Sucrose solubility in impure cane sugar solutions

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Technical summary

There is a growing interest in the industry in on-line measurement and use of supersaturation in crystallization control. Its accurate determination, however, requires reliable data on the solubility of sucrose in impure sugar solutions. Extensive research has led to a well established method for calculating this solubility in beet sugar syrups, based on syrup quality parameters. However, there seems to be much less information available on sucrose solubility in cane sugar syrups. Based on data collected by Thieme (the only source of data on cane sugar syrups known to this author) this paper reports attempts to determine the relevant quality parameters and extend the methodology, which proved its worth with beet syrups, to cane sugar solutions.

Introduction

It is well known to those involved with sugar processing, that supersaturation is the most important parameter when attempting to control, either manually or by an automatic control system, the process of crystallization.

It is well known, for example, that seeding a supersaturated sugar solution is the most critical part of crystallization, which determines to a great extent the quality and cost of the end product. It is also known that maintaining supersaturation is important throughout the course of the strike, if the quality to cost ratio is to be maximized[1]. However, this knowledge, is academic in most cases, simply because of the lack of reliable on-line measurement and use of supersaturation during the control of crystallization. Traditional instruments in use provide data only on certain syrup or massecuite parameters (for example: conductivity, resistance and capacity measured at radio frequencies, density, viscosity/consistency and water content of the syrup) which are more or less correlated to supersaturation, but are influenced by quite a few other parameters, the effects of which are neglected[2].

Supersaturation is simply defined as the amount of sugar in a sugar solution divided by the amount of sugar at saturation, assuming identical temperatures. Due to the fact that the amount of sugar dissolved and the amount required to saturate the solution at a given temperature strongly depend on the purity of the sugar solution (and figure also on the composition of the impurities), the impurities present play an important role in supersaturation. Changes in the composition of the impurities are reflected in the quality parameters to be discussed later[3].

There seems to be an increasing awareness in the industry nowadays of the potential value of measuring and exploiting supersaturation in crystallization control, as proved to this author by the many inquiries received after the publication of papers on the subject. Companies and universities based in Australia, India, France, USA, Canada and other countries have all given reports of new research projects on crystallization control. This change in attitude has been further advanced recently by the availability of the K-PATENTS process refractometer and its optional SeedMaster software, dedicated to the on-line measurement of supersaturation, coupled with automatic seeding capability[4].

Sucrose solubility in impure sugar solutions

In order to be able to calculate supersaturation accurately, all of the parameters which govern the sugar content at saturation in an impure solution (the denominator in the ratio mentioned above) have to be taken into account. These are: solids concentration, temperature, purity and the syrup quality parameters.

Sucrose solubility in impure beet sugar syrups has been investigated extensively by many researchers (Charles, Grut, Vavrinecz), and there seems to be a well established methodology (though rarely used on-line until SeedMaster became available, due to the lack of an instrument that could use it), by which solubility can be determined accurately and on-line. This is based on knowledge of sucrose solubility (g sucrose per 100 g of water) in pure sugar solutions, which depends on the temperature, and on the Wiklund-Vavrinecz solubility coefficient (SC), which is governed by the amount and composition of the impurities present in the solution[5]:

$$SC = m.NS/W+b+(1-b).\exp(-c.NS/W) \quad (1)$$

where

m , b , c are syrup quality parameters, and NS/W is the non-sugar to water ratio.

Typical data for beet syrups :
m : 0.13 - 0.25
b : 0.7 - 0.85
c : - 2.1 or -1.8 (usually one of these)
NS/W : 0 - 3.5

It was proved by Wiklund that the SC depends linearly on the NS/W ratio above NS/W=1.5, while the exponential term in the equation, determined by Vavrinecz, is most important at the lower end of the NS/W range, that is in syrups with higher purities. It was also found that the solubility coefficient does not depend on temperature. A typical SC over NS/W curve can be seen in Figure 1. It has to be noted here that

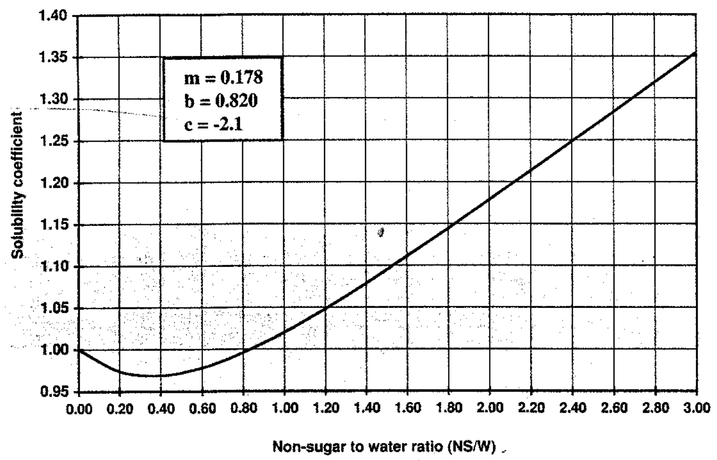

Figure 1. Solubility coefficient of typical beet syrups

with beet syrups the quality parameter, m, is positive, so solubility increases with increases in the NS/W ratio (NS/W > 1,5).

In using equation (1) to calculate the SC the difficulty comes from the knowledge (or, usually, the lack of knowledge) of the syrup quality parameters. In ideal cases these should be determined by the local laboratory as often as changes in syrup quality in local conditions (for example during the campaign period, or from campaign to campaign) justifies it. If there are no local data available, then typical figures can be used.

Grut's table, which lists solubility data versus temperature and purity is satisfactory for many beet growing areas and has been in use as typical data for beet sugar solutions for quite some time. Using his data, syrup quality parameters m, b and c have been determined and found to be as follows :

m: 0.178
b: 0.820
c: - 2.1

Sucrose solubility in impure sugar solutions (beet and cane, too) can be calculated as:

$$S(Q,T) = S(100,T).SC(Q, m, b, c) \quad (2)$$

where :

S(Q,T) is sucrose solubility of a syrup having;
Q % purity and
T°C temperature;
S(100,T) is sucrose solubility of pure (Q = 100 %) solutions at temperature, T°C
SC(Q, m, b, c) is the calculated saturation coefficient of the syrup with Q% purity and actual (locally determined) m, b and c parameters.

Solubility data for pure sucrose solutions (that is S(100,T)) can be found in data tables like those of Grut, though newer data collected by Vavrinecz are to be preferred.

The situation is quite different with cane sugar syrups, in the sense that there seems to be much less information in the relevant literature on sucrose solubility in impure cane sugar solutions. The few references available (at least those known to this author) seem to cite data collected by Thieme in Java[6,7] and are considered to be typical for cane sugar solutions.

Thieme's table

* lists sucrose solubility data in concentration by weight % for cane sugar syrups versus temperature and purity (like that of Grut for beet syrups),
* has no data in the 100 % to 92 % purity range, and
* has nothing to say about the syrup quality parameters: m, b and c.

When these solubility data are converted to g sugar per 100 g water, and those of purity into non-sugar to water ratios, and the figures are plotted, as in Figure 2 for T=70°C, it becomes apparent that these data contain errors which should be corrected. However, Thieme's data represent an important contribution to the subject, which also reveals an interesting difference between the two types of syrups: in contrast to beet syrups, sucrose solubility in cane syrups decreases as the NS/W ratio is increased.

In order to facilitate the introduction of more exact calculations on

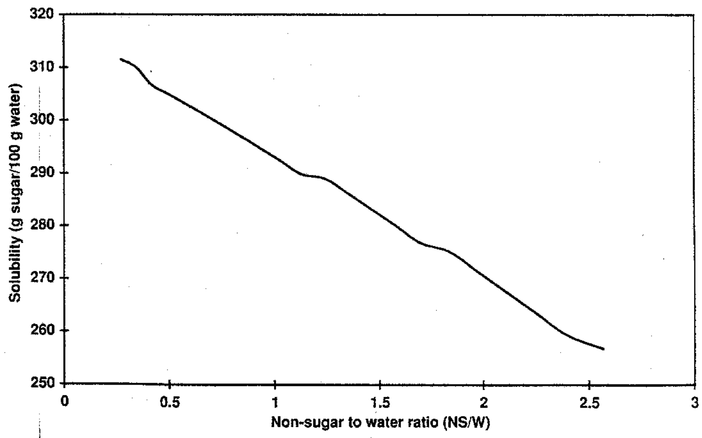

Figure 2. Thieme's original solubility data (T= 70°C)

Table I. Thieme's Table

Solubility in concentration by weight, %

T/Q	92	90	88	86	84	82	80	78	76	74	72
62	75.6	75.9	76.2	76.5	76.7	77	77.3	77.6	78	78.3	78.7
64	76	76.3	76.5	76.8	77.1	77.4	77.7	78	78.4	78.7	79
66	76.4	76.6	77	77.2	77.5	77.8	78.1	78.4	78.7	79.1	79.4
68	76.8	77.1	77.3	77.6	77.9	78.2	78.5	78.8	79.1	79.4	79.8
70	77.2	77.5	77.7	78	78.3	78.6	78.9	79.2	79.5	79.8	80.1
72	77.6	77.9	78.1	78.4	78.7	79	79.2	79.5	79.8	80.2	80.5
74	78	78.3	78.5	78.8	79.1	79.4	79.6	79.9	80.2	80.5	80.8
76	78.4	78.7	78.9	79.2	79.5	79.7	80	80.3	80.6	80.9	81.2
78	78.9	79.1	79.3	79.6	79.9	80.1	80.4	80.7	81	81.3	81.6
80	79.3	79.5	79.7	80	80.3	80.5	80.8	81.1	81.4	81.7	82

T/Q	70	68	66	64	62	60	58	56	54	52	50
62	79	79.3	79.7	80.1	80.4	80.8	81.1	81.4	81.7	82.1	82.4
64	79.4	79.7	80.1	80.4	80.8	81.1	81.4	81.7	82.1	82.4	82.7
66	79.7	80.1	80.4	80.8	81.1	81.4	81.7	82	82.4	82.7	83
68	80.1	80.4	80.8	81.1	81.5	81.8	82.1	82.4	82.8	83	83.4
70	80.5	80.8	81.1	81.4	81.7	82.1	82.4	82.7	83	83.3	83.7
72	80.8	81.1	81.5	81.8	82.1	82.4	82.7	83	83.3	83.7	84
74	81.2	81.5	81.8	82.2	82.5	82.8	83.1	83.4	83.7	84	84.3
76	81.6	81.9	82.2	82.5	82.8	83.1	83.4	83.7	84	84.3	84.6
78	81.9	82.2	82.6	82.9	83.2	83.5	83.8	84.1	84.4	84.7	85
80	82.3	82.6	82.9	83.2	83.5	83.8	84.1	84.4	84.7	85	85.3

supersaturation (and the use of SeedMaster) with cane sugar syrups, our aim in this paper is:

1. to calculate approximate solubility data in the 100 % to 92 % range of purities and
2. to determine the m, b and c parameters based on data collected by Thieme.

It should be noted that:

* these data are intended to be used only until more accurate figures become available;

* the m, b and c parameters should be determined by local laboratories in order to reflect local syrup quality.

Results

Extending the range of Thieme's table

Thieme's table (as shown in Table I) covers the temperature range from 62 to 80°C, and the range of purities from 92 to 42% (only to 50 % shown here). There are no data in the 100 to 92% purity range, which is quite important if higher purity syrups (refinery, A and B products) are to be covered.

In a paper discussing solubility data for cane sugar solutions[7] Ziegler discovered that Thieme's high purity values were slightly lower than those of Vavrinecz, and he proposed a minor upward adjustment of these values. His modified data are listed in Table II, which lists solubility in sugar to water ratio (S/W) versus temperature and purity.

Due to the fact that there are only two rows of data in the two tables with identical temperatures (70°C and 80°C), it was decided that only these would be used in further calculations.

By using the data in Table II, least-squares fits were determined as follows:

T = 70°C:

$$S/W = 0.01.(0.000572Q^3 - 0.133429Q^2 + 11.2742Q - 39.345) \quad (3)$$

$(R^2 = 0.9948)$

T = 80°C:

$$S/W = 0.01.(0.000525Q^3 - 0.127643Q^2 + 11.4125Q - 20.431) \quad (4)$$

$(R^2 = 0.9978)$

Table II. Thieme's table as modified by Ziegler: sugar to water ratios (S/W)

T/Q	100	90	80	70	60	50
65	3.06	2.96	2.82	2.71	2.61	2.5
70	3.25	3.14	2.99	2.93	2.81	2.62
75	3.46	3.33	3.2	3.11	2.97	2.76
80	3.69	3.56	3.43	3.35	3.17	2.97

Table III. Sucrose solubility in cane sugar solutions: sugar to water ratios (S/W)

T/Q	100	98	96	94	92	90	88	86	84
70	3.25	3.22	3.20	3.18	3.16	3.14	3.12	3.10	3.07
80	3.69	3.66	3.63	3.61	3.58	3.56	3.53	3.51	3.49
T/Q	**82**	**80**	**78**	**76**	**74**	**72**	**70**	**68**	**66**
70	3.05	3.03	3.01	2.98	2.96	2.93	2.91	2.88	2.86
80	3.47	3.44	3.42	3.40	3.38	3.36	3.33	3.30	3.28
T/Q	**64**	**62**	**60**	**58**	**56**	**54**	**52**	**50**	
70	2.83	2.81	2.78	2.75	2.72	2.70	2.67	2.64	
80	3.25	3.22	3.18	3.15	3.11	3.06	3.02	2.97	

Equations (3) and (4) can now be used to calculate solubility data in the complete Q = 100 - 50 % range of purities as listed in Table III.

Cane syrup quality parameters based on Thieme's data

Without going into full details, the cane syrup quality parameters were estimated by calculating:

1. the solubility in concentration by weight using data in Table III;
2. the non-sugar to water ratio, NS/W;
3. the solubility coefficient, SC, using Vavrinecz's data for pure solutions (S(100,T)).

Then plotting:

4. SC versus NS/W for NS/W ≥ 1.5 and determining the m and b parameters for the linear section;
5. (SC-m.NS/W-b)/(1-b) versus NS/W for NS/W ≤ 1.5, and determining the c parameter for the exponential term.

The procedure was completed for data valid for T=70°C and T=80°C with the following results:

T = 70°C
m = - 0.0655
b = 0.9780

T = 80°0,
m = - 00598
b = 0.9859

Average
m = -06265
b = 0.9820

It was also found that c = - 2.1 results in a very good fit. By taking the appropriate average values, syrup quality parameters for the adjusted Thieme data are:

m = - 0.06265
b = 0.9820
c = -2.1

Having determined the quality parameters for cane syrup represented (with slight adjustments) by Thieme's data, sucrose solubility for any temperature and purity can be calculated using Equation (2).

Discussion

It is instructive to study how calculated data compare with empirical figures. Figure 3 shows the calculated solubility coefficients versus the non-sugar to water ratios both from Thieme's original data and the ones calculated using Equation 2 and the syrup parameters given above. In both cases Vavrinecz's data for pure sugar solutions were used.

It can be seen that missing data in the high-purity region (Q=100 to 92% or NS/W= 0.00 to about 0.28) have been determined and the original Thieme solubility data have also been slightly adjusted upwards, as previously suggested by Ziegler to get better agreement with Vavrinecz's data (and with reality), which demands that SC = 1.00 at Q = 100 % or NS/W = 0.

It has already been mentioned that the solubility coefficient determined by Equation 1 does not depend on temperature. However, probably due to experimental errors, solubility coefficients calculated using Thieme's data do show a slight dependence on temperature.

It is logical to expect that the differences between the solubility coefficients of beet and cane sugar syrups should diminish as we approach 100 % purity. This can be seen in Figure 4, which depicts calculated data

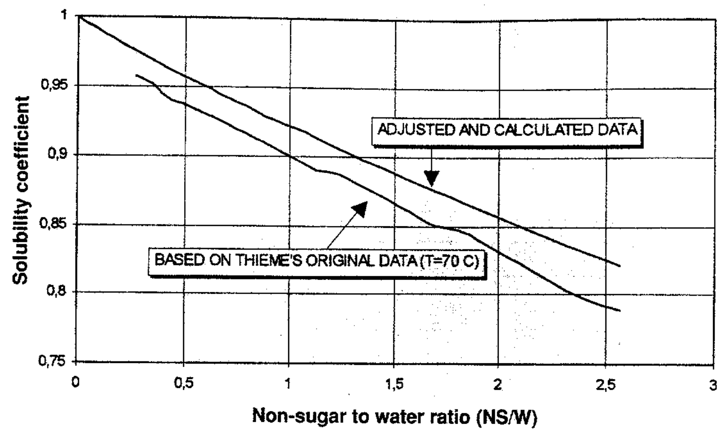

Figure 3. Solubility coefficients for cane syrups

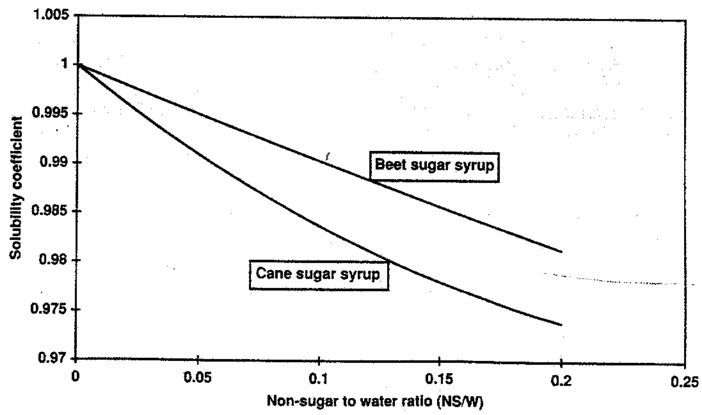

Figure 4. Solubility coefficients of typical beet and cane sugar syrups in the high purity (Q = 100 - 94%) region

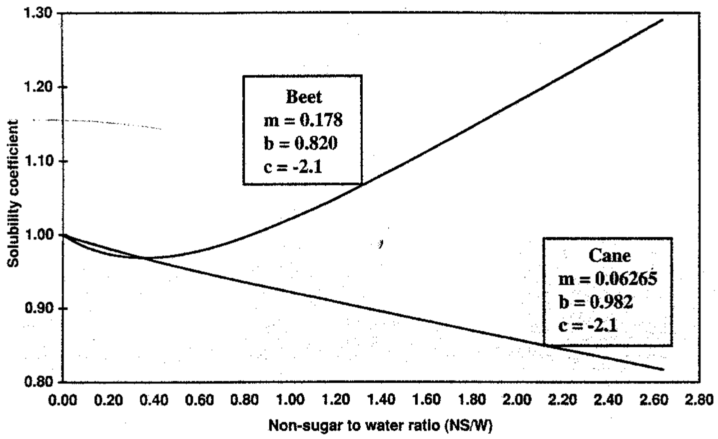

Figure 5. Solubility coefficients of typical beet and cane sugar solutions

for both typical beet (m = 0.178; b = 0.820; c = -2.1) and cane (m = -0.06265; b = 0.982; c = -2.1) sugar solutions. Differences in this region of purity are very small.

In order to give a broader picture, calculated solubility coefficients are shown in Figure 5, for a wider non-sugar to water range, which clearly shows how the difference between beet and cane sugar solutions increase as the non-sugar concentration increases.

Finally, for those who prefer to think in terms of purity rather than in non-sugar to water ratios, the solubility coefficient data of Figure 5 are represented in Figure 6 in terms of purity. This figure shows that the difference in the solubility coefficients between the two types of syrups is very small in the 100 to 90% range of purity, and begins to increase sharply only from about 88% purity.

It should be noted that Equations 1 and 2 completely define sucrose solubility in beet and cane sugar solutions. The accuracy of the calculation depends mostly on the knowledge and accuracy of the actual (local) syrup quality parameters, which should be determined by the local laboratory. This is a rather time-consuming operation, which requires appropriate laboratory equipment and careful analysis. However, if these local data are not available, typical ones can be used. Even this latter approach is much better than neglecting syrup quality parameters altogether. Even worse, although it happens quite often, is that claims are made that supersaturation is being considered, although in reality syrup quality, and even changes in mother liquor purity during the course of a strike, are being completely neglected.

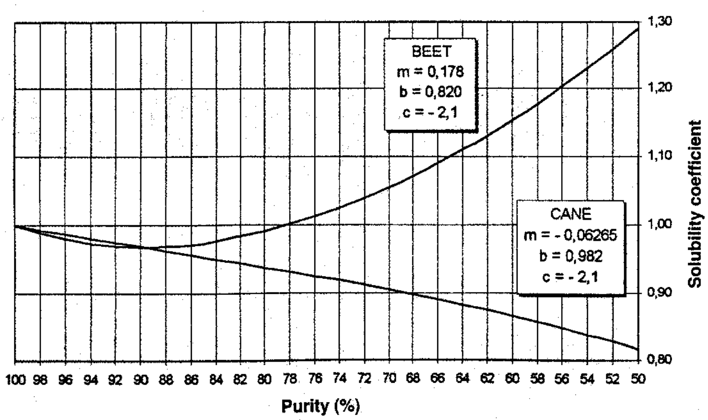

Figure 6. Solubility coefficients of typical beet and cane syrups

Conclusion

Calculation of supersaturation, which is the most important parameter in sugar crystallization, requires accurate, standardised methods. Based on the work of many researchers it has been possible to calculate supersaturation on-line in beet sugar syrups for some time. However, there are far fewer solubility data for impure cane sugar solutions, and behaviour of these syrups is somewhat different. Thus calculation of supersaturation in cane sugar solutions is only occasionally done, and never along the lines of the calculations which have proved successful with impure beet sugar solutions.

However, by extending and adjusting Thieme's original data, thought to be typical of cane sugar solutions, in order to achieve better conformity with the data of other researchers, quality parameters for this type of syrup have been determined. If local quality parameters are not available, these can be used in supersaturation calculations, applying the same methodology that has already been successfully used with beet sugar solutions.

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