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Sugar Monomer and Oligomer Solubility

Data and Predictions for Application to Biomass Hydrolysis

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Abstract

Oligomer solubility could potentially play an important role in controlling the rates and yields in the thermochemical hydrolysis of hemicellulose as a pretreatment for subsequent enzymatic conversion of cellulose. However, limited data or models are available to describe the aqueous solubility of sugar monomers and oligomers. In this work, we measured the solubilities of sugars common to many biomass feedstocks in the temperature range of 25–30°C. Then we reviewed solubility models for sugars from the open literature. Finally, we applied models to test their ability to describe this and other data reported in the literature. It was found that the solubility of sugar monomers was not well described by the ideal solubility law or other more complex models. However, with an empirical adjustment to the enthalpy of fusion, the ideal solubility law was able to approximately predict the solubility of cello-oligomers. Based on these results, solubilities for low molecular weight xylo-oligomers are predicted to investigate their possible importance in pretreatment and define further experimental measurements needed to improve our understanding of sugar and oligomer solubility.

Index Entries: Hydrolysis; oligomers; pretreatment; solubility; sugars.

Introduction

Lignocellulosic biomass has the potential to become a valuable raw material for the production of fuels and chemicals provided efficient and economical means are developed to convert them into marketable products. Biological processing offers a particularly promising path to realize such costs, and impressive improvements have been made *(1)*. However, further reductions in the cost of pretreatment and biological conversion of

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cellulose are essential to achieve this end. Elucidation of the fundamental mechanisms and the development of accurate predictive models would aid in identifying opportunities for significant advancements.

Hemicellulose hydrolysis, in which long chains of hemicellulose are depolymerized into oligomers and monomers, is often favored for the preparation of biomass for enzymatic cellulose conversion. This process is typically modeled as a first-order homogeneous reaction in which the polymer reacts to form monomers directly *(2)*. Such models neglect the true heterogeneous nature of the biomass/water pretreatment system. Furthermore, they suffer from inaccuracies and do not provide the insight needed to rationalize the next generation of technology that will be competitive in the marketplace, or the confidence to support commercial applications now or with more advanced approaches in the future.

Our group postulates that hemicellulose hydrolysis may be limited by the rate of mass transfer and solubility of the oligomers released from the solid. For example, if oligomers are only marginally soluble, oligomers of long-chain length would be unable to dissolve until those in solution are reacted to smaller units. This could explain some of the differences in yields realized in different reactor configurations. Knowledge of the solubility of oligomers would give researchers a tool to compare different configurations and would explain their theoretical limitations. However, to test this mechanism, data on the solubility of the five sugars in hemicellulose and their important oligomers are needed.

Some solubility information was found in the literature, but the data and predictive models were limited in the range of sugars and oligomers considered and sometimes contradictory. Jackson et al. *(3)* measured the solubility of α-(D)-glucose at 0.5–80°C, but the values differ from data reported by Taylor *(4)* in the temperature range of 20–65°C. Young *(5)* reported more values for the solubility of α-(D)-glucose, glucose monohydrate, and β-D-glucose in the temperature range of –17 to 63°C; his data agreed with Jackson et al. *(3)* data. Gabas et al. *(6)* reported solubilites for mannose and xylose at 25°C. More recently, Jacobsen *(7)* measured solubilities of glucose, xylose, and cellobiose in the temperature range of 25–47°C and found agreement with Taylor's *(4)* data for glucose and cellobiose. A number of researchers obtained data on the solubility of sugar mixtures and described their data with quasi-chemical models such as Universal Quasi-Chemical Model (UNIQUAC), Uniquac Functional-Group Activities Coefficients Model (UNIFAC), the Flory-Huggins model, and the Entropic Free-Volume *(8–15)*.

Fewer data are available in the literature for oligomers than for monomers. Taylor *(4)* performed a systematic study on the solubility of glucose, cellobiose, cellotriose, cellotetraose, and cellopentaose in the temperature range of 25–65°C and showed that solubilities drop off with increasing chain length, as one would expect. However, only an empirical fit is provided to describe his data; he does not present any experimental solubility data points or experimental SDs.

To develop a solubility and mass transfer model for hemicellulose hydrolysis, more information is needed on the solubility of monomers and particularly oligomers released in hydrolysis. Furthermore, it would be very valuable to be able to predict solubility at elevated temperatures typical for pretreatment by hemicellulose hydrolysis (1) because it would help to improve the efficiency of accessing such information and (2) because sugars would degrade during high-temperature solubility measurements. Thus, we initially focused on measuring the solubility of monomers present in biomass (arabinose, galactose, glucose, mannose, and xylose) and of cellobiose, the only oligomer of interest available at a reasonable cost, to provide a platform for evaluating leading models to determine how well they could predict the solubility data. We then applied the models to estimate the solubility of xylo-oligomers to evaluate whether solubility might play an important role in pretreatment by hemicellulose hydrolysis and to help define further data needs.

Materials and Methods

Chemicals

(D–)-arabinose, (D+)-cellobiose, (D+)-galactose, (D+)-glucose, (D+)-mannose, and (D+)-xylose were purchased from Sigma-Aldrich (St. Louis, MO). High-performance liquid chromatography (HPLC)-grade water from Fisher (Pittsburg, PA) was also used.

Determination of Solubility

Each of the sugars was mixed with deionized water in a 60-mL serum bottle (Fisher) in a ratio of about 2.5 wt% sugar in excess of the expected solubility (based on data in the literature or previous experimental data). The bottles were sealed with 20-mm stoppers (Fisher) and 20-mm tear-off aluminum crimp seals (Fisher). They were then fixed to a 12-in.-diameter, 4-in.-wide plastic wheel containing a 1 3/4-in.-deep groove. Up to nine bottles were fastened on to each side of the wheel using plastic ties. The wheel was mounted on a steel structure and connected by a chain to a Dayton DC gear motor (Niles, IL) operating at 50 rpm. The wheel was then immersed in a 12 × 24 × 20.5 in. water bath containing an Isotemp 2100 (Fisher) Immersion Circulator providing a temperature stability of ± 0.1°C and a pumping rate of 14 L/min.

To take samples, the motor was stopped periodically and the bottles were removed. After removing the caps, a sample was extracted with a 3-mL Luer-Lock, Beckton Dickinson syringe (Franklin Lakes, NJ). A 25-mm 0.5-μm Millipore filter (Bedford, MA) was then fastened to the end, and the liquor was pushed out onto a VWR aluminum weigh dish and quickly weighed on an OHAUS AS120 balance (Pinebrook, NJ) (repeatability of 0.1 mg) and diluted. Concentrations were measured on either of two systems: a Waters Separations Module 2695 (Milford, MA) using an Aminex HPX-87P column (Bio-Rad, Hercules, CA) with a Waters 2414 Refractome-

ter; or a Waters 717 autosampler, Aminex HPX-42A ion-exchange column, and a Waters 410 refractometer. An unpaired *t*-test was performed to determine when the change in concentration with time was undetectable.

Models

Ideal Solubility Model

The simplest method for predicting the solubility of carbohydrates is to use the ideal solubility law, the thermodynamic derivation of which is relatively straightforward *(16)*. For a component to be ideal, no solvent can appear in the solid phase*(8)* and the activity coefficient must be unity *(17)*. This implies that the solute does not form a hydrate at the given temperature, that the affinity between solute molecules is approximately the same as the affinity between solute and solvent molecules, and that the solute and solvent have similar molecular volumes *(16)*. With these assumptions, dissolution is thermodynamically equivalent to melting the solute, and the change in free energy of dissolution ($\triangle G_{dis}$) is equated to the change in free energy on melting ($\triangle G_f$) at the dissolution temperature. By assuming that there is no change in entropy, $\triangle G_f$ is equal to the change in enthalpy on melting ($\triangle H_f$) *(16)*. The resulting expression is as follows:

$$\ln(X) = \frac{-\triangle H_f}{R}\left(\frac{T_m - T}{T_m T}\right) + \frac{\triangle C_p}{R}\left(\frac{T_m - T}{T}\right) - \frac{\triangle C_p}{R}\ln\left(\frac{T_m}{T}\right) \quad (1)$$

Equation 1 is the first form of the ideal solubility law, in which X is the mole fraction of solute in solution at saturation, T is the absolute temperature, T_m is the melting point of the solute, R is the ideal gas constant, and $\triangle C_p$ is the heat capacity difference of the solute between pure solid and a subcooled liquid at the dissolution temperature. However, because the solute is thermodynamically stable only as a solid at the dissolution temperature, $\triangle C_p$ is difficult, and in some cases impossible, to determine. Thus, in the two most common forms of the ideal solubility law, an assumption about $\triangle C_p$ is necessary. The first assumption is that it can be set to zero, leading to *(16)*

$$\ln(X) = \frac{-\triangle H_f}{R}\left(\frac{T_m - T}{T_m T}\right) \quad (2)$$

A third equation is derived from empirical observation that the heat capacity difference $\triangle C_p$ can be better estimated by the entropy of fusion, $\triangle S_f$. Since $\triangle G_f = 0$ at the melting point and $\triangle H_f = T_m \triangle S_f = T_m \triangle C_p$, the first two terms in Eq. 1 can be eliminated, leading to *(16)*

$$\ln(X) = \frac{-\triangle H_f}{R T_m}\ln\left(\frac{T_m}{T}\right) \quad (3)$$

To apply the ideal solubility laws to oligomers, the enthalpy of fusion must be known. Unfortunately, a thorough search of the literature reveals

values for only monomers and a few dimers. Thus, it is necessary to estimate these values for oligomers. The enthalpy of fusion at the melting point temperature can be estimated by the entropy of fusion from the relation $\triangle H_f = T_m \triangle S_f$. Walden *(18)* observed that $\triangle S_f$ is about 13 cal/(K·mol) (54 J/(K·mol) for a large number of organic compounds. However, the values for $\triangle H_f$ calculated using Walden's value for $\triangle S_f$ are much less than the experimental values reported in the literature, for the monomers and dimers for which the fusion enthalpies are tabulated. Thus, $\triangle S_f$s were calculated from the experimental $\triangle H_f$s (*see* Table 1) and found to vary quite widely. However, note that the values do not vary appreciably between monomer and dimer.

With this in mind, values of $\triangle S_f$ that should not depend on chain length were bracketed between 60 and 100 J/(K·mol) and used in the ideal solubility law. For both the cello-oligomers and the xylo-oligomers, a minimum and maximum solubility was calculated using these two values for the fusion entropies, and these predictions were compared to experimental values available in the literature.

UNIQUAC/UNIFAC

Activities are often applied instead of concentrations to compensate for deviations from ideality in the liquid phase. Several methods have been devised to predict the activity that incorporate a combinatorial term (also called an *athermal* term), γ_i^C, that accounts for entropic effects arising from differences in size between solute and solvent molecules, and/or a residual term, γ_i^R, that accounts for energetic interactions such as Coulombic forces and hydrogen bonding that are very temperature dependent *(18)*. UNIQUAC and UNIFAC are two such models. They differ in the way in which the residual term is calculated *(19)*. Both methods treat the differential heat capacity as a linear function of temperature. UNIQUAC requires between five and six parameters for each component aside from water, and UNIFAC requires more parameters, depending on the number of functional groups.

Peres and Macedo *(8)* applied UNIQUAC to determine a wide variety of thermodynamic parameters for binary systems of D-glucose, D-fructose, and sucrose in water. The same group later compared the UNIQUAC predictions with those obtained from the Flory-Huggins and entropic free-volume models *(9–11)*. Gabas and Laguerie *(12)* applied UNIFAC to describe the solid-liquid-phase equilibria of the ternary system xylose, mannose, and water. Likewise, Abed et al. *(13)* used UNIFAC to describe the phase equilibria at saturation of mixtures of water, sucrose, and glucose along with water, sucrose, and fructose. Catte et al. *(14)*, and Spiliotis and Tassios *(15)* each created their own UNIFAC models using data from the literature. None of these groups examined the solubility of a binary, sugar monomer, or oligomer/water system over a wide temperature range, although many of them included data from other researchers.

Table 1
Experimental Fusion Enthalpies and Calculated Fusion Entropies with Experimental Melting Points and Fusion Enthalpy Values

Sugar	T_m (°C)	Fusion enthalpy (J/mol)	Fusion entropy (J/K·mol)
Arabinose	160[a]	35700[a]	82
Galactose	170[a]	43740[a]	99
Glucose	158[a]	32220[a]	75
Mannose	134[a]	24660[a]	61
Xylose	157[a]	31650[a]	74
Fructose	105[a]	30420[a]	80
Ribose	70[a]	21900[a]	64
Cellobiose	225[b]	31058[b]	62
Sucrose	165[a]	40356[a]	92

[a]From Roos *(22)*
[b]From Stanek et al. *(23)*.

Other Models

The Flory-Huggins model has been applied to predict sugar solubilities in some circumstances. It contains only a combinatorial term in the activity coefficent, assuming that deviations from ideality can be accounted for completely by the entropy of mixing, and requires knowledge of the molar volume of solution *(20)*. It is often applied to polymer solutions. The entropic free-volume model is a refinement of the Flory-Huggins model in which van der Waals volumes are used instead of molar volumes *(10)*.

Results and Discussion

The experimental solubilities are presented for the monomers arabinose, galactose, mannose, xylose, and glucose and for the dimer cellobiose at 20, 25, and 30°C in Table 2 along with SDs that ranged from 0.06 to 2.73% of the mean values. These data are reported as mole fractions according to the convention of Taylor *(4)*. The order of solubilities from most soluble to least soluble was mannose, xylose, glucose, arabinose, and galactose. The values also increased significantly with temperature. The solubility of arabinose displayed the greatest temperature dependence, increasing between 10 and 17% over a 5°C increment, and that of xylose showed the least temperature dependence, increasing by about 10% each 5°C increment. Expressed as mass fractions, the solubilities ranged from 28.22% for galactose at 20°C to 77.75% for mannose at 25°C.

Figure 1 shows the experimental values combined with values from the literature, where available, and values predicted by various models. For xylose and mannose, close agreement was found between the values reported in our work and those of Gabas and Laguerie *(12)*. Glucose is the only sugar considered herein for which the solubility over a wide range of

Table 2
Experimental Solubilities as Measured iIn Mole Fractions[a]

Sugar	Mole Fraction at Saturation		
	20°C	25°C	30°C
Arabinose	0.07400 (0.00110)	0.08160 (0.00060)	0.09530 (0.00110)
Galactose	0.00378 (0.00090)	0.04320 (0.00020)	0.05040 (0.00010)
Glucose	0.08029 (0.00219)	0.09447 (0.00114)	0.11386 (0.00017)
Cellobiose	0.00921 (0.00090)	0.00823 (0.00030)	0.00918 (0.00052)
Mannose	0.22241 (0.00079)	0.25884 (0.00374)	ND[b]
Xylose	0.11758 (0.00127)	0.12953 (0.00117)	0.14149 (0.00008)

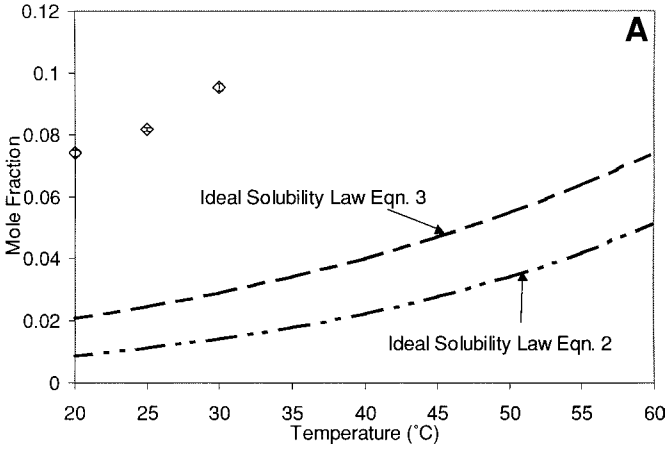
[a]SDs are given in parentheses.
[b]Not determined.

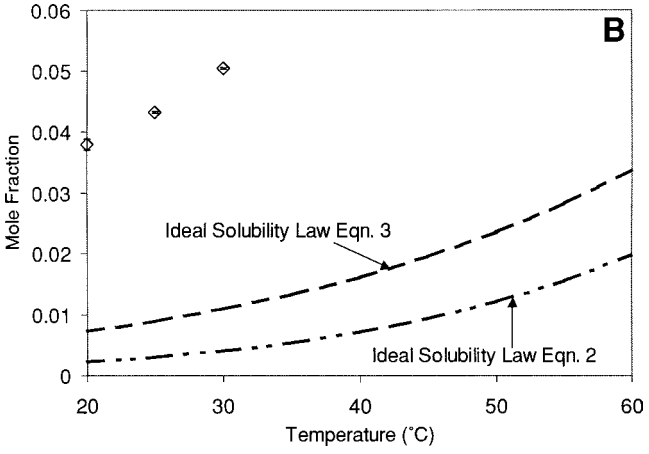
temperatures is well documented, but, as mentioned previously, there is substantial variation in the literature. As shown in Fig. 1C, reported solubilities of α-(D)-glucose cluster around two sets of values: those by Jackson et al. *(3)*, Peres and Macedo *(8)*, and Young *(5)*, vs those by Taylor *(4)*, and Jacobsen *(7)*. The values obtained in our work agreed with the latter group.

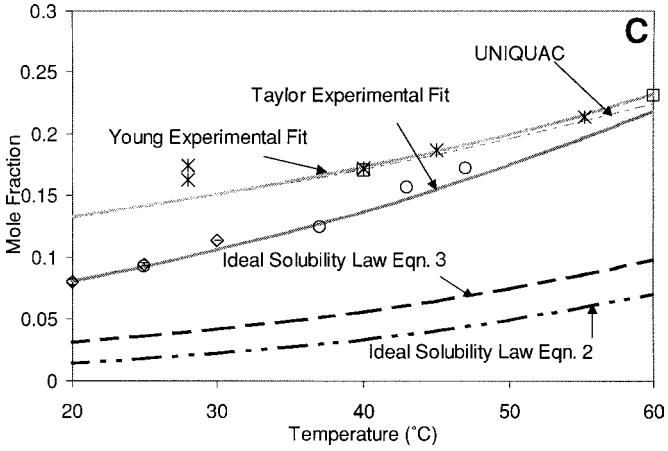
For all the sugars, the ideal solubility law Eqs. 2 and 3 underpredicted the actual solubility. In addition, the change in solubility with increasing temperature for the ideal predictions is much less than for the experimental solubilities. The first equation of the ideal solubility law was not used because values for $\triangle C_p$ are not tabulated. Equation 3 does a slightly better job than Eq. 2, a result consistent with the finding of Neau et al. *(16)*, implying that the differential heat capacity is better approximated by $\triangle S_f$ rather than simply set to zero. However, note that the ideal solubility law does predict the correct order of solubilities, from mannose to galactose, a sequence that corresponds to the order of the melting temperatures. This result implies that as T/T_m is greater, the solubility is greater, consistent with the idea that as the temperature approaches the melting point of a solute, more and more of the solute can be held in a liquid state (i.e., a solubilized state).

UNIQUAC was used to estimate glucose solubilities using parameters for the group volumes, surface area, and molecular interaction given by Peres and Macedo *(8)*. UNIQUAC agrees well with the empirical model reported by Young *(5)*, which is a cubic equation fit to his data. None of the other UNIQUAC or UNIFAC models were tested. In addition, the Flory-Huggins and the entropic free-volume models could not be used because they required data that were not available in the literature.

Experimental solubilities for cellobiose are given in Table 2. The SDs are much greater than for the monomers, ranging from 3.59 to 9.74% of the mean value. Because of these large experimental errors, the solubilities at 20, 25, and 30°C are indistinguishable. Part of the reason for this error is


A
Mole Fraction
Temperature (°C)
Ideal Solubility Law Eqn. 3
Ideal Solubility Law Eqn. 2
0.12
0.1
0.08
0.06
0.04
0.02
0
20
25
30
35
40
45
50
55
60


B
Mole Fraction
Temperature (°C)
Ideal Solubility Law Eqn. 3
Ideal Solubility Law Eqn. 2
0.06
0.05
0.04
0.03
0.02
0.01
0
20
30
40
50
60


C
UNIQUAC
Taylor Experimental Fit
Young Experimental Fit
Ideal Solubility Law Eqn. 3
Ideal Solubility Law Eqn. 2
Mole Fraction
Temperature (°C)
0.3
0.25
0.2
0.15
0.1
0.05
0
20
30
40
50
60

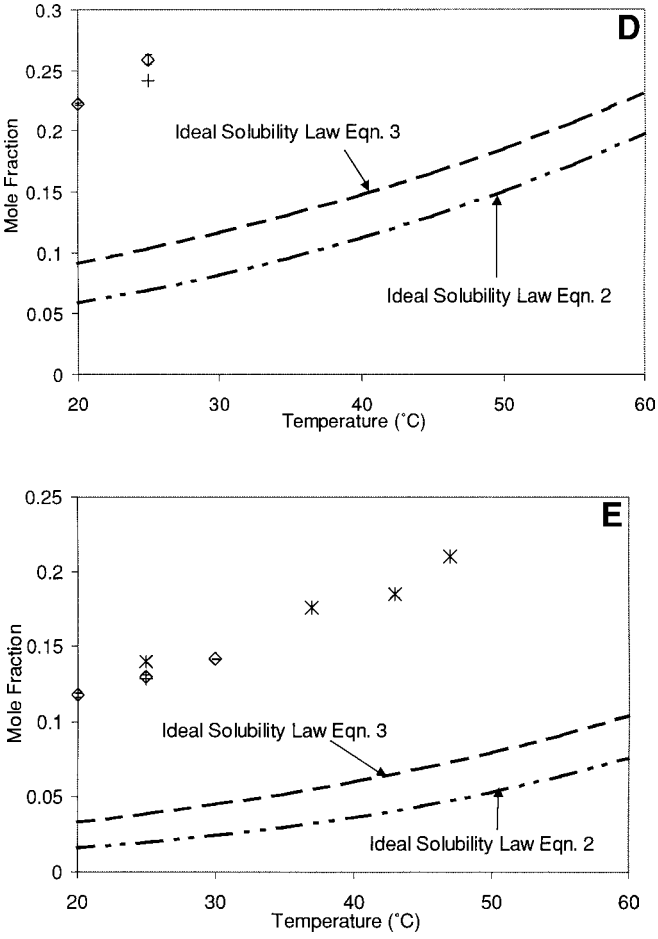


Fig. 1. Monomer solubilities vs temperature. **(A)** Arabinose solubility; **(B)** galactose solubility; **(C)** glucose solubility; **(D)** mannose solubility; **(E)** xylose solubility. (◇) This work; (○) Gabas *(6)*; (+) Jacobsen *(7)*; (×) Jackson et al. *(3)*; (□) Peres and Macedo *(8)*.

that the lower solubility of cellobiose makes it more prone to variations during weighing and analysis with HPLC. However, the values in this work do agree well with those reported by Taylor *(4)* and Jacobsen *(7)*, as shown in Fig. 2. For cellobiose and all the oligomers, Eq. 3 of the ideal solubility law was used to estimate their solubilities because Eq. 3 was observed to be more accurate than Eq. 2 for the monomers. Maximum and minimum values were used based on estimates of the entropies of fusion as discussed previously. Between 20 and 30°C, the ideal equation maximum underpredicts the solubility of cellobiose, but at higher temperatures, the maximum and minimum predictions do bracket the experimental solubilities.

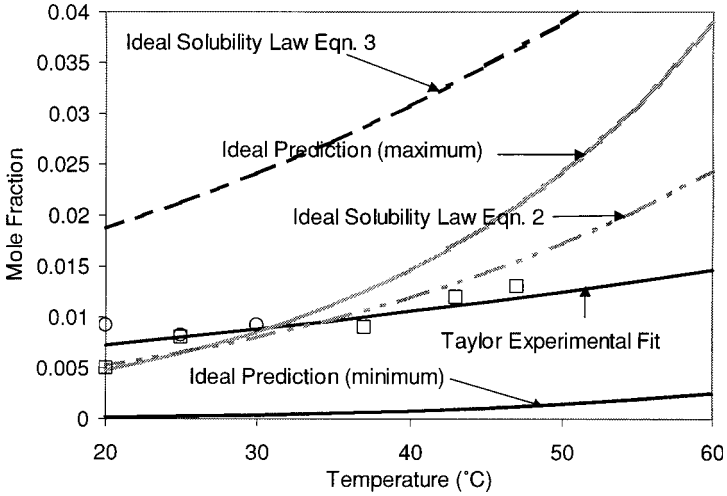


Fig. 2. Cellobiose solubility vs temperature. (○) This work; (□) Jacobsen *(7)*.

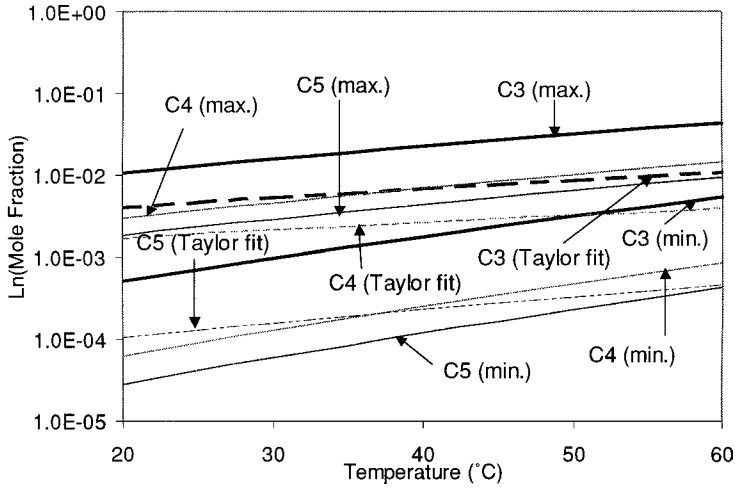


Fig. 3. Cello-oligomer solubilities vs temperature.

Figure 3 also shows the actual solubilities of cellotriose, cellotetraose, and cellopentaose as reported by Taylor *(4)*. For all of these oligomers, the actual solubility falls within the minimum and maximum limits in the temperature range of 20–60°C. Additionally, the predicted solubilities change more rapidly with temperature than the experimental solubilities, indicating that for elevated temperatures, the actual values may be less than both the predicted minimum and the predicted maximum.

The estimated values for the solubility of the xylobiose, xylotriose, xylotetraose, xylopentaose, and xylohexaose are given in Fig. 4. The solubilities are reported as mole fractions to make them comparable to the other solubility data and as mass fractions of xylose equivalents. The conversion is as follows:

$$oligo_{mass\ fraction} = \frac{oligo_{mole\ fraction} \times MW}{\left(oligo_{mole\ fraction} \times MW\right) + \left(1 - oligo_{mole\ fraction}\right) \times 18} \tag{4}$$

$$oligo\ (as\ xylose)_{mass\ fraction} = oligo_{mass\ fraction} \times \left(150 \times \mathrm{DP/MW}\right) \tag{5}$$

MW is the molecular weight of the oligomer and *DP* is the degree of polymerization of the oligomer. Figure 4 shows that all of the xylo-oligomers except for the trimer are predicted to have much greater solubilities than the corresponding cello-oligomer. At room temperature, the solubilities range from between 0.02 and 0.001 for xylobiose to 0.005 to 0.0001 for xylohexaose, corresponding to a range of mass percentages of about 1–20% for both species. This implies that, although they are much less soluble than the xylose monomer, they are at least moderately soluble at room temperature. When these predictions are extrapolated to 150°C, the predicted solubilities are very high. The minimum predicted solubilities of xylopentaose and xylohexaose at 120°C approach the experimental solubility of the most soluble monomer, mannose, at room temperature on the basis of mass fraction.

The next step was to compare these numbers with numbers expected in an uncatalyzed batch hydrolysis to estimate how solubility might influence hydrolysis. For example, for biomass containing 25% xylan (on a dry basis) in a batch system with 20% solids, the maximum oligomer mass percentage in the liquor would be 6.25% (expressed as xylan equivalents) at a yield of 100%. Converted to xylose equivalents, this maximum oligomer mass percentage is 7.1%. Figure 4 shows that at 120°C, the predicted minimum mass percentages for xylobiose to xylohexaose are all >55% (as xylose equivalents). Thus, for all oligomers with a degree of polymerization <6, the maximum expected oligomer concentration would be much less than the solubility of any one of the oligomeric components, and for temperatures exceeding 120°C, the solubility of any xylo-oligomer of chain length <6 is not expected to be a limiting factor in batch hydrolysis. However, higher molecular weight oligomers could still be a factor, but their solubility could not be predicted because their melting points are not known.

Conclusion

This work examined the solubilities of several monomers and oligomers expected in biomass hydrolysis. The monomers were very soluble in the temperature range of 20–30°C, with a mass fraction ranging from 28.22% for galactose at 20°C to 77.75% for mannose at 25°C. The order of solubilities

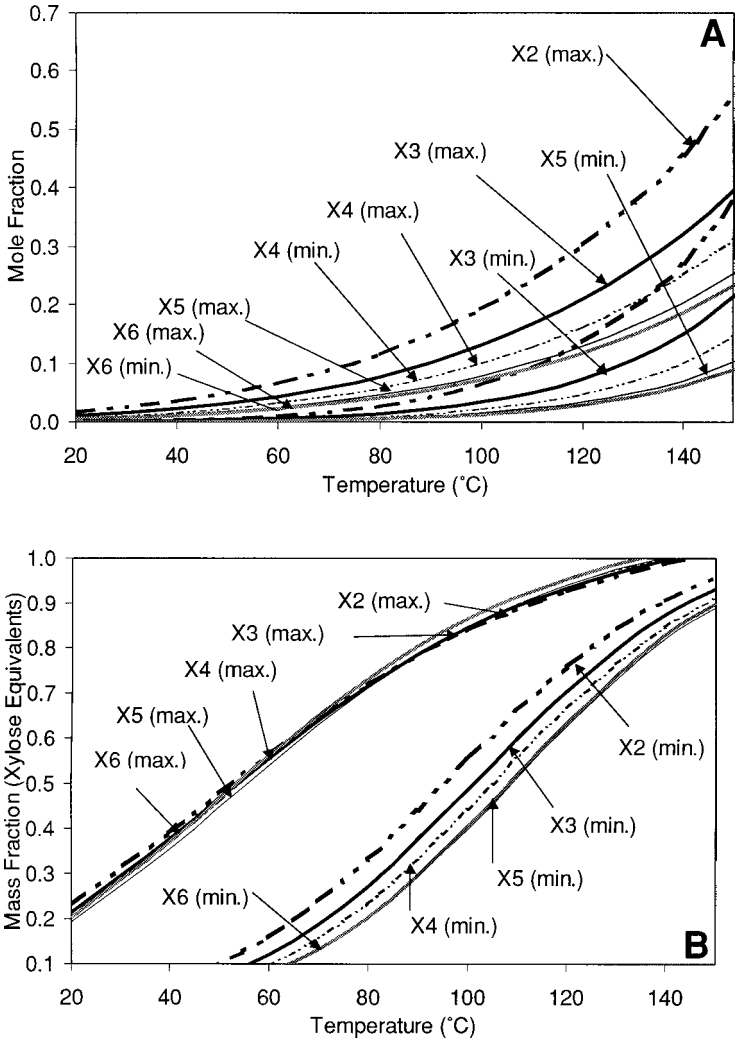


Fig. 4. Xylo-oligomer solubility vs temperature.

from most to least soluble is mannose, xylose, glucose, arabinose and galactose. All of the solubilities were strongly temperature dependent, increasing in solubility by at least 10% in a 5°C increment. The data developed were in close agreement with the values reported by most other researchers.

Neither Eq. 2 nor Eq. 3 of the ideal solubility law predicted the experimental solubilities closely, although both equations predicted the correct order of solubilities. UNIQUAC did closely predict some of the experimental values reported in the literature. UNIQUAC was simulated using the parameters reported by Peres and Macedo *(8)* and are presented in Table 3. Not enough information was available to estimate the solubilities of the other sugars using UNIQUAC, UNIFAC, Flory-Huggins, or the Entropic Free-Volume models.

Table 3
UNIQUAC Parameters *(9)*

Glucose fixed parameters	
T_0 (reference temperature)	298.15 K
T_m (melting point temperature)	425.15 K
$\triangle H$ (fusion enthalpy)	32432 J mol
$\triangle A$ (constant term for linear temperature dependent $\triangle C_p$)	139.5766 J/mol
$\triangle B$ (slope term for linear temperature dependent $\triangle C_p$)	0 J/(mol·K)

Size parameters (dimensionless)	Glucose	Water
Q_i (surface area parameter)	8.1528	0.92
R_i (volume parameter)	7.92	1.4

Interaction parameters (dimensionless) a_{ij}^0 *(constant term for linear temperature dependent interaction)*	Glucose	Water
Glucose	0	–68.6157
Water	96.5267	0

a_{ij}^t *(slope term for linear temperature dependent interaction)*	Glucose	Water
Glucose	0	–0.069
Water	0.277	0

The solubility of cello-oligomers was also investigated as a first step toward evaluating tools for predicting their behavior in solution. In the series cellotriose, cellotetraose, and cellopentaose, solubility drops rapidly with increasing chain length, and it was possible to bracket the actual solubilities with ideal solubility law predictions over the temperature range of 20–60°C, by approximating the entropy of fusion. This model was then applied to predict the solubilities of xylobiose, xylotriose, xylotetraose, xylopentaose, and xylohexaose, as shown in Fig. 4, but no experimental data on their solubilities were available for comparison. The ideal predictions estimate that the solubility of all the xylo-oligomers, except for the trimer, are greater than that of the corresponding cello-oligomer, with values at room temperature ranging from 1 to 20% by mass. At 120°C, the estimated mass percentages (as xylose equivalents) are all >55%. This implies that in the example conversion scheme discussed previously, the solubility of xylo-oligomers with a chain length of 6 or less is not likely to be a limiting factor.

Continuing work for this project will include taking experimental measurements of the solubilities of the xylo-oligomers, including longer-chain oligomers, and comparing the results to model predictions. We also plan to include measuring the enthalpies of fusion to test the ideal solu-

Table 4
Parameters Used in Study Models

Parameter	Units
Activity coefficient	Dimensionless
Athermal activity coefficient	Dimensionless
Differential heat capacity ($\triangle C_p$)	J/(g·K)
Enthalpy of fusion ($\triangle H_f$)	J
Entropy of fusion ($\triangle S_f$)	Dimensionless
Free energy of dissolution ($\triangle G_{dis}$)	J
Ideal gas constant (R)	J K-1 mol-1
Mass fraction	Dimensionless
Mass fraction of xylose equivalents	Dimensionless
Melting point temperature (T_m)	Dimensionless
Mole Fraction (X)	Dimensionless

bility law when applied to oligomers. Finally, the solubility of oligomers in multiple component systems will be examined, including mixed oligomer solutions; solutions containing xylose; solutions containing other sugars; solutions containing degradation products; and solutions containing other components present in biomass such as lignin, acetic acid, uronic acid, and extractives.

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