V_L	liquid specific volume, $cm^3\ mol^{-1}$
x	mole fraction in liquid phase
y	mole fraction in vapor phase
γ	activity coefficient
δ_{12}	$2B_{12} - B_1 - B_2$
ρ	liquid density, $g\ cm^{-3}$
ΔH_m	heats of mixing, $J\ mol^{-1}$
η	refractive index at 30 °C, using sodium D line
Θ	difference between the pure component boiling points
ϕ	intermolecular potential energy

Subscripts

1	component 1, benzene
2	component 2
B	benzene
D	1,2-dichloroethane
TR	1,1,1-trichloroethane
TE	1,1,2,2-tetrachoroethane
B-D	mixture of benzene–1,2-dichoroethane
B-TR	mixture of benzene–1,1,1-trichloroethane
B-TE	mixture of benzene–1,1,2,2-tetrachloroethane

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Corn Syrup Composition–Refractive Index–Dry Substance Relation: Development of a General Equation

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A general equation relating refractive index–dry substance–composition of corn syrups was developed from data published by the Corn Refiners Association. The composition information used was dextrose equivalents and saccharide distribution through DP7+. Using the equation, refractive index–dry substance tables for the reference syrups were computed which agreed well with the reference tables. The equation can be used to generate refractive index tables for new syrups or blends without extensive laboratory work.

Introduction

Wartman et al.[1] reported a study (sponsored by the Corn Refiners Association) of the relation between refractive index and dry substance for a variety of commercial corn syrups. The saccharide compositions and dextrose equivalents (DE) also were reported. Examination of the data suggested a functional relation between refractive index, dry substance, and composition.

Other investigators using previously reported syrup refractive index–dry substance tables have shown the effect of composition on the relation between refractive index and dry substance. Malinsky,[2] and Cakebread[3] expressed the dry substance determined by refractive index as a function of dextrose equivalent.

With the introduction of enzyme technology in the manufacture of corn syrup, a variety of syrup compositions have been produced, which differ from compositions obtained by simple acid hydrolysis of starch. Syrups of the same dextrose equivalent sometimes differ significantly in their saccharide composition. See, for example, the pairs of syrups 2 and 5, 3 and 6, and 9 and 10 in Wartman Table II.[1] It is apparent that the dextrose equivalent dependence of refractive index is not sufficient to explain all of the variation in the relationship with dry substance and that saccharide composition also must be

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Table I. Regression Coefficients, $A_{i,j}$

variable name	i	$j = 1$	$j = 2$	$j = 3$
DE	1	0.004 933	0	−0.000 831 1
dextrose	2	0.644 247	0.001 245 8	0
levulose	3	0.645 647	−0.002 343 1	0.002 939 2
DP2	4	0.644 247	−0.002 086 3	0
DP3	5	0.641 839	0	0
DP4	6	0.644 247	−0.003 898 2	0
DP5	7	0.644 247	0	0
DP6	8	0.644 247	0	−0.007 521 9
DP7+	9	0.644 247	-0.005 014 7	−0.002 333 2

considered. A suitable general relation would be useful for formulating refractive index–dry substance tables for syrups of other compositions not included in the recent study.

Experimental Section and Results

The data on which to base a general relation are available in Table II[1] and the supplementary tables of that study. A mathematical function, suggested by the work of Barber[4] and used by Wartman[1] can readily be modified by expansion to accommodate composition variables. The function, as used by Wartman was of the form

$$\frac{1}{n_D} = \frac{1}{n_{D,H_2O}}(1 + 0.0277701s)(1 - s) + (A_1 + A_2s + A_3s^2)s + (B_1s + B_2s^2)(t - 20) + (C_1 + C_2s)\left(\frac{su}{100}\right) \quad (1)$$

Where n_D = refractive index of the solution at temperature t °C, n_{D,H_2O} = refractive index of water at temperature t °C, s = grams of dry substance per gram of solution, and u = sulfated ash, percent dry basis.

A_1, A_2, and A_3 are coefficients characteristic of the particular syrup; B_1 and B_2 are temperature effect coefficients; C_1 and C_2 are ash effect coefficients.

The function can be expanded by introducing an additional term for each composition variable added. These additional terms have the general form $(A_{i,1} + A_{i,2}s + A_{i,3}s^2)c_i$, where $A_{i,1}$, $A_{i,2}$, and $A_{i,3}$ are regression coefficients, s = grams of dry substance per gram of solution, and c_i = grams of composition component per gram of solution.

These additional terms replace the second term in eq 1. Nine composition components were considered: dextrose equivalent, dextrose, levulose, and the Maltooligosaccharides DP2, DP3, DP4, DP5, DP6, and DP7+.

Since it was not the objective to develop a general relation including the effects of temperature and ash, the raw data of Wartman were adjusted, using her regression equations, to the base temperature of 20 °C and 0.0% ash. Data of other investigators for pure dextrose,[5] pure levulose,[6] and pure maltose[7] were included in the study.

The adjusted experimental data were fit to the function using a stepwise multiple linear regression program on an IBM 1130 computer. Eighteen nonzero coefficients were obtained, their values and the corresponding variables are shown in Table I. The functional form was

$$\frac{1}{n_D} = \frac{1}{n_{D,H_2O}}(1 + 0.0277701s)(1 - s) + \sum_{i=1}^{9}(A_{i,1} + A_{i,2}s + A_{i,3}s^2)c_i \quad (2)$$

where n_D = refractive index of the solution at 20 °C, 0.0% ash, n_{D,H_2O} = refractive index of water at 20 °C, s = grams of dry substance per gram of solution, c_i = grams of composition component (i) per gram of solution, and $A_{i,1}$, $A_{i,2}$, and $A_{i,3}$ = regression coefficients.

The standard deviation of residuals was 0.000 11 reciprocal refractive index units for the 123 observations used to develop the regression coefficients.

Table II. Comparison of Refractive Indices from Publications and by Calculation

material	dry substance, %	refractive index at 20 °C published	calculated	difference
syrup 1, 27 DE[4]	70	1.472 83	1.472 60	−0.000 23
syrup 2, 43 DE[4]	84	1.507 88	1.507 99	0.000 11
syrup 3, 55 DE[4]	84	1.505 26	1.505 09	−0.000 17
syrup 4, 33 DE[4]	84	1.510 40	1.510 49	0.000 09
syrup 5, 44 DE[4]	84	1.508 28	1.508 32	0.000 04
syrup 6, 49 DE[4]	84	1.506 80	1.506 58	−0.000 22
syrup 7, 65 DE[4]	84	1.503 38	1.503 51	0.000 13
syrup 8, 70 DE[4]	84	1.501 96	1.502 11	0.000 15
syrup 9, 95 DE[4]	74	1.471 77	1.471 83	0.000 06
syrup 10, 94 DE[4]	74	1.471 73	1.471 49	−0.000 24
syrup 11, 12 DE[4]	54	1.434 93	1.435 12	0.000 19
dextrose[5]	50	1.418 26	1.418 18	−0.000 08
maltose[7]	50	1.421 70	1.421 78	0.000 08
levulose[6]	50	1.418 15	1.418 08	−0.000 07

Table III. Comparison of Observed Refractive Index at 20 °C with the Value Calculated from Composition Data for Test Syrups

DE	75.2	85.4	25.5	29.0	53.5
dextrose	42.3	47.7	6.1	3.4	1.7
levulose	14.9	31.6	0.0	0.0	0.0
DP2	19.2	12.3	7.0	13.1	68.6
DP3	7.8	3.2	8.1	15.7	19.6
DP4	3.6	1.2	6.8	7.7	1.0
DP5	2.6	0.8	6.4	14.2	0.5
DP6	1.9	0.6	7.4	13.2	0.7
DP7+	7.7	2.6	58.2	32.7	7.9
ash	0.3	0.1	0.4	0.0	0.4
dry substance, %	79.20	74.57	78.25	74.72	82.49
calculated index	1.4883	1.4743	1.4956	1.4843	1.5017
observed index	1.4884	1.4747	1.4955	1.4846	1.5019

Refractive index tables were generated for the syrups and sugars used to develop the general regression equation. The actual DE and composition values for each material were used. For purposes of comparison, the calculated syrup refractive index values were adjusted for DE and ash to those for Tables VI–XVI of Wartman. The differences in refractive index (at maximum dry substance) between the published tables and those calculated (and adjusted) are in Table II and show generally good agreement.

The equation was tested also on a number of syrups prepared to reflect compositions departing from the common commercial ones. Some of the test syrups were purposely made and others were prepared by blending. Agreement between calculated and laboratory determined indices was good, as shown in Table III.

The utility of this general equation lies in reducing the work necessary when preparing a refractive index–dry substance table for a syrup of new composition. First, a tentative table can be computed using composition information. Second, the refractive index and dry substance of the syrup can be measured in the laboratory. Third, the difference between the measured and calculated indices can be used to correct the tentative table, at the measured dry substance and at all other concentrations by proportion.

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