



Original Research Paper

Solid-phase crystallization of spray-dried glucose powders: A perspective and comparison with lactose and sucrose

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ABSTRACT

The solid-phase crystallization growth kinetics of spray-dried sugar powders, including glucose, lactose and sucrose, have been studied from water-induced crystallization experiments at a relative humidity of 75% and temperatures from 15 to 40 °C on amorphous powders of these sugars produced in a laboratory-scale spray dryer (Buchi B290). All results have shown that the enthalpies and Gibbs Free Energies of activation of the sugars studied here increase during the crystallization process, suggesting that the binding energy needed for the formation of an activated complex increases as the moisture content decreases. The enthalpies of activation for glucose, lactose and sucrose crystallization have been compared by the Activated Rate equation and found to be $58 \pm 8 \text{ kJ mol}^{-1}$, $39 \pm 2 \text{ kJ mol}^{-1}$ and $68 \pm 4 \text{ kJ mol}^{-1}$, for glucose, lactose and sucrose, respectively. Similarly, the entropies of activation have been calculated as $-92 \pm 27 \text{ J mol}^{-1} \text{ K}^{-1}$, $-156 \pm 6 \text{ J mol}^{-1} \text{ K}^{-1}$ and $-60 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$ for glucose, lactose and sucrose, respectively. These different numerical values may be expected from the different structures of the sugars.

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1. Introduction

Yu [1] has stated that “Current research in the stabilization of amorphous solids focuses on: (i) the stabilization of labile substances (e.g., proteins and peptides) during processing and storage using additives, (ii) the prevention of crystallization of the excipients that must remain amorphous for their intended functions, and (iii) the selection of appropriate storage conditions under which amorphous solids are stable.” Our recent work (from [2–4]) has taken an additional perspective: (iv) exploiting crystallization behaviour during processing of carbohydrates to produce more stable products that are fully or partially-crystalline [5–9], so that further crystallization during storage is reduced or controlled [10], or so that other effects of crystallization (e.g. fat release) can also be used constructively [11].

It might be suggested that crystallization in the short time scales of spray drying might be difficult if not impossible. Woo et al. [12] and Fu et al. [13] have found small amounts of crystallinity in the single-drop drying of lactose droplets, from 3.44% to

5.89%, when dried at temperatures from 70 °C to 110 °C. The upper temperature limit is set by the behaviour of the glass filaments on which the droplets were suspended, although higher temperatures might have given larger temperature differences ($T - T_g$) that might have resulted in greater degrees of crystallinity. Fig. 1 shows why crystallization in short time scales might be possible, by showing the ratio of the crystallization time (Θ_g) at the glass-transition temperature (T_g) to the crystallization time (Θ_{cr}) at any other temperature (T) as predicted by the Williams–Landel–Ferry (WLF) equation (Williams, Landel and Ferry, 1955) [14]:

$$\ln \left(\frac{\Theta_g}{\Theta_{cr}} \right) = \frac{C_1(T - T_g)}{C_2 + (T - T_g)} \quad (1)$$

Here C_1 , C_2 are universal constants (−17.44 and 51.6, respectively). The temperature dependence illustrated in Fig. 1 is “super Arrhenius”, with the rates (as inverses of the crystallization times) potentially increasing by several orders of magnitude with small increases in the temperature differences ($T - T_g$).

At first sight, it might be thought that solid-phase crystallization could be explained in exactly the same way as conventional liquid-phase crystallization. During drying, the concentration of the solution increases, and conventional liquid-phase crystallization would be expected. This is the approach taken by Ben-Joseph and Hartel [15,16] during the drying of liquid films, and at first

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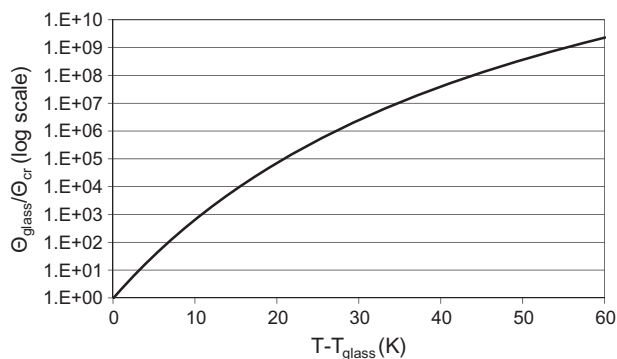


Fig. 1. The predicted ratio of the crystallization time (Θ_g) at the glass-transition temperature (T_g) to the crystallization time (Θ_{cr}) at any other temperature (T), according to the WLF equation.

sight, it would appear to be sufficient to explain the physical processes involved during crystallization and drying.

A conventional liquid-phase crystallization approach to predicting crystallization during spray drying has been used by Chiou and Langrish [17], Woo et al. [12] and Fu et al. [13] by using the difference between the concentration and the saturation concentration as a driving force for crystallization. While this approach has some qualitative merit in explaining the solid-phase crystallization process for sucrose-lactose mixtures [18], Chiou and Langrish [17] found that saturation-based analysis gave incorrect trends in predicting experimental spray-drying results for lactose, and Woo et al. [12] also found that “... the saturation-based analysis predicted that 70 °C drying condition will have higher proportion of crystals compared to the 110 °C condition; contrary to the experimental findings.” There is clearly more to the solid-phase crystallization process than simply following the same approach as used for conventional liquid-phase crystallization.

Crystallization of amorphous components in spray-dried powders does not occur spontaneously, despite evidence [19] that amorphous components have higher internal energies than their crystalline equivalents and tend to transform into these crystalline components if the temperature is high enough or if moisture is present. The absence of spontaneous transformation strongly suggests that there is the equivalent of an activation energy barrier to overcome between the amorphous and crystalline states. This view of crystallization as an activated-state (or activated-rate) process (ART, Activated-Rate Theory; [20–23]) is illustrated in Fig. 2.

Such activated-state (or activated-rate) processes have been studied extensively before, in the context of chemical reactions (transition-state theory; [24,25]). Wynne-Jones and Eyring [26]

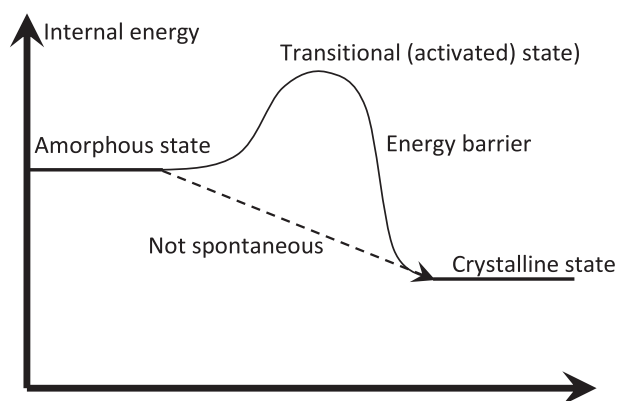


Fig. 2. Crystallization viewed as an activated-state process.

formulated an equation to calculate the rates of reaction in solution, in terms of thermodynamic quantities, such as the enthalpy of activation (ΔH^* , J mol⁻¹) and the entropy of activation (ΔS^* , J mol⁻¹ K⁻¹) as follows (the Eyring equation):

$$\ln\left(\frac{k}{T}\right) = -\left(\frac{\Delta H^*}{R}\right)\frac{1}{T} + \ln\left(\frac{k_B}{h}\right) + \left(\frac{\Delta S^*}{R}\right) \quad (2)$$

The reaction rate constant is k (s⁻¹), and ΔH^* (J mol⁻¹) and ΔS^* (J mol⁻¹ K⁻¹) are the enthalpy and entropy of activation, respectively. The absolute temperature is T (K), Boltzmann's constant is k_B (J/K), Planck's constant is h (Js), and the universal gas constant is R (8.314 J mol⁻¹ K⁻¹). A particular amount of energy is required in a chemical reaction to overcome an activation energy barrier for the reaction to occur. By making an analogy between the physical transformation in solid-phase crystallization and the chemical reaction in the transition-state model, a new way of quantitatively modelling the crystal-growth kinetics in solid-phase crystallization has been suggested by Das and Langrish [20–22] that uses a similar activated-rate (transition-state) approach to that used in chemical reactions. This approach is based on assuming that an activated or transition state occurs in solid-phase crystallization, which is formed when a certain amount of water is absorbed by amorphous materials, before crystallization starts. The Eyring equation (above) has been assumed to apply for calculating the enthalpy and entropy values of amorphous samples during crystallization. Water is frequently mentioned as a molecular lubricant (e.g. [1]), and the Activated-Rate Theory also regards water as being central to raising the internal energy of the amorphous material.

The form of the activated (transition) state is open to speculation. Judat and Kind [27], in a study of liquid-phase crystallization for barium sulfate, have concluded that:

“Particles at the early stages of growth shortly after the beginning of nucleation consist of many small nanocrystallites which have aggregated in a highly ordered manner. The diffraction pattern indicates many small-angle grain boundaries, whereas the particles at the end of the precipitation process are monocrystalline. This leads to the conclusion that barium sulfate grows according to a self-assembled aggregation mechanism followed by a fast recrystallization process”.

The point in the process between the “self-assembled aggregation mechanism” and the “fast recrystallization process” might be regarded as an activated state, according to the ART. The ART does not prescribe the exact physical form of the activated state.

Many previous theories for liquid-phase crystallization have suggested or implied aspects of this Activated-Rate Theory for solid-phase crystallization. For liquid-phase crystallization, the adsorption theory, which dates back to 1939, suggests that crystal growth is a discontinuous process, taking place by adsorption of layer upon layer on the crystal surface [28]. This theory is used still to describe crystal growth, although several modifications to the original theory have been proposed. Volmer's theory [28] suggests that, when the units of crystallising substance arrive at the face of the crystal, they are not immediately integrated into the lattice. Instead they merely lose one degree of freedom and are free to transfer over the crystal surface, which is called surface diffusion. They will loosely adsorb into a layer of integrating units at the interface, subsequently achieving dynamic equilibrium between this layer and the bulk solution [29]. The loss of freedom in approaching the crystal surface implies that some units of crystallizing material will be repelled by the surface, creating an effective activation-energy barrier. Kossel's model [30] of the growth of crystal face, which is a modification of the classical Volmer's theory, suggests that the flat crystal surface is made up of moving layers of monatomic height, which may contain one or more kinks.

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