Refractive Index, Viscosity, Density, and Solubility in the System Fructose + Ethanol + Water at 30, 40, and 50 °C

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Fructose may be recovered from aqueous syrups by crystallization through the addition of ethanol, which reduces the solubility of the fructose. The solubility of fructose in ethanol + water was determined at 30, 40, and 50 °C, over a range of ethanol concentrations. The amount of ethanol required for maximum yield is approximately 9 kg of ethanol/kg of water in the original fructose syrup. The refractive index, viscosity, and density of a wide range of fructose + ethanol + water solutions were determined to aid in the crystallization studies of the system.

Introduction

D-Fructose, $C_6H_{12}O_6$, is a monosaccharide used widely in the food industry because of its high sweetness relative to sucrose, and other useful properties, such as high viscosity, humectancy, and reactivity which promotes desirable color and flavor development in foods (Bates, 1942).

Fructose has been difficult to recover from fructose rich aqueous syrups by crystallization, due to its high water solubility (in excess of 4 g of fructose/g of water at 25 °C) and the resultant high viscosities of these solutions. Various patents (Mahoney, 1940; Dwivedi and Subodh, 1980; Bateman, 1984) have employed the addition of alcohols (ethanol, methanol, or 2-propanol) to concentrated fructose syrups to obtain crystalline fructose.

Published data on the solubility of fructose in ethanolic solutions are very limited. No systematic measurements of the other solution properties have been published. Johns et al. (1990) plotted a limited number of ternary solubility data, and these appear to be the most useful data available.

Experimental Section

Chemicals. U.S.P. grade D-fructose was obtained in bulk from A. E. Staley (Decatur, IL) and dried at 65 °C and 21 kPa for 24 h. It was found to be 99.8% (w/w) pure by high-performance liquid chromatography (HPLC).

Absolute anhydrous ethanol (CSR, Sydney, Australia) was determined to be 99.70% pure by Karl-Fischer titration. Water used was treated by reverse osmosis.

Experimental Procedures. The solubility of fructose in aqueous ethanol was measured at 30, 40, and 50 °C. The solutions were maintained at the desired temperature with an accuracy of ±0.5 °C. All determinations were made in either sealed glass Schott bottles or sealed and stirred glass crystallizers, into which a quantity of ethanol + water of known concentration was added. The ethanol concentration of the ethanol + water solution was known to an accuracy of 0.1 mg of ethanol/g of solution. All analyses are given in mass units, as for previous sugar solubilities (Reber, 1953; Gabas et al., 1988; Bockstanz et al., 1989).

For the bottles, sufficient anhydrous crystalline fructose was added to permit at least 50% excess of fructose over the amount needed to saturate the solution. For ϕ of 0.90−1.00, where ϕ is the mass fraction of ethanol in the absence of fructose, the sealed bottles were shaken at 200 rpm in an orbital shaker water bath, and samples were removed after 36, 42, and 48 h, filtered through a 0.45 μm cellulose acetate membrane, and analyzed for fructose content.

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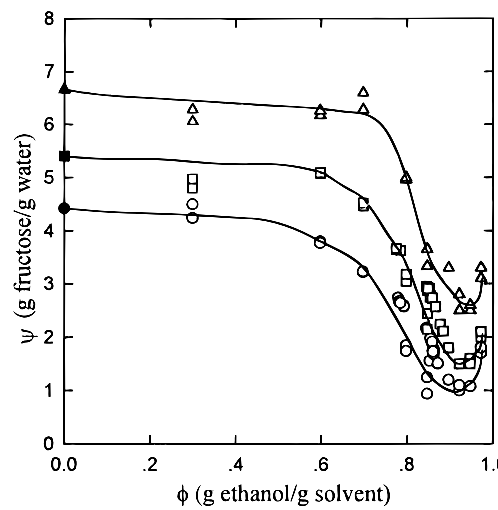

Figure 1. Solubility of D-fructose in aqueous ethanolic solutions: (○) 30 °C; (□) 40 °C; (△) 50 °C; filled symbols from Bates et al. (1942).

Table 1. Solubility of D-Fructose in Ethanol + Water at 30 °C

weight fraction of ethanol/(g of ethanol/g of solvent)	solubility/(g of D-fructose/g of soln) 30 °C	40 °C	50 °C
0.299	0.754	0.774	0.812
0.598	0.603	0.672	0.714
0.698	0.493	0.576	0.661
0.774[b]		0.451	
0.781[b]	0.370		
0.792[b]	0.359		
0.798	0.266	0.386	0.501
0.844[b]	0.230		
0.847	0.158	0.260	0.348
0.850[b]		0.300	
0.860[b]	0.206	0.278	
0.866[b]		0.256	
0.872[b]	0.162		
0.882[b]		0.203	
0.897	0.110	0.156	0.254
0.922	0.076	0.105	0.171
0.947	0.054	0.098	0.119
0.972	0.046	0.076	0.082
0.997	0.035	0.033	0.045

[a] Results are the average of two observations unless stated otherwise. [b] Average of several crystallization experiments.

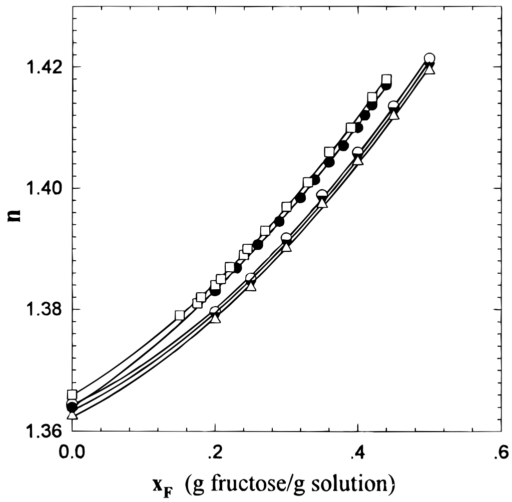

Figure 2. Variation of the refractive index of aqueous ethanolic fructose solutions with solvent composition: (●) 30 °C, E/W = 3.6; (□) 30 °C, E/W = 6.1; (△) 40 °C, E/W = 4.5; (▼) 40 °C, E/W = 6.0; (○) 40 °C, E/W = 7.5.

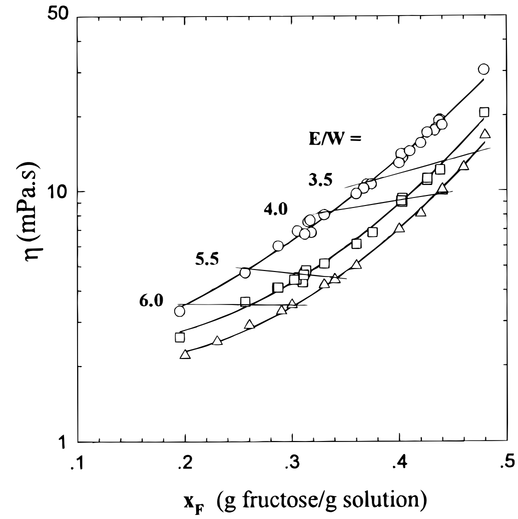

Figure 4. Viscosity of aqueous ethanolic fructose solutions. (○) 30 °C; (□) 40 °C; (△) 50 °C. Solubility lines for solvent compositions of E/W = 3.5−6.0 are shown.

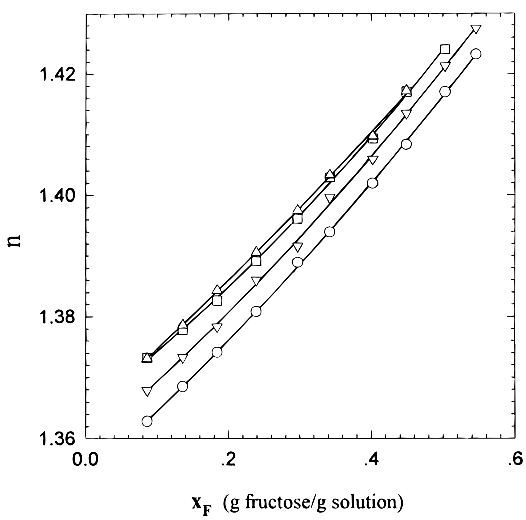

Figure 3. Effect of temperature on the refractive index of fructose solutions: (△) 25 °C; (□) 30 °C; (▽) 40 °C; (○) 50 °C.

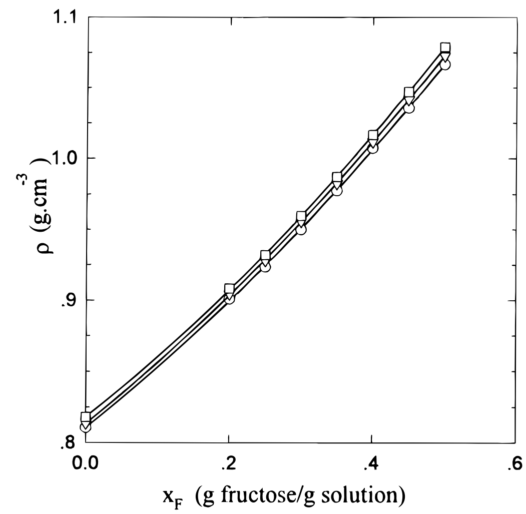

Figure 5. Density of aqueous ethanolic fructose solutions at 40 °C: (□) E/W = 4.5; (▽) E/W = 6.0; (○) E/W = 7.5.

Table 2. Refractive Index of D-Fructose + Ethanol + Water Solutions with an Ethanol/Water Ratio of 6

fructose concentration/ (g of fructose/g of soln)	solution refractive index			
	24 °C	30 °C	40 °C	50 °C
0.0860	1.3628	1.3679	1.3732	1.3731
0.1360	1.3685	1.3733	1.3778	1.3786
0.1840	1.3741	1.3783	1.3826	1.3843
0.2390	1.3808	1.3860	1.3891	1.3906
0.2970	1.3889	1.3916	1.3961	1.3975
0.3420	1.3939	1.3996	1.4029	1.4033
0.4020	1.4019	1.4059	1.4093	1.4097
0.4490	1.4083	1.4135	1.4170	1.4172
0.5030	1.4170	1.4213	1.4240	
0.5460	1.4232	1.4275		

For ϕ between 0.30 and 0.85, the solutions were very viscous and the bottles were held for 72 h at 100 rpm in a reciprocating shaking water bath with periodical hand shaking to ensure that fructose crystals did not form large conglomerates. Samples were taken from each bottle at 72, 73.5, and 75 h to ensure the saturation concentration was obtained.

With the crystallizer, for ϕ = 0.78−0.88, the saturation concentration was determined by mixing the solution at 600 rpm or more in a sealed crystallizer submerged in a thermostatically-controlled water bath. Samples were taken at 24, 25, and 26 h to determine the saturation fructose concentration. The concentrations were shown to be constant after 24 h to ±0.003 g of fructose/g of solution.

Table 3. Refractive Index of D-Fructose Solutions at 40 °C

fructose concentration/ (g of fructose/g of soln)	refractive index		
	E/W = 7.50	E/W = 6.00	E/W = 4.50
0.00	1.3645	1.3636	1.3625
0.20	1.3796	1.3790	1.3783
0.25	1.3851	1.3843	1.3836
0.30	1.3918	1.3910	1.3901
0.35	1.3989	1.3982	1.3974
0.40	1.4059	1.4052	1.4044
0.45	1.4135	1.4128	1.4119
0.50	1.4214	1.4202	1.4194

Fructose concentration was determined by duplicate total solids determinations performed at (65 ± 1) °C and 21 kPa (BSES, 1991). The accuracy (95% probable error) in each analysis was ±0.003 g of fructose/g of solution.

Refractive index measurements of solutions were made in triplicate on an Abbe refractometer with temperature control to within ±0.1 °C. The precision of the refractive index determination was ±0.0005 refractive index unit.

Table 4. Refractive Index of D-Fructose Solutions at 30 °C

ethanol/water ratio/(g/g)	fructose concentration/ (g of fructose/g of soln)	refractive index	ethanol/water ratio/(g/g)	fructose concentration/ (g of fructose/g of soln)	refractive index
3.60	0.00	1.3639	6.10	0.00	1.3660
	0.20	1.3830		0.15	1.3790
	0.23	1.3868		0.18	1.3820
	0.26	1.3907		0.20	1.3840
	0.29	1.3945		0.21	1.3850
	0.32	1.3984		0.22	1.3870
	0.34	1.4014		0.24	1.3890
	0.36	1.4043		0.25	1.3900
	0.38	1.4070		0.27	1.3930
	0.40	1.4100		0.30	1.3970
	0.41	1.4120		0.33	1.4010
	0.42	1.4137		0.36	1.4060
	0.44	1.4170		0.39	1.4100
				0.42	1.4150
				0.44	1.4180

Table 5. Viscosity of Aqueous Ethanolic Solutions of D-Fructose

temp/(°C)	ethanol/water ratio/(g/g)	fructose concn/ (g of fructose/g of soln)	viscosity/ (mPa·s)	temp/(°C)	ethanol/water ratio/(g/g)	fructose concn/ (g of fructose/g of soln)	viscosity/ (mPa·s)
30	3.40	0.3740	10.6		3.60	0.4380	18.8
	3.50	0.3120	6.70		3.70	0.3050	6.90
	3.50	0.4200	15.5		3.70	0.4030	13.5
	3.50	0.4370	19.0		3.70	0.4020	14.0
	3.50	0.4790	30.3		3.70	0.4100	14.4
	3.60	0.2870	6.00		3.70	0.4340	17.7
	3.60	0.3180	6.80		3.70	0.4400	18.3
	3.60	0.3170	7.60		3.70	0.4380	19.2
	3.60	0.3600	9.70		3.80	0.3150	7.50
	3.60	0.3670	10.2		3.80	0.4330	17.4
	3.60	0.3700	10.6		6.10	0.2560	4.70
	3.60	0.4000	12.9		6.40	0.1950	3.30
	3.60	0.4260	17.1		6.40	0.3300	8.00
40	3.70	0.4380	12.1		5.70	0.3750	6.80
	5.50	0.3120	4.70		5.70	0.4260	11.0
	5.50	0.3130	4.80		5.70	0.4790	20.4
	5.50	0.3300	5.10		5.80	0.2860	4.10
	5.60	0.3060	4.50		5.80	0.4280	9.30
	5.60	0.3110	4.60		5.90	0.2870	4.10
	5.60	0.3600	6.10		5.90	0.4030	9.30
	5.60	0.4030	9.00		6.40	0.2560	3.60
	5.70	0.3100	4.30		6.40	0.4260	11.2
	5.70	0.3020	4.40		7.70	0.1950	2.60
	5.70	0.3040	4.40		7.70	0.4020	9.10
50	5.50	0.2300	2.50		5.60	0.4200	8.10
	5.50	0.2600	2.90		5.60	0.4400	10.1
	5.50	0.2900	3.30		5.60	0.4600	12.4
	5.50	0.3000	3.50		5.70	0.4400	9.90
	5.50	0.3300	4.20		5.70	0.4800	16.6
	5.60	0.2000	2.20		6.00	0.3400	4.40
	5.60	0.4000	7.00		6.40	0.3600	5.00

Solution viscosity was measured in duplicate using a concentric cylinder viscometer (Rheomat 115), equipped with the low viscosity system 1054, to provide viscosity measurement in the range of 1−2000 mPa·s. A water bath maintained a constant temperature (±0.2 °C) in the viscometer. The viscosity was measured to an estimated ±3% relative error.

Solution density was measured at 40 °C, in duplicate, using a 10 cm^3 pycnometer. The precision of the density measurement was ±0.0002 $g·cm^{-3}$, which is considerably less important than the accuracy of the fructose concentration of the solutions measured (±0.0002 g of fructose/g of solution).

Results and Discussion

The solubility of D-fructose in ethanol + water is plotted in Figure 1. In anhydrous ethanol (ϕ of 0.997) the equilibrium fructose solubility, ψ, (expressed as g of fructose/g of water) was (12 ± 2) at 30 °C and 40 °C and (17 ± 2) at 50 °C. The solubility results are shown in Table 1.

Figure 1 shows there is little improvement in fructose crystal yield until ϕ is greater than 0.7. At ϕ above 0.7 the addition of ethanol significantly reduces the fructose solubility. Similar trends have been observed in sucrose, α-anhydrous glucose, D-xylose, and D-mannose (Reber, 1953; Gabas et al., 1988; Bockstanz et al., 1989).

The minimum mass ratio of D-fructose to water (ψ) at each temperature investigated occurred at $\phi = 0.92$. This minimum limits the maximum yield obtainable by the ethanolic crystallization of fructose. This limit is not sufficiently severe to limit the usefulness of alcoholic crystallization of fructose. This point does not represent the minimum solubility expressed as the mass fraction of D-fructose in solution, which occurs in pure ethanol ($\phi = 1$).

Increasing the temperature increased the fructose to water mass ratio (ψ) by approximately 25% per 10 °C for solutions of ϕ between 0 and 0.6, and by approximately 50% per 10 °C at $\phi = 0.9$.

The refractive index of solutions of fructose + ethanol + water at 30 and 40 °C is shown in Figure 2 for several

Table 6. Density of Aqueous Ethanolic Solutions of D-Fructose at 40 °C

fructose concn/ (g fructose/g of soln)	density		
	E/W = 7.5	E/W = 6.0	E/W = 4.5
0.0000	0.8106	0.8134	0.8180
0.2000	0.9008	0.9044	0.9083
0.2500	0.9235	0.9280	0.9320
0.3000	0.9500	0.9556	0.9596
0.3500	0.9775	0.9824	0.9870
0.4000	1.0072	1.0118	1.0168
0.4500	1.0355	1.0416	1.0472
0.5000	1.0666	1.0727	1.0789

ethanol/water (E/W) mass ratios in the solvent. The influence of temperature on the refractive index of solutions with $\phi = 0.857$ is shown in Figure 3. The refractive index of the fructose + ethanol + water system is strongly dependent on the fructose concentration, but relatively independent of ϕ. The refractive index of the ternary system is shown in Tables 2−4.

The viscosity of fructose + ethanol + water is shown in Figure 4. The viscosity was strongly (and nonlinearly) dependent on the fructose concentration, and relatively high viscosities may be obtained due to the high solubility of fructose in water. Although the viscosity of a solution of given fructose concentration will decrease with increasing temperature, the viscosity of a saturated fructose solution at a given ϕ may increase with increasing temperature, especially at low values of ϕ. This unusual behavior is due to the greatly increased fructose solubility at higher temperatures, overwhelming the tendency of high temperatures to lower solution viscosity. The viscosity of D-fructose + ethanol + water systems is shown in Table 5.

The densities of the fructose + ethanol + water solutions are shown in Figure 5. The solution density is strongly dependent on fructose concentration, and only weakly dependent on ϕ. The density results for this study are shown in Table 6.

Glossary

ϕ mass fraction of ethanol in the solvent

ψ mass of D-fructose per unit mass of water in solution

x_F mass of D-fructose per unit mass of solution

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