

Measurement and modeling of solid - liquid equilibrium in the system fructose + glucose + ethanol + water.

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ABSTRACT

Measurement and modeling of the solubility, and determination of preferred crystalline phases under different solvent and temperature conditions is essential information required at the beginning of crystallizer design. However this information is rarely available in the scientific literature, particularly for mixed solute and mixed solvent solutions. This paper describes methods and results for measuring and modeling solid-liquid equilibrium in the quaternary system fructose + glucose + ethanol + water at 30 and 40 °C. Experiments covered a range of solvent (ethanol + water) compositions from 40 weight percent ethanol to 80 weight percent ethanol. This range is suitable for determining solubilities under conditions likely to be found in alcoholic crystallization from high fructose syrups (HFS). The solubility results showed that addition of ethanol greatly reduces the solubility of both sugars over the entire range of compositions, as would be expected from the ternary systems glucose + ethanol + water and fructose + ethanol + water. The solubility also increases significantly with increasing temperature for all solvent compositions. The fructose + glucose + water system displays two invariant points, and thus three crystalline phases (glucose monohydrate, anhydrous glucose, and anhydrous fructose) over the range of solute compositions; however the system fructose + glucose + ethanol + water displays only one invariant point, where the preferred crystalline phase changes from anhydrous glucose to anhydrous fructose. It is believed that the ethanol in solution stabilizes the presence of water in the liquid phase with respect to the solid phase. The activity coefficient of the sugars in the solid phase could be determined from rigorous thermodynamic methods for both hydrated and anhydrous forms. The availability of solid-phase activity coefficients and solubility measurements at two temperatures allowed the system to be modeled using a UNIQUAC-type model.

1. INTRODUCTION

Fructose is a monosaccharide sugar that is widely used as a sweetener and food additive. The sweetness of its crystalline form is 1.8 times that of sucrose, although the sweetness of its non-crystallizing forms is not as high. Fructose is mostly sold as high fructose syrups (HFS) which are produced from starch. The starch is converted to glucose using alpha - amylase and glucoamylase, and the glucose syrup further reacted to a mixture of glucose and fructose using glucose isomerase. The equilibrium conversion of the last reaction is approximately 50 %, so the high fructose syrups have substantial quantities of glucose.

Crystalline fructose is currently produced from HFS by chromatographic separation to produce a 95 % (dry basis) fructose syrup, followed by either aqueous or aqueous – ethanolic crystallization. Fructose has extremely high solubility in aqueous solutions, and thus ethanol may be used to reduce the solubility of fructose, thus increasing yields and reducing solution viscosity in the crystallizer. Crystallization of these relatively pure fructose syrups is well understood, with significant research on the phase equilibrium and crystallization for aqueous solutions (Young *et al.*; 1952; Shiau and Berglund; 1987; Chu *et al.*; 1989), and aqueous ethanolic solutions (Flood *et al.*; 1996a; Flood *et al.*; 1996b; Flood *et al.*; 2000) already completed. Recently an investigation has begun which aims to crystallize and separate fructose and glucose directly from lower purity high fructose syrups: this research has required significant measurement and modeling of the solid liquid equilibrium in the system fructose + glucose + ethanol + water, which has been unavailable in the scientific literature.

Thermodynamic modeling of solid-liquid equilibrium has focused on two areas; the determination of activity coefficients at the solubility limit, and modeling of the liquid phase activity coefficients using available thermodynamic models. The first area has been solved for anhydrous crystalline forms for any solvent, and gives the well known equation:

$$\ln(\gamma_{\text{sup}} X_{\text{sup}}) = \left[\frac{-\Delta H}{R} + \frac{\Delta A - \Delta B T^0}{R} T_m + \frac{\Delta B}{2R} T_m^2 \right] \left(\frac{1}{T} - \frac{1}{T_m} \right) + \frac{\Delta A - \Delta B T^0}{R} \ln \left(\frac{T}{T_m} \right) + \frac{\Delta B}{2R} (T - T_m) \quad (1)$$

The ΔA and ΔB terms are related to the difference in the heat capacity of the pure liquid and the pure solid, via $\Delta C_p = \Delta A + \Delta B \times (T - T^0)$.

For hydrated crystalline forms, Catté *et al.* (1994) have developed a suitable equation based on the dilution enthalpy of the sugar: unfortunately their equation is only useful in binary sugar – water systems, and is not suitable for use in this study. Glucose monohydrate was not found in solutions containing ethanol, and hence their equation was not required.

Most current research involving modeling of solid-liquid equilibrium of sugars involves the UNIQUAC method, or modifications of this method (Catté *et al.*; 1994; Peres and Macedo; 1996, 1997a,b,c), although a UNIFAC method has also been attempted (Catté *et al.*; 1995). The modified UNIQUAC model of Peres and Macedo (1997a) has proved to be successful in the modeling of sugar solubility in mixed solvents (Peres and Macedo; 1997a,b; Flood; 2000). The UNIQUAC models break up the activity coefficient into a combinatorial part and a residual part;

$$\ln(\gamma_i) = \ln(\gamma_i^c) + \ln(\gamma_i^r) \quad (2)$$

This study uses the modified UNIQUAC model proposed by the group of Macedo. The combinatorial part is:

$$\ln(\gamma_i^c) = \ln \frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i} \quad \text{with } \phi_i \text{ defined as } \phi_i = \frac{x_i Z_i}{\sum_j x_j Z_j}, \quad Z_i = (R_i)^{2/3} \quad (3)$$

The UNIQUAC equation for the residual part is given by:

$$\ln(\gamma_i^r) = Q_i \left[1 - \ln \left(\sum_j \theta_j \tau_{ij} \right) - \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{ik}} \right] \quad \text{with } \theta_i = \frac{x_i Q_i}{\sum_j x_j Q_j} \quad (4)$$

The parameters τ_{ij} (commonly known as Boltzmann factors) are given in the modified UNIQUAC method as:

$$\tau_{ij} = \exp \left(-\frac{a_{ij}}{T} \right) \quad \text{where the } a_{ij} \text{ are fitting parameters, } a_{ij} = a_{ij}^0 + a_{ij}^1 (T - T^0) \quad (5)$$

Structural parameters for the molecules involved, and physical properties required for the solubility equation are given in Table 1.

Table 1. UNIQUAC structure parameters and physical properties for fructose, glucose, ethanol, and water.

Species	R_i	Q_i	Melting Temp. (K)	Enthalpy of Fusion (J/mol)	ΔA	ΔB
D-fructose	8.1529	8.004	378.15	33,000	320.0	0
D-glucose	8.1528	7.920	421.15	32,000	140.0	0
Ethanol	2.5755	2.588	a	a	a	a
Water	0.9200	1.400	a	a	a	a

^a Not required for the present study.

2. SOLUBILITY

Determining the solubility of solutes in solution is vitally important for crystallization design, however it is rare that accurate solubility data for industrially important systems is published. This is partly because the solubility is a function of many variables including temperature, solvent, co-solutes, and impurities. This section describes experimental methods to determine solubility in the mixed solute – mixed solvent system fructose + glucose + ethanol + water at 30 and 40 °C.

2.1 Solubility: Methods

The method used in the current study is the same as used in a previous study (Flood and Puagsa; 2000), of which a short discussion will be given here. The chemicals, D(-)-fructose, D-(+)-glucose anhydrous (both ACS grade), and ethanol anhydrous (99.9 % v/v, for analysis) were obtained from Carlo Erba Reagenti (Milan) and were used without further purification. Solutions were made by dissolving a quantity of fructose (below the solubility limit) in a known solution of ethanol + water. Glucose was added in at least 50 % excess of that needed for saturation. A range of experiments was performed to determine solubility between the limits given by the systems fructose + ethanol + water (see Flood *et al.*; 1996) and glucose + ethanol + water (Bockstanz *et al.*; 1989, and Peres and Macedo; 1997a). Solubility was approached using sealed glass Schott bottles held in a constant temperature (30 or 40 ± 0.2 °C) orbital shaking bath operating at 100 rpm (200 stroke). After 24 h the refractive index was measured every 6 h to test for equilibrium. Equilibrium was achieved within 7 days for all determinations.

The fructose and glucose concentration in equilibrated samples was determined by a HPLC method. In general it is preferable to measure solute concentrations in sugar systems using a gravimetric method such as the dry substance determination procedure (BSES; 1991), however in this study the determination of two solutes was required, and hence a separative method was preferred. Removal of the ethanol in solution was performed since it could interfere with the sugar peaks on the chromatogram and also partially react with the sugars during storage. Samples of approximately 1 mL were weighed, partially dried at room temperature for 17 h to remove the bulk of the ethanol, and then re-weighed. After drying the samples were diluted to approximately 1 % (w/v) by addition of a known amount of distilled water. All weights were determined to ± 0.1 mg. Diluted samples were filtered through a $0.45 \mu\text{m}$ syringe filter and then injected into a $250 \text{ mm} \times 4 \text{ mm}$ Aminex HPX-87C (Biorad, Bangkok) column using a water mobile phase at a flow rate of 0.3 mL/min . The column temperature was 80 °C, and detection was with a diode array detector measuring UV at 192 nm .

2.2 Solubility: Results and Conclusions

Results for the solubility of fructose and glucose in solutions of ethanol and water at 30 and 40 °C are given as ternary diagrams in Figure 1. Two axes give concentrations of glucose and fructose, and the third gives the concentration of the solvent, which is a known mixture of ethanol and water. The lines on the ternary diagram represent lines of constant solvent composition, in this case 0, 40, 60, and 80 weight % ethanol.

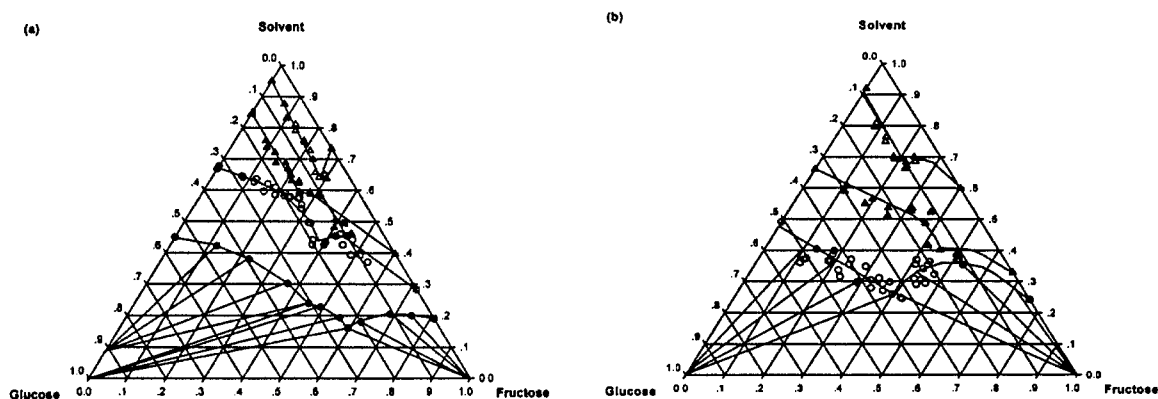


Figure 1. Solubility and preferred crystal phase in the system fructose + glucose + ethanol + water at 30 °C (a) (see Flood and Puagsa; 2000 for tabulated solubility data at 30 °C), and 40 °C (b). Solvent compositions: ● 0 weight % ethanol (aqueous, from Kelly; 1954); ○ 40 weight percent ethanol; ▲ 60 weight % ethanol; △ 80 weight % ethanol. Phases are indicated at 0 weight % ethanol at 30 °C (glucose monohydrate is ~ 9.1 % water) and 40 weight percent ethanol at 40 °C.

The solubility results show that the solubilities of fructose and glucose are both strong functions of temperature and solvent composition. The solubility of both sugars increases significantly over the 10 °C temperature range used in this study, and decrease markedly with increasing ethanol content in the solvent. In general, the minimum total sugar content at a particular temperature and solvent composition is where glucose appears as the

only solute, and the maximum is where fructose appears as the only solute. An exception to this is at 80 % ethanol, 30 °C, where there is a noticeable “salting in” effect: the maximum sugar content of 0.36 g sugar/g of solution is higher than the solubility of fructose in ethanol + water (0.266 g of fructose/g of solution) and that of glucose (0.050 g of glucose/g of solution).

It is also noticeable that while the fructose + glucose + water system has two invariant points (at 30 °C), the fructose + glucose + ethanol + water system appears to have only one invariant point for all solvent compositions studied. This will be discussed in greater detail in the crystal phase determination section.

3. CRYSTAL PHASE DETERMINATION

Crystal phase determination at different points of the phase diagram is important for industrial crystallizer design, as it enables the designer to choose a set of conditions resulting in the preferred product. The crystalline phase of the product will determine product purity (such as if the solvent is part of the crystal structure), crystal shape (which will influence the crystal – liquor separation process), and decomposition and melting temperatures. Sugar solutes may crystallize in a range of hydrate forms: the most likely forms for fructose and glucose are α -D-glucose anhydrous, α -D-glucose monohydrate, β -D-glucose anhydrous, D-fructose anhydrous (β -D-fructopyranose), D-fructose dihydrate, and D-fructose hemihydrate. Crystal phases in the system fructose + glucose + water were determined by Kelly (1954), and these phases are shown in Figure 1(a). β -D-fructopyranose is the preferred crystalline phase in the system fructose + ethanol + water between (at least) 30 to 50 °C.

3.1 Crystal Phase Determination: Method

Supersaturated solutions were made based on the results of the solubility work. (The supersaturated region for a particular solvent composition is the region below the solubility line in this figure). Points were chosen on either side of possible invariant points. Solutions were produced at 60 °C to dissolve the solute completely. After dissolution the samples were cooled to 40 °C, and seeded with a small amount of all likely preferred crystalline phases. Seeding was performed because sugar solutions have very large metastable regions and primary nucleation was unlikely at 20 °C subcooling. Seeding also resulted in large sized crystals, suitable for easy separation from solution.

Product crystals were vacuum filtered and then dried at 70 °C for 24 h, and then stored over silica gel. Higher temperatures were not used due to the melting point of glucose monohydrate (83 °C) and the decomposition temperature of fructose (~ 75 °C). It is believed that drying at this temperature could not alter the crystal phase from glucose monohydrate to anhydrous glucose. After drying the crystal phase was determined using X-ray diffraction (XRD). XRD was performed on a Bruker D5005 diffractometer using a copper anode. The 2θ range was 5 to 60°, using a step of 0.020°, and a step time of 0.6 s. In all cases there was excellent agreement between the intensity spectrum of the unknown and the intensity spectrum of the related compound in the XRD library.

3.2 Crystal Phase Determination: Results and Conclusions

The study of Kelly (1954) determined three phases in the system fructose + glucose + water at 30 °C. α -D-glucose monohydrate crystallizes at low fructose contents, up to the first invariant point. This crystalline form of glucose is approximately 9.1 % water, as shown on Figure 1(a). At high fructose concentrations (between the second invariant point and the glucose axis) anhydrous fructose is the preferred crystalline phase, and anhydrous glucose is the preferred crystalline phase between the two invariant points. The phases are shown on Figure 1(a).

In the system fructose + glucose + ethanol + water there is only one obvious invariant point, which suggests that only two distinct crystalline phases will be apparent. However, it was possible that a second invariant point still exists but was not evident, and hence phase determination was performed. At 40 °C, with a solvent composition of 40 % ethanol, it was determined that anhydrous glucose was the only crystalline phase to the left of the invariant point. To the right of the invariant point only anhydrous fructose crystallizes. This shows that (at least under these solvent conditions) there is only one invariant point in the system fructose + glucose + ethanol + water. Preferred crystalline phases are shown for 40 °C, 40 % ethanol in Figure 1(b). It appears that ethanol lowers the phase transition temperature (glucose monohydrate to anhydrous glucose) which is around 90 °C in aqueous solutions. This is probably due to ethanol increasing the affinity of water in the liquid phase.

4. THERMODYNAMIC MODELING

The modified UNIQUAC model was used to model solubility in the quaternary system fructose + glucose + ethanol + water. Two related ternary systems, fructose + ethanol + water and glucose + ethanol + water, have already been completed (Peres and Macedo, 1997b; Flood, 2000). The glucose-water, water-glucose, fructose-water, water-fructose, ethanol-water, and water-ethanol interaction parameters may be taken from these studies. The solubility of the third relevant ternary system, fructose + glucose + water, has not been studied since there is data only at 30 °C for this system. This is not significant; the fructose-glucose and glucose-fructose interaction parameters are set to zero in these studies. The relevant interaction parameters (from the earlier studies) are given in Table 2.

Table 2. Modified UNIQUAC interaction parameters for the system fructose + glucose + ethanol + water. (The first row is a_{ij}^0 and the second is a_{ij}^T . Only sugar-water parameters assume linear temperature dependence).

i / j	D-fructose	D-glucose	Ethanol	Water
D-fructose	0 0	0 0	-8.5681 ^b 0	58.5738 ^b 0.7329 ^b
D-glucose	0 0	0 0	53.5398 ^a 0	-68.6157 ^a -0.0690 ^a
Ethanol	159.6180 ^b 0	136.2574 ^a 0	0 0	207.4055 ^a 0
Water	97.3045 ^b 0.6761 ^b	96.5267 ^a 0.2770 ^a	-78.5272 ^a 0	0 0

^a From Peres and Macedo (1997b). ^b From Flood (2000).

This model fits the experimental data very well along the glucose axis (the ternary system fructose + ethanol + water) and along the fructose axis (the ternary system glucose + ethanol + water) as the model parameters were optimized using this experimental data in earlier studies. It is also likely that the model must fit the data reasonably well within the vicinity of these axes, where the second solute may be considered as only a low concentration impurity. Therefore it was decided a suitable (and quick) test of the model is whether the activity coefficients given by the model agree with the activity coefficients given by equation (1) at the invariant point for different temperatures and solvent compositions, where the error is likely to be close to the maximum error. There is one invariant point at each solvent composition (40, 60, and 80 weight percent ethanol) for each temperature (30 and 40 °C), and hence 6 points were tested. The results are given in Table 3.

Table 3. Comparison between the Modified UNIQUAC activity coefficient, and the experimental activity coefficient (determined from equation (1)) for the invariant points.

Temperature (K)	Solvent Composition (weight % ethanol)	Activity coefficients from experiment		Activity coefficients from Modified UNIQUAC	
		D-Fructose	D-Glucose	D-Fructose	D-Glucose
303.15	40.0	2.101	1.705	1.721	0.461
303.15	60.0	3.413	2.050	2.547	0.865
303.15	60.0	2.672	3.596	3.009	1.999
313.15	40.0	2.007	0.804	2.208	0.603
313.15	60.0	2.069	2.028	2.858	1.035
313.15	80.0	5.136	3.691	2.629	1.855

It can be noted that the Modified UNIQUAC model is quite poor at estimating the activity coefficients at the invariant points. This is particularly so for glucose, where the activity coefficient is significantly underestimated at all data points. This is despite the model predicting activity coefficients in the ternary sugar + ethanol + water systems very well. It is also clear that better predictions could be produced if the Modified UNIQUAC model was parameterized using the results of the current study. Further work is in progress to optimize the model in terms of the current quaternary solubility data, and to determine whether the re-optimized model still fits the ternary systems well. This work does call into question the ability of UNIQUAC type models to extrapolate from simple solutions to more complex ones. It is the author's own experience that UNIQUAC models do not extrapolate to temperatures outside the range of data used to optimize the model particularly well.

5. NOMENCLATURE

a_{ij}	UNIQUAC interaction parameter (K)	ΔC_p	Pure liquid heat capacity minus pure solid heat capacity (J/mol.K)
C_p	Heat capacity (J/mol.K)	ΔH_f	Enthalpy of fusion (J/mol)
Q	UNIQUAC group area parameter	ϕ	Molecular volume fraction
R	UNIQUAC group volume parameter	θ	Molecular surface area fraction
R	Universal gas constant (J/mol.K)	τ	UNIQUAC parameter
T	Absolute temperature (K)		
T_m	Melting temperature (K)		
T°	Reference temperature, set to 298.15 K	<i>Subscripts</i>	
x	Mole fraction of component	i, j, k	Property of component i, j, k
Z	Parameter for UNIQUAC model	sug	Property of a sugar
<i>Greek</i>		<i>Superscripts</i>	
γ	Activity coefficient	C	Combinatorial
$\Delta A, \Delta B$	Temperature dependencies	R	Residual

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