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Predicting phase equilibrium of aqueous sugar solutions and industrial juices using COSMO-SAC

Lucas T. Paese, Rafaela L. Spengler, Rafael de P. Soares, Paula B. Staudt *

Virtual Laboratory for Properties Prediction - LVPP, Chemical Engineering Department, Federal University of Rio Grande do Sul, Rua Ramiro Barcelos, 2777, Bairro Santana, CEP 90035-007, Porto Alegre, RS, Brazil

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ABSTRACT

COSMO-SAC model was used to predict bubble point pressure, bubble point temperature, water activity, freezing point depression and solubility of sugars in aqueous solutions. COSMO-SAC is based on quantum chemistry computations and has a high predictive character, not requiring a specific parameter calibration for each application. For most systems studied, the results obtained were close to experimental data, with relative mean errors varying from 0.1% to 6.4% for vapor–liquid equilibrium. Solubility results with COSMO-SAC presented the same tendency observed in experimental data, but with higher deviations, probably due to the fact that the loss of crystalline structure in sugars is a kinetic process more than a thermodynamic melting, and does not occur at a single temperature with a constant enthalpy value. COSMO-SAC model was also used to predict industrial juices water activity, bubble point temperature, and freezing point depression. Very low deviations from experimental data were observed for COSMO-SAC calculations, similar to those found for simpler sugar solutions.

1. Introduction

Carbohydrates, especially sugars, have been the subject of several studies over the years, mainly due to their strong presence in food industry and in biological systems (Taylor and Rowlinson, 1955; Shallenberger, 1978; Abed et al., 1992; Roos, 1993; Starzak and Mathlouthi, 2006; Elliott et al., 2007; Alavi et al., 2014). Understanding how sugar molecules interact with other substances is crucial, since sugars are usually found in solution in nature. These interactions can be calculated through activity coefficient models, as deviations from *ideality*. A behavior close to ideality happens in mixtures of similar components and, since this is not the case of sugars and water, advanced thermodynamic models can be useful tools (Prausnitz et al., 1998).

Different thermodynamic models have been proposed over the 20th century. They can be divided into predictive and non-predictive models. Non-predictive models, unlike predictive ones, are those where experimental data is only correlated (Gerber and Soares, 2010). For this reason, the model cannot be used to calculate mixture behavior not originally used in the correlation step. Non-predictive models for sugars were studied by Abderafi and Bounahmidi (1994), who used experimental bubble temperature data of aqueous sugar solutions to calibrate binary interaction parameters for Peng and Robinson (1976) and Kesler and Lee (1975) equations of state as well as NRTL (Non-Random Two-Liquid) (Renon and Prausnitz, 1968) activity coefficient

parameters. Peres and Macedo (1996) modified the combinatorial term of the existing UNIQUAC (UNIversal QUAsi-Chemical) model (Abrams and Prausnitz, 1975) and calibrated its parameters using the same experimental data of Abderafi and Bounahmidi (1994). Afterwards, other authors used non-predictive models for modeling sugar systems such as Jónsdóttir and Rasmussen (1999) using UNIQUAC model parameterized with molecular mechanics, Perozin et al. (2007) using Peng–Robinson modified by Stryjek and Vera (1986) and Alavi et al. (2014) using H-Wilson, H-NRTL and H-UNIQUAC, among others (Gray et al., 2003; Nowak et al., 2009; Martínez et al., 2011).

Nowadays, UNIFAC (UNIQUAC Functional-group Activity Coefficients) (Fredenslund et al., 1975) and its variants are the most popular models for calculating interactions among several components, including sugars (Starzak and Mathlouthi, 2006). UNIFAC has a more predictive character than the previously mentioned models because it is based on group contribution theory, which drastically reduces the amount of experimental data needed for parameter estimation. Further, behavior of substances with no experimental data available can still be computed if they consist of functional groups with known parameters. Several authors have proposed different functional group fragments for representing sugar molecules, such as Abed et al. (1992), Catté et al. (1995), Peres and Macedo (1997), Kuramochi et al. (1997), Spiliotis and Tassios (2000) and Tsavas et al. (2004).

Regarding the application of these models, calculation of some relevant properties in foods can be found in the literature. For instance, Vagenas and Marinos-Kouris (1992) used a modified version of the Wilson equation, with parameters determined from experimental data, for the calculation of water activity of high sugar content dry fruits. Abderafi and Bounahmidi (1999) used Peng–Robinson equation of state, with binary interaction parameters adjusted from binary, ternary and quaternary solutions of sugars, to calculate bubble temperature of beet and sugar cane juice. Gros and Dussap (2003) used the UNIFAC with a solvation model to predict water activity, osmotic pressure, decrease of melting point, increase of bubble temperature, pH and acidity of bovine milk.

A more recent alternative, with an even stronger predictive power, is the use of models based on COSMO (COnductor-like Screening MOdel) theory (Klamt and Schüürmann, 1993), like COSMO-RS (COSMO for Real Solvents) (Klamt, 1995) and COSMO-SAC (COSMO - Segment Activity Coefficient) (Lin and Sandler, 2002). The idea is to start with a molecule alone, surrounded by a perfect conductor to compute the so called σ-profiles. Then, put the molecules in mixture by a pairwise surface contact theory. Regarding applications related to sugar systems using COSMO based models, the literature is very sparse. Saldaña et al. (2012) used the COSMO-SAC model to calculate the solubility of glucose and lactose in water, obtaining only qualitatively acceptable results. Mohan et al. (2015) used the COSMO-RS model to calculate the solubility of sugars in ionic liquids. Xiong et al. (2015) used the COSMO-SAC model to predict the partition coefficients of fructose in water and C4 to C7 linear and branched alcohols.

In this work, a COSMO-SAC model with recent parametrization and σ-profiles was tested for the prediction of phase equilibria of binary, ternary, and quaternary aqueous solutions of glucose, sucrose, fructose, maltose, and lactose. Vapor–liquid and solid–liquid equilibrium, water activity, and freezing point depression experimental data were used to assess model quality. The study was also extended to industrial juices, where important properties were predicted and compared with experimental data.

2. Methodology

2.1. The COSMO-SAC model

In COSMO-SAC, as in many activity coefficient models, the activity coefficient is defined as a result of two contributions:

$$\ln \gamma_i = \ln \gamma_i^{\text{res}} + \ln \gamma_i^{\text{comb}} \tag{1}$$

where $\ln \gamma_i^{\text{res}}$ is the residual activity coefficient and $\ln \gamma_i^{\text{comb}}$ is the combinatorial contribution.

The residual part comes from a pairwise surface interaction theory. The starting point is to compute the induced surface charge densities around each molecule when surrounded by a perfect conductor, using the COSMO method. The results are the three-dimensional surfaces shown in Fig. 1.

However, for the actual computations these surfaces are first discretized into *segments* or *patches*. With this, the area of segments of similar charges can be accumulated in an histogram known as the σ-profile (also shown in Fig. 1).

Further, using the discrete segments, the residual contribution can be calculated as follows:

$$\ln \gamma_i^{\text{res}} = \sum_{m \in i} \frac{Q_m^i}{a_{\text{eff}}} \cdot \left(\ln \Gamma_m^s - \ln \Gamma_m^i \right) \tag{2}$$

where Q_m^i is the area of the segment m in a molecule i; a_{eff} is the standard segment surface area, which is the same for all molecules and is one of the universal parameters in this model; $\ln \Gamma_m^s$ is the logarithm of the activity coefficient of a segment m in solution and $\ln \Gamma_m^i$ in pure liquid, given by the so called *self-consistency* equations:

$$\ln \Gamma_m^s = - \ln \left[\sum_{n \in s} p_n^s \Gamma_n^s \exp \left(\frac{-\Delta W_{m,n}}{RT} \right) \right] \tag{3a}$$
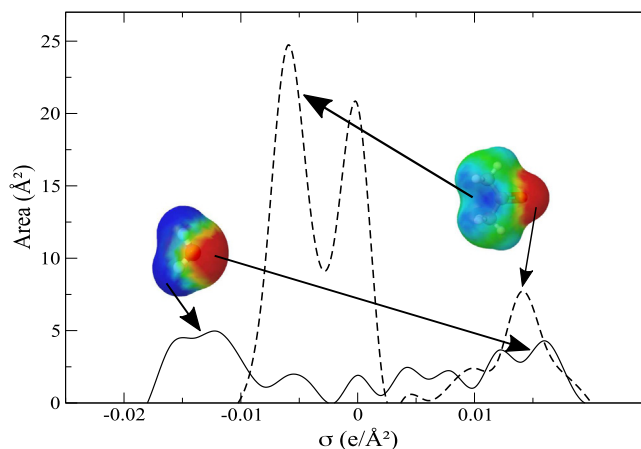

Fig. 1. σ-profiles of water (solid line) and acetone (dashed line).

$$\ln \Gamma_m^i = - \ln \left[\sum_{n \in i} p_n^i \Gamma_n^i \exp \left(\frac{-\Delta W_{m,n}}{RT} \right) \right] \tag{3b}$$

where the probability of finding a segment m in a mixture s (σ–profile of mixture) is given by:

$$p_m^s = \frac{x_i Q_m^i}{\sum_j x_j Q^j} \tag{4}$$

and the probability of finding a segment m in a pure liquid i (σ–profile of the pure compound) is:

$$p_m^i = \frac{Q_m^i}{Q^i} \tag{5}$$

where $Q^i = \sum_{m \in i} Q_m^i$ is the total cavity surface area of molecule i.

Finally, the interaction energy $\Delta W_{m,n}$ for each contact between segments m and n can be computed under different assumptions. Using the formulation of Lin and Sandler (2002), it is computed as a function of the segment charge densities σ_m and σ_n:

$$\Delta W_{m,n} = \left(\frac{\alpha'}{2} \right) (\sigma_m + \sigma_n)^2 + c_{\text{hb}} \max[0, \sigma_{\text{acc}} - \sigma_{\text{hb}}] \times \min[0, \sigma_{\text{don}} + \sigma_{\text{hb}}] \tag{6}$$

where α' is the constant for the misfit energy; c_{hb} is a constant for hydrogen bonding (HB); σ_{hb} is the sigma-value cutoff for hydrogen bonding; σ_{acc} and σ_{don} are the larger and smaller values of σ_m and σ_n.

In the present work, the combinatorial contribution was calculated using only the Flory–Huggins term:

$$\ln \gamma_i^{\text{comb}} = \ln \phi_i + 1 - \phi_i \tag{7}$$

where $\phi_i = R_i / \sum_j R_j x_j$ is the volume fraction; x_i is the mole fraction; and R_i is the COSMO cavity volume.

The procedure to obtain σ-profiles for substances studied in this work is described by Ferrarini et al. (2018) and deposited in the open source LVPP sigma-profile database available at https://github.com/lvpp/sigma. All required COSMO-SAC parameters were taken from the GMHB1808 multi-hydrogen bond parametrization, also freely available in that github repository.

The computational work necessary to evaluate activity coefficients with COSMO-SAC model was made with JCOSMO software, developed by Gerber and Soares (2010) and maintained by our group. For further information about COSMO-RS/SAC theory and applications, please refer to Klamt (1995), Lin and Sandler (2002), Soares (2011), Staudt et al. (2018).
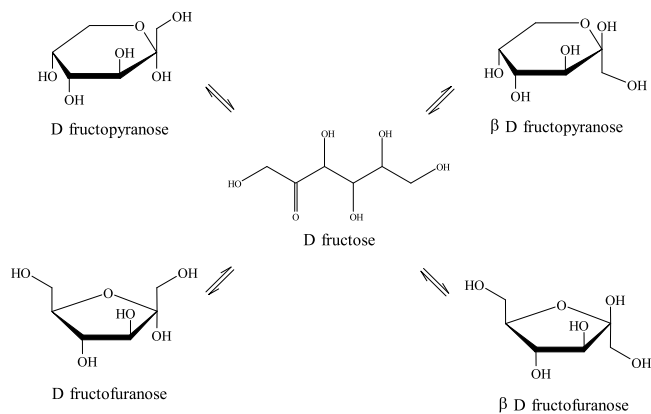
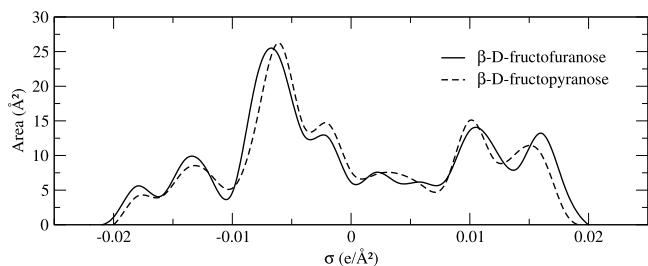**Fig. 2.** Fructose conformational isomerism in solution.

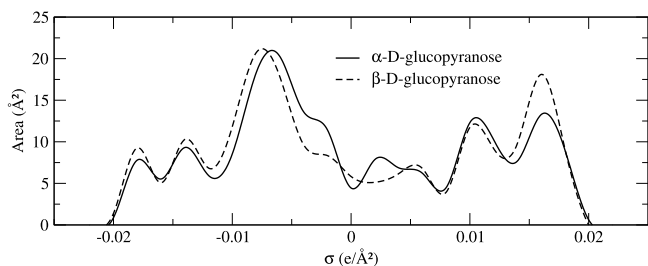**Fig. 3.** σ-profiles of β-D-fructopyranose and β-D-fructofuranose conformers.

Fig. 4. σ-profiles of α-D-glucopyranose and β-D-glucopyranose conformers.

2.2. Representing sugars with COSMO-SAC

Sugar molecules may show different conformations depending on temperature condition and solvent. For example, fructose in its crystalline form is only present as β-D-fructopyranose. When in solution, five possible conformers may appear in equilibrium (Flood et al., 1996), as shown in Fig. 2.

According to Flood et al. (1996), fructose in solution with water appears mostly in β-D-fructopyranose and β-D-fructofuranose forms. σ-profiles of both conformers were computed according to Ferrarini et al. (2018) methodology and are shown in Fig. 3.

As can be seen in Fig. 3, the σ-profiles of β-D-fructopyranose and β-D-fructofuranose are similar. In order to check how these nuances in σ-profiles impact in the results, phase equilibrium predictions for these different conformers are presented in Section 3.

Glucose molecules may also present α and β conformations of furanose and pyranose rings. In this case, pyranose form appears in the ratio of 99%, regardless of the temperature (Maple and Allerhand, 1987). However, this structure has two conformations, α and β, which are present in aqueous solution. σ-profiles of α-D-glucopyranose and β-D-glucopyranose conformers are shown in Fig. 4.

Comparing the σ-profiles of α-D-glucopyranose and β-D-glucopyranose of Fig. 4, again they are very similar and responses using these different structures are investigated in Section 3.

Other sugars investigated in this work, such as lactose and maltose, may also present different conformations in aqueous solution (Srisa-nga and Flood, 2004). However, due to a lack of detailed studies on this subject, the pyranose form was chosen to represent these sugars.

2.3. Vapor–liquid equilibrium (VLE)

Model performance in predicting isobaric or isothermal VLE was assessed through bubble temperature or bubble pressure computations, respectively. Considering the vapor phase as an ideal gas, the bubble temperature (or pressure) was calculated assuming the Modified Raoult's Law:

$$P y_i = x_i \gamma_i P_i^{\text{sat}} \tag{8}$$

where P is the total pressure, x_i and y_i are molar fractions of substance i in liquid and vapor phase, respectively, γ_i is the activity coefficient of substance i in the liquid mixture computed with COSMO-SAC, and P_i^{sat} is the saturation pressure of pure compound i at equilibrium temperature T.

Since sugars are not volatile, with negligible saturation pressure, it can be assumed that vapor consists in pure water and then Eq. (8) reduces to:

$$P = x_w \gamma_w P_w^{\text{sat}} \tag{9}$$

where the subscript w refers to water properties.

A flowchart for bubble temperature calculation is given in Supplementary Material as Fig. S1

2.4. Solid–liquid equilibrium

The solubility of sugars in a binary mixture with water was also evaluated, according to the following expression (Sandler, 1999):

$$\ln x_i = \frac{\Delta H_m}{R} \left(\frac{1}{T_m} - \frac{1}{T} \right) - \frac{\Delta C_p}{R} \left(1 - \frac{T_m}{T} - \ln \frac{T}{T_m} \right) - \ln \gamma_i \tag{10}$$

where x_i stands for sugar solubility (molar fraction in liquid phase); ΔH_m is the sugar fusion molar enthalpy at its melting temperature T_m; ΔC_p is the difference between the sugar heat capacity at liquid and solid phase at T_m; T is the equilibrium temperature, R the universal gas constant (8.314 J mol^{-1} K^{-1}); and γ_i is the sugar activity coefficient in the solution, calculated by COSMO-SAC.

Miller and de Pablo (2000) measured the heat capacity difference between amorphous solid and sub-cooled liquid for sucrose using DSC, but most ΔC_p data available in the literature are estimated with solubility experimental information using Eq. (10) (Ferreira et al., 2003; Ben Gaida et al., 2006). Besides, the first term of Eq. (10) (the one with ΔH_m) is dominant, since the second one has the tendency to approximately cancel out (Prausnitz et al., 1998). For these reasons we decided to neglect the second term of Eq. (10) for all sugars studied, and used the following form for solubility calculation:

$$\ln x_i = \frac{\Delta H_m}{R} \left(\frac{1}{T_m} - \frac{1}{T} \right) - \ln \gamma_i \tag{11}$$

Since Eq. (11) do not have a closed form solution for x_i (γ_i is temperature and composition dependent), the solubility of sugar in water is obtained using an iterative method. A flowchart illustrating the calculation steps used in this study is given in Supplementary Material as Fig. S2.

Table 1
Melting parameters of fructose, glucose and sucrose used in this work.

Sugar	Hurtta et al. (2004)				Lee et al. (2011)			
	(0.5 °C/min)		(10 °C/min)		2 °C/min		10 °C/min	
	ΔH_m (J/mol)	T_m (K)	ΔH_m (J/mol)	T_m (K)	ΔH_m (J/mol)	T_m (K)	ΔH_m (J/mol)	T_m (K)
Fructose	27311	383	31833	399	31154	380	33976	386
Glucose	32446	418	35004	428	33349	424	37600	431
Sucrose	41007	454	46005	462	42729	446	46939	459

Table 2
Approximate assumed compositions of fruit juices.

Reference	Juice	Fructose (w%)	Glucose (w%)	Sucrose (w%)
Abderafi and Bounahmidi (1999)	Beet	0	0	100
	Cane	0	0	100
Auleda et al. (2011)	Apple	62.0	22.0	16.0
	Peach	25.5	18.8	55.7
	Pear	52.5	39.0	8.5
Moura (1998)	Pineapple	14.0	23.0	63.0
	Tangerine	25.0	15.0	60.0
Velezmoro (1999)	Orange	26.9	25.0	49.0
	Tangerine	27.0	27.0	46.0
	Grapefruit	38.0	40.0	22.0

2.5. Freezing point depression

Freezing point depression is defined as the difference between freezing temperature of an aqueous solution and freezing temperature of pure water. Assuming that the solid crystals formed in the freezing process are pure water, solution freezing temperature can also be obtained by solving Eq. (10).

In this case, x_i is water molar fraction, ΔH_m is the enthalpy of fusion of pure water (6000 J/mol) at fusion temperature T_m (273.15 K), T is the freezing temperature of aqueous sugar solution, ΔC_p is the difference between the water heat capacity at liquid and solid phase at 273.15 K (38 J mol^{-1} K^{-1}), and γ_i is the activity coefficient of water in solution, obtained in this work with COSMO-SAC model.

The procedure to calculate freezing temperature of an aqueous sugar solution for a given water composition is available in Supplementary Material as Fig. S3.

2.6. Water activity

Water activity (a_w) is defined as the product between water composition, expressed as molar fraction x_w and its activity coefficient in a solution γ_w:

$$a_w = x_w \gamma_w \tag{12}$$

In food engineering applications it represents the water availability to chemical, physical and biochemical reactions in the material (Staudt et al., 2013). A crude interpretation would be that small values of water activity mean that water is bonded to the solutes in the media whereas values next to unity mean that water is mainly in free-form in the material solution.

Assuming again that sugars are not volatile and that the modified Raoult's law can represent the system equilibrium condition, we can estimate a_w as follows:

$$a_w = \frac{P}{P_w^{sat}} \tag{13}$$

where P is the solution vapor pressure, and P_w^{sat} is vapor pressure of pure water at the same temperature.

With Eq. (13), the value of a_w can be experimentally obtained measuring the vapor pressure above the water solution or material of interest.

2.7. Calorimetric properties of sugars

In order to assess the COSMO-SAC suitability to predict solubility of sugars in water, ΔH_m and T_m of each material must be known (see Eq. (10)). These values are usually obtained by Differential Scanning Calorimetry (DSC) analysis. However, in the particular case of sugars, the melting temperature and enthalpy obtained may vary substantially, depending on the heating rate used in the analysis (Hurtta et al., 2004; Lee et al., 2011) and on the source of the sugar used (Lu et al., 2017). Lee et al. (2011) suggested the use of the term "apparent melting" since the loss of sugar crystalline structure is due to a kinetic process rather than a thermodynamic melting.

In this study, melting parameters of sucrose, glucose and fructose of Lee et al. (2011) and Hurtta et al. (2004) were used to predict sugar solubilities in water using COSMO-SAC. These values were obtained via DSC experiments with heating rates of 0.5 °C/min, 2 °C/min and 10 °C/min, and present significant differences. Besides, different sugar sources were used. We decided to use different melting parameters to evaluate the difference in solubility results and the suitability of Eq. (11) to evaluate water–sugar solid–liquid equilibrium. Fructose, glucose and sucrose onset melting temperature and melting enthalpy used in this work are listed in Table 1.

2.8. Industrial juices

To predict industrial juices properties with an activity coefficient model a proper representation of material composition is required, usually a mixture of water and other dissolved components. Velezmoro (1999) predicted water activity in juices considering an aqueous solutions of fructose, glucose, sucrose and maltose. A similar approach was used by Auleda et al. (2011) and Peres and Macedo (1999), the authors took into account only fructose, glucose, and sucrose. Abderafi and Bounahmidi (1999) made a more refined representation, characterizing juices as an aqueous solution of sugars, aminoacids, ashes and carboxilic acids to predict bubble temperature of sugar cane and beet juices.

In this study, juices were assumed to consist in binary solutions of sucrose and water or quaternary solutions of water, fructose, glucose and sucrose. The approximate composition of each studied juice and the reference containing experimental equilibrium data are compiled in Table 2.

The juice properties assessed in this work were bubble temperature, water activity and freezing point depression. The knowledge of vapor–liquid equilibrium and freezing point depression curves are directly

(a)

(b)

(c)

(d)
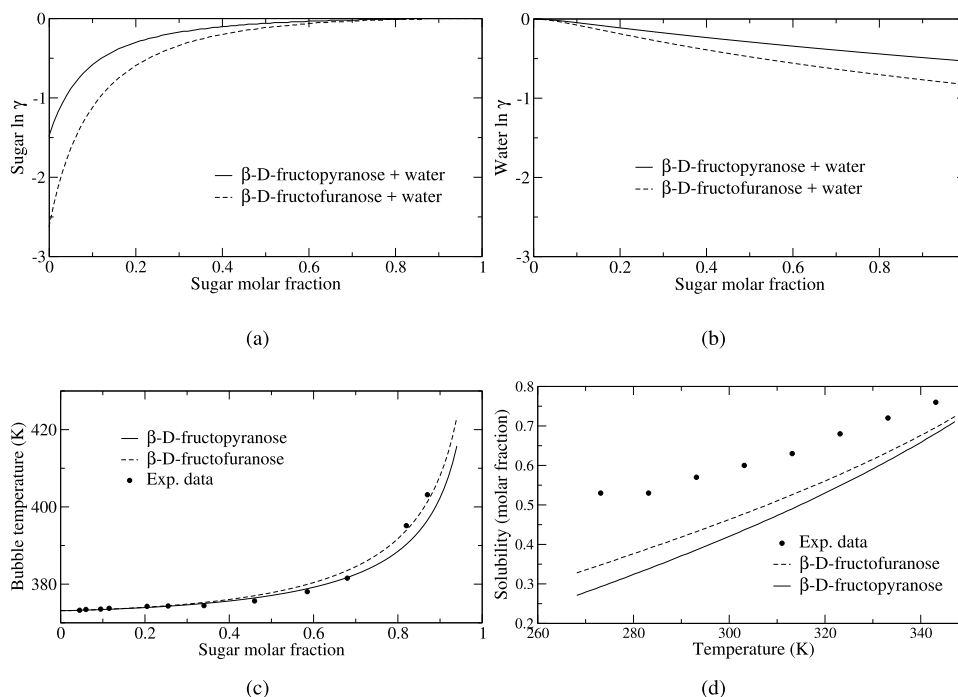
Fig. 5. (a) Logarithm of fructose activity coefficient at 298 K for pyranose and furanose forms in a binary mixture with water. (b) Logarithm of water activity coefficient at 298 K in solution with pyranose and furanose forms of fructose. (c) Bubble temperature of pyranose and furanose forms of fructose in solution with water at 1 bar. Experimental data from Abderafi and Bounahmidi (1994). (d) Solubility of pyranose and furanose forms of fructose in water. Experimental data from Nowak et al. (2009) and calorimetric properties from Hurtta et al. (2004).

correlated with concentration processes, either by water vaporization or by water crystallization, respectively. As already mentioned, water activity is the measure of water availability to microbiological growth and, therefore, is a very important parameter in food safety.

2.9. Prediction quality

Prediction quality was analyzed by the mean relative error (MRE), defined as follows:

$$\text{MRE (\%)} = \frac{100}{\text{NP}} \sum_{i=1}^{\text{NP}} \left| \frac{Y_i - \tilde{Y}_i}{Y_i} \right| \tag{14}$$

where Y_i and $\tilde{Y}_i$ are, respectively, experimental and model-predicted values of the parameters analyzed in experiment i, with NP being the number of experimental points. In the case of bubble point calculation Y means temperature or pressure, Y represents sugar molar fraction in solubility evaluation, freezing temperature in FPD problems or water activity (a_w).

3. Results and discussion

3.1. Sugar representation

As mentioned in Section 2.2, different conformations are expected for sugars, depending on temperature and solvent used. COSMO-SAC model needs a σ-profile of each molecule present in the mixture for calculating activity coefficients. Therefore, in this work, only one molecule was used to represent each sugar. A more comprehensive analysis was carried out for fructose and glucose in order to check which conformer better represents each sugar in water solution. Following studies from Flood et al. (1996) and Maple and Allerhand (1987), we compared molecules of β-D-fructopyranose and β-D-fructofuranose for representing fructose and the molecules of α-D-glucopyranose and β-D-glucopyranose for representing glucose.

As already shown in Fig. 3, different fructose conformers present similar σ-profiles. Fig. 5 presents how these nuances in σ-profiles influence water and sugar activity coefficient values in a binary mixture, calculated by COSMO-SAC. VLE and SLE predictions for each conformer are also depicted in Fig. 5, compared with experimental data from literature. Similar results were obtained for the two forms of fructose. The larger differences in activity coefficients shown in Fig. 5 at very dilute composition do not produce a considerable discrepancy in phase equilibrium calculations.

The same comparison was conducted with glucose conformers and results are shown in Fig. 6. For glucose, even smaller differences in activity coefficient and phase equilibrium calculations were obtained with COSMO-SAC for the two glucopyranose molecules. This fact was expected since the only difference between such forms is the position of one hydroxyl group.

Regarding VLE results, the errors obtained were very small for all tested molecules. Even though β-D-fructopyranose and β-D-glucopyranose conformations provided larger errors in the solubility test, they were selected to represent fructose and glucose, since according to Spiliotis and Tassios (2000) they appear in higher proportion in aqueous solution.

A more refined representation of the aqueous sugar solution could be achieved simultaneously solving a conformational equilibrium or assuming a mixture of possible conformers in the proportions studied by other authors (Flood et al., 1996; Maple and Allerhand, 1987; Shallenberger, 1978). However, this was left for future works for the sake of simplicity.

To summarize, Fig. 7 presents the chosen structures of the sugars analyzed in this work, as well as the three-dimensional distribution of induced charges and their σ-profiles needed for COSMO-SAC calculations.

(a)

(b)

(c)

(d)
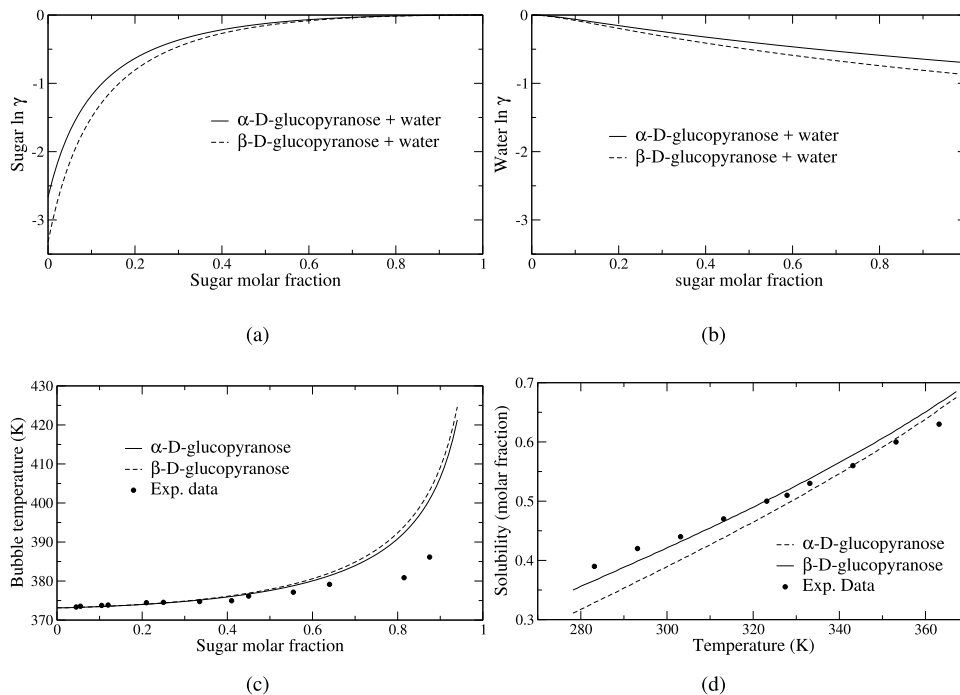
Fig. 6. (a) Logarithm of glucose activity coefficient at 298 K for α and β pyranose forms in a binary mixture with water. (b) Logarithm of water activity coefficient at 298 K in solution with α and β pyranose forms of glucose. (c) Bubble temperature of α and β forms of glucopyranose in solution with water at 1 bar. Experimental data from Abderafi and Bounahmidi (1994). (d) Solubility of α and β forms of glucopyranose in water. Experimental data from Nowak et al. (2009) and calorimetric properties from Hurtta et al. (2004).

(a) Fructose

(b) Glucose

(c) Sucrose

(d) Lactose

(e) Maltose
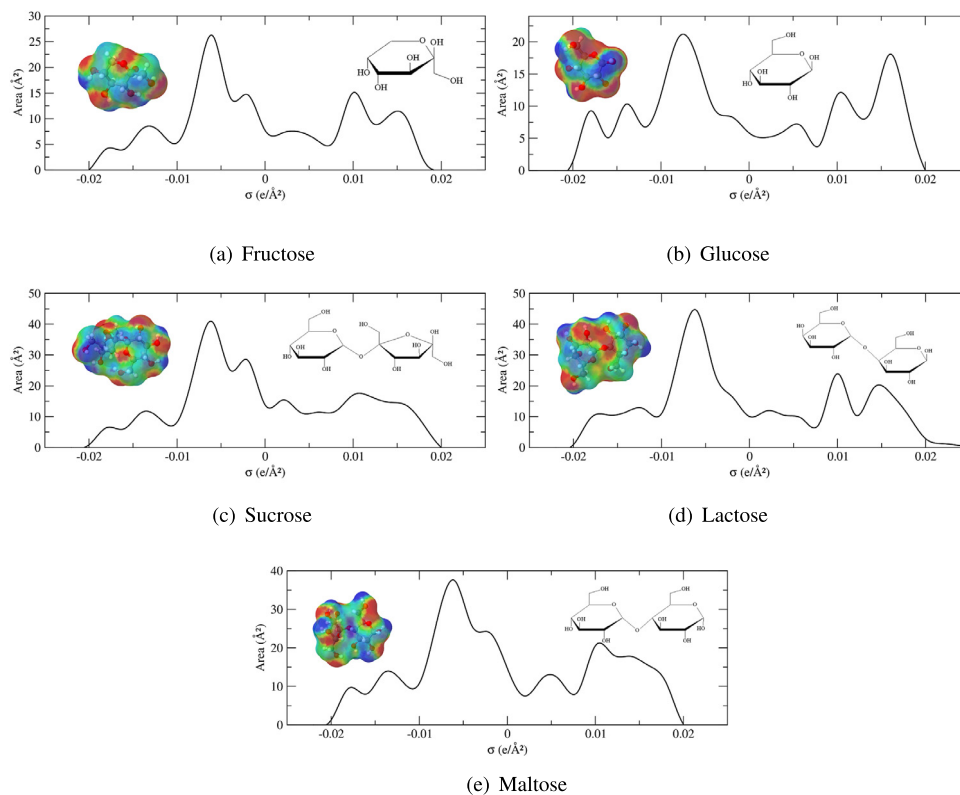
Fig. 7. Assumed conformer, three dimensional apparent induced surface charge densities, and σ-profiles for the sugars investigated in this work.
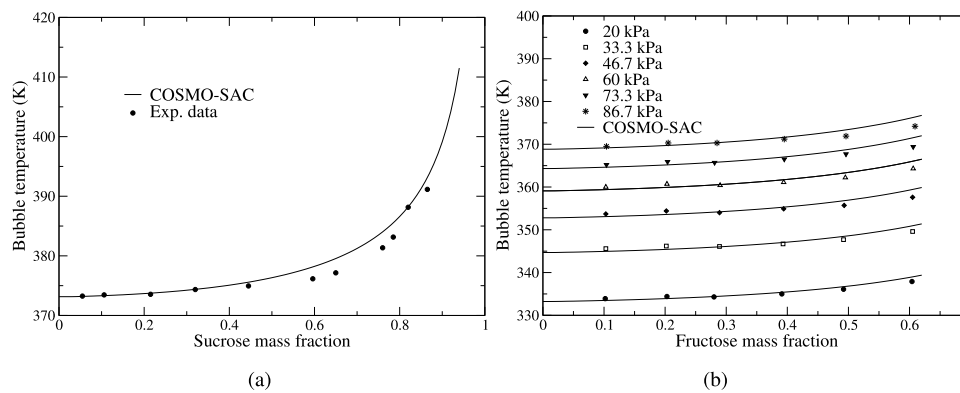
Fig. 8. (a) Experimental and calculated bubble temperature of (a) sucrose aqueous solution and (b) fructose aqueous solution as a function of sugar mass fraction. Experimental data from Abderafi and Bounahmidi (1994) and Maximo et al. (2010), respectively.

3.2. Phase equilibrium predictions

Binary, ternary and quaternary mixtures of glucose, sucrose, fructose, maltose and lactose with water were studied, by means of calculating phase equilibrium of solutions with COSMO-SAC model and comparing the results with experimental data from literature. Vapor–liquid equilibrium were evaluated as bubble pressure, bubble temperature and water activity and solid–liquid equilibrium were calculated as solutions freezing point depression and solubilities of sugars in water.

In Table 3 an overview of all binary systems studied and the maximum error found between predicted and experimental values is presented.

Table 4 shows ternary and quaternary mixtures studied here with MRE (%) values for each kind of phase equilibrium calculated with COSMO-SAC model.

According to the results of Tables 3 and 4, it is possible to confirm that COSMO-SAC model with parametrization GMHB1808 provides good predictions for phase equilibrium calculations of water solutions containing sugars. Larger MRE values are obtained for solubility predictions where only qualitative agreement was possible with COSMO-SAC. This outcome was already expected, since sugar melting does not occur at a single temperature with a single enthalpy (Lee et al., 2011).

Regarding bubble point temperature calculations, COSMO-SAC showed very good results with similar deviations encountered by other thermodynamic models fitted to experimental data. In the work of Abderafi and Bounahmidi (1994) Peng–Robinson, Lee–Kesler and NRTL were adjusted to predict VLE of water solutions containing fructose, glucose and sucrose at atmospheric pressure. Maximo et al. (2010) used UNIFAC-Lyngby to correlated isobaric (20 kPa to 93.3 kPa) data of fructose and glucose with larger MRE values than COSMO-SAC calculations. Isothermic VLE data were correlated using UNIQUAC and SAFT-VR models in the work of Baghbanbashi and Pazuki (2014), with similar errors for fructose and slightly smaller deviations for glucose, sucrose and maltose than those found in COSMO-SAC predictions. Errors between 1.6% and 6.4% found with COSMO-SAC are similar to the experimental uncertainty associated with pressure determination. Cooke et al. (2002) reported in their work that cumulative errors in equilibrium pressure determination were observed as the sugar concentration increases.

All these results are detailed in Supplementary Material (Table S1 to Table S5). It is worth mentioning that no binary interaction parameter is used in COSMO-SAC, being the results of this study purely predictive, and still similar results with other models from literature were obtained.

Taking sucrose and fructose as examples, bubble temperature predictions, compared with experimental data, are illustrated in Fig. 8.

All results referring freezing point depression (FPD) of sugar solutions are in very good agreement with experimental data, with all MRE under 1%. Responses for fructose and sucrose are shown in Fig. 9.
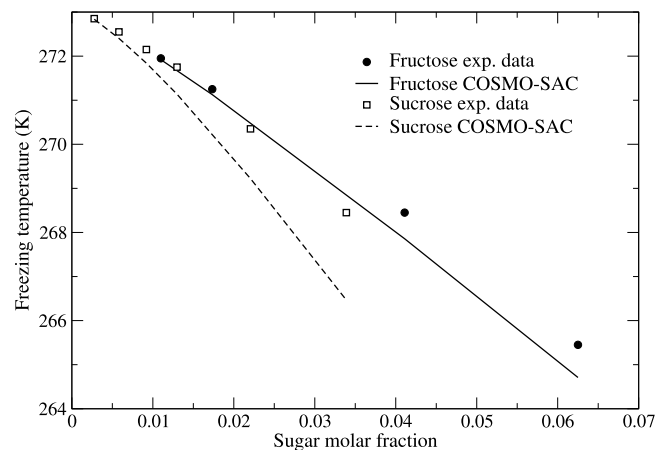

Fig. 9. Experimental and calculated freezing temperature of fructose and sucrose in water as a function of sugar molar fraction. Experimental data from Lerici et al. (1983).

It can be seen in Fig. 9 that larger differences between experimental and calculated temperature are observed as the sugar molar fraction increases. The bigger absolute deviation is 1.9 K for sucrose and 0.54 K for fructose, and mean absolute deviations are 0.68 K and 0.29 K, respectively.

The bigger error for water activity predictions in aqueous solutions in this study was around 5%, for binary mixture of water and glucose. For all other systems, including industrial juices, smaller deviations were found.

As already mentioned, solubility predictions presented larger deviations from experimental data. Fig. 10 shows the predicted solubility curves of glucose and fructose along with experimental data from Alves et al. (2007), Nowak et al. (2009) Macedo and Peres (2001) and Crestani et al. (2013). Results using calorimetric data from Lee et al. (2011), obtained using different heating rates, are represented by gray lines and from Hurtta et al. (2004) are represented by black lines. Solid lines are used for 0.5 °C/min and 2 °C/min parameters and dashed lines are used for 10 °C/min data (see Table 1).

Regarding glucose results, experimental data from literature are scatter at lower temperatures. COSMO-SAC model with Hurtta et al. (2004) melting parameters obtained using heating rate of 0.5 °C/min (black solid line) was able to predict the solubility of glucose with good agreement with experimental data in the entire temperature range. Melting parameters obtained using 10 °C/min (black dashed line) generate a different solubility curve. For the same heating rate of 10 °C/min, results using parameters from Lee et al. (2011) and Hurtta et al. (2004) have significant discrepancy, showing the influence of

Table 3
Binary systems studied in this work and the maximum MRE (%) between COSMO-SAC predictions and experimental values for phase equilibrium calculations.

| System	Phase equilibrium	T (K)	P (kPa)	NP	MRE (%)
Water + fructose	Bubble point	318–403	7.18–101.3	93	2.54
	Water activity	298	101.3	4	0.89
	FPD	264–271	101.3	11	0.13
	Solubility	273–343	101.3	17	44.3
Water + sucrose	Bubble point[a]	298–391	2.5–101.3	21	4.69
	Water activity	298	101.3	6	0.58
	FPD	266–272	101.3	13	0.36
	Solubility	283–373	101.3	12	33.6
Water + glucose	Bubble point	298–386	2.57–101.3	170	6.40
	Water activity	293–308	101.3	38	4.38
	FPD	262–271	101.3	7	0.40
	Solubility	283–363	101.3	18	13.4
Water + lactose	water activity	298	101.3	4	0.15
	FPD	272–273	101.3	4	0.01
Water + maltose	Bubble point	298–318	2.4–9.51	36	7.02

[a]Including beet and cane juices data.

Table 4
Ternary and quaternary systems studied in this work and the maximum MRE (%) between COSMO-SAC predictions and experimental values.

System	Phase equilibrium	T (K)	P (kPa)	NP	MRE (%)
Water + fructose + glucose	Bubble point	374–380	101.3	10	0.37
Water + sucrose + glucose	Bubble point	374–387	101.3	9	0.48
Water + sucrose + fructose	Bubble point	374–393	101.3	9	0.21
Water + sucrose + glucose + fructose	Bubble point	374–392	101.3	10	0.27
	Water activity[a]	298	101.3	40	2.53
	FPD[a]	247–272	101.3	41	3.27

[a]Quaternary mixture representing industrial juices.
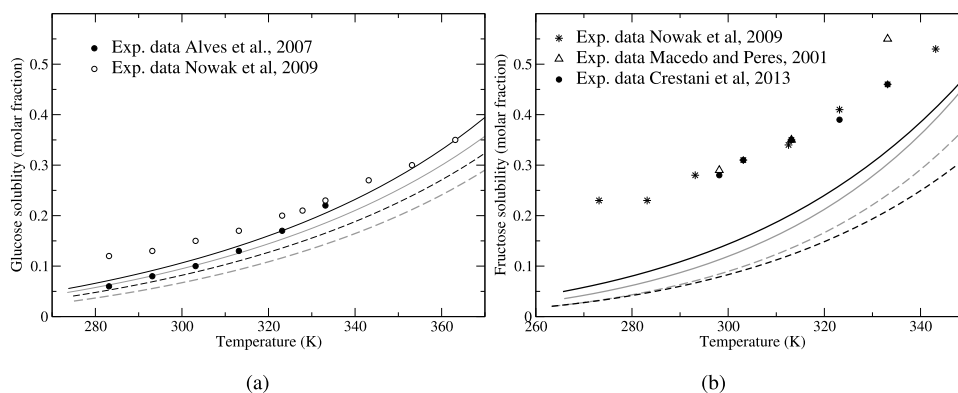
Fig. 10. (a) Glucose and (b) fructose solubility in water predicted with COSMO-SAC, using calorimetric data from Lee et al. (2011) (gray lines) and from Hurtta et al. (2004) (black lines). Solid lines are used for 0.5 °C/min and 2 °C/min and dashed lines for 10 °C/min..

sugar source. Difficulties in applying the thermodynamic theory for determination of sugar solubility are very clear in this case, since predictions using values from Lee et al. (2011) and Hurtta et al. (2004) give very different responses. As stated in the literature, sugar melting process does not occur at a single temperature with a single enthalpy value, and sugars obtained from different sources can present different properties.

For the case of fructose, experimental determinations are in good agreement among different authors, mainly Nowak et al. (2009) and Crestani et al. (2013). While the experimental data indicates that fructose is more soluble in water than glucose, COSMO-SAC predictions show similar solubilities for both substances. Thus, although in qualitative agreement in this case, the model under-predicted solubilities for all temperatures. This could be due to the uncertainties in the melting parameters, or due to a change in the conformation of this sugar, as suggested by Young et al. (1952), requiring further investigation in future works.

3.3. Juices

Vapor–liquid equilibrium (VLE), water activity and freezing point depression data were gathered and used to assess the prediction quality of COSMO-SAC calculations for industrial juices. Juices were considered as sugar solutions with composition accordingly to Table 2.

Results of bubble temperature for beet and cane juice presented a MRE of 0.96% and 0.58% compared to experimental data of Abderafi and Bounahmidi (1999). In terms of mean absolute error, a deviation of about 2 degrees was obtained between COSMO-SAC prediction and experimental data, with calculated temperatures always below expected values (see Fig. 11). This might be related to the assumption that all juice solids are sugars, neglecting the presence of fibers and other solids with considerable content. Considering juices as a mixture of sugars, salts, amino acids and carboxylic acids (as suggested by Abderafi and Bounahmidi (1999)), stronger interactions between juice components would be taken into account increasing the bubble temperature of the
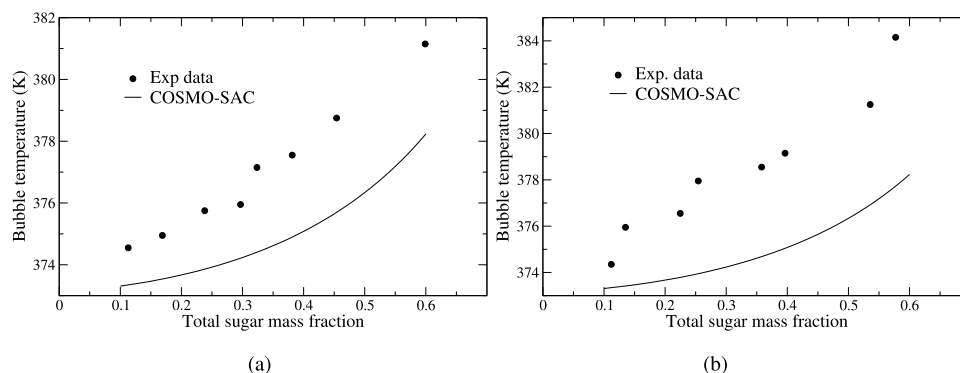
Fig. 11. Bubble temperature as a function of total sugar mass fraction for (a) cane and (b) beet juice. Experimental data from Abderafi and Bounahmidi (1999).
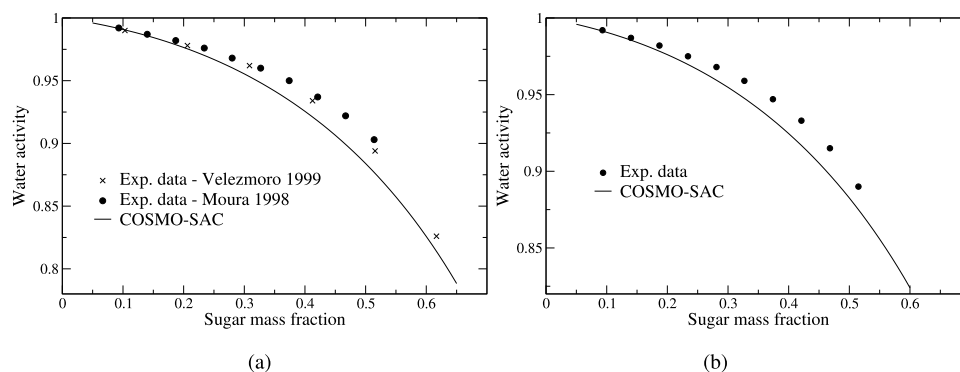

Fig. 12. Water activity of juices at 298 K as a function of total sugar mass fraction. (a) Tangerine juice with experimental data from Velezmoro (1999) and Moura (1998). (b) Pineapple juice with experimental data from Moura (1998).

system. Detailed results of VLE are given in Table S6 of Supplementary Material.

Water activity predictions of orange, tangerine, grapefruit, and pineapple juices were compared to data from Velezmoro (1999) and Moura (1998) and detailed results can be seen in Table S7 of Supplementary Material. COSMO-SAC provided a very good prediction for all studied juices. MRE values ranged from 1.06% for orange juice to 2.53% for pineapple juice. Fig. 12 shows that COSMO-SAC model was able to capture the behavior of juices water activity along all composition range. Although, for all cases, the model predicted a lower water activity for a given composition, meaning that the model is overestimating the interaction forces between sugars and water.

Finally, COSMO-SAC model was able to calculate the freezing temperature of juices with very low MRE (between 0.37% for apple juice and 3.27% for tangerine juice, see Table S8 of Supplementary Material) with results showing the same tendency of water activity outcome.

In general, similar values of MRE were obtained for sugar solutions and juices. This result is somehow expected due to the high water content of juices. A complete material description would be the best scenario and essential in describing more concentrated solutions or other materials like fruits, dried fruits, vegetables and so on.

4. Conclusions

Performance of the COSMO-SAC predictive activity coefficient model was assessed when applied to aqueous sugar solutions. Results concerning vapor–liquid equilibrium, freezing point depression, and water activity were in very good agreement with experimental data, with most average deviations under 1%. Higher discrepancies (between 1.6 and 6.4%) were found in isothermic VLE predictions, but still close to typical values of experimental uncertainties of phase equilibrium experiments. Concerning sugar solubility, the comparison with experimental data is more difficult. Even though predictions with glucose

were considered acceptable, greater discrepancies were observed for fructose and sucrose solubility. One explanation could be the fact that the loss of crystalline structure in sugars does not occur at a single temperature, with a single enthalpy value, suggesting a kinetic process more than a thermodynamic melting. Finally, COSMO-SAC model was applied to calculate properties of industrial juices. All results were in very good agreement with experimental data. Observed deviations might be associated with the assumption that all material solids are represented by sugars, and better results could be achieved using a more detailed juice composition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.jfoodeng.2019.109836.

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