

Sucrose in the Concentrated Solution or the Supercooled “State”: A Review of Caramelisation Reactions and Physical Behaviour

M. A. C. Quintas · J. F. Fundo · C. L. M. Silva

Abstract Sucrose is probably one of the most studied molecules by food scientists, since it plays an important role as an ingredient or preserving agent in many formulations and technological processes. When sucrose is present in a product with a concentration near or greater than the saturation point—i.e. in the supercooled state—it possesses high potentialities for the food industry in areas as different as pastry industry, dairy and frozen desserts or films and coatings production. This paper presents a review on critical issues and research on highly concentrated sucrose solutions—mainly, on sucrose thermal degradation and relaxation behaviour in such solutions. The reviewed works allow identifying several issues with great potential for contributing to significant advances in Food Science and Technology.

Keywords Supercooled sucrose · Relaxation behaviour · Caramelisation reaction

Introduction

Sucrose and its supercooled solutions are of utmost importance in areas as different as food and pharmaceutical

industries or cryopreservation of biological systems. It is probably one of the most studied molecules by food scientists, since it plays an important role as an ingredient or preserving agent in many formulations and technological processes.

When sucrose is present in a product with a concentration near or greater than the saturation point—i.e. in the supercooled state—it possesses high potentialities for the food industry in areas as different as pastry industry, dairy and frozen desserts or films and coatings production.

The use of sucrose concentrated solutions on confectionery is considered by many as an art only mastered by great chefs in trendy restaurants, or older women who devoted their lives to cooking in small pastry shops located in small villages. However, this could not be farther from the truth: there is a lot of science behind the production of sugar syrups. Such production involves the use of high temperatures with subsequent water evaporation. The extent of sugar degradation and the final water content in sugar syrups are critical parameters that influence aroma, sweet taste, mouthfeel and texture of the final pastry products [92]. Sweet creams, produced essentially with egg yolk and sugar are an example of the importance of concentrated sucrose solutions in pastry [49]. This kind of product can be used in pastry and toppings, or consumed as a sweet dessert, and also a basis for production of several different desserts, like fruit and nut custards. In order to provide the typical structure, colour, aroma, smoothness and consistency of this kind of product, sugar syrups have a crucial importance since its viscosity influences all these characteristics.

The use of amorphous sucrose in coating or infusion of nut products is also a traditional application of supercooled sucrose. Furthermore, amorphous sucrose is important in frozen food products, especially in ice creams [55, 57]. In

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these products, control of ice crystal growth is important for stability during storage and consumer acceptance. In most cases, increased sugars concentration is able to control or even reduce ice crystallisation [57, 120].

Sucrose has also been studied for its plasticising effect in films, including plasticising fish myofibrillar proteins to produce packaging biomaterials by thermal compression-moulding [35] or, more recently in edible coatings applied to fresh cut carrots slices [133], and in white asparagus during cold storage [130]. Also, sucrose was used as coating ingredient for a method of encapsulation purified egg yolk immunoglobulins from immunised hens using a fluidised bed granulator [10].

This paper aims at reviewing the main aspects related to physical-chemical properties of supercooled sucrose. More specifically, of the relevant research that contributed to the development of a deeper understanding of chemical and physical properties of such supersaturated solutions. Namely:

1. The effect of heat treatment of sucrose in high concentrations and the kinetics of caramelisation reaction;
2. The physical behaviour of supersaturated sucrose solutions;
3. The systematisation and understanding of the underlying phenomena in these systems, by means of different mathematical modelling approaches.

The Effect of Heat Treatment on Supercooled Sucrose

The Caramelisation Reaction

Reaction Mechanism

Sucrose thermal degradation is an important reaction in the food industry, since it is responsible for either important characteristics of the final food products or can influence the yield of obtainable white sugar in sugar manufacture. This degradation may occur by two different major reaction pathways: the Maillard reaction, which takes place in the presence of amino acids, and caramelisation, that occurs when sucrose is heated at high temperatures [16].

Caramelisation, which is the common name for a group of complex reactions, has been studied by several authors. In the past decades, great insight was gained on the reactions mechanism [32, 84, 106].

The caramelisation reaction occurs in the presence or absence of catalysts (acids, basis or salts and impurities). It can be observed in diluted or concentrated solutions (amorphous state), and in the crystal form, leading to many different pathways. Each possible pathway may be

predominant under given environmental conditions. In this review, we focus on the case where sucrose in very concentrated solutions (above saturation at room temperature) is heated at high temperatures in the absence of impurities and at neutral pH. Under these conditions, the effect of heat is similar to the effect of using lower temperatures in acidic conditions and the reaction mechanisms can be considered to be identical [84]. This is due to the formation of weak acids during sucrose hydrolysis.

The first step in the caramelisation reaction is sucrose hydrolysis (please see Fig. 1a). This takes place by protonation of the glycosidic linkage [32, 42, 84, 106]. The H^+ used in this reaction step can be derived from water (or even sucrose) dissociation at high temperatures and also from acidic reaction products [42, 76, 106].

Under neutral conditions, sucrose hydrolysis yields D-glucose and a fructose oxocarbenium ion [32, 42, 76, 106]. This fructose carbocation can react with: (1) a water molecule to form fructose and regenerate the catalyst H^+ , or (2) another carbohydrate molecule present in solution (sucrose, glucose, fructose or even another fructose carbocation) to form oligosaccharides. Moreover, this fructose carbocation may undergo non-specific reactions to form a wide range of products, including: anhydrosaccharides, 5-hydroxymethyl-furfural (HMF) and organic acids [32, 42, 106].

The oligosaccharide and anhydrosaccharide components of caramel have been extensively studied [38, 39, 80–82, 102]. However, the extent of production of these substances is dependent on reaction conditions and is typically favoured by extreme acidic/high temperatures reaction conditions [5, 81, 82].

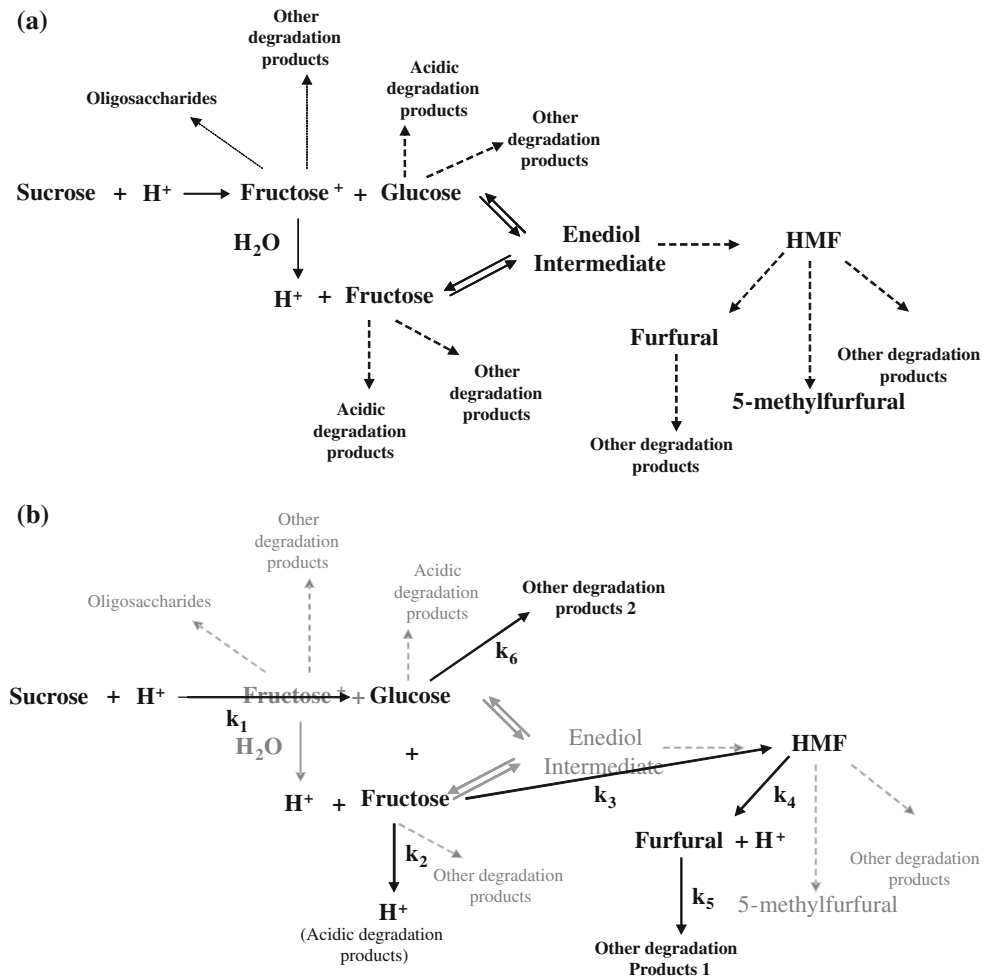
Further degradation of fructose and glucose is responsible for the formation of other compounds, especially to HMF [5, 32, 42, 70, 76, 84, 126]. The mechanism of such reaction is generally accepted to be an open chain β -elimination mechanism, which proceeds via an enediol intermediate to 3-deoxyhexulose [32, 70]. With the further development of the caramelisation reaction, HMF can be degraded to other products, including: (1) furfural, via fragmentation reaction (with indirect subsequent H^+ release) and (2) 5-methylfurfural, via reduction reaction [5, 32, 70, 84].

The simplified mechanism of sucrose caramelisation reaction at high temperatures and neutral pH can then be generally described by the scheme in Fig. 1a).

Colour Changes During Sucrose Thermal Degradation

Non-enzymatic browning is the general cause of a food product darkening due to any reaction not owed to enzymatic activity. Although this includes several reaction types, such as lipid oxidation or ascorbic acid degradation,

Fig. 1 Schematic representation of sucrose caramelisation mechanism: **a** based on literature search and **b** proposed reaction pathways based on experimental data and multiresponse modelling procedures [96]



non-enzymatic browning is mainly associated with carbohydrate degradation reactions, such as the Maillard and caramelisation reactions [16].

Colour changes due to the Maillard reaction are extensively described in literature [11, 14, 24, 37, 64, 75, 105, 113]. On the other hand, caramelisation-related colour development has been less studied [23, 25].

The typical brown colour developed during caramelisation is attributed to the production of polymeric products during the reaction course. HMF and furfural are pointed out as precursors of such polymers [70].

Colour changes together with HMF content have been studied for numerous food systems, such as fruit juices and purees [19, 30, 50, 61, 66, 103, 129], dairy products [27, 71, 86], baked goods [98, 99], infant foods [46, 53, 101], honey [127] and model Maillard systems [28, 29, 118].

However, few studies have tried to correlate HMF content with colour development. Most of such studies only report the observation or not of a linear correlation between such factors [26, 45]. In even fewer cases, the possibility of an exponential correlation is addressed [100], and one study reported the use of a power law to describe

such correlation [74]. Recently, it was shown that colour changes during caramelisation reaction presented and autocatalytic behaviour similar to sucrose degradation kinetics under the same conditions. Moreover, the contribution of HMF content to colour changes can be described by a fractional conversion model (for L/L₀) or a power law model (for total colour difference) [97].

Caramelisation Reaction Kinetics

Sucrose Degradation Behaviour

The Maillard reaction kinetics has been widely studied in the food science field [11, 25, 64, 132]. Caramelisation, on the other hand, is considered to follow a more simple reaction pathway and, consequently, fewer studies have been dedicated to its kinetics.

Caramelisation reaction is influenced by pH, impurities (e.g. salts or other sugars like glucose or fructose) and solution's sucrose concentration. Several authors approached these aspects [32, 43, 76, 84, 106, 135]. Most of those works are in a range of low sucrose concentration (<70%

(w/w)), relatively low processing temperatures (<85 °C), presence of impurities and/or acidic or alkaline media [84]. A first-order model is often used to describe the heat degradation of sucrose under such conditions [25, 135].

There is little information on the kinetics of sucrose thermal degradation at high concentrations. A study was carried under these conditions, the research was related to acidic saturated solutions and a first-order reaction was observed [114].

However, in some cases, like specific confectionery products [36] or sugar boiling during white sugar production [106], high concentrated sucrose solutions are heated at high temperatures and neutral pH. In such cases, a lag phase on sucrose degradation occurs [32, 42, 76]. This behaviour has been modelled assuming a pseudo-first-order reaction for concentrated sucrose thermal degradation in the presence of different salts [42]. A lag phase was also observed in a study of cane juice stored at factory room temperature, where the sucrose degradation was due to the combined action of microbial, enzymatic and chemical reaction (acidic degradation) [41]. This type of behaviour was also found in thermal degradation of sucrose in sub-critical water (high pressure and high temperature conditions) [54].

The lag phase and consequent sinusoidal behaviour observed in pure, high concentrated and neutral solutions treated at high temperatures, suggests an autocatalytic type reaction.

This autocatalytic nature is probably due to two main factors:

1. formation of weak acids during the first step of sucrose hydrolysis, that decreases solutions' pH, thus accelerating the reaction [70, 76, 90] and
2. molecular mobility. In the last decade, scientists started to realise the importance of molecular mobility, influenced by temperature and amount of water molecules in the system, in typical food reactions [13, 67, 69, 121]. In sucrose hydrolysis, water can act as a solvent or reactant [73]. In concentrated solutions, there is a decreased molecular mobility in the system as well as a deficit in the available water molecules for the reaction to occur, which may explain the existence of a lag phase. Furthermore, studies on sucrose crystals indicate that sucrose degradation products depress the melting point, leading to a type of autocatalysis reaction by the increased molecular mobility [91]. In the amorphous state, the increase of molecular mobility during the reaction may also be explained by lower molecular weights of the degradation products (i.e. fructose and glucose) when compared with sucrose.

Recently, these two hypothesis were confirmed: a significant effect of both temperature and water content (i.e.

system's molecular mobility) on the lag time was observed [93] and a relationship between caramelisation kinetics and H⁺ production was identified [96].

Product Formation Behaviour

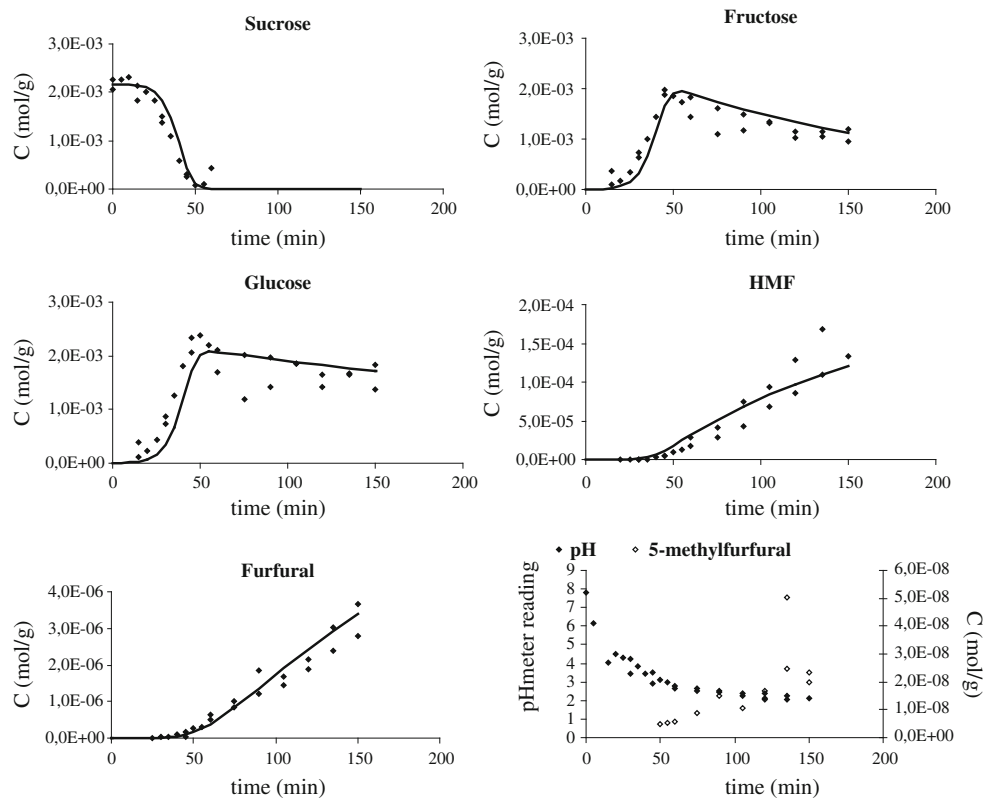
Studies on kinetics of caramelisation products formation are much less common and are usually related with HMF production [7, 74]. Furthermore, such studies are carried under first-order kinetics reaction conditions, i.e. in diluted acidic solutions. However, an induction period has been observed in non-enzymatic browning of freeze dried model systems containing sucrose [68, 73], probably due to the above-mentioned low molecular mobility in these systems.

Modelling the Kinetics of the Complete Caramelisation Reaction

Due to the large number of reaction pathways and even larger number of products formed during the caramelisation reaction, kinetic studies based on the caramelisation reaction mechanism are complex. The complexity of the reaction makes the use of multiresponse modelling [17, 125] very attractive, since it also allows clarifying the main reaction pathways that directly depend on the process conditions: this modelling approach accounts for kinetic information of both reactants and products involved in the reaction, resulting in insightful parameter estimation and, consequently, in more accurate model predictions. This method was applied to the mathematical description of the sucrose caramelisation reaction [96], based on the mechanisms referred in literature (Fig. 1a). The pathway proposed in Fig. 1b fulfilled multiresponse regression analysis of the experimental data and the proposed model successfully described the experimental data (Fig. 2).

Nevertheless, it is convenient to consider that the mathematical model can only be "tentatively entertained" [18]. As an example, the determined pathway (Fig. 1b) has been described by several authors when discussing the higher reactivity of fructose over glucose [5, 7, 74, 76, 84, 106]. However, other pathways may emerge, if different processing conditions are used. This was observed for very low water content sucrose solutions, where the ability of the global model to predict caramelisation kinetics under such extremely low water content was impaired [96]. These conclusions are a good example of the use of mathematical models, not merely with predictive purposes, but aiming at including fundamental principles, allowing a better understanding of the complex chemical changes occurring during heating of sucrose.

Fig. 2 Multiresponse model prediction (*line*) and experimental data (*dots*) of sucrose, fructose, glucose, HMF, furfural, 5-methylfurfural and pH of heat processed solutions. Example for a 25.30% (w/w) water content sucrose solution processed at 140 °C [96]



Physical Behaviour of Supercooled Sucrose

Significant Phenomena in Supercooled Sucrose

The physical state of all materials results from its composition (mainly molecular weight and water content), thermal history and temperature. These factors directly influence systems' molecular mobility, which is responsible for systems' physical properties. In food systems, molecular mobility, together with food microstructure, is also responsible for other quality attributes, like chemical reactivity and organoleptic characteristics [77].

When a liquid is cooled below the melting temperature, and crystallisation is avoided, a rubbery region or supercooled melt "state" is observed. With further cooling of the system, the "glassy state" is achieved at the glass transition temperature (T_g).

The glass transition temperature has been described as the temperature at which molecules take at least 100 s to move from one position to another [22]. T_g is also considered as the temperature upper limit for physical stability of a material, which supports the great importance that food scientists dedicate to this subject [121] and is dependent on both composition and solid content of a material [47]. Not without contestation [115], the "glassy state" is generally accepted to be an isoviscosity state, with viscosity (η_g) approximately 10^{12} Pa s [2], resembling

more a transparent brittle solid than a free flowing liquid [107]. Glasses have also been described as non-equilibrium amorphous solids that lack long-range spatial order, typical of crystalline structures [52]. The transition from the supercooled liquid to the glassy state is not considered by some authors as a true thermodynamic transition [88] (at least in the conventional sense), since there is no observable difference in the molecule structure, but instead an increase on the relaxation time, which becomes infinite at experimental time scale. Others [48, 107] consider a second-order thermodynamic transition, since glass transition presents no latent heat of phase transition and a step-change discontinuity in the heat capacity.

Rheological Measurements and Viscosity in Supercooled Sucrose Solutions

Highly concentrated sucrose solutions can be achieved by using high temperatures (above melting temperature) for short periods of time, followed by fast cooling [20, 59, 65]. This procedure leads to extremely high viscosity and amorphous solutions, with decreased molecular mobility, thus preventing crystallisation [116]. However, the material is in a metastable state: shearing promotes collision between its molecules, leading to nucleation and consequent crystal growth [56, 117]. This metastable nature of highly concentrated sucrose solutions confines the use of

steady-state flow measurements to characterise the rheological properties of such solutions. Due to the increasing shear involved in such experiments, crystallisation is faster and there is a change in the rheological behaviour during the measurements. This kind of phenomenon has been mentioned, when discussing the difficulty of the use of rheological methods in crystallisation studies [58].

Sucrose solutions behave as Newtonian fluids [83], and this behaviour has been reported for concentrations up to 78% (w/w) [108]. For higher sucrose concentrations, most studies mainly focus on viscosity of at temperatures below 20 °C, avoiding sample's fast crystallisation [15, 31, 85]. At room temperature (20–80 °C), viscosity of concentrated sugar solutions has been studied using cone and plate rheometry and the falling sphere methods [122]. However, a mixture of sucrose/fructose (87.5/12.5% (w/w)) was used, expanding the sugar concentration range without crystallisation.

To assess viscosity of sucrose solutions from 70 to 85% (w/w) in a wide temperature range (0–90 °C), avoiding crystallisation, creep test has been successfully applied [94]. Creep test can be used to assess the maximum Newtonian viscosity of a material, if time is sufficiently long to attain viscous flow. In this transient test, a small instantaneous stress is applied to the sample, and the response of strain is observed along time. After stress removal, the recovery of strain is also an indication of the rheological behaviour of the material in study [124]. The stress applied to the sample is rather low, thus minimising the disturbance in the system.

In amorphous materials such as supercooled sucrose solutions, molecular mobility is reflected on the systems viscosity, which in turn is mainly proportional to the time scale of the relaxation time. Molecular relaxation behaviour in the supercooled “state” has interested scientists for long time. Experimentally, there have been observed, mainly, two types of temperature dependence behaviour in the supercooled “region”: (1) the traditionally called Arrhenius behaviour, where viscosity varies exponentially with the reciprocal of temperature, and (2) the VFT behaviour, where viscosity temperature dependence presents a non-linear behaviour in the Arrhenius plot [3]. These different behaviours have been classified as strong (Arrhenius following) and fragile (VFT following) supercooled liquids [2]. Strong liquids are usually tetrahedral network structures, with small changes in heat capacity at the glass transition temperature. On the other hand, fragile liquids do not present directional bonds, often have ionic or aromatic character and present sharp changes in heat capacity at the glass transition temperature. The fragility concept has been proposed to measure the deviation from strong behaviour in the “supercooled state” and to characterise the steepness of the temperature dependence of viscosity [3].

The concept of free volume [34, 40] and the entropy-controlled cooperative motions approach [1] are good examples of theories developed to describe strong/fragile relaxation behaviour. However, these theories do not consider the experimentally observed dynamical singularity in the response of a supercooled system at a critical (or divergence) temperature, T_c ($T_c > T_g$) [52].

The experimental determination of T_c using rheological measurements is difficult. The torque of most commercial rheometers is not able to support such high viscosities. In order to measure viscosity near T_g , it is necessary to replace the transducer [119] or recur to comparison techniques that introduce a larger experimental error [115]. Literature values of T_g/T_c can be found typically around 0.8 [8]; for semi-rigid polymers this ratio was found to be around 0.9 [111] and studies on glycerol indicated an approximate 0.75 ratio [115]. For sucrose solutions, T_g/T_c was found to be approximately 0.86, in a wide concentration range [31].

More recently, the random walk approach was used to develop a model that is able to describe relaxation temperature dependence in both strong and fragile liquids [8, 9]. This approach has been successfully applied in supercooled sucrose solutions [95].

Sucrose Crystallisation

Sucrose crystallisation is an important phase transition in food industry and several research works have been dedicated to this subject.

Crystallisation is related with the formation of a crystalline lattice structure. Typically, this occurs in four steps: (1) generation of a supersaturated state; (2) nucleation, i.e. the formation of the lattice structure; (3) growth, i.e. subsequent growth of nuclei until equilibrium is attained; and (4) recrystallisation, i.e. reorganisation of the crystalline structure to a lower energy state [58]. In highly concentrated sucrose solutions and at room temperature and higher, crystallisation phenomenon, as well as its kinetic behaviour, temperature and water content dependence, have been largely discussed [56, 58, 59, 117].

Mathematical Modelling in the Supercooled State

In the area of quality/safety loss kinetics during storage and processing, some remarkable examples of the effort made to draw food scientists' attention to the benefits of accurate modelling and reporting of experimental data are available (e.g. [6, 72, 78, 109]). Later works [33, 131] also played a critical role on alerting to the importance of estimates precision and quality of the regression. However, regression analysis is less common in works describing molecular relaxations in food products. Many studies in this area fit models with “universal constant” parameters (e.g. [122])

and extrapolate such “description” to “predict” relaxation outside the experimental range (e.g. [21]). Moreover, studies on estimates precision are extremely rare [87].

Empirical Modelling of Molecular Relaxation

Temperature Dependence Following Arrhenius Type Behaviour Viscosity dependence on temperature for Newtonian fluids is extensively described using an Arrhenius type equation [12]. This is an empirical model, developed from the theory of the liquid state, based on the movement of molecules through the formation of “holes” in the system [44]. The Arrhenius model has been successfully applied to describe the viscosity temperature dependence of various food products, such as clarified fruit juices [51, 60, 62, 134], vegetable oils in solution [63] and molasses [128]. For sucrose solutions, this type of behaviour has been reported for low concentrations (up to 60%)—i.e. solutions with real “liquid like” behaviour [93].

Temperature Dependence Deviating from Arrhenius Behaviour At temperatures near the glass transition, more specifically in the T_g to $T_g + 100$ °C range, experimental data of fragile glass-forming liquids show markedly deviation from Arrhenius behaviour. This behaviour has been described by several mathematical functions (e.g. the Vogel–Fulcher–Tammann (VFT) equation [2]). However, food scientists have shown a preference for using the Williams, Landel and Ferry (WLF) empirical model to describe the viscosity temperature dependence (Eq. 1) in the above-mentioned temperature range [47, 136]:

$$\log \eta = \log \eta_{\text{ref}} - \frac{c_1(T - T_{\text{ref}})}{c_2 + T - T_{\text{ref}}} \quad (1)$$

The constants c_1 and c_2 became “universal”, respectively, with the values of 17.44 and 51.6 °C, using T_g as reference temperature.

The WLF model has been used to describe the viscosity temperature dependence of several food materials, mainly at sub ambient temperatures, such as amorphous isomalt [104], sucrose solutions [15, 31, 85] and solutions of other low molecular weight carbohydrates, such as glucose, fructose, sorbitol, xylitol [79] and trehalose.

The use of the “universal” constants c_1 and c_2 is limited, and Williams, Landel and Ferry themselves cautioned for the indiscriminate use of T_g as reference temperature, since small differences in measured T_g could lead to a deviation in the curve behaviour [136]. Other authors also questioned the universality of these constants, when developing a molecular-kinetic theory to explain the temperature dependence of relaxation behaviour in glass-forming liquids [1]. In this study, a similar expression to the WLF model (Eq. 1) was found. However, c_1 was dependent on

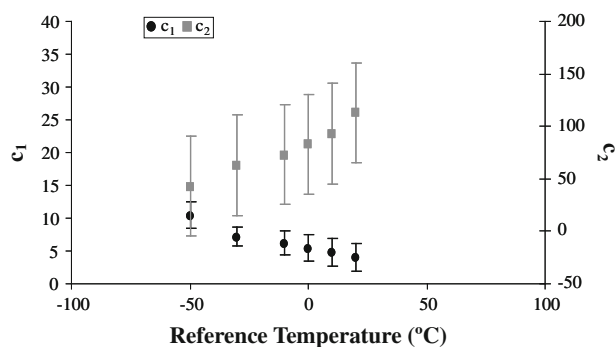


Fig. 3 Reference temperature effect on the WLF c_1 and c_2 parameters (79.93% (w/w) sucrose concentration). The bars indicate the 95% confidence interval limits [94]

T_{ref} and on the nature of the material itself, and c_2 dependent on both T_{ref} and process temperature (T).

The use of universal c_1 and c_2 constants to describe relaxation behaviour in supercooled systems was also questioned by other researchers, which found Gordon–Taylor type concentration dependencies for both c_1 and c_2 [20]. In polymers, several works have also reported c_2 “constants” far from universal [4]. More recently, another work demonstrated that a better prediction of the viscosity is achieved if the reference temperature, used in the WLF model, is within the experimental data range, and c_1 and c_2 are model parameters [87]. This approach has been successfully applied in honeys [123].

For supersaturated sucrose solutions the WLF model successfully described the observed behaviour [94]. Moreover, a minimum value for the estimates standard error ($\log \eta_{\text{ref}}$, c_1 and c_2) was observed when the reference temperature was close to the lowest temperature used in the experimental determination of viscosity (example in Fig. 3) and this is in accordance with Peleg [87]. In addition, it was observed that when the reference temperature is fixed, c_1 is dependent on the concentration, whereas c_2 does not present statistically significant concentration dependence (example in Fig. 4). These findings were in agreement with Adam and Gibbs [1] conclusions.

The Random Walk Approach to Modelling Molecular Relaxation

As already discussed, Arkipov and Bassler’s proposed a random walk (RW) approach for describing molecular relaxation in supercooled liquids. A random walk is a statistical tool that can be used to predict the final state of a system when a physical phenomenon, usually associated with movement, occurs in a complex way. It is constituted by steps of the same length and, at each point, the probability of displacement into another point is independent of the actual position and equal for all new probable locations.

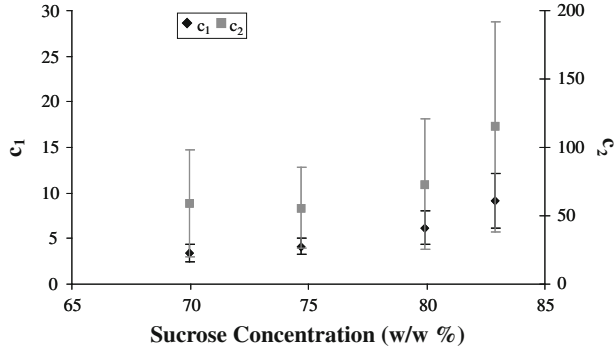


Fig. 4 Concentration dependence of the WLF c_1 and c_2 parameters, using 0 °C as reference temperature. The bars indicate the 95% confidence interval limits [94]

This approach has been successfully applied to semi-rigid polymers [111] and it is based on a random walk modelling of molecular movements in the system. To some extent, it is possible to affirm that this is a model based on “movement mechanism” and a parallelism can be established with the mechanistic modelling of chemical reactions kinetics. Herein, a small summary of this modelling approach is presented.

Arkhipov and Bassler’s random walk approach [8, 9] considers that a unit structure (i.e. a molecule or a subunit embedded in the molecular environment) in the configurational space, due to existing strong interactions, cannot change its position without the adjacent structures movement and, consequently, a transition in the configurational space occurs. This transition can be considered as a jump of a unit structure in a highly complex energy landscape. After each jump, the structural unit finds a new environment and the configurational space phase memory is lost. This “no memory” process can be modelled as a random walk on a disordered network of hopping sites in configurational space, characterised by a broad distribution of energies. Considering that the energy of a structural unit depends on a large number of configurational co-ordinates, each one varying randomly, a normalised function can be realistically assumed for the distribution of possible metastable states. Arkhipov and Bassler defined the random variable (E) as the energy to supply to a structural unit for the unit to “jump” to another site in the configurational space. Considering a random walk, the jump frequency of structural units can be determined using a master equation for the normalised energy distribution function of the structural units [8].

Being the viscosity proportional to the inverse of the jump frequency, the temperature dependence of viscosity for fragile glass-forming liquids in the higher temperature regime (or “real liquid”, where the energy landscape is fluctuating at a frequency large enough to allow an unit jump to an adjacent site, and the activation energy of a

jump upward in energy is the difference between sites energies ($T > T_c$)) is then given by [8, 9]:

$$\eta = \eta_{0\text{RW}} 2^{(2\beta-1)/2(\beta-1)} \frac{1}{\beta} \Gamma\left(\frac{1}{\beta}\right) \left(\frac{T_{0\text{RW}}}{T}\right) \times \exp\left[(\beta-1)\left(1-2^{-1/(\beta-1)}\right)\left(\frac{T_{0\text{RW}}}{\beta T}\right)^{\beta/(\beta-1)}\right] \quad (2)$$

where β is a shape parameter of the normalised distribution of the random variable (E), Γ is the gamma function, $\eta_{0\text{RW}}$ accounts for the contribution of structural unit jumps towards viscosity and $T_{0\text{RW}}$ is a temperature that reflects the spread of the self-energies of the structural units.

This equation was successfully applied for describing the temperature dependence of supercooled sucrose solutions viscosity (Fig. 5). The obtained results are relevant for the physical interpretation of the observed phenomena (Table 1): (1) $\eta_{0\text{RW}}$, which is proportional to the structural units jumps contribution to viscosity, increased with sucrose content (i.e. with number of sucrose molecules in the solution) and (2) the spread of the self-energies of the structural units due to configurational disorder, which is described by $T_{0\text{RW}}$, decreased with increasing sucrose content [95].

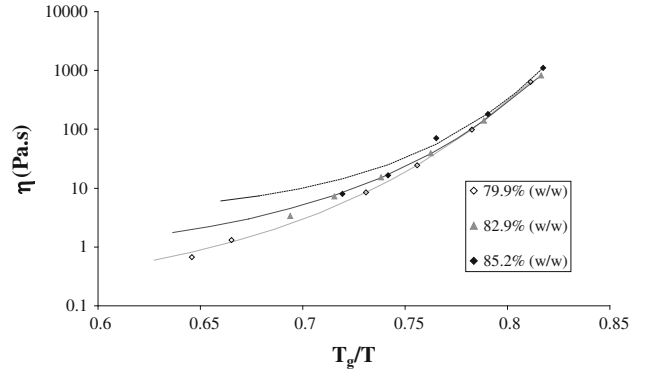


Fig. 5 Random walk model fitting to experimental data of viscosity for three sucrose concentration levels: 79.9% (w/w), solid grey line; 82.9% (w/w), solid black line and 85.2% (w/w), dashed line [95]

Table 1 Results from fitting the random walk (RW) model to experimental data, at different sucrose concentrations [95]

Sucrose concentration (w/w)	Estimated parameters			
	$\eta_{0\text{RW}}$	$T_{0\text{RW}}$	β	m_{RW}
79.9	6.88×10^{-3}	541.64	1.16	118.61
82.9	2.13×10^{-2}	502.05	1.13	151.46
85.2	4.03×10^{-2}	455.23	1.09	285.46

'Fragility' is a term that tries to capture the deviation of Arrhenius behaviour in the "supercooled state". Several methods have been proposed to "measure" fragility of a system, i.e. to characterise the steepness of the temperature dependence of viscosity [3]. The most popular form is to measure the slope (m) of the VFT (or WLF) equation near T_g [3, 21, 89, 112, 115]:

The RW model also allows the description of the function steepness through the β parameter. In fact, strong glass-forming fluids behaviour (Arrhenius-like) show $\beta \rightarrow 2$ and fragile glass-forming liquids behaviour (VFT-like) indicates $\beta \rightarrow 1$ [9]. Furthermore, a correlation of the fragility index β and m has been successfully established [110]:

$$m_{RW} = \frac{1}{\ln 10} \left[\left(\frac{2 - \beta}{2(\beta - 1)} \right) + \beta \left(\frac{T_{0RW}}{\beta T_g} \right)^{\beta/(\beta-1)} \right] \quad (3)$$

In supercooled sucrose solutions, the fragility index (β) was found to be significantly affected by solution concentration (Table 1; [95] and approached 1 with increasing sucrose content as reported in literature [4, 9]. Furthermore, it was possible to determine an m_{RW} (from Eq. 3) in agreement with literature values of sucrose solutions fragility [21]. These reported results are even more significant when the small concentration range of the study is considered, and are a good indication of the potential of the random walk (RW) approach to the study of molecular relaxation behaviour in the supercooled "state", using only high temperature regime data.

Academically, this study presents a great potential for investigating reactions and phase transitions in such systems. Application of such knowledge may help, in the future, the development of stable food products with improved functionality.

Summary and Future Research Trends in Supercooled Sucrose Solutions

This paper reviewed critical issues and research on highly concentrated sucrose solutions. Concerning sucrose thermal degradation in such solutions, two main topics were addressed: (1) autocatalytic behaviour of degradation kinetics (2) and description of the caramelisation reaction, i.e. sucrose degradation and product formation. As for the relaxation behaviour of the supercooled sucrose solutions, main topics are: (1) the rheological properties of highly concentrated sucrose solutions at ambient temperatures, (2) currently used theories of the viscosity temperature dependence with special emphasis on a critical assessment

of the use of c_1 and c_2 "universal" constants and T_g as reference temperature, to describe viscosity temperature dependence in WLF type behaviour and (3) the random walk approach on description of sucrose relaxation behaviour in the supercooled "state".

The reviewed works allow identifying several issues with great potential for contributing to significant advances in Food Science and Technology.

Greater insight into the mechanism of sucrose thermal degradation can be gained by performing experiments measuring other reaction products, e.g. the organic acids. The study of the reaction mechanism under different processing conditions (e.g. high/extremely low water content and different initial pH) may also reveal different reaction pathways. The kinetic modelling procedures here presented can be enhanced by studies on improving parameters and predictions precision by optimal experimental design. Special relevance should be given to multiresponse regression procedures, where optimal experimental designs were not yet applied in the food science area.

Studies on the effect of sucrose degradation on viscosity of solutions and its effect on temperature and water content behaviour may contribute to a better understanding of the relationship between composition and physical behaviour. Such understanding is a potential key area in food studies in the next years.

The random walk approach to molecular mobility of supercooled systems may prove to be useful to study and predict other processes. The random nature of molecular collision during crystallisation makes such phenomena of great interest to observe using a random walk approach. The diffusion in supercooled and glassy systems may also be studied using this approach—such studies may be extremely useful in understanding and predicting important properties of a food product, like, for example, controlled release of functional ingredients in the digestible track.

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