EFFECT OF IMPURITIES ON SUCROSE CRYSTAL SHAPE AND GROWTH

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ABSTRACT

Sucrose crystal growth rate is a subject which attracted the interest of researchers both for its theoretical and practical importance. It is generally admitted that two major steps govern this process: the diffusion of sucrose from the bulk solution to crystal/solution interface on the one hand and the incorporation of sucrose molecules in the crystal after release of hydration water on the other. The second step seems the most critical as it necessitates disassociation of hydration water molecules and their diffusion in the bulk solution.

Hydrophilic impurities like oligo- and polysaccharides, because of their affinity for water and for sucrose itself, exert a major effect on the shape and rate of growth of sucrose crystals.

Experimental results are reported to show the specific effect of some selected impurities on the shape and rate of growth of sucrose crystals. Likewise, the role of water on crystallisation rate is discussed.

KEYWORDS: Sucrose; crystal growth, crystal shape, impurities, oligosaccharide, polysaccharide.

INTRODUCTION

The rate of growth of sucrose crystals has been used as a typical example in the study of the mechanism of crystallisation [1]. It was generally represented by a sequence of transport followed by a sequence of integration of the sucrose molecules into the surface of crystal. The first important investigations in this field are due to *Kukharenko* [2]. From careful experiences performed with relatively large crystals (1 to 12g of weight) grown in supersaturated sucrose solutions initially "sterilised" by overheating to eliminate the possible clustering of solute molecules which might lead to spontaneous nucleation, Kukharenko [2] obtained reliable rates of growth expressed in $mg.m^{-2}min.^{-1}$ by use of a shape factor $k = S/m^{2/3}$ (with S: crystal surface; m: mass of crystal). *VanHook* [3,4] contribution in the field of sucrose crystal growth is particularly significant. Using simple devices (0.5 – 1 litre beakers placed in thermostated bath and agitated), he extended the work of *Kukharenko* to temperatures as high as 100°C. He observed that transport phenomena are essential in determining growth rates below 50°C. Above this temperature transport is rate limiting. At low temperatures, the surface incorporation prevails and the rate of growth of sucrose crystals is first order and virtually independent of supersaturation, viscosity and agitation [5]. The kinetic order increases as temperature increases and then decreases again. *Bennema* [6] using the BCF theory of surface diffusion could account for the second order growth at intermediate temperatures. The linear dependence at higher temperatures is due to slower transport step of the diffusion-surface integration combination which describes crystal growth [7]

The effect of impurities on crystal habit and growth was also studied by *VanHook* [8], especially for raffinose which was found to be preferentially adsorbed on the surface of growing sucrose crystals and not built in the normal crystal lattice [9]. *Aquilano* et *al* [10] observed and described the effects of KCl, NaBr and raffinose on crystal growth and habit. These authors found that growth inhibition is not explained by surface adsorption but by kink poisoning at specific site where sucrose is bound with its fructose unit to the impurity. Polysaccharides where found to decrease the rate of growth of sucrose crystals due to an increase of viscosity of mother solution and also to a reduction of the rate of incorporation of molecules into the growing crystal [11]. Macromolecular impurities such as polysaccharides and colorants (melanoïdins) can also be included in the crystal in case of rapid growth

according to a "finger" growth type where cavities are created at the surface of the crystal which are closed to include the macromolecular impurities [12].

Another parameter to take into account in interpreting sucrose crystal growth is the hydration water. Migration of this fraction of water to the bulk solution after release from sucrose molecules during their integration to the crystal was proposed as the controlling step of growth [13]. Sucrose crystal growth is in fact comparable to a hurdle race where the hurdles are the energy barriers due to convection, volume diffusion, adsorption, dehydration and surface alignment [14]. Alignment of molecules and the disassociation of hydration water are not instantaneous which explains the pulsation mechanism of sucrose crystal growth [15].

We report in this paper our results as well as some data from the literature to illustrate the effect of some selected impurities on the growth rate and the morphology of sucrose crystals. Factors such as the supersaturation of solution and size of macromolecular impurities are studied. In all cases, growth rates are decreased in presence of impurities.

MATERIALS AND METHODS

Highly pure sucrose crystals with sizes 0.86 and 1.50 mm where complimentary given by Cristal Union, Sugar beet factory of Bazancourt (France).

Pure polysaccharides arabinogalactan from larch and dextran (MW=73000 kg/mol) where Sigma products used without any further purification.

Macromolecules obtained by ultrafiltration of press water from the sugar factory of Bazancourt where concentrated and freeze-dried before utilisation in the growth experiments. These macromolecules correspond to retention fraction on membranes with thresholds of 3.5; 10 and 45 kg/mol.

Macromolecules obtained by ultrafiltration of second runoffs in sugar factory (> 10000 kg/mol) where also used. These impurities are a mixture of colorants and polysaccharides concentrated in the mother liquor of second strike of sugar crystallisation process

The "end to end" method of crystallisation was used to follow the growth rate and the morphology of crystals was analysed with Lucia software of image analysis [16] after acquisition of the images of crystals with a camera microscope connected to a PC.

The "end-to-end" method consists in growing the sucrose crystals in sample tubes filled with supersaturated solutions. The growing crystals are selected under camera microscope and heated at work temperature prior to introduction in the tubes. The sample tubes containing crystals and saturated solution are fixed on a disc rotating at 6 rpm placed in a thermostated (30°C) box. Supersaturation and the percentage of impurity are varied and the dimensions a, b, and c of crystals determined with image analysis before and after growth. An average rate of growth along each of the axis a, b, and c is calculated and expressed in μm/min. In order to express growth in the usual rate unit ($mg.m^{-2}.min^{-1}$) a shape factor was calculated and found comparable to that of *Bubnik and Kadlec* [17], i.e. 0.713. Growth rate is expressed by R = 0.713 Lg where Lg is the linear growth rate.

RESULTS AND DISCUSSION

Effect of impurities on the shape of sucrose crystals

Crystal habit modification may have as its origin the shape properties of the sucrose molecule itself [18].Sucrose molecule is flexible in aqueous solution [Fig.1] and this flexibility was demonstrated [19] using low-angle X-ray diffraction and Raman spectroscopy. A wide range of molecular structures was observed in crystals and complexes involving a

sucrose moiety. The shape with lowest energy is generally derived from the calculation of the energy of the molecule obtained when rotating the glycosyl and fructosyl moieties of the sucrose molecule around the glycosidic linkage C-O-C. The flexibility of sucrose molecules in different environments is mainly due to the numerous conformations adopted by the fuctofuranosyl ring. Moreover, most of impurities found to exert a significant influence on sucrose crystal shape and rate of growth have structure features that have similarities with the sucrose molecule itself.

- oligosaccharides:

Oligosaccharides including in their molecular structure a sucrose moiety (raffinose, kestoses, nystose) are found as impurities in beet sugar syrups. Experimental work [20] using these oligosaccharides as additives allowed understanding of their effect on sucrose crystal shape and rate of growth. Raffinose (α-D-galactopyranosyl (1- 6) α - D –glucopyranosyl (1 – 2) β-D – fructofuranoside) which contains glucose and fructose rings attached with the same (1-2) linkage as sucrose proceeds through selective adsorption at the surface of sucrose standard (flat) crystal (Fig.2). The sucrose moiety of raffinose replaces a sucrose at a kink and the remaining monosaccharide (galactose) emerging from the surface prevents the integration of other sucrose molecules to the poisoned face. Even at low concentrations, raffnose engenders an elongated needle along (010) axis (Fig. 3). Explanation of the specific effect of raffinose on sucrose crystal shape was attributed to the compatibility between a molecule of raffinose and the sucrose conformation at the different sucrose crystal faces [1; 20]. Maximum compatibility was found to occur on the polar (110) face and the minimum with the ($\overline{1}\,\overline{1}$0) form. Raffinose also interferes with non polar (100) and (101) forms. The role of raffinose on sucrose crystal growth was also approached at a molecular level using the "growth cell" model and semiempirical quantum mechanical calculations [21]. Equilibrium state of hydrogen binding of raffinose to (10$\overline{1}$) crystal face was proposed (Fig.4). From the energy of formation of the structures involving or not raffinose, it was found that the most stable (lower energy) configuration is obtained with raffinose [21], which means that adsorption of raffinose is spontaneous. Beside polarity of crystal faces and the probability of adsorption of raffinose, hydration arguments are scarcely invoked in the interpretation of crystal growth studies.

We have recently emphasized the role of water in the mechanism of crystal growth. In fact, incorporation of sucrose molecules only concerns desolvated sucrose. Desolvation occurs at the surface of the crystal prior to integration into the crystal lattice. When sucrose-sucrose bonds are established, there is a release of hydration water. The kinetics of dehydration of sucrose molecules and the diffusion of water from crystal surface to the bulk solution becomes a limiting factor to growth. This phenomenon is considerably aggravated when a hydrophilic impurity like raffinose is adsorbed at a face of sucrose crystal. Raffinose crystallizes as a pentahydrate [22]. When it is found as an impurity in sucrose solution, its structure is relaxed: no intramolecular hydrogen bonds remain in its sucrose moiety. However, its affinity for water is very high. At least 2 water molecules are bound to oxygen atoms O(2) and O(5) in the gucosyl ring of raffinose. The very slow removal of these hydration water molecules makes the kinetics of growth of the poisoned face very low, which allows a higher speed of other faces and leads to needle shaped crystals.

The fructo-oligosaccharides (1-kestose, neokestose and nystose) were also found to induce unusual rhombic growth habit when added at low concentration to aqueous sucrose solutions. A mode of adsorption similar to that of raffinose was proposed [20] for fructo-oligosaccharides. The sucrose moiety of these oligosaccharides was supposed to replace a sucrose molecule in the crystal while the remaining monosaccharides (fructofuranose) prevent the adsorption of new sucrose molecules arriving from the solution to contribute to growth of

the crystal face. The efficacy of these "blocking" additives is enhanced by the particular conformation change and affinity for water of the fructofuranosyl residues. The faces of crystal the most affected by fructo-oligosaccharides are $(\bar{1}\,\bar{1}0)$; (011) for 1-kestose and (100); (110); $(0\bar{1}\,\bar{1})$ for neokestose. The retardation of growth of these faces leads to typical habits of sucrose crystals reported in Fig. 5.

-polysaccharides

Generally the polysaccharides studied at the laboratory as impurities affecting growth and shape of sucrose crystals are those naturally found in cane and beet sugar syrups. Dextrans are among the major impurities present in cane and pectins in beet. Dextrans are present in cane products simultaneously with glucose and fructose. Their influence on the shape of sucrose crystals is manifested by an elongation along c-axis. However, no synergistic effect was observed with the influence of glucose and fructose [23]. Each impurity seems to have its own influence on growth and merely affects the adsorption of the other impurity. *Bubnik et al.* [23] following the rate of growth along c and b axis derived from the experimental results a model equation for the ratio c/b as a function of dextran concentration . In pure sucrose solution the ratio c/b is equal to 0.7. It reaches 3 times this value in presence of 3g dextran/100g water. As may be observed in Figure 6, the elongation along c axis exceeds 3 times the length of b when sucrose crystals are grown in presence of dextrans.

In the model system containing water sucrose, dextrans and invert sugar (glucose + fructose) as well as in the more complex system constituted by saturated cane sugar syrup, the water fraction is just enough to hydrate each of the solutes and almost no free water is left. In these conditions diffusion of sucrose molecules decreases and tends towards zero. Crystal growth is therefore mainly controlled by the release of hydration water and its diffusion from the surface of crystal to the bulk. Such a diffusion necessitates the presence of mobile water which might be limitant if hydration water is tightly bound to solutes.

Depending on the impurity (invert sugar or dextran) in the solution, the ratio c/b might change, showing an increase as dextran concentration increases followed by a decrease observed when invert sugar increases in presence of low amounts of dextran [23]. This change can be assigned to the possible change in affinity for water of each of the impurities when concentration is varied. It is also an explanation to the contradictory results published by different authors on the effect of impurities in technical cane syrups on the shape of sugar crystals.

Effect of impurities on the rate of growth

To compare growth rates along the various crystallographic axis, it is needed that initial crystal dimensions are known. The average dimensions for a standard (flat) sucrose crystal grown in the laboratory [17] are: $L_b : L_c : L_a = 1.60 : 1.0 : 0.73$.
We measured L_b, L_c, and L_a, the lengths along the 3 axes for 100 crystals grown in beet sugar factory and found an average value of $L_b/L_c = 1.33$. Depending on the mean size of crystal, a slight decrease on L_b/L_c is observed. Growth rates R_b, R_c and R_a of sucrose crystals are also obtained from the measurement of the linear dimensions L_b, L_c and L_a. Knowing the initial L_b/L_c ratio, it is possible to follow the elongation ratio after measuring growth rates. Overall rate of growth of sucrose crystal R is expressed in $mg/m^2.min$. It is obtained using the following expression:

$$R = Cr_{(i)} - Cr_{(i-1)}/[S_{(i-1)}]*[\theta_{(i)} - \theta_{(i-1)}]$$

Where $Cr_{(i)}$ and $Cr_{(i-1)}$ is crystal weight at instant $\theta_{(i)}$ and $\theta_{(i-1)}$ respectively ; S is the surface of crystal obtained from size or mean aperture (M.A.) as: S = 0.4/M.A.

Effect of process impurities on overall rate of growth

Comparison of the effect of polysaccharide impurities dextran (MW = 73000) and arabinogalactan added in pure sucrose solution at the same concentration 5 g impurity % g water is reported in Fig. 7 for overall growth rate. As may be observed, the effect of dextran in decreasing the growth rate of sucrose crystals as a function of supersaturation is much higher than that of arabinogalactan. The latter polysaccharide is taken as a model for beet pectin. The effect on growth in presence of this model compound is comparable to that obtained with beet pectin [24] which were not found detrimental to crystal growth when added to factory sucrose syrup, but they might act as clorant carriers and provoke inclusion of colour. This effect of pectins was demonstrated by use of pectinases which contributed to the reduction of colorant inclusion [24].

In addition to the study of the effect of impurities from the commerce (dextran, arabinogalactan (Sigma products), *Pautrat et al.* [25] have used freeze dried ultrafiltration retentates obtained from sugar process thin juice and second strike runoffs. The same proportion of impurity (5g%g water) was used and the measured rate of growth reported in Fig.8. As expected impurities reduce the rate of growth. However, concentrated thin juice impurities have a more pronounced effect than runoffs. This might have as its origin the presence of low molecular weight (LMW) macromolecules (degraded pectins and the non polymerised colorants HADP (Hexose Alkaline Degradation Products) in thin juices. In runoffs, the impurities are mainly constituted by high molecular weight (HMW) condensation products like melanoïdins and polymerised HADP as well as caramel. The lower the molecular weight of impurity, the higher its adsorption on crystal faces and the higher its retarding effect on growth. Impurities from runoffs, although having less blocking effect are generally implied in the mechanism of inclusion of colour inside the crystal through a "finger" type of crystal growth which imprisons the droplets of HMW colorants remaining at the surface of growing sucrose crystals [12] without changing the crystal shape.

Effect of macromolecules from press water on rate of growth along b and c axes

Three factions of macromolecules were obtained by ultrafiltration of the water resulting from pressing at high pressure (….kPa) the exhausted beet cossettes. This press water is entirely recycled in the diffusion extractor without any further treatment. The impurities extracted by pressure in this water are also recycled. The 3 fractions of macromolecules have different molecular weights (3.5 – 10 and 45 kg/mol). They were freeze dried and added as impurities in pure sucrose solutions to check their effects on crystal growth. From monosaccharide composition, these fractions are composed of pectins and hemicelluloses. Figure 9 shows the rate of growth along axis b for sucrose crystals with initial size (M.A.) equal to 0.86 mm. in presence of 0.5g of macromolecules % water. Growth rate follows a 2nd order kinetics as can be expected for a BCF type of growth. The same trend was observed by *Maurandi* [26] for a NS/W ratio of 0.9. Decrease in the rate of growth with macromolecules from press water seems less important than that observed with process impurities (thin juice and runoffs). For example at a supersaturation σ = 1.08, growth rate in pure sucrose solution R = 821 g/m^2.min. This value becomes equal to 421 in presence of the highest molecular weight fraction (45 kg/mol), which corresponds to 50% decrease in growth rate. Fractions at 3.5 and 10 kg/mol molecular weights give a comparable retarding effect of the crystal growth along the b axis.

Comparison of the rates of growth along c and b axes when macromolecules with 45 kg/mol MW are added into growth solution is reported in Fig 10. The rate of growth along b

axis is higher than along c axis. For a supersaturation equal to 1.12, for example, the growth along b axis is nearly double of that along c axis. Compared to the growth in pure sucrose solution the trend is the same. This result confirms the fact that pectin fractions found in the press water do not have a noticeable effect on the shape of crystal although the overall growth is decreased.

CONCLUSION

Adsorption of impurities on the faces of sucrose crystals seems specific and particularly harmful to growth for low molecular weight impurities like oligosaccharides. These oligomers of sugars show a high affinity of faces of the sucrose crystal where sucrose molecules adopt the same conformation as their sucrose moieties. By blocking some of the faces of the crystal they provoke a relative increase in growth of other faces, which ends with special forms like the needles elongated along b axis in presence of raffinose and the rhomboedric shapes obtained in presence of kestoses. Among macromolecules, dextran gives the most important decrease in growth. It provokes an elongation along c axis. Other hetero - polysaccharides like pectin, hemicellulose or arabinogalactan exert a lesser retarding effect on sucrose crystal growth. The absence of compatible conformation of monosaccharide residues with that of sucrose is very likely at the origin of lower adsorption.

On the other hand, the release of hydration water from the sucrose molecules integrated into the crystal lattice and the need of a certain mobility for this water fraction to diffuse to the bulk solution might be the clue to explain the retarding effect of impurities to the growth of sucrose crystals.

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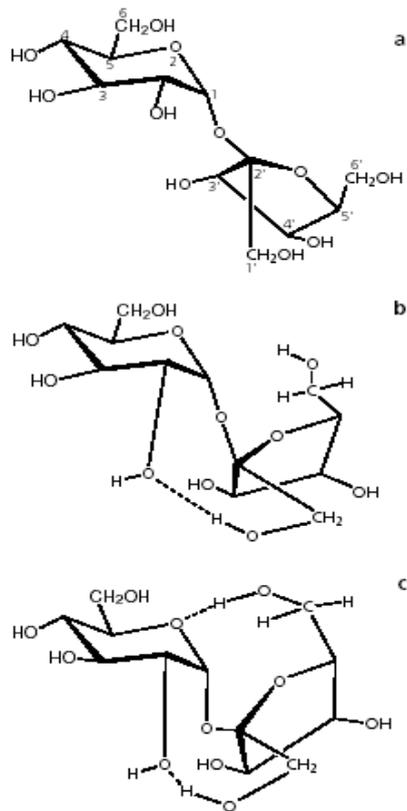
Figure 1 : Flexibility of sucrose molecule around the glycosidic bond: a) no intra-molecular H bonds in dilute solution; b) 1 H-bond in intermediate concentration; c) 2 intra-molecular H-bonds in the saturated solution (and in the crystal) (from Ref. 19)
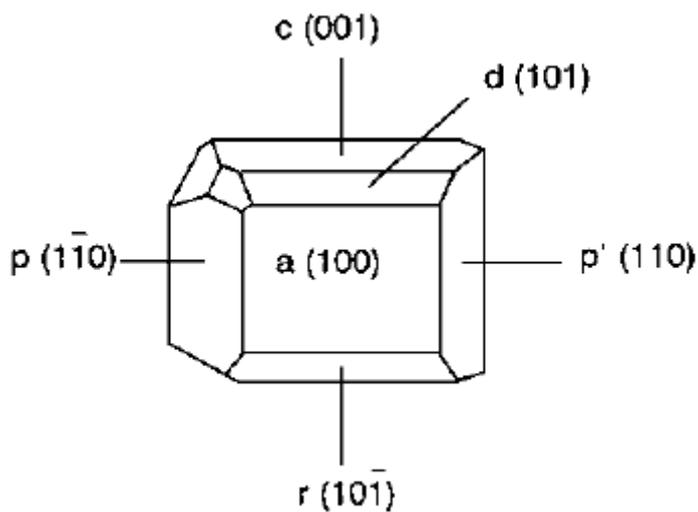

Figure 2: Standard shape of sucrose crystal showing important crystal faces (Ref. 20)

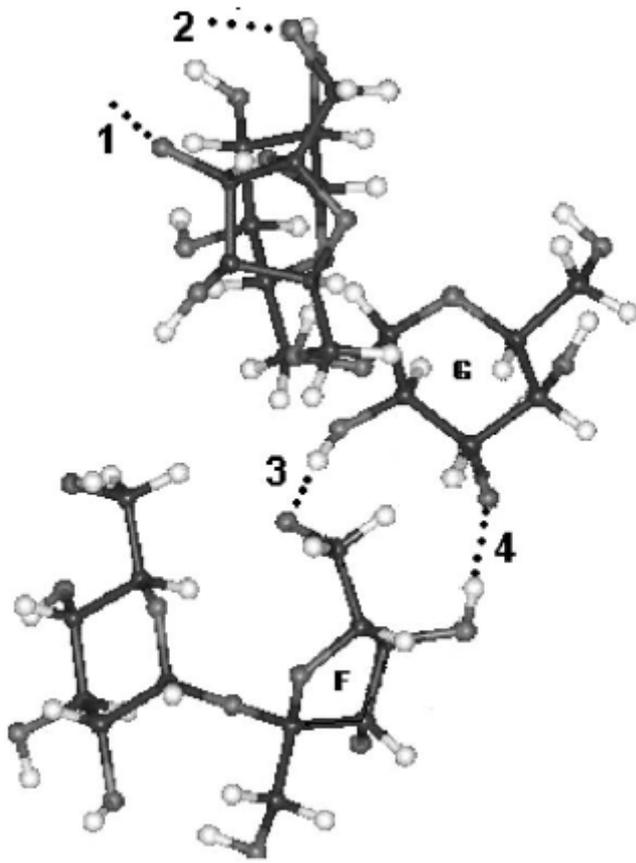Figure 3 : Sucrose crystal grown in presence of raffinose (Ref. 20)

Figure 4: Hydrogen bonding between raffinose and sucrose at equilibrium state according to interaction model reported in Ref. 21.
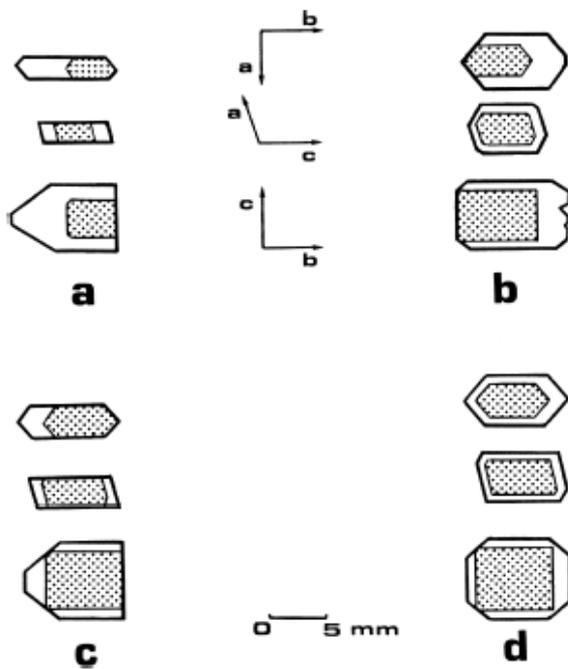
Figure 5: Growth habits of sucrose crystal modified by: (a) neo-kestose (20g/100g water); (b) 1-kestose (20g/100g water); (c) neo-kestose + 1-kestose 1:1; (d) neo-kestose + 1-kestose 1:5.
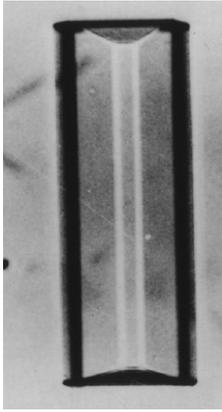
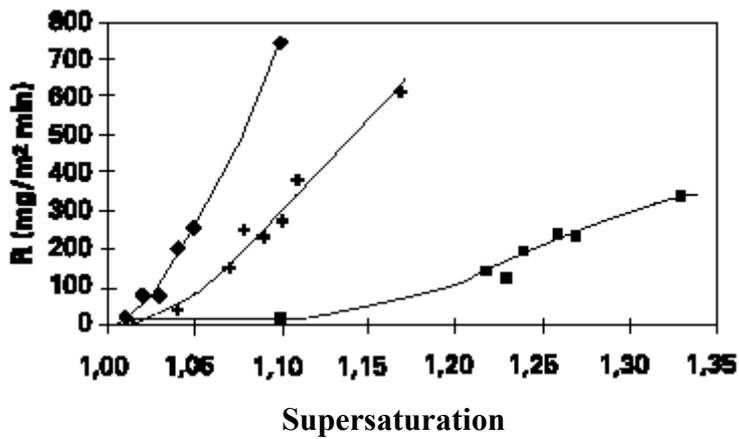Figure 6: Crystal od sucrose grown in presence of dextran

Figure 7: Rate of growth of sucrose crystals in pure solution (■), in presence of arabinogalactan (**x**), and in presence of dextran (◆) (Ref. 25)
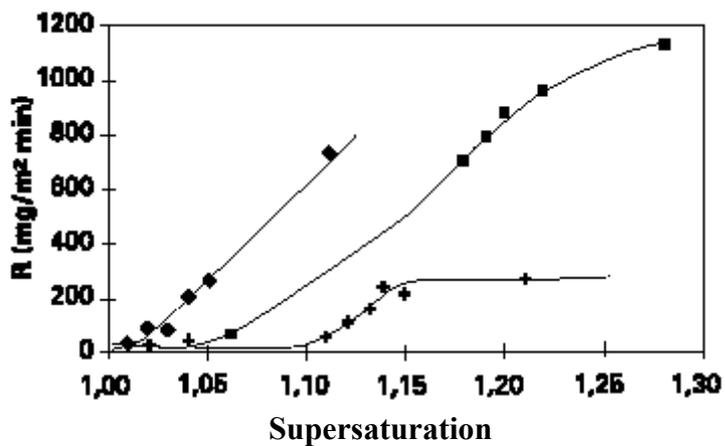

Figure 8: Rate of growth of sucrose crystals in pure solution (■), in presence of second runoffs retentate(◆) and in presence of thin juice retentate (+) (Ref. 25)
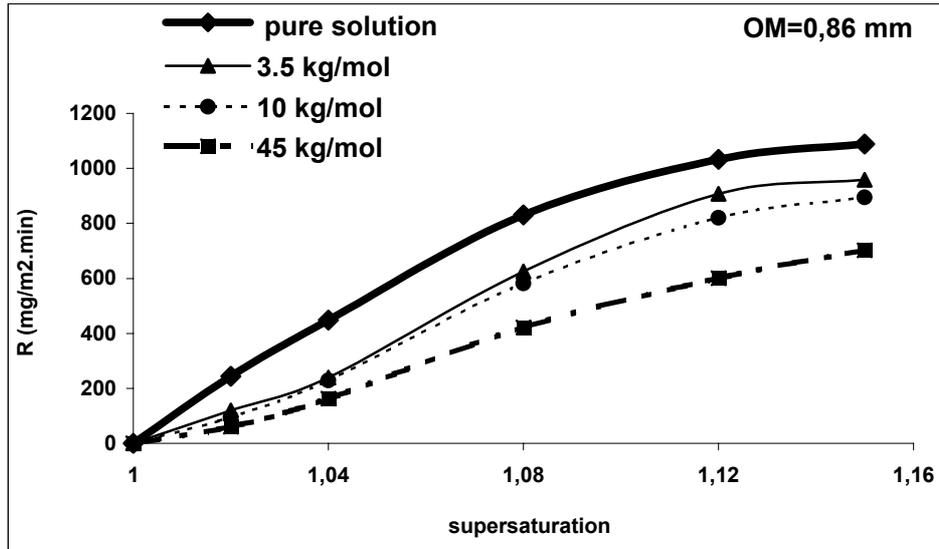
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Figure 9: Rate of growth of sucrose crystals (initial size = 0.86 mm) in pure solution and in presence of press water macromolecular impurities
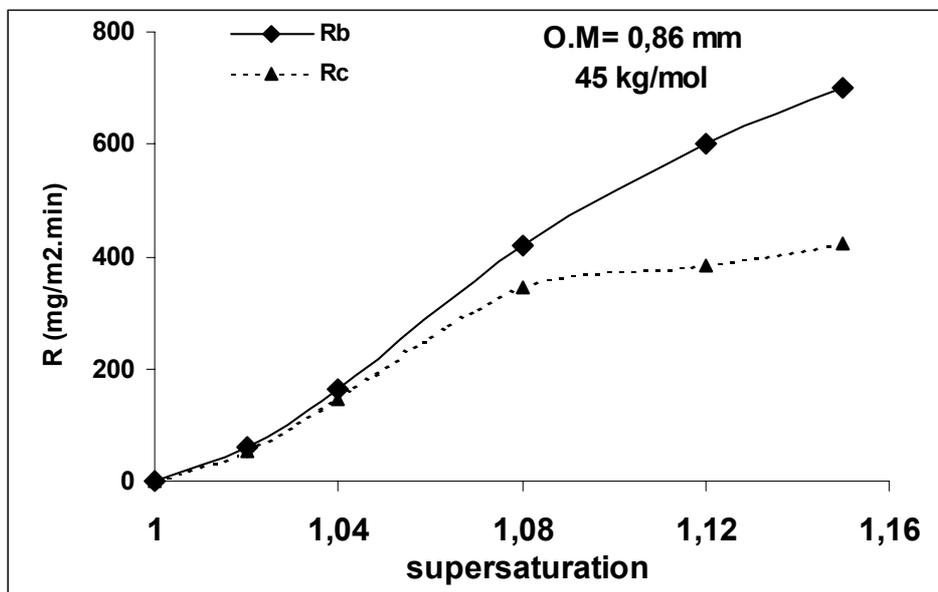

Figure 10: Rate of growth of sucrose crystals (initial size = 0.86 mm) in presence of press water macromolecules (45 kg/mol) along b and c axis.