Experimental and modelling studies on the synthesis of 5-hydroxymethylfurfural from sugars

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Experimental and modelling studies on the solubility of D-arabinose, D-fructose, D-glucose, D-mannose, sucrose and D-xylose in methanol and methanol-water mixtures*

Abstract

The solubilities of D-glucose, D-arabinose, D-xylose, D-fructose, D-mannose and sucrose in methanol and methanol-water mixtures (<25 wt% water) were determined at temperatures between 295 and 353 K using a unique high-throughput screening technique. The data were modelled with a UNIQUAC framework with an average error between calculated and experimental data of 3.7%. The results provide input for the design of efficient chemical processes for the conversion of these sugars into valuable biobased building blocks in methanol-water mixtures.

6.1 Introduction

Lignocellulosic biomass is considered an attractive renewable source for the production of biofuels and biobased chemicals and intense research and development activities have been performed the last decade to identify techno-economically viable routes. Well-known examples are the conversion of lignocellulosic biomass to bioethanol as a second generation biofuel, and the conversion of C6-sugars to platform chemicals like 5-hydroxymethylfurfural (HMF) and levulinic acid.1-4

For most of these conversions, water was the initial solvent of choice as it is considered environmentally benign and a good solvent for monomeric sugars. Especially aqueous fermentation of sugars to biofuels and biobased chemicals will play an important role.5 There are, however, significant disadvantages for using water as solvent for chemical processes. General disadvantages of using water as the solvent for any chemical process are the high cost of its removal due to its high heat of vaporisation (2.4 kJg\(^{-1}\))6 and its corrosiveness at elevated temperatures. The importance of a more classical chemocatalytic approach to the conversions of sugars is expected to gain momentum.7 For some high-potential chemocatalytic processes the carbon yields in water cannot meet techno-economic targets due to excessive by-product formation. Alternative solvents have been explored, especially in the case of the production of furans from sugars.1

Unfortunately, the solubility of monomeric sugars in common organic solvents is rather limited and sugars typically only dissolve well in high-boiling polar aprotic solvents such as DMSO and NMP. However, the relatively high boiling points of these solvents result in serious issues in the product work-up and therefore lower boiling solvents are favoured. As such, the use of lower alcohols is currently extensively explored in the development of carbohydrate (pre-)treatment and conversion processes, such as the organosolv processes using ethanol8 (boiling point 351 K, heat of vaporisation 0.84 kJg\(^{-1}\))6 and sugar dehydration to 5-hydroxymethylfurfural derivatives.1, 9 Saka and co-workers have looked extensively into cellulose and lignocellulosic biomass pre-treatment in methanol10, 11 (boiling point 338 K, heat of vaporisation 1.11 kJg\(^{-1}\)).6 Research by Bicker et al.9 and Avantium12 has shown that methanol is the solvent of choice for the production of 5-hydroxymethylfurfural (HMF) and its methyl ether (MMF).
Experimental and modelling studies on the solubility of D-arabinose, D-fructose, D-glucose, D-mannose, sucrose and D-xylose in methanol and methanol-water mixtures

For the development of efficient green processes solvent usage and recycle should be minimised and as such there is a large incentive for performing reactions in highly concentrated solutions. For this purpose, detailed solubility data of the sugars in solvents other than water are required. Limited research has been performed on the solubility of sugars in alcohols, see Table 1 for an overview. The majority of the studies focus on glucose and fructose solubilities using methanol and ethanol as the solvent. The emphasis is mainly on alcohol-water mixtures and less on the pure alcohols. Furthermore the temperature ranges for individual studies are often very narrow. Limited attention is given to higher alcohols and to other sugars.

**Table 1. Overview of research studies on sugar solubility in alcohols**

<table>
<thead>
<tr>
<th>Sugar</th>
<th>Solvent</th>
<th>Temperature range (K)</th>
<th>Model type</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Galactose</td>
<td>Ethanol/water</td>
<td>273, 288 and 303</td>
<td>UNIFAC</td>
<td>13</td>
</tr>
<tr>
<td>Xylose and mannose</td>
<td>Ethanol and ethanol/water</td>
<td>278, 288 and 298</td>
<td>UNIFAC</td>
<td>14</td>
</tr>
<tr>
<td>Glucose, fructose, xylose, galactose, mannose, sucrose</td>
<td>Methanol, ethanol, n-propanol, n-butanol, t-pentanol</td>
<td>298-398</td>
<td>UNIFAC</td>
<td>15</td>
</tr>
<tr>
<td>Glucose, fructose, sucrose</td>
<td>Methanol, methanol/ethanol and methanol/water and Ethanol/water</td>
<td>298, 313, 333</td>
<td>UNIFAC</td>
<td>16</td>
</tr>
<tr>
<td>Fructose</td>
<td>Methanol, methanol/ethanol, methanol/water and Ethanol/water</td>
<td>298, 313, 333</td>
<td>UNIFAC and UNIQUAC</td>
<td>17</td>
</tr>
<tr>
<td>Sucrose</td>
<td>Ethanol and ethanol/water</td>
<td>310</td>
<td>UNIQUAC</td>
<td>18</td>
</tr>
<tr>
<td>Fructose and glucose</td>
<td>Ethanol/water</td>
<td>303</td>
<td>UNIQUAC</td>
<td>19</td>
</tr>
<tr>
<td>Glucose</td>
<td>Methanol, ethanol, methanol/water, methanol/ethanol</td>
<td>313 and 333</td>
<td>UNIQUAC</td>
<td>20</td>
</tr>
<tr>
<td>Glucose, fructose, sucrose</td>
<td>Methanol, methanol/ethanol and methanol/water and Ethanol/water</td>
<td>298, 313, 333</td>
<td>UNIQUAC</td>
<td>21</td>
</tr>
<tr>
<td>Glucose, fructose, galactose</td>
<td>Ethanol and ethanol/water</td>
<td>295, 303, 313</td>
<td>UNIQUAC</td>
<td>22</td>
</tr>
</tbody>
</table>
In this paper, a systematic study is presented on the solubility of a range of C6 and C5 sugars (D-arabinose, D-fructose, D-glucose, D-mannose and D-xylose) and one disaccharide (sucrose) in methanol and methanol-water mixtures containing up to 25 wt% water. The sugars are shown in Scheme 1 in which the monosaccharides are presented in their pyranose forms as it is likely that these will be the most abundant tautomers in water and in methanol.\textsuperscript{23, 24}

To the best of our knowledge, this is the most extensive study reported in this field so far, allowing a proper comparison of the solubilities of the sugars under study at a wide range of conditions. The experiments were performed using a unique Avantium high-throughput device (Crystal16\textsuperscript{TM}). A wide range of temperatures (295-353 K) and methanol-water ratios (0-25 wt%) were applied. The equipment allows sixteen parallel experiments at temperatures higher than the boiling point by measuring within a closed vial. The solubility data were modelled using a UNIQUAC model.

\begin{scheme}
\centering
\includegraphics[width=\textwidth]{sugar_structures.png}
\caption{The sugars tested in this study, with all monosaccharides in their pyranose forms}
\end{scheme}
6.2 Experimental section

6.2.1 Chemicals

Sucrose (99.6%) was obtained from Fluka. All other sugars (pure D-form) were obtained from Sigma-Aldrich at >99% purity. Methanol was obtained from Fisher and was HPLC gradient grade. Milli-Q grade water was used for all experiments.

6.2.2 Solubility measurements

All experiments were performed using the Avantium Pharmatech Crystal16™ equipment. This equipment has been specifically designed for determining clear points and cloud points for crystallisation studies. It consists of four heating blocks with magnetic stirring, with four slots each for standard 1.6 mL HPLC vials. Validation of the equipment showed that the temperature of the liquid in the vial was always within 1 K of the set point temperature for the complete temperature range of the experiments. Each reactor has a light source and a sensor. The equipment determines the percentage of light passing through the vials allowing for automatic turbidity measurements and thus for the determination of the clear points and cloud points of the solutions under investigation.

The software provided with the Crystal16™ equipment allows for automatic and regulated temperature increase and cooling sequences. Here, one cycle consisted of heating up at a rate of 3 K/h to 353 K, followed by cooling at a rate of 1 or 2 K/min to 268 K. The experiments generally consisted of 3 cycles. Solutions were prepared from weighed amounts of all components, making the error in sample preparation significantly less than 1%. The experiments were performed at approximately 1 mL scale. After the experiments the vials were weighed to check for loss of the solvent by evaporation due to leakage. Significant loss of solvent was not observed.
6.2.3 UNIQUAC modelling

From thermodynamics the well-known equation for the solubility of a solid in a liquid is obtained as: \(^{25}\)

\[
\ln(\gamma_i x_i) = \frac{\Delta H_{f,i}}{R} \left(\frac{T_{f,i} - 1}{T}\right) - \frac{\Delta C_{p_i}}{R} \left(1 - \frac{T_{f,i}}{T}\right) + \ln \left(\frac{T_{f,i}}{T}\right)
\]

(1)

where \(\gamma_i\) and \(x_i\) denote the activity coefficient and the molar fraction of the solute in the liquid phase. \(\Delta C_{p_i}\) denotes the difference of the solute's specific heat in the solid and liquid phases, \(T\) is the actual temperature and \(T_{f,i}\) the fusion point temperature. Equation (1) is obtained with the assumptions that the solid phase that is in equilibrium with the solution consists of the pure solute and that \(\Delta C_{p_i}\) is independent of the temperature in the range of \(T\) to \(T_{f,i}\).

Equation (1) can be used to evaluate the experimental results if a model for the activity of the solute is implemented. Here the UNIQUAC model formulation\(^ {26}\) was chosen to model the activity coefficients because of its suitability for the systems under investigation, i.e. a highly polar, non electrolyte, low pressure mixture that contains both large and small molecules.\(^ {27}\) From Equation (2) \(\ln \gamma_i\) is calculated:

\[
\ln \gamma_i = 1 - \phi_i + \ln \phi_i - 5 q_i (1 - \frac{\phi_i}{\theta_i} + \ln \frac{\phi_i}{\theta_i}) + q_i (1 - \ln S_i - \sum_j x_j \frac{\phi_j}{\theta_j} \frac{\tau_{ij}}{S_j})
\]

(2)

where \(\phi\) and \(\theta\) depend on the volume and surface area parameters \(r_i\) and \(q_i\), and \(S\) also on the binary parameters \(\tau_{ij}\) (see list of symbols). The values of the parameters \(r_i\) and \(q_i\) were taken from Poling et al.\(^ {27}\) (Table 2).

The adjustable binary parameters are defined in terms of binary energy interaction parameters \(A_{ij}\):

\[
\tau_{ij} = \exp(-A_{ij}/T)
\]

(3)

where in general \(A_{ii} = A_{jj} = 0\) and \(A_{ij} \neq A_{ji}\). The values of the parameters \(A_{ij}\) were obtained by fitting the calculated solubilities of equations (1)-(2) to the measured ones using a standard Newton routine for non-linear optimisation.
Experimental and modelling studies on the solubility of D-arabinose, D-fructose, D-glucose, D-mannose, sucrose and D-xylose in methanol and methanol-water mixtures

The physical properties of the carbohydrates mentioned in equation (1), i.e. the heat of fusion, the temperature of fusion and the solid-liquid specific heat difference, were taken from literature when available, or estimated following literature (Table 3).

**Table 2.** UNIQUAC parameters \( r_i \) and \( q_i \)

<table>
<thead>
<tr>
<th></th>
<th>( M ) [g/mol]</th>
<th>( r_i )</th>
<th>( q_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>32.04</td>
<td>1.9011</td>
<td>2.048</td>
</tr>
<tr>
<td>water</td>
<td>18.01528</td>
<td>0.92</td>
<td>1.40</td>
</tr>
<tr>
<td>arabinose</td>
<td>150.13</td>
<td>6.7089</td>
<td>6.492</td>
</tr>
<tr>
<td>fructose</td>
<td>180.16</td>
<td>8.1589</td>
<td>8.004</td>
</tr>
<tr>
<td>glucose</td>
<td>180.16</td>
<td>8.1558</td>
<td>7.92</td>
</tr>
<tr>
<td>mannose</td>
<td>180.16</td>
<td>8.1558</td>
<td>7.92</td>
</tr>
<tr>
<td>sucrose</td>
<td>342.30</td>
<td>14.5586</td>
<td>13.764</td>
</tr>
<tr>
<td>xylose</td>
<td>150.13</td>
<td>6.7089</td>
<td>6.492</td>
</tr>
</tbody>
</table>

**Table 3.** Physical properties of the sugars used in this study

<table>
<thead>
<tr>
<th>sugar</th>
<th>( \Delta H_f ) [kJ/mol]</th>
<th>( T_f ) [K]</th>
<th>( \Delta C_p ) [J/mol.K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>arabinose</td>
<td>35.78(^{28})</td>
<td>435(^{29})</td>
<td>120(^b)</td>
</tr>
<tr>
<td>fructose</td>
<td>33.0(^{30})</td>
<td>378(^{30, 31})</td>
<td>120(^a)</td>
</tr>
<tr>
<td>glucose</td>
<td>32(^{28, 30, 32})</td>
<td>420(^{29, 32})</td>
<td>120(^a)</td>
</tr>
<tr>
<td>mannose</td>
<td>24.7(^{28})</td>
<td>404(^{28, 29})</td>
<td>120(^a)</td>
</tr>
<tr>
<td>sucrose</td>
<td>46.2(^{28})</td>
<td>452(^{29, 31})</td>
<td>254(^{33})</td>
</tr>
<tr>
<td>xylose</td>
<td>31.7(^{28})</td>
<td>420(^{28, 29, 31})</td>
<td>120(^a)</td>
</tr>
</tbody>
</table>

\(^a\) estimated by Ferreira et al.\(^{15}\)
\(^b\) estimated following Ferreira et al.\(^{15}\)
6.3 Results and discussion

6.3.1 Experimental studies

The solubility of the six sugars in methanol and methanol/water mixtures (0-25 wt% water) was studied at temperatures in the range of 298-353 K. Determination of the solubility of fructose at a water content higher than 10 wt% proved not possible due to stirring issues as a results of the high solid loading required by the high solubility under those conditions. The experimental results, combined with the modelled solubilities (vide infra) are shown in Figures 1-6. As expected the solubility of the sugars increased with temperature and water content. Of the sugars tested, sucrose shows by far the lowest solubility in methanol, followed by glucose and arabinose with almost equal solubility, xylose, mannose and fructose. The order was the same in methanol containing 10 wt% water, with the exception that glucose now possessed significantly better solubility than arabinose.

![Figure 1. The solubility of glucose in pure methanol and methanol/water mixtures containing up to 25 wt% water](image)
Experimental and modelling studies on the solubility of D-arabinose, D-fructose, D-glucose, D-mannose, sucrose and D-xylose in methanol and methanol-water mixtures

Figure 2. The solubility of arabinose in pure methanol and methanol/water mixtures containing up to 25 wt% water

Figure 3. The solubility of xylose in pure methanol and methanol/water mixtures containing up to 25 wt% water
Figure 4. The solubility of fructose in pure methanol and methanol/water mixtures containing up to 10 wt% water.

Figure 5. The solubility of mannose in pure methanol and methanol/water mixtures containing up to 25 wt% water.
Experimental and modelling studies on the solubility of D-arabinose, D-fructose, D-glucose, D-mannose, sucrose and D-xylose in methanol and methanol-water mixtures

**Figure 6.** The solubility of sucrose in pure methanol and methanol/water mixtures containing up to 25 wt% water

### 6.3.2 Modelling studies

The UNIQUAC binary energy interaction parameters were obtained by matching the calculated to the measured solubilities and the results are given in Table 4. The data were modelled on a mass basis to avoid possible complications due to density changes.

**Table 4.** Modelled UNIQUAC binary energy interaction parameters.

<table>
<thead>
<tr>
<th>$A_{ij}$</th>
<th>Methanol</th>
<th>water</th>
<th>arabinose</th>
<th>fructose</th>
<th>glucose</th>
<th>mannose</th>
<th>sucrose</th>
<th>xylose</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>0</td>
<td>-13.88</td>
<td>79.48</td>
<td>-6.64</td>
<td>92.31</td>
<td>13.72</td>
<td>43.73</td>
<td>37.67</td>
</tr>
<tr>
<td>water</td>
<td>167.19</td>
<td>0</td>
<td>57.73</td>
<td>65.91</td>
<td>-124.81</td>
<td>6558.79</td>
<td>-127.48</td>
<td>306.31</td>
</tr>
<tr>
<td>arabinose</td>
<td>112.39</td>
<td>-1.34</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>fructose</td>
<td>171.59</td>
<td>48.58</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>glucose</td>
<td>122.22</td>
<td>380.87</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>mannose</td>
<td>226.14</td>
<td>-225.16</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>sucrose</td>
<td>187.87</td>
<td>410.38</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>xylose</td>
<td>152.50</td>
<td>-164.80</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
</tbody>
</table>
A parity plot of experimental versus calculated values for 323 datapoints is shown in Figure 7. This figure clearly shows that the model fits the experimental results very well.

The modelling results for all sugars are given in Figures 1-6. The measured solubilities show consistent trends and the data points are all very close to the model lines, again indicating that the model fits the data very well. Deviations between the model and experimental data in the figures are mainly due to small differences in the actual water concentration in the solutions and not due to modelling inaccuracies. For instance, in the specific case of Figure 1 at 15 wt% water, the experimental points above the line were actually obtained at 16.1 wt% water in methanol and those below that at 15.6 wt% water, whereas the line represents the model prediction at a 15 wt% water content. The actual water contents were used in the model.

The average absolute error between the calculated model and the experimental data was 3.7%, which shows that the obtained models are accurate representations of the solubilities of these sugars in methanolic mixtures. As such, the high throughput technology is very well suited for this type of solubility research.

### 6.3.3 Literature comparison

The solubility of fructose, glucose and sucrose in methanol and methanol-water mixtures has been reported (Table 1). Figures 8-10 show a comparison of the experimental solubility data
obtained in this study with those previously reported. In addition, the model lines are provided. For fructose (Figure 8) agreement between our and the literature data is in general good in the range 310-325K. In addition, the combined data are predicted well using the model provided in this paper. However, at both the high and low end of the temperature range, some deviations between our model and the experimental literature data are observed. We were not able to obtain datapoints for fructose in this temperature regime (max 10 wt% fructose loading) making comparison cumbersome.

**Figure 8.** Comparison of fructose solubility vs. temperature in pure methanol (0%) and methanol with 10% by weight water (10%). Symbols: closed symbols: 0% water; open symbols: 10% water; ▲: Montañes et al.\textsuperscript{22}; ●, ◊: Macedo and Peres\textsuperscript{17}; □, ■: this work. Lines: calculated according to the model of this work.

In Figure 9 the experimental glucose data and the model developed in this work are compared with the results from literature. In pure methanol, our experimental data and those obtained by Montañes et al.\textsuperscript{22} and Macedo and Peres\textsuperscript{20} are in agreement, though the literature results are consistently slightly higher. The glucose solubilities in methanol with 10 wt% water at 313 and 333 K reported by Macedo and Peres\textsuperscript{20} are only slightly above the model line obtained in this work. At 20 wt% water content the results reported by Macedo and Peres\textsuperscript{20} are significantly higher than the model line obtained in this work.
Figure 9. Comparison of glucose solubility vs. temperature in pure methanol (0%) and methanol with 10% and 20% by weight water (10%, 20%). Symbols: closed symbols: 0% and 20% water; open symbols: 10% water; ▲: Montañes et al.\textsuperscript{22}, ◆: Macedo and Peres\textsuperscript{20}; □, ■: this work. Lines: calculated according to the model of this work.

In Figure 10 the sucrose solubility data and model from this work are compared to results from literature. At all three water concentrations given, the data reported by Macedo and Peres\textsuperscript{20} are exactly in line with the model and data obtained in this work.

Figure 10. Comparison of sucrose solubility vs. temperature in pure methanol (0%) and methanol with 10% and 20% by weight water (10%, 20%). Symbols: closed symbols: 0% and 20% water; open symbols: 10% water; ◆: Macedo and Peres\textsuperscript{20}; □, ■: this work. Lines: calculated according to the model of this work.
6.4 Conclusions

The solubilities of six sugars in methanol and methanol-water mixtures (< 25 wt% water) were successfully determined using a unique method employing Avantium high-throughput technology. This allowed the measurement of many datapoints with high accuracy and reproducibility at a wide temperature range and even above the boiling point of the solvent. The data were successfully modelled using the UNIQUAC model. The results provide valuable input for the development of efficient processes for biomass conversions in methanol, and methanol water mixtures.

6.5 Symbols

\[ A_{i,j} \] UNIQUAC binary energy interaction parameter, K

\[ \Delta C_p \] solid-liquid difference of specific heat, J mol\(^{-1}\) K\(^{-1}\)

\[ \Delta H_f \] heat of fusion, J mol\(^{-1}\)

\[ q_i \] UNIQUAC surface area parameter

\[ r_i \] UNIQUAC volume parameter

\[ S_i \] UNIQUAC parameter, \( S_i = \sum_k x_k \phi_k \tau_{k,i} \)

\[ T_f \] temperature of fusion, K

\[ x \] molar fraction, -

\[ \phi_i \] UNIQUAC parameter, \( \phi_i = r_i / \sum_k x_k r_k \)

\[ \theta_i \] UNIQUAC parameter, \( \theta_i = q_i / \sum_k x_k q_k \)

\[ \tau_{i,j} \] UNIQUAC binary interaction parameter
6.6 References


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