Ultrasonic and Magneto Kinetics of Crystallization of Sucrose

THESIS

SUBMITTED TO

BABASAHEB BHIMRAO AMBEDKAR UNIVERSITY
(A CENTRAL UNIVERSITY)
LUCKNOW

BABASAHEB
BHIMRAO
AMBEDKAR
UNIVERSITY

LUCKNOW

प्रज्ञा शील करुणा

ESTABLISHED 1996

FOR THE DEGREE OF

Doctor of Philosophy

IN

APPLIED CHEMISTRY

Submitted by

Satya Prakash Gupta

M.Sc. Chemistry
Enrollment No. 856/12

Under the Supervision of

Prof. Kaman Singh

DEPARTMENT OF APPLIED CHEMISTRY
SCHOOL FOR PHYSICAL SCIENCES
BABASAHEB BHIMRAO AMBEDKAR UNIVERSITY
VIDYA VIHAR, RAE BARELI ROAD, LUCKNOW-226 025

2018

SUMMARY

Crystallization of sucrose is an important process on which the efficient performance and economics of sugar industry is primarily depends. Fundamental and applied work on various aspects of sucrose crystallization has therefore been the subject of major research work in the past.

Kinetic of crystallization of sucrose attracted the attention of many research workers for obtaining data for design of pans, [De Coudry, 1946, Holven, 1942] crystallizers, etc. for use in sugar industry, they also concentrate for finding out the phenomenon occurring during crystallization.

There are many problems during sugar processing particularly in crystallization step such as occurrence of latent period, excessive viscosity of the processing fluids and scale formation on the heating surfaces. These problems have received much attention several years ago, unfortunately till date there is no effective solution.

Induction period exist in the initial interval of time during crystallization. The induction period referred to decrease rate of sugar crystallization process in the initial interval of time leading to incomplete exhaustion of sucrose from the mother liquor. The occurrence of induction period in the crystallization processes presents a serious draw back and it hampers the economy of the industry. The most important study of the latent period on the kinetics of crystallization of sucrose was studied by Van Hook [Van Hook, 1944] and other [Ramaiah *et al*, 1961].

The study of thermodynamic data enables one to get deep insight into the phenomenon operative during crystallization. The recommendation of the international commission for uniform method of sugar analysis (13^{th} session held at Hamburg, 1962) rightly emphasizes the need for work on the determination of thermodynamic properties of crystallization of sucrose. The detail investigations have been carried out in the past. During our research work the change in free energy (ΔG), heat content (ΔH) and entropy change (ΔS) is calculated. The significance of these thermodynamical quantities in an

apparently physical process of transfer of sucrose molecules from the solution phase onto the seed crystal is discussed in detail in our research work.

High viscosity reduces the effective extraction of sucrose crystal from the mother liquor (industrial terms: massecuite and molasses). The viscosity of the mother liquor increases abruptly when low purity massecuite is cooled, and at the minimum temperature sucrose crystals cannot be separated effectively from molasses in the centrifuge. The option to reduce the viscosity of the massecuite is either by dilution or by heating the massecuite sufficiently to lower its super-saturation. However, dilution of the molasses leads to the loss of sucrose crystals due to its high solubility, whereas, heating of the massecuite may lead to sucrose loss due to inversion.

Scale is defined the precipitation of undesired solid material such as calcium phosphate, calcium carbonate, calcium oxalate, calcium sulphate and other minerals at phase interface. In sugar industry this occurs on the heat exchanger surface of the heater evaporator and pans. Scale formation inside the pipe/tube during evaporation process is the inevitable problem which is difficult to manage and control under the operational condition. As a result of progressive accumulation of scale on heated surface, the heat transfer coefficient considerable declines with time causing significant economic loses.

The calcium in solution is derived either from dissolution from natural resources, or from chemical deliberately added during clarification of juice. $CaCO_3$ become less soluble at higher temperatures and on heating, CO_2 escapes favoring the bicarbonate decomposition reaction which causes $CaCO_3$ to precipitate.

The reaction in the formation [J. Peric, *et al*, 1996] of $CaCO_3$ can be straight forwardly represented as:

$$2HCO^-_3 \longrightarrow CO_3^{2-}+CO_2+H_2O \qquad (1)$$

$$Ca^{2+} +CO_3^{2-} \longrightarrow CaCO_3 \qquad (2)$$

Relevant literature survey on purposed topic has revealed that there is a need of an investigation on the effect of ultrasonics during crystallization of sucrose. The aim of proposed study is to determine the effect of ultrasonics on the sucrose crystallization

from its aqueous solution. Therefore, keeping in view the aforesaid problems of the sugar industry during crystallization, we propose the following :-

I. To study the kinetics of crystallization of sucrose from aqueous solution with/without the use of ultrasonics/PMF.

II. The effect of ultrasonic on induction (latent) peried occuring on crystalization of sucrose.

III. A comparative study on kinetics of crystallization of sucrose will be studied in absence and presence of ultrasonics.

IV. The proposed work will be extended on industrial scale for improved crystallization (sonocrystalizatoin) during sugar processing.

V. The viscosity, purity, conductivity, pH and other relevant parameters will be determined before and after ultrasonics irradiation/PMF application.

VI. Thermodynamics parameters related with sonocrystallization of sucrose employing ultrasoics and PMF will be investigated.

The proposed work has academic as well as industrial importance. Kinetic and thermodynamic data are considered to be very important in physical chemistry. Eyring equation and Arrhenius equations were not found applicable as long as induction period persists during crystallization, however, employing ultrasonics, induction period can be eliminated and in such a situation Eyring or Arrhenius equations can be applied to crystallization process. Thermodynamic parameters provide valuable information regarding any process. Hence, low values of ΔG^o and ΔS^o during crystallization can be explained, on this basis of solution and solid state structure [G.M. Brown, *et al,* 1963, 1973] and transport properties [K. Singh, *et al*, 1999, 2003, 2005] of sucrose. Additionally, the proposed work has industrial importance as to where industrial crystallization, scale formation on heating surface and control or minimization of excessive viscosity of fluids can be managed by the proposed techniques in this thesis such as ultrasonic and pulse magnetic field.

The organization of the thesis is given below:

Chapter 1: General introduction and review of literature

Chapter 2: Methodology

Chapter 3: The effect of high intensity focused ultrasound (HIFU) on the kinetics of crystallization of sucrose: Elimination of latent period

Chapter 4: Application of ultrasonics on viscosity and scale control: An eco-friendly technique for saving energy in the sugar industry

Chapter 5: Application and potential of pulsed magnetic field (PMF) in controlling scale formation in cane sugar processing

Chapter 6: Reducing viscosity of molasses and massecuite with pulsed magnetic field (PMF)

The study will brodly follow the scheme as given above. The summary of research work carried out is as follows:

Chapter 1

In this proposed work, attempt has been made to understand the effect of ultrasonic and pulsed magnetic field on crystallization of sucrose. Keeping in view the above problem of the sugar processing, following have been proposed:

i. The effect of ultrasonic on induction period occurring during crystallization of sucrose.

ii. A comparative study on crystallization of sucrose with and without ultrasound

iii. The viscosity and scale information will studied before and after ultrasonic irradiation and PMF application.

iv. Thermodynamic parameter related with sonocrystallization of sucrose employing ultrasonic and PMF treatment.

Chapter 2

Following instrumental techniques have been carried out for the removal of induction period characterization of scale and reduction in viscosity of molasses and massecuite.

i. Scanning electron microscopy: SEM examination provides information about surface features of scale form on evaporator body.

ii. Fourier Transform Infrared (FT-IR) spectroscopy. It is used to identify the chemical species present as scale on evaporator body.

iii. Digital Viscometer: Viscosity of the molasses and massecuite was determined with the help of Brookfiled viscometer.

iv. Refractometer: Digital Refractometer was used to measure the refreative index of supersaturated sugar solutions.

v. Ultrasonicator: Ultrasonicator was used to carry out crystallization in the presence of ultrasonic wave.

Chapter 3

The application of a technique to eliminate the latent period during crystallization of sucrose by high intensity focused ultrasound **(**HIFU) was investigated in this chapter. Employing HIFU (20 kHz, 750W) to crystallization of sucrose, latent period was eliminated and it was found to obey first order kinetics (K ~10^{-5} sec^{-1}) in the temperature range of 30-50°C. Employing Arrhenius equation, the average energy of activation (E_a) estimated as 5.0 kcal/mole. Traditional knowledge indicates that that crystallization is sufficiently spontaneous; however, the magnitude of "K" and other thermodynamic quantities of the process indicate that crystallization is actually a slow process. Generally, chemical reactions which posses low rate constants, need high energy of activation. On the contrary, the energy of activation is appreciably less. The energy of activation with rate constant of the order of 10^{-5} sec^{-1} could be predicted of the order of 20 kcal/mole at 27 °C. The low energy of activation for crystallization of sucrose is of interest. A very

interesting elucidation can be had from neutron diffraction data [G.M. Brown, *et al,* 1963, 1973] and transport property [K. Singh, *et al,* 1999, 2003, 2005] of the sucrose which is discussed in details in this chapter.

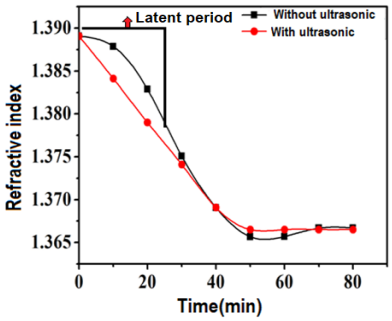

Fig. 1. Graph illustrating elimination of latent period by HIFU (20 kHz, 750 W) during crystallization of sucrose (S= 1.13)

The present study concludes that occurrence of latent period (20-25 min) during crystallization of sucrose can be eliminated by high intensity focused ultrasound (20 kHz, 750W). This aspect of the HIFU is very important from practical point of view and it can be applied to initiate and control crystallization on industrial scale and moreover, intentional seeding which is common in industrial crystallization processes could be avoided if operation is carried out under the influence of ultrasound. Furthermore, it is a non-chemical device and easy to operate as well. As long as latent period persists, observed data are not amenable to follow first order kinetics. However, crystallization of sucrose under the influence of power ultrasound was found to obey first order kinetics in the temperature range of 30-50°C. The magnitude of the velocity constant $K \simeq 10^{-5}sec^{-1}$ is surprisingly of a low order as the crystallization process is thought to be very fast. For reactions with $K \simeq 10^{-5}$ sec^{-1}, the energy of activation could be predicated to be of the order of 20.0 k cal/mole. The low value of energy of activation (5.0 kcal/mole) recorded for sonocrystallization of sucrose is of significance and throws light on the mechanism of the process. In solution state, the glucose and fructose units rotate independently around ether linkage whereas in the crystalline state, the formation of the hydrogen bonds restricts the rotational movements, consequently; it reduces entropy.

Chapter 4

Excessive viscosity of the processing fluids and scale formation in evaporators are two major problems faced by the sugar technologists. High viscosity reduces the effective extraction of sucrose crystal from the mother liquor. The deposition of $CaCO_3$ which is commonly known as scale costs billions of rupees to the world wide economy. This problem has received much attention from several years; unfortunately, to date there is no effective solution yet. The first experimental evidence with proposed theory of ultrasound (US) on scale reduction or control is presented here. The SEM analysis of the scale implied that the ultrasonic treatment suppresses the formation of calcite crystals (hard) and prefers vaterite; a thermodynamically least stable (soft) polymorph. The results are consistent with the literature model of $CaCO_3$ crystallization. The laboratory experiment coupled with commercial trials is confirmed to be beneficial for process control and significant energy saving during sugar manufacturing. A complete mechanism and explanations are offered to explain the experimental results. A technique to reduce or control scale formation employing an eco-friendly technique employing ultrasonics during sugar processing is developed [K. Singh, *et al*, 2016, V. K. Singh, *et al*, 2013].

Industrial application of ultrasound in sugar processing leads to the following important conclusions:

(a) Viscosity of massecuite and final molasses was reduced by 30-35%.
(b) Changes the physical configuration of the scaling from hard, dense to soft, porous sludge type.
(c) The SEM analysis of the scale implied that the US treatment suppresses the formation of calcite crystals (hard) and prefers vaterite; a thermodynamically least stable (soft) polymorph. The results are consistent with the literature model of $CaCO_3$ crystallization.
(d) Chemical consumption to clean and descale the evaporators was reduced significantly.
(e) Time to clean up the evaporators and labour cost is reduced significantly
(f) Colour and sulphur contents were found to reduce.

(g) The laboratory experiment coupled with commercial trials is confirmed to be beneficial for process control and significant energy saving during sugar manufacturing.
(h) The theory proposed here is consistent with the experimental results.

Chapter 5

The deposition of calcium carbonate commonly known as scale costs billions of dollars to the world wide economy. This is also a customary problem for cane sugar processing across the world. The present work is essentially an extension of our earlier work on the effect of pulsed magnetic field on cane molasses and massecuite. A suitable magnetic field pulse can effectively reduce scale formation and also changes the nature of the scale formed. Examining the physical characteristics of scale samples revealed that the scale after PMF treatment was found to be loose, soft sludge type and easily de-scalable. The FTIR spectrum of the scale samples after PMF treatment presents the characteristic absorption peaks of vaterite at 1112 and 1134 $cm^{-1.}$ No characteristic peaks belonging to calcite at 713 and 876 cm^{-1} were detected after PMF treatment. However, partial characteristic peaks belonging to aragonite were appeared after treatment at 649.4 cm^{-1}. The Scanning Electron Micicrograph (SEM) image clearly demonstrates the vaterite image after PMF treatment [K. Singh, *et al*, 2016]. Thus, application of PMF plays a crucial role to sugar evaporators changing the nature of scale from hard (calcite) to soft (vaterite) which is easily de-scalable.

The application of a suitable magnetic field pulse in cane sugar evaporators leads to following important conclusions:-

a) The physical configuration of the scale changes from hard and dense to soft, porous sludge type which is easily de-scalable.
b) The SEM images demonstrate that a large amount of thermodynamically least stable vaterite is formed after PMF treatment.
c) The FT-IR spectral finger print for the identification of carbonate polymorphs after PMF treatment demonstrate the characteristic absorption peaks of vaterite at

1112 and 1134 cm^{-1}; a thermodynamically least stable polymorph of calcium carbonate.

d) Thus applications of a suitable PMF suggest that the PMF application could lead to an energy saving process for cane sugar manufacturing.

Chapter 6

Laboratory and industrial tests were conducted on reducing viscosity of cane molasses and massecuite with pulsed magnetic field (PMF). Employing PMF treatment, viscosity was reduced by 40-45% in comparison with untreated materials. It is hypothesized that in response to PMF treatment, non-sugar components (molecules) in the molasses and massecuite aggregate leading to changes in the rheological property of the fluids. The 5 minute PMF at 0.15 tesla (T) produced maximum viscosity reduction (40-45%). After about 3 hours viscosity begins to rise and after 10 to 12 hours after the PMF treatment returns to the original value. These laboratory studies coupled with some commercial trials suggest that the PMF application [K. Singh, *et al*, 2016] could lead to an energy saving process for cane sugar manufacturing.

a) With the PMF treatment, viscosity of massecuite and final molasses was reduced significantly, by 40 to 45%.
b) Application and re-application of PMF may help in effectively transporting the concentrated fluids (molasses and massecuite) in the sugar process.
c) The laboratory experiments support commercial trials, confirmed the expected benefits for process control and energy savings during sugar manufacturing**.**
d) The present study clarifies the existing controversy regarding the suitability of magnetic fluid conditioners or even permanent magnets in the sugar manufacturing process. The use PMF provides reproducible data on viscosity of the molasses and massecuite.

REFERENCES

- A. Van Hook, Kinetics of sucrose crystallization: Pure sucrose solutions, *J. Ind. Eng. Chem.* 36 (1944) 1042.
- De Coudray, Crystallization of sugar, *Sugar*, 41 (1946) 36.
- G.M. Brown, H.A. Levy, Sucrose: Precise determination of crystal and molecular structure by neutron diffraction. *Science.* 141 (1963) 921-923.
- G.M. Brown, H.A. Levy, Further refinement of the structure of sucrose based on neutron-diffraction data. *Acta Cryst.* B29 (1973) 790-797.
- Holven, Supersaturation in sugar boiling operations. continuous automatic measurement, *Ind. Eng. Chem.* 34 (1942) 1-4.
- H.W. *Anderson,* B. Carberry, H.F. Stauton, B.C. Sutradhar, crystallization of adpic acid , U.S. *Patent*, 5471001 (1995).
- J. Peric, M. Vicak, R. Krstulovic, L. Brecevic, D. Kar1j, M. Vicak, R. Krstulovic, L. Brecevic, D. Karlj, Phase transformation of calcium carbonate polymorphs, *Thermochem Acta*. 277 (1996) 175.
- K. Singh, M. Prasad, solid phase conductivity of commercial plantations white sugar (PWS) crystal, *J. Indian Chem. Soc.* 76 (1999) 49-50.
- K. Singh, S. Mohan, Kinetic study of crystal coloration during crystallization of sucrose, *Ind. J. Chem. Tech*. 10 (2003) 386-390.
- K. Singh, M. Prasad, Solid state conductance in sucrose and its allied crystalline products, J. *Ind. Chem. Soc*. 82 (2005) 437-440.
- K. Singh, A. Kumar and S. P. Gupta, Effect of ultrasonics on morphology of precipitated calcium carbonate (PCC) for controlling scale formation in cane sugar processing: Laboratory scale experiment, *Proc. Sug. Tech. Asso. India,* 74 (2016) 579-587.
- K. Singh, B. Chandra, S.P. Gupta, A. Kumar, Application and potential of a pilsed magnetic field in controlling scale formation in cane-sugar processing, *Proc. Int. Soc. Sug. Can. Tech*. 29, (2016) 566-571.
- K. Singh, B. Chandra, S.P. Gupta, Reducing viscosity of molasses and massecuite with pulsed magnetic field (PMF), *Int. Sugar J*. 118 (2016) 26

- N.A. Ramaiah , S.K. Sanyal, Further studies on the occurrence of induction periods in crystallization of sucrose, *Proc. Sug. Tech. Assos. Ind*. 30 (1962), 147-150.
- V. K. Singh, S. K. Verma, B. Chandra, S. P. Gupta, K. Singh, Application and potential of power ultrasound (pus) in sugar manufacturing: a non-chemical green technology, *J. Pure Appl. Ultrason. 35* (2013) 137-140.