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# Viscosity of Multicomponent Solutions of Simple and Complex Sugars in Water

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Sugar is a key ingredient widely used in food industries mainly in the form of solution in water. Due to different physical and chemical properties, different simple and complex sugars are mixed together to obtain the optimal mixture mainly in terms of freezing point and sweetness capability. Aiming to measure some of these relevant properties, in this paper viscosity data and starting freezing temperature have been measured for a wide range of binary, ternary, and quaternary sugar solutions in water. The onset freezing temperature for solutions was calculated from DSC data, applying a new iterative numerical technique. From viscosity data, a method was developed to calculate the viscosity of multicomponent aqueous solutions of simple and complex sugars, also including temperature effects. The proposed model estimates the viscosity of a multicomponent solution by assuming the summability of the contribution from binary solution viscosity and introducing pairwise interaction parameters. The values of these parameters, as a function of temperature and composition, have been estimated from experimental data of binary and ternary solutions. Quaternary solution data have been used to check the model in a predictive way. The resultant predictions were good (error below 15 %) for diluted solutions, but agreement fails for concentrated solutions. Therefore, another parameter, taking into account ternary interactions, was added, and the model results fit the experimental data within a 10 % maximum error over the entire concentration and temperature range.

## Introduction

Sugars are key ingredients for several areas of food production, such as the confectionery,[1] the ice cream production,[2] and the bakery[3] industries. It is well-known that monosaccharides with the same molecular weight show either different behavior or different thermodynamic properties, such as solution freezing point, sweetening capability, and viscosity. This aspect can be fructuously used by the manufacturers with the aim to obtain a solution having the desired sweetening ability or viscosity by mixing different simple and complex sugars. To reduce trials in this concern, it would be helpful to have a predictive model that is able to predict the viscosity of the multicomponent solution on the basis of the viscosity of the binary water−sugar solution, and a thermodynamic model has been recently proposed to predict these properties.[4]

Even though nonelectrolyte solutions (such as sugars in water) have been investigated from different points of view,[5−6] only a few models have been proposed for viscosity prediction of the binary solution. Mathlouthi and Genotelle (1995)[5] proposed an additive mixing rule, whereas Chirife and Buera (1997)[7] based their model on the extension of the electrolyte solution theoretical model. Even though different mixtures of sugars are widely used in the food industry, especially for ice cream production, the open literature reports only a few viscosity measurements of multicomponent sugar in water solutions, as a function of composition and temperature.[8] In this single case, theoretical modeling is based on isopiestic binary solution value summability.[4]

With the aim to fill the gap in the available measured properties, first, DSC (differential scanning calorimetry) measurements have been performed to determine the onset freezing temperature of any mixture. In this way, the minimum temperature at which no solid phase is present, i.e., the lower-temperature boundary to perform monophase measurements, was identified. Viscosity measurements were then performed on binary, ternary, and quaternary mixtures at various temperatures above their freezing point. The aim was to correlate the viscosity of the multicomponent solution to those of the binary mixtures at the same sugar molar fraction and temperature, by using a simple mixing rule including binary or ternary interaction parameters.

Data of binary solutions have been used to identify a model to calculate the viscosity of a single sugar in water solution as a function of temperature and sugar mass fraction. On this basis, a general model, based on mixing rules and binary interaction parameters, is proposed to calculate the viscosity of multicomponent sugar solutions at different temperatures. Interaction parameters have been calculated and fitted using ternary solution data, and the application to quaternary solutions in a predictive way showed that ternary interactions were not negligible when increasing the sugar content. Therefore, the model has been improved including another parameter depending upon the sugar type and temperature.

## Materials and Methods

***Sample Preparation.*** Samples were prepared by adding, to distilled water, powder sugars of laboratory grade (> 99 %): D(+)-glucose (abbreviated "Gl") from BDH (UK), D(+)-galactose ("Ga") from Fluka (Switzerland), sucrose ("Su"), and fructose ("Fr") from Alfa Aesar (UK). Solutes were gently added to water at 40 °C while stirring with a magnetic stirrer (ARE

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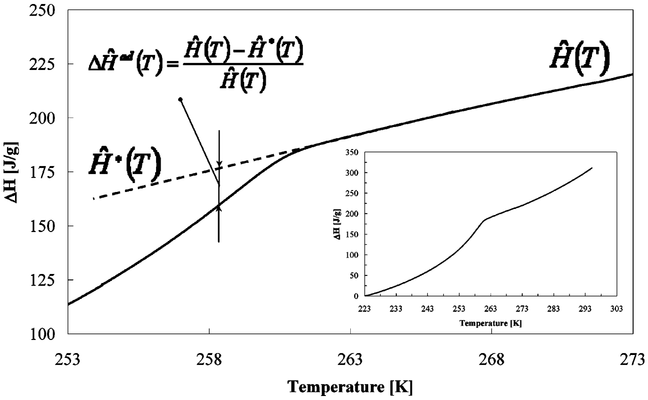

**Figure 1.** Enthalpy curve and onset freezing temperature calculation. Example for fructose 70 % [w/w] solution.

Velp Scientifica, Italy). After complete dissolution, samples were left for 1 h in a controlled temperature bath at 4 °C. Binary mixture concentration ranges (w/w %) were: Fr, 5 % to 70 %; Ga, 5 % to 50 %; Gl, 5 % to 50 %; and Su, 10 % to 60 %.

Ternary solutions were prepared for any pair of sugars at the following concentrations (w/w %): 10 % - 10 %, 20 % - 10 %, 10 % - 20 %, 20 % - 20 %, 30 % - 20 %, 20 % - 30 %, 30 % - 30 %.

Quaternary solutions were prepared for the following combination of sugars, Fr/Gl/Su, Fr/Ga/Su, and Ga/Gl/Su, at the following concentrations (w/w %), 5 % - 5 % - 5 %, 10 % - 10 % - 10 %, 15 % - 15 % - 15 %, and 20 % - 20 % - 20 %.

***Freezing Point Determination.*** Differential scanning calorimetric (from now on abbreviated as DSC) measurements (TA60 Shimadzu, Japan) have been performed to determine the initial freezing point of each solution. A sample weighing between 10 and 15 mg was placed in an aluminum open pan (volume 29.2 mm$^3$) and quenched at −50 °C. The measurement started by increasing the temperature with a 2 °C·min$^{-1}$ heating rate up to −35 °C and standing for 5 min at this temperature. Afterward, the sample was heated with a 2 °C·min$^{-1}$ heating rate up to 20 °C; at this temperature, water evaporation was still reasonably negligible. The raw instrument output was the power supplied to the sample *W*, and applying the energy balance without energy loss, the sugar enthalpy change can be directly calculated by integrating the *W* vs time curve.

All the calculated enthalpy variations, assuming zero enthalpy at −50 °C, show a sigmoid shape (Figure 1), indicating that the solution does not have a single freezing temperature. While cooling, progressive ice formation makes the solution more and more concentrated, decreasing the freezing temperature as a consequence.[9]

To determine the lower-temperature limit for viscosity measurements, avoiding the presence of ice crystals, the evaluation of the initial starting freezing temperature, $T_f$ (temperature when the freezing process starts), is needed. The following iterative procedure was used to estimate $T_f$: starting from higher and going to lower temperatures, a first estimation $T_f^*$ was obtained by visual inspection, where the measured enthalpy $\hat{H}(T)$ curve diverges from local linearity. A local linearization is done in the range [$T_f^*$; $T_f^* + 3$ °C] and the parameters (slope and intercept) of the enthalpy straight line $\hat{H}^*(T)$ were calculated (Figure 1). The linear $\hat{H}^*(T)$ was then calculated over the whole temperature range, and the dimensionless difference $\Delta\hat{H}^{ad}(T)$ between the calculated linear and the measured value was determined.

$$\Delta\hat{H}^{ad}(T) = \frac{\hat{H}(T) - \hat{H}^*(T)}{\hat{H}(T)} \tag{1}$$

**Table 1. Initial Freezing Point for Binary Solutions**

| sugar w/w % | fructose $T_f$ °C | sucrose $T_f$ °C | D(+)-galactose $T_f$ °C | D(+)-glucose $T_f$ °C |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 5 | −0.2 | −0.5 | −1.7 | −0.1 |
| 10 | −0.6 | −0.9 | −1.9 | −0.2 |
| 20 | −2.9 | −1.5 | −3.9 | −3.5 |
| 30 | −5.0 | −2.9 | −4.2 | −4.2 |
| 40 | −7.8 | −4.5 | −6.6 | −8.0 |
| 50 | −10.5 | −9.3 |  | −12.0 |
| 60 | −12.0 | −13.0 |  |  |

The new value of $T_f$ is determined by assuming a minimum difference criterion, compromising between the calculated and experimental data accuracies

$$\Delta\hat{H}^{ad}(T_f) \leq 0.005 \tag{2}$$

The process was repeated assuming the calculated $T_f$ as the new estimation, and less than five cycles were always sufficient for converging to a constant $T_f$ value.

***Viscosity Measurements.*** Viscosity measurements were performed using a controlled-strain rheometer (ARES-RFS, TA Instruments, USA), equipped with a bob and cup geometry (bob diameter 32 mm, gap 1 mm). Temperature was controlled by means of a thermostatic bath (Julabo, USA) by circulating a mixture of ethylene-glycol and water in the external jacket of the cylinder. The sample was stored in a controlled-temperature bath (Julabo, USA) at the same temperature as the measurements for 2 h, and after loading onto the cylinder, it was left for a further 180 s to equilibrate the temperature.

Flow curves have been measured in the shear rate range 0.1 to 1000 s$^{-1}$, sampling five points for each shear rate decade. A preliminary "step shear rate" test, for the more viscous solutions at low temperatures, showed that 10 s was enough to reach the steady state when the shear rate is at the lower boundary of the range (0.1 s$^{-1}$); this waiting time was therefore fixed for all measurements after changing the shear rate.

The steady shear viscosity was measured during 10 s, and all the data were automatically elaborated from the instrument as the average in this considered measuring interval.

Measurements were performed at 20 °C, 10 °C, 5 °C, 0 °C, −5 °C, and −10 °C when the two last values were higher than the freezing point of the solution.

All samples showed Newtonian behavior in the investigated range, being the viscosity constant with respect to the applied shear rate. Every test was performed three times, and a single average value was calculated as the arithmetic average of all the measured data over the entire shear rate range. The reproducibility of data was rather good, showing a maximum standard error within 5 %.

## Binary Solutions

***Freezing Point.*** According to the proposed technique, data for the freezing temperatures of the binary mixtures are reported in Table 1 with a maximum error of 5 %. Except for D(+)-glucose, data have been compared to some open literature data available for low sugar content solutions[10] showing a similar trend (Figure 2).

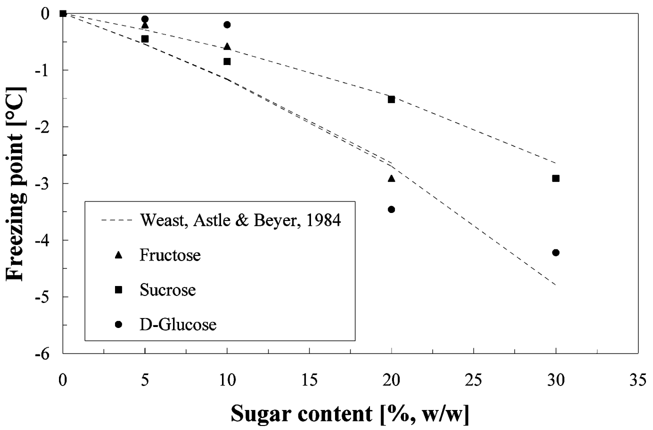

**Figure 2.** Freezing point of a binary mixture compared to literature data.

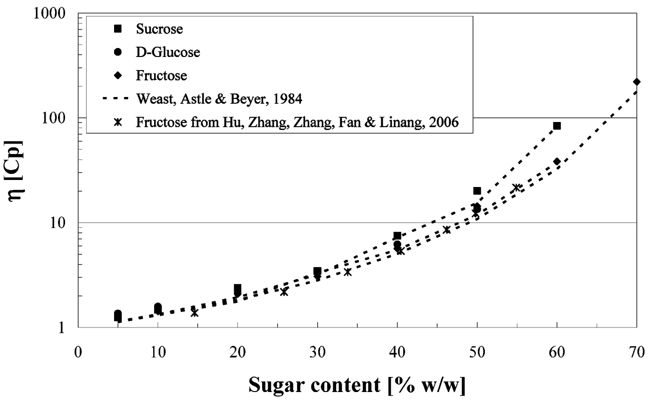

**Figure 3.** Comparison between experimental data and a literature reference for viscosity of sucrose, fructose, and D(+)-glucose solutions at 293 K.

***Viscosity.*** Viscosity data for binary mixtures are reported in Table 2. A good agreement was found when experimental results were compared with some open literature data[8,10] at room temperature (Figure 3) and, only for fructose, with data at different temperatures and sugar contents (Figure 4, comparison with open literature data[11]).

Data have been fitted according to the evidence that viscosity depends upon $T$ according to a classic activated process,[12] and it may be calculated assuming a reference temperature $T_0$

$$\eta(T, x) = \eta_0(x)\cdot e^{\left(\frac{E_a(x)}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)} \tag{3}$$

$T_0$ was assumed to be 293 K, and both the pre-exponential parameter and activation energy were assumed to be dependent on the sugar molar concentration $x$. The best fit curves were determined, using commercial software (TableCurve 3D-Jandel

**Table 2. Viscosity Data for Binary Solutions**

| | | fructose | | D(+)-galactose | | D(+)-glucose | | sucrose | |
|---|---|---|---|---|---|---|---|---|---|
| sugar | temp | viscosity | std. error | viscosity | std. error | viscosity | std. error | viscosity | std. error |
| [w/w %] | K | mPa•s | mPa•s | mPa•s | mPa•s | mPa•s | mPa•s | mPa•s | mPa•s |
| 5 | 293.15 | 1.26 | 0.12 | 1.397 | 0.093 | 1.36 | 0.14 | 1.246 | 0.082 |
| 5 | 283.15 | 1.681 | 0.042 | 1.699 | 0.042 | 1.76 | 0.15 | 1.72 | 0.16 |
| 5 | 278.15 | 1.999 | 0.066 | 2.077 | 0.086 | 1.98 | 0.17 | 1.91 | 0.19 |
| 5 | 273.15 | 2.345 | 0.061 | 2.42 | 0.11 | 2.39 | 0.25 | 2.450 | 0.14 |
| 10 | 293.15 | 1.43 | 0.15 | 1.52 | 0.15 | 1.58 | 0.18 | 1.48 | 0.14 |
| 10 | 283.15 | 1.991 | 0.087 | 2.107 | 0.033 | 2.02 | 0.14 | 2.02 | 0.14 |
| 10 | 278.15 | 2.440 | 0.078 | 2.40 | 0.12 | 2.470 | 0.173 | 2.472 | 0.055 |
| 10 | 273.15 | 2.89 | 0.14 | 2.779 | 0.13 | 2.908 | 0.13 | 2.978 | 0.22 |
| 15 | 293.15 | – | – | 1.77 | 0.13 | – | – | – | – |
| 15 | 283.15 | – | – | 2.469 | 0.088 | – | – | – | – |
| 15 | 278.15 | – | – | 2.77 | 0.10 | – | – | – | – |
| 15 | 273.15 | – | – | 3.325 | 0.077 | – | – | – | – |
| 20 | 293.15 | 2.092 | 0.053 | 2.10 | 0.10 | 2.13 | 0.11 | 2.38 | 0.18 |
| 20 | 283.15 | 2.859 | 0.093 | 2.76 | 0.19 | 2.930 | 0.097 | 3.01 | 0.16 |
| 20 | 278.15 | 3.39 | 0.22 | 3.37 | 0.20 | 3.46 | 0.19 | 3.48 | 0.15 |
| 20 | 273.15 | 4.20 | 0.12 | 4.27 | 0.13 | 4.30 | 0.24 | 4.42 | 0.10 |
| 30 | 293.15 | 3.07 | 0.16 | 3.27 | 0.28 | 3.46 | 0.11 | 3.46 | 0.17 |
| 30 | 283.15 | 4.45 | 0.15 | 4.57 | 0.24 | 4.83 | 0.12 | 5.06 | 0.10 |
| 30 | 278.15 | 5.50 | 0.11 | 5.34 | 0.13 | 5.94 | 0.11 | 5.99 | 0.12 |
| 30 | 273.15 | 6.39 | 0.33 | 6.93 | 0.29 | 8.17 | 0.10 | 7.19 | 0.21 |
| 30 | 268.15 | 7.97 | 0.13 | 8.95 | 0.55 | – | – | – | – |
| 40 | 293.15 | 5.67 | 0.12 | 6.11 | 0.15 | 6.21 | 0.11 | 7.53 | 0.27 |
| 40 | 283.15 | 8.07 | 0.15 | 9.00 | 0.21 | 9.63 | 0.27 | 11.31 | 0.51 |
| 40 | 278.15 | 10.84 | 0.22 | 11.17 | 0.20 | 11.19 | 0.81 | 14.22 | 0.23 |
| 40 | 273.15 | 14.02 | 0.35 | 14.56 | 0.43 | 15.28 | 0.22 | 19.81 | 0.42 |
| 40 | 268.15 | 18.51 | 0.17 | 18.84 | 0.50 | – | – | 25.48 | 0.29 |
| 50 | 293.15 | 14.33 | 0.29 | – | – | 13.43 | 0.20 | 20.09 | 0.50 |
| 50 | 283.15 | 19.44 | 0.48 | – | – | 20.52 | 0.56 | 31.33 | 0.39 |
| 50 | 278.15 | 25.27 | 0.35 | – | – | 26.54 | 0.52 | 42.93 | 0.41 |
| 50 | 273.15 | 35.06 | 0.19 | – | – | 37.31 | 0.47 | 66.8 | 1.0 |
| 50 | 268.15 | 54.8 | 1.2 | – | – | 50.80 | 0.72 | 92.4 | 1.8 |
| 60 | 293.15 | 38.31 | 0.43 | – | – | – | – | 83.9 | 1.4 |
| 60 | 283.15 | 72.0 | 1.5 | – | – | – | – | 153.1 | 2.0 |
| 60 | 278.15 | 103.4 | 2.0 | – | – | – | – | 228.9 | 21 |
| 60 | 273.15 | 148.7 | 2.4 | – | – | – | – | 316.5 | 3.5 |
| 60 | 268.15 | 238.0 | 3.7 | – | – | – | – | 491.8 | 6.4 |
| 70 | 293.15 | 220.7 | 4.6 | – | – | – | – | – | – |
| 70 | 283.15 | 509.4 | 5.6 | – | – | – | – | – | – |
| 70 | 278.15 | 843 | 12 | – | – | – | – | – | – |
| 70 | 273.15 | 1418 | 42 | – | – | – | – | – | – |
| 70 | 268.15 | 2446 | 81 | – | – | – | – | – | – |
| 70 | 263.15 | 4270 | 140 | – | – | – | – | – | – |

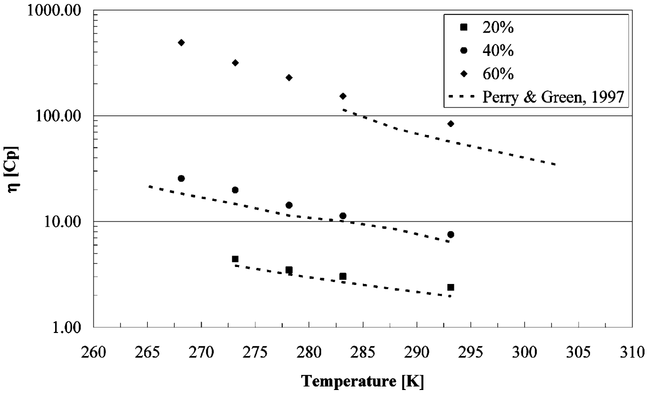

**Figure 4.** Comparison between experimental data and a literature reference for viscosity of a sucrose solution in water at different temperatures and sugar contents.

**Table 3. Fitting Parameters of Equations 3 to 5**

| | $a$ | $b$ | $c$ | α | $\beta$ | $r^2$ |
|---|---|---|---|---|---|---|
| | | | Fructose | | | |
| value | −0.1286 | 28.92 | 0.0433 | 3387.1 | 125254 | 0.999 |
| std. error | 0.3709 | 4.71 | 0.5647 | 518.4 | 14511 | |
| | | | D(+)-Galactose | | | |
| value | 0.0944 | 24.72 | −1.0089 | 2696.9 | 261926 | 0.999 |
| std. error | 0.0410 | 1.88 | 0.9337 | 157.4 | 46179 | |
| | | | D(+)-Glucose | | | |
| value | −0.0165 | 33.93 | 2.6455 | 2816.3 | 212736 | 0.999 |
| std. error | 0.1138 | 3.66 | 1.2329 | 375.5 | 47671 | |
| | | | Sucrose | | | |
| value | −0.3864 | 73.39 | 1.8710 | 3988.2 | 320711 | 0.998 |
| std. error | 0.4329 | 15.19 | 2.3405 | 674.2 | 128542 | |

**Table 4. Initial Freezing Point for Ternary Solutions**[a]

| | | soln 1 | soln 2 | soln 3 | soln 4 | soln 5 | soln 6 |
|---|---|---|---|---|---|---|---|
| sugar A | sugar B | $T_f$ | $T_f$ | $T_f$ | $T_f$ | $T_f$ | $T_f$ |
| [w/w %] | [w/w %] | °C | °C | °C | °C | °C | °C |
| 10 | 10 | −1.3 | −1.2 | −0.3 | −1.7 | −0.5 | −0.1 |
| 10 | 20 | −3.3 | −3.2 | −1.1 | −3.2 | −1.8 | −2.3 |
| 20 | 10 | −3.4 | −4.0 | −2.8 | −2.7 | −2.3 | −2.0 |
| 20 | 20 | −7.0 | −7.4 | −4.5 | −7.1 | −5.4 | −5.4 |
| 20 | 30 | −13.7 | −13.0 | −9.0 | −12.0 | −9.1 | −8.6 |
| 30 | 20 | −11.8 | −11.4 | −10.2 | −12.1 | −9.8 | −9.2 |
| 30 | 30 | − | − | −15.0 | −18.9 | −14.9 | −15.5 |

[a] Solution (soln) number: Sugar A, Sugar B; 1, Fr−Ga; 2, Fr−Gl; 3, Fr−Su; 4, Ga−Gl; 5, Ga−Su; 6, Gl−Sa.

Sci., USA), as follows

$$\ln[\eta_0(x)] = \frac{(a + b\cdot x)}{(1 + cx)} \tag{4}$$

$$\frac{E_a(w)}{R} = \alpha + \beta x^2 \tag{5}$$

Table 3 shows fitting parameters for each sugar; a good agreement was found between measured and calculated values, as shown in Figure 5 (maximum error below 10 %).

## Ternary Solutions

***Freezing Point.*** According to the proposed technique, data of freezing temperatures of the ternary mixtures are reported in Table 4 showing a maximum error of 5 %.

***Viscosity.*** Viscosity data for ternary solutions are reported in Table 5. Experimental data have been correlated with the solution composition and temperature by averaging the viscosity of the binary solutions. The proposed mixing rule includes the contribution of the viscosity of every binary solution containing the same amount of each sugar as the multicomponent solution. Referring to a general multicomponent solution $S_1-S_2-S_3-A$, where $S_i$ is solute and A is the solvent, the overall sugar molar fraction $x_t$ is

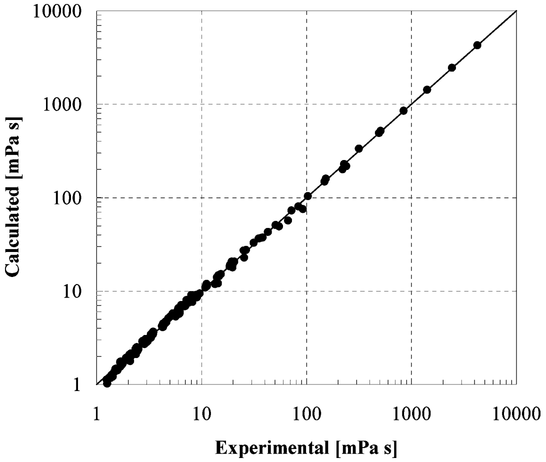

**Figure 5.** Comparison of viscosity data of a binary solution from experimental data and prediction of eqs 3 to 5.

$$x_t = \frac{\sum_i n_S i}{\sum_i n_S i + n_A} \tag{6}$$

where $n$ is the number of moles. For the same solution, the equivalent binary solution molar fraction for each sugar $\bar{x}_i$ can be calculated as follows considering only the $i$th sugar and water

$$\bar{x}_i = \frac{n_S i}{n_S i + n_A} \tag{7}$$

$\chi_i$, the molar fraction of the $i$th sugar in the solution on a water-free basis, avoiding water moles can be expressed as

$$\chi_i = \frac{n_S i}{\sum_j n_{S_j}} \tag{8}$$

Using these definitions, for the viscosity of a multicomponent solution, the following mixing rule is proposed

$$\log_{10}\eta(x_t) = \sum_i[\chi_i \log_{10}\eta_i(\bar{x}_i)] + \frac{1}{2}\sum_i\sum_{j\neq i}(\chi_i\chi_j k_{ij}) \tag{9}$$

where $k_{ij}$ is the binary interaction parameter, taking into account nonideal behavior as a result of binary interactions.

It was observed that $k_{ij}$ depends, in principle, upon temperature, composition, and the sugar pair, and if a reciprocity rule is assumed (i.e., $k_{ij} = k_{ji}$), eq 9 can be employed to evaluate $k_{ij}$ as

$$k_{ij} = \frac{\sum_i[\chi_i \log_{10}\eta_i(\bar{x}_i)] - \log_{10}\eta(x_t)}{\chi_i\chi_j} \tag{10}$$

**Table 5. Viscosity Data for Ternary Solutions**

| | | | $T = 20$ °C | | $T = 10$ °C | | $T = 5$ °C | | $T = 0$ °C | | $T = -5$ °C | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | sugar A | sugar B | viscosity | std. error | viscosity | std. error | viscosity | std. error | viscosity | std. error | viscosity | std. error |
| | [w/w %] | [w/w %] | mPa•s | mPa•s | mPa•s | mPa•s | mPa•s | mPa•s | mPa•s | mPa•s | mPa•s | mPa•s |
| fructose (A) − D(+)-galactose (B) | 10 | 10 | 2.16 | 0.08 | 2.93 | 0.08 | 3.46 | 0.10 | 4.00 | 0.14 | − | − |
| | 10 | 20 | 3.32 | 0.11 | 4.61 | 0.13 | 5.70 | 0.17 | 6.78 | 0.13 | − | − |
| | 20 | 10 | 3.18 | 0.12 | 4.44 | 0.16 | 5.59 | 0.09 | 6.68 | 0.10 | − | − |
| | 20 | 20 | 5.85 | 0.14 | 8.70 | 0.17 | 10.66 | 0.14 | 13.97 | 0.18 | 19.11 | 0.36 |
| | 20 | 30 | 12.65 | 0.13 | 20.43 | 0.38 | 27.17 | 0.64 | 36.57 | 0.73 | 49.64 | 0.93 |
| | 30 | 20 | 12.23 | 0.38 | 19.93 | 0.40 | 27.34 | 0.47 | 35.22 | 0.83 | 53.14 | 0.72 |
| | 30 | 30 | 32.89 | 1.62 | 65.91 | 1.11 | 90.67 | 0.92 | 148.5 | 4.7 | 236.0 | 10.0 |
| fructose (A) − D(+)-glucose (B) | 10 | 10 | 2.17 | 0.17 | 2.86 | 0.15 | 3.55 | 0.11 | 4.39 | 0.14 | − | − |
| | 10 | 20 | 3.41 | 0.09 | 4.72 | 0.17 | 5.84 | 0.26 | 7.19 | 0.15 | 8.96 | 0.43 |
| | 20 | 10 | 3.35 | 0.16 | 4.65 | 0.22 | 5.58 | 0.09 | 7.23 | 0.31 | 9.05 | 0.30 |
| | 20 | 20 | 6.07 | 0.05 | 8.84 | 0.10 | 11.07 | 0.16 | 13.97 | 0.23 | 18.47 | 0.20 |
| | 20 | 30 | 13.34 | 0.65 | 21.69 | 0.50 | 28.60 | 0.41 | 39.07 | 0.91 | 51.10 | 1.20 |
| | 30 | 20 | 12.88 | 0.32 | 20.94 | 0.36 | 26.43 | 0.76 | 37.07 | 0.68 | 52.40 | 0.66 |
| | 30 | 30 | 31.30 | 1.60 | 57.80 | 2.30 | 90.60 | 2.30 | 136.6 | 3.1 | 200.4 | 4.4 |
| fructose (A) − sucrose (B) | 10 | 10 | 2.21 | 0.10 | 2.89 | 0.09 | 3.44 | 0.11 | 4.16 | 0.11 | − | − |
| | 10 | 20 | 3.42 | 0.13 | 4.77 | 0.07 | 5.69 | 0.21 | 7.17 | 0.12 | − | − |
| | 20 | 10 | 3.33 | 0.07 | 4.58 | 0.09 | 5.39 | 0.10 | 6.91 | 0.12 | − | − |
| | 20 | 20 | 6.13 | 0.09 | 8.72 | 0.28 | 10.48 | 0.41 | 14.95 | 0.45 | 19.62 | 0.12 |
| | 20 | 30 | 14.02 | 0.19 | 22.96 | 0.49 | 31.15 | 0.68 | 41.45 | 1.28 | 61.62 | 0.87 |
| | 30 | 20 | 14.07 | 0.23 | 22.25 | 0.37 | 27.74 | 0.36 | 36.62 | 0.47 | 47.19 | 0.77 |
| | 30 | 30 | 47.90 | 0.84 | 85.70 | 2.00 | 127.3 | 4.7 | 194.7 | 3.8 | 315.0 | 12.0 |
| D(+)-galactose (A) − D(+)-glucose (B) | 10 | 10 | 2.14 | 0.08 | 2.94 | 0.10 | 3.53 | 0.19 | 4.49 | 0.20 | − | − |
| | 10 | 20 | 3.40 | 0.12 | 4.82 | 0.18 | 5.94 | 0.13 | 6.99 | 0.19 | − | − |
| | 20 | 10 | 3.29 | 0.11 | 4.73 | 0.12 | 5.66 | 0.14 | 6.68 | 0.26 | − | − |
| | 20 | 20 | 5.90 | 0.08 | 8.72 | 0.38 | 10.61 | 0.26 | 13.83 | 0.24 | 18.01 | 0.22 |
| | 20 | 30 | 13.59 | 0.19 | 21.74 | 0.19 | 28.09 | 0.67 | 37.39 | 0.75 | 54.27 | 0.70 |
| | 30 | 20 | 13.50 | 0.42 | 21.75 | 0.50 | 28.24 | 0.53 | 37.51 | 0.85 | 52.00 | 1.30 |
| | 30 | 30 | 39.23 | 0.39 | 70.76 | 0.66 | 98.15 | 0.12 | 133.7 | 3.10 | 179.7 | 3.3 |
| D(+)-galactose (A) − sucrose (B) | 10 | 10 | 2.14 | 0.14 | 2.98 | 0.09 | 3.54 | 0.12 | 4.27 | 0.09 | − | − |
| | 10 | 20 | 3.58 | 0.09 | 4.98 | 0.10 | 5.97 | 0.16 | 7.45 | 0.13 | − | − |
| | 20 | 10 | 3.40 | 0.09 | 4.84 | 0.10 | 5.98 | 0.11 | 7.55 | 0.03 | − | − |
| | 20 | 20 | 6.14 | 0.10 | 9.48 | 0.46 | 12.01 | 0.14 | 15.80 | 0.10 | 21.35 | 0.11 |
| | 20 | 30 | 15.68 | 0.23 | 24.93 | 0.63 | 33.26 | 0.49 | 41.74 | 0.70 | 61.15 | 0.68 |
| | 30 | 20 | 14.98 | 0.39 | 24.47 | 0.44 | 31.82 | 0.88 | 42.15 | 0.81 | 59.70 | 1.00 |
| | 30 | 30 | 53.00 | 1.10 | 95.80 | 1.00 | 128.9 | 1.3 | 200.2 | 4.5 | 322.7 | 3.3 |
| D(+)-glucose (A) − sucrose (B) | 10 | 10 | 2.27 | 0.06 | 2.98 | 0.11 | 3.53 | 0.13 | 4.37 | 0.23 | − | − |
| | 10 | 20 | 3.55 | 0.14 | 4.92 | 0.19 | 5.89 | 0.15 | 7.42 | 0.20 | 9.26 | 0.27 |
| | 20 | 10 | 3.47 | 0.23 | 4.89 | 0.13 | 5.75 | 0.22 | 7.47 | 0.13 | 9.23 | 0.30 |
| | 20 | 20 | 6.46 | 0.12 | 9.42 | 0.14 | 12.03 | 0.17 | 15.42 | 0.21 | 19.58 | 0.11 |
| | 20 | 30 | 16.05 | 0.28 | 24.59 | 0.41 | 33.15 | 0.60 | 46.22 | 0.50 | 63.90 | 1.50 |
| | 30 | 20 | 14.50 | 0.37 | 23.08 | 0.37 | 31.72 | 0.45 | 43.33 | 0.48 | 59.31 | 0.64 |
| | 30 | 30 | 52.96 | 0.93 | 100.2 | 2.1 | 131.2 | 2.3 | 191.8 | 1.5 | 332.4 | 4.9 |

$k_{ij}$ was found to be dependent upon temperature and overall molar fraction for each sugar pair but weakly dependent upon the relative amount of the two sugars, also justifying the reciprocity assumption. The following dependence is proposed as the "best fitting" of data

$$k_{ij}(x_t, T) = \frac{1}{2\left(k_1 + \frac{k_2}{T^2} + k_3 x_t\right)} \qquad (11)$$

Values of parameters, as calculated using the same commercial software, are reported in Table 6 for the sugar pairs investigated. Data calculated from eqs 9 to 11 have been compared with experimental data in Figure 6, and a good agreement was found (maximum error of 9.5 %).

## Quaternary Solutions

***Freezing Point.*** Freezing temperatures of the quaternary mixtures are reported in Table 7, and a maximum experimental error of 5 % was found.

***Viscosity.*** Viscosity of quaternary solutions has been measured following the above proposed method, and experimental results are reported in Table 8; data have also been compared to predictions of the proposed model. It is worthy to point out that in this case the model is purely predictive because binary

**Table 6. Fitting Parameters of Equations 9 to 11**

| | $k_1$ | $k_2$ | $k_3$ | $r^2$ |
|---|---|---|---|---|
| | | Fructose−D(+)-Galactose | | |
| value | 0.1616 | −14482 | 0.0166 | 0.997 |
| std. error | 0.0105 | 768 | 0.0003 | |
| | | Fructose−D(+)-Glucose | | |
| value | 0.1519 | −13341 | 0.0164 | 0.996 |
| std. error | 0.0136 | 1004 | 0.0003 | |
| | | Fructose−Sucrose | | |
| value | 0.0865 | −9432 | 0.0123 | 0.995 |
| std. error | 0.0122 | 894 | 0.0003 | |
| | | D(+)-Galactose−D(+)-Glucose | | |
| value | 0.1012 | −10307 | 0.0176 | 0.996 |
| std. error | 0.0167 | 1226 | 0.0004 | |
| | | D(+)-Galactose−Sucrose | | |
| value | 0.1014 | −10152 | 0.0116 | 0.993 |
| std. error | 0.0104 | 759 | 0.0002 | |
| | | D(+)-Glucose−Sucrose | | |
| value | 0.1043 | −10683 | 0.0121 | 0.997 |
| std. error | 0.0095 | 697 | 0.0002 | |

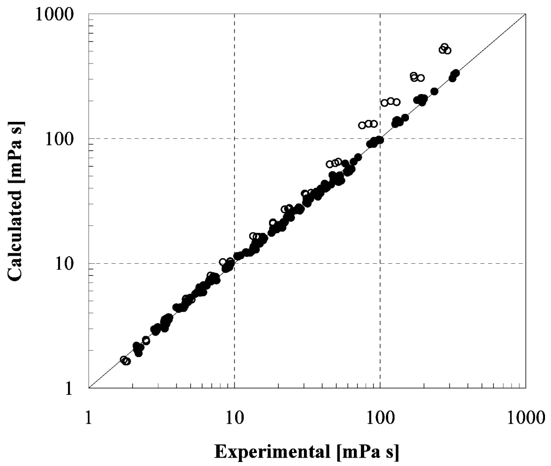

**Figure 6.** Comparison of viscosity data of ternary solutions (closed circles) and quaternary solutions (open circles) from experimental data and prediction of eqs 9 to 11.

**Table 7. Initial Freezing Point for Quaternary Solutions**[a]

| sugar A | sugar B | sugar C | soln 1 | soln 2 | soln 3 |
|---|---|---|---|---|---|
| | | | $T_f$ | $T_f$ | $T_f$ |
| [w/w %] | [w/w %] | [w/w %] | °C | °C | °C |
| 5 | 5 | 5 | −0.8 | −0.8 | −1 |
| 10 | 10 | 10 | −2.43 | −2.27 | −2.67 |
| 15 | 15 | 15 | −7.07 | −6.59 | −7.46 |
| 20 | 20 | 20 | −16.14 | −16.18 | −16.88 |

[a] Solution (soln) number: Sugar A, Sugar B, Sugar C; 1, Fr−Ga−Gl; 2, Fr−Ga−Sa; 3, Ga−Gl−Su.

interaction parameters were used as calculated from eqs 10 to 11 for every pair of sugars in the quaternary solution.

Figure 6 shows the comparison between experimental data and values calculated from the predictive model: a good agreement (error below 15 %) was found for solutions with a weight fraction of sugars up to 0.45, whereas a much larger error in prediction (maximum 95 %) was found when the model was applied to 60 % sugar content solutions.

The failure of predictions at high concentrations may be explained because only binary interactions are taken into account by the model. In fact, although for diluted solutions the effect of ternary interactions may be neglected, they have to be accounted for when increasing the sugar content.

In this respect, the model has been amended taking into account also ternary interactions using a $m_{ijk}$ parameter as follows

$$\log_{10}\eta(x_t) = \sum_i[\chi_i \log_{10}\eta_i(x_i)] + \frac{1}{2}[\sum_i\sum_{j\neq i}(\chi_i\chi_j k_{ij})] + \frac{1}{2}(\chi_i\chi_j\chi_k m_{ijk})_{i\neq j\neq k} \qquad (12)$$

Using the same technique as that in eq 10, parameters $m_{ijk}$ have been calculated for the quaternary investigated system from eq 12.

Also, this interaction parameter was found to be dependent upon temperature, total sugar mass fraction, and type of (group of three) sugars. The following correlation has been proposed to interpolate calculated $m_{ijk}$ values

$$m_{ijk}(x_t, T) = \frac{1}{m_1 + m_2T^3 + m_3\ln(x_t)} \qquad (13)$$

Table 9 reports values of the parameters calculated from eq 13.

The effect of the ternary interaction parameters improves the model prediction capability, reducing the maximum difference between estimated viscosity and experimental values to less than 10 % as shown in Figure 7.

## Conclusions

In this paper, viscosity measurements and starting freezing points of a wide range of sugars (either mono- or disaccharides) in water solutions have been presented. DSC measurements have been interpreted using an iterative procedure to estimate the freezing temperature of aqueous solutions that does not show a clear and sharp transition. The criterion is based on an estimate of the point where the enthalpy curves diverge from local linear behavior.

As for viscosity, all samples showed Newtonian behavior, and a classic “Arrhenius-type” activated process rule has been adopted to interpolate viscosity data against temperature for binary solutions. A simple model has also been proposed, which is able to calculate the viscosity of ternary and quaternary sugar solutions, starting from the viscosity of binary solutions using pairwise interaction parameters. Data from experiments on ternary solutions have been used to evaluate $k_{ij}$ values, and the model has been tested to predict quaternary solution behavior.

The interaction parameters $k_{ij}$ showed a strong nonlinear dependence on the total amount of sugar, type of sugar, and temperature, but a fair dependence has been found on the relative amount of the two involved sugars. Therefore, an exponential dependence was assumed on sugar amount and temperature, revealing the possibility to assume an “Arrhenius-type” activated process. Application of the model to ternary solutions showed

**Table 8. Viscosity Data for Quaternary Solutions**

| | composition | | | $T$ = 20 °C | $T$ = 20 °C | $T$ = 10 °C | $T$ = 10 °C | $T$ = 5 °C | $T$ = 5 °C | $T$ = 0 °C | $T$ = 0 °C | $T$ = −5 °C | $T$ = −5 °C |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | [w/w] | | | viscosity | std. error | viscosity | std. error | viscosity | std. error | viscosity | std. error | viscosity | std. error |
| | % | % | % | mPa·s | mPa·s | mPa·s | mPa·s | mPa·s | mPa·s | mPa·s | mPa·s | mPa·s | mPa·s |
| fructose<br>D(+)-galactose<br>sucrose | 5 | 5 | 5 | 1.75 | 0.15 | 2.48 | 0.18 | 2.82 | 0.13 | 3.42 | 0.11 | – | – |
| | 10 | 10 | 10 | 3.37 | 0.15 | 4.66 | 0.16 | 5.76 | 0.11 | 6.87 | 0.29 | – | – |
| | 15 | 15 | 15 | 9.36 | 0.55 | 13.46 | 0.16 | 18.44 | 0.15 | 23.85 | 0.68 | 33.61 | 0.49 |
| | 20 | 20 | 20 | 49.26 | 0.31 | 83.49 | 1.07 | 118.44 | 1.26 | 170.3 | 1.9 | 277.6 | 2.7 |
| fructose<br>D(+)-glucose<br>sucrose | 5 | 5 | 5 | 1.84 | 0.04 | 2.48 | 0.04 | 2.94 | 0.10 | 3.35 | 0.12 | – | – |
| | 10 | 10 | 10 | 3.38 | 0.05 | 4.64 | 0.16 | 5.85 | 0.09 | 7.20 | 0.12 | – | – |
| | 15 | 15 | 15 | 8.36 | 0.16 | 14.74 | 0.11 | 18.48 | 0.10 | 23.42 | 0.24 | 30.50 | 0.30 |
| | 20 | 20 | 20 | 45.20 | 0.49 | 75.31 | 2.00 | 107.36 | 3.18 | 172.2 | 2.7 | 268.8 | 4.1 |
| D(+)-galactose<br>D(+)-glucose<br>sucrose | 5 | 5 | 5 | 1.80 | 0.04 | 2.49 | 0.09 | 2.89 | 0.08 | 3.33 | 0.13 | – | – |
| | 10 | 10 | 10 | 3.48 | 0.10 | 5.09 | 0.15 | 5.92 | 0.10 | 7.16 | 0.24 | – | – |
| | 15 | 15 | 15 | 9.40 | 0.29 | 14.21 | 0.24 | 18.44 | 0.11 | 22.15 | 0.21 | 31.07 | 0.64 |
| | 20 | 20 | 20 | 51.65 | 0.80 | 90.85 | 1.59 | 129.87 | 1.26 | 190.7 | 2.3 | 290.7 | 5.9 |

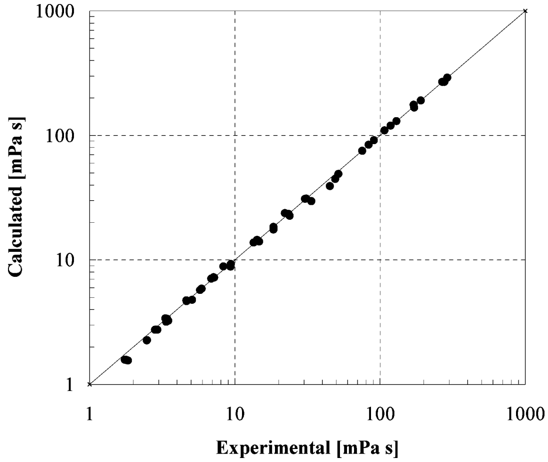

**Figure 7.** Comparison of viscosity data of a quaternary solution from experimental data and prediction of eqs 9 to 13, including ternary interaction parameters.

**Table 9. Fitting Parameters of Equation 13**

| | $m_1$ | $m_2 \cdot 10^{-09}$ | $m_3$ | $r^2$ |
|---|---|---|---|---|
| | Fructose−D(+)-Galactose−Sucrose | | | |
| value | 0.6000 | −9.01 | 0.2194 | 0.997 |
| std. error | 0.1286 | 2.96 | 0.0546 | |
| | Fructose−D(+)-Glucose−Sucrose | | | |
| value | 0.7297 | −3.91 | 0.3258 | 0.921 |
| std. error | 0.1711 | 2.10 | 0.0761 | |
| | D(+)-Galactose−D(+)-Glucose−Sucrose | | | |
| value | 0.9820 | −11.01 | 0.3831 | 0.919 |
| std. error | 0.2083 | 3.36 | 0.0916 | |

a good agreement between prediction and experimental data (maximum error within 9.5 %). A similar comparison for quaternary solutions revealed a good agreement only for relatively low overall sugar concentrations (up to 45 % overall content, with a maximum error of 15 %). On the contrary, with an increase in the sugar content, the model overestimates the viscosity with a maximum error of 95 %. This evidence was ascribed to the adopted mixing rule because only binary interaction parameters were considered, whereas ternary interactions should start to be relevant in quaternary solutions when increasing the sugar content.

Therefore, a ternary interaction parameter $m_{ijk}$ has been included in the model leading to a suitable tool to predict the viscosity of ternary and quaternary solutions of simple and complex sugars within 10 % of maximum error. These results are rather interesting because they can be directly used when proposing new ingredient formulations.

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