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Physical state, molecular mobility and chemical stability of powdered dairy formulations

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ABSTRACT

The chemical stability of valuable nutrients like the essential amino acid lysine is an important factor regarding the nutritional quality of dairy powders. So far, the stability concepts based on the water activity or on the glass transition temperature are mainly used to predict the stability of dairy powders. However, these concepts often only partly predict the stability of food products. Therefore, the aim of this study was to complement the established stability concepts by the molecular mobility as measured by low resolution ^{1}H NMR to fill this gap. Glass transition and crystallization of lactose were measured by differential scanning calorimetry. The delay of lactose crystallization was a function of the glass transition temperature and could be modeled by the Williams–Landel–Ferry equation. Lactose crystallization kinetics could not be modeled by the Avrami equation which indicates the formation of different crystal forms. The molecular mobility measured by low resolution ^{1}H NMR proved to be a fast and easy to handle method for the characterization of dairy powders. The transversal relaxation time showed a sharp increase above the glass transition temperature and increased further in the crystalline state. However, the crystallization conditions affected the transversal relaxation time in the crystalline state which indicated the formation of different crystal forms in accordance with the observations of the lactose crystallization kinetics. Furthermore, crystallization led to a step increase of the second moment. Hence, low resolution ^{1}H NMR could also be used to analyze the crystalline structure. The extent of lysine loss in three different dairy formulations after a thermal treatment could be explained by taking into account the physical state together with the molecular mobility. Thus, it can be concluded that both the physical state and the molecular mobility are decisive for the chemical stability of dairy powders.

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1. Introduction

The stability of sensitive ingredients during the production and storage of food products is a major concern for high-quality food products. In order to ensure the preservation of nutrients and to minimize degradation reactions of sensitive ingredients, the circumstances that lead to these product deteriorations have to be identified. Understanding the mechanisms allows optimizing the product characteristics as well as the processing and storage conditions with regard to the product quality. For instance, Tolkach and Kulozik (2007) developed a reaction kinetics model for the denaturation of β-lactoglobulin that allowed a targeted choice of heating conditions in order to create desired functional properties. By determining the inactivation kinetics of dairy fermentation bacteria during convective drying and during isothermal heating, Ghandi, Powell, Chen, and Adhikari (2012) could differentiate between the impact of dehydration and thermal stresses on the survival rate.

In milk products available lysine, an essential amino acid, represents an important nutrient that is decisive for their nutritional value. Lysine is necessary for the protein synthesis in the human metabolism, especially in the liver (Tome & Bos, 2007). However, lysine is only available to the human metabolism if its ε-amino group is free (Meade, Reid, & Gerrard, 2005; Moughan & Rutherfurd, 2008; van Boekel, 1998). This amino group is mainly blocked by the early Maillard reaction with the reducing sugar lactose in dairy products. As lysine loss occurs already at rather gentle conditions, e.g. during spray drying and storage (Chavez-Servin, Castellote, & Lopez-Sabater, 2008; Ferrer, Alegria, Farre, Abellan, & Romero, 2000; Finot, 1983; Malec, Gonzales, Naranjo, & Vigo, 2002; Schmitz, Gianfrancesco, Kulozik, & Foerst, 2011), it is a good indicator for the chemical stability of powdered dairy products. Storage and spray

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drying were shown to be the critical points concerning lysine loss in powdered dairy products.

Several concepts exist to characterize the chemical stability. The water activity concept is based on the idea that chemical or biological stability is a function of the water activity and that a food product is most stable at its monolayer water content (Rahman, 2010). A stability map with bacterial growth, yeast growth, non-enzymatic browning reactions, etc. as a function of the water activity can be drawn (Rahman, 2009; Roos, 2002). However, water activity alone cannot explain stability in many cases. Schmitz et al. (2011) for example have shown that the loss of available lysine in model infant formula is not only determined by the water activity but to a large extent also by the physical state. The physical state is taken into account by the glass transition concept. The glass transition concept takes the glass transition temperature as reference temperature for stability (Champion, Le Meste, & Simatos, 2000; Rahman, 2010; Roos, 2010). In the glassy state below the glass transition temperature the viscosity reaches high values and, consequently, the mobility is limited. Thus, the rate of diffusion controlled reactions is normally slow which results in a good stability. These concepts can be used to establish state diagrams, as it was for example done by Vuataz (2002) for milk, as a tool to predict the stability or to optimize processing.

However, the concepts mentioned above often fail to predict the stability of sensitive products. For instance, Aschenbrenner, Kulozik, and Foerst (2012) concluded that there was no direct link between glass transition and microbial inactivation. Difficulties are often encountered to find a clear correlation between glass transition and microbial activity, enzymatic or non-enzymatic reactions, e.g. the oxidation of ascorbic acid (Lin et al., 2006). This weak point can be overcome by including the molecular mobility in the stability concept (Champion et al., 2000; Lin et al., 2006). Data available in literature on chemical or microbiological stability as related to molecular mobility is so far rather scarce. Acevedo, Schebor, and Buera (2008) related non-enzymatic browning kinetics in potato starch to glass transition and molecular mobility. They determined higher non-enzymatic browning rates in the rubbery state compared to the glassy state concomitant with an increasing molecular mobility and attributed the decrease in the non-enzymatic browning rate at higher water contents to the appearance of very mobile water. Foerst, Reitmaier, and Kulozik (2010) demonstrated that the transition from liquid-like to solid-like behavior during drying as evaluated by means of molecular mobility measurements coincided with the critical water content for a protective effect of sorbitol on the survival of lactic acid bacteria. Hinrichs et al. (2004) linked molecular mobility to the water binding capacity of whey protein concentrates. This knowledge can serve to minimize the extent of syneresis in dairy products. Yoshioka and Aso (2007) concluded for the chemical stability of amorphous pharmaceuticals that depending on the degradation reaction global mobility as determined for example by differential scanning calorimetry and/or local mobility measured for example by nuclear magnetic resonance can be decisive for the chemical stability.

In this study, we focused on a model dairy formulation that on the one hand is prone to the loss of available lysine due to its high content of lysine-rich proteins and of lactose and that on the other hand easily tends to phase transitions, i.e. glass transition and crystallization, which is accompanied by a change in molecular mobility. The molecular mobility as measured by low resolution ^{1}H-NMR was related to the water activity and the physical state as well as to the chemical stability expressed by the loss of available lysine. The conditions used are not only relevant for the storage period but first of all for conditions that a particle experiences during spray drying. Thus, the importance of a combined concept of water activity, physical state and molecular mobility can be demonstrated.

2. Materials and methods

2.1. Production of the model dairy formulation

The amorphous milk based model system was prepared by reconstituting skim milk powder, whey protein isolate, lactose, potassium citrate and sodium hydrogenphosphate in deionized water (Table 1) as described by Schmitz et al. (2011). The standard composition was characterized by a lactose:protein ratio of 5:1 and a whey protein:casein ratio of 60:40. This composition is typical of specialized dairy powders as for example infant formula. The solution was frozen (−40 °C) and freeze-dried (0.37 mbar, >48 h, freeze-dryer Delta 1–24 LSC, Martin Christ, Osterode, Germany) in order to obtain a homogeneous amorphous powder without application of heat. Aliquots of the freeze-dried powders were stored over saturated salt solutions (Table 2) to adjust the water activity at 25 °C for at least 7 days until equilibrium was reached.

2.2. Loss of available lysine

The equilibrated samples were transferred to hermetically closed heating containers (Ø 50 mm, height 8 mm) and heated in a water bath at 70–90 °C for 30 min. The samples were subsequently cooled down to room temperature in ice water. For the quantification of available lysine, samples were reconstituted in deionized water to 10% (w/w) dry matter. Samples that were not analyzed immediately after heating were frozen at −40 °C till analysis.

The *o*-phthaldialdeyhde (OPA) method was used to assess available lysine as described by Schmitz et al. (2011). OPA forms a fluorescent isoindole with β-mercaptoethanol and a free amino group, in this case with the ε-amino group of lysine, at alkaline conditions. The amount of free amino groups, i.e. available lysine, is directly proportional to the detected fluorescence intensity when the impact of the amino groups of free amino acids and small peptides is substracted.

2.3. Water content and water activity

The water content (X) was measured by Karl–Fischer Titration (Karl–Fischer Titrator, Titro Line KF, Schott, Mainz, Germany). Analyses were carried out at 40 °C in a 1:1 mixture of Hydranal®-Formamid dry and Hydranal®-Methanol Rapid (Sigma-Aldrich, Steinheim, Germany). Samples were stirred for 5 min to equilibrate the system and then titration was done with Hydranal®-Composite 5 (Sigma-Aldrich, Steinheim, Germany). The titrator was calibrated with Hydranal®-Water Standard (Sigma-Aldrich, Steinheim, Germany). The water activity (a_w) was determined at 25 °C using a water activity meter (a_w-sprint TH500, Novasina AG, Lachen, Switzerland).

2.4. Sorption isotherm

Aliquots of the freeze-dried powders with known water contents were stored for at least 7 days over saturated salt solutions (Table 2) at 25 °C to adjust the water activity. The samples were weighed

Table 1
Composition of dry matter of the model dairy formulations.

Composition	Standard composition	High lactose content	Low lactose content
Lactose:protein ratio	5:1	7:1	3:1
Whey protein:casein ratio	60:40	60:40	60:40
Skim milk powder [%]	22.2	16.8	32.8
Whey protein isolate [%]	8.4	6.4	12.4
Lactose [%]	68.3	75.8	53.7
Potassium citrate [%]	1.0	1.0	1.0
Sodium hydrogenphosphate [%]	0.1	0.1	0.1

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