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# Effect of saccharides on glass transition temperatures of frozen and freeze dried bovine plasma protein

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ABSTRACT

In this study, to preserve the integrity of plasma protein, protective agents, such as saccharides are added to produce a glassy (vitrified) state. Differential scanning calorimetry (DSC) was used to measure the glass transition ($T_g$), crystallization temperatures ($T_c$) of the solid freeze–dried bovine plasma protein and the glass transition temperature ($T'_g$) of the protein freeze solution, with the addition of inulin as protective agent, comparing the behavior with glucose and sucrose. The results indicated that transition temperatures increased with the molecular weight of the saccharide, conferring inulin a stabilizing effect at higher storage temperature. The $T'_g$ and the water plasticizing effect were estimated by means of two theoretical models: Miller/Fox and Gordon/Taylor extended for multi-component systems. The determination of the glass transition temperatures is useful in defining a freeze–drying cycle and storage stability of plasma protein concentrates.



## 1. Introduction

The use of inulin and its derivatives in the food industry is in constant increase mainly by their technological and nutritional benefits. These benefits are, fat and sugar replacement, low caloric bulking agent, texturing and water-binding agent and it has a prebiotic activity (Kip et al., 2006; Ronkart et al., 2009). Commercial inulin is mainly extracted from chicory root and is available as a spray-dried powder product. In a previous work, we investigated the inulin capacity as protective agent of proteins during freeze–drying process, and it was demonstrated that the denatured proteins percentage was reduced preserving their conformation, and consequently, their functional properties, even during storage (Rodriguez Furlán et al., 2010).

Freeze–drying is the main process used to produce stable proteins, which are unstable in aqueous solution with limited shelf life. An appropriate choice of stabilizers (saccharides) is needed to protect the proteins from denaturation during processing, as well as to provide a glassy matrix required for long-term storage stability in the dried solid (Costantino et al., 1998; Liao et al., 2004; Passot et al., 2005). Primary drying is the most time consuming stage of the process. It should be carried out at the maximum allowable temperature usually associated to the glass transition temperature of the maximally freeze concentrated solution ($T'_g$). Below this temperature a glassy state that behaves as an amorphous solid is obtained. If the temperature of the frozen system rises above the $T'_g$, the material becomes less viscous and freeze–drying may cause the loss of the porous structure and product collapse (Chen and Oakley, 1995; Passot et al., 2005).

In the freeze–dried sample, water is removed and the solute concentration in the matrix increases, obtaining a material with an amorphous structure that exhibits a glass transition temperature ($T_g$) (Chen and Oakley, 1995; Shah and Schall, 2006). The $T_g$ can be defined as a second order phase change temperature at which sample properties change from glassy state to rubbery state (Gallegos Infante et al., 2005; Noel et al., 1995; Roos, 1995). It is also defined in kinetic terms as the temperature below which the viscosity of a liquid is at least $10^{13}$–$10^{14}$ Pa s (Chen and Oakley, 1995; Katkov et al., 2006). Besides, it has been assumed that amorphous products are stable in their solid, glassy state below $T_g$ with a high internal viscosity. As the temperature is increased above $T_g$, various properties of the materials may change, like an increase in the molecular mobility and a decrease in the viscosity, often resulting in a crystallization event of the added solute increasing also food deterioration (Gallegos Infante et al., 2005; Roos, 1995; Shah and Schall, 2006). Therefore, the $T_g$ determines the product stability during storage (Katkov and Levine, 2004).

Both transitions $T'_g$ and $T_g$ are important parameters in the development of the freeze–drying cycle because not only ensures

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product stability and quality, but also allow to improve the efficiency of the manufacturing process (Chen and Oakley, 1995; Passot et al., 2005; Shah and Schall, 2006; Tattini et al., 2005).

Differential scanning calorimetry (DSC) is a tool used to characterize the freeze–drying behavior of protein formulations. There are limited data for the glass transition temperatures of multi-component mixtures and few studies comparing experimental and predicted values of $T_g$ for such mixtures (Shah and Schall, 2006).

The objectives of the present work were: to apply DSC analysis to assess the effect of different saccharides (glucose, sucrose and inulin) on several transition temperatures: (a) the glass transition temperature of the maximally concentrated frozen solutions ($T_g'$) of bovine plasma protein and to compare the experimental results with the predictive equations of Miller/Fox and Gordon/Taylor extended for multi-component systems; (b) the glass transition ($T_g$) of the freeze dried multi-component mixtures with the objective of improving the lyophilization cycle; (c) the onset crystallization

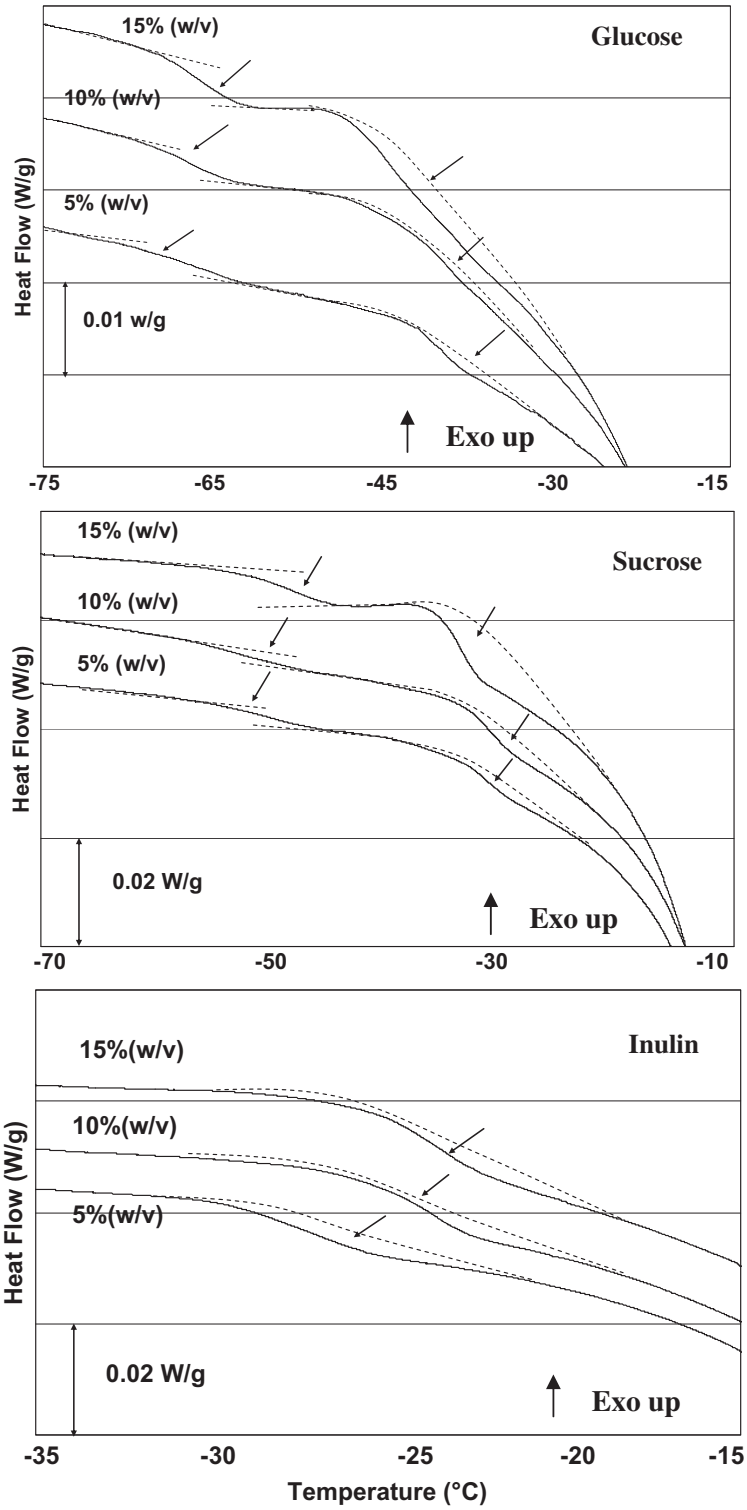


**Fig. 1.** DSC thermograms for freeze bovine plasma protein–saccharide solutions. Down-arrows indicate $T_g'$.