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# Modeling and measurements of solid–liquid and vapor–liquid equilibria of polyols and carbohydrates in aqueous solution

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**Abstract**

The solubilities of five saccharides in water have been measured at various temperatures. This includes the monosaccharides xylose and galactose, and the disaccharides maltose monohydrate, cellobiose and trehalose dihydrate. A method that uses interaction energies and interaction parameters calculated with molecular mechanics methods has shown to give good predictions of the phase behavior of a variety of mixtures, including glycols and small saccharides in aqueous solution. The method is completely predictive, as the strength of the molecular interactions is determined with a theoretical method in the absence of any phase equilibrium data. For calculating solubilities, experimental values for the melting points and the heats of fusion of the compounds under study are, however, necessary. The solubilities of the five saccharides listed above, raffinose and *meso*-erythritol in water were calculated with this method. The calculated solubilities are in reasonably good agreement with experiment, and in the case of *meso*-erythritol, which is a polyalcohol (polyol), and galactose, the agreement between prediction and experiment is excellent. Also the vapor pressures of water over several polyols and saccharides in aqueous solution have been predicted with this method, giving results in excellent agreement with the experimental values. 

*Keywords:* Molecular simulation; Vapor–liquid equilibria; Solid–liquid equilibria; Polyols; Saccharides

## 1. Introduction

The use of molecular simulation techniques and molecular structure calculations for predicting properties of interest for the chemical industry is becoming more and more important.

A method that involves calculation of interaction energies and interaction parameters between molecules using molecular mechanics methods has been shown to be successful for predicting vapor–liquid equilibria (VLE) for a variety of mixtures. This involves various organic mixtures,[1–4] polymer solutions[5,6] and saccharides in aqueous solution.[3,7] Also the solid–liquid equilibrium (SLE) of saccharides in aqueous solution can be predicted with the method.[7] We have named the method TIEC (Theoretical Interaction Energy Calculations).

A basic finding is that it is possible to predict phase behavior of large systems by studying small subsystems, where the important interactions are included. In previous publications,[3,7,8] very interesting results were obtained with the so-called transference principle. By calculating interaction parameters for the water–1,2-ethanediol system, it is possible to predict VLE for aqueous solution of glycols and saccharides, and the solubilities of glucose and sucrose in aqueous solution. 1,2-Ethanediol can be considered as a functional subunit of the larger glycol and sugar molecules, and the water molecule is so small that it can only interact with a small part of the larger molecule. This is similar to results obtained for polymer solutions,[5] where interaction parameters are determined between the solvent and a model compound of similar size as the solvent molecule that contains one or two repeat units of the polymer molecule. It is thus possible to predict phase

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behavior of large systems by studying small subsystems, provided that the most important interactions are taken into account.

Here the work is extended to cover both the VLE and SLE of aqueous solutions of several saccharides and polyols. These two classes of compounds have significant structural similarities. Polyols are oligomers made up of $–CH_xOH$ ($–CH_2OH$ and –CHOH) units, and the saccharides studied here are mostly made of $–CH_xOH$ units and a few –CHO– units. These compounds form strong hydrogen bonds with one another and with water, which leads to higher order structure of some sort, as in the case of pure liquid water.

Despite the fact that carbohydrates are very important molecules, both from industrial and biological points of view, there is a considerable lack of experimental data in the literature. An important part of our research has been the acquisition of such experimental data. The vapor pressure of water over several saccharides and polyols in aqueous solution has been measured.[9,10] Of special interest is a systematic study of glucose oligomers, ranging from (+)-D-glucose (Glc) to maltopentaose ($(\alpha$-D-glucopyranosyl-$(1\rightarrow4))_4$-D-glucopyranose) in aqueous solution. For these mixtures, both the vapor pressures and the molar heats of mixing have been measured.[9] Vapor pressures for (−)-D-fructose (+)-raffinose, *meso*-erythritol, xylitol and D-sorbitol in aqueous solution have also been measured.[10]

In addition, solubilities of five different mono- and disaccharides in aqueous solution at various temperatures, have been measured using an isothermal technique. These five compounds are the monosaccharides (+)-D-xylose and (+)-D-galactose and the disaccharides (+)-maltose monohydrate, (+)-cellobiose and (+)-trehalose dihydrate. The disaccharides are all made of two glucose units, only differing in the type of glycosidic linkage. The measured solubility data are presented in this manuscript, along with the model calculations.

There is a lack of good predictive models for describing the phase behavior of larger carbohydrate molecules and other strongly interacting molecules. The strength of our approach is the very fundamental way of examining the intermolecular interactions on an atomic level, which gives us valuable information about the molecules involved. The purpose of this article is to examine the predictive ability of the existing model in the light of the new experimental information available. In the following text and in the abstract, all the saccharides are named by their trivial name.

## 2. Experimental and thermodynamic models

*Vapor pressure measurements.*—Vapor pressure of water over several polyols and saccharides in aqueous solution have been measured. Description of the technique used and the experimental data have been published elsewhere.[9,10]

Here the predicted vapor pressures are compared with measured values at 317.99 K, for the following three polyols; *meso*-erythritol, xylitol and sorbitol and three saccharides; fructose, raffinose[10] and cellobiose.[9]

*Solubility measurements. — Materials.* For the solubility measurements, twice-deionized water was used. (+)-D-Galactose, (+)-D-xylose and (+)-trehalose dihydrate were supplied by Fluka, with a minimum purity of 99%, and (+)-maltose monohydrate and (+)-cellobiose were supplied by Sigma, with minimum purities of 99 and 98%, respectively. The purities are given as weight percents. All the saccharides were dried under vacuum at 60 °C and used without further purification.

*Apparatus and procedure.* The solubilities of the saccharides mentioned above in water were measured using an isothermal technique, which is described in detail in previous publications.[11–15] Measurements were taken at the following temperatures: 298.15, 308.15, 318.15, 328.15, 338.15, 348.15, 358.15 K. The accuracy of the temperature measurements is estimated to be $\pm 0.1$ K.

As explained in previous publications,[11–15] each experimental point is an average of three different results obeying one of the following criteria: if the experimental solubility is less than 0.2 wt%, then the maximum deviation allowed (from the average) must be less than 3%; if the experimental solubility is between 0.2 and 10 wt%, then the standard deviation(s) of the three measurements should be less than 0.005; for solubilities higher than 10 wt%, the standard deviation should be less than 0.001.

*Thermodynamic models.*—Vapor pressures of water over a group of saccharides, and the solubilities of the sugars in aqueous solution are calculated. In all cases, the activity coefficients are calculated with the UNIQUAC method[16,17] using the theoretically obtained interaction parameters calculated with the TIEC method.

The vapor pressures ($P$) of water are calculated by the modified Raoults' law

$$P = x_1\gamma_1 P_1^{\mathrm{sat}}, \tag{1}$$

where $x_1$ is the water mole fraction, $\gamma_1$ the is activity coefficient of water and $P_1^{\mathrm{sat}}$ is the vapor pressure of pure water.

The solubility of an anhydrous saccharide in aqueous solution is calculated with the following equation,[18]

$$\ln(\gamma_2 x_2) = \frac{\Delta H_{m_2}}{R}\left(\frac{1}{T_{m_2}} - \frac{1}{T}\right) - \frac{\Delta C_{p_2}}{R}\ln\left(\frac{T_{m_2}}{T}\right) - \frac{\Delta C_{p_2} T_{m_2}}{R}\left(\frac{1}{T_{m_2}} - \frac{1}{T}\right) \tag{2}$$

where $\gamma_2$ is the activity coefficient and $x_2$ is the mole fraction of the sugar in the liquid phase, respectively. $\Delta H_{m_2}$ is the enthalpy of fusion, $T_{m_2}$ is the melting point of the solid compound, $\Delta C_{p_2}$ is the heat capacity difference between the pure liquid and the pure solid phase, $T$ is the temperature of the mixture and $R$ is the gas constant.

For several of the saccharides, the solid phase is most stable in a hydrated form. The solubility of the hydrated form of the saccharide can be calculated with the following equation, taking both the saccharide and the water activity into account.

$$\begin{aligned}&\ln(\gamma_2 x_2) + n_h \ln(\gamma_1 x_1)\\ &= \frac{\Delta H_{m_3}}{R}\left(\frac{1}{T_{m_3}} - \frac{1}{T}\right) - \frac{\Delta C_{p_3}}{R}\ln\left(\frac{T_{m_3}}{T}\right)\\ &\quad - \frac{\Delta C_{p_3} T_{m_3}}{R}\left(\frac{1}{T_{m_3}} - \frac{1}{T}\right) + \ln\left(\gamma_2(T_{m_3})\frac{1}{1+n_h}\right)\\ &\quad + n_h \ln\left(\gamma_1(T_{m_3})\frac{n_h}{1+n_h}\right)\end{aligned} \tag{3}$$

$n_h$ is the number of water molecules per saccharide molecule in the solid phase. $\Delta H_{m_3}$ is the enthalpy of fusion and $T_{m_3}$ is the melting point of the saccharide in its hydrated form and $\Delta C_{p_3}$ is the heat capacity difference. As heats of fusion and heat capacities are included in the calculation of solubilities, reliable experimental values need to be available for the compounds of interest. The two last terms of the equation take account of the saccharide and the water activity in the solid phase. Eqs. (2) and (3) are hereinafter referred to as model 1.

Catté et al.[19] proposed an alternative method for calculating the solubilities of saccharides in water, using the so-called asymmetrical convention and replacing the heat of fusion by heat of dilution. The equations proposed by Catté et al.[19] are as follows,

$$\begin{aligned}&\ln(\gamma_2 x_2) - \ln(\gamma_2^{\infty})\\ &= \frac{\Delta H_{d_2}(T_{m_2})}{R}\left(\frac{1}{T_{m_2}} - \frac{1}{T}\right) - \frac{\Delta C_{p_2}}{R}\ln\left(\frac{T_{m_2}}{T}\right)\\ &\quad - \frac{\Delta C_{p_2} T_{m_2}}{R}\left(\frac{1}{T_{m_2}} - \frac{1}{T}\right) - \ln(\gamma_2^{\infty}(T_{m_2}))\end{aligned} \tag{4}$$

where $\Delta H_{d_3}(T_{m_2})$ is the enthalpy of dilution, defined as the difference in between the enthalpy of a solution at infinite dilution and the enthalpy of the pure solid phase. $\Delta C_p$ is the corresponding heat capacity difference ($\Delta C_{p_2} = \Delta C_{p_2}^{\infty} = C_{p_2}^{\infty} - \Delta C_{p_2}^{S}$). Heats of dilution are normally given at $T^0 = 298.15$ K in the literature. $\Delta H_{d_2}$ is thus calculated with the following expression: $\Delta H_{d_3}(T_{m_2}) = \Delta H_{d_2}(T^0) + \Delta C_{p_2}(T_{m_2} - T^0)$. Catté et al. used the literature value at 298.15 K in their model, which is significantly different from the value at the melting point.

The solubility of the hydrated form of the saccharide is calculated as,

$$\begin{aligned}&\ln(\gamma_2 x_2) + n_h \ln(\gamma_1 x_1) - \ln(\gamma_2^{\infty})\\ &= \frac{\Delta H_{d_3}(T_{m_3})}{R}\left(\frac{1}{T_{m_3}} - \frac{1}{T}\right) - \frac{\Delta C_{p_3}}{R}\ln\left(\frac{T_{m_3}}{T}\right)\\ &\quad - \frac{\Delta C_{p_3} T_{m_3}}{R}\left(\frac{1}{T_{m_3}} - \frac{1}{T}\right) + \ln\left(\gamma_2(T_{m_3})\frac{1}{n_h+1}\right)\\ &\quad + n_h \ln\left(\gamma_1(T_{m_3})\frac{n_h}{n_h+1}\right) - \ln(\gamma_2^{\infty}(T_{m_3}))\end{aligned} \tag{5}$$

where the subscripts 1, 2 and 3 refer to water, anhydrous sugar and hydrated sugar, respectively. $\Delta H_{d_3}(T_{m_3})$ is the enthalpy of dilution of the hydrated saccharide ($\Delta H_{d_3}(T_{m_3}) = \Delta H_{d_3}(T^0) + \Delta C_{p_3}(T_{m_3} - T^0)$), likewise $T_{m_3}$ is the melting point and $\Delta C_{p_3}$ is the heat capacity difference. There are, however, two problems with this method. Firstly, heats of dilution are normally measured at 298.15 K, and thus heats of dilution at the melting point need to be calculated. This can introduce errors if either the heat capacity difference or the melting point is not well determined. A much more serious problem arises from the activity coefficients at infinite dilution, which are significantly more difficult to determine accurately than activity coefficients in solution. Catté's model (Eqs. (4) and (5)), is hereinafter referred to as model 2.

*Calculation of the interaction parameters.*—A method for calculating interaction energies between pairs molecules, using molecular mechanics methods has been developed. Based on these energy values, UNIQUAC interaction parameters ($A_{12}$ and $A_{21}$) are calculated by,

$$A_{ji} = \frac{\Delta U_{ji} - \Delta U_{ii}}{q_i R} \tag{6}$$

where $\Delta U_{ji}$ is the interaction energy between two molecules, $q_i$ is the UNIQUAC surface area parameter, and $R$ is the gas constant. For determining a pair of interaction parameters for a binary mixture, a reliable value of the interaction energy needs to be determined for each of the three different molecular pairs which occur in the mixture. Interaction energies ($\Delta U_{12}$, $\Delta U_{11}$ and $\Delta U_{22}$) are thus determined for one pair of unlike molecules (components $1+2$) and two different pairs of like molecules (components $1+1$ and $2+2$). This method has been available for many years,[1] but recently we have named it the TIEC method.

Two molecules can be oriented in many way relative to one another, and each molecule can occur as many conformers (equilibrium conformations). The most energetically favorable internal orientations of the molecular pairs, as well as their conformational flexibility, need to be taken into account. Two different procedures have been developed for determining the interaction energies. With the direct search procedure, a

number of molecular pairs are energy minimized using starting geometries generated through a specific pattern.[1,2] The Monte Carlo search procedure uses Monto Carlo methods for generating initial geometries, followed by energy minimizations.[3,7] See the previous publications for a detailed description of these methods.

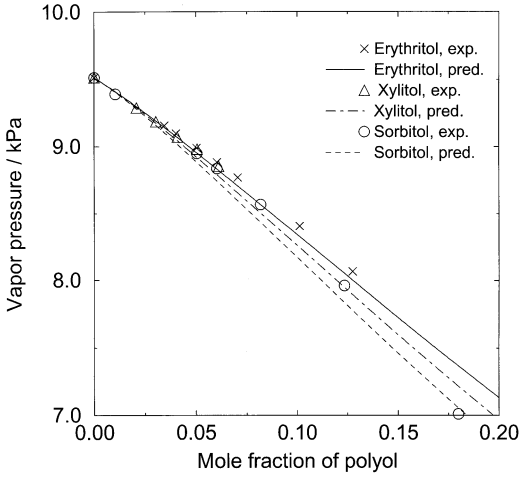


Fig. 1. Vapor pressures of water over *meso*-erythritol, xylitol and sorbitol in aqueous solution at 317.99 K.

Table 1
Rms deviations between the experimental and calculated vapor pressure data shown in Figs. 1 and 2

| System | No. of data points | rms deviations (%) |
|---|---|---|
| Water | 8 | 0.6 |
| –*meso*-erythritol | | |
| Water–xylitol | 6 | 0.6 |
| Water–sorbitol | 8 | 2.2 |
| Water–fructose | 8 | 0.5 |
| Water–cellobiose | 10 | 0.2 |
| Water–raffinose | 5 | 0.3 |

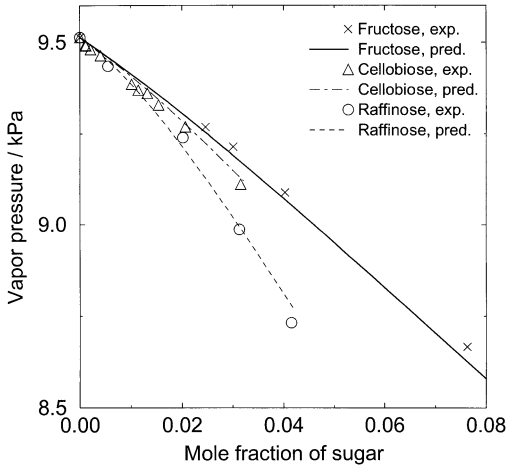


Fig. 2. Vapor pressures of water over D-fructose, cellobiose and raffinose in aqueous solution at 317.99 K.

It has shown that it is possible to determine interaction energies and interaction parameters for small subsystems and use these parameters for accurate predictions of the phase behavior of systems containing much larger molecules made of the same or similar functional groups. It has been shown that the water–1,2-ethanediol system can be used as a model system for various glycol and mono- and disaccharide molecules in aqueous solution.[2,7] Here we examine how well this approach, the so-called transference principle, applies to a number of polyols and saccharides in aqueous solution. The parameter values obtained for the water(1)–1,2-ethanediol(2) system ($A_{12} = 396$ K and $A_{21} = -334$ K)[3] are used in all the following calculations.

## 3. Results and discussion

*Vapor–liquid equilibria.*—Vapor pressures of water over aqueous solution of three polyols, *meso*-erythritol, xylitol and sorbitol have been measured and calculated at 317.99 K, using interaction parameters determined with the TIEC method. The results are shown on Fig. 1 and the rms deviations are given in Table 1. (One data point for sorbitol is missing from the figure.) Good agreement with the experimental data is obtained. For erythritol and xylitol, the rms deviation between the calculated and the experimental data points is 0.6%, but for sorbitol it is 2%. The experimental data points are given in a separate publication.[10] It is thus also possible to predict the phase behavior of these polyols using interaction parameters determined for the water–1,2-ethanediol system. It should be mentioned that VLE measurements could be taken into the metastable supersaturated region before crystallization took place.[10]

Furthermore, water vapor pressure over several saccharides in aqueous solution at 317.15 K have been calculated. This includes fructose, a monosaccharide, the disaccharide, cellobiose, and the trisaccharide, raffinose (see Fig. 2 and Table 1). (For fructose three additional data points, measured at higher concentration, are not shown on the figure.) In addition, vapor pressures of water over aqueous solutions of different glucose oligomer, glucose, maltose, maltotriose, maltotetraose and maltopentaose have been studied previously.[8,9] Maltose and cellobiose differ only in the type of glycosidic linkage, and the vapor pressure curves of these compounds are identical.

For fructose, maltose,[8] cellobiose and raffinose, the calculated vapor pressures are in excellent agreement with the experimental values at 317.99 K, with rms deviations smaller than 1%. For the higher glucose

Table 2
Experimental solubilities of sugar in water, in g anhydrous saccharide in 100 g of solution

| Temperature (K) | D-Galactose | D-Xylose | Maltose | Cellobiose | Trehalose |
|---|---|---|---|---|---|
| 298.15 | 32.561 | 58.091 | 42.669 | 14.229 | 47.658 |
| 308.15 | 37.042 | 59.746 | 49.177 | 15.716 | 54.680 |
| 318.15 | 42.371 | 64.082 | 56.554 | 18.636 | 60.651 |
| 328.15 | 48.038 | 68.649 | 62.642 | 21.626 | 66.496 |
| 338.15 | 54.181 | 73.361 | 69.433 | 25.716 | 75.053 |
| 348.15 | 61.068 | 78.023 | 75.428 | 30.340 | 80.722 |
| 358.15 | | | | | 81.605 |

Table 3
Volume (*ri* ), surface area (*qi* ) parameters and molecular weight of the saccharides in their anhydrous form

| Component | $CH_xOH$/monosaccharide units | $q_i$ | $r_i$ | $M_w$ (g/mol) |
|---|---|---|---|---|
| Water | | 0.9200 | 1.400 | 18.015 |
| *meso*-Erythritol | 4 | 4.3626 | 3.872 | 122.12 |
| Xylitol | 5 | 5.3395 | 4.684 | 152.15 |
| Sorbitol | 6 | 6.3164 | 5.496 | 182.17 |
| Xylose | Xyl | 4.8259 | 4.028 | 150.13 |
| Glucose | Glu | 5.8028 | 4.840 | 180.16 |
| Galactose | Gal | 5.8028 | 4.840 | 180.16 |
| Fructose | Fru | 5.8029 | 4.924 | 180.16 |
| Cellobiose | Glu–Glu | 10.7895 | 8.752 | 342.30 |
| Maltose | Glu–Glu | 10.7895 | 8.752 | 342.30 |
| Trehalose | Glu–Glu | 10.7895 | 8.752 | 342.30 |
| Raffinose | Gal–Glu–Fru | 15.5568 | 12.748 | 504.44 |

The structural parameters are calculated using Bondi's method.[23]

oligomers[8] the agreement is not as good, although reasonably good in the lower concentration range.

*Solid–liquid equilibria*.—The solubilities of xylose, galactose, maltose, cellobiose and trehalose in water have been measured. Xylose and galactose are monosaccharides. Maltose, cellobiose and trehalose are disaccharides made up of two glucose units, only differing in the glycosidic linkage, as discussed previously.

The experimental solubilities obtained for the different sugars in water in the temperature range from 298.15 to 258.15 K with 10 K interval are given in Table 2. It can be seen that the solubility increases monotonically with temperature.

Literature values are available for maltose throughout the temperature range,[20] and a few values are available for cellobiose.[21] As shown on the graphs, there is very good agreement between our results and the literature values.

The solubilities have been calculated using two thermodynamic approaches, the more traditional method, model 1, and the method proposed by Catté, model 2. In both cases the activity coefficients are calculated with the UNIQUAC method, using the theoretically determined interaction parameters. The UNIQUAC surface area and volume parameters, and the molecular weight of the saccharides in their anhydrous form are given in Table 3. The thermodynamic data used in the calculation are listed in Table 4. For some substances, more than one value for the melting point and/or heat of fusion was available in the literature. In these cases, the most recent measurement was chosen. It is important to mention that model 1 is expected to give more accurate results, as no activity coefficients at infinite dilution need to be calculated.

The solubilities of erythritol can be found in the literature.[20] It is seen in Fig. 3, that the solubilities predicted with model 1 are in excellent agreement with the experimental values, and calculated solubilities obtained with model 2 are somewhat underestimated.

The experimental and calculated solubilities of six saccharides in aqueous solutions at various temperature are shown on Figs. 4–9. This includes the five saccharides for which solubility data has been measured, as well as raffinose.[20] The two monosaccharides, xylose and galactose, appear in their anhydrous form within the entire temperature range. For these two sugars there is good agreement between the solubility curve calculated with model 1 and experimental solubilities,

Table 4
Experimental thermodynamic data used for calculating solubilities

| Component | $T_m$[24,25] (K) | $\Delta H_m$[22,24] (kJ/mol) | $\Delta C_p$[26,25] (J/mol/K) | $\Delta H_d(T^0)$[26,25] (kJ/mol) | $\Delta H_d(T_m)$ (kJ/mol) |
|---|---|---|---|---|---|
| *meso*-Erythritol ($C_4H_6O_4$) | 392.15[22] | 40.3 | 124 | 22.4 | 34.0 |
| D-Xylose ($C_5H_{10}O_5$) | 416.15 | 31.7 | 97 | 10.1 | 21.5 |
| D-Galactose ($C_6H_{12}O_6$) | 436.15 | 43.8 | 139 | 17.2 | 36.4 |
| Cellobiose ($C_{12}H_{22}O_{11}$) | 495.15 | 54.8 | 263 | 6.5 | 58.3 |
| Maltose monohydrate ($C_{12}H_{22}O_{11}$)·$H_2O$ | 377.15 | 45.4 | 231 | 15.6 | 33.8 |
| Trehalose dihydrate ($C_{12}H_{22}O_{11}$)·2 $H_2O$ | 368.15 | 48.1 | 241 | 19.1 | 36.0 |
| Raffinose pentahydrate ($C_{18}H_{32}O_{16}$)·5 $H_2O$ | 358.15 | 89.2 | 355 | 52.2 | 73.5 |

and in the case of galactose, the agreement is excellent. For the disaccharides maltose and trehalose, fairly good predictions are obtained with model 1, but for cellobiose, which is also a disaccharide, the agreement is poor. In a previous study the solubilities of glucose and sucrose have been determined,[7] giving excellent agreement with experimental values.

By examining the measured values for the heat of fusion, and in comparing those to the solubility data, it can be seen that there is a connection between these two properties. Heats of fusion for maltose and trehalose are very similar in magnitude, and the solubility curves are also very similar. It is observed that the heats of fusion are 8–12 kJ/mol larger in magnitude than the heats of dilution at the melting point for all the sugars except for cellobiose. Cellobiose is also the only compound for which the calculated solubility with model 1 differs largely from the experimental curve, and thus it is possible that the measured value for the heat of fusion of cellobiose[22] is incorrect. Because saccharides, containing more than one monosaccharide unit, decompose easily before melting, their heats of fusion are difficult to measure accurately. As a simple test, we adjusted the heat of fusion of cellobiose according to the observations made for the other compounds, and a better agreement between model calculations and experiment was obtained. The adjusted value is 70.0 kJ/mol, compared to 54.8 kJ/mol in Ref. 22. It must be emphasized that this parameter adjustment is a simple test and should only be considered as such.

For all the mono- and disaccharides the solubilities are significantly underestimated with model 2. The difference between the curves obtained with the two thermodynamics models, is, however, relatively similar from one compound to another, except for cellobiose.

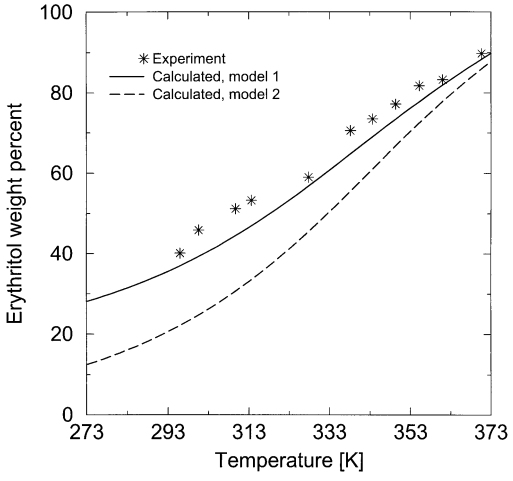


Fig. 3. Solubilities of *meso*-erythritol in water.

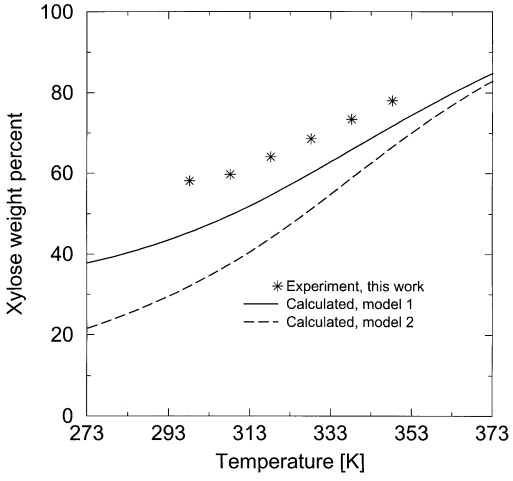


Fig. 4. Solubilities of xylose in water.

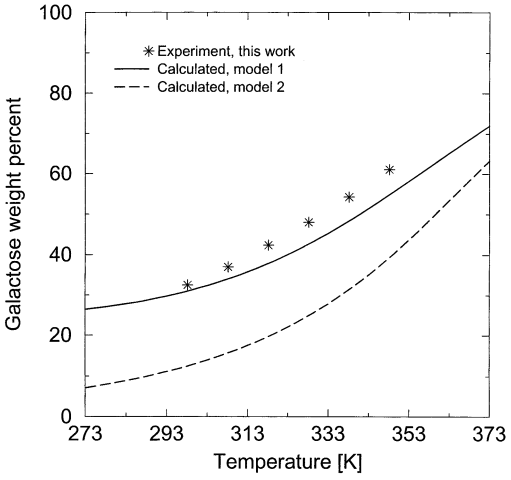


Fig. 5. Solubilities of D-galactose in water.

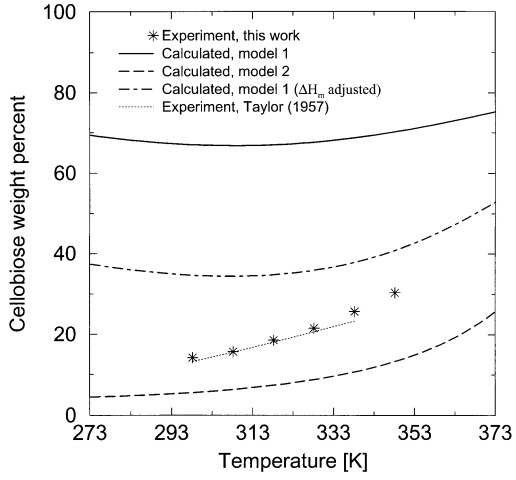


Fig. 6. Solubilities of cellobiose in water.

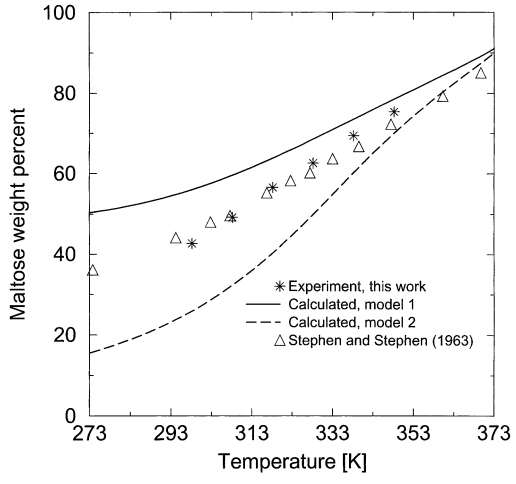


Fig. 7. Solubilities of maltose in water.

As discussed before, model 2 includes the activity coefficient at infinite dilution, which is significantly more difficult to predict than activity coefficients at finite concentrations. Unpublished results for asymmetrical activity coefficient data show that our simple approach does not adequately predict properties depending on the sugar activity coefficient at infinite dilution.

For raffinose the solubilities in water are overestimated significantly in the lower temperature range with model 1, whereas the results are reasonably good at 313.15 K and above. The curve obtained with model 2 also underestimates the solubilities of raffinose.

These results show clearly that it is possible to describe the behavior of saccharides in aqueous solution with interaction parameters determined for the water–1,2-ethanediol system. For the solubilities, the method should be considered as a way to get a reasonable estimate of the solubility at a given temperature, rather than an accurate method for prediction of solubilities.

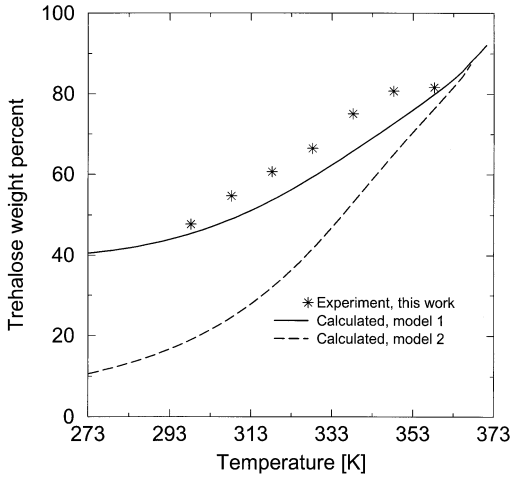


Fig. 8. Solubilities of trehalose in water.

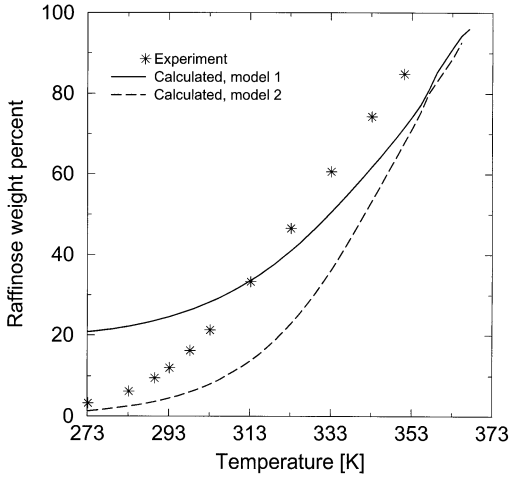


Fig. 9. Solubilities of raffinose in water.

If accurate experimental values for the heat of fusion and the melting point for a saccharide are available, predictions of the solubility at a given temperature should be possible with acceptable accuracy.

As discussed by Jónsdóttir and Rasmussen,[7] the water experiences the solution to be closer to ideal than the saccharide. This is mainly due to the size difference of the molecules. Properties like solvent activities (vapor pressures) and boiling temperatures of saccharides in aqueous solution depend primarily on how the solvent experiences the surrounding solution. A property like solubility depends, on the other hand, primarily on how the saccharide "sees" its surroundings. For small saccharides like glucose, the water activity coefficient is close to one, i.e., the solution is close to being ideal. The larger the saccharide becomes, the larger becomes the negative deviation from ideal solution behavior.[9,10]

## 4. Conclusions

In this paper both VLE and SLE of various polyols and saccharides in aqueous solution are predicted using UNIQUAC interaction parameters calculated with molecular mechanics methods. The saccharide molecules are treated as polymers containing $–CH_xOH$ and –CHO– units as building blocks. Interaction parameters determined for the water(1)–1,2-ethanediol(2) system are used, together with the volume and surface area parameters of the molecule considered.

The predicted vapor pressures are in excellent agreement with experiment for all the systems studied here. Solubilities of one polyol and six saccharides were calculated with two different approaches. The traditional approach, labeled model 1, uses the heat of fusion of the saccharide. A recently proposed method, which is derived within asymmetrical convention, uses the heat of dilution instead. This method, which is labeled model 2, also uses the calculated activity coefficients at infinite dilution, which makes the model less accurate.

For model 1 the calculated solubilities of the polyols and the monosaccharides are in good agreement with experiment, whereas for the larger saccharides an acceptable agreement with experiment is obtained. Taking account that the simulations have been carried out for a much smaller model system, the results must be considered good. The predictive ability of the method is limited by the availability of good experimental values for the heat of fusion and the melting point for the saccharide of interest.

In the case of model 2, the calculated solubilities are significantly underestimated compared to experiment. Although heats of dilution can be measured more easily than heats of fusion, the use of infinite dilution activity coefficients make model 2 less accurate. The traditional more approach, model 1, should thus be preferred.

## 5. List of symbols

| | | | |
|---|---|---|---|
| $\Delta U_{ij}$ | interaction energy | $\Delta H_m$ | heat of fusion |
| $A_{ij}$ | interaction parameter | $\Delta H_d$ | enthalpy of dilution |
| $q_i$ | surface area fraction | $Tm$ | melting temperature |
| $r_i$ | volume fraction | $T^0$ | room temperature |
| $R$ | gas constant | $\Delta C_p$ | heat capacity difference |
| $T$ | temperature | $a_1$ | solvent activity |
| $x_i$ | mole fraction | $\gamma_i$ | activity coefficient |

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