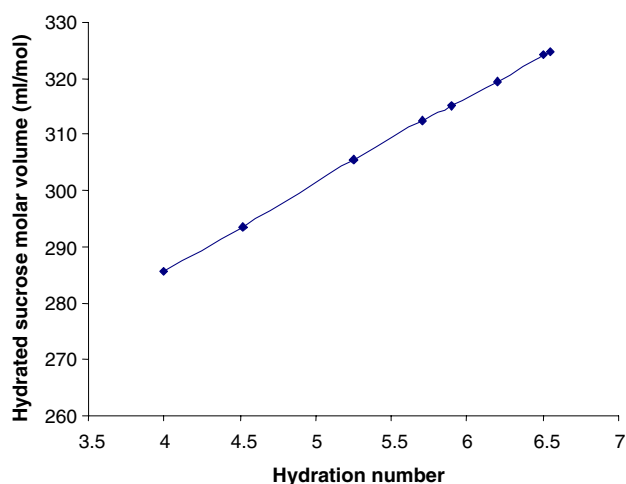|	Sucrose concentration (% w/w)								
	0	5	10	20	30	40	50	60	70
Density	0.99984	1.02005	1.04098	1.0851	1.13243	1.18319	1.23754	1.29559	1.35733
Hydration number	–	**6.55**	**6.5**	**6.2**	**5.9**	**5.7**	**5.25**	**4.52**	**4**
Total water mass (g)	–	95	90	80	70	60	50	40	30
Bound water mass (g)	–	1.72368	3.42105	6.52632	9.31579	12	13.8158	14.2737	14.7368
Free water mass (g)	–	93.2763	86.5789	73.4737	60.6842	48	36.1842	25.7263	15.2632
Solution volume (ml)	–	98.0344	96.0633	92.1574	88.3057	84.5173	80.8055	77.1849	73.6741
Free water volume (ml)	–	93.2912	86.5928	73.4854	60.6939	48.0077	36.19	25.7304	15.2656
Hydrated sucrose molar volume (ml)	–	**324.717**	**324.176**	**319.571**	**315.05**	**312.431**	**305.437**	**293.548**	**285.617**

Fig. 6. Variation of molar volume of hydrated sucrose with hydration number at 0 °C.

At 0 °C: The relation between molar volume of sucrose at 0 °C and n_h is linear up to 40% mass concentration

$$V_{hS,0} = 219.5 + 16.5n_h \tag{4}$$

Above 40% ($n_h > 5.5$), $V_{hS,0}$ deviates from linearity (Table 6 and Fig. 6). At 0 °C, the values of apparent density of sucrose and molar volume of bound water are, respectively, 1.559 g/ml and 16.45 ml/mol H_2O. It should also be noted that the apparent density (1.559) is comparable to that obtained from extrapolation at concentration = 100% and 0 °C.

4. Density and hydration in aqueous solutions of monosaccharides, glucose and fructose

The first part of this work was devoted to sucrose for which literature data (ICUMSA official tables of density, papers on hydration and water activity reviewed in introduction) is available in a large domain of concentrations and temperatures. It was possible, starting from accurate density tables and hydration numbers to determine the relation between density and the volume occupied in solution by sucrose molecules on the one hand and water molecules on the other. For a good fit, it was needed that the shrinkage of hydration water molecules is accounted for. This relation can be written as follows:

$$100/\rho_{sol} = S/\rho_s + (100 - S)/\rho_w - \Delta V \tag{5}$$

where ρ_{sol} is solution density; ρ_s is sucrose apparent mass density in solution; ρ_w pure water density; S concentration in g sugar % g solution and ΔV, defined above is given by the following equation:

$$\Delta V = n_h \times (S/M) \times (18.02/\rho_w) \times 0.092 \tag{2}$$

The applicability of the above equations to mono- and disaccharides might be of practical use in food industry. The sugars chosen for this purpose are the monosaccharides (D-glucose and D-fructose) on the one hand, and the disaccharides maltose and trehalose on the other. All these sugars differ from one another quantitatively and qualitatively as concerns their hydration.

Table 7
Relations between density, mass concentration and hydration of D-glucose in aqueous solution; estimation of molar volume of D-glucose in solution

	Glucose concentration (% w/w)				
	37.12	41.42	51.15	57.58	61.55
Density	1.1586	1.17962	1.22992	1.26463	1.28702
Water activity	0.9354	0.9220	0.8819	0.8462	0.8155
Hydration number	**2.45**	**2.32**	**2.08**	**1.87**	**1.83**
Solution volume (ml/100 g)	86.311	84.773	81.306	79.075	77.699
Bound water mass (g)	9.0997	9.6182	10.6632	10.7469	11.2389
Free water mass (g)	53.7814	48.9569	38.182	31.6766	27.2089
Free water volume (ml)	53.8784	49.0452	38.2509	31.7337	27.258
Volume of hydrated glucose (ml)	32.4327	35.7278	43.0552	47.3411	50.4409
Molar volume of hydrated glucose (ml/mol)	**157.4**	**155.4**	**151.6**	**148.1**	**147.6**

Table 8
Relations between density, mass concentration and hydration of D-fructose in aqueous solution; estimation of molar volume of D-fructose in solution

	Fructose concentration (% w/w)			
	52.63	63.83	71.43	76.92
Density[a]	1.24406	1.3077	1.35332	1.37145
Water activity	0.8712	0.7895	0.6947	0.6004
Hydration number	**2.24**	**1.92**	**1.72**	**1.50**
Solution volume (ml/100 g)	80.382	76.470	73.892	72.916
Bound water mass (g)	11.7781	12.2259	12.3158	11.5197
Free water mass (g)	35.5904	23.9443	16.2556	11.5572
Free water volume (ml)	35.6545	23.9875	16.2849	11.5781
Volume of hydrated fructose (ml)	44.7274	52.4827	57.6074	61.3375
Molar volume of hydrated fructose (ml/mol)	**153.1**	**148.1**	**145.3**	**143.7**

[a] Bubnik et al. (1995).

Published experimental water activity coefficients for monosaccharides are not accurate enough to allow estimation of hydration numbers especially for dilute solutions. This is why the values calculated in Tables 7 and 8 are based on literature data (Cooke et al., 2002) above a concentration of 37% for D-glucose and 52% for D-fructose. Hydration numbers are obtained by application of Eq. (2) using density values from Bubnik, Kadlec, Urban, and Bruhns (1995). Results reported in Fig. 7 give values for n_h ranging from 3.83 to 1.89 for D-fructose and 3.56–1.35 for D-glucose at concentrations between 5% and 70%. These values slightly higher for D-fructose than D-glucose are comparable to literature.

Estimation of the volume of hexoses in aqueous solution was performed using the same procedure as for sucrose. Apparent density is found identical for both hexoses ($\rho = 1.526$ g/ml) and slightly lower than that of sucrose (Tables 7 and 8).

From the data reported in Table 7, it is possible to deduce the relation between molar volume of hydrated D-glucose (V_g) and hydration number n_h. Shrinkage of hydration water volume was found equal to 10%

$$V_g = 118.05 + 16.2n_h \qquad (6)$$

Likewise, the specific mass of non-hydrated D-glucose in solution is

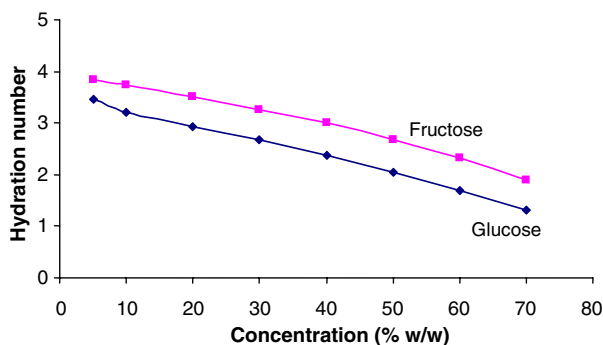$$\rho_g = 160.16/116.05 = 1.526 \qquad (7)$$

Table 8 allows finding a relation between molar volume of hydrated fructose (V_f) and hydration number (n_h) and the volume shrinkage for hydration water in D-fructose solutions was 10.8%

$$V_f = 118.0 + 16.10n_h \qquad (8)$$

The differences in hydration numbers and volume shrinkage of hydration water show a higher compatibility of D-fructose with water structure, which was already demonstrated using different experimental techniques (Mathlouthi et al., 1980).

5. Density and hydration in aqueous solutions of disaccharides, maltose and trehalose

5.1. Maltose molar volume in solution and hydration at 20 °C

Hydration numbers are obtained by application of Eq. (2). Results reported in Fig. 8 for maltose and trehalose give values for n_h comparable to that found by previous workers (Lerbret et al., 2005). The n_h values are comparable to that of sucrose above a concentration of 40% and the difference between the two sugars and sucrose increases rapidly in dilute solution. The causes of this difference are very likely a better accuracy of the sucrose literature

Fig. 7. Variation of hydration number of fructose and glucose in function of mass concentration.
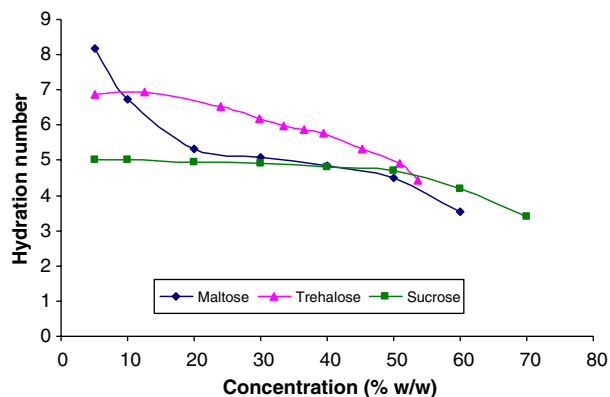

Fig. 8. Variation of hydration number in function of mass concentration of sucrose, maltose and trehalose in aqueous solution.

data, on the one hand and the higher flexibility of sucrose molecule in water on the other.

We have estimated the volume occupied by a molecule of maltose in function of the density of aqueous solution at 20 °C (*Handbook of chemistry and physics* (69th ed.), 1988–1989) and the water activity obtained as the ratio p/p_0, $p_0 = 3.152$ kPa, taken from saturated water vapour tables and p, the value of water vapour pressure over maltose solution given by Cooke et al. (2002). Results for mass concentrations between 40% and 60% (range of concentrations where a_w is determined with sufficient accuracy) are reported in Table 9. From this table, it is possible to establish the relation between maltose molar volume and hydration number

$$V_{\text{maltose}} = 220.46 + 16.46 n_h \qquad (9)$$

Values of molar volume of maltose (220.5 ml/mol) and that of hydration water (16.46 ml/mol) are comparable to results found for sucrose. Likewise, the value of specific mass of maltose in concentrated aqueous solution was found equal to 1.550 g/ml (1.549 for sucrose).

5.2. Hydration number of maltose from density – comparison to previous work

The method applied to sucrose solutions, based on density data and hypothesis on volume contraction of hydra-

tion water which allowed determination of hydration numbers in a wide range of concentrations (Table 2) was applied to maltose aqueous solutions between 0% and 60%. Results are summarised in Table 10.

The results of calculation of hydration numbers are compared to data from literature in Table 11. It may be observed that the difficulty of measurement of water vapour pressure (Cooke et al., 2002) over dilute solutions yields values of n_h largely higher than that obtained using our "density method" or the values obtained by molecular dynamic simulation (Lerbret et al., 2005). The hydration numbers based on our method of exploitation of density data at 20 °C lie between the results obtained at 0 °C and 100 °C by Lerbret et al. (2005), except for dilute solution. Discrepancies very likely originate from geometric criteria chosen by Lerbret et al. (2005) in their simulation. We have only made the comparison with the type I geometric criteria which stand for strong H-bonds (O–H···O distance < 3.4 Å and bond angle = 160°).

5.3. Trehalose hydration from density

Whereas density tables exist for sucrose for more than a century, data relative to solution properties of trehalose are recent. For sucrose, the accuracy of data is guaranteed by the International Commission of Unified Methods of Sugar Analysis (ICUMSA, 1994) which allows them to

Table 9
Estimation of the volume occupied by a maltose molecule for different mass concentration at 20 °C

	Maltose concentration (% w/w)			
	44.57	50.32	53.08	57.47
Density	1.2008	1.2322	1.2475	1.2717
Water vapour pressure (kPa)	2.9934	2.9483	2.922	2.8723
Solution water activity	0.94970	0.93537	0.92703	0.91125
Hydration number	**4.75**	**4.29**	**4.09**	**3.79**
Water fraction (g/100 g of solution)	55.43	49.68	46.92	42.53
Bound water mass (g)	11.146	11.349	11.424	11.473
Free water mass (g)	44.284	38.331	35.496	31.057
Solution volume (ml)	83.279	81.158	80.164	78.635
Free water volume (ml)	44.364	38.4	35.56	31.113
Hydrated maltose volume (ml)	38.916	42.758	44.604	47.522
Maltose molar volume (ml/mol)	**298.87**	**290.86**	**287.64**	**283.05**

Table 10
Hydration number of maltose for various concentrations at 20 °C

	Maltose concentration (% w/w)							
	0	5	10	20	30	40	50	60
Density	0.9982	1.0183	1.0385	1.0806	1.1267	1.1766	1.2304	1.2855
Solution volume (ml)	–	98.203	96.293	92.541	88.755	84.991	81.274	77.791
Total mass of water (g)	–	95	90	80	70	60	50	40
Volume of maltose (ml)	–	3.2250	6.4499	12.8999	19.3498	25.7998	32.2497	38.6997
ΔV(solution − maltose) (1)	–	94.978	89.843	79.641	69.405	59.191	49.025	39.091
Mass total water/water density (2)	–	95.171	90.162	80.144	70.126	60.108	50.090	40.072
(2) − (1)	–	0.193	0.320	0.503	0.721	0.917	1.066	0.981
Bound water (mol)	–	0.11903	0.19666	0.30958	0.44395	0.56461	0.65582	0.60384
Hydration number	–	**8.17**	**6.75**	**5.31**	**5.08**	**4.84**	**4.50**	**3.45**

Table 11
Comparison of hydration numbers of maltose in aqueous solution

	Maltose concentration (% w/w)							Reference
	5	10	20	30	40	50	60	
Hydration number at 25 °C	–	14	8.4	6	5	4.3	3.6	Cooke et al. (2002)
Hydration number at 0 °C	–	6.6	6.4	6	5.6	5.2	5	Lerbret et al. (2005)
Hydration number at 100 °C	–	5	4.8	4.5	4.3	4.1	3.6	Lerbret et al. (2005)
Hydration number at 20 °C	8.17	6.75	5.31	5.08	4.84	4.50	3.45	This work

Table 12
Molar volume of trehalose in aqueous solution for various concentrations at 20 °C

	Trehalose concentration (% w/w)										
	0.00	5.12	12.54	23.92	29.85	33.49	36.46	39.45	45.34	50.85	53.66
Density[a]	0.9982	1.01870	1.04999	1.10128	1.12960	1.14760	1.16275	1.17836	1.20956	1.24108	1.25490
Total water mass (g)	100	94.88	87.46	76.08	70.15	66.51	63.54	60.55	54.66	49.15	46.33
Hydration number	–	6.88	6.94	6.52	6.2	5.99	5.86	5.76	5.31	4.91	4.44
Bound water mass (g)	–	1.85	4.58	8.20	9.73	10.55	11.24	11.95	12.67	13.13	12.53
Free water mass (g)	–	93.02	82.87	67.87	60.41	55.95	52.30	48.59	41.99	36.01	33.79
Solution volume (ml)	–	98.16	95.23	90.80	88.52	87.13	86.00	84.86	82.67	80.57	79.68
Free water volume (ml)	–	93.19	83.03	67.99	60.52	56.05	52.40	48.68	42.07	36.08	33.86
Hydrated trehalose volume (ml)	–	4.97	12.21	22.81	28.01	31.09	33.61	36.18	40.61	44.50	45.83
Trehalose molar volume (ml/mol)	–	332.30	333.29	326.40	321.17	317.72	315.56	313.95	306.58	299.54	292.32

[a] Elias and Elias (1999).

be adopted as official methods in commercial transaction. Among the more or less complete set of data on trehalose density, we have chosen the values reported by Elias and Elias (1999). Using these density data, we have applied the same reasoning as for sucrose to obtain the characteristics of trehalose in aqueous solution at 20 °C, especially the hydration number (Table 12). It was also possible to calculate the specific mass of anhydrous trehalose in aqueous solution, found equal to 1.559, slightly higher than that of sucrose (1.549). Such difference can be assigned to the conformation differences between the two molecules.

On the other hand, if we compare hydration numbers calculated in this work using the "density method" to molecular dynamics simulation results, we find our values obtained at 20 °C between the simulations values at 0 and 100 °C. (Lerbret et al., 2005).

To account for the special affinity of trehalose for water, hydration number variation in function of mass concentration was represented in Fig. 9 and the values of n_h extrapolated at high concentration. On the same graph, total water in solution expressed as number of water molecules per trehalose was also plotted in function of concentration. It is remarkable to note that the intersection of the two curves corresponds to the composition of trehalose dihydrate (90% or $2H_2O$/trehalose), which means that for this concentration all water is bound.

6. Conclusion

Using density tables of mono- and disaccharides in aqueous solution allowed obtaining of hydration numbers, molar volumes and specific mass of the non-hydrated sugar molecules. The different calculations assume that water in solution is either in the first hydration shell of solute with a volume shrinkage of about 9% for disaccharides and 10% for monosaccharides or free having the same density as pure water. Density data are accurate enough, especially for sucrose, to allow evidencing of such structural details as the folding around glycosidic bond from the molar volumes determined in function of concentration. The same formalism was applied to D-fructose and D-glucose in aqueous solution. It was possible to determine that D-fructose exhibits higher hydration than D-glucose at all concentrations and a better compatibility with water structure. Although maltose and trehalose are comparable to sucrose
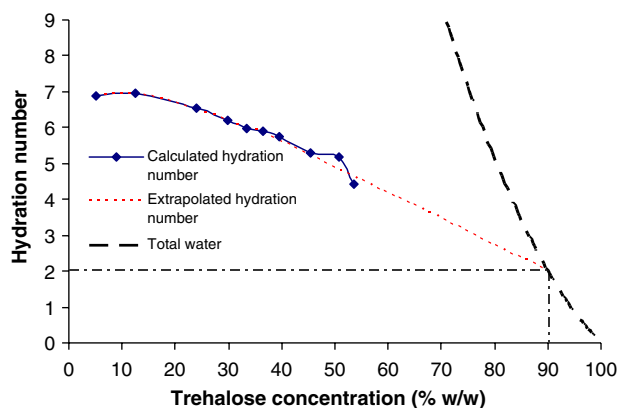

Fig. 9. Variation of calculated and extrapolated hydration number and total water as a function of trehalose concentration.

as disaccharides, they show different hydration behaviour. Their hydration numbers are higher than that of sucrose in the whole range of concentrations investigated. In the region of concentrations above 30%, where density and activity coefficients are more accurate, the hydration numbers of trehalose remain the highest among disaccharides. Another characteristic of trehalose is the possibility to show the convergence of hydration water and total water at a concentration corresponding to the composition of trehalose dihydrate.

Our approach based on simple hypothesis concerning hydration water and free water in aqueous solution of mono- and disaccharides and the utilisation of accurate density tables brings a further piece of information to the unveiling of properties of the complex water–sugar system. It is particularly interesting to show that our "density method" is precise enough to allow differentiating the hydration of the investigated sugars and describing some molecular features like flexibility around the glycosidic bond.

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