Kinetics of Sucrose Crystallization:
Mechanism of the Reaction in Real Massecuites[1]

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Although the activity interpretation of sucrose crystallization, already sueessfully applied to pure sucrose solutions and synthetic massesuites (11)[3], does not require any mechanical or molecular model, it does imply (*11d*) an independence of any structural nature or transport behavior in the operating medium, it is therefore necessary to establish this suggested independence to warrant continued application of the activity theory to the ultimate practical goal of pan boiling and crystallization, it has been demonstrated with pure sucrose solution, and intimated for impure syrups (*11c*), that crystallization rates are determined by some interfacial reaction rather than an interboundary one. That is, as frequently suggested in sugar literature but often overlooked, diffusion and viscosity are not primary rate controlling factors in the crystallization of sucrose. It is the intention of this paper to examine the role of diffusion and the reciprocally related viscosity as controlling factors in determining the velocity of crystallization of sucrose from real massecuites.

Methods

Massecuites were made up from various beet and cane final molasses. Most, of the results herein reported are for a typical non-Steffens beet molasses (East Grand Forks factory of Americal Crystal Sugar Company) and a Cuban blackstrap (Pennsylvania Sugar Company). Solubilities were determined by Brown's (*1*) method; good correlation being obtained between drying and refractometric methods of determining dry substance when the latter method was previously standardized with the particular molasses under consideration. Grut's (*2*) tables of solubilities were found to apply to these beet syrups within reasonable variation, and the pattern suggested by Thieme (*10*) for cane syrups was also confirmed, although deviations from his average curve are marked.

The rate of adjustment of non-saturated massecuites was followed refractometrically where possible and by a modified Nees' technique in others. These methods have been shown to yield comparable results (7. *11b*). To display significant differences most experiments were performed at an effective purity of 75 percent (*4*). Stock solutions of both the cane and beet molasses were made saturated at 30° C. at this nominal purity. In subsequent over saturating, undersaturating, or addition of contaminants, etc., the impurity-to-water ratios of these base molasses were retained constant.

Saturation coefficients are expressed as oversaturations—the quotient of sucrose/water ratio in the actual massecuites to the same ratio in the same syrup when saturated at the same temperature. This is accepted practice in the cane industry and, in the light, of previous experience for interpretive purposes, is considered superior to ordinary supersaturation coefficients (ratio of sucrose percentages), although frequently not as convenient.

The monomoleeularity of the crystallization rate from these real massecuites was good for one-half to two-thirds of the total life. Thereafter the rate fell sharply. This behavior is similar, but the freedom from secondary reactions is not as extensive (to 3/4 life) as has been observed with pure sucrose solutions *(11a)*.

Diffusivities were measured by the Northrup-McBain (*11d*) porous disc technique. True purities of the resultant solutions were ascertained by the semi-micro method of Scales (5). Since only approximate viscosities were needed, rising bubble tubes w^{T}ere considered adequat..

Results and Discussion

1. Rates of Deposition of Different Crystalline Faces, and Comparison of Solution and Crystallization Rates.—Distorted and abnormal sucrose crystals are more frequently produced from impure syrups, thus suggesting an unequal and variable growth of the various faces. This is quite the opposite to a uniform rate of growth expected on the basis of a simple diffusion theory.

One might expect the dissolution of a crystal to be entirely eontrolled by a diffusion mechanism involving the dissipation of an adhering of film of saturated solution (*3b*). This is apparently the case with sucrose, as subsequent experiments reveal. But in comparing the rate of crystallization from pure sucrose solutions with that of dissolution at the same saturation potential, it is observed (*4*) that the former is a much slower process than the latter, again suggesting the inoperation of a diffusion mechanism as primary in the crystallization process. The same relative effect was observed with natural syrups in the present investigation; for example :

a. Refraetometric technique—beet fillmass—75 purity, 30° C. Oversaturation and undersaturation 1.06 and 0.94 respectively

$$\frac{\text{Solution velocity (observed)}}{\text{Crystallization velocity (observed)}} = \frac{1.7}{1}$$

At 60 percent purity and 40° C a ratio of 2.1 was observed for this same molasses.

b. Microscopic technique—cane massecuite—75 purity, 25° C Oversaturation and undersaturation 1.12 and 0.88 respectively

$$\frac{\text{Solution velocity}}{\text{Crystallization velocity}} = \text{Between 1 and 2 with no stirring; above 3 at 1,000 r.p.m.}$$

2, Diffusivities.—The diffusivities and relative viscosities of the standard cane and beet molasses at 75 nominal purily and 0.96 underwit oration were determined at 80° and 63° C. Additional sucrose was added to some of these same syrups to give an oversaturation of 1.15 at the respective temperatures, and the rates of crystalization from these syrups were then determined. The results are given in table 1 together with pertinent calculations and information; the conclusion, as with pure syrups, is that, crystallization is invariably the slower process and therefore rate controlling, or very largely so. The temperature coefficients are comparable to a few values available in the literature *(3a, 6)* on the effect of various salts on the diffusion of sucrose.

Table 1.—Diffusivities, crystallization velocities, etc. of a cane and a beet syrup at comparable oversaturations and purities.

	Cane		Beet	
	30° C.	63° C.	30° C.	63° C.
Diffusivities—Integral, cm²/day	0.21	0.44	0.43	0.96
Diffusivities—pure sucrose (11d)	0.46	0.80	0.41	0.91
Relative viscosities	1	1.84 (55° C)	3.5	7.15 (55° C)
Relative crystallization velocity	1	4.1	0.78	2.56
Energy of activations, calculated from:				
Diffusivities		4.6		5.0 kCal/mol
Viscosities		5.2		6.7
Solution velocity		5.7 (pure cube)[b]		2.1 (low)
Crystallization velocity		7.5		8.8

The rate of solution of sucrose in an undersaturated beet molasses (S = 0.94) was ascertained at 30° and 40° C. and at 75 nominal purity in each case. The observed velocity at 40° C. was larger than that at 30° C. by a factor of 1.11. This 10° coefficient is considerably smaller than the 1.33 reported by Sandera and Mircev *(9)* for the leaching of pure cube sugar. However, both low values (corresponding to energies of activation of 2.1 and 5.7 kCal. respectively) emphasize the relative rapidity of the solution process and suggest the domination of a physical step. This situation emphasizes the need for close and uniform temperature conditions in boiling work *(12)* ; for any local overheating will reduce pan capacity much more significantly than an equivalent supersaturation condition can undo in the same time.

3. Effects of Stirring.—Generally speaking, a physically controlled process is more dependent on the rate of agitation, within the system than is a chemically controlled system. That is, in the exponential curve—Velocity $= \propto (N)^{\beta}$, where N is the rate of stirring, and $\propto$ and β are constants, the exponent is of small magnitue if interfacial reactions control, while it approaches more nearly unity if a transport mechanism dominates. In the previous investigations *(11c)* of pure sucrose solutions, exponents of the order of 0.25 were typical, which was taken lo indicate the controlling influence of an interbouudary reaction. In the present instance the standard cane molasses was investigated, and the data presented in figure 1 are for two complete experiments in which effectively different stirring
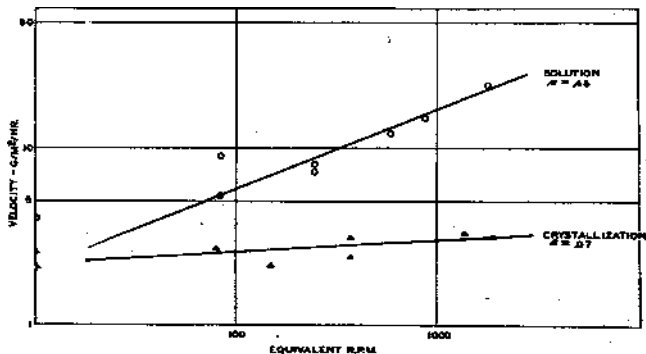

Figure 1,—Solution and crystallization velocities for standard cane massecuite. Both at same displacement from saturation.

speeds were realized by cementing the crystals to be grown at different distances along a common spindle.

The exponent (approximately 0.5) for solution, which process is expected to be a diffusion-controlled one, is not. quite the perfect value of one (0.8 is more the typical limiting value (8), but the low value for crystallization, especially when compared to the higher solution value, is quite convincing in regard to the difference in the *modu   operandi.*

For beet fillmasses, the limited data of Hungerford (4) gives exponents less than 0.12 when evaluated according to the above expression. This low value is again indicative of the absence of diffusion (and viscosity) control.

4.   Effect of **Additional Impurities.**—**A** comparison of the effects of colloids on the viscosity and on the crystallization rate of sucrose from syrups is very revealing in the present connection. Approximimately 5 percent by weight of caramel was added to the standard beet molasses at an oversaturation of 1.15**.** The viscosity of the syrup was diminished (0.8 of original value), while the crystallization rate dropped to 54 percent of its original value. In similar manner, an amount of gum acacia sufficient to increase the viscosity of this molasses six-fold effected no change in the crystallization rate (observed 3 percent increase). The melassigenic behavior of these and other constituents are thus directly contrary to what one would expect were a physical (diffusion or viscosity) process the primary controlling factor in sucrose crystallization.

The effects of these same two materials on the solution velocity of sucrose was ascertained to concur with the expectation that diffusion is the controlling factor in this case; namely, it was found that caramel had little influence on the rate of solution whereas acacia impeded the process tremendously.

Summary and Conclusion

The rate of growth of sucrose from real massecuites, as well as from pure solution (*11*), is determined primarily by some interfacial (homogeneous, chemical) reaction rather than an interboundary (heterogeneous, physical) reaction.

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Literature Cited

1. (a) Brown, R. F.; Sharp .J. E. and Dahiberg,, H. A. Determition of Solubility of Sucrose in Beet House Sirups. Ind. and Eng. Chem. 20: 1230. 1028.

   (b) Brown, R. J. and Nees, A. R. Solubility of Sucrose in Beet House Sirups. Ind. and Eng. Chem. 25: 555. 1933.

2. Grut, E. W. Investigations of Supersaturation and Viscosity in Refrigerators for the First Product. Listy Cukrovar 56:37, 53, 62, 77. Zeitschrifl fur Zuckerindustrie Ceckoslovak Republic 61 :356, 373, 437, 445. 1937.

3. (a) Hlerzfeld, A. Theory of Diffusion. Zeitschrift Vereins Deutsche Zuckerindust rie 322. 1889.

   (b) Hixson, A. W. Mixing and Agitation. Ind. and Eng. Chem. 23. 823, 1002, 1160. 1931.

4. Hungerford, E. H. Seasonal and District Variations in the Rate of Crystallization of Sucrose From Beet, House Sirups. Proc. Amer. Soc. Sug. Beet Tech. 3:499. 1942.

5. . (a) Isbell, H. S.. Pigman, W. W., and Frush, H. L. Reducing Powers of Various Sugars. Jour, of Res., National Bureau of Standards 24: 241. 1940. (At the recommendation of Dr. F. W. Zerban.)

   (b) Jackson, R. F., and McDonald, E. J. Copper Reduction of Various Sugars in Citrare-Corbonate Solution. Jour, of Res., National Bureau of Standards 34: 213. 1945.

6. Janacek, O. Physical and Chemical Basis in Diffusion. Listy Cukrovar 57: 265. 1939.

7. Nees, A. R. and Hungerford, E. H. Raffinose. Ind. and Eng Chem. 26: 462. 1934.

8. Perry, J. H. Chemical Engineering Handbook, New York 1941.

9. Sandera, B. K. and Mircev. Solution Rates of White Sugar.

Zeitschrif t fur Zuckerindustrie Ceckoslovak Republic 60:233. 1935-36.

10. Thieme, J. G.   Studies in Sugar Boiling.   Facts About Sugar, New York.   1928.

11. Van Hook, A.   Kinetics of Sucrose Crystallization.

   (a) Ind. and Eng. Chem. 36:1042, 1048.   1944.

   (b) Ind. and Eng. Chem. 37:782.   1945.

   (c) Ind. and Eng. Chem. 38 :50.   1945.

   (d) Ind. and Eng. Chem. 67:370.   1945.

12. Webre, A.   Circulation in Vacuum Pans.

   (a) Mechanical. Engineering 58:99.   1936.

   (b) Spencer-Meade Handbook 8th Ed.   X. Y.   1945.