

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  $\rho_1$  = initial density,  $\rho_2$  = 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).

#### ACKNOWLEDGMENT

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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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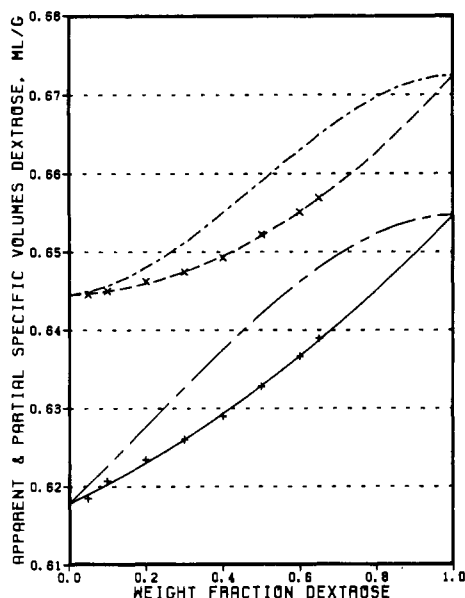
A specific volume model, based on apparent specific solute volumes, is developed for aqueous solutions containing dextrose, fructose, sucrose, DP2, DP3, and DP4+. Multiple linear least-squares analysis is presented of data from a density study that is reported in the preceding paper in this issue. For 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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**Figure 1.** Apparent and partial specific volume of dextrose solutions at 20 and 80 °C [based on Schliephake (1965)]. Curves: observed apparent specific volumes of dextrose at 20 °C (+) and 80 °C (x); [(—) and (---)] smoothed curves through the observations at 20 and 80 °C, respectively; [(—) and (---)] partial specific volumes of dextrose at 20 and 80 °C, respectively.

of component partial specific volumes. The effects of temperature, composition, and saccharide type are shown for the partial specific volume of water. The extreme limits in composition for the saccharide partial specific volumes are compared to literature values. These extrapolations provide partial validation for the specific volume model. The partial specific quantities are useful model diagnostic tools. Compositional effects of DP3 are not very well established. Precision during prediction is not seriously affected for solutions having less than 20% dry substance DP3.

The apparent specific volume is a very useful way to represent solution specific volume. The apparent specific volume for a saccharide solute in water (Lewis et al., 1961) is

$$\phi V_s = (V - w_1 v_{s1}^0) / w_2 \quad (1)$$

By rearrangement of this expression, the solution volume is

$$V = v_{s1}^0 w_1 + \phi V_s w_2 \quad (2)$$

The solution specific volume is

$$V_s = V / (w_1 + w_2) \quad (3)$$

(see Abbreviations Used for symbol definitions). Figure 1 illustrates the concentration dependence of the apparent specific volume of dextrose in water. The data are based on the 20 and 80 °C density measurements of Schliephake (1965). The smoothed curves through the data are the least-squares fits of the form

$$\phi V_s = \epsilon_1 + \epsilon_2 x_2 + \epsilon_3 x_2^2 + \epsilon_4 x_2^3 \quad (4)$$

This cubic form in  $x_2$  adequately accounts for curvilinear effects seen in  $\phi V_s$  at all temperatures.

Generalizing to a solution containing  $q$  saccharides and ash, the specific volume can have the form

$$V_s = v_{s1}^0 x_1 + \phi V_{s,ash} x_{ash} + \sum_{i=2}^{q+1} \phi V_{si} x_i \quad (5)$$

Nonaqueous constituents, i.e., the dry substance compo-

nents, are assumed to provide a common effect on each apparent specific volume:

$$\phi V_{si} = \epsilon_{1i} + \epsilon_{2i} s + \epsilon_{3i} s^2 + \epsilon_{4i} s^3 \quad (6)$$

The specific volume described by eq 5 applies to a specified temperature,  $t$ . To account for temperature effects, the corresponding specific volume change between temperature  $t_0$  and  $t$  is

$$V_s(t) - V_s(t_0) = \Delta(t, t_0) x_1 + \sum_{i=2}^{q+1} [\phi V_{si}(t) - \phi V_{si}(t_0)] x_i \quad (7)$$

where

$$\Delta(t, t_0) = v_{s1}^0(t) - v_{s1}^0(t_0)$$

The temperature dependence of each saccharide's apparent specific volume is taken to vary linearly with temperature:

$$\phi V_{si}(t) - \phi V_{si}(t_0) = (t - t_0)(\beta_{1i} + \beta_{2i} s + \beta_{3i} s^2 + \beta_{4i} s^3) \quad (8)$$

The temperature effect for water is treated exactly and that of the ash neglected. Analysis later indicates that approximation 8 will not properly account for all the temperature dependence. It is expedient to replace the difference in specific volume of pure water by  $\Delta(t, t_0)$  times  $(1 + \alpha_1 s + \alpha_2 s^2 + \alpha_3 s^3)$  rather than introduce second-order temperature effects to the saccharide apparent specific volumes. Therefore, small nonlinearities in  $V_s$  with respect to temperature are conveniently represented as a dry substance correction.

#### EXPERIMENTAL DATA

Wartman et al. (1984) have studied the density-dry substance relation of 18 syrup mixtures. Using 100 mL volume pycnometers, they were able to measure densities to  $\pm 5 \times 10^{-5}$  g/mL (assuming weighing errors of  $\pm 0.002$  g). Refer to their paper for experimental details.

Selecting temperatures of 15.55, 20.00, 40.00, and 60.00 °C, they reported densities for each syrup type at four dry substance (DS) levels ranging from 10 to 80% DS. Percent DS is determined indirectly from 20 °C refractive index measurements by backward interpolation of the refractive index-DS model found in the Appendix of Wartman et al. (1980). Corrections are necessary, however, in their reciprocal refractive index relationship. The sign of the temperature contribution, which has the factor  $(t - 20)$ , should be changed from plus to minus. Furthermore, a sulfated ash term,  $0.0168As^2$ , should be subtracted from the right side of the relationship. Refractive index reproducibility of  $\pm 0.00005$  corresponds to  $\pm 0.02$  error in percent DS.

High-pressure liquid chromatography was used by Wartman et al. (1984) to determine saccharide distributions. This compositional information is used to calculate the dry substance and to perform density modeling.

Density data for solutions of dextrose, fructose, invert sugar, and sucrose, taken from the literature, have been included in the present analysis (Wartman et al., 1984).

#### RESULTS

The statistical analysis follows a two-stage model building strategy. First, a specific volume-temperature relationship is developed. Next, a specific volume-composition model at base temperature  $t_0 = 20$  °C is determined. The minimum number of pseudocomponents is determined at each stage. Initially, all components that are resolved chromatographically (dextrose, fructose, sucrose, DP2, DP3, DP4+) are treated as contributing distinct apparent specific volumes. (An example of a logical pseudocomponent is DP2+, which combines DP2, DP3,

Table I. Parameter Estimates for Equations 9 and 13<sup>a</sup>

j	10 <sup>4</sup> β <sub>ij</sub>			
	dextrose, j = 1	fructose, j = 2	sucrose, j = 3	DP2+, j = 4
1	6.05790	8.01021	4.96852	5.50896
2	1.38848	-0.305881	4.31398	2.38307
3	-11.69530	-7.40144	-14.56460	-11.44500
4	6.72079	2.8377	7.73088	5.68493

$${}^a \alpha_1 = -0.383087. \quad \alpha_2 = -1.365900. \quad \alpha_3 = 1.646390.$$

and DP4+ as a single component.) There are 565 cases of data used in our analysis (379 experimental and 186 literature cases).

In the first modeling stage, the expression

$$V_s(t) - V_s(20) - \Delta(t,20)(1-s) = \Delta(t,20)(1-s)(\alpha_1 + \alpha_2 s + \alpha_3 s^2) s + (t-20) \sum_{i=1}^q (\beta_{1i} + \beta_{2i} s + \beta_{3i} s^2 + \beta_{4i} s^3) x_{i+1} + \text{error} \quad (9)$$

describes the assumed specific volume-temperature model plus error. Analysis is based on a zero-intercept multiple linear least-squares fitting procedure. After several passes, the analysis indicates that the number of components could be reduced from 6 to 4. Included saccharides are dextrose, fructose, sucrose, and DP2+. Inclusion of the  $\alpha$  terms in the model decreases the residual root mean square error (RRMSE) from  $1.49 \times 10^{-4}$  to  $5.6 \times 10^{-5}$  mL/g [403 degrees of freedom (df) for residuals]. When the  $\alpha$  terms are omitted from the model, the extreme levels in the high percent DS sucrose data are outliers in the modeling. Furthermore, the corn syrup data systematically undercorrects the not 20 °C data to the observed 20 °C densities. Generally, the  $\alpha$  terms provide a common nonlinear temperature correction for the total dry substance. A standard deviation of replicate error (estimated from the residuals of neighboring observations) is  $3.6 \times 10^{-5}$  mL/g. For a low specific volume syrup (density = 1.4 g/mL), this replicate error is close to  $3 \times 10^{-5}$  mL/g, the standard error estimate for the measurement; see Table I for estimates for the  $\alpha$ 's and  $\beta$ 's for the four saccharides.

Statistical analysis of the 20 °C corrected density data (ash corrected) follows in a similar fashion. This analysis, based on eq 5, is defined by the expression

$$V_s(t) - [V_s(t) - V_s(20)]_{\text{calcd}} - v_{s1}^0(20)(1-s) - 0.287(1 + 0.58s)sA = \sum_{i=1}^q (\epsilon_{1i} + \epsilon_{2i} s + \epsilon_{3i} s^2 + \epsilon_{4i} s^3) x_{i+1} + \text{error} \quad (10)$$

Apparent specific volumes for all six saccharides were required to adequately account for variation in the dependent variable (left-hand side of eq 10). When the full eq 10 is modeled, a RRMSE value of  $1.95 \times 10^{-4}$  mL/g is obtained (541 residual df). Residuals analysis suggests internal consistency of the data. A variable selection procedure based on "best subset regression" and the Cp criteria (Daniel and Wood, 1980) simplifies this model somewhat by excluding three terms with high order in  $s$  (RRMSE =  $1.95 \times 10^{-4}$  mL/g, 544 residual df). A relatively large RRMSE, as compared to the internal estimate of error,  $4.5 \times 10^{-5}$  mL/g, remains. The source of the unexplained variability resides largely as small systematic errors in samples 3, 14, 15, 18, 19 and the literature dextrose [see Wartman et al. (1984), Table I, for sample identification]. Model inadequacy is not likely because the experimental plan has four levels of DS per syrup type and the model has four parameters per component to account for DS effects; see Table II for estimates of  $\epsilon$  coefficients for the six saccharide components.

Table II. Parameter Estimates for Equations 10 and 11

saccharide (j)	10 <sup>2</sup> ε <sub>ij</sub>			
	i = 1	i = 2	i = 3	i = 4
dextrose (1)	62.0432	0.627519	4.60687	-2.12504
fructose (2)	61.2753	0.992279	2.70443	
sucrose (3)	61.6979	-0.299045	4.92218	-2.41932
DP2 (4)	60.9621	3.081050		
DP3 (5)	59.6075	9.158810	-21.31450	17.10960
DP4+ (6)	60.6680	-2.774940	8.47427	-3.04761

## DISCUSSION

The apparent specific volume,  $\phi V_s(t)$ , of dextrose, fructose, sucrose, DP2, DP3, and DP4+ in aqueous solutions at  $t = 20$  °C is determined to be of the form in eq 6 with the  $\epsilon$  parameters shown in Table II. Specific volumes,  $V_s(20)$ , of saccharide solutions may be calculated according to an expression similar to eq 5. Thus

$$V_s(20) = 1.00177(1-s) + 0.287(1 + 0.58s)x_{\text{ash}} + \sum_{i=1}^6 (\epsilon_{1i} + \epsilon_{2i} s + \epsilon_{3i} s^2 + \epsilon_{4i} s^3) x_{i+1} \quad (11)$$

where dry substance,  $s$ , is defined by

$$s = x_{\text{ash}} + \sum_{i=1}^6 x_{i+1} = 1 - x_1 \quad (12)$$

Specific volumes,  $V_s(t)$ , between 15.55 and 60 °C can be determined by

$$V_s(t) = V_s(20) + \Delta(t,20)(1 + \alpha_1 s + \alpha_2 s^2 + \alpha_3 s^3) \times (1-s) + (t-20) \sum_{i=1}^4 (\beta_{1i} + \beta_{2i} s + \beta_{3i} s^2 + \beta_{4i} s^3) x_{i+1} \quad (13)$$

where the  $\alpha$ 's and  $\beta$ 's are found in Table I.

Derivation of the partial specific volumes expressions for the components in a binary saccharide-water mixture can be found in the Appendix. The partial specific volume of dextrose,  $v_{s2}(x_2, t)$ , and the apparent specific volume of dextrose,  $\phi V_s(t)$ , at 20 and 80 °C are shown in Figure 1. The data are those of Schliephake (1965). The curves are calculated from the least-squares estimates of  $\epsilon$ 's that result from fitting his  $\phi V_s$  vs.  $x_2$  data (excluding  $x_2 = 0$  data) to expression 4 at each temperature. As should be the case, the second term in expression 19, which accounts for the differences between  $v_{s2}$  and  $\phi V_s$ , vanishes at the limits of  $x_2$ .

Figure 2 shows the compositional dependence of solution specific volume and component partial specific volumes of dextrose solutions at 20 and 60 °C. The parameters for dextrose are taken from Tables I and II. The specific volume quantities are related by

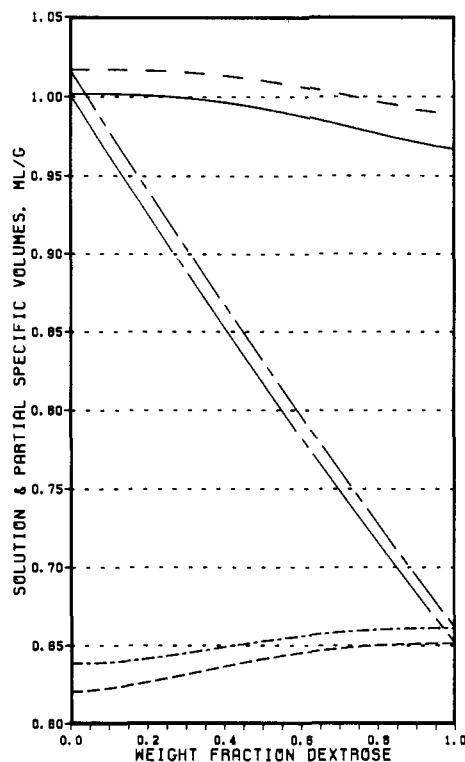
$$V_s = v_{s1} x_1 + v_{s2} x_2 \quad (14)$$

and

$$dV_s/dx_2 = v_{s2} - v_{s1} \quad (15)$$

where  $dV_s/dx_2$  is the slope to the tangent line of the  $V_s$  curve at a given  $x_2$ . The slope in the dilute limit is  $\epsilon_1 - v_{s1}^0$ .

The partial specific volume of water,  $v_{s1}(x_2, t)$ , being a bulk property of all water present in the mixture, varies with composition. It measures the change in solution that occurs when added water is proportioned over all molecular aggregations within the solution. In the dilute limit, the state of aggregation is hydrogen-bonded "structured" water where  $v_{s1} = v_{s1}^0$ . In the concentrated limit of a glassy saccharide, the probability of water hydrogen bonded to itself is small and water is hydrogen bonded to the hydroxyl groups on the saccharide. The corresponding  $v_{s1}$  is  $v_{s1}^0 - (\epsilon_2 + 2\epsilon_3 + 3\epsilon_4)$ . Table III presents the limits of



**Figure 2.** Solution and component partial specific volumes of dextrose solutions at 20 and 60 °C vs. weight fraction of dextrose. Curves: [(---) and (—)] partial specific volumes of water at 60 and 20 °C, respectively; [(---) and (—)] solution specific volumes at 60 and 20 °C, respectively; [(---) and (—)] partial specific volumes of dextrose at 60 and 20 °C, respectively.

**Table III.** Partial Specific Volume of Water,  $v_{s1}(x_2)$ , mL/g, in Saccharide Solutions

	20 °C, $v_{s1}(0) = 1.0018$		60 °C, $v_{s1}(0) = 1.0170$	
	$v_{s1}(1)$	$v_{s1}(0) - v_{s1}(1)$	$v_{s1}(1)$	$v_{s1}(0) - v_{s1}(1)$
dextrose	0.9671	0.0347	0.9882	0.0289
fructose	0.9378	0.0640	0.9778	0.0392
sucrose	0.9789	0.0229	0.9991	0.0179
DP2	0.9710	0.0308	0.9985	0.0186
DP3	0.8232	0.1786	0.8507	0.1664
DP4+	0.9515	0.0503	0.9790	0.0381

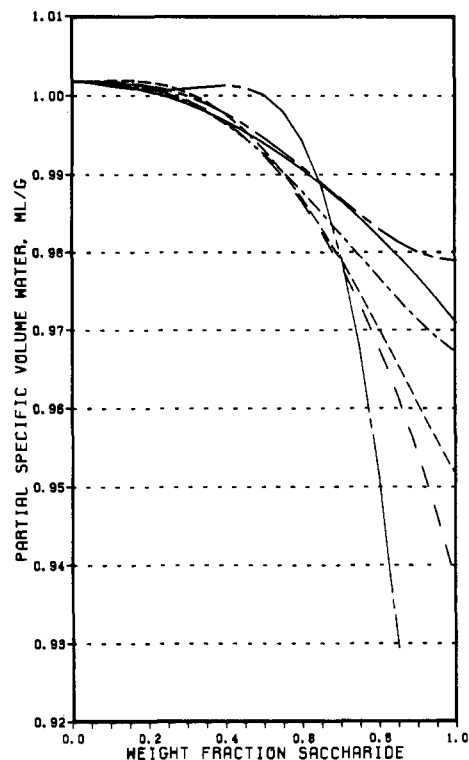
**Table IV.** Volume Properties of Saturated Solutions of Saccharides at 20 °C

	dextrose	fructose	sucrose
$x_2$	0.6065	0.794	0.6710
$R^a$	6.5	2.6	4.7
$v_{s1}$	0.9875	0.9684	0.9881
$v_{s2}$	0.6457	0.6463	0.6365
$V_s$	0.7802	0.7127	0.7522
$F^b$	0.4980	0.2799	0.4322
$F/R$	0.08	0.11	0.09

<sup>a</sup> $R$  = ratio of water molecules to saccharide residues. <sup>b</sup> $F$  =  $v_{s1}x_1/V_s$  = volume fraction of water.

$v_{s1}(x_2, t)$  at 20 and 60 °C for six saccharides. The differences,  $v_{s1}(0, t) - v_{s1}(1, t) = \epsilon_2 + 2\epsilon_3 + 3\epsilon_4$ , measure the "specific volume" of water tightly bound to each saccharide.

The volume of water aggregated on each saccharide in dilute solution cannot be specified because the volume of solution occupied by water,  $v_{s1}x_1$ , has contributions mainly from solvent "structured" regions rather than water-saccharide aggregations. However, at the solubility limit of the saccharide, nearly all water is aggregated to the saccharide. The 20 °C solubility limit data for dextrose, fructose, and sucrose are shown in Table IV. The volume



**Figure 3.** Partial specific volume of water in binary saccharide-water mixtures at 20 °C vs. weight fraction of saccharide. Curves: (---) sucrose; (—) DP2; (---) dextrose; (---) DP4+; (---) fructose; (---) DP3.

**Table V.** Partial Specific Volume of Saccharides in Infinitely Dilute Aqueous Solution at 25 °C

saccharide	$v_{s2}(0, 25)$ , mL/g	
	present work	Høiland and Holvik (1978)
dextrose	0.6230	0.6200 ± 0.0012, 0.6227, 0.6211, 0.6189
fructose	0.6163	
sucrose	0.6190	0.6182 ± 0.0029, 0.6141, 0.6132
DP2	0.6119	0.6135 ± 0.0029, 0.6100
DP3	0.5984	
DP4+	0.6090	

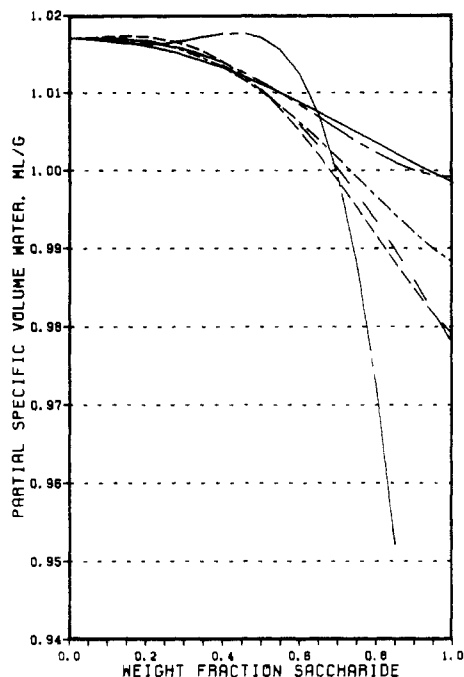
**Table VI.** Partial Specific Volume of Saccharides

saccharide	$v_{s2}(x_2)$ , mL/g, at 20 and 60 °C					
	$v_{s2}(0)$			$v_{s2}(1)$		
	60 °C	20 °C	difference	60 °C	20 °C	difference
dextrose	0.6388	0.6204	0.0184	0.6614	0.6515	0.0099
fructose	0.6389	0.6127	0.0262	0.6623	0.6497	0.0216
sucrose	0.6310	0.6170	0.0140	0.6488	0.6390	0.0098
DP2	0.6258	0.6096	0.0162	0.6490	0.6404	0.0085
DP3	0.6123	0.5961	0.0162	0.6541	0.6456	0.0085
DP4+	0.6229	0.6067	0.0162	0.6417	0.6332	0.0085

fraction  $F$ , estimates what proportion of the water-saccharide aggregation is water. The ratio,  $F/R$ , is approximately 0.1 because it compares the water proportion on an equal  $R$  basis.

Figures 3 and 4 show the compositional relations of  $v_{s1}(x_2, t)$  for six different saccharide solutions at  $t = 20$  and  $60$  °C, respectively. As Table III has shown, each saccharide has a unique intercept on the ordinate at  $x_2 = 1$ . In general,  $v_{s1}$  increases with increasing temperature. This change in  $v_{s1}$  results from an increase in  $v_{s1}$  and a decrease in the magnitude of  $\epsilon_2 + 2\epsilon_3 + 3\epsilon_4$ . Hence, differences in  $v_{s1}$  among the saccharides are reduced at elevated temperature, but they remain distinct.

The partial specific volume of a saccharide,  $v_{s2}(x_2, t)$  increases as a function of  $x_2$  from the infinitely dilute value,  $\epsilon_1$ , to the concentrated limit ( $x_2 = 1$ ),  $\epsilon_1 + \epsilon_2 + \epsilon_3 + \epsilon_4$ .



**Figure 4.** Partial specific volume of water in binary saccharide-water mixtures at 60 °C vs. weight fraction of saccharide. Curves: (—) sucrose; (---) DP2; (· · ·) dextrose; (- · - ·) DP4+; (- - -) fructose; (— · —) DP3.

Høiland and Holvik (1978) reported partial molal volumes,  $\bar{v}_2$ , of saccharides in infinitely dilute aqueous solutions at 25 °C. Our partial specific volumes,  $v_{s2}(0,25)$ , are compared with literature values in Table V. The 20 and 60 °C values of  $v_{s2}(x,t)$  at the composition limits are shown in Table VI. Values of  $v_{s2}(0,20)$  suggest a very compact structure in contrast to the glassy and crystalline states for the saccharides. This is particularly true for DP2, DP3, and DP4+. Neal and Goring (1970) have suggested that maltose undergoes hydrophobic folding in dilute solution. Thermal effects tend to wash out differences between monosaccharides and between sucrose and DP2. Parks et al. (1928) determined  $V_s = 0.6566$  mL/g for glassy dextrose at 20 °C. Our extrapolated value,  $v_{s2}(1,20) = 0.6515$  mL/g, is intermediate between that and anhydrous crystalline  $\alpha$ -D-glucose (0.6402 mL/g). They reported the coefficient of thermal expansion to be  $\alpha_v = 3.7 \times 10^{-4}$  (°C) $^{-1}$  above 60 °C. We estimate  $\alpha_v$  from the expression

$$\alpha_v = [v_{s2}(1,60)/v_{s2}(1,20) - 1]/40 \quad (16)$$

to be  $3.8 \times 10^{-4}$  (°C) $^{-1}$ . Schwers (1911) studied the specific volume of glassy sucrose from -14.55 to 114.70 °C. Our extrapolated value,  $v_{s2}(1,20) = 0.6396$  mL/g, lies between his value, 0.6593 mL/g, and crystalline sucrose's value (0.6357 mL/g). The ratio of Schwer's specific volumes,  $V_s(60)/V_s(20) = 1.0130$ , compares well with our ratio,  $v_{s2}(1,60)/v_{s2}(1,20) = 1.0153$ .

The above considerations are part of the general model validation process where the extrapolation capabilities of the solution specific volume model have been examined. Furthermore, the partial specific volume relations provide a general formalism for this model. These partial quantities help point out weakness in the model. For example, DP3 never exceeds 20% DS in any data case. Hence, parameter estimation might be poor for its  $\epsilon$ 's. The  $v_{s1}$  curve for DP3 in Figures 3 and 4 bears this out. For DP3,  $v_{s1}(x_2)$  should not exceed  $v_{s1}^0$ . Furthermore,  $v_{s1}(x_2 = 1)$  is very low relative to DP4+. (Correspondingly,  $v_{s2}$  has a spurious minimum less than  $\epsilon_1$ .) Hence, DP3 is inconsistent with the other saccharides. Nevertheless, the term  ${}^\phi V_{s6}x_6$

in eq 5 has sufficient precision for mixtures where  $x_6$  is less than 0.2.

A general word of caution is necessary concerning extrapolations to the high concentration limit. For example, Figures 3 and 4 show the partial specific volume of water,  $v_{s1}(x_2)$ , extending above the experimental limits of  $x_2$ , i.e.,  $x_2 > 0.7$ . However, the extrapolated partial specific volumes of dextrose and sucrose at the high concentration limit,  $v_{s2}(x_2 = 1)$ , range between measured glassy and crystalline specific volumes.

In summary, the solution specific volume-composition-temperature data of commercial corn syrup mixtures is analyzed. A model, based on apparent specific volumes of the component saccharides, is used. Relations are derived that describe the partial specific volumes of binary saccharide-water mixtures,  $v_{s1}$  and  $v_{s2}$ , in terms of composition, temperature, and the various parameters of apparent specific volumes. Partial specific volumes of water and saccharides are discussed in the dilute solution limit, at the saccharide solubility limit, and at the high concentration limit.

#### APPENDIX

**Partial Specific Volumes of a Binary Mixture.** The mixture volume has the partial specific volume form

$$V = v_{s1}w_1 + v_{s2}w_2 \quad (17)$$

where the partial specific volumes are partial derivatives of  $V$  with respect to one component's weight holding the other component's weight constant, i.e.

$$v_{s1} = \partial V / \partial w_1 \quad v_{s2} = \partial V / \partial w_2 \quad (18)$$

The physical interpretation of the partial specific volume is as follows. The partial specific volume of solvent is that volume change that occurs when 1 g of solvent is added to the solution consisting of  $w_1$  grams of solvent and  $w_2$  grams of solute. An analogous statement holds for the solute.

The partial specific volume of the solute, taking expressions 2 and 4 into account, is given by

$$v_{s2} = {}^\phi V_s + (\epsilon_2 + 2\epsilon_3x_2 + 3\epsilon_4x_2^2)x_1x_2 = \epsilon_1 + 2\epsilon_2x_2 + (3\epsilon_3 - \epsilon_2)x_2^2 + (4\epsilon_4 - 2\epsilon_3)x_2^3 - 3\epsilon_4x_2^4 \quad (19)$$

By use of a similar differentiation, the partial specific volume of solvent is given by

$$v_{s1} = v_{s1}^0 - (\epsilon_2 + 2\epsilon_3x_2 + 3\epsilon_4x_2^2)x_2^2 \quad (20)$$

These partial quantities have the following limits: at  $x_2 = 0$ ,  $v_{s1} = v_{s1}^0$  and  $v_{s2} = \epsilon_1$ ; at  $x_2 = 1$ ,  $v_{s1} = v_{s1} - (\epsilon_2 + 2\epsilon_3 + 3\epsilon_4)$ , and  $v_{s2} = \epsilon_1 + \epsilon_2 + \epsilon_3 + \epsilon_4$ .

The effects of temperature on the partial quantities [ $i = 1$  (solvent) or 2 (solute)] can be expressed by

$$v_{si}(t) = v_{si}(t_0) + \partial[V(t) - V(t_0)] / \partial w_i \quad (21)$$

where

$$\partial[V(t) - V(t_0)] / \partial w_1 = \Delta(t, t_0)[1 + \alpha_1x_2 + \alpha_2x_2^2 + \alpha_3x_2^3 - (\alpha_1 + 2\alpha_2x_2 + 3\alpha_3x_2^2)x_1x_2] - (t - t_0)x_2^2(\beta_2 + 2\beta_3x_2 + 3\beta_4x_2^2) \quad (22)$$

$$\partial[V(t) - V(t_0)] / \partial w_2 = \Delta(t, t_0)x_1^2(\alpha_1 + 2\alpha_2x_2 + 3\alpha_3x_2^2) + (t - t_0) \times [\beta_1 + \beta_2x_2 + \beta_3x_2^2 + \beta_4x_2^3 + (\beta_2 + 2\beta_3x_2 + 3\beta_4x_2^2)x_1x_2] \quad (23)$$

Hence, the solution volume, as expressed by a partial specific volume relationship (17), can now be calculated at any specific temperature and composition.

The specific volume,  $V_s$  of the saccharide-water mixture exhibits a very strong dependence on the saccharide weight

fraction (see Figure 2). The slope to the tangent line of the  $V_s$  curve at some  $x_2$  describes the change in  $V_s$  resulting from a change in  $x_2$ . This slope, the ratio of these changes, can be related to partial specific volumes and the apparent specific volume parameters by the expressions

$$dV_s/dx_2 = (v_{s2} - V_s)/x_1 = v_{s2} - v_{s1} = \epsilon_1 - v_{s1}^\circ + (2\epsilon_2 + 3\epsilon_3x_2 + 4\epsilon_4x_2^2)x_2 \quad (24)$$

$$dV_s/dx_1 = (v_{s1} - V_s)/x_2 = -dV_s/dx_2 \quad (25)$$

In the dilute limit ( $x_2 = 0$ ),  $dV_s/dx_2$  is equal to  $\epsilon_1 - v_{s1}^\circ$ . In the high concentration limit ( $x_2 = 1$ ),  $dV_s/dx_2$  is equal to  $\epsilon_1 - v_{s1}^\circ + 2\epsilon_2 + 3\epsilon_3 + 4\epsilon_4$ .

**Abbreviations Used:** A, weight fraction of dry substance that is sulfated ash; DS, dry substance, weight fraction of nonaqueous components; DP $_i$ , saccharide consisting of  $i$  monomers (dextrose units); DP4+, component consisting of tetrasaccharides and saccharides of higher DP (degree of polymerization);  $dV_s/dx_2$ , derivative of specific volume with respect to the saccharide weight fraction;  $F$ , volume fraction of water in solution;  $q$ , number of saccharide components;  $R$ , ratio of water molecules to saccharide residues in solution;  $s$ , weight fraction of dry substance (saccharides plus ash) in solution;  $t$ , temperature in degree Celsius;  $t_0$ , base temperature, 20 °C;  $V$ , solution volume, mL;  $V_s$ , solution specific volume, mL/g;  ${}^\circ V_{si}$ , apparent specific volume of the  $i$ th saccharide in water, mL/g;  $v_{s1}$ , partial specific volume of water, mL/g;  $v_{s1}^\circ$ , specific volume of pure water, i.e., 1.00177 mL/g at 20 °C;  $v_{si+1}$ , partial specific volume of only the  $i$ th saccharide in water, mL/g;  $w_1$ , weight water, g;  $w_2$ , weight saccharide, g;  $x_1$ , weight fraction of water;  $x_2$ , weight fraction of solute in binary mixture;  $x_{i+1}$ , weight fraction of the  $i$ th saccharide in solution;  $x_{ash}$ , weight fraction of ash in solution;  $\alpha_1$ ,  $\alpha_2$ ,

and  $\alpha_3$ , parameters associated with higher order thermal effects of dry substance;  $\alpha_v$ , coefficient of thermal expansion of liquid, (°C)<sup>-1</sup>;  $\beta_{ij}$ , temperature parameter of ( $i - 1$ ) order in  $s$  for apparent specific volume of the  $j$ th saccharide;  $\epsilon_{ij}$ , compositional parameter of ( $i - 1$ ) order in  $s$  for apparent specific volume of the  $j$ th saccharide;  $\Delta$ , difference in specific volume of water at temperature  $t$  and  $t_0$ , mL/g;  $\partial$ , symbol for partial differentiation; ash, ash component (on inorganic sulfate basis);  $s$ , specific; 1, water component; 2, saccharide solute in binary mixture;  $v$ , volume;  $\phi$ , apparent;  $^\circ$ , pure component.

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**Registry No.** Dextrose, 50-99-7; fructose, 57-48-7; sucrose, 57-50-1.

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## High-Performance Liquid Chromatographic Determination of Furfural in Orange Juice

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A high-performance liquid chromatographic (HPLC) method to quantify the amount of furfural in orange juice has been developed. It was found necessary to separate furfural from interfering compounds by distilling the juice. The distillate was injected on a Du Pont Zorbax ODS column. The furfural was eluted with water-methanol (70:30 v/v). Detection was by absorbance at 280 nm. A linear response was obtained from 12 to 20 000 ppb. The minimum detectable level of furfural in orange juice is 2 ppb. Compared to traditional colorimetric methods of furfural analysis, the HPLC procedure was more precise, had a wider range, and could be run in less time with safer reagents.

Processed orange juice and orange concentrate are susceptible to color, flavor, odor, and nutritional changes if stored for extended periods above refrigerated (4 °C) temperatures. Many chemical tests have been suggested to indicate storage abuse (Dinsmore and Nagy, 1971; Nagy and Nordby, 1970). A test that is widely accepted as an indication of general flavor changes in citrus juices

subjected to storage temperature abuse is the test for furfural (Dinsmore and Nagy, 1972, 1974). This test was chosen because furfural is virtually nonexistent in fresh citrus juice, whereas large amounts of furfural have been reported in citrus juices stored at improper temperatures (Kirchner and Miller, 1957; Rymal et al., 1968; Dinsmore and Nagy, 1971).

Furfural content is useful as an off-flavor indicator, although it does not cause the off-flavor developed during temperature abuse of citrus juices (Tatum et al., 1975). A strong relationship between flavor change in orange and grapefruit juice and furfural content has been shown (Nagy

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