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# Measurement and Correlation of the Solubility of Carbohydrates in Subcritical Water

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The measurement and correlation of the high-temperature aqueous solubilities of three different carbohydrates (glucose, maltose, xylose, etc.) between 293 and 453 K are reported in this study. Sugar solubilities were measured by a continuous-flow technique in which the sugar is saturated at various temperatures in a stream of flowing hot water. Sugar solubilities were measured on the diluted samples taken in the “saturation plateau” region of the solubility measurement technique. Because of a large increase in the 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 an adjustment of the dilution water rate were necessary. The determined sugar solubility values compare favorably with existing data below the boiling point of water and provide nonexistent data over the above temperature range above the boiling point of water. The resultant sugar solubility trends were modeled empirically or by use of a modified Apelblat equation or the A-UNIFAC model.

## Introduction

Carbohydrate physicochemical data, particularly their properties in solution such as solubility, play a major role in the design and optimization of chemical engineering processes. The need for such data in the food industry, where they are used as sweeteners, in the pharmaceutical field, and, more recently, in relation to biomass conversion processes<sup>1,2</sup> supports the need for an extended carbohydrate solubility database. For example, in the latter field, Wyman and colleagues<sup>3,4</sup> 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 the sugar solubility impact on solids loading and the subsequent sugar yield in connection with post-hydrolysis precipitation of the carbohydrate oligomers.

A comprehensive search of sugar solubility data as a function of the temperature in the literature reveals a paucity of values at higher temperatures and very limited data above the boiling point of water, i.e., in the subcritical region where it is constrained by pressure.<sup>5</sup> This lack of sugar solubility values probably occurs for two reasons: (1) the experimental difficulties in making measurements at higher temperatures; (2) the susceptibility of carbohydrates to thermal degradation at these high temperatures. Much of the existing sugar solubility data is taken at temperatures below 373 K<sup>6–11</sup> or in binary solvent systems such as ethanol–water mixtures.<sup>12–14</sup> Although a few exceptions do exist in the literature, as taken from the Yalkowsky and He compendium<sup>15</sup> and other sources,<sup>16</sup> data on the temperature dependence of the sugar solubility in water up to and beyond its boiling point are lacking, which compromises attempts to theoretically predict or model its solubility as a function of the temperature.

An additional factor to consider when attempting to measure carbohydrate solubilities at higher temperatures is the expo-

ponential increase of the sugar solubility, particularly beyond the boiling point of water. These trends are verified in Figure 1 for select sugars as a function of the increasing temperature, where a secondary axis was required to quantify the increasing solubility for the sugars glucose, maltose, and lactose, up to temperatures of 473 K.<sup>8,17,18</sup> Such sugar solubility data in hot compressed water above its boiling point are limited, although recently Jonsdotir et al.<sup>19</sup> have measured the aqueous solubilities for several mono- and disaccharides up to 358 K.

To alleviate the above situation, we have developed a new approach to measuring the solubilities of carbohydrates as a function of the temperature and above the boiling point of water using a modification of the dynamic-flow method reported by Miller and Hawthorne.<sup>20</sup> Variations of this method have been reported by others who embrace the range of solute solubilities on a mole fraction scale from 10<sup>−6</sup> to 10<sup>4</sup>, which includes solutes exhibiting very low solubilities in water (i.e., hydrocarbons<sup>21,22</sup>) to inorganic salts<sup>23</sup> over a wide temperature range from ambient to 683 K. Recently, we have reported the solubilities of thermally sensitive flavonoid solutes in subcritical water to temperatures of 413 K<sup>24</sup> using a similar methodology.

The measured carbohydrate solubility data have been correlated empirically as well as modeled using a modified Apelblat equation<sup>25</sup> or a A-UNIFAC (modified UNIQUAC functional-group activity coefficient) model (which takes into consideration association effects between carbohydrates and water by introducing a specific term in the original UNIFAC equation based on the Wertheim associating theory).<sup>26</sup> These predictive approaches are compared to the current solubility values, as well as data from the literature to predict saccharide solubilities as a function of the temperature and molecular structure.

## Experimental Section

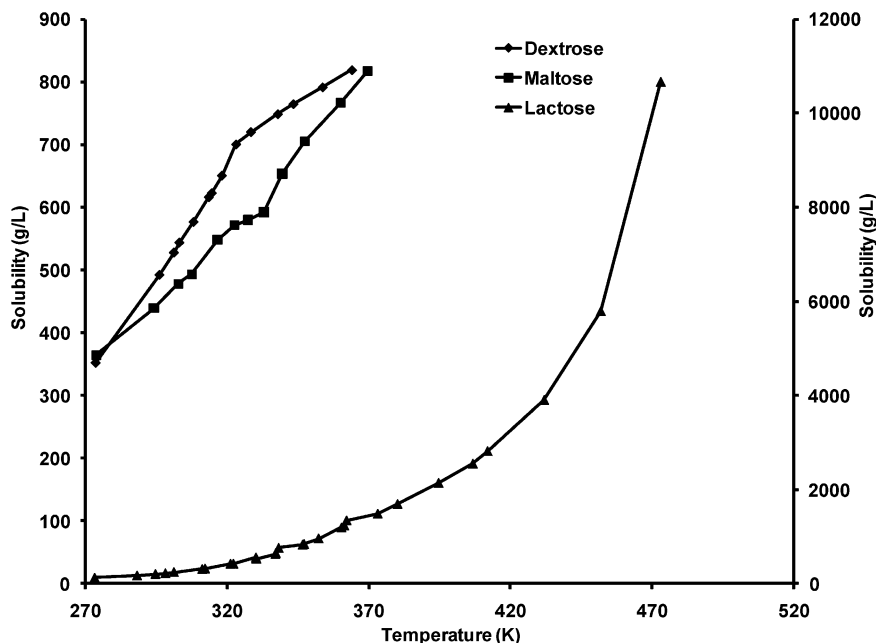
**Materials.** The sugar standards used for solubility measurements in subcritical water, D-(+)-xylose, and D-(+)-maltose monohydrate were obtained from Sigma (St. Louis, MO). Glucose was obtained from Fisher Biotech (Wembley, Australia). The sea sand dispersant was acquired from EMD (Gibb-

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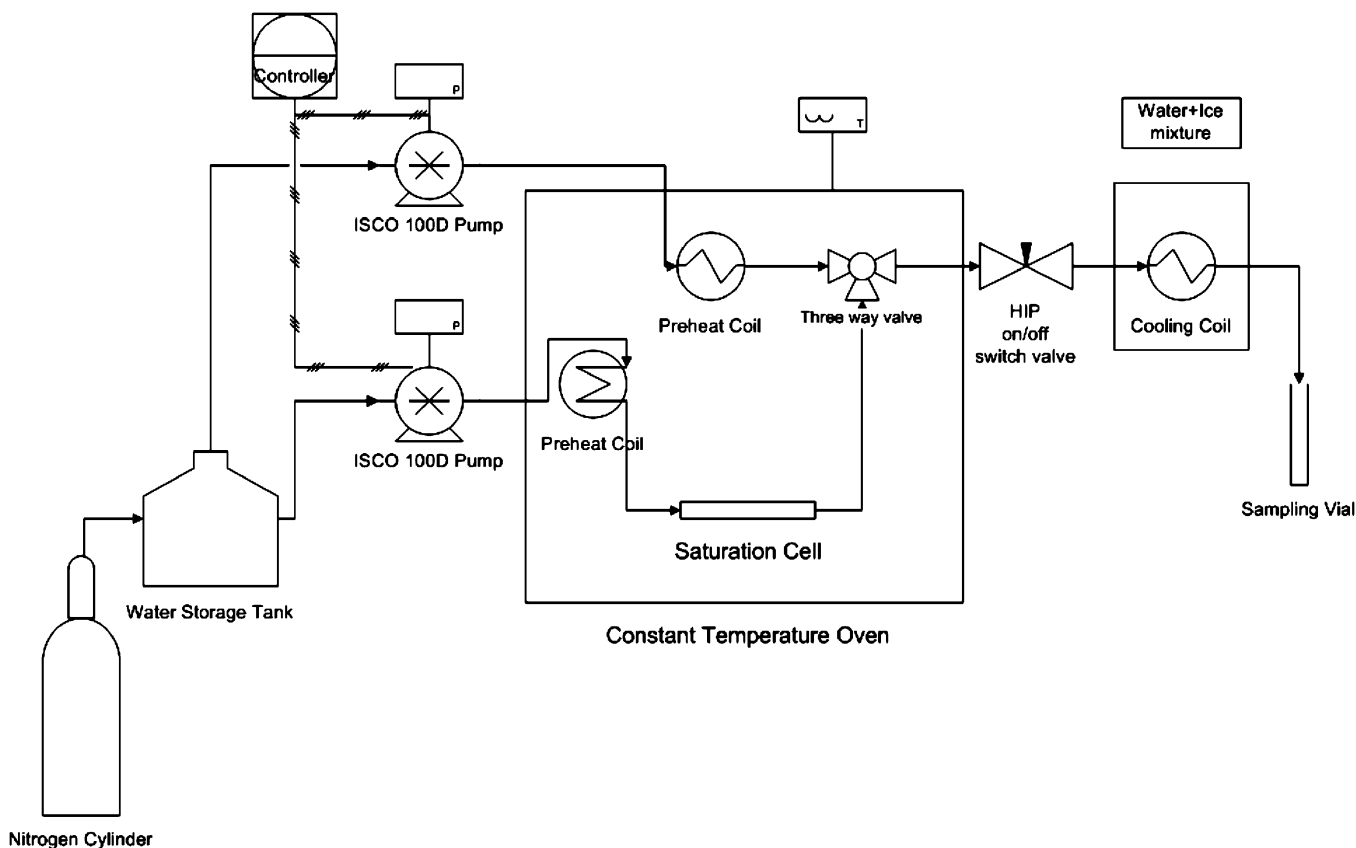
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**Figure 1.** Solubility of glucose, maltose, and lactose as a function of the temperature in water: dextrose and maltose (left ordinate); lactose (right ordinate). Sugar solubilities are in grams per liter.<sup>16–18</sup>



**Figure 2.** Schematic of the dynamic-flow apparatus for measuring solute solubilities in subcritical water.

stown, NJ). For the experiments described, 18.2 MΩ·cm ultrapure water of quality registering 1–5 ppb TOC and <0.001 EU/mL pyrogen levels was produced in-house using a laboratory water purification Milli-Q Synthesis A10 unit (Millipore, Bellerica, MA). This water was then placed in the water storage tank (Figure 2), where it was blanketed with nitrogen to avoid absorption of air.

**Solubility Measurements.** Our method relies on the establishment of a transient solubility plateau as a function of time

(or water passage), in which the sugar is saturated at various temperatures in a stream of flowing hot water. The length of time for this saturation plateau can be optimized by carefully controlling such factors as the size of the saturator cell, the amount of sugar in the cell, the flow rate of water through the cell, and the time of the experiment. High-performance size-exclusion chromatography (HPSEC) with a refractive index detector was used to measure the sugar solubility in diluted samples taken during the “saturation” region of the sugar

solubility measurement technique. These samples have been precisely diluted with an auxiliary stream of water from another syringe pump to avoid precipitation of the sugar in the flowing hot water stream as it reaches ambient temperatures. A throttling valve was placed in-line at the exit of the diluted saturated sugar solubility stream to maintain at least adequate pressure to keep the hot water in its subcritical state. This, along with the described dilution of saturated sugar samples, proved adequate to prevent sugar precipitation in the lines after the equilibrium cell as well as formation of a second water phase.

The experimental apparatus for measuring the aqueous solubility of the sugars is shown in Figure 2. The solubility saturation cells described below were placed in a Hewlett-Packard model 5890 oven to provide precise temperature control. Three solubility cells were used throughout the course of this study depending on the expected solubility of the candidate sugar, which is also temperature-dependent. The cells in order of their use were 10 mL (3.4 cm length  $\times$  2.0 cm i.d.), 22 mL (15.2 cm length  $\times$  2.0 cm i.d.), and 50 mL (33.0 cm. length  $\times$  1.4 cm i.d.), with the latter cell being from Applied Separations, Inc. (Allentown, PA). The oven temperatures were accurately measured using a J-type thermocouple coupled to an Omega DP703 thermocouple microcomputer (Stanford, CT). The sugar solute and sand were manually mixed in a 1:2 ratio (by weight) and then added to the saturation cell. An ISCO model 100D syringe pump (Lincoln, NE) was used to pump water from an Alloy Products pressurized reservoir held under nitrogen pressure, at a constant flow rate between 0.1 and 0.5 mL/min through a 1.5 m  $\times$  0.159 cm o.d. preheating coil (contained in the oven) to the saturation cell placed in the oven. Because of a large increase in the 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 an adjustment of the dilution water rate (pump tubing to the mixing tee in Figure 2) were necessary. A mixing tee [High Pressure Equipment Inc. (HIP), Erie, PA, P/N no. HIP15-23AF1] was installed in the oven between the outlet of the saturation cell and the external cooling coil to allow introduction of an excess dilution solvent. For this purpose, an ISCO model 100D syringe pump operating in the constant flow mode was used to supply an excess of water at a flow rate varying between 0.4 and 2.0 mL/min into one port of the mixing tee.

An ISCO SFX 200 controller (Lincoln, NE) was used to control the flow rate of both of the solvent pumps. The system pressure was recorded on the ISCO SFX 200 controller. An on/off switching valve (HIP, Erie, PA, P/N no. HIP19-11AF1) was placed at the outlet from the oven and used as a back-pressure regulator to throttle the water flow rate and prevent conversion to its vapor state. The sugar-saturated solution exiting from the saturation cell contacted the excess dilution solvent (water) at the mixing tee inside the oven to prevent precipitation of the sugars when the solution exits the oven into a ice bath cooling reservoir and then into a sampling vial. The flow rate of the excess solvent was adjusted in order to maintain a dilution factor of 4 throughout the solubility experiments. After a 10–20 min equilibration period at the desired temperature (higher temperatures required shorter equilibration time, a higher pump flow rate, and, hence, lower sampling time intervals), 5–10 fractions were collected every 2–5 min. The fractions were diluted appropriately, and 0.2 mL of the diluted solution was mixed with 3.8 mL of the HPSEC mobile phase and analyzed using HPSEC. The aqueous solubility of the sugars was calculated using eq 1 in terms of the mole fraction.

$$x_s(\text{mole fraction}) = \frac{1}{1 + \left[ \frac{M_s}{M_w} \left( \frac{1}{S(\text{g/L})} - 1 \right) \right]} \quad (1)$$

where  $M_s$  and  $M_w$  are the molecular weights of the sugars and water, respectively, and  $S$  is the aqueous solubility of the sugar in grams per liter of solvent determined from a calibration curve.

Solubility measurements in water for glucose, xylose, and maltose were carried out between 293 and 453 K at approximately 20 K intervals. For every solubility determination at a particular temperature, triplicate measurements were made. Degradation of the sugar solutes was checked by observing the color of the concentrated sugar solutions collected in the sample vials because they were collected after the exiting the solubility cell. HPSEC as described below was also used to check for the appearance of additional peaks indicative of sugar decomposition.

**HPLC Analysis.** A HPSEC system consisting of a Waters model 515 pump and a Waters model 2414 refractive index detector (Waters Corp., Milford, MA), along with a Waters model 717 autosampler, was used for analysis of the diluted sugar samples. Two Shodex columns, OHPak SB-802 and SB-804 HQ (Shodex, Kawasaki, Japan), were used in this method, and they were held at a constant temperature of 328 K during analysis. The refractive index detector was maintained at a temperature of 313 K. The HPSEC mobile phase was 0.003 M  $\text{NaN}_3$  and 0.1 M  $\text{NaNO}_3$ . The injection volume was 100  $\mu\text{L}$ , and all samples were filtered through a nylon 5  $\mu\text{m}$  membrane before injection. Chromatographic data were processed using Waters Empower software.

## Results and Discussion

**Sugar Solubility Variation with Temperature.** The sugar solubility data in grams per liter for the three different sugars in this study are shown in Table 1. This includes the data for dextrose and maltose shown in Figure 1. For all three sugars, there is a monotonic but significant increase in the sugar solubility with temperature up to close to the boiling point of the solvent. At approximately the boiling point of water, there is close to a 5-fold increase in the solubility of all three sugars over the range of 373–453 K relative to their recorded solubilities at 373 K, exponentially reaching values close to 5000 g/L. A comparison of these experimental solubility data with values from the literature values (Table 1) agrees best with the data from the Yakowsky and He compendium,<sup>15</sup> showing an increase in the solubility with increasing temperature; although the reported literature values for glucose are slightly higher than our experimental data, they are slightly less for maltose and for the single literature data point for xylose for comparison. These sugar solubility trends with the temperature are similar to those found for the sugar solubilities plotted in Figure 1 taken from the literature, although there are differences in the comparison of one set of sugar solubility data with other data. This is apparent when one looks at the dispersion of values listed in Table 1 for the three sugars, which, in part, justifies the experimental work reported in this study. This variance in the sugar solubility values is, in part, due to myriad of experimental approaches utilized in trying to measure the sugar solubilities as a function of the temperature and is no more apparent than in the dispersion of literature values given at 298 K.

All of the aqueous sugar solubility measurements as a function of the temperature, as noted previously, were performed in triplicate. The standard deviations in the aqueous solubility of

**Table 1. Comparison of Literature and Experimental Values for Sugar Solubilities as a Function of the Water Temperature**

temperature (K)	xylose (g/L)		glucose (g/L)		maltose monohydrate (g/L)	
	literature	this work	literature	this work	literature	this work
298	432, <sup>15</sup> 1220, <sup>12</sup> 670 <sup>19</sup>	463	479, <sup>15</sup> 1033, <sup>8</sup> 607, <sup>10</sup> 818 <sup>33</sup>	466	438, <sup>15</sup> 601, <sup>11</sup> 1080, <sup>33</sup> 493 <sup>19</sup>	507
315	733 <sup>19</sup>	649	615, <sup>15</sup> 1630, <sup>8</sup> 673 <sup>10</sup>	564	524, <sup>15</sup> 630 <sup>19</sup>	655
335	913 <sup>19</sup>	853	737, <sup>15</sup> 2880 <sup>8</sup>	698	636, <sup>15</sup> 854 <sup>19</sup>	736
356		1140	815, <sup>15</sup> 4280 <sup>8</sup>	735	750 <sup>15</sup>	900
377		1640		1160		1560
396		2080		2160		2740
417		2630		2940		3250
438		3610		3410		3820
456		4240		na		5010

the sugars and the thermodynamic properties of dissolution were calculated using eq 2,

$$\text{RSD} = \sqrt{\frac{\sum_{i=1}^n (X_{g,i} - \bar{X}_g)^2}{n-1}} \quad (2)$$

where  $X_{g,i}$  = solubility or other thermodynamic property (such as enthalpy, entropy, or Gibbs free energy) for the  $i$ th sample at a particular temperature for a selected solute,  $\bar{X}_g$  = average solubility or other thermodynamic property for a selected solute at a particular temperature, and  $n$  = number of replicates.

Carbohydrate solubilities from this study are tabulated in Table 1 in grams per liter for comparison purposes. For the sugar solubility values given in Table 1, the standard deviation ranged from approximately 0.5% to as high as 43% in one case (xylose between 356 and 377 K). The average relative standard determination for all of the data was 11.5%, with the larger deviations occurring in the xylose data, which largely reflect data taken by two different individuals. For the solubility data taken in the saturation plateau region, triplicate analysis of the sugar solubility typically yielded a 2% relative standard deviation.

Initially, when solubility measurements were made above 413 K, it became apparent that some degradation of the sugars was occurring, which was reflected in the unexpectedly low solubility values for the sugars. Examination of the contents of the saturation cell revealed a char formation on the sand support, resulting in a dark color of the collected extracts. Carbohydrate stability studies have shown that significant degradation occurs when aqueous solutions are heated for a prolonged time over 373 K.<sup>27</sup> There can also be an increase in the amount of degradation products for concentrated sugar solutions because of pH changes, which will increase the degradation rate of sugars.<sup>28</sup> Moreover, the disaccharide structure of the carbohydrate studied (maltose monohydrate) is more unstable than those of xylose and glucose because of its tendency to hydrolyze to a monosaccharide compound. As noted in the Experimental Section, this problem was overcome by adjusting the flow rate of pure water through the cell, which was increased 5-fold. The flow rate through the saturation cell was adjusted to 0.5 mL/min and the flow rate at the mixing tee to 2 mL/min, thereby maintaining a dilution factor of 4-fold. Consequently, the experimental time was reduced to 3 min of equilibration, with samples taken every 1 min for 5 min. Using these conditions, the sugar degradation was minimized, as judged by the disappearance of additional peaks in the HPSEC profile because only the peak of the carbohydrate solute was observed in the HPSEC profile when using refractive index detection. Adjustment of the ratio of the water flow rate to the saturation cell to the flow rate from the dilution pump is critical in optimizing the reported method and will depend on the thermal stability

of the solute under examination at the chosen temperature for the solute solubility measurement.

**Correlation and Modeling of Solubility Data.** Because of the exponential-like dependence of the sugar solubility (in g/L) with temperature, the recorded sugar solubilities in water were converted to mole fractions and plotted as the logarithm of the mole fraction sugar solubility versus the reciprocal of the absolute temperature, as shown in Figure 3. This resulted in a relatively linear relationship that could be used for approximating the aqueous solubility of these sugars as a function of the temperature. Note also in Figure 3 that the sugar solubility decreases with the molecular weight of the solute.

In order to properly correlate the solubility trends of sugars in water with temperature, a literature search was conducted to examine previous attempts for correlating highly polar solute solubilities in aqueous solution. It was found that the cubic equations for correlating more nonpolar solute solubilities in water as a function of the temperature<sup>21,22</sup> were inadequate, particularly beyond the boiling point of water, and resulted in an unacceptable agreement with our experimental values as well as literature data. Additional solubility studies in our laboratory have shown reasonable agreement between experimentally determined solubilities for flavonoid compounds in hot water up to 413 K and a modified Apelblat equation used for similar studies in the literature.<sup>24</sup> Phase equilibria in sugar solutions have been correlated by the A-UNIFAC model, as reported in the literature by Ferreira et al.,<sup>26</sup> and for that reason, we decided to use these models to correlate our experimental data.

The temperature dependence of the aqueous solubilities of the three sugars were correlated with a modified Apelblat-type equation,<sup>29,30</sup> as given in eq 3,

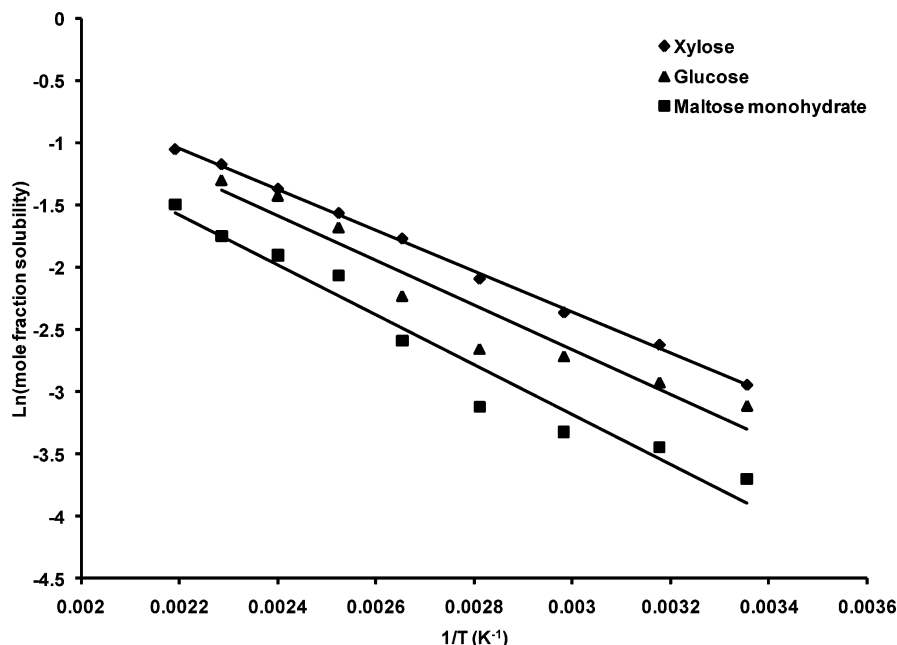
$$\ln(x_s) = A + \frac{B}{T} + C \ln(T) \quad (3)$$

where  $x_s$  is the mole fraction solubility of the carbohydrate in water at temperature  $T$  (K) and  $A$ ,  $B$ , and  $C$  are empirically derived constants. These empirically derived constants for determining the aqueous solubility of the three sugars as a function of the temperature are provided to five significant figures (for a better estimation accuracy) in Table 2. The last column in Table 2 tabulates the absolute average deviation (AAD) between the experimental sugar solubilities and those calculated using the modified Apelblat equation, and this was calculated using eq 4,

$$\text{AAD} = \frac{1}{N} \sum_{i=1}^N \left( \frac{x_i^{\text{calcd}} - x_i^{\text{exptl}}}{x_i^{\text{exptl}}} \right)^2 \quad (4)$$

where  $x_i^{\text{exptl}}$  and  $x_i^{\text{calcd}}$  are the individual temperature-dependent sugar solubility values determined experimentally and those





**Figure 3.** Variation of the natural logarithm of solubility (mole fraction) of sugars as a function of the reciprocal of temperature (K).

**Table 2.** Fitting Parameters for the Modified Apelblat Equation

solute	A	B	C	AAD <sup>a</sup>
xylose	-110.28	3958.06	16.57	0.230
glucose	1.565	-543.75	-10.17	0.069
maltose monohydrate	15.45	4404.38	-106.24	0.054

<sup>a</sup> AAD is the absolute average deviation between the experimental and theoretical sugar solubility values calculated using eq 4.

calculated using the modified Apelblat equation, respectively, and  $N$  is the number of determinations.

As noted above, the above-measured solubility data were also correlated using the A-UNIFAC model. The sugar solubility in water in this case can be estimated considering the sugar equifugacity 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 (eq 5):

$$\ln(x_s/\gamma_s) = -\frac{\Delta H_m}{RT_m} \left( \frac{T_m}{T} - 1 \right) + \frac{\Delta C_p}{R} \left( \frac{T_m}{T} - 1 \right) + \frac{\Delta C_p}{R} \ln \left( \frac{T}{T_m} \right) \quad (5)$$

where  $T_m$  and  $\Delta H_m$  are respectively the carbohydrate normal melting temperature and the enthalpy of the solute and  $\gamma_s$  is its activity coefficient in the aqueous phase. No temperature dependence for  $\Delta C_p$  (the difference between the heat capacities of the pure liquid and solid carbohydrate) was assumed. In order to convert the sugar mole fractions ( $x_s$ ) to concentration (g/L), the densities of solution are necessary. Solution densities ( $\rho$ ) at each experimental temperature were estimated using eq 6:

$$\rho = \rho_{\text{water}} \times \text{water volume fraction} + \rho_{\text{sugar}} \times \text{sugar volume fraction} \quad (6)$$

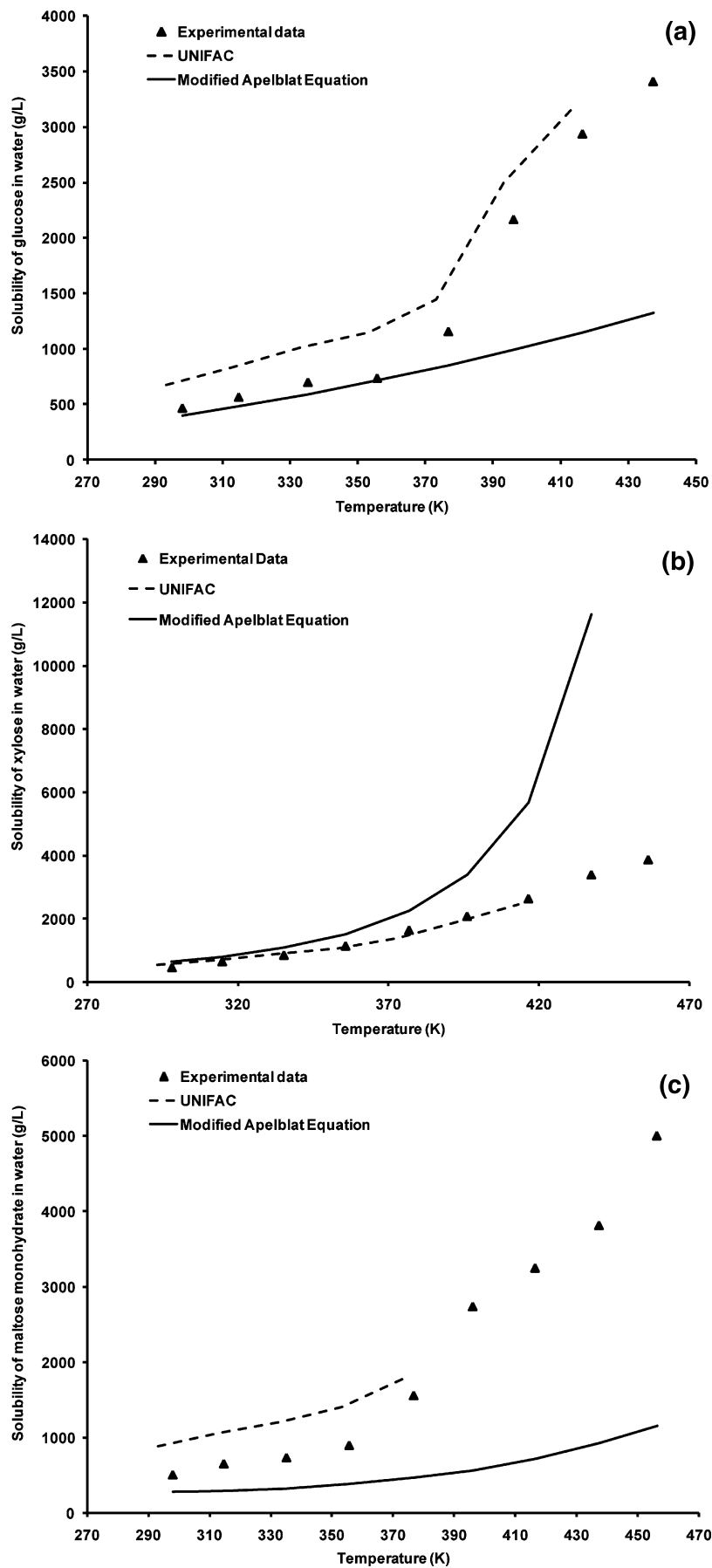
A linear variation of  $\rho_{\text{sugar}}$  with temperature was assumed using values between 298 and 373 K. The activity coefficient of the solute,  $\gamma_s$ , was predicted using the A-UNIFAC model, as described in the literature.<sup>31</sup> The carbohydrate pure-component physical properties used for this model are given in Table 3.

**Table 3.** Carbohydrate Physicochemical Property Data Used in the A-UNIFAC Modeling

carbohydrate	$T_m$ (°C)	$\Delta H_m$ (J/mol)	$\Delta C_p$ (J/mol·K)
glucose	150.15	32 248	120
xylose	150.15	31 650	120
maltose·H <sub>2</sub> O	106.15	45 400	231

Parts a–c of Figure 4 show a comparison between the solubilities measured in this study and those predicted using both the modified Apelblat equation and the A-UNIFAC model. As can be seen in Figure 4a–c, the Apelblat-modeled aqueous solubility data below about 353 K give reasonable agreement with the experimentally derived data for glucose, while for xylose, there is also good agreement up to 353 K. The correlation of experimental data for maltose with the Apelblat equation is much poorer over the entire temperature range; i.e., the modified Apelblat equation predicts much lower values than those obtained experimentally. For these reasons, it was decided to apply the A-UNIFAC model to see if a better agreement between the experimental values and theoretically predicted sugar solubilities could be achieved.

A comparison of the predicted solubility trends with temperatures for the three sugars using a A-UNIFAC model shows that this equation more closely predicts the trend of the experimental sugar solubility data with temperature. For two of the three sugars (glucose and maltose), the UNIFAC model predicts somewhat higher values for the solubility of sugars as a function of the temperature than those obtained experimentally, while for xylose, there is excellent agreement throughout the entire temperature range up to 420 K (Figure 4b). The more limited temperature range when the A-UNIFAC model was applied to maltose was due to the fact that the A-UNIFAC model was only applied up to the melting points of the respective sugars, i.e., maltose having a lower melting point than either glucose or xylose. The relatively better agreement using A-UNIFAC to model the temperature dependence of the sugar solubilities over an extended temperature range is due to its use of a solution thermodynamic model employing solute activity coefficients and hence where both solute and solvent physicochemical properties are considered. The poorer agreement between the experimental and predicted sugar solubilities



**Figure 4.** Comparison of experimentally determined aqueous solubilities (g/L) of sugars as a function of the temperature (K) with those predicted using A-UNIFAC and a modified Apelblat equation: (a) glucose; (b) xylose; (c) maltose.

when employing the modified Apelblat equation is because it is simply an empirical equation used to fit solute solubility data. Correlation of the polar solute solubilities over such an extended temperature is difficult, but hopefully the results obtained in this study will see additional application of the A-UNIFAC approach.

The thermodynamic properties of dissolution for the sugars at different temperatures were calculated using the equations given by Queimada et al.<sup>32</sup> For the calculation of the molar enthalpy ( $\Delta H_{\text{sol}}$ ), molar entropy ( $\Delta S_{\text{sol}}$ ), and molar Gibbs free energy ( $\Delta G_{\text{sol}}$ ) of the solution from the experimentally determined carbohydrate solubility values in water, it is assumed that the activity coefficient of the solute is unity. The molar enthalpy of the solution can be calculated from the Gibbs–Helmholtz equation, as shown in eq 7,

$$\Delta H_{\text{sol}} = RT^2 \left( \frac{d \ln x_s}{dT} \right)_P \quad (7)$$

where  $R$  is the universal gas constant,  $T$  is the temperature (K), and  $x_s$  is the experimentally measured solubility of the sugar on a mole fraction scale. The differential term in eq 6 is calculated by determining the slope of the straight line obtained by plotting the natural logarithm of the aqueous solubility of the compound, expressed in mole fraction units, as a function of the temperature. The molar Gibbs free energy and entropy of solution can then be calculated using eqs 8 and 9, respectively.

$$\Delta G_{\text{sol}} = -RT \ln(x_s)_P \quad (8)$$

$$\Delta S_{\text{sol}} = \frac{\Delta H_{\text{sol}} - \Delta G_{\text{sol}}}{T} \quad (9)$$

The thermodynamic properties of the solution for the sugars, as calculated using eqs 7–9, are listed in Table 4. The root-mean-square deviation (RSD) for all of the thermodynamic properties of the solution, listed within parentheses in Table 4, was calculated using eq 2.

Subsequently, the specific heat capacity at constant pressure ( $C_p$ ) can be calculated by measuring the slope obtained by plotting the enthalpy of solution ( $\Delta H_{\text{sol}}$ ) versus temperature, as given in eq 10.

$$C_p = \frac{\partial(\Delta H_{\text{sol}})}{\partial T} \quad (10)$$

As indicated in Table 4, the free energies of solution,  $\Delta G_{\text{sol}}$ , for all three sugars are positive and of similar magnitude for xylose and glucose, although the values for xylose relative to glucose are less over the entire temperature range. The  $\Delta G_{\text{sol}}$  values for maltose are larger than those for the monomeric sugars as a function of the temperature and, similar to glucose and xylose, decrease with increasing temperature. The enthalpy of solution,  $\Delta H_{\text{sol}}$ , increases linearly with the temperature for all three sugars; the  $\Delta H_{\text{sol}}$  trend for xylose is that the temperature is smaller in magnitude than that recorded for glucose and maltose, which have a similar magnitude in  $\Delta H_{\text{sol}}$  with temperature. It is apparent from eq 10 that the enthalpies of solution for the three sugars as a function of the temperature can be expressed as follows:

$$\Delta H_{\text{sol}} = A + C_p(T/K) \quad (11)$$

From eq 11, the heat capacities at constant pressure,  $C_p$ , can be estimated, and these are presented in Table 5, along with the empirical constants  $A$  and the goodness of fit ( $R^2$ ) obtained

**Table 4. Thermodynamic Properties of Dissolution of the Sugars as a Function of the Temperature**

temperature (K)	$\Delta H_{\text{sol}}$ (kJ/mol) <sup>a</sup>	$\Delta G_{\text{sol}}$ (kJ/mol) <sup>a</sup>	$\Delta S_{\text{sol}}$ (kJ/mol·K) <sup>a</sup>
Xylose			
298	8.92 (±0.02)	7.30 (±0.02)	5.44 (±0.25)
315	9.95 (±0.06)	6.92 (±0.08)	9.62 (±0.09)
335	11.3 (±0.06)	6.67 (±0.10)	13.8 (±0.03)
356	12.7 (±0.09)	6.42 (±0.18)	17.7 (±0.10)
377	14.3 (±0.07)	5.74 (±0.18)	22.6 (±0.05)
396	15.8 (±0.04)	5.23 (±0.12)	26.6 (±0.05)
417	17.4 (±0.03)	4.79 (±0.11)	30.3 (±0.05)
438	19.2 (±0.01)	4.28 (±0.05)	34.1 (±0.07)
456	20.9 (±0.01)	4.01 (±0.07)	37.0 (±0.06)
Glucose			
298	10.4 (±0.003)	7.71 (±0.004)	8.92 (±0.07)
315	11.6 (±0.002)	7.65 (±0.003)	12.4 (±0.06)
335	13.1 (±0.001)	7.56 (±0.002)	16.6 (±0.05)
356	14.8 (±0.001)	7.85 (±0.002)	19.4 (±0.04)
377	16.6 (±0.02)	7.00 (±0.05)	25.4 (±0.04)
396	18.3 (±0.02)	5.55 (±0.06)	32.2 (±0.05)
417	20.2 (±0.006)	4.93 (±0.03)	36.8 (±0.04)
438	22.3 (±0.004)	4.72 (±0.02)	40.2 (±0.03)
Maltose Monohydrate			
298	10.9 (±0.006)	9.17 (±0.007)	5.91 (±0.19)
315	12.2 (±0.001)	9.17 (±0.001)	5.91 (±0.10)
335	13.8 (±0.002)	9.26 (±0.003)	13.6 (±0.08)
356	15.6 (±0.003)	9.23 (±0.004)	17.8 (±0.07)
377	17.5 (±0.03)	8.15 (±0.06)	24.7 (±0.01)
396	19.3 (±0.03)	6.94 (±0.09)	31.2 (±0.09)
417	21.3 (±0.008)	6.56 (±0.03)	35.5 (±0.05)
438	23.5 (±0.01)	6.39 (±0.04)	39.2 (±0.05)
456	25.6 (±0.003)	5.62 (±0.01)	43.8 (±0.04)

<sup>a</sup> RSD values from the mean of replicate measurements listed within the parentheses were calculated using eq 2.

**Table 5. Heat Capacity at Constant Pressure for Sugars in Water**

solute	$C_p$ (kJ/mol·K)	$A$ (kJ/mol)	$R^2$
xylose	0.0757	−13.201	0.997
glucose	0.0857	−15.980	0.997
maltose monohydrate	0.0927	−15.661	0.996

by drawing a linear trendline across  $\Delta H_{\text{sol}}$  plotted as a function of the temperature for each sugar. The heat capacities decrease with increasing carbon number for the sugars and are lower than the estimated values of  $\Delta C_p$  for the same sugars as those given in Table 3 that were used in the A-UNIFAC model. The entropies for sugar dissolution are computed as the difference in  $\Delta H_{\text{sol}}$  and  $\Delta G_{\text{sol}}$ , as noted in eq 9, and change rather significantly with increasing temperature, increasing in magnitude for all sugars 4.5–6.8-fold depending on the sugar moiety.

## Conclusions

The dynamic-flow technique described here for measuring the saturation solubilities of sugars at temperatures above and below the boiling point of water can be widely applied to a diverse number of solute–solvent systems. Successful implementation of the method relies on an appreciation of the need to optimize the technique with respect to minimizing the residence time of the solute in the saturation cell because, at higher temperatures, the possibility of the superimposition of solute degradation can exist that will complicate accurate solute (sugar) solubility measurements. Using this technique, we have successfully measured carbohydrate solubilities in pressurized water above its boiling point, where a paucity of data now exists. For this particular class of solutes, i.e., sugars, it appears that the A-UNIFAC model provides a reasonable approximation of the variation of the sugar solubility with increasing temperature.



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