

Role of water in sucrose crystallization¹

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Received 3 December 1997

Abstract

The rate of sucrose crystallization in supersaturated solutions is known to include at least two steps: the diffusion of sucrose from the bulk solution to the thin layer at the interface crystal/solution and the incorporation of sucrose molecules in the crystal after the release of their hydration water. Among the energy barriers encountered in the ‘hurdle race’ of the crystallization process, viscosity seems to be a minor hurdle and the disassociation of hydration water a major one. We will attempt to show that the dehydration of sucrose molecules prior to their incorporation into the crystal plays an important part in the crystallization process and propose to conceive the mechanism of crystal growth as mainly based on the release of water molecules and their diffusion in the bulk solution rather than a migration of sucrose from the solution to the crystal. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Crystallization; Hydration water; Hydrogen bonds; Nucleation; Crystal growth

1. Introduction

Sucrose crystallizes in supersaturated aqueous solutions. The appearance of nuclei generally occurs after the organization of hydrated sucrose molecules in swarms during the period of prenucleation.

If nucleation is considered as a step of establishing sucrose–sucrose hydrogen bonds, there is a need to make sure that potential H-bond sites are not occupied by hydration water. During crystal growth, incorporation of sucrose molecules to the crystal lattice also requires that hydration water molecules be disassociated. This step seems to constitute a higher energy barrier to crystal growth than the barriers of diffusion or viscosity. Although classical crystallization theory considers the sucrose concentration gradient as the driving force for crystal growth, it is possible to find arguments in favor of a crystallization mechanism based on the transfer of water molecules from the interface crystal/boundary layer of mother liquor to the bulk of solution.

Before developing this new point of view, we first recall previous work on hydrogen bonds in aqueous sugar solutions as well as nucleation and sucrose crystal growth.

2. Hydrogen bonding in sucrose crystal and solution

2.1. Sucrose crystal

The nature of intra- and intermolecular bonds in the crystal is the same as that between water and sucrose, namely H-bonds. These hydrogen bonds are linear O–H...O or bifurcated with two or three sites of binding. Brown and Levy (1963), using neutron diffraction, have shown the existence of two intramolecular H-bonds for sucrose molecules in the crystal network (see also Hanson et al., 1973).

Among the eight possible sites of H-bonds in a sucrose molecule, seven were characterized from crystallography including the two intramolecular bonds (see Table 1). The group Og(4)–H is only marginally implied in the hydrogen bonding of the crystal (Brown and Levy, 1973). The fructosyl moiety of sucrose seems preponderant in establishing H-bonds as may be observed in Table 1. The absence of H-bonds at carbon-4 allows Og(4)–H a higher freedom of vibrational motion which is manifested by an individualized OH vibration in the region of OH stretchings on the FTIR spectra of sucrose crystal and concentrated solution (Mathlouthi et al., 1986).

Moreover, the hydrogen bonding in sucrose is strengthened by the cooperatively and polarisability of H-bond chains as was reported previously (Jeffrey, 1992, Engelsen et al., 1995). Studying the conformational flexibility of

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¹ Presented at the Second International Meeting of the Portuguese Carbohydrate Chemistry Group.

sucrose shows that sucrose is more rigid than other disaccharides. Rather than sucrose conformation in vacuo or in computer, it is more relevant to study experimentally the sucrose structure in the aqueous medium.

2.2. Sucrose–water interactions

2.2.1. Molecular dynamics simulation

Recent molecular dynamic simulations have shown that intramolecular hydrogen bonds do not exist in dilute aqueous solutions (Immel and Lichtenthaler, 1995). Two maxima in radial distribution between hydrogen and oxygen atoms have been observed at 1.8 and 3.2 Å. They have been assigned to H-bonds between either the sucrose oxygen and one of the protons in H₂O or between the same oxygen and the other proton (Immel and Lichtenthaler, 1995).

The presence of a water bridge between glucose and fructose residues in the sucrose molecule in highly concentrated solutions has also been obtained by the same authors using molecular dynamic (MD) simulation. This water molecule seems to have a relatively long lifetime at the scale of simulation experiment and might play a role in sucrose crystallization as it could be the last hydration water molecule to disassociate prior to incorporation in the crystal (Immel and Lichtenthaler, 1995).

2.3. Experimental results

Using X-ray diffraction and laser-Raman spectroscopy, we have shown that the sucrose molecule can adopt two conformations depending on the concentration of aqueous solution (Mathlouthi, 1981). Below about one-third of saturation concentration, water–water interactions are preponderant and the sucrose molecule is fully hydrated including no intramolecular H-bonds. Between one- and two-thirds of saturation concentration, hydrated sugar molecules move closer to each other, folding starts and a first intramolecular H-bond takes place. Above two-thirds of

saturation concentration, the conformation of sucrose becomes comparable to that in the crystal involving two intramolecular H-bonds. This was derived from the variation of the Raman frequency for $\delta(\text{C–O–C})$ bending as concentration is increased (Mathlouthi et al., 1980) (see Fig. 1).

Recent work using ¹H NMR and ¹⁷O NMR established the existence of four regions of different water mobilities in the 5%–80% (w/w) sucrose concentration range (Richardson et al., 1987) (see Fig. 2). From 5% to 40% (region I), rapid exchange of water molecules is observed. From 40% to 60% (w/w), water–sucrose and sucrose–sucrose interactions are found. The stability of NMR signal (III) corresponds to solubility equilibrium. Supersaturation corresponds to increased ¹⁷O relaxation and decreased water mobility (IV) (see Fig. 2). Other experimental evidence of the increased order in concentrated sugar solutions is known: the work of Tikhomiroff and Heitz (1965), based on viscosity and dielectric measurements, demonstrates the existence of a ‘prenucleation’ step of formation of swarms of sucrose molecules (protonuclei) prior to the starting of nucleation and growth in supersaturated solutions.

2.4. Sucrose crystallization

Apart from the kinetic and thermodynamic aspects of crystallization, it should be noted that the unit operation called crystallization is also an art. Van der Sluis (1989) has shown that the precise knowledge of the arrangement of solvent molecules around the crystal and the understanding of solute–solvent interactions allow elucidation of crystal growth and shape.

2.4.1. Nucleation

Interactions between sucrose molecules to form a nucleus consist of a series of equilibria until the critical size is reached. However, before reaching the critical radius of

Table 1
Hydrogen bonds in sucrose crystal (Brown and Levy, 1973)

Bonds (O–H...O)	Distances (Å)			Angle (O–H...O (°))
	O–H	H...O	O...O	
Intramolecular				
O1(f)–H...O2(g)	0.974	1.851	2.781	158.6
O6(f)–H...O5(g)	0.972	1.895	2.850	167.1
Intermolecular				
O2(g)–H...O6(f)	0.972	1.892	2.855	170.2
O3(g)–H...O3(f)	0.959	1.907	2.862	172.8
O6(g)–H...O4(f)	0.956	1.921	2.848	162.9
O3(f)–H...O4(f)	0.969	1.908	2.864	168.5
O4(f)–H...O1(f)	0.976	1.760	2.716	165.4
OH non-bonded				
O4(g)H	O2(f)	2.309	2.838	116.6
	O3(g)	0.912	2.534	103.0
	O6(g)	2.539	3.373	152.1

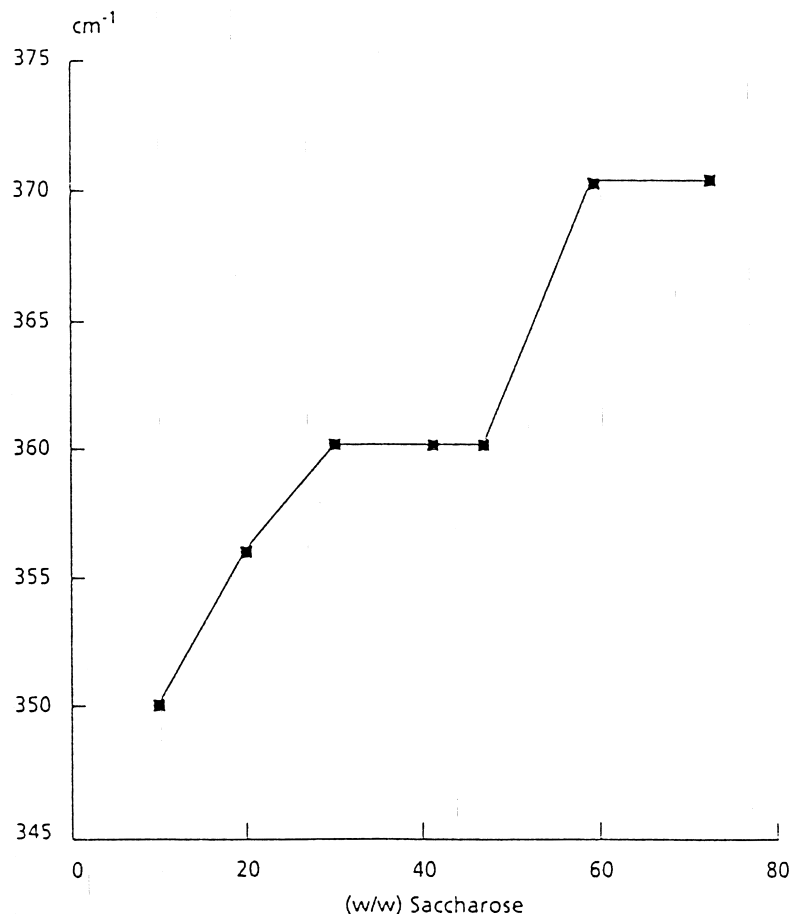


Fig. 1. Variation of Raman frequency corresponding to (C–O–C) bending as a function of concentration (Mathlouthi et al., 1980).

nucleus, embryos are formed as hexamers (Kelly and Mak, 1975). Regular stacking of sucrose molecules around embryos is at the origin of the nuclei of about 80–100 molecules ($r_c \approx 20 \text{ \AA}$). The rate of passing from embryo to nucleus is lower than that of embryo formation. It is possible that embryos exist in undersaturated solutions at the range of concentrations from 44% to 67% (w/w) at 20°C (2/3 to saturation). The frequency of collision of these embryos leads to a probability of appearance of critical nuclei given by:

$$J = \frac{kT}{h} \exp\left(\frac{\Delta S}{R}\right) \exp\left(-\frac{\Delta H}{RT}\right)$$

The first term in this relation is a universal term. In the second term, the variation of entropy plays a major role. There is a need for a high ΔS for at least two reasons: the evolution from disorder to order on the one hand and the evacuation of hydration water on the other.

2.5. Crystal growth

Nucleation depends on supersaturation in a critical way and becomes explosive at a supersaturation of about 1.5–1.6 (Van Hook and Bruno, 1949) in homogeneous solution, whereas crystal growth follows a much slower variation in

function of supersaturation. In non-seeded syrups, the average growth rate is an adjustment between nucleation and growth (see Fig. 3).

Growth is generally described as a heterogeneous process including two steps: (1) diffusion from bulk solution to the boundary layer of immobile mother liquor at the surface of the crystal; (2) incorporation of sucrose molecules in the crystal. The rate of the first step is described by Fick's

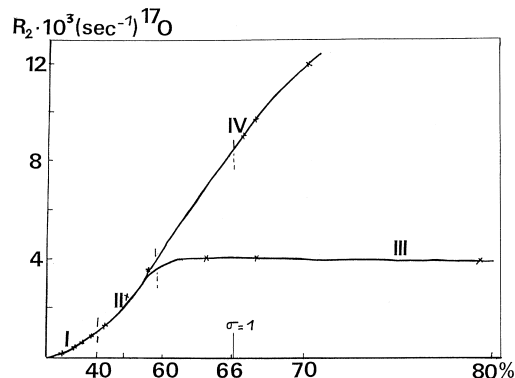


Fig. 2. ^{17}O relaxation as a function of sucrose concentration. Region I, 5%–40% rapid exchange; II, 40%–60% water–sucrose and sucrose–sucrose interactions; III, solubility equilibrium; IV, decrease in water mobility in supersaturated solution (Richardson et al., 1987).

first law:

$$V_D = k_D(C - C_1)/d \quad (1)$$

where V_D is the quantity of sugar which diffuses to the crystal per unit surface of crystal and unit of time, C and C_1 are, respectively, concentrations of solution and of thin layer around the crystal which thickness is d ; k_D is diffusion coefficient.

The second step is expressed by:

$$V_R = k_R(C_1 - C_0)^2 \quad (2)$$

where C_1 is sucrose concentration in the vicinity of the crystal and C_0 , the concentration of solution (saturated) at the contact of the crystal. K_R is a constant for the incorporation of molecules in the crystal (Silin, 1958).

Combining Eq. (1) and Eq. (2) yields an expression for the overall rate of growth where the unknown concentration C_1 at a short distance from the crystal is eliminated:

$$V = \frac{k_D}{d} \left[\frac{k_D}{2dk_R} + \Delta C - \sqrt{\frac{k_D}{dk_R} \left(\Delta C = \frac{k_1}{4dk_R} \right)} \right] \quad (3)$$

where $\Delta C = C - C_0$

This equation is comparable to that proposed by Frank (1949). Other authors express V_R as $V_R = K_R(C_1 - C_0)$ which yields a simpler relation for V :

$$V = (C - C_0) \left(\frac{d}{k_D} + \frac{1}{k_R} \right) \quad (4)$$

For temperatures above 45°C, k_R is preponderant, so that $1/k_R$ is negligible compared to $1/k_D$. Replacing the diffusion coefficient k_D in Eq. (4) by the expression

$$k_D = \frac{kT}{6\pi\eta r}$$

established for dilute solutions leads to the classical relation:

$$V = \frac{k \cdot T \cdot C_0 (\sigma - 1)^x}{\eta^y} \quad (5)$$

where T is temperature in K, η viscosity in mPa·s, C_0 the ratio sugar/water given in solubility Tables, σ the saturation coefficient, and x and y are constants. Comparing the rates of growth obtained by application of Eq. (5) with experimental results permits determination of empirical

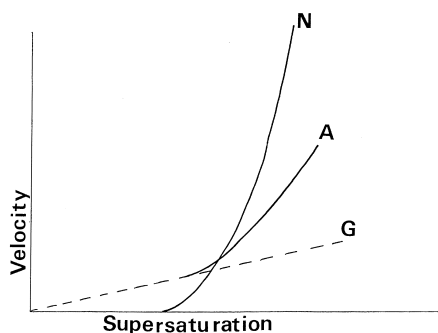


Fig. 3. Schematic representation of the rate of crystal growth as an adjustment between the rates of nucleation and growth.

parameters x and y in the following relation:

$$V = \frac{10^{0.0183T} \cdot C_0 (\sigma - 1)^{1.5}}{\eta^{0.731}} \quad (6)$$

Experimental data obtained by Kukharenko (1928) fit well with the rates calculated by use of Eq. (6). It may be noticed that $\eta^{0.731}$ is much lower than the viscosity of saturated sucrose solution. Such empirical exponent used for viscosity as well as that of supersaturation questions the preponderance of diffusion based on Fick's law and Stokes–Einstein relations in the crystallization process.

It seems, according to Van Hook (1977) that sucrose crystallization implies at least two energy barriers, one due to diffusion and the other to the incorporation of sucrose molecules into the crystal. Preponderance of one or the other barrier depends on temperature. Below 45–50°C, incorporation is the limiting step, whereas at higher temperatures, diffusion becomes preponderant (see Fig. 4).

3. Hydration water and sucrose crystal growth

3.1. Hydration in concentrated sucrose crystallization

Most work on hydration of sucrose molecules was undertaken on dilute solutions. The hydration number generally admitted is $n = 5\text{H}_2\text{O}/\text{sucrose}$ (Bressan and Mathlouthi, 1994). Using such a value for n allows calculation of water activity (a_w) from the relation:

$$a_w = \frac{55.51 - w}{55.51 - w + m}$$

where $w = nm$ is the total number of hydration water molecules, m being the molality of sucrose solution (Akhumov, 1975), n was found equal to 5 below a concentration of 1.8 M (38%, w/w). Such a concentration barrier is also found using other techniques like viscosity or vibrational spectroscopy. It is the limit between dilute solutions where water–water and water–sugar interactions are preponderant and the concentrated solutions where sugar–sugar interactions are manifested. The more

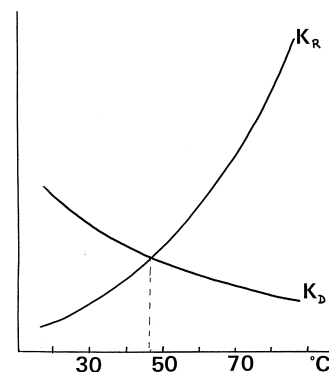


Fig. 4. Schematic evolution of diffusion coefficient (K_D) and integration (to the crystal) coefficient (K_R) as a function of temperature.

concentrated the aqueous sucrose solution, the lower the free water available for dissolution, whereas hydration water is maintained constant around $3\text{H}_2\text{O}/\text{sucrose}$ (see Fig. 5). For supersaturation $\sigma = 1.4$ at 80°C , only 30% of water is free when calculated from solubility curves, hydration water being deduced from water activity tables of Norrish (1966).

When concentration is increased, it is obvious that Stokes–Einstein formalism of viscous flow is no more applicable. This was observed as early as 1945 by Van Hook and Russel (1945) who could not correlate experimental diffusion coefficient measurements with Stokes–Einstein relation. They concluded that hydrogen bonds between sucrose molecules in concentrated solutions is so strong that it hinders completely the free diffusion of molecules. English and Dole (1950) after determination of diffusion coefficients in the range of concentration 0%–81% at 25 and 35°C , have concluded that diffusion in concentrated solutions is not due to viscous flow, but to the transfer of water molecules from one sucrose molecule to another by rotation of these sugar molecules and establishment of transfer of water molecules similar to ‘Grotthuss chain’. Therefore, water diffuses in the concentrated solution and the sucrose molecules remain immobile.

3.2. Structural features in aqueous sucrose solution

The structure of water has been thoroughly studied for several decades. However, the precise nature of the

molecular association has not been elucidated. Apart from unusual properties like maximum of density at 4°C , minimum of heat capacity at 37°C , etc., vicinal water was also found to show discontinuities in its physical properties at temperatures of 15, 30, 45 and 60°C (Drost-Hansen and Lin Singleton, 1989). In aqueous sucrose solution, the solute not only strongly binds water molecules in its hydration sphere, but it also orients water molecules at a long distance. Although ‘structure maker’ and ‘structure breaker’ concepts are questionable, interpretation of such physical properties as molar volume and compressibility allowed Bernal and Van Hook (1986) to demonstrate the electrorestricive hydration of sucrose which means that hydrogen bonding between water and sucrose is as strong as that found for strong electrolytes.

Moreover, solvation and dissolution of solutes is due to the polarity of solvents and proceeds according to a charge transfer mechanism (Gurikov, 1986). For carbohydrates, molecular association with the solvent is only made through OH groups. They have the same nature as OHs in water. Hydration of sugars increases with the number of equatorial OHs (Uedeira et al., 1990). In the case of sucrose, the folding of the sucrose molecule, when its concentration is increased, only leaves five potential sites for hydration.

Assuming that sucrose molecules are spheres with a diameter equal to 8 \AA and that water molecules have a diameter of 2.8 \AA , it is possible to calculate the volume of these spheres for a solution at supersaturation $\sigma = 1.10$ and

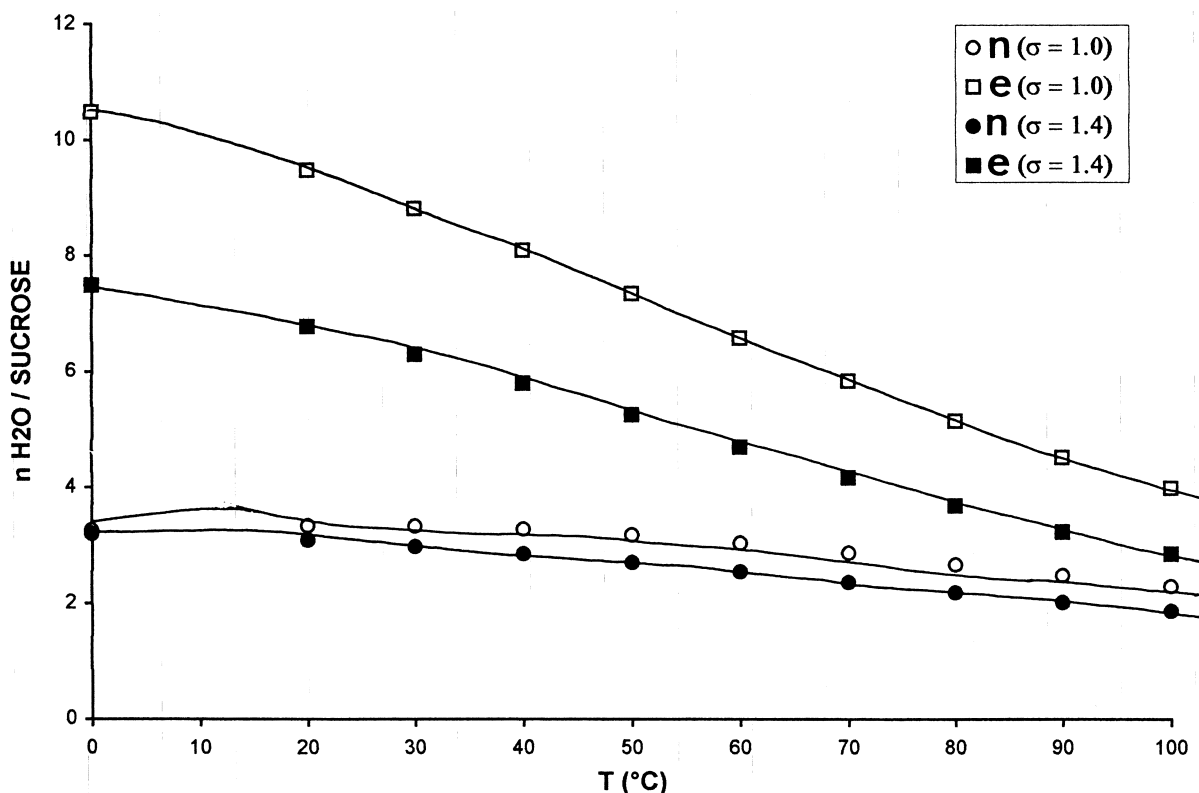


Fig. 5. Number of molecules of hydration water (n) and dissolution water (e) at supersaturations $\sigma = 1$ (○) and 1.4 (●).

temperature = 70°C. In such industrial conditions, the volume of a sucrose molecule is around 161.5 cm³ and that occupied by water is 6.9 cm³. At $\sigma = 1.110$ and $T = 70^\circ\text{C}$, concentration is 78.15% (w/w) and the density is 1.37 g/cm³. For 100 cm³, the mass of sucrose in solution is 107 g and that of water 30 g, the volumes being, respectively $(161.5 \times 107)/342 = 50.5 \text{ cm}^3$ and $(6.9 \times 30)/18 = 11.5 \text{ cm}^3$ which corresponds to 38% of vacuum.

According to Bernal (1968), the volume occupied by randomly disposed spherical balls is around 64%, which corresponds to 36% of vacuum. In a polyhedral regular arrangement, the volume occupied may reach 74.1%. If the balls are shaken and left to randomly occupy the space, 39% of vacuum is found (Scott, 1960). The smaller the balls, the larger the volume of vacuum; thus, the calculated 38% of vacuum in sucrose solution is plausible. This accounts for a structure in solution where sucrose molecules are close to each other and very likely form swarms of molecules, as proposed by Tikhomiroff (1965). The packing of molecules and the electrorestrictive character of H-bonds, hardly allow viscous flow of sucrose molecules from the bulk solution of crystal/solution interface.

3.3. The mechanism of crystal growth: role of water

The model generally admitted for crystal growth is the so-called B.C.F. (Burton and Cabrera, 1951) model which supposes that in spiral growth the time spent by molecules in the boundary layer is longer than that needed for their incorporation. Van Hook (1977) describes this step as a step of 'peregrination' of solute from solution to their site fixation (kink) on the crystal. This implies volume diffusion of sucrose molecules in the film surrounding the crystal, their adsorption, and then their surface diffusion to the site of fixation. Bennema (1969) has examined the importance of surface diffusion as compared to volume diffusion and concluded that four energy barriers are found before accession of sucrose to the incorporation site. These are due to diffusion to surface layer, leaving this layer after desolvation, making a 'diffusion jump' at the surface before incorporation in a kink of the crystal. Therefore, crystal growth looks like a hurdle race where the hurdles are energy barriers due to convection, volume diffusion, adsorption, surface diffusion, dehydration and molecular alignment (Van Hook, 1977). At low temperatures, below 40–50°C, the energy barrier of incorporation is much higher than at high temperature. This originates from the energy needed to dehydrate sucrose molecules and to align them properly before incorporation. The molecular arrangement in the vicinity of the crystal seems far from precisely defined. The role of hydration water is admitted, which seems to control the rate of growth through the activation energy of the desolvation step. Moreover, diffusion of sucrose molecules in the boundary layer around the crystal cannot be used as the only driving force for crystallization. Diffusion constants were found to tend towards 0 when concentration

reaches 76%–80% (w/w) (English and Dole, 1950, Heitz, 1975). However, the multistep (desolvation, alignment, integration) mechanism of growth seems more plausible (Bennema, 1969). In all events, the Stokes–Einstein diffusion model is unapplicable, even if it is adjusted through sophisticated models like the adhesion-slipping model (Grunwald et al., 1976).

Rather than trying to adapt the diffusion model, it seems more relevant to take, as the driving force for crystal growth, the desolvation of sugar molecules and the transfer of hydration water from the vicinity of the crystal to the bulk of solution. The mechanism of transfer, the energy potential controlling it and the type of resistance to this transfer are not known. However, an hypothesis can be put forward:

(1) It may be assumed that each time that a gradient is created, the flow naturally proceeds in the direction favourable to equilibrium. If we suppose that the activity of water at the crystal/solution interface is that of a saturated one (a_{w0}), and that water activity in the bulk solution is lower (a_{w1}), migration of water should proceed from crystal surface to bulk solution as a function of $(a_{w0} - a_{w1})$. The same process can be assumed for sucrose in the opposite direction with gradient $(a_{s1} - a_{s0})$. However, the distance between hydrated sucrose molecules being very weak, and their binding being strong, it is hardly conceivable that diffusion can take place in such a medium. The migration of water molecules could be due to molecular rotation of sucrose molecules and the transfer of water molecules as proposed by English and Dole (1950). Some other arguments may be given in favor of this model, such as the rapid development of faces (110) and $(\bar{1}10)$ corresponding to fructose moieties around which water molecules are more mobile. Alignment of molecules seems to favour the sucrose conformation where sucrose–sucrose bonds are stronger than sucrose–water bonds. Alignment of molecules and desolvation are not instantaneous, which explains the pulsation crystallization of sucrose.

(2) If incorporation of sucrose molecules only concerns desolvated molecules, and if this step controls the growth rate, at least below 50°C, one can approach crystallization as a desolvation (dehydration) mechanism. Observing the crystallization thermograms (see Fig. 6) published by Tikhomiroff and Heitz (1965), one can question the origin of the endothermic peak observed for homogeneous crystallization. We think that the first endothermic step is needed for the unavoidable step of endothermic desolvation which is followed by the exothermic step of interface creation. When interfaces already exist (heterogeneous crystallization), the heat released by the incorporation of sucrose molecules to the crystal largely compensates the heat needed for water–sugar H-bond breakage (see Fig. 6). The general shape of the thermogram observed in Fig. 6 for homogeneous crystallization is comparable to that observed for dehydration kinetics where the discontinuity is called the Smith–Topley effect (Bertrand, 1976). Although the thermodynamic phenomenon reported in

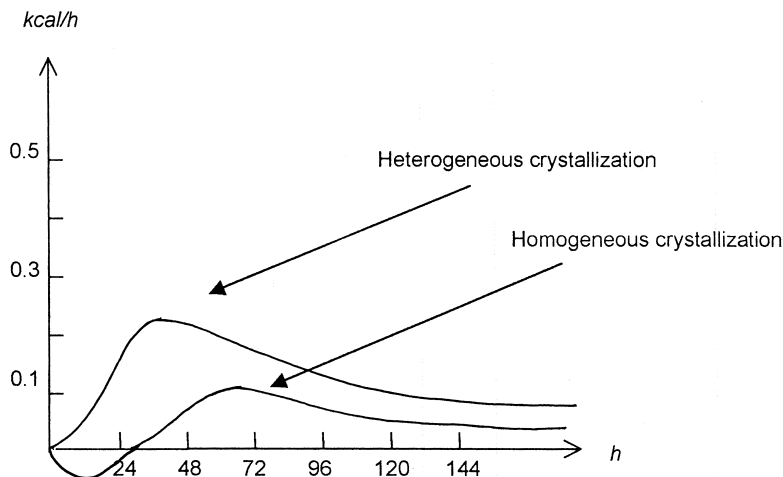


Fig. 6. Sucrose crystallization thermograms (Tikhomiroff and Heitz, 1965).

Fig. 6, and the dehydration kinetics discontinuity are different, some similarities may be found. Water vapour pressure in supersaturated solution is low. When sucrose–sucrose bonds are established and interfaces created, there is a release of water molecules and augmentation of water vapour pressure. The variation of dehydration rate in function of water vapour pressure and the heat flow accompanying this phenomenon are parallel. The role of dehydration kinetics is an additional obstacle to crystal growth. The release of dehydration water may even yield an undersaturated solution at the surface of the crystal as was observed for a large sucrose crystal by use of FTIR spectroscopy and attenuated total reflection (ATR) technique (Pautrat, 1997).

4. Conclusion

An attempt is made to show the role of water structure and sucrose–water interactions in the mechanism of crystallization. Interpretation of results obtained from literature sources and the proposition of the hypothesis allow the conclusion that migration of hydration water from the crystal surface to the bulk solution is very likely the controlling step in sucrose crystal growth. Such hypotheses are starting to be demonstrated by use of ATR–FTIR techniques, followed by a fractal analysis of FTIR spectra. These ideas are in agreement with those emitted by Van Hook (1981a), Van Hook (1981b), Van Hook (1983). They may stimulate collaborative research in the fields of molecular simulation, molecular interactions and the industrial crystallization of carbohydrates.

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