ARTICLES

Relationship between Density, Temperature, and Dry Substance of Commercial Corn Syrups, High-Fructose Corn Syrups, and Blends with Sucrose and Invert Sugar

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A study of the dry substance–density–temperature relationship has been made for a variety of commercial corn syrups including 42, 55, and 90% fructose syrups and blends with sucrose and invert sugar. Dry substance was determined by the refractive index at 20 °C. Densities, for a range of dry substance levels, were measured at 15.55, 20, 40, and 60 °C. The results of 18 product types are presented in the form of tables and are used to generate model equations relating density, composition, temperature, and dry substance of the samples. Density values were also converted to Baumé units and commercial Baumé and presented in tabular form as related to dry substance.

Previous work (Wartman et al., 1976; Wartman et al., 1980; Kurtz and Eliason, 1979) has established the relationship between refractive index, composition, and dry substance (DS) of a variety of corn syrups, high-fructose corn syrups and blends with sucrose, medium invert (MI) syrup, and 63 dextrose equivalents (DE) corn syrup. In the current investigation, an additional relationship was established between DS, composition, density, and temperature. The latter relation has allowed tables of Baumé and commercial Baumé to be generated. Furthermore, DS temperature correction factors were calculated to provide means to reduce densities measured at any temperature to densities at 20 °C. Similar correction factors allow such adjustments for Baumé units as well.

Each syrup was analyzed at four different DS levels, generally covering the range of 20–80% DS. Due to solubility characteristics, the ranges covered with the 12 DE and the 60/40 blend of 63 DE/HFCS 42 syrups were 10–40 and 20–60%, respectively. The densities were measured on all syrups and dilutions at 15.55 (60 °F), 20, 40 °C, and 60 °C. The refractive index at 20 °C and the composition of the syrup were used to determine the actual DS of syrups and dilutions.

Mathematical expressions were developed by using multiple linear regression to represent the information gathered in the density study. Two relationships were established: (1) the temperature dependence of the density and (2) the compositional dependence of the density at 20 °C. Working tables were produced that can be conveniently used to obtain the DS from densities measured at 20 °C as well as obtaining DS from Baumé units or commercial Baumé. The equations are presented in the following paper (Maxwell et al., 1984).

EXPERIMENTAL SECTION

Samples. Samples of nine corn syrups, three high-fructose corn syrups, sucrose, and invert sugar were collected by the Moffett Technical Center of CPC International, Inc., Summit-Argo, IL, from member companies of the CRA (Corn Refiners Association). Blends of fructose syrups with sucrose, invert sugar, and corn syrup were prepared. Aliquots from identical syrup batches were delivered to this laboratory for density–DS studies and to the laboratories of Clinton Corn Processing Co., Clinton, IA, A. E. Staley Manufacturing Co., Decatur, IL, CPC International, Inc., Summit-Argo, IL, and Amstar Corp., Dimmit, TX, for analysis by liquid chromatography (HPLC) to determine composition. Description of these products and their composition are given in Table I. In addition, the composition data on identical product types previously used for refractive index studies (Wartman et al., 1976, 1980) are presented in Table II for ease of comparison. The products are at times listed only by the numbers assigned in Table I.

Experimental Details. The refractive index was measured as previously described by Wartman et al. (1976). The instrument was calibrated with a standard test piece at the start of the investigation, subsequently checked twice during the experiment, and rechecked at the conclusion. Glass-distilled water was used as a check each day when refractive indices were measured. The difference between the observed and the standard value of water was used as a correction factor for observed values. The dry substance was calculated from the composition, refractive index, and the formula derived previously by Wartman et al. (1980). Dilutions were therefore not made quantitatively since the refractive index value determined the actual DS. Brief heating in a microwave oven increased the fluidity of some of the more viscous samples and aided in some dilutions to ensure homogeneity. Those samples showing evidence of crystallization were subjected to the same treatment, and the dilutions were made immediately upon redissolution. The sucrose standards were prepared as previously described by Wartman et al. (1980).

The determination of density of corn syrup by a pycnometer is exceedingly difficult because of the high viscosity. A modified pycnometric technique was reported by Brown and Zerban (1941) wherein a molasses sample was topped off with water to fill the pycnometer. Xylene

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Table I. Composition of Syrups Used in Current Study (Percent of Dry Substance)

sample no.	syrup description	dextrose	fructose	DP2	sucrose	DP3	DP4+	ash
1	12 DE, CS (maltodextrin)	0.6		2.4		4.6	92.4	0.40
2	28 DE, CS	8.2		8.8		10.2	72.8	0.30
3	42 DE, CS, AC	18.3		13.9		12.2	55.6	0.40
4	55 DE, CS, AC	8.1		13.9		12.2	55.6	0.40
5	32 DE, CS, DC	9.1		9.8		9.7	71.4	0.30
6[a]	42 DE, CS, DC	7.6		33.2		27.5	31.7	0.20
7	55 DE, CS, DC	10.0		50.7		14.5	24.8	0.30
8	63 DE, CS, DC	37.0		30.9		10.8	21.3	0.50
9[a]	42 DE, CS, DC	7.6		33.2		27.5	31.7	0.20
10	95 DE, CS, DC	94.6		3.1		0.5	1.8	0.10
11	HFCS 42	52.6	41.4	3.8		0.5	1.7	0.03
12	HFCS 55	40.4	54.5	4.0		0.4	0.7	0.03
13	HFCS 90	5.8	92.2	1.7		0.1	0.2	0.03
14	50% MI/50% HFCS 55	34.1	40.8	1.9	21.9	1.0	0.3	0.03
15	75% MI/25% HFCS 42	34.1	30.4	1.8	31.8	1.5	0.4	0.03
16	50% MI/50% HFCS 42	40.4	33.9	1.8	21.8	1.2	0.9	0.04
17	60% 63 DE, CS/40% HFCS 42	42.8	16.4	19.9		6.7	14.2	0.3
18	75% 63 DE, CS/25% HFCS 42	40.7	10.3	23.8		8.1	17.1	0.4
19	50% sucrose/50% HFCS 42	25.7	20.6	1.3	50.8	0.4	1.2	0.02

[a] Syrups 6 and 9 are the same syrups. Densities were measured twice and both sets of data used in the regression analysis.

Table II. Composition of Syrups in Previous Studies (1, 3)[a] (Percent of Dry Substance)

sample	syrup description	dextrose	fructose	DP2	sucrose	DP3	DP4+	ash
1	12 DE, CS (maltodextrin)	0.9		2.5		4.0	92.6	0.40
2	28 DE, CS	9.2		8.7		7.8	74.3	0.40
3	42 DE, CS, AC	19.6		14.4		11.6	54.4	0.40
4[b]	50 DE, CS, DC	30.7		17.9		12.2	39.2	0.40
5	32 DE, CS, DC	10.0		14.5		9.6	65.9	0.40
6	42 DE, CS, DC, HM	7.5		39.5		14.7	38.3	0.40
7	50 DE, CS, DC	8.6		51.6		14.5	25.3	0.40
8	63 DE, CS, DC	39.2		30.5		6.6	23.7	0.40
9[c]	70 DE, CS, DC	47.2		27.2		5.2	20.4	0.40
10	95 DE, CS, DC	92.4		3.8		0.7	3.1	0.50
11	HFCS 42	49.0	43.2	3.9		0.2	3.7	0.05
12	HFCS 55	40.3	55.4	3.0		0.4	0.9	0.05
13	HFCS 90	7.7	90.8	1.2		0.1	0.2	0.05
14	50% MI/50% HFCS 55	35.1	41.3	1.1	20.9	0.9	0.7	0.05
15	75% MI/25% HFCS 42	34.3	30.9	0.6	31.8	1.4	1.0	0.05
16	50% MI/50% HFCS 42	39.5	35.2	0.9	21.5	1.1	1.8	0.05
17	60% 63 DE, CS/40% HFCS 42	42.9	17.2	18.9		6.1	14.9	0.5
18	75% 63 DE, CS/25% HFCS 42	41.2	11.2	22.3		7.5	17.8	0.50
19	50% sucrose/50% HFCS 42	24.9	22.1	0.7	50.2	0.1	2.0	0.05

[a] The order in which the syrups are listed corresponds to the order in Table I and not the original publications. [b] The composition of sample 4 was quite different from the current 50 DE, CS, DC syrup. [c] Number 9 had no equivalent syrup used in the current study.

was selected for topping off in this study because it has a low solubility in the syrups, has a low volatility, and is less dense than the syrups.

The density determinations were performed as follows. Gay-Lussac pycnometers of a total volume of approximately 100 mL were calibrated by using degassed, deionized water. Wider neck pycnometers had been constructed for the more viscous samples. Each was fitted with a ground glass stopper with a capillary bore.

A preweighed pycnometer was partially filled by aid of a narrow stem funnel, stoppered, and reweighed. Xylene was introduced through the capillary bore by means of a syringe to give an overflow. The order of incubation was first placing the pycnometers in the 60 °C bath (to facilitate removal of trapped air bubbles), then at 15.55 °C, then at 20 °C, and finally at 40 °C. Excess xylene was allowed to overflow or additional xylene was introduced as the samples equilibrated. Subsequently each pycnometer was weighed until two weighings agreed within 0.002 g. After ambient temperature was reached, the xylene was removed through aspiration and samples for the refractive index measurement were immediately taken from the interior of the syrup and applied to the refractometer prism with a Teflon stirring rod or a plastic dropper. The following formulas were used to calculate density or specific gravity in vacuum:

$$\text{specific gravity } (t, °\text{C}) \text{ (air)} = \text{weight of the syrup}/[\text{weight of water} - [\text{weight of xylene}/\text{sp g of xylene } (t, °\text{C})]] \quad (1)$$

$$\text{specific gravity } (t, °\text{C}) \text{ (vacuum)} = \text{sp g } (t, °\text{C}) \text{ (air)} - 0.0012[\text{sp g } (t, °\text{C}) \text{ (air)} - 1] \quad (2)$$

$$\text{density } (t, °\text{C}) \text{ (vacuum)} = \text{sp g } (t, °\text{C}) \text{ (vacuum)} \times \text{the density of water } (t, °\text{C}) \text{ (vacuum)} \quad (3)$$

The density of the batch of xylene used throughout the study was determined by using three different pycnometers at each temperature. The values did not vary by more than ±0.00002 from the average at any temperature.

The temperature control for both the density and refractive index determinations was maintained by use of Brinkman/Lauda Model K-2/R thermostatic circulating water baths. The temperature was monitored by A.S.T.M. No. E-1 centigrade thermometers graduated to 0.1 °C and read with the aid of a reading lens to ±0.02 °C. The method was validated by use of standard sucrose solutions prepared gravimetrically.

Table III. Comparison of Results of Refractive Index and Specific Gravity of Sucrose Solutions

std sucrose by wt	n^{20}_D obsd	n^{20}_D lit.	Δ	sp gravity, 20 °C, obsd (vacuum)	sp gravity, 20 °C, vacuum lit.[a]	Δ
0	1.33299	1.33299				
9.99	1.34783	1.34781	+0.00002	1.03993	1.03994	−0.00001
19.94	1.36385	1.36374	+0.00009	1.08284	1.08262	+0.00022
39.99	1.39984	1.39985	−0.00001	1.17865	1.17854	+0.00011
27.20	1.37622	1.37616	+0.00006	1.11598	1.11576	+0.00022
45.38	1.41055	1.41054	+0.00001	1.20709	1.20675	+0.00034
50.00	1.42008	1.42009	−0.00001	1.23197	1.23179	+0.00018
50.12	1.42033	1.42034	−0.00001	1.23215	1.23245	−0.00030
62.81	1.44849	1.44838	+0.00011	1.30597	1.30549	+0.00048
40.14	1.40012	1.40013	−0.00001	1.17954	1.17931	+0.00023
66.79	1.45762	1.45770	−0.00008	1.33033	1.32965	+0.00018

[a] The International Commission for Uniform Methods of Sugar Analysis (1966).

Table IV. Density Table for Dry Substance in Corn Syrups and High-Fructose Corn Syrups

dry substance, %	dextrose equiv: maltose:	density, 20 °C in vacuum 28	32	42 13	42 33	55 40	55 50	63	95	fructose content 42	55	90
68		1.3483	1.3471	1.3446	1.3439	1.3411	1.3416	1.3366	1.3269	1.3295	1.3298	1.3324
70		1.3612	1.3600	1.3574	1.3567	1.3537	1.3544	1.3491	1.3389	1.3415	1.3418	1.3445
72		1.3742	1.3730	1.3703	1.3697	1.3665	1.3673	1.3617	1.3510	1.3536	1.3539	1.3567
74		1.3874	1.3862	1.3834	1.3828	1.3794	1.3804	1.3745	1.3632	1.3659	1.3662	1.3690
76		1.4007	1.3995	1.3966	1.3961	1.3925	1.3936	1.3874	1.3756	1.3783	1.3786	1.3815
78		1.4142	1.4130	1.4099	1.4096	1.4057	1.4070	1.4005	1.3882		1.3911	1.3940
80		1.4278	1.4266	1.4234	1.4232	1.4191	1.4206	1.4137	1.4008		1.4038	1.4067
82		1.4416	1.4403	1.4371	1.4370	1.4326	1.4344	1.4272	1.4137			1.4194
84		1.4555	1.4542	1.4508	1.4509	1.4462	1.4484	1.4407	1.4266			

Table V. Commercial Baumé Table for Dry Substance in Corn Syrups and High-Fructose Corn Syrups: Commercial Baumé = 140 °F/60 °F + 1°Be′

commercial Baumé	dextrose equiv: maltose	dry substance, % 28	32	42 13	42 33	55 40	55 50	63	95	fructose content 42	55	90
36		66.44	66.60	66.99	67.10	67.53	67.45	68.24	69.86	66.99	70.09	70.09
37		68.35	68.51	68.91	69.01	69.47	69.36	70.19	71.87	72.00	72.12	72.12
38		70.26	70.43	70.84	70.93	71.41	71.28	72.14	73.89	74.03	74.15	74.16
39		72.18	72.35	72.78	72.86	73.36	73.22	74.11	75.93	76.07	76.19	76.12
40		74.12	74.30	74.73	74.80	75.33	75.16	76.09	77.97		78.25	78.27
41		76.08	76.25	76.69	76.74	77.31	77.10	78.08	80.02		80.32	80.35
42		78.04	78.22	78.67	78.70	79.29	79.06	80.08	82.09			82.44
43		80.02	80.20	80.66	80.67	81.31	81.03	82.09	84.17			
44		82.02	82.19	82.66	82.65	83.32	83.01	84.11	86.26			

RESULTS

The water refractive index taken each day varied from the standard value at 20 °C of 1.33299 by an average of −0.00001 (range +0.00002 to −0.00004). The results of the refractive index and specific gravity of sucrose solutions at 20 °C are given in Table III.

Multiple regression analysis of the raw data led to the development of the model equations relating density, temperature, and composition described in the following paper (Maxwell et al., 1984). Data for all syrups, pure sucrose, dextrose, fructose, and invert are available in Table I of the supplementary material (see paragraph at end of paper regarding supplementary material). The difference between observed and calculated densities indicates that the equation is adequate and that the data are consistent internally. Published data for standard sucrose, dextrose, fructose, and invert by The International Committee for Uniform Methods of Sugar Analysis (1966), Schliephake (1965) U.S. Department of Commerce (1942), and Snyder and Hattenberg (1963) are included in this table since these were used in developing the mathematical relationships. In the course of the model development, dry substances were derived from refractive index values by use of the refractive index–dry substance model reported in the Appendix of Wartman et al. (1980).

Regression analysis led to the development of a model relationship for all syrups by Maxwell et al. (1984). The equations were used to generate working tables (supplementary Tables II–XX), which facilitate obtaining DS values directly from observed densities at 20 °C. These tables also give Baumé (140 °F/60 °F) and commercial Baumé dry substance relationships for each syrup.

A correction factor was obtained mathematically for density measurements taken at temperatures other than 20 °C (supplementary Tables XXI–XXVIII). Observed densities are to be multiplied by these factors to obtain densities at 20 °C. A relationship between density, refractive index, and composition was developed from a reexpression of the specific refraction function and provided an additional means of demonstrating the internal consistency of the data. A detailed description of the statistical analysis will be presented in a subsequent publication.

$$\text{Baumé } 60\ °\text{C}/60\ °\text{F} = 145 - \frac{145}{\text{sp g}(60\ °\text{C}/60\ °\text{F})} \quad (4)$$

where 145 = the Baumé modulus and sp g = specific gravity in vacuum at 60 °F. Commercial Baumé is defined as follows: use a spindle calibrated at 60 °F but make the measurement at 140 °F and then add 1.00 to the 140 °F reading.

Correction factors for Baumé readings observed at temperatures other than 60 °F were obtained by using the equation

$$\Delta\text{Baumé} = \left(\frac{1}{\rho_2} - \frac{1}{\rho_1} - \frac{0.000028\Delta t}{\rho_1}\right)M \quad (5)$$

where ρ_1 = initial density, ρ_2 = final density, 0.000028 = cubic expansion coefficient of glass, and M = 145 (the Baumé modulus). The factors are to be added to the observed values. These numbers are given in supplementary Tables XXIX–XXXIV.

The previously published tables of refractive index and dry substance were for a set of corn syrups and blends similar to those in this study. However, the saccharide compositions of similar materials were not identical in the two studies. If density tables were prepared by using the compositions in the current work, then there would be an inconsistency with respect to the refractive index tables. For example, determined refractive index and density on a material would yield slightly different values for dry substance from the two tables. Therefore, the density and Baumé tables were calculated with the equations in this report but by using the saccharide compositions reported in the refractive index study.

Tables IV and V summarize the density, dry substance, composition, and commercial Baumé data for the most commonly traded syrups in the dry substance region of industrial and commercial interest.

Abbreviations Used: AC, acid conversion; CS, corn syrup; DC, dual conversion; DE, dextrose equivalent; DS, dry substance; HFCS, high-fructose corn syrup; HM, high maltose; MI, medium invert; DP2, DP3, and DP4+, disaccharides, tri saccharides and higher saccharides in the glucose series. For a more extensive explanation of these terms, see Wartman et al. (1976, 1980).

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Supplementary Material Available: Raw data tables of percent dry substance, density, and refractive index on all syrups and dilutions, calculated density, Baumé and commercial Baumé for dry substance every 2% of all syrups, density and temperature relationships for all syrups every 5 °C, and Baumé temperature corrections for all syrups every 5 °F (40 pages). Ordering information is given on any current masthead page.

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Specific Volume (Density) of Saccharide Solutions (Corn Syrups and Blends) and Partial Specific Volumes of Saccharide–Water Mixtures

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A specific volume model, based on apparent specific solute volumes, is developed for aqueous solutions containing dextrose, fructose, sucrose, DP2, DP3, and DP4+. Multiple linear least-squares analysis is presented of data from a density study that is reported in the preceding paper in this issue. For the case of binary water–saccharide mixtures, component partial specific volumes, v_{s1} and v_{s2}, are derived. These partial quantities are used as a diagnostic tool to examine the model. Extrapolations of v_{s2} are compared to the literature values for sucrose and dextrose at dilute and concentrated limits. DP2 is compared at the dilute saccharide limits. All other estimates have never been reported. The composition and temperature variations in v_{s1} depend on saccharide type.

Wartman et al. (1984), in their density study of commercial corn syrups, high-fructose corn syrups, and blends with sucrose and invert sugar, have provided a wealth of information on the effects of composition and temperature on solution specific volume, V_s (reciprocal of density).

The present paper proposes a thermodynamic model for V_s based on apparent specific volumes of the saccharide solutes and presents a least-squares analysis of the data based on that model. The resultant model may be used in a predictive sense, i.e., to generate density tables for particular saccharide distributions at different dry substance and temperature levels.

For the case of binary saccharide–water mixtures, the form of the solution specific volume is reexpressed in terms

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