Solubility of Carbohydrates in Subcritical Water

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ABSTRACT

Carbohydrate solubility in water as a function of temperature is important in a wide range of applications in food, pharmaceutical, as well as biofuels technology. Both experimental solubility data along with thermodynamic modeling are required for optimizing the processing of materials containing, e.g., to optimize sugar oligomer-monomer production in biomass conversion processes. This study presents an extensive experimental study on the measurement of high temperature aqueous solubilities of different carbohydrates (glucose, maltose, xylose, etc.) between 20 and 200°C. Sugar solubility data in the subcritical water region above the boiling point of water is of particular interest since carbohydrate polymers in various biomass (cellulose, hemicellulose) are frequently hydrolyzed under subcritical water conditions.

Sugar solubilities were measured by a modification of the Miller-Hawthorne [1] continuous flow technique in which the sugar is saturated at various temperatures in a stream of flowing hot water. HPSEC was used to measure sugar solubility in diluted samples taken during the "saturation" region of solubility measurement technique. Due to the large increase in sugar solubility with temperature – particularly above the boiling point of water – adjustments in the size and amount of solute in the saturation cell as well as adjustment of the dilution water rate from a second pump were necessary. The obtained sugar solubility values compare favorably with existing data below the boiling of water – there is no data available for comparison at higher temperatures. Above 160°C, some degradation of the sugars occurs resulting in an apparent lowering of sugar solubility, but this can be alleviated by making the adjustments given described in the experimental section.

The measured solubility data have been correlated using A-UNIFAC model (which takes into consideration association effects between carbohydrates and water by introducing a specific term in the original UNIFAC equation based on Wertheim associating theory)[2] - and with data from the literature to predict polysaccharide solubilities as a function of temperature and molecular structure.

INTRODUCTION

The development of more evironmentally-benign methods for biomass production and other liquid renewable fuels based on a "green" pressurized fluids platform technology has been discussed by King et al.[3]. The topic has been reviewed recently by Rogalinski et al [4] where it has been noted that carbohydrate-containing natural biopolymers derived from biomass must be solubilized and hydrolyzed simultaneously to lower oligomeric sugars, and prefereably monomeric sugars, for eventual fermentation to bioethanol. Other investigators [5-7] have conducted studies to produce monomeric sugars from model carbohydrate polymers or biomass to liquid fuels, or studied sugar conversion to carbochemicals [8].

Wyman and colleagues [9-10] have emphasized the importance of sugar solubility and its role in controlling the rates and yields in the thermochemical hydrolysis of cellulosic-based polymers as well as its impact on solids loading and subsequent sugar yield due to post hydrolysis precipitation of the resulting sugar oligomers.

There is limited sugar solubility data in hot compressed water above its boiling point, but data from several studies [11-12] have been plotted in Figure 1 as a function of temperature. It is apparent from Figure 1 that sugar solubilities in water increase as a function of temperature, and at least for lactose, increase substantially with temperature above the boiling point of water. More recently Jonsdottir et al [13] have measured solubilities for several mono- and di-saccharides up to 85°C. This data is often determined in conjunction with the need for sugar solubilities required for dissolution and crystallization studies of excipients in the pharmaceutical industry [14], however sugar solubility data at much higher temperatures is required for biomass processing research.

Here the solubility of glucose, maltose monohydrate and xylose in subcritical water is presented between 20 and 200°C using a modification of the Miller and Hawthorne [1] continuous flow technique. Some of the measured solubility data have been correlated using the A-UNIFAC model [15], which takes into consideration the association effects between carbohydrates and water by introducing a specific term in the original UNIFAC equation [16] based on Wertheim associating theory.
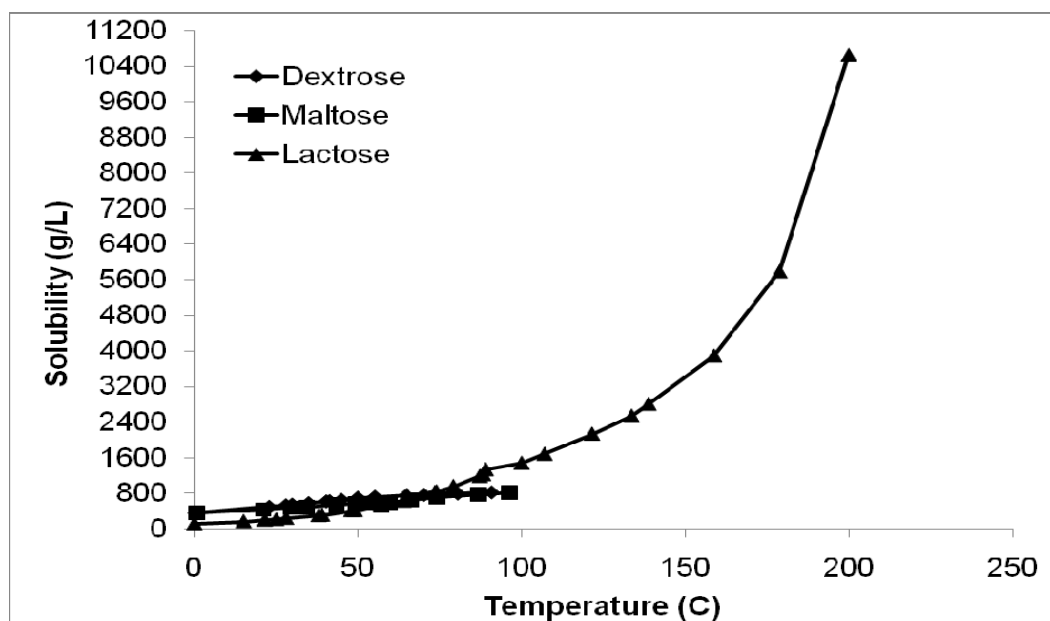

Figure 1. Solubility (g/L)of common sugars as a function of temperature [9-10].

MATERIALS AND METHODS

Samples and reagents
Sugar standards used for solubility measurements in subcritical water, D-(+)-xylose and D-(+)-maltose monohydrate, were obtained from Sigma (St. Louis, MO, USA). Glucose was purchased from Fisher Biotech (Wembley, Australia). Sea sand (washed) was acquired from EMD (Gibbstown, NJ, USA). 18.2 MΩcm Ultrapure water quality with 1–5 ppb TOC and < 0.001 EU/mL pyrogen levels (Milli-Q) was produced in-house using a laboratory water

purification Milli-Q Synthesis A10 system (Millipore, Bellerica, MA, USA) was used throughout this study. This water was then placed in the water storage tank shown in Figure 2 where it was blanketed with nitrogen to avoid absorption of air.

Solubility measurements in subcritical water
Solubility measurements in water of glucose (DP1), maltose monohydrate (DP2) and xylose (DP1) were carried out between 20 and 200°C at approximately 20°C intervals. The experimental procedure is based in a modification of the Miller-Hawthorne [1] continuous flow technique (Figure 2). The sugar solute was mechanically-mixed with the sea sand in a 1:2 proportion of sugar:sand and then packed into one of the saturation cells (12, 20 or 50 mL in volume), which was then connected to the flow system as shown in Figure 2. The experimental procedure involved sampling every 5 minutes with water delivered at a flow rate of 0.1 mL/min by an Isco 100D pump through a saturation cell. Due to the large increase in sugar solubility with temperature – particularly above the boiling point of water – adjustments in the size and amount of solute in the saturation cell as well as adjustment of the dilution water rate (pump tubing to the mixing tee in Figure 2) were necessary. The saturated solution exiting from the cell contacted excess solvent (water) flowing at a rate of 0.4 mL/min in a mixing tee inside the oven (HP Series II 5890 Gas Chromatograph, Hewlett-Packard, Palo Alto, CA, USA) to prevent precipitation of sugars when the solution exited the oven through a cooling coil into a sampling vial. The first sample is taken after 15 minutes of equilibration with the next sampling taken every 5 minutes over a 25 minute period. Every experimental measurement at a specific temperature were run in triplicate. For measurements at 140°C, some degradation of the sugars occurred. To overcome this problem the flow rate was increased five-fold and experimental time reduced five-fold.

High performance size exclusion chromatography (HPSEC) using a Waters 2414 refractive index detector (Milford, MA, USA) coupled with two Shodex OH Pac SB-802 and SB-804 HQ columns (Shodex, Kawasaki, Japan) was used to measure sugar solubility in diluted samples taken during the "saturation plateau" region of solubility measurement technique. The mobile phase employed in HPSEC analysis was 0.003 mol/L NaN_3 and 0.1 mol/L $NaNO_3$). All samples were filtered before injection into the HPSEC system.
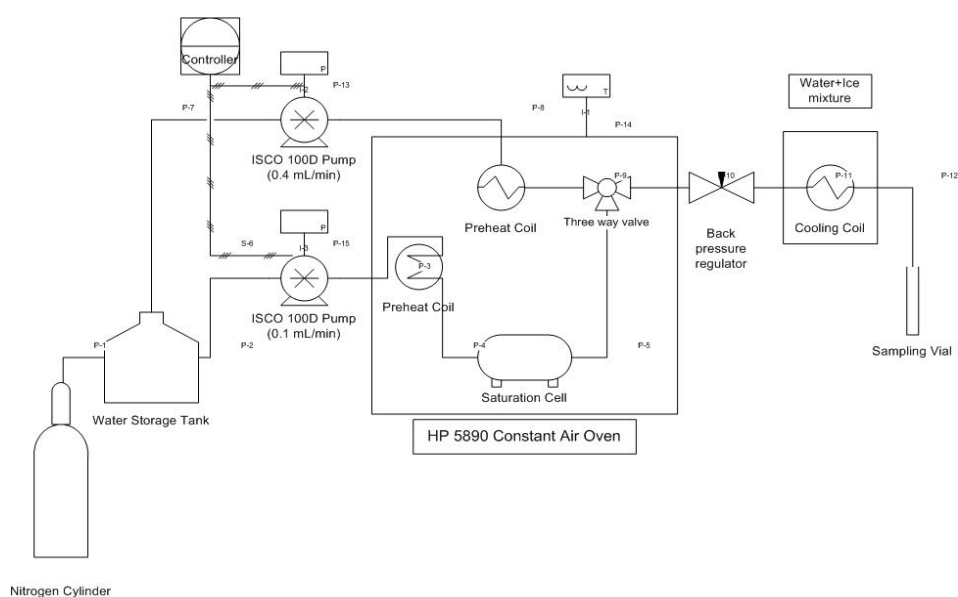

Figure 2. Solubility measurement apparatus

RESULTS AND DISCUSSION

Experimental data obtained for three different sugars: glucose, xylose, and maltose, using the above described approach are shown in Figure 3. For all three sugars, there is a monotonic but significant increase in sugar solubility with temperature up to the boiling point of the solvent. At approximately the boiling point of water, there is close to a ten-fold increase in the solubility of all three sugars in the range of 100 – 200°C relative to their recorded solubilities at 100°C. A comparison of the experimental solubility data with literature values (Table 1) taken from the extensive Yakowsky and He [14] compendium show an increase in solubility with increasing temperature; although the reported literature values for glucose are slightly higher than our experimental data, and slightly less for maltose and for the single literature data point for xylose used for comparison. These solubility trends a function of temperature are similar to those found for other recorded sugar solubilities in the literature (Figure 1), although there are differences in comparing one set of sugar solubility data with another. This in part justifies the experimental work reported in this study. For the select solubility data given in Table 1 and Figure 3, the standard deviation was approximately 2% of the mean value for triplicate determinations.
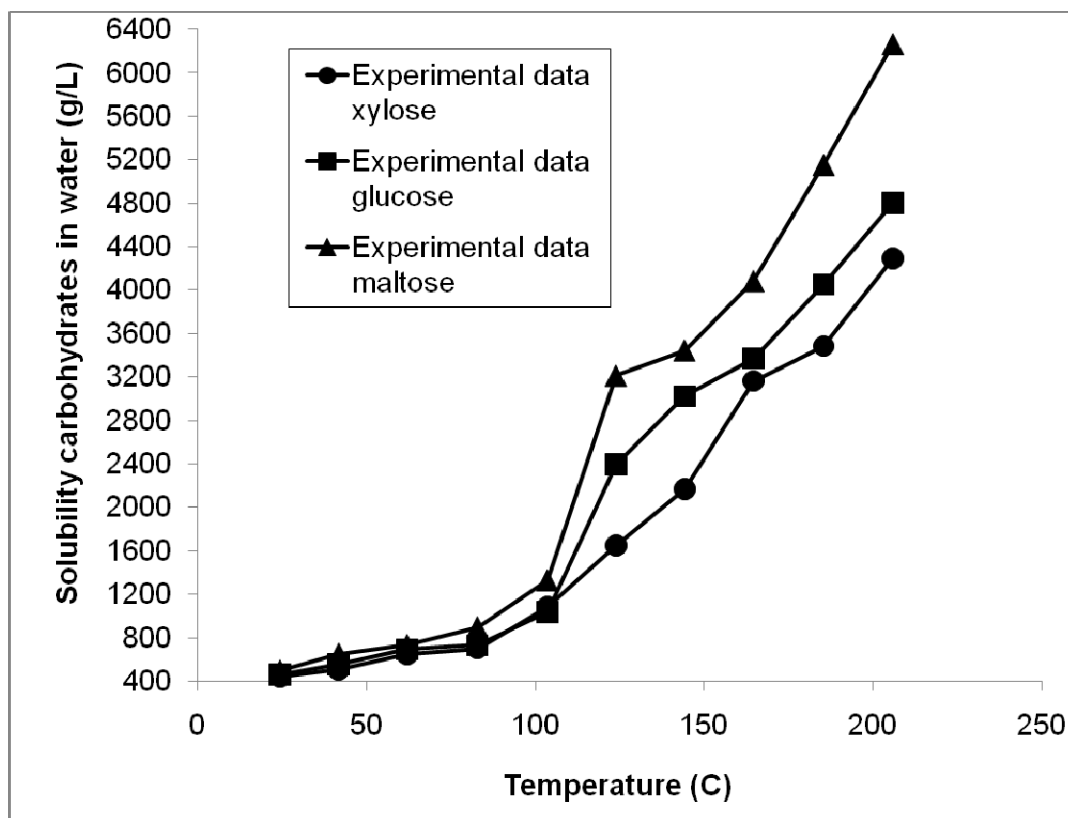

Figure 3 Saccharide solubility in g/L vs. temperature.

Select solubility data for the three different carbohydrates are summarised in Table 1. Typical sugar solubilities between 20 – 140°C range from approximately 470 – 3000 g/L for glucose and from 500 – 3500 g/L for maltose monohydrate. These sugar solubility values compare favorably with existing data below the boiling of water – there is no data available for comparison at higher temperatures. For xylose, the solubility data range between 445 – 2170

g/L, and comparison with the one data point from the literature with our experimentally-determined value are very close.

Table 1. Carbohydrates' solubilities in water

Temperature (°C)	Glucose (g/L)		Maltose·H₂O (g/L)		Xylose (g/L)	
	Literature	this work	Literature	this work	Literature	this work
20	479.2[14]	465.5	438.2[14]	499.5	432.2[14]	446.1
40	615.4[14]	564	523.8[14]	654.7		513.6
60	736.8[14]	697.8	636.4[14]	735.5		654.2
80	814.8[14]	734.9	750.2[14]	899.8		705.6
100		1044		1330.5		1086.9
120		2404		3215.0		1653.9
140ᵃ		3028		3447.8		2171.4

ᵃ Flow-rate 5 times than in previous experiments

Initially when making solubility measurements above 140°C, it became apparent that some degradation of the sugars was occuring which was reflected in the anaomolously low solubility values for the sugars. Examination of the contents of the saturation cell revealed a char on the sand support and collected extracts were dark in color. Carbohydrate stability studies have shown that significant degradation occurs when aqueous solutions are heated for a prolonged time over 100°C [17]. There can also be an increase in the amount of degradation products for concentrated sugar solution due to pH changes which will increase the degradation rate of sugars [18]. Moreover, the disaccharide structure of the carbohydrate studied (maltose monohydrate) is more unstable than xylose and glucose due to the tendency to hydrolyze to the monosaccharide. As noted in the experimental section, this problem was overcome by adjusting the flow rate of pure water through the cell which was increased five-fold. The flow rate through saturation cell was adjusted to 0.5 mL/min and flow rate at mixing tee to 2 mL/min, thereby maintaining a dilution factor of four-fold. Consequently the experimental time was reduced to 3 minutes of equilibration with sampling inacted every minute for 5 minutes. This technique minimized sugar degradation as judged by the disappearance in HPSEC analysis of additional peaks, since only the peak of the carbohydrate solute was observed in the HPSEC profile.

The above measured solubility data were correlated using A-UNIFAC model. Sugar solubility in water can be estimated considering the sugar equi-fugacity condition between the solid (pure sugar) and liquid (water + sugar) phases. At temperatures below the sugar melting point, the carbohydrate mole fraction x_s in the aqueous phase can be calculated using the following expression:

$$\ln(x_s / \gamma_s) = -\frac{\Delta H_m}{R T_m}\left(\frac{T_m}{T} - 1\right) + \frac{\Delta C_p}{R}\left(\frac{T_m}{T} - 1\right) + \frac{\Delta C_p}{R}\ln\left(\frac{T}{T_m}\right) \qquad (1)$$

where T_m and ΔH_m are, respectively, the carbohydrate normal melting temperature and enthalpy and γ_s is its activity coefficient in the aqueous phase. In addition, no temperature dependence for ΔC_p (the difference between the heat capacity of the pure liquid and solid carbohydrate) was assumed. In order to convert the sugar mole fractions (x_s) to concentration (g/L), solution densities were necessary. Solution densities (ρ) at each experimental temperature was estimated using the following equation :

$$\rho = \rho_{water} * \text{water volume fraction} + \rho_{sugar} * \text{sugar volume fraction} \qquad (2)$$

A linear variation of ρ_{sugar} with temperature was assumed using values at 25°C and 100°C.

The activity coefficient of the solute, γ_s, was predicted using the A-UNIFAC model [15] as described in the literature [2, 19]. The carbohydrate pure component physical properties are given in Table 2 below.
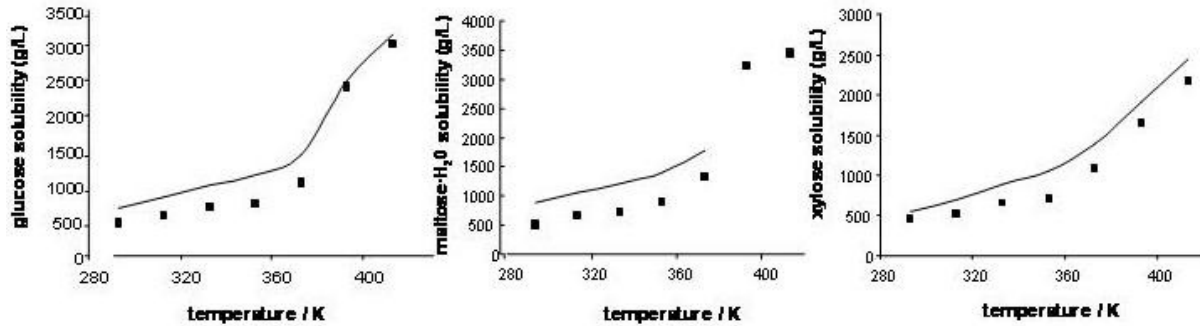

Figure 4. Carbohydrates solubilities. (——) A-UNIFAC model predictions; (—■—) experimental data.

Figures 4 shows a comparison between the solubilities measured in this study and those predicted using Eq. (1) and the A-UNIFAC model. As can be deduced from Figure 4, this thermodynamic modeling approach provides a reasonable prediction of sugar solubility in subcritical water at temperatures below the carbohydrate melting point – the predicted values being higher than the experimentally-recorded sugar solubilities .

Table 2. Carbohydrate physical properties

Carbohydrate	T_m (°C)	ΔH_m (J/mol)	ΔC_p (J/mol K)
Glucose	150.15	32248	120
Xylose	150.15	31650	120
Maltose·H₂O	106.15	45400	231

CONCLUSIONS

Accurate measurement of carbohydrate solubilities over a wide range of temperatures (20 to 200°C) were carried out using the above described system in our laboratory. The obtained solubility data as a function of temperature follows trend previously reported in the literature [11-14]. These measurements correlate reasonably well with the solubility trend predicted using the A-UNIFAC model.

ACKNOWLEDGMENTS

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