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LACTOSE CRYSTALLIZATION IN COMMERCIAL WHEY POWDERS
AND IN SPRAY-DRIED LACTOSE

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Abstract

Two kinds of whey powder, one containing only amorphous lactose, and the other containing precrystallized lactose, and spray-dried amorphous lactose were examined for particle structure by scanning electron microscopy. Lactose crystallization under 75% relative humidity was studied by X-ray diffraction analysis. Scanning electron microscopy appeared to detect changes due to lactose crystallization on the smooth surface of the particles examined. Lactose crystallization started within 30 minutes after exposure to the humid atmosphere. Both α-lactose hydrate and β-lactose crystals were detected in the spray-dried amorphous lactose by X-ray diffraction within 40 minutes under the humid conditions. Only crystals of α-lactose hydrate developed in the whey powders. Additional crystallization of lactose in the amorphous portion of precrystallized whey powder was seen by scanning electron microscopy but increased crystallinity was not clearly detected by X-ray diffraction analysis. Several physical treatments involving storage at -20 to 55°C along with a desiccating agent, failed to crystallize β-lactose in the whey powders. It is hypothesized that the presence of milk serum solids inhibited the crystallization of β-lactose.

Introduction

Utilization of whey is attracting the attention of researchers and manufacturers in the dairy industry because of a) the effective utilization of whey proteins and lactose (Zall, 1984), and b) whey disposal problems. Lactose is being used for various purposes, including as a constituent in dairy foods (Hobman, 1983; Zadow, 1983). Whey powder is the main product produced from whey. The whey drying process has been summarized by many researchers (Webb and Whitlter, 1948; Hall and Hedrick, 1971; Morrissey, 1975). Some reports showing the particle structure of whey powder have been published (Ruma and Henstra, 1971a; Roezman, 1979; Linko et al., 1981, Saltmarch and Labuzza, 1980a, b; Saito and Taguchi, 1980), although they are not as numerous as those concerning the structure of skim milk powder particles (Verhey, 1972; Ruma, 1978; Roezman, 1979; Saito, 1985). The composition of whey varies slightly depending on the type of cheese that is made due to differences in processing. Demineralization processes using either ion exchange resin or electric dialysis may be applied to whey depending on the requirements of the users of the whey powder. This is another reason for variation in the composition of the whey powder. Lactose, however, is always the major constituent of whey powder, being present at 65 to 88% (Hall and Hedrick, 1971) by mass. Properties of lactose are reflected in the behavior of the whey powder particles. There are two types of whey powder in respect to the physical state of lactose. One type contains the amorphous form of lactose, and the other type contains both the crystalline and the amorphous forms. In either type, whey proteins are dispersed in a continuous phase of amorphous lactose having the β/α ratio of 1.25 (Roezman and Schaik, 1975). Since lactose in the amorphous state is highly hygroscopic, the whey powder which is spray-dried without the crystallization of lactose is also highly hygroscopic. On the other hand, a whey powder in which crystallization of lactose is allowed to take place before and/or after drying is considerably less hygroscopic and flows easily. The properties of whey powder in relation to the characteristics of lactose, particularly its physical state, have been discussed in other publications (Nickerson, 1974; Hynd, 1980; Parkinson, 1980).

It generally has been accepted that in spray-dried milk powder lactose occurs in the amorphous state and crystallizes as α-lactose hydrate in skim milk powder as reviewed by King (1985), in whole-

Key Words: Whey powder, amorphous lactose, spray-dried lactose, lactose hydrate, beta-lactose, X-ray diffraction, crystallization, scanning electron microscopy.
milk powder (Troy and Sharp, 1930; Saito, 1985), and in buttermilk powder (Kalab, 1980) by moisture uptake from the atmosphere. Lactose crystallization is also important in whey powder and must be controlled for desired flow and solubility characteristics. Amorphous lactose in whey powder behaves like that in skim milk powder with respect to the transition into its crystalline form (Roetman, 1979; Saltmarch and Labuza, 1980a,b). The processes usually applied to produce dried milk and whey powder cannot lead to the crystallization of β-lactose (Webb and Whittier, 1948). In a few cases, however, crystalline β-lactose was detected in dried milk (Knoop and Samhammer, 1962), and in drum-dried whey (Sharp, 1938; Sharp and Doob, 1941). Crystals of β-lactose also developed in whole milk powder stored in a sealed metal can at 60°C (Wärsch et al., 1984), and that stored at low humidity at 37°C for 5 months (Saito, 1985). Saito (1986) also treated instant skim milk powder in the same manner as the whole milk powder, and found crystals of β-lactose and α-lactose hydrate, even though the X-ray diffraction peaks showing crystallization were lower in the skim milk powder than in the whole milk powder. Subsequent storage under 75% relative humidity at 37°C for 2 days resulted in the disappearance of β-lactose crystals and an increase of α-lactose hydrate crystals in the instant skim milk powder, whereas no change (and thus no formation of α-lactose hydrate) was observed in the whole milk powder. In other literature (Knoop and Samhammer, 1962), formation and detection of β-lactose crystals have been described only in a limited number of whole milk powders, but never in other spray-dried products such as skim milk powder and whey powder.

Some patents describe a process where seeding a partially crystallized whey with β-lactose at a temperature above 93.3°C was applied to prepare a dried whey in which lactose crystallized in the β-form (Webb and Whittier, 1948). Many procedures to crystallize β-lactose from aqueous solutions have been published (Olino et al., 1983). Crystalline β-lactose also was detected in amorphous lactose after moisture uptake (Herrington, 1934) and on the surface of crystals of α-lactose hydrate (Sharp, 1938).

In a previous paper (Saito, 1985), lactose crystallization in whole milk powders and skim milk powders as well as the structure of the powder particles were studied. The present paper extends the previous work, and includes a study of the particle structures of whey powder and spray-dried lactose, and the effect of milk constituents on the crystallization of lactose.

Materials and Methods

Whey powders: Three commercial spray-dried powders were used. Lactose was present only in the amorphous form in two of them (ordinary whey powder and partially demineralized whey powder). In the third powder (precrystallized whey powder), lactose was partially crystallized prior to drying. Spray-dried lactose: A 33% lactose solution was kept at 70°C for 1 h and then was spray-dried (drying air: 160°C at Inlet, 90°C at outlet).

The materials described above were packed in a polyethylene bag, then placed in another polyethylene bag along with a drying agent (silica gel), and kept at room temperature until used. Scanning electron microscopic examination was carried out without any fixation procedure. The samples were sprinkled on a piece of double adhesive tape attached to a specimen holder, coated with gold by an ion-sputtering method, and observed in a JEOI-25 SII scanning electron microscope (SEM) operating at an accelerating voltage of 15 kV. A computerized X-ray diffractometer (Rigaku GeigerFlex RADIA, Cu Target) was used to obtain X-ray diffraction patterns. The forms of crystalline lactose were determined by comparing X-ray diffraction patterns with published patterns (Knoop and Samhammer, 1962; Buma, 1987; Saito, 1985).

Relative humidity (RH) of 75% was provided by placing a saturated sodium chloride solution in a closed container (Rockland 1960) at room temperature.

To learn how rapidly the lactose crystallized, the following procedures were attempted. Small amounts of the two powders, were adhering to a double adhesive tape on a specimen holder for SEM and kept under humid conditions (75% RH) for 30 min and then coated with gold. Samples were also packed in a shallow dent on a glass plate, which served as a sample holder for X-ray analysis, and kept for 40 min at 75% RH prior to analysis by X-ray diffraction.

Results

Structure of whey powder particles

Whey powder particles seemed to be more fragile than skim milk powder particles and were easily damaged by the electron beam in a way similar to that demonstrated by Kalab and Emmons (1974). SEM demonstrated that particles of ordinary and demineralized whey powders were spherical (Fig. 1). Demineralization apparently had no effect on particles structure. Surface folds and dents such as those observed in skim milk powder (Roetman, 1979; Saito, 1985) were not present in whey powder particles. Their absence had already been mentioned by Buma and Henstra (1971a). Buma and Henstra showed vacuoles of various sizes (Fig. 1B). Thin streaks, which could be a type of crack, were observed on the surface of particles (Figs. 1A, C). It is unknown how these streaks formed. The occasional presence of thin streaks was also in agreement with the observations of Buma and Henstra (1971a).

The precrystallized whey powder particles contained spherical particles and lactose crystals covered with amorphous lactose and other constituents such as whey proteins (Fig. 2). A somewhat squared structure was observed in some of the spherical particles suggesting inclusion of lactose crystals even in the particles (Fig. 2A). Small pieces of dust-like material, probably parts of crushed particles, were adhering to the surface of the powder particles (Figs. 2A, B). Some crystals were covered only slightly with other constituents (Fig. 2C), but contained small holes in the surface which were probably caused by evaporation of water from the covering material, i.e., amorphous lactose involving whey proteins and salts.

Structure of spray-dried lactose particles

Particles of spray-dried lactose were intact spheres of various sizes having smooth surfaces (Fig. 3) as was shown earlier by Roetman (1979) and Buma and Henstra (1971b). Deformed particles were rarely observed, even though some of the large particles carried small particles on them (Fig. 3B).
Crystallization of lactose under humid conditions

Amorphous lactose in the ordinary as well as in the demineralized whey powder and in spray-dried lactose crystallized easily by uptake of moisture under a 75% RH.

SEM observations of the particles of whey powder (Fig. 4A) and spray-dried lactose (Fig. 4B) attached on specimen holders and exposed to 75% RH for 30 min revealed that lactose crystallization was initiated on the surface of the particles within such a short time. However a sample, of about 5 g, placed in a small beaker (4.2 x 6.0 cm, height of powder: 0.6 cm) and kept under 75% RH for 30 min at room temperature did not show the peaks of lactose crystals in X-ray diffraction pattern. Crystallization of lactose during 30 min might be limited to the surface portion of particles in the upper zone and not detected by X-ray diffraction. Thus, scanning electron microscopy was more sensitive than X-ray diffraction analysis for detecting initial crystallization of lactose in whey powder particles.

The X-ray diffraction pattern for spray-dried lactose (packed in a dent of a sample holder for X-ray analysis and exposed to 75% RH for 40 min) showed the formation of crystals of α-lactose hydrate and β-lactose. Such patterns, which would correspond to lactose crystals, could not be shown by X-ray diffraction in the two whey powders under study.

Lactose crystals developed sufficiently within 1 day under 75% RH in both whey powders and in spray-dried lactose. Electron micrographs of the whey powders and the spray-dried lactose kept for 10 h and for 3 - 6 days in the humid atmosphere are shown in Figs. 5 and 6. Additional crystallization of lactose in the precrystallized whey powder seemed to proceed only to a small extent and produced tiny crystals on the surface of the original crystals as well as on the spherical particles (Figs. 5C,D). Spray-dried lactose retained its spherical structure after crystallization (Figs. 6A,C) but the inner
structure consisted just of an aggregate of lactose crystals (Figs. 6A, B).

According to the X-ray diffraction patterns, the crystals formed in spray-dried lactose were a mixture of \( \alpha \)-and \( \beta \)-forms (Fig. 7A) similar to the \( \alpha \)-crystals of spray-dried milk powder (Knoop and Samhammer, 1962), whereas the crystals in ordinary whey powder (Fig. 7B) were \( \alpha \)-lactose hydrate.

In the case of the precrystallized whey powder, in which some of the lactose had crystallized as \( \alpha \)-lactose hydrate (Fig. 7D), the proof of the additional uptake of moisture. The changes in X-ray diffraction patterns, however, were small and did not clearly demonstrate any additional crystallization of lactose (Fig. 7C).

To find a physical treatment which might promote the development of \( \beta \)-lactose crystals, as in the case of the whey powder, spray-dried lactose for 6 months at 37°C and 55°C together with a desiccating agent (silica gel) was attempted. The samples were also stored at -20°C to 30°C for 6 months. All these treatments failed to cause the crystallization of either \( \alpha \)-lactose hydrate or \( \beta \)-lactose. The samples treated as above produced lactose crystals in the same manner as the untreated sample by subsequent exposure to 75% RH for 1 day.

Discussion

Particles of spray-dried lactose were almost ideal spheres. On the other hand, the ordinary whey powder containing only amorphous lactose contained some deformed particles. This deformation was probably related to the particle size and to the presence of whey proteins. The latter might affect the passage of moisture from the interior of the particles to the surface at the time of drying. The particles of skim milk powder, whole milk powder, and whey powder were similar in that they all were spherical, but differed in surface structure. Buma and Henstra (1971b) reported that casein micelles may cause folds and dents on the surface of skim milk powder particles. According to their results, the smooth surface of whey powder particles was due to the absence of casein.

Only \( \alpha \)-lactose crystallized as a monohydrate in whey powders after moisture uptake. Impurities, i.e., whey proteins and salts, must influence the initiation and progression of the crystallization process in various ways. Nickerson and Moore (1974) demonstrated that demineralized whey accelerated the crystallization of \( \alpha \)-lactose from supersaturated solutions, even though the continued presence of the impurities depressed the rate of crystal growth. It has been reported that \( \beta \)-lactose could retard the growth rate of \( \alpha \)-lactose hydrate (Michaels and van Kreveld, 1966).

In the case of precrystallized whey powder, the crystallization of lactose under humid conditions was much less noticeable than in the whey powder which contained only amorphous lactose. Precrystallized whey powder contains not only crystalline lactose but also amorphous lactose, in which whey proteins and salts are concentrated. Crystallization of lactose from the amorphous state may be retarded by whey proteins and \( \beta \)-lactose. Further growth of precrystallized lactose crystals may not be anticipated because of contamination of the crystal surface with impurities. Therefore, the growth of lactose crystal was limited.

Bushill et al. (1965) demonstrated an unusual crystal form of lactose, an anhydrous molecular compound consisting of \( \alpha \)-lactose and \( \beta \)-lactose in a molecular ratio of 5:3, in a spray-dried lactose solution after absorption of moisture and its subsequent loss. In the present study, the X-ray diffraction patterns of spray-dried lactose kept under humid conditions consisted of a combination of typical patterns of \( \alpha \)-and \( \beta \)-forms, i.e., there were peaks at 2\( \theta \) = 22.00°, 16.40° (\( \alpha \)-form), and 2\( \theta \) = 23.0°, 25.1°, 30.1° (\( \beta \)-form); whereas 2\( \theta \) = 22.0°, which was a typical peak for the unusual crystalline form reported by Bushill et al. (1965), was missing. The crystals, which appeared in the particles of spray-dried lactose after the uptake of moisture were, therefore, a mixture of \( \alpha \)-lactose hydrate and \( \beta \)-lactose, and not the anhydrous molecular compound. It is, however, possible that the unusual crystalline form develops after subsequent drying and/or prolonged storage.

Since amorphous lactose is in a supersaturated state of both \( \alpha \)-and \( \beta \)-lactose, both forms may crystallize if right conditions to initiate crystallization exist. No information about the crystallization of \( \beta \)-lactose form in an amorphous state is available at present. Storage at relatively high temperatures did not succeed in initiating the crystallization of \( \beta \)-lactose unlike in the case of whole milk powder (Würsch et al., 1984; Saito, 1985). Only the uptake of moisture produced crystals of \( \beta \)-lactose as a mixture of \( \alpha \)- and \( \beta \)-forms in spray-dried lactose. The formation of \( \beta \)-lactose crystals in an amorphous state is available at present.

The literature available suggests that the crystallization of \( \beta \)-lactose from amorphous state is favored in whole milk powder (Würsch et al., 1984; Saito, 1985; Saito 1986) but not in skim milk powders and in whey powders. Milk fat might help the crystallization of \( \beta \)-lactose but it interferes with the movement of moisture and retards the crystallization of \( \alpha \)-lactose as monohydrate.

The crystallization of amorphous lactose in whey powder and spray-dried lactose causes caking of them, but makes their physical properties more stable with respect to moisture uptake. Thus the crystallization of amorphous lactose, with subsequent grinding procedure, could provide rather stable types of whey powders and spray-dried lactose which are easy to handle.

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Whey powder and crystallization of lactose

Fig. 7 (above). X-ray diffraction patterns of whey powders and spray-dried lactose. A = Spray-dried lactose, B = ordinary whey powder, C, D = precrystallized whey powder. A, B, C = kept under 75% RH at room temperature for 1 day. D = not exposed to the humid condition. Arrows show characteristic peaks of α-lactose crystal.

Figs. 4 - 6. Scanning electron micrographs. Bars = 10 μm.

Fig. 4. Ordinary whey powder (A) and spray-dried lactose (B) kept under 75% RH at room temperature for 30 min.

Fig. 5. Whey powders kept under 75% RH at room temperature for 10 h (A), 3 days (B), and 6 days (C, D). A, B = ordinary whey powder, C, D = precrystallized whey powder. Arrow shows tiny crystals produced on the original crystal after moisture uptake.

Fig. 6. Spray-dried lactose kept under 75% RH at room temperature for 10 h (A), 3 days (B), and 6 days (C). I = inner portion, S = particle surface.
References


Discussion with Reviewers

M. Kalab: "Somewhat squared structure" inside the particles (Fig. 2A) would mean that crystallization took place before the particles were formed. I doubt it that Fig. 2A shows a lactose crystal because that structure has no attribute of a crystal such as sharp edges, smooth planes etc., but has holes.

Author: Squared structure inside the particles means that crystallization took place before the particles were formed. In the manufacturing of precrystallized whey powder, lactose crystals are dispersed in saturated lactose solution which contains salts and whey proteins, before spray-drying. Therefore, all of the lactose crystals are covered, more or less, with a continuous layer of amorphous lactose which formed from the saturated lactose solution after drying. Some of the relatively small crystals of


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Lactose may be included in the particles and give a squared appearance at the surface of the particle.

On the other hand, large crystals covered with amorphous lactose show the shape of lactose crystals but not sharp edges and smooth planes, typical for crystals, because amorphous lactose containing whey proteins and salts covers them.

M. Kalab: What are the practical implications of this study?
Author: Crystallization of amorphous lactose stabilizes the physical properties of whey powder and spray-dried lactose. This is convenient for users and may provide a new way in their usage. For instance, caking of spray-dried lactose containing chemicals, such as pesticide, is avoided by crystallization of amorphous lactose followed by subsequent grinding. If we could crystallize amorphous lactose in whey powder as β-lactose, even though we did not succeed, the usage of whey powder may be expanded.

Thus, crystallization of amorphous lactose has some practical implications. So I plan to continue this research to control crystallization behavior of amorphous lactose.