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Variable hydration of small carbohydrates for predicting equilibrium properties in diluted and concentrated solutions

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Abstract

A physical–chemical model is proposed to describe the equilibrium properties of binary and multicomponent water–carbohydrate mixtures.

The chemical part of the model accounts for the hydration equilibrium of carbohydrate with the formation of carbohydrate n-water molecules in a single stage process; n, the hydration number, and K, the hydration equilibrium constant, are the two independent parameters in this part.

The physical part of the model is the UNIFAC group-contribution model as modified by Larsen et al. (I.E.C. Research, 26 (1987) 2274–2286). The original functional groups and the structural and interaction parameter values are maintained and introducing new groups such as pyranose rings, furanose rings and osidic bonds was not necessary.

The model is compared to experimental data including water activity, osmotic coefficients, activity coefficients, freezing and boiling point temperatures and solubility for binary systems containing xylose, glucose, mannose, galactose, fructose, sucrose, maltose, lactose and trehalose and for food products containing sugars.

Keywords: Sugars; Hydration number; Equilibrium properties; Physical–chemical model; Solubility

1. Introduction

Carbohydrates are one of the most abundant classes of organic compounds that can be found on earth. This large natural resource has long interested chemists and biochemists because of its predominant role in a variety of areas, including biological and industrial applications. An important fraction of carbohydrates is made up of the smaller building units, namely sugar monomers and oligomers, and their use in solvents such as water or alcohols is mainly associated with the processing and the preservation of foods.

This study focuses on the phase behaviour of sugars in aqueous solutions, which plays a major role in the sugar and food industries. Thus, industrial sugar juices can be considered as aqueous solutions of four pseudo-components: sugar, amino acid, carboxylic acid, and mineral matter called ash. The sugar pseudo-component is represented by sucrose, glucose and fructose, the three most important pure substances concerned, the amino acid pseudo-component by aspartic acid and glutamic acid, the carboxylic pseudo-component by lactic acid and succinic acid, and mineral matter by NaOH and KCl. Osmotic dehydration is a food processing operation used in the preparation of intermediate moisture foods (IMF). It has been introduced as a pre-treatment, in conventional fruit and vegetable processing, to improve quality and reduce energy costs, and is used in new fish

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or meat products processing. It involves contact of food with concentrated aqueous solutions containing sugars (sucrose, glucose, fructose,...), sorbitol, lactitol, PEG or salts.

The preservation and shelf-life of sugar-rich food products are also directly related to sugar–water interactions. The hydration of sugars is a decisive factor for properties such as water activity, glass transition temperature, melting temperature, solubility, and osmotic pressure. For example, the composition of honey, mainly sugars and water, is responsible for many its physicochemical properties, such as viscosity, hygroscopicity and granulation. Most honeys are supersaturated solutions of glucose which have a tendency to crystallise spontaneously at room temperature in the form of glucose monohydrate; the crystallisation of honey, often called granulation, is an undesirable process in liquid honeys, and water content and water activity are the major factors influencing honey conservation quality and stability.

Despite their importance, to date relatively few thermodynamic data are available for sugars, which is the reason why the correlation or prediction of phase equilibrium data is of major interest, and a series of attempts have been made over the past 20 years to model the thermodynamics of solutions.

The resulting models of solutions can roughly be assigned to two general categories; either physical or chemical models. Physical models suppose that all deviations from the ideal solution are due to physical properties such as the relative size of the individual molecules and the physical forces or interactions between them. They are based on the lattice theory of solutions, as proposed by Guggenheim, Flory and others. This category of models includes the equations of Wilson, NRTL and UNIQUAC and, in some aspect, the group-contribution models derived such as ASOG and UNIFAC.

Chemical models describe deviation from ideal mixtures as a result of chemical reactions (association or hydration) occurring between solvent and solutes molecules. The chemical theory of solutions provides a reasonable approximation whenever there is evidence that strong chemical forces, for example appreciable hydrogen bonding between like and unlike components, operate in a liquid mixture.

One of the conclusions given by Prausnitz, Lichtenthaler and de Azevedo in their reference book (1999) is that "careful study has shown that for accurate work both physical and chemical forces must be taken into account. However, the dividing line between physical and chemical forces cannot easily be determined with rigor and as a result, it is often necessary to make an essentially arbitrary decision on where that line is drawn".

The majority of models specially developed for or applied to the description of phase equilibrium of sugar mixtures fall into the physical model category and follow a group-contribution approach, mainly because of their predictive (rather than correlative) properties. They have been used successfully to model binary and multicomponent aqueous solutions of sugars, mainly in the region of dilute solutions (Achard, Gros, & Dussap, 1992; Catté, Dussap, Achard, & Gros, 1994; Le Maguer, 1992; Peres & Macedo, 1996, 1997). However, as stated by Starzak, Peacock, and Mathlouthi (2000), none of these models are able to predict the water activity coefficient γ_w in the sucrose-water system at vapour–liquid equilibrium, that is, along the boiling curve, in the region of very high sucrose concentrations.

To our knowledge, only two physical–chemical models have been proposed for sugar–water mixtures in past years. Catté, Dussap, and Gros (1995) developed a physical–chemical UNIFAC model for aqueous solutions of sugars. The physical part is provided by the UNIFAC-Larsen group-contribution model, and the chemical part describes the hydration equilibria between water and sugar and the conformational equilibria. The physical part is described in terms of three new UNIFAC groups, pyranose ring, furanose ring and osidic bond, used to represent the sugar molecules. The chemical part of the model assumes equilibrium hydration of sugar in a single step process: the hydration numbers are fixed with a simple rule (equal to OH groups that are not in axial position), and the partial molar Gibbs energy of the hydrogen bonds was identified. This model is only applicable to sugar mixtures. More recently, the A-UNIFAC model was applied to phase equilibrium in sugar solutions by Ferreira, Brignole, and Macedo (2003). Three contributions to excess Gibbs energy are considered in the A-UNIFAC model (Mengarelli, Brignole, & Bottini, 1999), the conventional residual and combinatorial contributions, plus an association term based on Wertheim's theory for fluids with highly directive attractive forces (Wertheim, 1984, 1986). For the association term, a unique OH-associating group is considered, allowing a straightforward extension to multicomponent mixtures. Three new main groups are defined: the sugar ring (pyranose and furanose), the osidic bond and the hydroxyl ring group. This model was applied to mixtures of sugars in mixed solvents (water and alcohols) considering the same OH-associated group for all alcohols in water.

In a critical review on hydration number and water activity models for the sucrose–water system, Starzak et al. (2000) gave a detailed evaluation of the existing chemical models of water activity from Scatchard (1921), Stokes and Robinson (1966), Schönert (1986a, 1986b) and Van Hook (1987), including their predictive ability for dilute solutions and their behaviour in the region of high sucrose content. They suggested developing a chemical model including a sucrose association mechanism (clustering) together with sucrose hydration and (eventually) water dimerization (Starzak & Mathlouthi, 2002).

In this paper, we investigate the capabilities of a physical–chemical model for multicomponent sugar-mixtures, with straightforward extension to electrolytes and non-electrolytes mixtures. The model assumes equilibrium hydration of sugars with the formation of sugar-*n* hydrates in a single-step process where n is the hydration number.

2. Model

The chemical and the physical theories are extremes. In certain limiting cases, each theory provides a satisfactory approximation. The model developed here attempts to allow for a smooth transition between the limit of a "physical" solution to the other limit of a "chemical" solution.

To illustrate this, we consider a simple case, a binary solution of sugar S and water where complexes form according to

$$\mathrm{S} + n\mathrm{H_2O} \leftrightarrow (\mathrm{S}, n\mathrm{H_2O}), \tag{1}$$

where n is the hydration number, i.e. the number of water molecules in the solvated complex with sugar.

The equilibrium constant is related to the activities of the three species

$$K = \exp\left(\frac{-\Delta G^0}{RT}\right) = \frac{\gamma_{\mathrm{Sh}} x_{\mathrm{Sh}}}{\gamma_{\mathrm{Sl}} x_{\mathrm{Sl}} a_{\mathrm{w}}^n}, \tag{2}$$

where x_{Sh} and x_{Sl} correspond to the mole fraction of the sugar n-hydrate and free sugar respectively.

This leads to an immediate problem, which is how the apparent mole fractions z_{S} and z_{w} and the apparent activity coefficients are related to the "true" mole fractions x_{Sh} and x_{Sl} and to the "true" activity coefficients. Prigogine and Defay (1954) demonstrated that apparent activity coefficients and apparent mole fractions are related to true activity coefficients and true mole fractions by

$$\gamma_{\mathrm{w}}^a = \frac{\gamma_{\mathrm{w}} x_{\mathrm{w}}}{z_{\mathrm{w}}}, \tag{3}$$

and

$$\gamma_{\mathrm{S}}^a = \frac{\gamma_{\mathrm{Sl}} x_{\mathrm{Sl}}}{z_{\mathrm{S}}}. \tag{4}$$

From material balances with the definition of true mole fractions and apparent mole fractions, we get

$$z_{\mathrm{S}} = \frac{x_{\mathrm{Sh}} + x_{\mathrm{Sl}}}{1 + n x_{\mathrm{Sh}}}, \tag{5}$$

with the corresponding sum equations

$$z_{\mathrm{S}} + z_{\mathrm{w}} = 1, \tag{6}$$

and

$$x_{\mathrm{Sh}} + x_{\mathrm{Sl}} + x_{\mathrm{w}} = 1. \tag{7}$$

When provided the equilibrium constant K value, the hydration number n and an appropriate expression for computing true activity coefficients, and knowing the apparent mole fraction z_{S}, the system of Eqs. (2), (5)–(7) can be solved for the unknowns z_{w}, x_{Sh}, x_{Sl} and x_{w}. Eqs. (3) and (4) provide γ_{w}^a and γ_{S}^a.

The physical model relaxes the assumption that the "true" chemical species form an ideal solution. Expression for Gibbs excess energy of the mixture (water, sugar and sugar n-hydrates) and for the "true" activity coefficients are obtained from the UNIFAC group-contribution model of Larsen, Rasmussen, and Fredenslund (1987). This modified UNIFAC model was used in this study because of its performance in treating mixtures containing water and because of its robustness with respect to temperature dependency. In the model, interaction parameters were not modified and no new group was added.

An average equivalent hydration number in the mixture is defined as

$$n_{\mathrm{eq}} = n\frac{x_{\mathrm{Sh}}}{x_{\mathrm{Sh}} + x_{\mathrm{Sl}}} = n\frac{\frac{\gamma_{\mathrm{Sl}}}{\gamma_{\mathrm{Sh}}} K a_{\mathrm{w}}^n}{1 + \frac{\gamma_{\mathrm{Sl}}}{\gamma_{\mathrm{Sh}}} K a_{\mathrm{w}}^n}. \tag{8}$$

This model was extended to multicomponent mixtures.

2.1. Phase equilibria studies

This work studied two kinds of fluid phase equilibria for sugar solutions: vapour-liquid and solid–liquid equilibria.

The vapour-liquid equilibrium of aqueous solutions containing sugars requires calculation of water and sugar activity coefficients, water activity a_{w}, osmotic coefficient ϕ, vapour pressure of the mixture and boiling point temperature. Water activity is given by

$$a_{\mathrm{w}} = \gamma_{\mathrm{w}} x_{\mathrm{w}} = \gamma_{\mathrm{w}}^a z_{\mathrm{w}}, \tag{9}$$

and the osmotic coefficient is defined by

$$\phi = -\frac{x_{\mathrm{w}}}{x_{\mathrm{S}}} \ln a_{\mathrm{w}}. \tag{10}$$

Assuming the vapour phase is ideal, boiling point temperature is calculated iteratively from

$$P = P_{\mathrm{w}} = \gamma_{\mathrm{w}} x_{\mathrm{w}} P_{\mathrm{w}}^0, \tag{11}$$

where P_{w}^0, the saturated vapour pressure of water, is taken from the international DIPPR data bank (1984).

The solid–liquid equilibrium calculations afford the freezing point depression and solubility. The freezing point depression of a sugar–water mixture of known composition can be calculated iteratively using

$$\ln a_\mathrm{w} = \frac{\Delta H_\mathrm{f,w}}{R}\left[\frac{1}{T_\mathrm{f,w}} - \frac{1}{T_\mathrm{f,mix}}\right] - \frac{\Delta C_\mathrm{p,w}}{R}\ln\left[\frac{T_\mathrm{f,w}}{T_\mathrm{f,mix}}\right] - \frac{\Delta C_\mathrm{p,w}}{R}\left[1 - \frac{T_\mathrm{f,w}}{T_\mathrm{f,mix}}\right], \tag{12}$$

where $T_\mathrm{f,w}$ is the pure water freezing temperature, equal to 273.15 K, $T_\mathrm{f,mix}$ is the freezing point of the mixture. $\Delta H_\mathrm{f,w}$ is the enthalpy of fusion at $T_\mathrm{f,w}$, and $\Delta C_\mathrm{p,w}$ is the difference in the heat capacities of liquid water and ice at $T_\mathrm{f,w}$, assumed to be constant in the range $T_\mathrm{f,w} - T_\mathrm{f,mix}$. Their values, 6002 J mol^{-1} and 38.03 J mol^{-1} K^{-1}, respectively, are taken from Ferro Fontan and Chirife (1981) and Peres and Macedo (1996).

The solute solubility in water at T is obtained from

$$\ln(\gamma_\mathrm{S}^a z_\mathrm{S}) = \ln(\gamma_\mathrm{Sl} x_\mathrm{Sl}) = -\frac{\Delta H_\mathrm{f,s}}{R}\left[\frac{1}{T} - \frac{1}{T_\mathrm{m,S}}\right] + \frac{\Delta C_\mathrm{p}}{R}\left[\frac{T_\mathrm{m,S}}{T} - 1\right] + \frac{\Delta C_\mathrm{p}}{R}\ln\left[\frac{T}{T_\mathrm{m,S}}\right], \tag{13}$$

where $T_\mathrm{m,S}$ is sugar melting temperature and $\Delta H_{\mathrm{f},s}$ is heat of fusion of sugar. ΔC_p is the difference in the heat capacity of the pure hypothetical liquid and the pure solid sugar at T. ΔC_p is generally considered as a linear function of temperature (Catté et al., 1994; Ferreira et al., 2003; Spliotis & Tassios, 2000).

The available phase diagrams of carbohydrate–water systems show that some sugars (e.g. glucose and fructose) have a hydrated solid form, in addition to the anhydrous solid form, with transition occurring at a precise temperature T_t. In this case, two different equations are used according to whether the temperature is lower or higher than T_t (Catté et al., 1994), Eq. (13) and the following equation:

$$\ln(\gamma_\mathrm{S}^a z_\mathrm{S}) + n_\mathrm{h}\ln(\gamma_\mathrm{w} x_\mathrm{w}) = \left(-\frac{\Delta H_\mathrm{f,S}^\mathrm{hyd}}{R} + \frac{\Delta C_\mathrm{p}^\mathrm{hyd}}{R} T_\mathrm{m,S}^\mathrm{hyd}\right) \times \left[\frac{1}{T} - \frac{1}{T_\mathrm{m,S}^\mathrm{hyd}}\right] + \frac{\Delta C_\mathrm{p}^\mathrm{hyd}}{R}\ln\frac{T}{T_\mathrm{m,S}^\mathrm{hyd}} + \ln\left[\frac{1}{1+n_\mathrm{h}}\gamma_\mathrm{S}(T_\mathrm{m,S}^\mathrm{hyd})\right] + n_\mathrm{h}\ln\left[\frac{n_\mathrm{h}}{1+n_\mathrm{h}}\gamma_\mathrm{w}(T_\mathrm{m,S}^\mathrm{hyd})\right], \tag{14}$$

where n_h is the number of water molecules in the hydrated solid form.

In the UNIFAC model, as with group-contribution models, molar excess energy and the activity coefficients are calculated with respect to the so-called symmetrical convention, i.e. mole fraction scale and a reference state corresponding to the pure (hypothetical) liquid for all species at T and P of the system. Conversion equations

Table 1
Hydration numbers *n* suggested for some saccharides and the corresponding measurement methods

	Viscosity measurements	Dielectric and magnetic relaxation	Ultrasonic and acoustic measurements	Dynamic molecular simulation
Fructose	3.01[e,m] 3.26[g,m]	16.5[k]	8.8[c]	–
Glucose	3.01[g,m] 3.16[e,m] 3.26[f,m]	3.7[b] 5–6[a] 18.6[k]	8.4[c]	–
Maltose	11.7[h]	5[b] 5.9[l] 27.2[k]	14.2[h] 14.5[c]	–
Trehalose	12.1[h]	6.6[l]	15.2[h] 15.3[c]	7.8–27.5[j] 8[j]
Sucrose	5.3[d]	25.2[k]		11.7[i]
	11.2[h]		13.8[h]	7.8–27.5[j]
	6.14[e,m]		13.9[c]	6.8[j]

[a] Franks et al. (1973).
[b] Suggett (1976).
[c] Galema and Høiland (1991).
[d] Mathlouthi and Reiser (1995).
[e] Mathlouthi et al. (1996).
[f] Hutteau and Mathlouthi (1998).
[g] Mathlouthi and Hutteau (1999).
[h] Branca et al. (2001).
[i] Ekdawi-Sever et al. (2001).
[j] Engelsen et al. (2001).
[k] Uedaira and Uedaira (2001).
[l] Matsuoka et al. (2002).
[m] Estimation from the relation of Herkovits and Kelly (1973): $n = (1000 \cdot B/v - M_2\nabla_2)/18$ where B is the viscosity coefficient of the solute, v is the kinematic viscosity and $M_2\nabla_2$ the partial molar volume of the solute.

Table 2
Experimental database

	Water activity (a_w)	Freezing temperature (T_f)	Boiling temperature (T_b)	Osmotic coefficient (Φ)	Activity coefficient (γ_S)	Solubility
Xylose						
N	34	–	–	34	34–35	8
T range (°C)	25	–	–	25	25	22.5–75
w_s range (%)	1.5–33.8	–	–	1.5–33.8	1.5–33.8	54–78
D-*Fructose*						
N	68	75	16	12	–	45
T range (°C)	25	−1.3–(−30)	100–130	25	–	−3.8–50
w_s range (%)	5–78	0.5–69	8.3–98.5	21–78	–	44.7–86.7
Galactose						
N	–	–	–	18	18	8
T range (°C)	–	–	–	25	25	25–75
w_s range (%)	–	–	–	1.7–38.6	1.7–38.6	32.5–61
D-*Glucose*						
N	87	42	6	45	23	40
T range (°C)	25	−5–(−20)	100–104.8	25	25	−12–80
w_s range (%)	0.5–70.8	30–63	3.47–60	1.8–49.3	1.8–64.3	30.8–81.4
Mannose						
N	–	–	–	23	23	4
T range (°C)	–	–	–	25	25	20–35
w_s range (%)	–	–	–	1.77–51.9	1.77–51.9	74–79.5
Maltose						
N	53	60	–	13	53	23
T range (°C)	25	−0–(−5.4)	–	25	25	0.6–96.5
w_s range (%)	0.5–52.3	0.5–44	–	5–44	3.3–49.8	35.8–85.1
Sucrose						
N	157	49	42	11	51	66
T range (°C)	25	−0.01–(−15)	100.2–130	25	25	−13.9–100
w_s range (%)	0.5–95	0.17–67	0.14–95	25.5–67.2	3.3–67.2	63.6–82.9
Trehalose						
N	12	–	–	–	–	11
T range (°C)	25	–	–	–	–	10–85
w_s range (%)	16–72	–	–	–	–	42.3–81.6

w_S (%) is the mass percentage of sugar.

are necessary when experimental data are given using asymmetrical convention in the molal scale. Thus

$$\gamma_S^m = \frac{\gamma_S}{\gamma_S^\infty} x_w, \tag{15}$$

where γ_S^m refers to the activity coefficient in the molal scale.

2.2. Sugar hydration number values

It is well known that carbohydrates have a very high affinity for water. It is the nature of their interactions with this solvent that is responsible for most of their biological features including gel formation, sweet taste induction, storage, stabilisation and adherence.

Sugar hydration has been investigated for many years and several measurement methods have been used to calculate overall sugar hydration and its dependence on sugar concentration.

Table 3
Physical parameters related to sugars: heat of fusion ($\Delta H_{f,s}$), melting temperature ($T_{m,S}$) and difference of heat capacities of the pure hypothetical liquid and the solid state (ΔC_p)

Sugar	$\Delta H_{f,s}$ (J/mol)	$T_{m,s}$ (K)	ΔC_p (J/mol/K)
Xylose	31,650[g]	423.15[g]	120.00[g]
Fructose	20,500[h]	377.15[b]	120.00[g]
Fructose dihydrate	32,504[h]	293.87[d]	158.03[g]
Galactose	43,800[f]	436.15[f]	139.00[f]
Glucose	30,000[h]	419.10[b]	120.00[g]
Glucose monohydrate	36,002[h]	344.30[c]	166.03[g]
Maltose monohydrate	38,000[h]	377.15[f]	231.00[e]
Sucrose	45,000[h]	458.15[a]	221.60[d]

[a] Raemy and Schweizer (1983).
[b] Lide (1991).
[c] Ross (1993).
[d] Catté et al. (1994).
[e] Miller and de Pablo (2000).
[f] Jónsdóttir et al. (2002).
[g] Ferreira et al. (2003).
[h] Values estimated in this work.

One of the first attempts (Robinson & Stokes, 1961) considered the carbohydrates present in aqueous solutions as quasi-ideal solutes. Their thermodynamic properties can be expressed as a simple series of hydration equilibria. The number of these equilibria is equal to the number of oxygen atoms present in the sugar molecule.

Many later studies (Lemieux, 1971) tried to pinpoint the existence of a close relationship between hydration phenomena and the stereochemistry of sugars in solution. Franks, Ravenhill, and Reid (1972) demonstrated this assumption by experimental measurements of compressibility and partial molar volume of diluted solutions. This was later confirmed by calorimetric and dielectric measurements (Franks, Reid, & Suggett, 1973).

Nuclear magnetic resonance (NMR) and dielectric resonance (DR) studies concluded that, in aqueous solu-

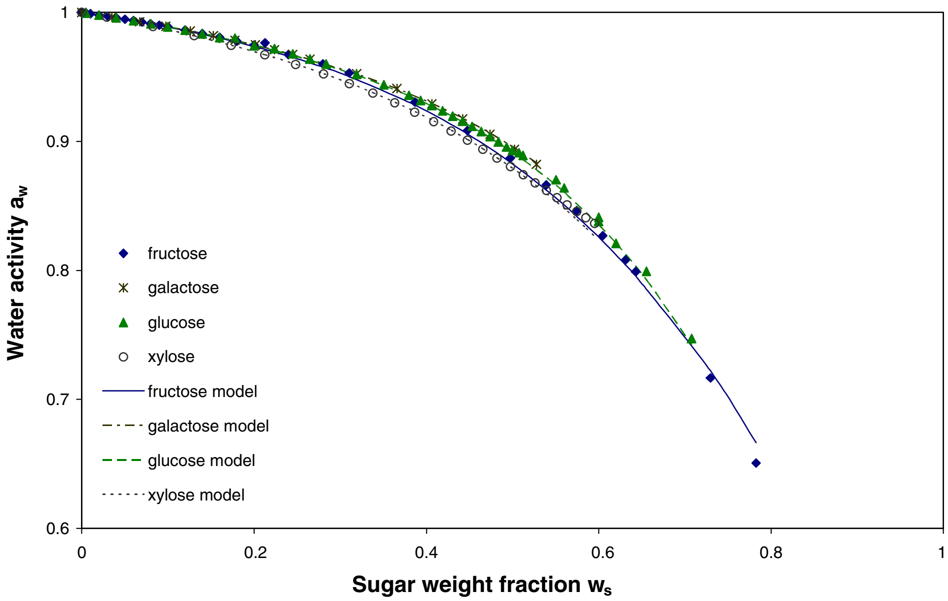

Fig. 1. Experimental and calculated water activity of water-monosaccharide mixtures at 298.15 K: ◆, D-fructose (Rüegg & Blanc, 1981; Weast, 1973); $*$, galactose (values obtained from Gibbs-Duhem equation); ▲, D-glucose (Ferro Fontan & Chirife, 1981; Rüegg & Blanc, 1981; Taylor & Rowlinson, 1955; Weast, 1973); ○, xylose (Uedaira & Uedaira, 1969).

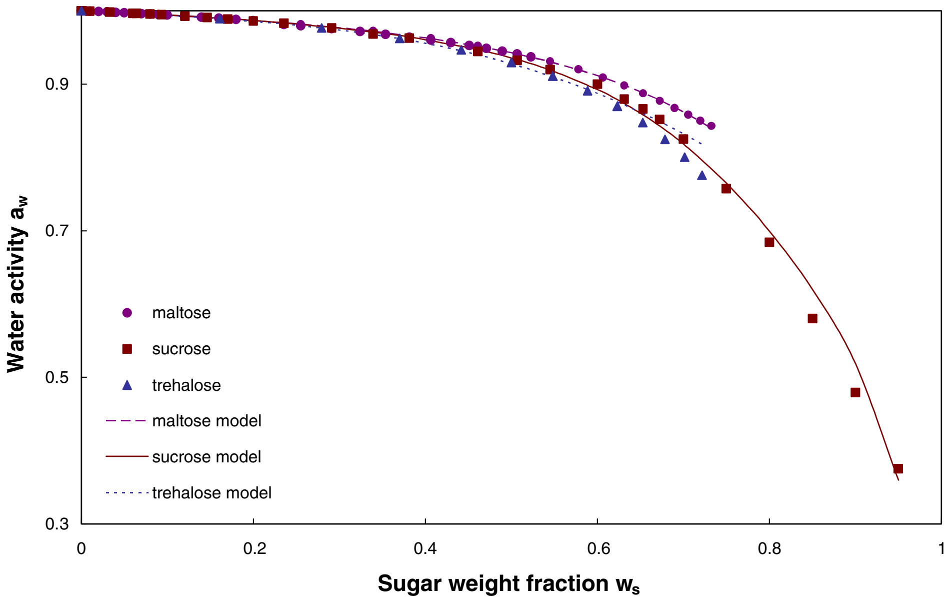

Fig. 2. Experimental and calculated water activity of water–disaccharide mixtures at 298.15 K: ●, maltose (Uedaira & Uedaira, 1969); ■, sucrose (Lee & Jackson, 1973; Robinson & Stokes, 1955; Rüegg & Blanc, 1981; Weast, 1973); ▲, trehalose (Sato et al., 2004).

tions of glucose, each OH group generally forms at least two hydrogen bonds with water (Harvey, Symons, & Naftalin, 1976). This was confirmed in studies by Harvey and Symons (1978). However, it was difficult to observe differences between the hydration phenomena of hexose isomers.

Using partial molar volume and compressibility measurements, Høiland and Holvik (1978) deduced that the number of OH groups in the equatorial position and their relative position on the molecule play a major role in hydration phenomena in sugars.

Galema, Blandamer, and Engberts (1990, 1992) and Galema and Høiland (1991) confirmed the stereo chemical nature of sugar hydration by measuring compressibility and expansibility. They suggested that the hydration phenomena are related to the relative position of OH groups on site 2 and site 4 of the hexose molecule.

More recently, Branca et al. (2001) experimentally quantified the basic hydration behaviour of three disaccharides – trehalose, maltose and sucrose – as a function of concentration and temperature using density, viscosity and sound velocity measurements. The viscosity and ultrasound data revealed that, in comparison to the other disaccharide solutions, the trehalose/water system is characterized by the highest interaction strength parameter values of the hydration number. These results are in good agreement with those obtained by dynamic molecular simulation.

Engelsen, Monteiro, de Penhoat, and Perez (2001) coupled the advanced techniques of NMR with molecular simulation dynamics using explicit water molecules to study the hydration of two disaccharides, trehalose and sucrose. They found that the hydration patterns of these sugars are quite different. A very strong localised hydration site was shown to be a major feature of sucrose hydration, and this was accompanied by a distribution of solvent molecules that display a high degree of anisotropy. There have also been other reported cases of solvent anisotropy (Leroux, Bizot, Brady, & Tran, 1997). It should be noted that in order to fully understand the results from modern experimental perturbation methods, it is essential to have a reliable theoretical model of solvation dynamics and it would appear that molecular dynamics provides the most promising technique for this purpose.

Despite the various numerous structural studies and attempts at molecular modelling to account for water–sugar interactions, it remains difficult to accurately quantify the number of water molecules that hydrate sugar molecules. Thermodynamic methods generally give one value in the equilibrium state, whereas perturbation methods give numbers which depend on the time scale of the perturbation. Thus, there is considerable variation

Table 4
Hydration number and equilibrium constant for mono- and disaccharides

	n	K	MSE
Xylose	1.33 ± 0.22	0.52 ± 0.30	1.10×10^{-5}
Fructose	3.39 ± 0.02	1.74 ± 0.05	3.59×10^{-5}
Glucose	1.93 ± 0.03	1.65 ± 0.05	1.26×10^{-5}
Galactose	1.81 ± 0.35	1.14 ± 0.64	9.87×10^{-5}
Maltose	4.48 ± 0.02	0.88 ± 0.02	3.45×10^{-5}
Sucrose	3.13 ± 0.02	5.03 ± 0.03	3.05×10^{-3}
Trehalose	5.80 ± 0.02	3.09 ± 0.03	1.08×10^{-3}

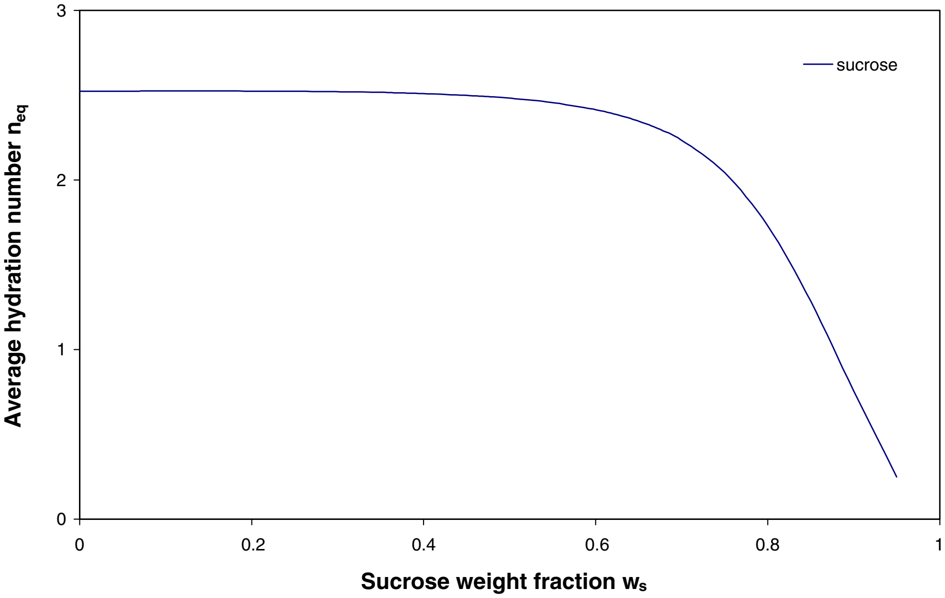

Fig. 3. Variation of the calculated average hydration number with sucrose concentration at 298.15 K.

depending on the measurement method used, as indicated in Table 1 for a few sugars. This disparity is even greater if all hydration numbers published for sucrose (varying from 1.8 (NMR) to 21 (NIR) are included (Starzak et al., 2000)).

Therefore, it is not yet possible to set the hydration number values a priori for carbohydrates to represent hydration of these compounds in aqueous solutions.

2.3. Fitting procedure and database

The remaining adjustable parameters in the model for each non-electrolyte component were n and K, i.e. hydration number and equilibrium constant. These were estimated based on an experimental database for binary water carbohydrate systems (Table 2). Parameters n and K were calculated for each sugar by using a Gauss–

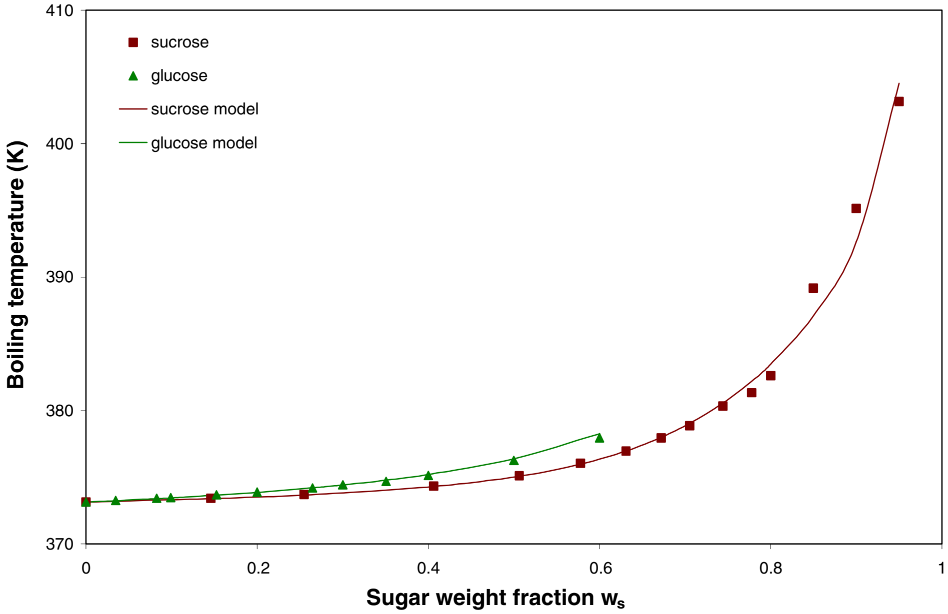

Fig. 4. Experimental and calculated boiling temperature of sucrose–water and D-glucose–water mixtures: ■, sucrose (International Critical Tables, 1926; Pancoast & Junk, 1980); ▲, D-glucose (International Critical Tables, 1926; Pancoast & Junk, 1980).

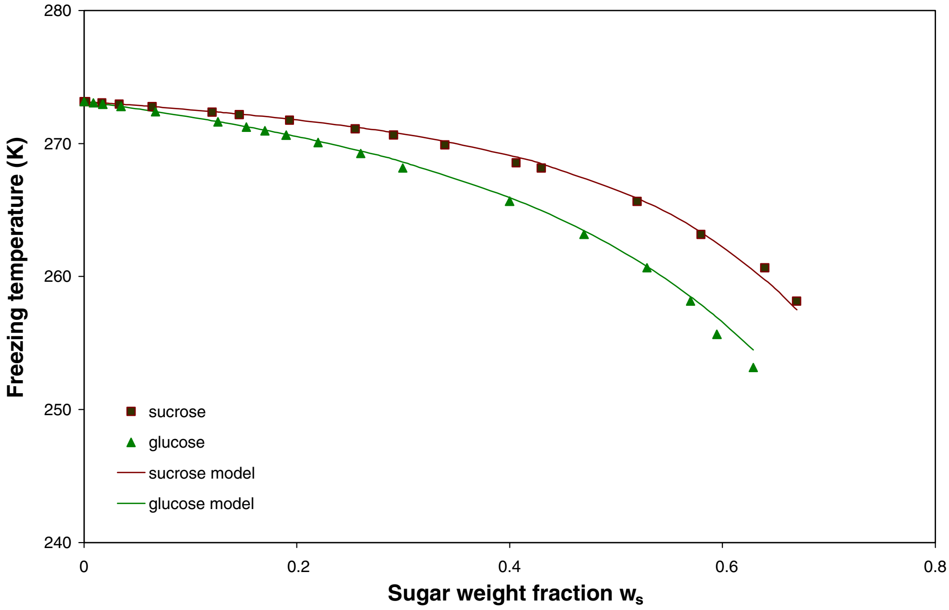

Fig. 5. Experimental and calculated freezing temperature of sucrose–water and D-glucose–water mixtures: ■, sucrose (Ferro Fontan & Chirife, 1981; International Critical Tables, 1926); ▲, D-glucose (Ferro Fontan & Chirife, 1981; International Critical Tables, 1926; Pancoast & Junk, 1980).

Newton method to minimize the following objective function

$$F = \sum^{N} (a_{w_{\exp}} - a_{w_{\text{calc}}})^2, \tag{16}$$

where exp and calc refer respectively to experimental values from the database and calculated values, and N is the number of data points. The data used as experimental water activity data were equilibrium relative humidity data, boiling point temperature or boiling point elevation measurements transformed by Eq. (11) and freezing point measurements from Eq. (12). Some of the activity coefficients of the solutes were used after numerical transformation using the Gibbs–Duhem equation.

The standard deviations for n and K were obtained from the variance–covariance matrix values at the min-

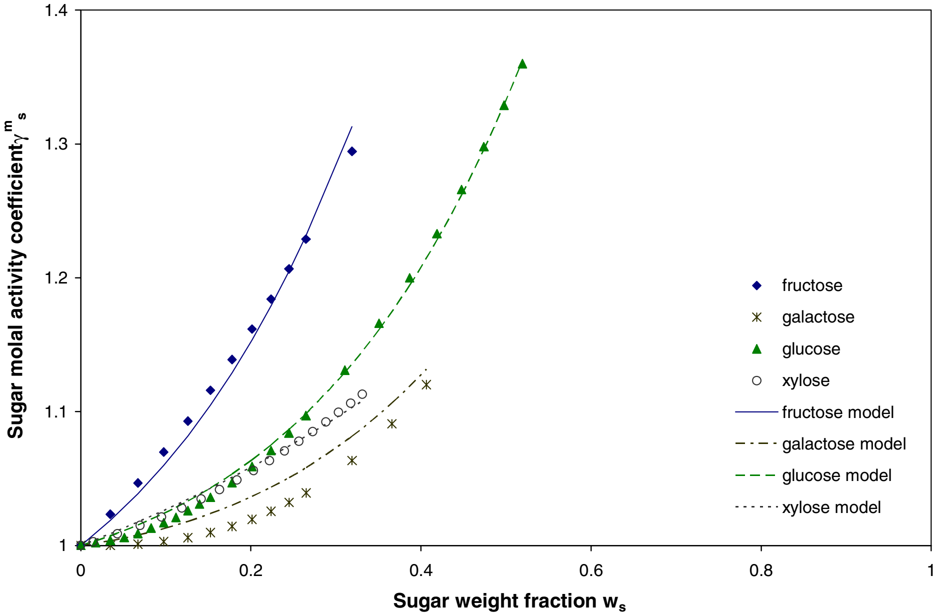

Fig. 6. Experimental and calculated sugar coefficient activity of water–monosaccharide mixtures at 298.15 K: ◆, D-fructose (values obtained from Gibbs-Duhem equation); *, galactose (Miyajima et al., 1983); ▲, D-glucose (Miyajima et al., 1983); ○, xylose (Uedaira & Uedaira, 1969).

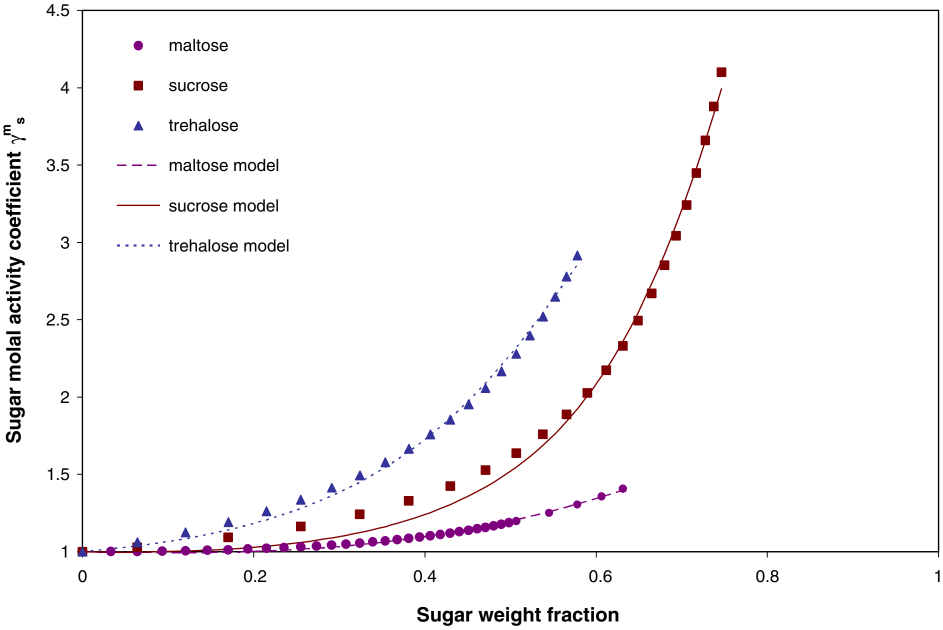

Fig. 7. Experimental and calculated sugar coefficient activity of water–disaccharide mixtures at 298.15 K: ●, maltose (Uedaira & Uedaira, 1969); ■, sucrose (Robinson & Stokes, 1955; values obtained from Gibbs–Duhem equation); ▲, trehalose (values obtained from Gibbs–Duhem equation).

imum of the objective function. The mean square error (MSE) was defined by

$$\mathrm{MSE} = \frac{1}{N-p}F, \tag{17}$$

where p is the number of identified parameters.

The thermodynamic data necessary in the model for the prediction of solubility are presented in Table 3.

3. Results

3.1. Correlation

The correlation results obtained for water activity in binary aqueous solutions of xylose, D-fructose, D-glucose, galactose, and sucrose, trehalose, and maltose are presented in Figs. 1 and 2 and the corresponding n and K values are given in Table 4. For mannose and lactose, data were too scarce to allow the simultaneous

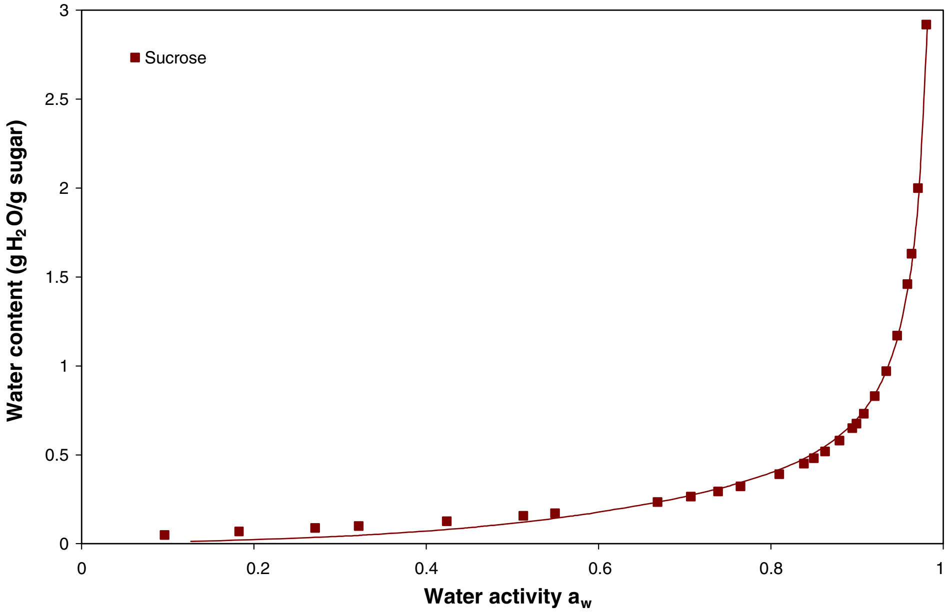

Fig. 8. Sorption isotherm of the sucrose–water system (Norrish, 1966; Bressan & Mathlouthi, 1994).

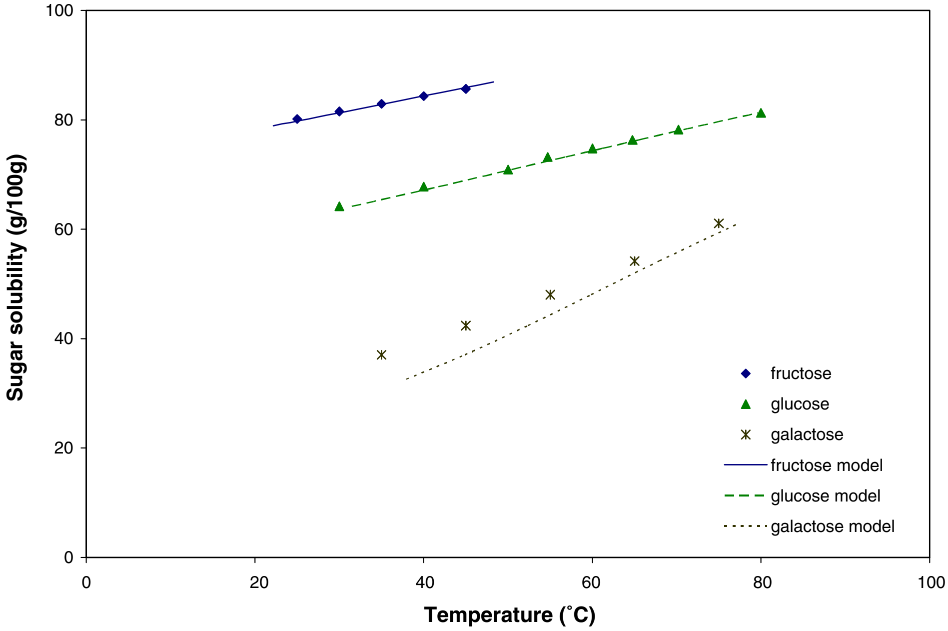

Fig. 9. Anhydrous monosaccharides solubility in water versus temperature: ♦, D-fructose (Pancoast & Junk, 1980; Young et al., 1952); ▲, D-glucose (Pancoast & Junk, 1980; Stephen & Stephen, 1963; Young, 1957); ∗, galactose (Jónsdóttir et al., 2002).

determination of n and K. The distinction between isomers is obtained through n and K values.

As expected, the average hydration number calculated by Eq. (8) varies depending on sugar concentration. Fig. 3 shows for sucrose the sharp decrease in sucrose hydration above 0.6 sucrose weight fraction which corresponds to water activity below 0.9.

The boiling temperature prediction for sucrose and glucose solutions is presented in Fig. 4; the boiling point temperature is well represented over the whole concentration range.

Fig. 5 shows the performance of the model in describing freezing temperatures for the same solutions.

A comparison between the asymmetrical molal activity coefficients calculated using the proposed model and Eq. (15), and the ones published in the literature is shown in Figs. 6 and 7. The figures show a satisfactory agreement, essential to the prediction of solubility data.

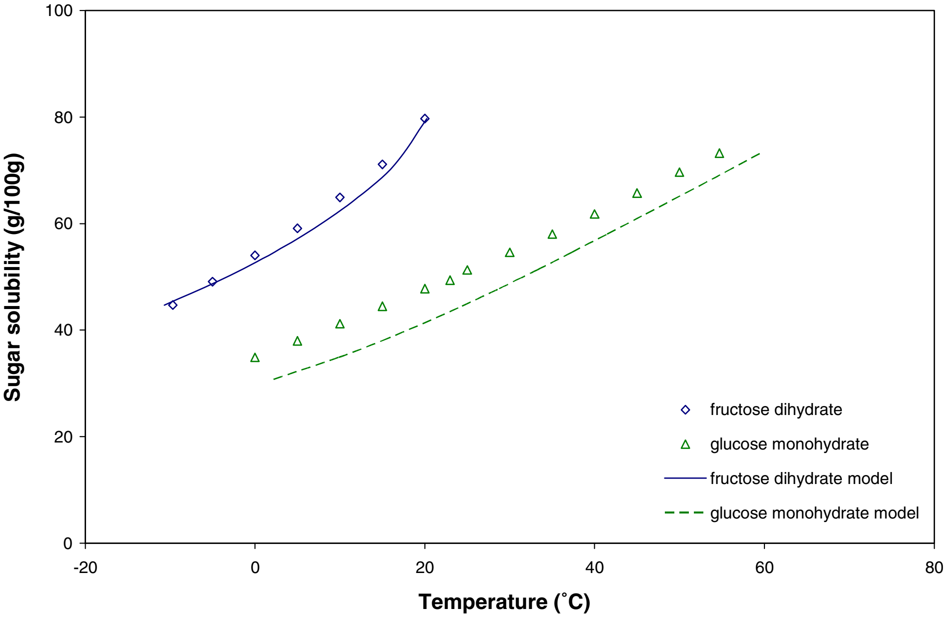

Fig. 10. Hydrated monosaccharides solubility in water versus temperature: ◇, fructose dihydrate (Young et al., 1952); △, glucose monohydrate (International Critical Tables, 1926; Pancoast & Junk, 1980; Young, 1957).

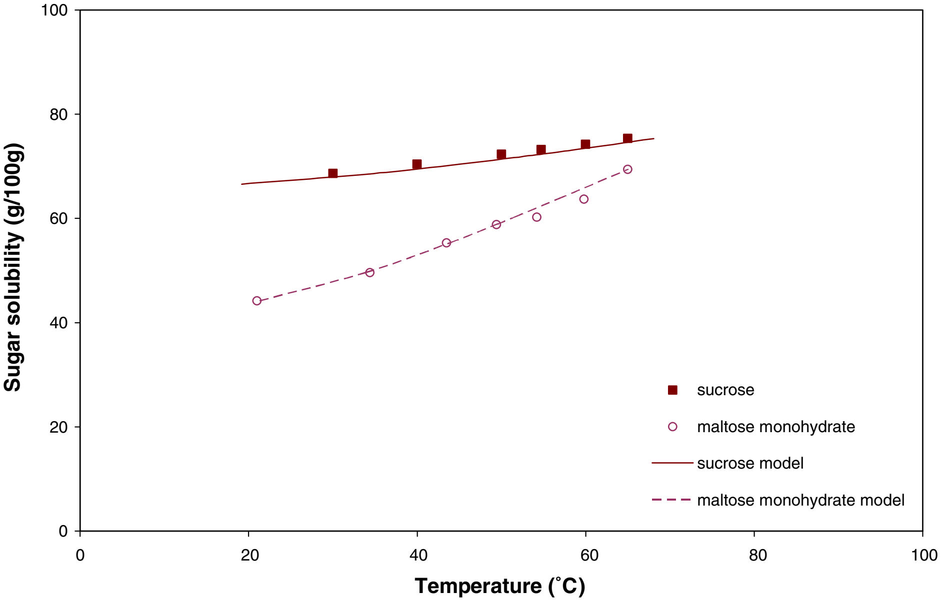

Fig. 11. Disaccharides solubility in water versus temperature: ■, sucrose (Pancoast & Junk, 1980; Young, 1957); ○, maltose monohydrate (Pancoast & Junk, 1980; Stephen & Stephen, 1963).

3.2. Prediction

The set of parameters identified when correlating was used to predict several thermodynamic properties of binary and multicomponent mixtures and of different types of juices and honeys.

The model was first used to obtain the sorption isotherm for the sucrose–water system (Fig. 8) in the regions of high ($0.75 \leqslant a_w \leqslant 1.0$) and intermediate ($0.30 \leqslant a_w \leqslant 0.75$) moisture content. The prediction is the more satisfactory, as this representation is very sensitive to the weaknesses of models.

The model predictions for sugar solubility are also dependant on the estimation of the enthalpy of fusion, melting point temperature and heat capacity difference between the liquid and solid states (Table 3). For the mono- and the disaccharides the results are presented in Figs. 9–11. This gives the phase diagrams for glucose and fructose (Fig. 12) which show the existence of hydrated forms (glucose, $1H_2O$ and fructose, $2H_2O$) and

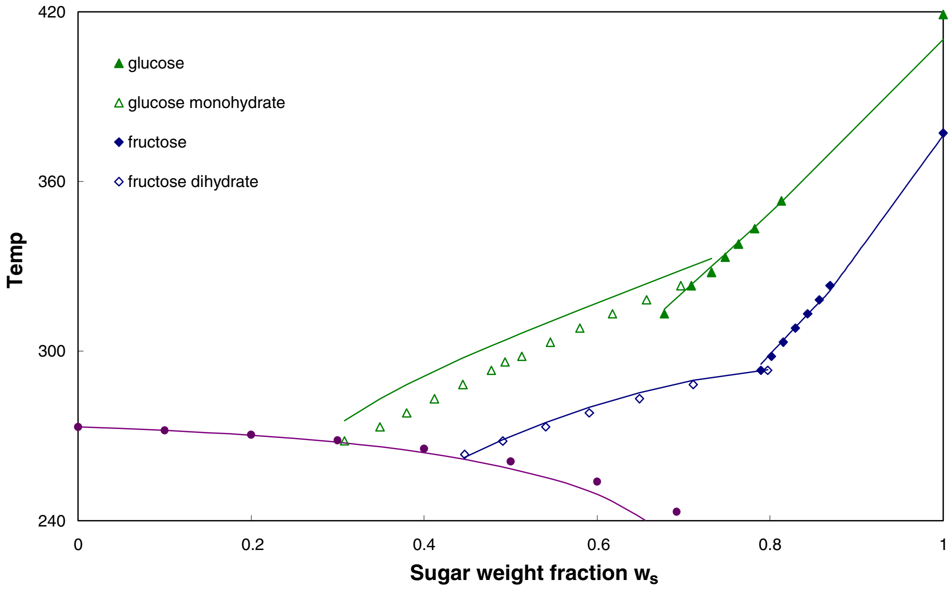

Fig. 12. Phase diagram of D-glucose–water and D-fructose–water systems at atmospheric pressure: ▲, D-glucose (Pancoast & Junk, 1980; Stephen & Stephen, 1963; Young, 1957); △, glucose monohydrate (International Critical Tables, 1926; Pancoast & Junk, 1980; Young, 1957); ◆, D-fructose (Pancoast & Junk, 1980; Young et al., 1952); ◇, fructose dihydrate (Young et al., 1952).

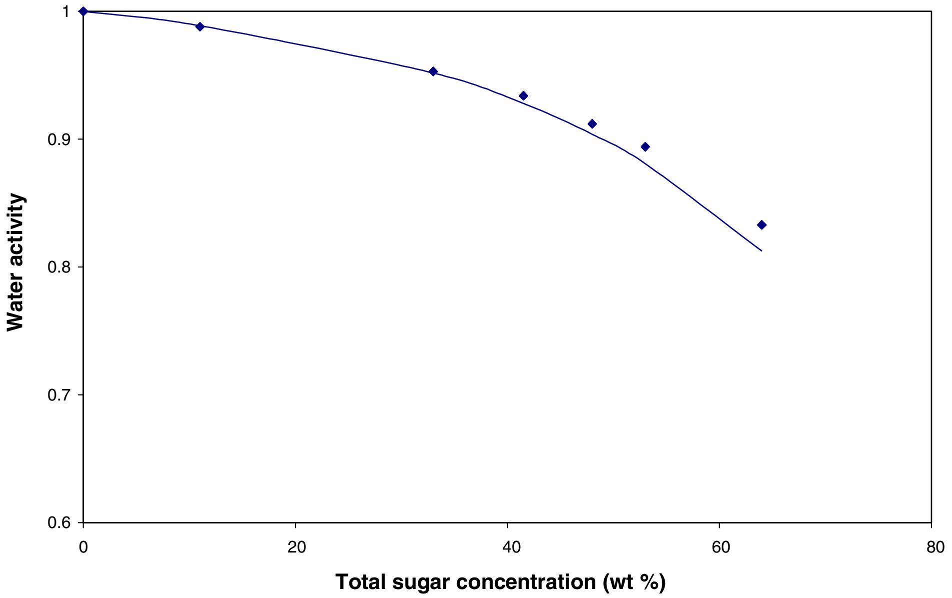

Fig. 13. Experimental and calculated water activity for an apple juice at 298.15 K (Ferro Fontan et al., 1981).

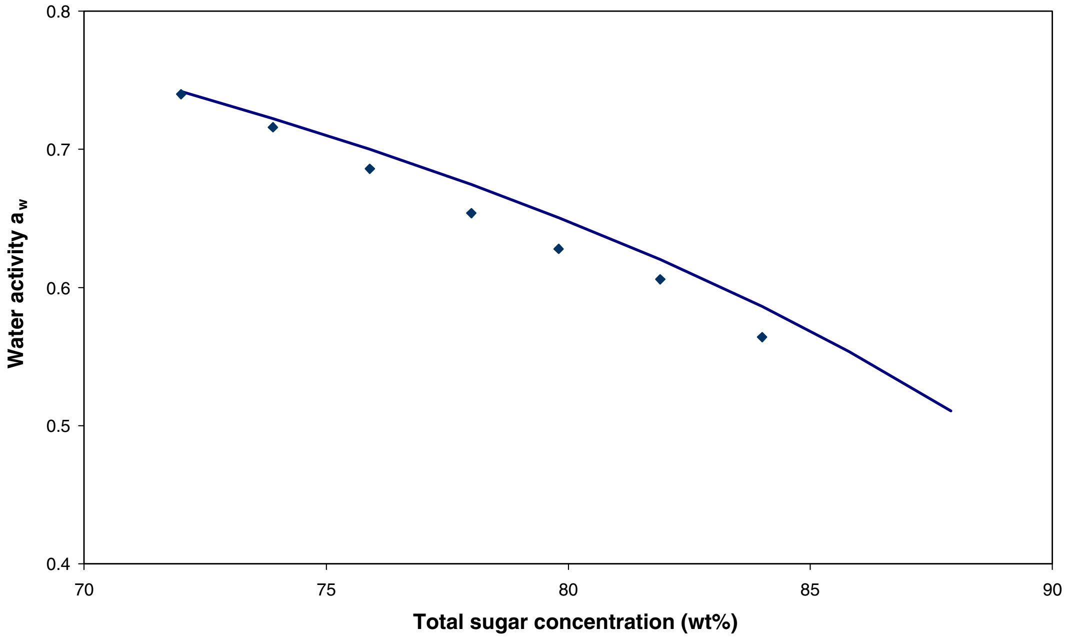

Fig. 14. Experimental and calculated water activity in synthetic honey at 298.15 K (Rüegg & Blanc, 1981).

Table 5
Carbohydrate concentration of some Greek honeys and prediction of their water activities (Lazaridou et al., 2004)

Botanic/geographical origin	Moisture content (g/100 g)	Proportion of major sugars (w_s, %)				Experimental water activity	Calculated water activity
		Fructose	Glucose	Maltose	Sucrose		
Honeydew (pine)/Thasos	18.9	38.92	30.19	7.029	0.91	0.610	0.643
Honeydew (pine)/Thasos	18.3	39.36	34.07	7.23	1.03	0.615	0.621
Honeydew (pine)/Thasos	15.4	40.70	35.72	12.41	0	0.57	0.568
Honeydew (pine)/Evia	14.8	40.94	35.15	7.17	1.93	0.663	0.563
Honeydew (fir)/Vytina	13.3	45.54	30.79	7.45	2.92	0.561	0.595
Honeydew (fir)/Vytina	15.2	44.88	30.48	6.96	2.48	0.609	0.572
Floral/Livadia	13.8	42.98	36.06	6.92	0.24	0.528	0.542
Floral/Livadia	15.1	41.21	35.42	7.32	0.95	0.55	0.568
Floral (Orange blossom)/Argos	16.2	41.21	38.26	3.58	0.74	0.584	0.582
Floral (Orange blossom)/Argos	17.9	41.41	36.02	3.94	0.73	0.577	0.610

anhydrous forms. The transition temperature is determined where the two solubility curves intersect and the eutectic point temperature is at the junction of the solubility and freezing lines; note that the model is able to represent the metastable line observed experimentally, far below the eutectic point.

Finally, the model was applied to multicomponent mixtures which are more representative of food products. Water activity in a concentrated apple juice (Ferro Fontan & Chirife, 1981) was well predicted (Fig. 13). The synthetic liquid honeys studied by Rüegg and Blanc (1981), activity of which ranged between 0.55 and 0.8, were well represented (Fig. 14) in comparaison with prediction given by published models (Ferreira et al., 2003). It was similar for the prediction of water activity in Greek honeys of different geographical and botanical origins (Table 5) studied by Lazaridou, Biliaderis, Bacandritsos, and Sabatini (2004).

4. Conclusion

A physical–chemical model of activity coefficient was proposed. This model can be considered as a second approximation form of the chemical solution theory (Sandler, 1994) as it not only considers that hydration introduces new species in solution (chemical part) but also accepts that this solution is non-ideal at elevated concentration. This model gives better estimates at high concentrations than classical physical models at the expense of two parameters, hydration number and equilibrium constant, which must be estimated from equilibrium properties of binary solutions.

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