LOW RESOLUTION $^1$H-PULSED NMR FOR SUGAR CRYSTALLIZATION STUDIES

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Abstract- The stability of food and other labile biological systems containing sugars has been related to the amorphous characteristics of the matrices which they formed, being inversely related to the degree of crystallization. It is thus necessary to explore the applicability of simple, non-destructive and reliable methods to analyze sugar crystallization. Solid fat content is a well-established AOCS method to study solid content in lipid systems. However, there are no literature reports on the use of this method to analyze sugar crystallization. Crystallization kinetics of concentrated trehalose and trehalose/salts solutions was followed by proton pulse nuclear magnetic resonance ($^1$H p-NMR). Three different concentrations ($X_t$= 0.60, 0.63 and 0.66) of trehalose solutions were crystallized to 25, 20, 15, 10 and 5°C and the degree of crystallization was investigated by following the index of solids with time. Crystallization rate was determined by a combined effect of supercooling and molecular diffusion. By analyzing trehalose systems by $^1$H p-NMR, it was possible to confirm the effect of divalent cations on retarding sugar crystallization.

Keywords- NMR, Crystallization, Trehalose Solutions, Divalent cations

I. INTRODUCTION

Sugars have frequently been used in food and pharmaceutical fields for protecting both proteins and cells during freezing and drying due to their ability to form glasses, to mimic the hydrogen bonding character of water, to increase the surface tension of the bulk solvent, to prevent thermotropic phase separations in lipid bilayers, and to prevent the fusion of membranes (Conrad and de Pablo, 1999). Trehalose is a nonreducing disaccharide of glucose. It occurs naturally in many organisms which suffer dehydration stresses. Trehalose’s success as a cryoprotectant has been attributed to its strong interaction with water and lipid membranes, its unique chemical stability, and its glass-forming behavior when amorphous (Crowe et al., 1996). The stabilizing effect of sugars has been inversely related to the degree of crystallization (Suzuki et al., 1997; Cardona et al., 1997). Divalent cations were reported to delay crystallization kinetics of sugars (Mazzobre and Buera, 1999).

The crystallization of sugars is also important in the food industry as evidenced by the many processes where the degree of crystallinity of sugars is critical to acceptance of the final product, i.e., storage stability and quality of milk powders are significantly affected by the physical state of lactose, one of the main components in regular milk powders (Jouppila and Roos, 1994). Crystallization of lactose in ice-cream, condensed milk and milk powders is considered undesirable, while in products such as milk chocolate lactose crystallization is desirable. Likewise sucrose crystallization evidenced by graining in boiled sweets is considered to be a defect whereas the fine crystals present in fondant icing are desirable because they help enable the icing to retain its shape in confectionery products (Hartel and Shastry, 1991; Hartel, 1992).

The control of lactose and sucrose crystallization during processing is important for a wide variety of products and there is a need for a suitable method to determine the degree of crystallization which would occur under specific processing conditions (Kedward et al., 1998). Nuclear Magnetic Resonance (NMR) is a noninvasive technique often used for the examination of biological systems. This technique allows the determination of relaxation effects of protons containing in different states. Low resolution $^1$H-pNMR is widely employed to determine the solid/liquid ratio in fats (AOCS official method). However, no previous references have been found for the application of this technique to determine the degree of crystallization in sugar solutions. The most common techniques in sugar studies are the evaluation of spin-spin and spin-lattice relaxation times. The experiments involve the study of a one phase systems and are usually performed in dehydrated systems (Cornillon, 2000) or vitreous systems (Rubin et al., 1990). Diffusion of sugars in aqueous solutions was also investigated performing spin echo and spin-spin relaxation experiments (Martin et al., 1999) and the determination of soluble solids content in fruits (Cho et al., 1993; Keener et al., 1997) by NMR was also reported.

The aim of the present work was to analyze the applicability of low resolution proton pulse nuclear magnetic resonance ($^1$H p-NMR) to describe crystallization behavior of sugars. Isothermal