Modeling Thermodynamic Properties of Aqueous Single-Solute and Multi-Solute Sugar Solutions with PC-SAFT

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The Perturbed-Chain Statistical Association Fluid Theory is applied to simultaneously describe various thermodynamic properties (solution density, osmotic coefficient, solubility) of aqueous solutions containing a monosaccharide or a disaccharide. The 13 sugars considered within this work are: glucose, fructose, fucose, xylose, maltose, mannitol, mannose, sorbitol, xylitol, galactose, lactose, trehalose, and sucrose. Four adjustable parameters (three pure-sugar parameters and a k_{ij} *between sugar and water that was allowed to depend linearly on temperature) were obtained from solution densities and osmotic coefficients of binary sugar/water solutions at 298.15 K available in literature. Using these parameters, the sugar solubility in water and in ethanol could be predicted satisfactorily. Further, osmotic coefficients and solubility in aqueous solutions containing two solutes (sugar/sugar, sugar/salt) were predicted (no additional* k_{ij} *parameters between the two solutes) reasonably. The model was also applied to predict the solubility of a sugar in a solvent mixture (e.g., water/ethanol) without additional fitting parameters.* © 2013 American Institute of Chemical Engineers *AIChE J*, 59: 4794–4805, 2013

Keywords: sugar, sugar alcohol, aqueous solutions, activity coefficient, osmotic coefficient, solubility, perturbed-chain statistical association fluid theory, modeling, prediction

Introduction

The knowledge of thermodynamic properties and phase equilibria of sugar solutions is indispensable for food, pharmaceutical, and cosmetic industries. Due to the high viscosity of concentrated sugar solutions, measuring thermodynamic data is difficult, time (and cost)-consuming in many cases.

Nevertheless, thermodynamic properties of aqueous sugar solutions are broadly available in the literature. Solution densities have usually been measured based on the vibrating-tube principle. Vapor-pressure depressions, activity coefficients, or osmotic coefficients have been determined by vapor-pressure measurements or isopiestic methods in most cases. In this manner, Taylor and Rowlinson measured vapor pressures and solution densities of glucose/water solutions already in 1955.[1] Solubility was determined by applying the all-gravimetric method to most of the sugar systems. For example, the group of Macedo measured sugar solubilities in water, alcohols, and solvent mixtures.[2] All these experimental methods are reliable as they have been proven to be highly accurate. The existing database provided in the literature is, thus, broad and accurate enough to apply precise state-of-the-art thermodynamic models.

Since the 1970s, thermodynamic properties of sugar solutions have been correlated, modeled, and predicted. Two types of thermodynamic models for the description of the phase behavior of sugar solutions have been developed so far: excess Gibbs-energy (g^E) models and equations of state (EOS). In 1971, Chandrasekaran and King[3] used the two-suffix Margules equation to describe water activity coefficients in binary, ternary, and quaternary sugar solutions. However, they only accounted for sugar/water interactions and neglected sugar–sugar forces in their modeling approach. Later, Franks[4] showed that solute–solute interactions are important and proposed an experimental assessment via coefficients in the series expansions of the excess free energy and enthalpy.

From the beginning of the 1990s, many research groups started to apply more modern g^E models to describe sugar solutions. The group of Macedo correlated and predicted thermodynamic properties of aqueous sugar solutions. They applied a modified UNIQUAC approach to model aqueous solutions containing one sugar (glucose, fructose, or sucrose). Based on this, they could predict vapor–liquid and solid–liquid equilibria in aqueous solutions containing more than one sugar[5] and in aqueous solutions containing one sugar and a second solvent.[2] Later, they considered also a

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modified UNIFAC approach[6] with the same purpose. Comparing UNIQUAC and UNIFAC, it could be observed that the latter provides poorer agreement to experimental data, especially with respect to the simultaneous description of osmotic coefficients and solubility. Nonetheless, a large number of different systems could be modeled with a satisfactory agreement to experimental data. Further, also Spiliotis and Tassios developed a modified UNIFAC model, called S-UNIFAC.[7] Comparing the approaches of Peres and Macedo with S-UNIFAC[6] suggests that both models provide similar results for aqueous sugar solutions. Until 2000, the only predictive models (which are also applicable to nonaqueous sugar solutions) were these two UNIFAC approaches. On the basis of this fact, UNIFAC models to describe sugar solutions were further developed. Ferreira et al.[8] developed the A-UNIFAC model, which explicitly accounts for association effects in mixtures containing sugars, alcohols, and water. Good predictions were obtained for vapor−liquid equilibria and solid−liquid equilibria of ternary and quaternary systems with sugars in mixed solvents. A-UNIFAC has been further applied also by other researchers to sugar solutions.[9] S-UNIFAC was extended by Tsavas et al.,[10] which used a different combinatorial term compared to S-UNIFAC. Their model, mS-UNIFAC, is more reliable for mixtures with molecules that differ significantly in size. Enzymatic reactions could, thus, be described with mS-UNIFAC, which failed with S-UNIFAC. mS-UNIFAC was further applied to model the glucose solubility in water and alcohols.[11]

In contrast to the broad application of g^E models, EOS have only been seldom used for the modeling of phase equilibria in sugar systems. Velezmoro et al.[12] used the classical Peng–Robinson as well as a modified Peng–Robinson approach to model water activities in binary sucrose/water, glucose/water, fructose/water, and maltose/water solutions. Water activity was then predicted for a quaternary mixture (sucrose, glucose, fructose, and water) with an average relative deviation (ARD) of 1.3 and 0.5% for the classical and the modified Peng–Robinson EOS, respectively. Thus, it was shown that an EOS yields comparable results to g^E models like original UNIFAC. Abderafi and Bounahmidi[13] modeled vapor–liquid equilibria of binary, ternary, and quaternary mixtures of sucrose, glucose, fructose, and water. By comparing g^E models (non-random two-liquid model (NRTL)) with EOS (Peng–Robinson and Lee–Kesler), they stated that EOS gave better descriptions of binary systems and a better prediction of the boiling-point curve for quaternary mixtures.

Summing up, only few models have been shown to give quantitatively predictive results for phase equilibria of sugar solutions. All the aforementioned models use a lot of parameters, which were fitted to a high amount of experimental data. This work aims at the development of a predictive modeling strategy for sugar solutions based on three pure-component parameters, which are adjusted to a minimal set of experimental data. These parameters are applied to predict single-sugar solubility in pure solvents (water, ethanol, or methanol) and in solvent mixtures (water/ethanol, water/methanol) as well as osmotic coefficients in aqueous solutions containing two or more sugars. This study uses the Perturbed-Chain Statistical Association Fluid Theory (PC-SAFT) framework because it has already proven flexibility and performance in modeling complex systems containing biomolecules (amino acids,[14–16] osmolytes,[17] urea[18]) as well as electrolytes[19–22] in aqueous solutions. The pure-component parameters of the sugars were determined by fitting to experimental solution densities and osmotic coefficients of binary sugar/water mixtures only. With these parameters, it was the clear focus of this work to predict thermodynamic properties and phase behaviors of multi-component sugar solutions in a broad range of temperature and composition. That is, in this work, PC-SAFT is applied to model such systems to which parameters have not been fitted to.

Thermodynamic Modeling

The PC-SAFT EOS

The PC-SAFT model is based on a perturbation theory. This type of theories uses a reference system, which in case of PC-SAFT is the so-called hard-chain fluid. A hard chain consists of a set of joint hard spheres that only interact via repulsion forces. Deviations from that reference system, as for example, attractive interactions (e.g., due to van der Waals forces, hydrogen bonds, or charges) are considered as independent, additive perturbations to the reference system. Due to the fact that PC-SAFT considers the hard chain as reference system instead of the hard-sphere system, it is particularly suitable to describe sugar molecules, which are chain-like and nonspherical molecules.

The residual Helmholtz energy of original PC-SAFT $a^{\text{PC-SAFT}}$ is obtained as the sum of the contribution of the reference system hard chain (hc) and the contributions originating from the perturbations due to attractive forces

$$a^{\text{PC-SAFT}} = a^{\text{hc}} + a^{\text{disp}} + a^{\text{assoc}} \tag{1}$$

a^{disp} and a^{assoc} account for the Helmholtz-energy contributions due to van der Waals (dispersive) and associative interactions, respectively. In this work, the expressions for a^{disp} and a^{assoc} are used as in the original PC-SAFT model.[23] Equation 1 is applied to systems with uncharged components (e.g., sugar/water). In systems that also contain ions, the expression a^{ion} is used as in the original electrolyte Perturbed-Chain Statistical Associating Fluid Theory (ePC-SAFT)[19] yielding

$$a^{e\text{PC-SAFT}} = a^{\text{PC}-\text{SAFT}} + a^{\text{ion}} = a^{\text{res}} \tag{2}$$

In this work, the Coulomb contribution a^{ion} that accounts for charged species is described by a Debye–Hückel term. The inclusion of all energy contributions denoted by Eq. 2 will be applied only in the Result sections containing Table 3 to account for effects in systems with inorganic ions.

To describe a solution of one sugar i in water, the model requires five pure-component parameters for the sugar, all of them having a physical meaning: the number of segments m_i^{seg}, the diameter of the segments σ_i, the van der Waals-interaction (dispersion) energy parameter between segments of two different molecules $u_i \cdot k_B^{-1}$, as well as association-energy and association-volume parameters $\varepsilon^{A_iB_i} \cdot k_B^{-1}$ and $\kappa^{A_iB_i}$. The number N_i^{assoc} of association sites per molecule is fixed according to the number of OH groups in a sugar, and thus, not treated as an adjustable parameter.

To extend the model to multicomponent mixtures, conventional Lorentz–Berthelot—combining rules are used for two components i and j

$$\sigma_{ij} = \frac{1}{2}\left(\sigma_i + \sigma_j\right) \tag{3}$$

$$u_{ij}=\sqrt{u_i u_j}\cdot\left(1-k_{ij}\right) \tag{4}$$

k_{ij} in Eq. 4 is a binary parameter that can be used to correct for deviations from the geometric mixing rule of the dispersion-energy parameter. For solute/solvent mixtures (e.g., sugar/water), this parameter is determined by fitting to binary data, for example, osmotic coefficients or solution densities. In case of ternary systems, each of the binary pairs has to be considered and adjusted to appropriate data. In case of a solvent 1/solvent 2 pair, the k_{ij} should be fitted to liquid–liquid equilibrium or vapor–liquid equilibrium data.

The k_{ij} in Eq. 4 was applied in this work to sugar/water and to water/ethanol pairs only. The k_{ij} values for sugar/solute, sugar/ethanol, and ion/water pairs were set to zero. Dispersive interactions between two ions were neglected. a^{ion} was only applied for Coulomb forces caused by the presence of inorganic ions. For sugar/water solutions, the k_{ij} parameter was allowed to depend on temperature

$$k_{ij}(T)=k_{ij,298.15\text{K}}+k_{ij,T}\cdot(T-298.15\text{K}) \tag{5}$$

Here, $k_{ij,298.15}$ is the interaction parameter at 298.15 K and $k_{ij,T}$ accounts for the temperature dependence of k_{ij}. According to the results of our previous works on biomolecules[15] these parameters are best fitted to solution data (solution densities, activity or osmotic coefficients, solubilities). In this work, only osmotic coefficients and solution densities were used to estimate the pure-component parameters for each sugar (references listed in Table 2).

The combining rules proposed by Wolbach and Sandler[24] were used in this work to describe the association between a sugar and water

$$\varepsilon^{AiBj}=\frac{1}{2}\left(\varepsilon^{AiBi}+\varepsilon^{AjBj}\right) \tag{6}$$

$$\kappa^{AiBj}=\sqrt{\kappa^{AiBi}\kappa^{AjBj}}\left(\frac{\sqrt{\sigma_i\sigma_j}}{0.5\left(\sigma_i+\sigma_j\right)}\right)^3 \tag{7}$$

Calculation of thermodynamic properties with PC-SAFT

Once the residual Helmholtz energy $a^{\text{PC-SAFT}}$ of a system is known, other thermodynamic properties can be derived by applying classical thermodynamics.[25] Among them is the compressibility factor Z, which can be determined with the derivation of $a^{\text{PC-SAFT}}$ with respect to the system density ρ

$$Z=1+\rho\left(\frac{\partial\left(a^{\text{PC-SAFT}}/k_BT\right)}{\partial\rho}\right) \tag{8}$$

The residual chemical potential $\mu_i^{\text{PC-SAFT}}$ of component i is obtained by

$$\frac{\mu_i^{\text{PC-SAFT}}}{k_BT}=\frac{a^{\text{PC-SAFT}}}{k_BT}+Z-1+\left(\frac{\partial\left(a^{\text{PC-SAFT}}/k_BT\right)}{\partial x_i}\right)-\sum_{j=1}^{N}x_j\left(\frac{\partial\left(a^{\text{PC-SAFT}}/k_BT\right)}{\partial x_j}\right) \tag{9}$$

Finally, the fugacity coefficient ϕ_i of component i can be determined using the expressions in Eqs. 8 and 9

$$\ln j_i=\frac{\mu_i^{\text{PC-SAFT}}}{k_BT}-\ln Z \tag{10}$$

The fugacity coefficients obtained from Eq. 10 can be used to calculate activity coefficients. Water activity coefficients γ_w are calculated by

$$\gamma_w=\frac{\varphi_w(x_w)}{\varphi_{0w}(x_w=1)} \tag{11}$$

where φ_w is the fugacity coefficient of water in the mixture (at the mole fraction of water x_w) and $\varphi_{0\text{w}}$ stands for the fugacity coefficient of pure water at the same temperature. Osmotic coefficients are calculated by

$$\phi=-\frac{1000\ln\left(x_w\gamma_w\right)}{M_w\sum_{i\neq w}\nu_i m_i} \tag{12}$$

with M_w being the molecular weight of water in [g mol^{-1}]. The molality in mol kg^{-1} is denoted with m_i, and ν_i represents the number of species per solute, in this work $\nu_\text{sugar}=1$ and $\nu_\text{salt}=\nu_\text{cation}+\nu_\text{anion}=2$.

For solubility calculations, a phase-equilibrium condition between the liquid and the solid phase has to be applied. Assuming a pure solid phase, the mole fraction of sugar in the liquid phase (its solubility) can be calculated by[26]

$$x_i^L=\frac{\varphi_{0i}^L}{\varphi_i^L}\cdot\exp\left\{\frac{\Delta h_{0i}^{SL}}{RT_{0i}^{SL}}\left(1-\frac{T_{0i}^{SL}}{T}\right)-\frac{\Delta c_{p,\text{i}}}{R}\left[1-\frac{T_{0i}^{SL}}{T}+\ln\left(\frac{T_{0i}^{SL}}{T}\right)\right]\right\} \tag{13}$$

$\varphi_{0i}{}^\text{L}/\varphi_i{}^\text{L}$ is the ratio of the fugacity coefficients of the sugar i as pure substance (as a hypothetical subcooled liquid) and in the mixture, respectively. $\varphi_i{}^\text{L}$ depends on temperature and on the kind and composition of the solvent (mixture), as well as on the concentration of the sugar i. $\Delta h_{0i}{}^{\text{SL}}$ is the melting enthalpy and $T_{0i}{}^{\text{SL}}$ is the melting temperature of the pure sugars. The influence of the difference in the heat capacities of the solid and the hypothetical subcooled liquid $\Delta c_{p,i}$ was explicitly accounted for in this work. The $\Delta c_{p,i}$ values were assumed to be independent of temperature. For most of the sugars considered in this work, exact melting properties are available in open literature. However, some sugars decompose before

Table 1. PC-SAFT Parameters for Water, Ethanol, and Ions Used within This Work

Substance	m_i^{seg}	σ_i/Å	$u_i\cdot k_\text{B}^{-1}$/K	$\varepsilon^{\text{AiBi}}\cdot k_\text{B}^{-1}$/K	κ^{AiBi}	k_{ij} with water	Ref.
Water	1.2047	[a]	353.95	2425.7	0.0451	–	14
Methanol	1.5255	3.2300	188.90	2899.5	0.0352	−0.085	22
Ethanol	2.3827	3.1771	198.24	2653.4	0.0324	−0.049[b]	22
Na^+	1.0000	2.4122	646.05	–	–	–	22
Cl^-	1.0000	3.0575	47.29	–	–	–	22

[a] For water, a temperature-dependent segment diameter $\sigma = 2.7927 + 10.11\exp(-0.01775\,T) - 1.417\exp(-0.01146\,T)$ was used.[14]

[b] For modeling water/ethanol systems, additional binary water/ethanol interaction parameters were applied according to.[22]

Table 2. Pure-Sugar and Binary Sugar/Water PC-SAFT Parameters. The Deviations ARD Between Modeled and Experimental Data are Given for Solution Densities ρ, Solubilities m, and Osmotic Coefficients ϕ in (%) Together with the References for the Experimental Data

Sugar/ Parameter	m^{seg}	σ (Å)	$u \cdot k_B^{-1}$/K	N^{assoc}	$\varepsilon^{\text{AiBj}} \cdot k_B^{-1}$/K	κ^{AiBj}	T^{SL}/K	$\Delta h^{\text{SL}} \cdot R^{-1}$/K	$\Delta c_p \cdot R^{-1}$	$k_{ij,298.15\text{ K}}$ (H_2O)	$k_{ij,T}$ (H_2O)	ρ ARD (%)	Ref.	ϕ ARD (%)	Ref.	m ARD %	Ref.
Glucose	6.626	2.986	244.53	10	5000	0.1	423.2[27]	3900.7[28]	14.4[8]	−0.0524	2.24E-4	0.61	1	0.53	29	2.61	30
Fructose	7.387	2.849	237.19	10	5000	0.1	378.227	3130.78	11.931	−0.0555	1.40E-4	0.28	32	0.84	12	3.91	33
Xylose	6.012	2.888	283.22	8	5000	0.1	416.228	3601.128	11.734	−0.0342	2.58E-4	0.04	35	1.43	35	0.92	36
Galactose	6.478	2.950	244.91	10	5000	0.1	436.028[a]	5265.0[28a]	16.7[34]	−0.0495	4.24E-4	0.01	37,38	0.12	29	2.83	36
Sucrose	14.886	2.827	297.39	16	5000	0.1	598.528[b]	2863.228[b]	30.539	−0.0371	2.56E-4	0.90	40,41	1.80	42	1.56	43
Sorbitol	7.230	2.960	226.94	12	5000	0.1	384.044[a]	3848.744	3.444	−0.0591	9.33E-5	0.60	41	1.35	45,46	6.52	47
Xylitol	6.250	2.910	242.24	10	5000	0.1	367.548	4050.848	9.348	−0.0492	2.00E-4	0.03	49	0.86	50	6.25	51
Mannitol	7.230	2.935	227.03	12	5000	0.1	439.152	6653.452[a]	16.753	−0.0607	2.20E-4	0.05	41	0.21	54	7.74	47,54
Fucose	5.662	3.030	252.99	8	5000	0.1	–	–	–	−0.0538	–	0.68	1	0.65	55	–	–
Maltose	14.063	2.853	305.30	16	5000	0.1	439.228[c]	6960.528[b]	25.128	−0.0333	1.20E-4	0.23	35	0.21	35	4.22	36
Mannose	7.738	2.801	297.82	10	5000	0.1	390.128[c]	2968.528[a]	15.628	−0.0327	3.70E-4	0.03	32	0.06	29	3.13	8
Lactose	14.337	2.811	319.21	16	5000	0.1	498.027	7988.5[d]	28.739	−0.0321	1.84E-4	0.05	56	0.95	[e]	0.70	57
Trehalose	13.692	2.856	319.85	16	5000	0.1	443.028[c]	5846.2[d]	22.628	−0.0274	2.19E-4	0.02	Held and Sadowski, submitted	0.59	Held and Sadowski, submitted	4.90	58

[a] Value refitted to experimental solubility data within 4% deviation to experimental value.
[b] Value refitted to experimental solubility data at 298.15 K in water.
[c] Value refitted to experimental solubility data at 298.15 K in water within 8% deviation to experimental value.
[d] No literature data available, fitted to experimental solubility at 298.15 K in water.
[e] No literature data available, calculated according to Eq. 16, see Table 3.
[f] No literature data at 273.15 K available, calculated according to Eq. 16.

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melting. In this case, these properties were fitted to experimental solubility data (see next section).

In this work, solubility data will be presented in molality m (moles of sugar per kg of solvent s), which can be converted from the mole fraction of the sugar x_i by

$$m_{i \neq s} = \frac{1000 x_i}{x_s M_s} \tag{14}$$

PC-SAFT parameter estimation for sugars

In this work, systems containing solvents (water, ethanol), inorganic ions (Na^+, Cl^-), and sugars were modeled. The solvents and the ions have already been parameterized earlier.[22] For the sake of completeness, these parameters are given in Table 1.

Within PC-SAFT, the sugars were considered as chains consisting of identical uncharged spheres. Each OH group was assigned with two association sites, mimicking the proton-donor site and the proton-acceptor site. For example, for glucose, a 5:5 association scheme was applied. Both association-site types were assumed to have the same energy and volume parameters ($\varepsilon^{\text{AiBi}} \cdot k_B{}^{-1}$ and κ^{AiBi}). In a preliminary investigation within this study, a sensitivity test was carried out to investigate the influence of the association parameters on the model performance. As a result, it was proven that setting the association parameters to fixed values still allows for satisfactory modeling of sugar/water systems. That is, $\varepsilon^{\text{AiBi}} \cdot k_B{}^{-1}$ and κ^{AiBi} were not treated as adjustable pure-component parameters. Setting $\varepsilon^{\text{AiBi}} \cdot k_B{}^{-1}$ and κ^{AiBi} to 5000 K and 0.1, respectively, yielded the best results for modeling solution densities and osmotic coefficients in sugar/water systems as well as for predicting sugar solubilities in water. Thus, these values were applied in this study for all the sugars.

Thus, in this work, only three pure-component PC-SAFT parameters (segment number, segment diameter, dispersion-energy parameter) for the sugars and a k_{ij} between sugar and water were determined by fitting to experimental solution-density and osmotic-coefficient data. Experimental data were taken from literature.

For solubility calculations (see Eq. 13), the melting enthalpy, the melting temperature, and the $\Delta c_{p,i}$ values of the pure sugars are required. The latter were directly inherited from literature (references: see Table 2) for all considered sugars. For most of the sugars, melting properties given in literature were directly used for solubility calculations. In some cases, these values were allowed to change up to 8% for accurate solubility calculations (see Table 2 footnotes). However, for some sugars, the experimental melting properties are highly uncertain (due to decomposition before melting, for example, for trehalose, lactose, and sucrose). In

Table 3. ARD Values (%) Between (e)PC-SAFT Predicted and Experimental Osmotic Coefficients for Solutions Containing Two Solutes at 298.15 K

Aqueous solution of:		m_1 range	m_2 range	ϕ range	ARD	
Sugar (1)	Cosolute (2)	mol kg^{-1}	mol kg^{-1}	(Exp.)	%	Ref.
Sucrose	Glucose	0.3–2.8	0.5–3.5	1.10–1.26	8.2	59
Glucose	Mannitol	0.0–1.0	0.0–1.0	1.00–1.01	0.2	60
Glucose	Sorbitol	0.0–7.1	0.0–7.2	1.00–1.16	0.5	60
Mannitol	Sorbitol	0.0–0.8	0.0–7.2	1.00–1.16	0.6	60
Mannitol	NaCl	1.2–1.3	0.8–5.2	0.93–1.20	1.9[a]	61

[a] Data $m_2 < 1.6$ mol kg^{-1} was discarded.

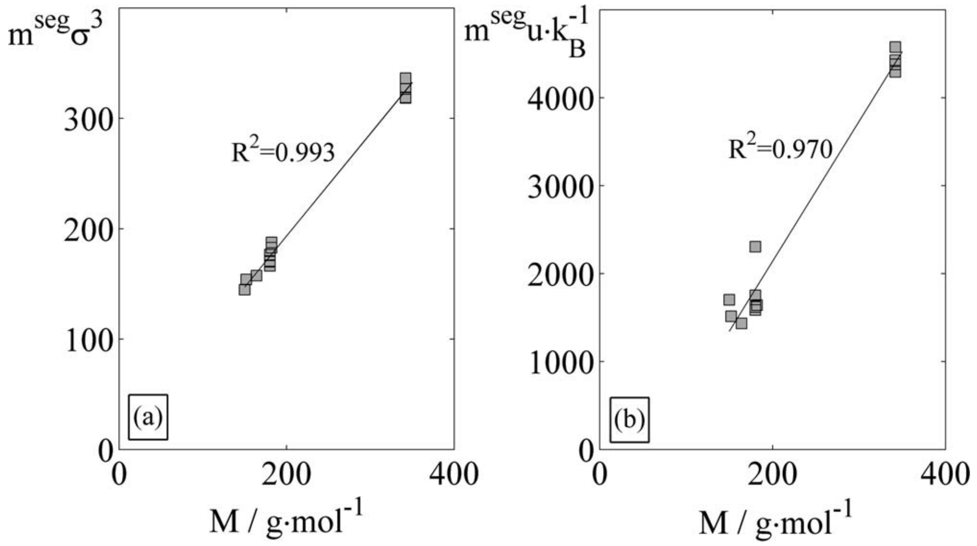

Figure 1. Dependence of the pure-sugar PC-SAFT parameters ($m^{seg}\sigma^3$) and ($m^{seg}u \cdot k_B^{-1}$) on the molecular weights of the sugars considered in this work.

these cases, the melting properties Δh_{0i}^{SL} and T_{0i}^{SL} were fitted to experimental solubility data under the consideration of $\Delta c_{p,i}$ values given in literature.

The PC-SAFT parameters for the sugars, the reference for the experimental data, and the accuracy of the fitting procedure are listed in Table 2. The accuracy is expressed via absolute relative deviations ARD between modeled and experimental data, calculated by

$$\text{ARD}=100 \cdot \frac{1}{\text{NP}}\sum_{k=1}^{\text{NP}}\left|\left(1-\frac{y_k^{\text{calc}}}{y_k^{\text{exp}}}\right)\right| \tag{15}$$

where y represents solution density, osmotic coefficient, or sugar solubility, respectively. Considering the ARD values in Table 2, it can be stated that all the considered thermodynamic properties of the sugar systems can be accurately described with PC-SAFT. Globally, the ARDs for all considered systems are very small ($\text{ARD}_{\text{density}} = 0.23\%$, $\text{ARD}_{\text{osmotic coefficient}} = 0.61\%$) with the highest error appearing in the solubility predictions ($\text{ARD}_{\text{solubility}} = 4.87\%$). Presumably, this is caused by the experimental uncertainty (about 3%) as well as by the higher temperature range compared to densities and osmotic coefficients. Moreover, solubility was not used for the pure-component parameter estimation. Thus, this result is satisfactory as the properties vary in a broad concentration and temperature range. These parameters provide the basis for modeling aqueous sugar solutions with more than one dissolved component. The PC-SAFT parameters for the sugars were analyzed with respect to any dependency on the molecular weight. As it can be easily observed in Figure 1, linear trends were observed for the parameters ($m^{seg}\sigma^3$) vs. M and ($m^{seg}u \cdot k_B^{-1}$) vs. M.

Results and Discussion

Thermodynamic properties of binary sugar/water solutions

Using the parameters in Tables 1 and 2, densities, osmotic coefficients, and solubilities can be modeled with high precision for sugar/water solutions. Overall ARDs for these properties are given in Table 2. As a representative example, Figure 2 illustrates experimental data and modeling results of three thermodynamic properties for aqueous glucose

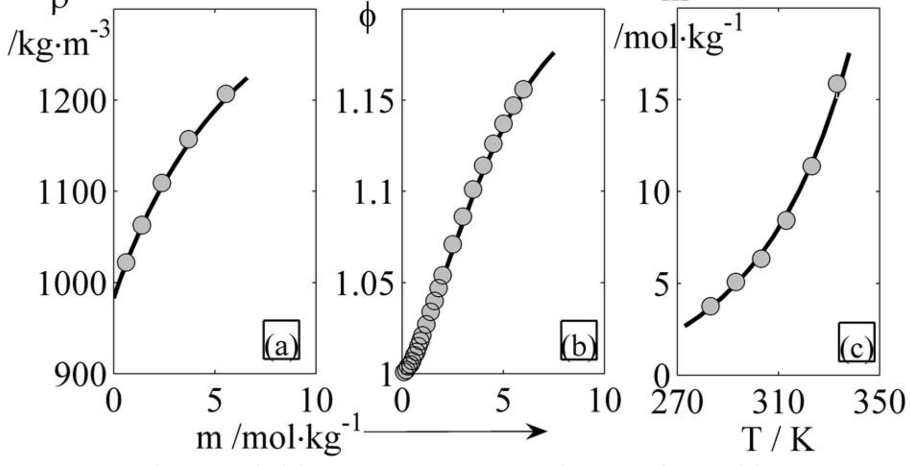

Figure 2. (a) Solution densities (298.15 K), (b) osmotic coefficients (298.15 K), and (c) solubility of glucose in water.

Symbols represent experimental data with references from Table 2, lines correspond to PC-SAFT calculations.

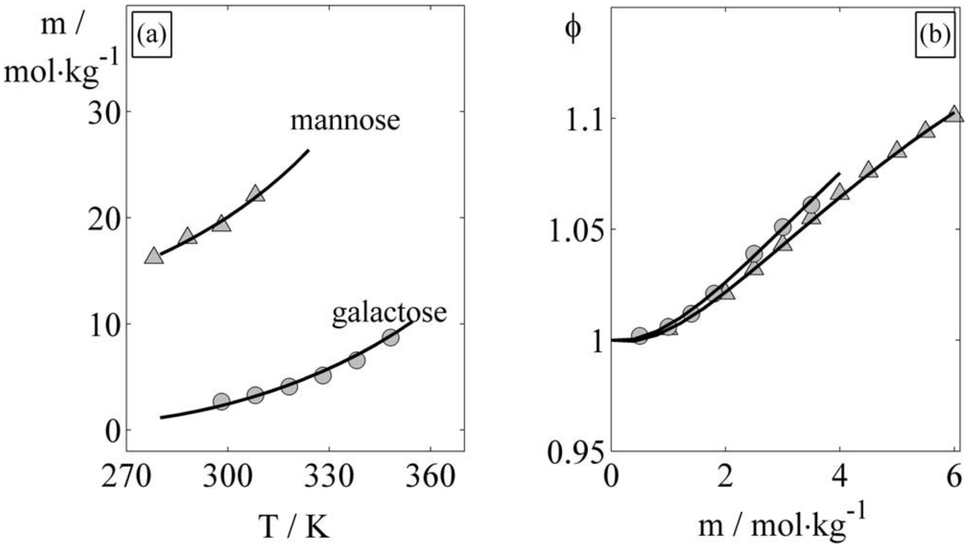

Figure 3. Properties of sugar/water systems.

Symbols are experimental data with references from Table 2 (galactose/water: circles, mannose/water: triangles), lines correspond to PC-SAFT calculations. (a) Solubility of sugar in water and (b) osmotic coefficients of sugar/water solution at 298.15 K.

solutions. As can be seen, solution densities and osmotic coefficients can be described simultaneously with PC-SAFT.

For modeling the solubility of glucose in water, the melting properties and the Δc_p value found in literature were directly used in Eq. 13. As solubility data were not included in the parameter fitting, the result shown in Figure 2c is a pure prediction. This is a typical result for binary sugar/water systems.

Despite of the very similar structure and the same molecular weight of isomeric sugars, the solubility in water may vary strongly. This is shown for the D-aldohexoses galactose and mannose (both having the chemical formula $C_6H_{12}O_6$) in Figure 3a. Whereas the solubility of mannose is very high in the considered temperature range, it is much lower for galactose (roughly eight times lower at 298.15 K). In contrast, osmotic coefficients of galactose/water and mannose/water solutions are more or less equal (Figure 3b).

To show that PC-SAFT is able to capture the temperature dependence of osmotic coefficients and solubility at the same time, Figure 4 compares experimental data and PC-SAFT calculations for these properties in xylitol/water and sucrose/water solutions. The osmotic coefficients of these sugar solutions decrease linearly with temperature. In contrast, solubility increases nonlinearly with temperature (especially for xylitol). One consequence on this is that mainly the melting properties (especially T^{SL}) determine the shape of the solubility curve. It can be observed that both, osmotic coefficients and solubility can be modeled simultaneously, and thus, the parameter sets in Table 2 are physically meaningful. Considering Figure 4, it can be observed that experimental osmotic coefficients of sorbitol solutions monotonically increase with the sugar concentration, whereas the model shows nonmonotonic behavior. However, it has to be stated that experimental data at low concentration are

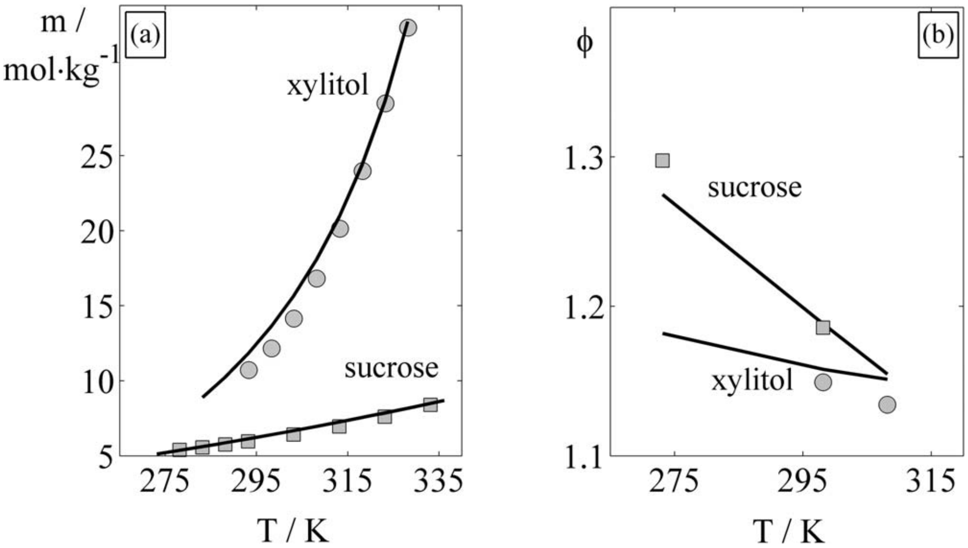

Figure 4. (a) Solubility of sugar in water and (b) osmotic coefficients of sugar/water solutions.

Symbols are experimental data (circles: xylitol, squares: sucrose). Osmotic coefficients are at 9.83 m for xylitol and at 2 m for sucrose solutions. Lines correspond to PC-SAFT with references from Table 2.

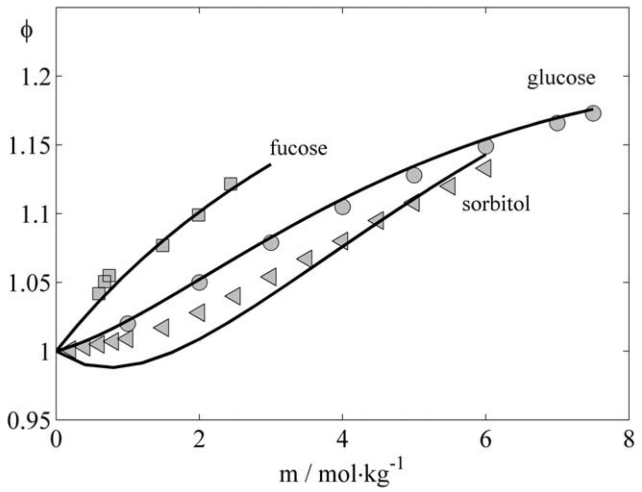

Figure 5. Osmotic coefficients of aqueous sugar solutions as function of sugar molality at 298.15 K.

Symbols represent experimental data with references from Table 2 (glucose: circles, sorbitol: triangles, fucose: squares), lines correspond to PC-SAFT calculations.

known to be uncertain by at least 0.5%. The fact that also the experimental data in the xylitol/water show nonmonotonic behavior makes it hard to state whether the experimental uncertainty of osmotic coefficients in the sorbitol/water system is too high or the model does not capture the effect correctly.

In sugar solutions at low-sugar molalities, ϕ deviates only weakly from unity, which was observed also for other biomolecule solutions in previous work.[15] However, highly concentrated sugar solutions (e.g., relevant for juices) deviate more strongly from the ideal behavior. In Figure 3b, it was shown that osmotic coefficients of binary galactose/water and mannose/water solutions are almost equal. A very similar behavior can be observed for osmotic coefficients of other binary sugar/water solutions.

In general, osmotic coefficients of sugar solutions are close to or higher than unity. That is, sugar and water interact strongly with each other. The increase of osmotic coefficients with increasing sugar molality is in most cases less pronounced at small molalities and higher in high-concentrated regions; this leads to the typical s-shaped behavior of osmotic coefficients (see e.g., Figure 3b).

Influence of Functional Groups of Sugars on Osmotic Coefficients of Sugar/Water Solutions. In general, sugars considered in this work are composed of hydrophilic groups (especially OH and O) that are attached to a C5 or C6 backbone. The general dependence of osmotic coefficients on the number of carbon atoms (chain length) and on the number of functional polar groups is discussed by examining the trends of osmotic coefficients for several sugar solutions at 298.15 K in the following sections.

Influence of OH Groups. The influence of polar groups, which might form hydrogen bonds (especially OH) on osmotic coefficients is usually strong in biomolecule/water solutions.[15]

The experimental and modeled osmotic coefficients for glucose, sorbitol, and fucose aqueous solutions are illustrated in Figure 5. All these sugars are C6 backboned. Glucose possesses 5 OH groups and a terminated O-group, whereas one additional hydroxyl group is present in sorbitol compared to glucose (glucose $C_6H_{12}O_6 \rightarrow$ sorbitol $C_6H_{14}O_6$). Although the osmotic coefficients are very similar for glucose/water and sorbitol/water solutions, slightly lower osmotic coefficients are observed for a solution containing the sugar with a higher number of OH groups. That is, decreasing the number of OH groups from 5 to 4 (glucose $C_6H_{12}O_6 \rightarrow$ fucose $C_6H_{12}O_5$) causes increased osmotic coefficients for fucose solutions ($\phi_{\text{glucose/water}} < \phi_{\text{fucose/water}}$) of equal molality. This finding is in qualitative accordance with the behavior of amino-acid solutions,[15] however, less pronounced. This behavior is captured quantitatively by PC-SAFT. It can be observed that the experimental osmotic coefficients increase with the sugar concentration for sorbitol/water solutions. However, PC-SAFT shows a slight nonmonotonic behavior. This might be due to the uncertainty of experimental data at low-sugar concentrations. However, there is indeed one sugar/water system with such a minimum (xylitol/water). Thus, it is hard to state whether the experimental uncertainty is in this case too high or if the model does not capture the effect in the sorbitol/water system correctly. It should be mentioned that this deviation between model and experiment is very low (<1%, see Table 2).

Influence of CH_3 Groups. Pentoses (e.g., xylose) possess five carbon atoms in their backbones, whereas six carbons are present in the hexoses (e.g., fucose). Comparing xylose and fucose (both of them having four OH groups), the influence of adding a methylene group to the sugar's backbone (xylose $C_5H_{10}O_5 \rightarrow$ fucose $C_6H_{12}O_5$) on osmotic coefficients can be investigated (Figure 6). It can be observed that increasing the number of CH_3 groups causes higher-osmotic coefficients of the respective aqueous solutions, that is, $\phi_{\text{fucose/water}} > \phi_{\text{xylose/water}}$. This behavior is expected as it was also observed in amino-acid solutions.[15]

Comparing aldopentose (xylose) with aldohexose (glucose), both, a methylene as well as an OH-group is added to the aldopentose. As shown before, these groups cause opposite effects and it cannot be easily estimated, which is the stronger one. Comparing osmotic-coefficient data, however, it can be stated that the experimental osmotic coefficients are higher for

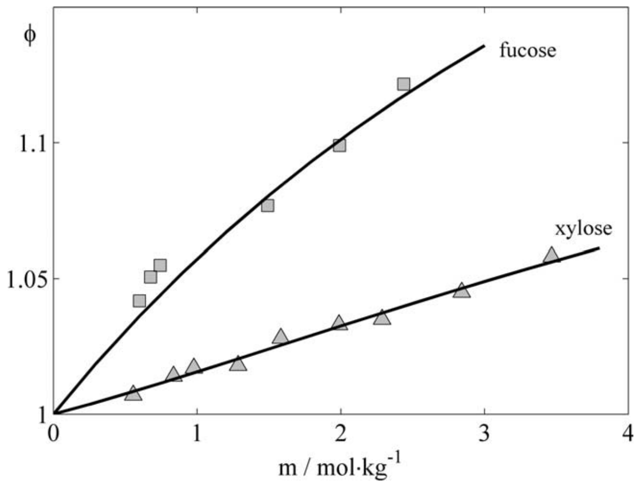

Figure 6. Osmotic coefficients of aqueous sugar solutions as function of sugar molality at 298.15 K.

Symbols represent experimental data with references from Table 2 (xylose: triangles, fucose: squares), lines correspond to PC-SAFT calculations.

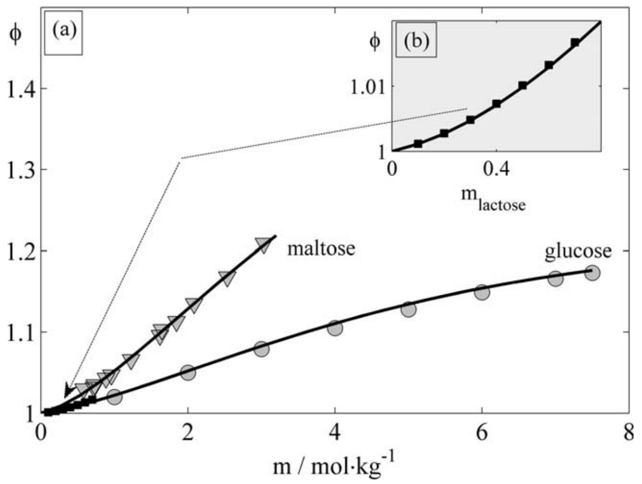

Figure 7. Osmotic coefficients of aqueous sugar solutions as function of sugar molality at 298.15 K.

Symbols represent experimental data with references from Table 2 (glucose: circles, maltose: triangles, lactose: squares), lines correspond to PC-SAFT calculations. (b) Data and modeling for lactose/water solutions.

hexose than for pentose solutions ($\phi_{\text{glucose/water}} > \phi_{\text{xylose/water}}$). Thus, the effect of OH-groups is obviously overcompensated by the influence of an increased number of methylene groups.

Influence of Sugar Dimerization. Investigating the osmotic coefficients of glucose and maltose (which consists of two glucose monomers) solutions in Figure 7 reveals a strong influence of osmotic coefficients on the presence of sugar dimers. Compared to its monomer, maltose causes much higher osmotic coefficients at equal conditions. It can be observed that the ϕ data follow a mixing rule that is the sum of three osmotic-coefficient contributions: ideal, excess of binary system monomer 1/water, and excess of binary system monomer 2/water

$$\phi_{\text{dimer/water}} = \underbrace{1}_{\text{ideal}} + \underbrace{(\phi_{\text{monomer1/water}} - 1)}_{\text{excessmonomer1/water}} + \underbrace{(\phi_{\text{monomer2/water}} - 1)}_{\text{excessmonomer2/water}} \tag{16}$$

This holds also true for the other dimers (see Table 2) for which ϕ data were available and which were considered in this work.

Using Eq. 16, osmotic coefficients were calculated for lactose/water solutions for which experimental data are not available so far. The so-determined osmotic coefficients of lactose/water solutions are shown in Figure 7b. For cases where experimental data are not available (herein: osmotic coefficients of lactose/water solutions at 298.15 K), the application of Eq. 16 might be an appropriate alternative. The behavior of maltose/water and the other disaccharide/water solutions is captured quantitatively with PC-SAFT (ARDs in Table 2).

Osmotic coefficients of solutions containing two or three solutes

Up to this point, binary solutions containing only one sugar have been investigated. Model parameters have been fitted for monosaccharides, sugar alcohols, and disaccharides.

In the following, the applicability of PC-SAFT for modeling osmotic coefficients of aqueous solutions containing two solutes will be discussed briefly. In the literature, osmotic coefficients are available for the systems mannitol/NaCl/water, glucose/sucrose/water, mannitol/sorbitol/water, glucose/mannitol/water, and glucose/sorbitol/water at 298.15 K (references in Table 4). All these literature data were measured using an isopiestic method. That is, within one measurement series, both of the solute molalities varied, which does not allow for presenting the results in a two-dimensional m,ϕ-diagram. Thus, the modeling results are presented in Table 3 for each of the considered ternary two-solute systems in terms of the ARD value between model and data.

Considering the ARD values in Table 3, it can be stated that binary interaction parameters k_{ij} for sugar/solute pairs are not required for modeling these data, even at high sugar or cosolute molalities. The results were obtained by using only the pure-component parameters from Tables 1 and 2 and the k_{ij} values between sugar and water (see Table 2). As it becomes obvious from Table 3, the osmotic coefficients of solutions containing two solutes could be predicted quantitatively with PC-SAFT. The untypically high ARD value of the osmotic coefficients for sucrose/glucose solutions (8.2% in Table 4) might be due to experimental uncertainty in the data used for the calculations.

With these parameters also the osmotic coefficients of a quaternary sorbitol/mannitol/glucose/water system[60] could be modeled quantitatively with an ARD value of 0.5%.

Table 4. ARD Values/% Between (e)PC-SAFT Predicted and Experimental Sugar Solubilities in Ethanol/Water, Methanol/Water, and Ethanol/Methanol Mixtures

Solvent 1	Solvent 2	Sugar	T/K	wt %$^{\text{sugar-free}}$ of solvent 2	ARD m/%	Ref.
Water	Ethanol	Lactose	298.15	90–100	14.78	62
Water	Ethanol	Maltose	310.15	75–100	14.68	9
Water	Ethanol	Mannose	298.15	50–100	18.60	9
Water	Ethanol	Sucrose	310.15	62.5–100	13.01	63
Water	Ethanol	Mannitol	310.15	25–100	24.71	63
Water	Ethanol	Trehalose	298.15	80–100	33.41	9
Water	Ethanol	Xylitol	298.15	25–100	12.13	64
Water	Ethanol	Galactose	303.15	10–100	12.28	65
Water	Ethanol	Sorbitol	310.15	5–100	21.03	63
Water	Ethanol	Xylose	298.15	30–100	30.12	9
Water	Ethanol	Fructose	298.15	11–100	15.07	66
Water	Ethanol	Glucose	313.15	10–100	8.00	67
Water	Methanol	Xylitol	298.15	25–100	11.98	2
Ethanol	Methanol	Glucose	313.15	10–100	37.08	2

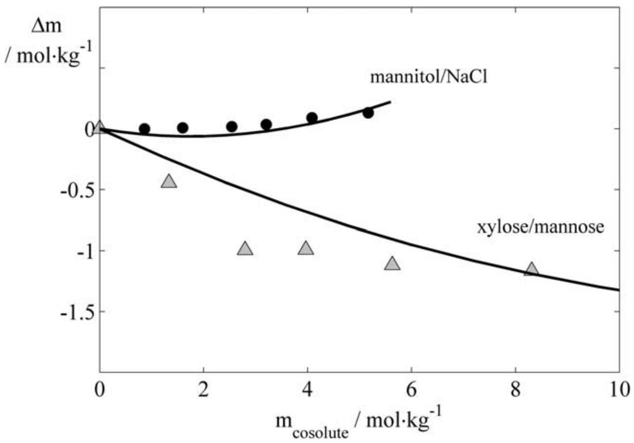

Figure 8. Solubility at 298.15 K of mannitol in the presence of NaCl (circles), and of xylose in the presence of mannose (triangles), presented as solubility differences Δm of the sugar solubility in the ternary and the binary sugar/water system.

Symbols represent experimental data (stars: mannitol/NaCl[61], triangles: xylose/mannose[69]), lines are pure predictions with ePC-SAFT ($k_{ij}=0$ between sugar and cosolute).

Solubility of sugars in multi-solute solutions

In a previous publication,[68] it was shown that amino-acid solubilities in multisolute aqueous solutions can be predicted based on the pure-component parameters of the amino acids only. For most of the systems, no fitting parameters (i.e., k_{ij} between two amino acids) had to be introduced. For example, for aqueous solutions composed of valine/leucine or valine/alanine, quantitative solubility predictions ($k_{ij}=0$) were possible at temperatures between 298.15 and 333.15 K.

Figure 8 illustrates the influence of cosolutes on the aqueous sugar solubility at 298.15 K, presented as solubility difference Δm of the sugar solubility in the presence and absence of the cosolute, respectively. It can be seen that NaCl causes a slight salting-in behavior of mannitol in aqueous solutions. In contrast, adding mannose to saturated xylose solutions reveals a strong salting-out effect. Without applying k_{ij} parameters between sugar and cosolute, these behaviors were well predicted with ePC-SAFT. Moreover, in the case of mannitol/NaCl/water, it can be concluded that ePC-SAFT allows for simultaneous predictions of osmotic coefficients (Table 4) and sugar solubility in multisolute solutions.

It is known from literature that there are some solutes that cause salting-in phenomena at low concentrations and salting-out at higher concentrations, and vice versa. It can be observed from Figure 8 for the mannitol/NaCl system that the experimental Δm values are monotonically increasing, whereas the model predicts negative Δm values at low NaCl concentrations before becoming positive at higher NaCl concentrations. It can be argued whether this observation is due to experimental error (3% at least) or due to model inaccuracies at low NaCl concentrations.

Solubility of sugars in pure alcohol and in solvent mixtures

Besides the modeling of sugar solubility in multisolute aqueous solutions, also modeling the solubility in ethanol and in alcohol/water mixtures is of academic and industrial interest. Experimental data are fairly available, as several research groups carried out measurements and modeling of such data.

In a first step, solubility calculations of sugars in pure alcohols were carried out to evaluate whether a k_{ij} interaction parameter between sugar and ethanol is necessary. For glucose/ethanol solutions, the ARD value between experimental[67] and PC-SAFT calculations is below 3% (related to molality) at 313 K. Thus, a k_{ij} between sugar and ethanol was not applied in this work. The obtained PC-SAFT results are then pure predictions.

Besides modeling sugar solubility in pure solvents, also the solubility in solvent mixtures is of interest. Literature data are available for many sugars in water/ethanol mixtures. Figure 9 shows the solubility of glucose and of fructose in water/ethanol mixtures at 313.15 K. It can be observed from the experimental data that adding water to pure ethanol causes a continuous increase of the sugar solubility. Moreover, the solubility curves show a slight s-shape. Experimental solubility data for other sugars in solvent mixtures[63–66] indicate that these observations are typical for sugar solubility in water/ethanol mixtures.

Applying PC-SAFT to these systems allows for an accurate prediction of the sugar solubility. This is illustrated in Figure 9 for the solubility of glucose and fructose in ethanol/water mixtures as two representative examples. Similar predictive results were obtained for the solubility of sorbitol, galactose, xylitol, and mannitol in water/ethanol mixtures (experimental data from[63–66]). For xylose, trehalose, mannose, maltose, and lactose slight deviations between predicted and experimental solubility data[9,62,63] in water/ethanol mixtures were observed. For these sugars, the solubility in ethanol is predicted too low, resulting in underestimated solubilities for compositions with larger amounts of alcohol. Table 4 lists ARD values obtained by predicting sugar solubilities in different solvent systems at different temperatures. For these predictions, the k_{ij} values between a sugar and ethanol as well as between a sugar and methanol were set to zero.

In sum, it can be stated that the proposed modeling and the sugar parameters provide high accuracy for

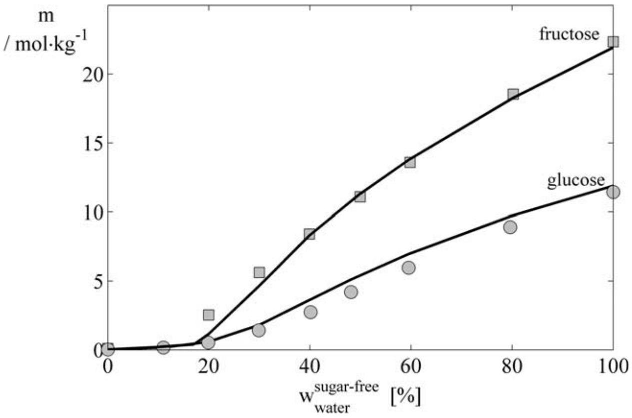

Figure 9. Solubility of glucose at 313.15 K (circles) and fructose at 298.15 K (squares) in ethanol/water mixtures depending on the sugar-free wt % of water in the mixed solvent.

Symbols are experimental data[2], lines represent PC-SAFT predictions.

thermodynamic properties and phase equilibria of sugar solutions. PC-SAFT has been shown to be quantitatively predictive over large ranges of concentration and temperature for very different systems.

Conclusions

In this work, thermodynamic properties and phase equilibria of aqueous sugar solutions were modeled with the PC-SAFT model. In sum, 13 sugars were considered: glucose, fructose, fucose, xylose, maltose, galactose, mannitol, mannose, sorbitol, xylitol, lactose, trehalose, and sucrose. Only four adjustable parameters (three pure-component parameters and a k_{ij} between sugar and water that was allowed to depend linearly on temperature) were fitted to experimental solution densities and osmotic coefficients of binary sugar/water mixtures at 298.15 K. To preserve the associative behavior of the sugars, the number of association sites was set according to the number of OH groups in each sugar and the association parameters were set to constant values for all sugars. This strategy allowed for highly precise modeling of solution densities and osmotic coefficients of binary sugar/water solutions.

With the same set of parameters, the sugar solubility in water and in ethanol and in methanol could be reasonably predicted for most of the sugars. In some cases (especially for the disaccharides), also the melting enthalpy and/or the melting temperature had to be slightly readjusted compared to the experimental values. Binary interaction parameters k_{ij} between sugars and ethanol or sugars and methanol were set to zero. To prove the predictive applicability of PC-SAFT also to more complex systems, osmotic coefficients and sugar solubility in aqueous solutions containing two solutes (e.g., two sugars or sugar + salt) were modeled without introducing additional k_{ij} parameters for sugar/solute pairs. Furthermore, the model has shown to predict the solubility of a sugar in a solvent mixture of water and ethanol or water and methanol, again without fitting additional parameters. For most of these multi-component mixtures, PC-SAFT allowed quantitative prediction of the experimental data. For a few exceptions, the predictions showed only qualitative agreement with experimental data, with deviations slightly higher than experimental uncertainties.

In general, this work shows that PC-SAFT and the proposed sugar parameters allow for quantitative modeling predictions in complex multi-component sugar solutions with a minimum of four adjustable parameters, fitted solely to densities and osmotic coefficients.

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Symbols

Roman symbols

a = Helmholtz free energy per total particle number, J
Δc_p = heat capacity difference between solid and hypothetical subcooled liquid sugar, J (mol K)$^{-1}$
Δh^{SL} = melting enthalpy, J mol^{-1}
k_B = Boltzmann constant, $1.38065 \cdot 10^{-23}$ J/K
k_{ij} = binary interaction parameter
$k_{ij,T}$ = slope of the temperature-dependent binary interaction parameter, K^{-1}
$k_{ij,298.15\ K}$ = binary interaction parameter at 298.15 K
m = molality (moles of solute i per kg of solvent), mol kg^{-1}
M = molecular weight, g mol^{-1}
N_i^{assoc} = number of association sites of component i
m^{seg} = number of segments
n = number of moles
R = ideal gas constant, J (mol K)$^{-1}$
T = temperature, K
T^{SL} = melting temperature, K
x = mole fraction
V = volume, m^3
Z = compressibility factor

Greek letters

γ_i = symmetric activity coefficient of component i (related to pure component)
φ_i = fugacity coefficient of component i
$u\ k_B^{-1}$ = dispersion-energy parameter, K
$\varepsilon^{AiBi} \cdot k_B^{-1}$ = association-energy parameter, K
κ^{AiBi} = association-volume parameter
μ_i = chemical potential of component i
ϕ = osmotic coefficient
ρ = density, kg m^{-3}
σ_i = segment diameter of component i, Å

Subscripts

i, j = component indices
T = function of temperature
seg = segment
s = solvent
W = water
0 = pure substance

Superscripts

assoc = association
disp = dispersion
hc = hard chain
ion = ionic
m = based on molality
res = residual

Abbreviations

ARD = average relative deviation
EOS = equation of state
(e)PC-SAFT = (electrolyte) Perturbed-Chain Statistical Association Fluid Theory.

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