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Simulation of the effect of hydrogen bonds on water activity of glucose and dextran using the Veytsman model

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ABSTRACT

Carbohydrates exhibit either van der Waals and ionic interactions or strong hydrogen bonding interactions. The prominence and large number of hydrogen bonds results in major contributions to phase behavior. A thermodynamic framework that accounts for hydrogen bonding interactions is therefore necessary. We have developed an extension of the thermodynamic model based on the Veytsman association theory to predict the contribution of hydrogen bonds to the behavior of glucose–water and dextran–water systems and we have calculated the free energy of mixing and its derivative leading to chemical potential and water activity. We compared our calculations with experimental data of water activity for glucose and dextran and found excellent agreement far superior to the Flory–Huggins theory. The validation of our calculations using experimental data demonstrated the validity of the Veytsman model in properly accounting for the hydrogen bonding interactions and successfully predicting water activity of glucose and dextran. Our calculations of the concentration of hydrogen bonds using the Veytsman model were instrumental in our ability to explain the difference between glucose and dextran and the role that hydrogen bonds play in contributing to these differences. The miscibility predictions showed that the Veytsman model is also able to correctly describe the phase behavior of glucose and dextran.

1. Introduction

Carbohydrates are structurally complex food biopolymers. They exhibit van der Waals and ionic interactions as well as strong, specific interactions such as hydrogen bonds. Hydrogen bonds dominate phase behavior in many instances. An understanding of the phase behavior of mixtures of carbohydrates and the solubility of monosaccharides, oligosaccharides and polysaccharides in water is important in food science, and food product development. Phase changes include gelation, melting, crystallization and glass transitions which affect the texture, stability, processability and shelf life of many foods.

Phase separation has been observed in several carbohydrates including dextran, starch, amylose, amylopectin, locust bean gum (LGB) and guar gum in aqueous solutions individually or in their mixtures (Kalichevsky, Orford, & Ring, 1986; Kalichevsky & Ring, 1987; Garnier, Schorsch, & Doublier, 1995; Ahmad & Williams, 2001; Zimeri & Kokini, 2003a; Zimeri & Kokini, 2003b; Zimeri & Kokini, 2003c). However, the thermodynamic basis of these phenomena are not well understood and are the object of continuous scientific debate (Icoz & Kokini, 2007a).

Hydrogen bonding plays a crucial role in determining the phase behavior of carbohydrate polymers and their miscibility/immiscibility (Icoz & Kokini, 2007a). When polymer/polymer hydrogen bonding is stronger than water/polymer hydrogen bonding, the polymer molecules aggregate and are immiscible. When the opposite happens, the polymer usually disperses in water.

Various models have been developed in order to describe bonding interactions in biopolymer mixtures (Catte, Dussap, & Gros,

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1995; Mengarelli, Brignole, & Bottini, 1999; Starzak, Peacock, & Mathlouthi, 2000; Ben Gaida, Dussap, & Gros, 2006), and also in mixtures ranging from low molecular weight molecules such as alcohols and hydrocarbons (Asprion, Hasse, & Maurer, 2001; Asprion, Hasse, & Maurer, 2003a; Asprion, Hasse, & Maurer, 2003b), to polymer blends (Coleman, Graf, & Painter, 1991; Coleman & Painter, 1995; Painter & Coleman, 2000). These approaches can be roughly subdivided into two general classes, as "chemical" and "physical".

Physical models such as the Wilson, NRTL and UNIQUAC models treat hydrogen bonds as strong, physical interactions. They often postulate different types of hydrogen bonding locations on a molecule. The resulting set of predictive equations is usually quite complex and involves a number of adjustable parameters that need to be measured or estimated from thermodynamic data.

A chemical theory proposed by Dolezalek (1908) and later models developed by Heidemann and Prausnitz (1976) and Acree (1984) on the other hand, treat the mixture by considering the equilibrium distribution of hydrogen-bonded species. The distribution of the associated species is usually described in terms of equilibrium constants related, to the enthalpy and entropy of hydrogen-bond formation. These species are allowed to mix randomly and the physical interactions between them (e.g., dispersion forces) are described by separate parameter(s). An advantage of this approach is the separation of hydrogen bonds from van der Walls or weak polar interactions, thus accounting for their very different chemical forces and temperature dependencies: for example, dispersion forces often vary as $1/T$, while hydrogen bonds follow the van't Hoff relationship. Nevertheless, even in this approach there are still a number of unknown parameters usually obtained by a fit to thermodynamic data. Often these parameters only provide a good description of the data set from which they were obtained and have limited applicability for other even similar mixtures.

Previous work by Painter and colleagues on synthetic polymers has focused on hydrogen bonding based association models for the prediction of primarily hydrogen bonded synthetic polymer solutions and blends (Coleman et al., 1991; Coleman & Painter, 1995; Painter & Coleman, 2000). It has been shown that the contribution of hydrogen bonds to the free energy of mixing depends only on the number of hydrogen bonds of each type. One consequence of this result is that when the solvent is non-polar the equilibrium constants can be measured using FT-IR, thus reducing the number of adjustable parameters needed to describe phase behavior. It was found that group contributions to solubility parameters describing dispersion and weak polar forces, could be used in conjunction with these equilibrium constants to predict phase behavior (Coleman et al., 1991).

Initial applications of the association theory to predict phase behavior in polysaccharide blends have also been conducted. on blends formed by two dextrans of different molecular weight and inulin–amylopectin systems (Icoz & Kokini, 2007b; Icoz & Kokini, 2008). The use of the model necessitated approximations that led to semi-accurate thermodynamic predictions.

The division of approaches into "chemical" and "physical" is clearly artificial, and they simply are alternative ways of describing the same thing. This was demonstrated by Veytsman in 1990, who developed a lattice model that describes how hydrogen bonds are distributed between donor and acceptor groups. It was subsequently shown that the results obtained using association models (which can be related to Flory's lattice model) are identical to those obtained using Veytsman statistics (Coleman & Painter, 1995; Painter & Coleman, 2000). However, the latter approach is more easily and transparently applied to mixtures where the components have multiple donor and acceptor sites (Park, Veytsman, Coleman, & Painter, 2005).

In this paper, we present an extension of the Veytsman contact theory to predict the contribution of hydrogen bonds on the water activity and we developed a phase diagram for glucose–water system and the carbohydrate dextran in water. The glucose–water system was used as a simpler model to obtain the data for the modeling of the more complex dextran–water system. This enables molecular level understanding of the contribution of hydrogen bonding to the phase behavior of carbohydrate mixtures. Free energy of mixing together with its second derivative was calculated in order to predict the phase behavior of glucose water and dextran water solutions.

2. Miscibility theory

2.1. The free energy of mixing for a system involving hydrogen bonds

The free energy of mixing ΔF_{mix} for a mixture of solvent/molecules involving hydrogen bonds can be expressed as the sum of the free energy of mixing due to non-specific interactions ΔF_{NHB}, and the free energy of mixing due to hydrogen bonds ΔF_{HB} (Veytsman, 1990):

$$\Delta F_{mix} = \Delta F_{NHB} + \Delta F_{HB} \tag{1}$$

2.2. The hydrogen bonds contribution: Veytsman lattice model

In the Veytsman lattice model (1990) a single molecule of each species occupies a number of cells and has a number of H-donor and H-acceptor sites. Veytsman's combinatorial approach allows counting the number of hydrogen bonds distributed between the donor and acceptor groups in the mixture. The model assumes that a donor site of an ith kind can form an H-bond with an acceptor site of a jth kind only if the active sites occupy adjacent cells on the lattice. Such a bond is referred to as an (i and j) bond. The first index refers to the donor group and the second one to the acceptor group.

The following expression for the free energy of hydrogen bonding from the contribution of the components in a mixture is obtained (Veytsman, 1990):

$$\frac{F_{HB}}{VRT} = \sum_{i=1}^{k}\sum_{j=1}^{k} m_{ij} + \sum_{i=1}^{k} n_i a_i \ln\left(\frac{n_i d_i - \sum_{j=1}^{k} m_{ij}}{n_i d_i}\right) + \sum_{j=1}^{n} n_j a_j \ln\left(\frac{n_j a_j - \sum_{i=1}^{k} m_{ij}}{n_j a_j}\right) \tag{2}$$

The stoichiometric equations are written as:

$$m_{ij} = K_{ij}\left(n_i d_i - \sum_k m_{ik}\right)\left(n_j a_j - \sum_k m_{kj}\right) \tag{3}$$

where m_{ij} is the number of moles of (i and j) hydrogen bonds per unit volume where i is the donor group coupled with the acceptor species j; n_i is the number of moles of reference units (molecules or monomer) of i kind per unit volume, d_i is the number of donor groups of ith kind per unit (molecule or segment), a_j is the number of acceptor groups of jth kind per unit (molecule or segment), V is the total volume of the mixture, R is the universal gas constant and T is the absolute temperature. The quantities K_{ij} are the equilibrium constants for the formation of hydrogen bonds of each type. The values n_i can be expressed through the molecular masses

w_i, the densities ρ_i and volume fractions ϕ_i of the corresponding components:

$$n_i = \frac{\phi_i \rho_i}{w_i} \tag{4}$$

The chemical potential of the ith species in the mixture is related to the free energy according to the following equation:

$$\frac{\mu_i}{\mathrm{VRT}} = \frac{\partial}{\partial n_i}\left(\frac{F}{\mathrm{VRT}}\right)_{T,P,n_j} \tag{5}$$

where μ_i is the chemical potential of the ith component in the mixture, n_i and n_j are the number of moles of the ith and jth species, respectively. The derivative is calculated with respect to the number of moles of the ith component, keeping the temperature, pressure and the number of moles of the jth species constant.

Combining Eqs. (2) and (5), the chemical potential for the hydrogen bonding contribution in the mixture can be written as:

$$\frac{\mu_{i,\mathrm{HB}}}{\mathrm{RT}} = V_{m,i}\sum_{ij} m_{ij} + d_i \ln\left(\frac{n_i d_i - \sum_k m_{ik}}{n_i d_i}\right) + a_j \ln\left(\frac{n_j a_j - \sum_k m_{kj}}{n_j a_j}\right) \tag{6}$$

where $V_{m,i}$ is the molar volume of the ith species calculated as the ratio between the molecular masses w_i and the density ρ_i.

2.3. Application of Veytsman lattice model to carbohydrate solutions

Hydrogen bonds can be formed between one unit and another of the same compound (self-association) as well as between one unit of one compound and another of the second compound (inter-association). Therefore four kinds of HBs occur in these systems. These are: solvent–solvent (*ss*), solvent–carbohydrate (*sc*), carbohydrate–solvent (*cs*) and carbohydrate–carbohydrate where the subscripts *s* and *c* identify the solvent (water) and the carbohydrate (glucose or dextran), respectively. The above interactions are described by the corresponding constituent equilibrium constants: K_{ss}, K_{sc}, K_{cs} and K_{cc}.

The stoichiometric equations for solvent/carbohydrate mixture are:

$$m_{ss} = K_{ss}(n_s d_s - m_{ss} - m_{sc})(n_s a_s - m_{ss} - m_{cs}) \tag{7}$$

$$m_{sc} = K_{sc}(n_s a_s - m_{ss} - m_{sc})(n_c a_c - m_{cc} - m_{sc}) \tag{8}$$

$$m_{cs} = K_{cs}(n_c d_c - m_{cc} - m_{cs})(n_s a_s - m_{ss} - m_{cs}) \tag{9}$$

$$m_{cc} = K_{cc}(n_c d_c - m_{cc} - m_{cs})(n_c a_c - m_{cc} - m_{sc}) \tag{10}$$

where $K_{sc} \neq K_{cs}$ and $m_{sc} \neq m_{cs}$.

K_{sc} is usually different from K_{cs} because of the difference in the electronegativity of the molecular environment of a proton donor group and a proton acceptor group leading to the formation of hydrogen bonds. Similarly m_{sc} and m_{cs} are usually different because they depend on the number of donors and acceptors on the representative units thus strongly dependent on the chemical structure of the interacting species. If the number of donors are different from the number of acceptors, then even in a symmetric system (when $K_{sc} = K_{cs}$), m_{sc} and m_{cs} will be different.

The expression of the free energy of hydrogen bonds is given as follows:

$$\frac{F_{\mathrm{HB}}}{\mathrm{VRT}} = m_{ss} + m_{sc} + m_{sc} + m_{cc} + n_s \ln((\nu_s{}^d)^{d_s} \times (\nu_s{}^a)^{a_s}) + n_c \ln((\nu_c{}^d)^{d_c} \times (\nu_c{}^a)^{a_c}) \tag{11}$$

The chemical potential contribution of the solvent derived hydrogen bonds:

$$\frac{\mu_s, \mathrm{HB}}{\mathrm{RT}} = V_{m,s}(m_{ss} + m_{sc} + m_{cs} + m_{cc}) + d_s \ln \nu_s^d + a_s \ln \nu_s^a \tag{12}$$

Similarly for the carbohydrate:

$$\frac{\mu_c, \mathrm{HB}}{\mathrm{RT}} = V_{m,c}(m_{ss} + m_{sc} + m_{cs} + m_{cc}) + d_c \ln \nu_c^d + a_c \ln \nu_c^a \tag{13}$$

where $V_{m,s}$ and $V_{m,c}$ are the molar volume of the solvent and carbohydrate, respectively; m_{ss}, m_{sc}, m_{cs} and m_{cc} are the moles of hydrogen bonds per unit volume of the solution, n_s and n_c are the number of moles of solvent and of carbohydrate per unit volume of the solution, d_s and d_c and a_s and a_c are the number of donors and acceptors per each representative unit of solvent and carbohydrate.

The quantities $\nu_s{}^d$, $\nu_c{}^d$, $\nu_s{}^a$ and $\nu_c{}^a$ are the fractions of free donor and acceptor groups for the solvent and carbohydrate, respectively defined according to the following equations:

$$\nu_s{}^d = \frac{n_s d_s - m_{ss} - m_{sc}}{n_s d_s} \quad \nu_c{}^d = \frac{n_c d_c - m_{cc} - m_{cs}}{n_c d_c} \tag{14}$$

$$\nu_s{}^a = \frac{n_s a_s - m_{ss} - m_{cs}}{n_s a_s} \quad \nu_c{}^a = \frac{n_c a_c - m_{cc} - m_{sc}}{n_c a_c} \tag{15}$$

Eq. (11) only provides the term of the free energy of hydrogen bonds in the (solvent/carbohydrate) mixture. The overall contribution of hydrogen bond formation to the change in the free energy of mixing $\Delta F_{\mathrm{HB}}/\mathrm{VRT}$ is obtained by subtracting the expression for the free energy of hydrogen bonding in the pure state:

$$\frac{\Delta F_{\mathrm{HB}}}{\mathrm{VRT}} = \frac{F_{\mathrm{HB}}}{\mathrm{VRT}} - \frac{F_{\mathrm{HB_0}}}{\mathrm{VRT}} \tag{16}$$

The free energy in the pure state F_{HB_0} is expressed according to Eq. (17) below:

$$\frac{F_{\mathrm{HB_0}}}{\mathrm{VRT}} = (1 - \Phi_c) \times [F_{\mathrm{HB}}(0)] + \Phi_c \times [(F_{\mathrm{HB}}(1)] \tag{17}$$

where Φ_c is the volume fraction of the carbohydrate and $F_{\mathrm{HB}}(0)$ and $F_{\mathrm{HB}}(1)$ are the values of the F_{HB} calculated from Eq. (11) at $\Phi_c = 0$ and $\Phi_c = 1$, respectively.

Similarly, the overall contribution of the chemical potential for the solvent and the carbohydrate is then expressed as:

$$\frac{\Delta \mu_{s,\mathrm{HB}}}{\mathrm{RT}} = \frac{\mu_{s,\mathrm{HB}}}{\mathrm{RT}} - \frac{\mu_{s,\mathrm{HB_0}}}{\mathrm{RT}} \tag{18}$$

$$\frac{\Delta \mu_{C,\mathrm{HB}}}{\mathrm{RT}} = \frac{\mu_{C,\mathrm{HB}}}{\mathrm{RT}} - \frac{\mu_{C,\mathrm{HB_0}}}{\mathrm{RT}} \tag{19}$$

where $\mu_{s,\mathrm{HB_0}}/\mathrm{RT}$ and $\mu_{c,\mathrm{HB_0}}/\mathrm{RT}$ are expressions for the chemical potential of the hydrogen bonds for the solvent and the carbohydrate in the pure state calculated from Eqs. (12) and (13) at $\Phi_c = 0$ and $\Phi_c = 1$, respectively.

2.4. Non-specific contribution: The free energy of mixing and the chemical potential for water

The term describing non-specific contributions to the free energy of mixing for a solution is expressed by the Flory–Huggins theory (Flory, 1953; Painter & Coleman, 1997):

$$\frac{\Delta F_{\mathrm{FH}}}{\mathrm{RTV}} = (1 - \Phi_C) \times \frac{\rho_S}{w_S} \times \ln(1 - \Phi_C) + \Phi_C \times \frac{\rho_C}{w_C} \times \ln \Phi_C + \chi \frac{\rho_S}{w_S} \times \Phi_C \times (1 - \Phi_C) \tag{20}$$

Similarly the overall non-specific contribution of the chemical potential for water is given by Eq. (21) (Painter & Coleman, 1997) reported below:

$$\frac{\Delta\mu_{s,\mathrm{FH}}(\Phi)}{\mathrm{RT}} = \ln(1-\Phi) + \left(1-\frac{1}{M}\right)\Phi + \Phi^2\chi \tag{21}$$

where M is the degree of polymerization of the polymer defined as the ratio between the molar volume of the component and the reference volume (solvent i.e. water molar volume) and χ is the Flory–Huggins interaction parameter.

The Flory–Huggins interaction parameter is related to the Hildebrand solubility parameters of the solvent (δ_s) and polymer (δ_p) (Painter & Coleman, 1997) according to:

$$\chi = \frac{V}{\mathrm{RT}}\left(\delta_s - \delta_p\right)^2 \tag{22}$$

The total contribution of the chemical potential for water is obtained as:

$$\frac{\Delta\mu_{s,\mathrm{tot}}(\Phi)}{\mathrm{RT}} = \frac{\Delta\mu_{s,\mathrm{HB}}(\Phi)}{\mathrm{RT}} + \frac{\Delta\mu_{s,\mathrm{FH}}(\Phi)}{\mathrm{RT}} \tag{23}$$

where the two terms on the right hand side of Eq. (23) are the Flory–Huggins and hydrogen bonding term expressed by Eqs. (18) and (21), respectively.

3. Materials and methods

3.1. Solutions preparation

Anhydrous dextrose (D-Glucose) and dextran (M_w 70,000) were purchased from EMD (Millipore, MA, USA) and Sigma-Aldrich (St. Louis, MO, USA), respectively. Distilled water was used as solvent in the preparation of the solutions. Initial moisture content of the glucose powder and dextran were determined by drying in a convection oven at 105 °C for 24 h. The moisture was found to be 10 and 16 ± 0.04% in glucose and dextran, respectively. Determination of the initial moisture content was carried out in triplicate. To prepare the solutions, the powders were dissolved in water using magnetic stirring at room temperature until total dissolution occurred. Powders were weighed using a Mettler Toledo analytical balance with ±0.1 mg precision in different concentration ranges. For glucose, because experimental data was available in the literature in the range of 30–65% (Bui, Nguyen, & Muller, 2003), solutions in the range of 10–30% and 65–80% w/w were prepared. For concentrations higher than 50% it was necessary to heat the mixture for the glucose to dissolve. For dextran, solutions were limited to the range of 10–55% w/w. In this range it was possible to obtain homogenous and transparent solutions. At mass fractions higher than 55% w/w the formation of dextran–water homogenous solutions could not be made and there was phase inversion where the dextran remained in the form of a white wet mud. In the region above 55% the water activity of the dextran powder/mud needed to be measured. This data was available in a previous study in our laboratory (Icoz, 2008).

3.2. Water activity measurements of glucose and dextran solutions

Experimental water activities of aqueous glucose and dextran solutions were measured at 25 °C in an Aqualab series 4TE (Decagon Devices, Pullman, WA, USA), dew point water activity meter with controlled temperature. The instrument allows measurements of water activity (a_w) between 0.030 and 1.000 in the temperature range of 15–50 °C. Measurements were taken in triplicates and the average values were used for predictions.

3.3. Particle density measurements

The apparent particle density of dextran and glucose powders was measured at 25 °C with a gas/helium pycnometer (AccuPyc 1330, Micrometrics) using 1 cm^3 insert. The values obtained were 1.54 and 1.026 g/cm^3 for glucose and dextran, respectively.

3.4. Determination of Veytsman model parameters for carbohydrate–water systems

In order to use the model the number of donors and acceptors per representative unit as well as the equilibrium constants describing hydrogen bonds for both self-association and inter-association are needed. Four equilibrium constants are necessary, each of them describing a type of hydrogen bonding interaction: K_{ss} (water–water), K_{sc} (water–carbohydrate), K_{cs} (carbohydrate–water) and K_{cc} (carbohydrate–carbohydrate) (Eqs. (7)–(10)). In order to easily distinguish between glucose and dextran, in the definition of K_s, the subscript c has been replaced with g and d to refer to glucose and dextran, respectively. We will discuss below how all the modeling parameters were obtained for both glucose and dextran aqueous systems.

3.4.1. Estimation of the number of donors and acceptors on the water and glucose reference units

A water molecule has the ability to form four hydrogen bonds, two bonds as a donor and two as an acceptor because of its "oxygen lone–pair orbitals"(Markovitch & Agmon, 2008).

The glucose molecule has five hydroxyl groups (OH) and one ether oxygen atom. Therefore each molecule of glucose has five hydrogen donor groups and six hydrogen acceptor groups. Thus the number of donor and acceptor sites per molecule of water is $d_s = a_s = 2$ and for glucose $d_g = 5$, $a_g = 6$.

3.4.2. Estimation of the magnitude of equilibrium constants of hydrogen bonds for glucose–water systems

3.4.2.1. Self-association equilibrium constants for glucose–glucose and water–water hydrogen bonds. K_{ss} and K_{gg} were estimated from IR spectroscopy measurements of the free OH groups conducted earlier in Painter's group (Coleman & Painter, 1995 and Luck, 1980).

Following the methodology presented by Icoz and Kokini (2007b), the experimental hydrogen bond equilibrium constant available for 2-propanol (CH_3—CHOH—CH_3) (Coleman & Painter, 1995) was used as a reference for the equilibrium constant of a single glucose–glucose hydrogen bond. This self-association equilibrium constant from IR measurements has the dimensionless value of 57.6 (Coleman & Painter, 1995).

In Veytsman model K_{gg} has the units of cm^3/mol, since it refers to the molar volume of glucose per OH group. In order to obtain the correct value of K_{gg} the value of 57.6 has been multiplied by a factor equal to the molar volume of each OH group in the glucose molecule. The molar volume of 116.99 cm^3/mol was calculated using the density of 1.54 g/cm^3 experimentally determined as described in Section 3.3. This value has been divided by the number of hydroxyl groups (OH = 5) on the glucose molecule, thus obtaining the molar volume of 23.40 cm^3/mol per OH group. The value of 57.6 was then multiplied by this factor, obtaining the final value of K_{gg} equal to 1348 cm^3/mol.

For water, the dimensionless experimental value $K_{\text{self-assoc\_exp}}$ obtained by IR spectroscopy measurements of the free OH is 94.74 (Luck, 1980). Similarly, the value of K_{ss} was obtained using the molar volume of water equal to 18.02 cm^3/mol divided by the "equivalent" number of hydroxyl groups (OH = 2) on the water molecule (since the oxygen atom on the water molecule has two lone pairs of electrons). Thus the value of K_{ss} = 856 cm^3/mol was obtained.

Table 1
Input parameters used in the simulation of water activity data of aqueous glucose solutions.

Input parameters		
Variation intervals of K_{sg} and K_{gs}	Step of K_{sg} and K_{gs}	Value of χ
Constant value 0	1	0.01
[0, 855]	1	0.01
[856, 1348]	1	0.01
[1349, 2696]	1	0.01

Table 2
Input parameters used in the simulation of water activity data of aqueous dextran systems.

Input parameters		
Variation intervals of K_{dd}	Step of K_{sg} and K_{gs}	Values of χ
[0, 270]	1	0.35
[271, 674]	1	0.35
[674, 1348]	1	0.35
[1349, 2020]	1	0.35

3.4.2.2. Inter-association constants for equilibrium hydrogen bonding and Flory–Huggins interaction parameter for glucose–water solutions. The values of the inter-association dimensionless equilibrium constants for water–glucose and glucose water bonds are not experimentally measurable by IR spectroscopy due to the presence of water (which absorbs very strongly in the infrared region) and to the partial/total immiscibility of glucose in the inert solvent such as cyclohexane or toluene used in the IR measurements. As a result, the approach developed above to estimate the self-association equilibrium constants (Section 3.4.2.1) could not be used to estimate the values of K_{sg} and K_{gs}.

Therefore we developed an alternative approach using a curve fitting procedure of the available experimental water activity data as a function of the volume fraction of glucose, Φ_g. The curve fitting procedure uses a dedicated mean square error (MSE) minimization algorithm, minimizing MSE as a function of K_{sg} and K_{gs} for the array of experimental points. This algorithm has been implemented in a program called "minsearch"© written in C language. Based on an "exhaustive search method", minsearch iteratively searches for the optimal values of the constants in a selected interval. At each cycle, the equilibrium constants are increased of a value equal to a specified step. More specifically, for each trial pair of K_{sg} and K_{gs} the concentrations of the hydrogen bonds in the mixtures, m_{ss}, m_{sg}, m_{gs} and m_{gg} (moles of HBs per unit volume of the solution) are determined by numerically solving the stoichiometric equations (Eqs. (7)–(10)). The values obtained for hydrogen bonds concentrations, m_{ij} and the chosen value of the Flory–Huggins interaction parameter χ are then used to calculate the overall change of the chemical potential for water using Eq. (23). The procedure is repeated for other trial pair. The mean squared error MSE for all points is estimated and the values where MSE is smallest are obtained. The interval [0, 2696] with step = 1 was selected for the constants where the limits are expressed in cm^3/mol. This interval was the same for both K_{sg} and K_{gs}. In order to reduce the computational time, the selected interval was divided in three subintervals called variation intervals according to the selected step of 1: [0, 855]; [856, 1348], and [1349, 2696] using the values of K_{ss} equal to 856 cm^3/mol and K_{gg} equal to 1348 cm^3/mol calculated as explained in Section 3.4.2.1. As the maximum value of the interval we have selected 2696 cm^3/mol calculated as double the value of the K_{gg}. In all the calculations, χ was assumed equal to 0.01 because of the high solubility of glucose in water. In the predictions, the value of M in Eq. (21) was equal to 6.5 as obtained by the ratio between the molar volume of glucose (116.99 cm^3/mol) and the molar volume of water (18.02 cm^3/mol). In order to clarify the effect of K_{sg} and K_{gs} on the magnitude of water activity the case of only self-association was investigated by setting both the constants K_{sg} and K_{gs} to zero. The input parameters of minsearch used for the MSE calculation are summarized in Table 1.

3.4.3. Estimation of Veytsman model parameters for dextran

The methodology developed for glucose has been extended to dextran–water solutions. Dextran is a glucose polymer and its repeating units have three hydroxyl groups and two ether oxygen atoms. The number of donors and acceptors were determined by using the single repeating unit (monomer) of dextran. Accordingly every monomer of dextran has three donor groups and five acceptor groups: $d_c = 3$ and $a_c = 5$.

Dextran monomers also need four equilibrium constants: K_{ss} (water–water), K_{sd} (water–dextran), K_{ds} (dextran–water) and K_{dd} (dextran–dextran). In this case we used for the equilibrium constants of dextran–water and water–dextran the optimal values obtained for glucose–water systems. It is reasonable to assume that the strength of the hydrogen bonds formed between glucose and water is equal to the strength of the hydrogen bonds formed between dextran monomer and water because of the similar chemical structure of glucose and dextran monomer. The procedure described in Section 3.4.2.2 was used to determine the optimal values of average dextran–dextran hydrogen bonding interaction equilibrium constant K_{dd}. We also used the value of 0.35 for the χ parameter. This average value is reported as being commonly observed for a large number of polymers (Sperling, 2006). The simulations were carried out first by using the water activity data corresponding to the low volume fraction, complete solution region. We fitted the constant K_{dd} in the interval: [0, 2020] with step = 1.

The maximum value of 2020 cm^3/mol was obtained by applying the same methodology used for glucose to calculate its self-association equilibrium constant as described in Section 3.4.2.1. For dextran the molar volume of dextran monomer used was 162.06 cm^3/mol.

Simulations were also carried out using the degree of polymerization for dextran i.e. $M = 3786$ as obtained by the ratio of the molar volume of the polymer and the molar volume of the solvent. The parameters used in the simulations for dextran–water systems are summarized in Table 2.

The value of 270 for K_{dd} originated from earlier studies by Shenoy, Arrighi, and Cowie (2008) showing that the equilibrium constant for hydrogen bonding for a polymer could be as little as 1/5th that of the monomer.

For glucose–water solutions the simulation algorithm was applied to the whole water activity range. This is theoretically sound since glucose remains completely soluble in the concentration range that we studied. However, dextran at low moisture contents, exhibits glassy or crystalline phases. Thus it is not possible to use the same association constants to predict phase behavior in this concentration range. For this reason, only the water activity data in the complete solution region i.e. up to a volume fraction of dextran were simulated.

3.5. Calculation of thermodynamics properties (free energy of hydrogen bonds, total free energy of mixing and its second derivative)

We have developed a dedicated algorithm to numerically solve the stoichiometric equations (Eq. (7)–(10) in Section 2.3) obtaining as output the concentration of hydrogen bonds mij as a function of glucose and dextran volume fraction and to calculate the free energy of hydrogen bonds in the mixture. This algorithm has been implemented in a dedicated program called "hbcalculator"©

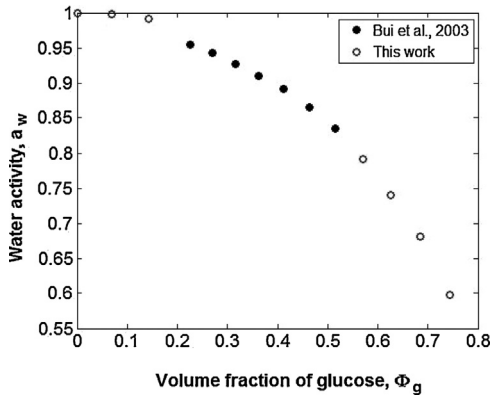

Fig. 1. Experimental water activity data of aqueous glucose solutions vs volume fraction of glucose, Φ_g.

written in C language. The total free energy of mixing was estimated by adding this contribution and the Flory–Huggins term in Eq. (1). Analytical calculation of the second derivative of the total free energy of mixing as a function of glucose and dextran volume fraction is non-trivial, so we used numerical differentiation. For this purpose, a dedicated algorithm has been developed and implemented in another dedicated program "D2bincalculator"© also written in C language.

4. Results and discussion

4.1. Calculations of inter-association constants from water activity data

In Fig. 1 the water activity (a_w) of glucose–water mixtures measured in this study is plotted together with the experimental data reported by Bui et al. (2003) versus the volume fraction of glucose, Φ_g. The correspondence between our measurements and literature values is remarkable and the data nicely superimpose. In the lowest volume fraction range at Φ_g between 0.1 and 0.2, water activity of glucose–water solutions is close to 1.0. As the volume fraction of glucose increases further, water activity decreases as measured here and reported by others (Chirife & Del-Pilar, 1994; Chirife & Buera, 1995; Chirife & Buera, 1996).

The graphical comparison between the experimental data corresponding to the whole solution region and the predicted values of the water activity of glucose–water mixtures versus the volume fraction of the monosaccharide Φ_g is shown in Fig. 2.

The results of the simulations obtained with $K_{sg} = K_{gs} = 0$ are plotted in Fig. 2a. When inter-association of glucose with water is neglected and only self-association is assumed to occur, the model fails to predict the reduction in water activity values of glucose–water mixtures. The predicted water activities erroneously increase at increasing glucose volume fraction, Φ_g.

Table 3
Results of the simulation by using the water activity data in glucose–water solutions.

Variation intervals of K_{sg} and K_{gs}	K_{sgopt}	K_{gsopt}	MSE
Constant value 0	0	0	0.6662
[0, 855]	855	855	0.0894
[856, 1348]	1180	*910*	0.0052
[1349, 2696]	1349	1349	0.1193

The formation of hydrogen bonds (K_{sg} and $K_{gs} > 0$) reduces the water activity values as shown in Fig. 2b. When inter-association is introduced, the results of the simulations become consistent with the experimental observations and the degree of the inter-association plays a crucial role in the ability of the model to predict the observed magnitude of water activity and its reduction at increasing glucose volume fraction, Φ_g (Fig. 2b).

The best agreement between predictions and experimental data is achieved at $K_{sg} = 1180$ and $K_{gs} = 910\,cm^3/mol$ with the smallest MSE = 0.0052, as shown in Fig. 2b. These values of K_{sg} and K_{gs} are close to each other indicating that each hydrogen bond formed between water and glucose molecules has about the same strength ($\sim \ln K_{sg} = 7.07$ and $\ln K_{gs} = 6.80$). This is intuitively reasonable considering that each equilibrium constant describes the formation of hydrogen bonds between the donor and the acceptor of each hydroxyl group. If K_{sg} and K_{gs} were smaller than K_{ss} water molecules would be strongly attracted to one another. This condition would then prevent glucose from interacting with water and as a result glucose would be insoluble in water contrary to what we experimentally observe. The fact that K_{sg} and K_{gs} are higher than K_{ss} reflects the fact that water predominantly associates with glucose both as donor and acceptor. The values of K_{sgopt}, K_{gsopt} and MSEs are summarized in Table 3. Further increase of K_{sg} and K_{gs} from their best values does not improve the accuracy of the predictions as shown by the increase of the MSE in Table 3.

4.2. Calculations of distribution of hydrogen bonds in glucose–water solutions and the effect of the magnitude of the inter-association/self-association ratio

The concentration of hydrogen bonds (moles/cm^3) for each type of interaction m_{ss}, m_{sg}, m_{gs} and m_{gg}, formed in the glucose–water mixture as predicted by Veystman model at different values of K_{sgopt} and K_{gsopt} are shown in Fig. 3. If only self-association occurs in the mixture $m_{sg} = m_{gs} = 0$ because in Eqs. (8) and (9) both the

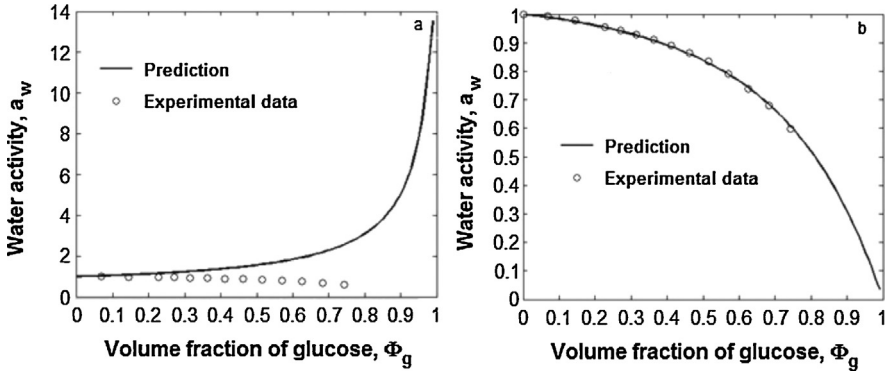

Fig. 2. Simulation of water activity of aqueous glucose solutions with Veytsman model at: (a) imposed $K_{sg} = K_{gs} = 0$ and (b) $K_{sg} = 1180$ and $K_{gs} = 910\,cm^3/mol$.

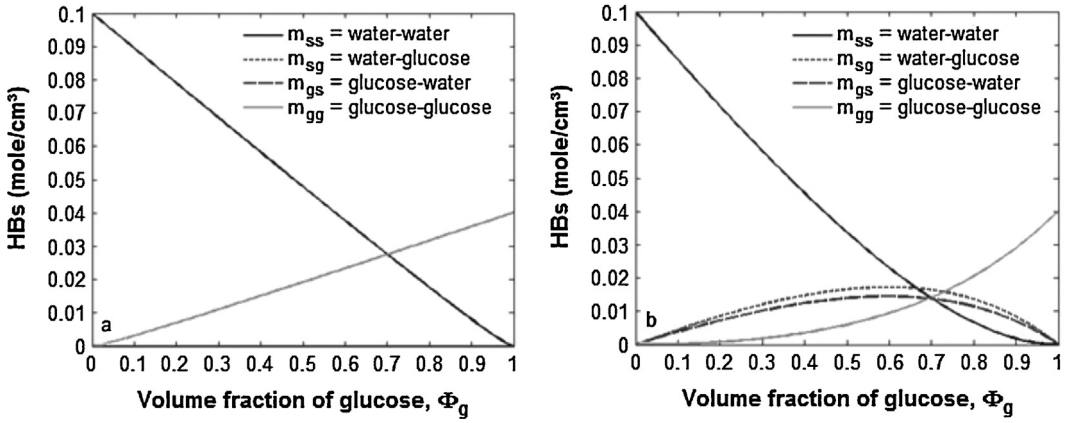

Fig. 3. Predicted concentrations of hydrogen bonds (moles/cm^3) in aqueous glucose solutions with Veytsman model at: (a) $K_{sg} = K_{gs} = 0$ and (b) $K_{sg} = 1180$ and $K_{gs} = 910$ cm^3/mol.

constants K_{sg} and K_{gs} are equal to zero (Fig. 3a). No hydrogen bonds are formed between water and glucose molecules. The concentration of hydrogen bonds formed between solvent molecules (m_{ss}), decreases linearly with the volume fraction of glucose, Φ_g.

On the other extreme the interactions per unit volume between glucose–glucose molecules m_{gg}, increase linearly from zero to the maximum value of 0.040 mol/cm^3 when the mixture is composed only of glucose. As the mixture becomes more concentrated, due to the disappearance of water molecules in the mixture, less hydroxyl (OH) groups form hydrogen bonds with water, while the presence of more OH groups on glucose molecules will increase the glucose–glucose molecular interactions resulting in an increase of the concentration of hydrogen bonds formed between glucose molecules.

The concentration of hydrogen bonds in the glucose–water mixtures at $K_{sg} = 1180$ cm^3/mol and $K_{gs} = 910$ cm^3/mol is shown in Fig. 3b. As for the case of $K_{sg} = K_{gs} = 0$ water–water molecular interactions, m_{ss} decrease while glucose–glucose hydrogen bonds m_{gg} increase with increasing values of the volume fraction of the monosaccharide. In addition, as the mixture becomes more concentrated in glucose, the formation of hydrogen bonds between water and glucose molecules also occurs and the curves describing the concentration of m_{sg} and m_{gs} exhibit a maximum. The hydrogen bonds in the system increase with the volume fraction of glucose until a maximum value, above which they start to decrease due to saturation of the system.

It is interesting to note, that m_{sg} is slightly higher than m_{gs}. The higher concentration of hydrogen bonds formed between each molecule of water and each molecule of water glucose is an indicator of the easier diffusion of water into the glucose than glucose into water. This finding is qualitatively in agreement with the results of Lee, Debenedetti, and Errington (2005) in their molecular simulation study of hydration of glucose, trehalose and sucrose. In all cases a slightly higher average number of acceptor bonds per carbohydrate molecule with water was found. This could be explained by "the entropic contribution which arises from the fact that an acceptor bond can be formed in two equivalent ways (two H atoms per water molecule), whereas there is only one choice of H atom in a donor bond" (Lee et al., 2005).

4.3. Calculations of dextran–dextran self-association constant from water activity data

The water activity data for glucose and dextran–water systems are shown in Fig. 4. It is well known that dextran values are higher than glucose–water values throughout the volume fraction range showing a considerably greater interaction between glucose and water compared to dextran and water.

For dextran, simulations of water activity data were carried out using for K_{sd} and K_{ds} the best values obtained with glucose–water solutions i.e. 1180 cm^3/mol and 910 cm^3/mol, respectively. χ was kept constant at 0.35 as indicated before. The results are shown in Fig. 5.

The best fit was obtained for $K_{dd} = 1503$ cm^3/mol in the full complete solution region with MSE = 0.006. This value is somewhat higher than the value for glucose indicating a higher strength of hydrogen bonds formed between each repeating unit thus limiting the degree of molecular interaction between dextran and

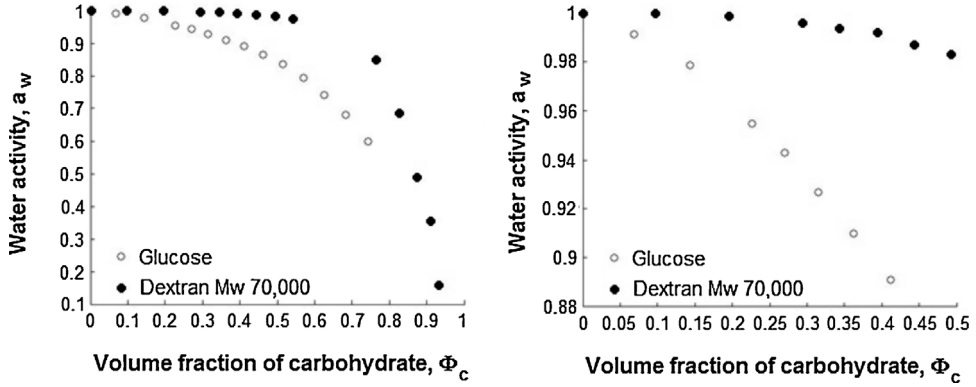

Fig. 4. Experimental water activity data of glucose–water solutions and dextran–water systems vs volume fraction of the carbohydrate Φ_c in the whole investigated range. The Figure on the right is the expanded inset.

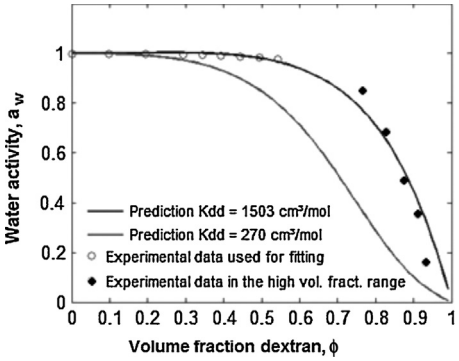

Fig. 5. Simulation of water activity of aqueous dextran solutions with Veytsman model at K_{dd} = 1503 cm^3/mol and K_{dd} = 270 cm^3/mol with M = 3776 and χ = 0.35 in the complete dilution solution range.

water. This is in agreement with what we observe experimentally. In the low volume fraction region, as shown in Fig. 4 the water activity values for dextran are considerably higher than glucose indicating more "free water" in case of dextran solutions than glucose.

The comparison between the results obtained in the complete solution and the concentrated/partially aggregated regions, shows that Veytsman model predicts the experimental observations very well in the low volume fraction region, and an equally good agreement between the simulations and the experimental data is obtained in the high dextran volume fraction region. It is possible that there is a dependence of K_{dd} on the volume fraction of dextran and several different best values of K_{dd} would be obtained by fitting separately different volume fraction regions.

We have also simulated the data using the Shenoy scaling concept of taking 1/5th of the monomer K_{gg} (glucose) value for dextran giving us 270 cm^3/mol. This simulation fits the experimental data well in the dilute solution region only also shown in Fig. 5. This is expected since the Shenoy approximation holds true only where polymer/polymer interactions are not promoted by molecular crowding which is observed when the concentration of the polymer in solution increases. The high flexibility of dextran chains (Nordmeier, 1993) prevents self-association to such a high degree in the dilute solution region that hydrogen bonding interactions between the dextran monomers are highly limited. The best fit value of the K_{dd} increases to 1503 cm^3/mol as we include data which are in the region where molecular interactions between dextran molecules are forced because of increasing crowding. This result shows that there is an effect of removing water leading to increasing dextran–dextran interactions. The presence of a high volume fraction of water in the highly dilute region limits the interaction between dextran molecules. As the content of water decreases the dextran monomers are forced to interact with each other, thus explaining the increase of K_{dd} in this region. At the same time, since dextran is hygroscopic, the degree of interaction between water and dextran is not affected thus explaining why there is no change in the values of K_{sd} and K_{ds}. The values of $K_{dd\text{opt}}$ and MSEs for each case are summarized in Table 4.

Table 4
Results of the simulation by using the water activity data in dextran–water systems.

Variation intervals of K_{dd}	$K_{dd\text{opt}}$	MSE
[0, 270]	270	0.08773
[271, 674]	674	0.04890
[674, 1348]	1348	0.00936
[1349, 2020]	1503	0.00579

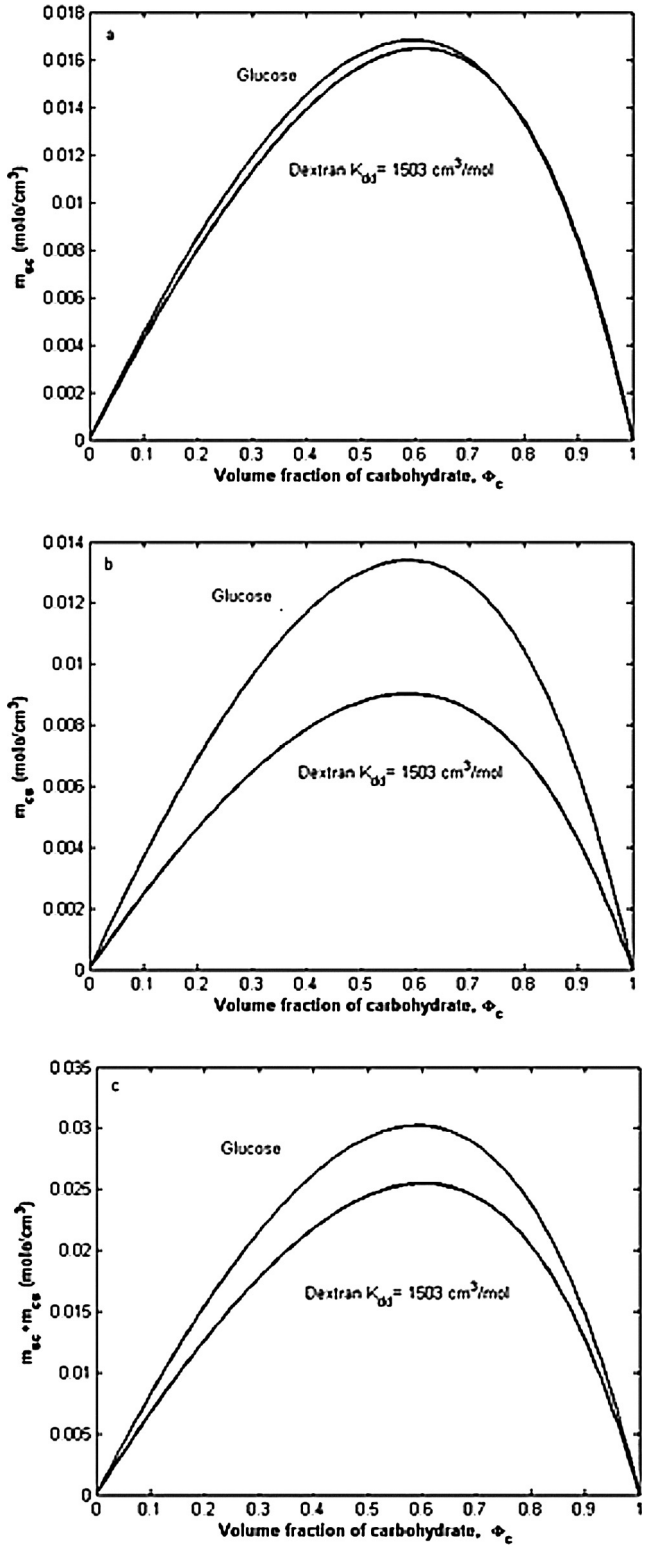

Fig. 6. Predicted concentrations of (a) water–carbohydrate hydrogen bonds m_{sc}, (b) carbohydrate–water hydrogen bonds m_{cs} and, (c) the sum of water–carbohydrate and carbohydrate–water hydrogen bonds $m_{sc} + m_{cs}$ in aqueous glucose and dextran solutions with Veytsman model.

4.4. Calculations of the distribution of hydrogen bonds in dextran–water solutions using the Veytsman model and the effect of the magnitude of the inter-association/self-association ratio

Fig. 6 shows the concentration of the inter-association hydrogen bonds between water–dextran and dextran–water respectively, as

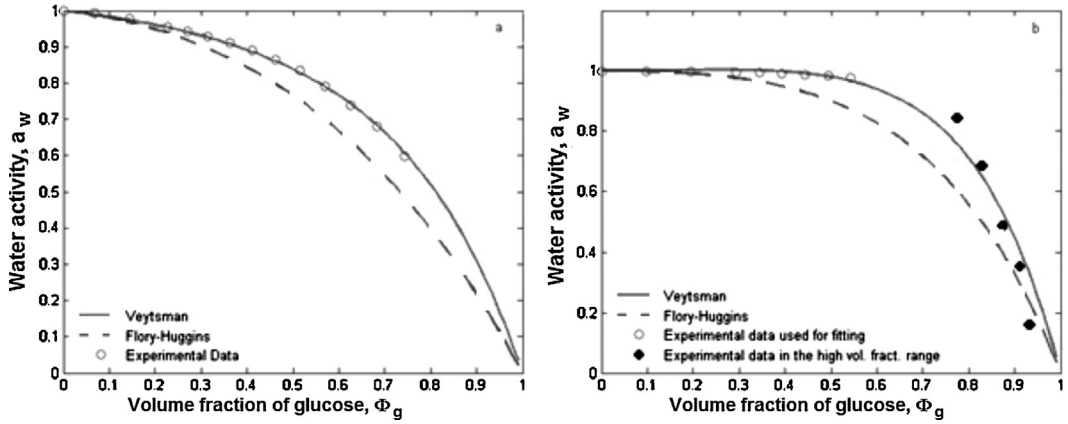

Fig. 7. Comparison of the simulations of water activity with Veytsman model and the Flory–Huggins theory of (a) aqueous glucose solutions at K_{sg} = 1180 cm^3/mol, K_{gs} = 910 cm^3/mol and imposed χ = 0.01, (b) aqueous dextran solutions at K_{dd} = 1503 cm^3/mol and imposed χ = 0.35 using the fitting procedure in the low volume fraction range.

a function of carbohydrate volume fraction. The values corresponding to glucose–water and water–glucose were also plotted on the same graph. We observe that for water–donor bonds, the values of m_{sg} and m_{sd} are very close to each other (Fig. 6a) with m_{gs} being slightly higher than m_{ds}. The number of acceptors on each glucose molecule is 6 and on the dextran monomer is 5 and these values are very close to one another.

In contrast m_{gs} is significantly higher than m_{ds} (Fig. 6b). The fact that m_{ds} values are smaller than m_{gs} is reflected in the rapid drop of water activity when glucose volume fraction increases compared to that of dextran and reflects the higher inter-association between glucose molecules and water as a result of the higher number of donors on glucose (5) molecules compared to that of dextran (3).

We observe, however, that in order to better explain the differences in the experimental water activity between glucose and dextran, it might be more appropriate to consider the sum of the interactions between water–carbohydrate and carbohydrate–water as a function of the volume fraction of carbohydrate (Fig. 6c).

According to the curves describing the m_{ds} and m_{gs}, the number of hydrogen bonds formed between dextran and water is smaller than in case of glucose, thus explaining why more free water is available with dextran in the higher water activity region. This reflects what we observed with the individual m_{gs} and m_{ds} data but the consideration of the total water–carbohydrate and carbohydrate–water interactions gives the impact of the magnitude of the complete interaction.

4.5. Comparison between the Flory–Huggins theory and the Veytsman model for glucose–water and dextran–water solutions

In order to evaluate the significance of hydrogen bonds in contributing to the water activity of glucose–water and dextran–water systems, simulations of the water activities of both glucose and dextran–water mixtures were also carried out by using only the expression for the Flory–Huggins chemical potential (Eq. (21)), and comparing that with the Veytsman theory.

For glucose–water solutions, the results of the calculations are shown in Fig. 7a. There is clearly a considerable difference between the predictions and the water activity experimental data when using the Flory–Huggins theory. The Flory–Huggins model under predicts the experimental observations and fails in the whole volume fraction range showing the importance of hydrogen bonding contributions.

For dextran–water, water activity comparison between the predictions and experiments is shown in Fig. 7b. The Flory–Huggins theory still fails to predict the experimental water activity data as shown by the significant discrepancy observed between the calculated values and measured ones.

The comparison between the results obtained by using the Flory–Huggins theory and the Veytsman model shows that the Flory–Huggins theory without hydrogen bonding is inadequate in terms of accurately describing the water activity of both glucose–water and dextran–water systems and the importance of the hydrogen bonding contributions. The formation and

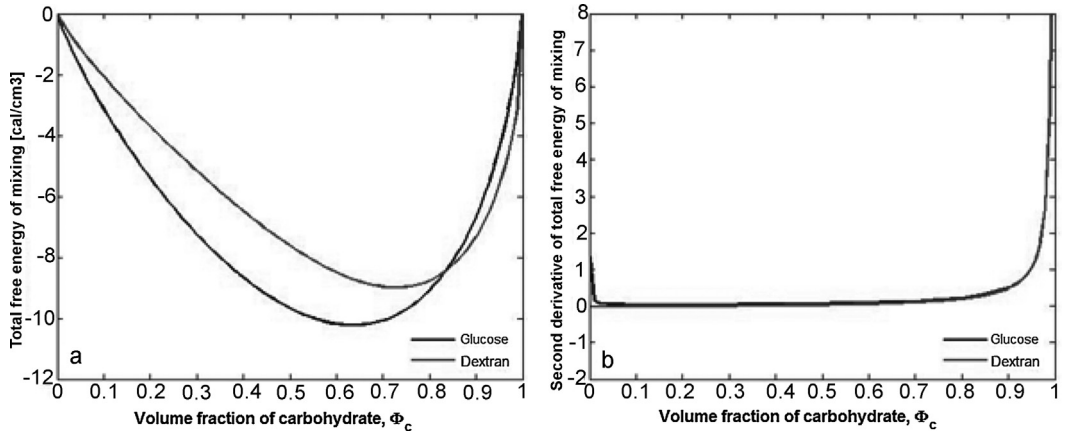

Fig. 8. Predicted (a) total free energy of mixing and (b) second derivative of total free energy of mixing of aqueous glucose solutions and dextran systems with Veytsman model.

distribution of hydrogen bonds in the mixture plays a key role; only the addition of the contribution of hydrogen bonds results in a correct prediction.

4.6. Thermodynamics predictions of the total free energy of mixing and its second derivative in glucose–water and dextran–water solutions

The contribution of hydrogen bonds to the total free energy of mixing as predicted by the model was calculated using the values of all four equilibrium constants as described in Section 3.5 for both glucose–water and dextran–water solutions/mixtures. The total free energy of mixing was obtained by adding the Flory–Huggins term (Eq. (20)) to the Veytsman calculation for hydrogen bonding contribution.

It is well known that the phase behavior is determined by both the signs of the total free energy of mixing ΔF_{mix} and its second derivative with respect to the composition $\partial^2 \Delta F_{mix}/\partial \Phi^2$ (Painter & Coleman, 1997). The curves of the free energy and its second derivative for glucose–water and dextran water mixtures versus the volume fraction of the carbohydrate, Φ_c are graphed in Figs. 8a and b, respectively. The predictions reveal negative values of the total free energy of mixing throughout the whole volume fraction region of these mixtures (Fig. 8a).

The second derivative results are positive (Fig. 8b), clearly indicating that glucose–water and dextran–water solutions are miscible. The comparison of the relative magnitudes of the curves for glucose and dextran show that the total free energy of mixing of glucose is lower i.e. more negative than for dextran up to approximately volume fraction of 0.85. Above this volume fraction there is no significant difference in the magnitude being the value for dextran slightly smaller than in case for glucose. The difference in the magnitude of the free energy of mixing for water–glucose compared to the dextran–water system shows that water–dextran system is less miscible.

5. Conclusions

In this work the Veytsman association model has been applied for the first time to water soluble carbohydrate mixtures including a more simple glucose solution and a more complex dextran–water system by specifically accounting for hydrogen bonding molecular interactions. We calculated the free energy of mixing and its derivative giving the chemical potential which led to the calculation of water activity.

The results of our calculations demonstrated the validity of the model in predicting the water activity. In contrast the Flory–Huggins theory without hydrogen bonds is unable to predict water activity showing the need to account for the hydrogen bonding in order to obtain correct predictions. Our calculations of the concentration of hydrogen bonds proved to be useful in explaining the difference between glucose and dextran and the role that hydrogen bonds play in contributing to these differences.

The miscibility predictions showed that the Veytsman model is also able to correctly describe the phase behavior of glucose and dextran.

Our methodology can be applied to other carbohydrate mixtures composed of monosaccharide as well as carbohydrate polymers. This work represents an improvement in the current knowledge in understanding polysaccharide phase behavior. Our future investigations will focus on understanding how to extend the model to other carbohydrates and to multicomponent carbohydrate systems and validate these concepts with more complex carbohydrate mixtures to facilitate development of novel food products.

Acknowledgements

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