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LACTOSE CRYSTALLIZATION IN SPRAY-DRIED MILK POWDERS EXPOSED TO ISOBUTANOL

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Abstract

A study was undertaken to establish whether suspension of dry milk powder in isobutanol and l-octanol during particle size analysis and preparation for scanning electron microscopy introduced artifacts. The median, volume-based diameter, \(d_{v,0.5}\), of spray-dried milk powders containing 27-67% lactose changed over time of exposure to isobutanol. No changes in median diameter were observed when powders were exposed to l-octanol. Changes in particle size resulted from solubilization of amorphous lactose and/or recrystallization of lactose on the particle surface. Both \(\alpha\)- and \(\beta\)-lactose were formed during contact with isobutanol as indicated by X-ray diffraction and scanning electron microscopy. The magnitude of the characteristic peaks for \(\alpha\)- and \(\beta\)-lactose and scanning electron micrographs indicated that the amount of lactose crystal formed was proportional to the initial amount of amorphous lactose in the sample. l-Octanol was determined to be a suitable suspension medium for sizing of milk powders containing lactose.

Key Words: Lactose, crystallization, milk powder, isobutanol, laser diffraction, particle size analysis, X-ray diffraction, scanning electron microscopy.
higher than 10%, only the α-lactose monohydrate is formed. Methanol is suitable for the removal of the water of crystallization from the α-lactose monohydrate to form anhydrous α-lactose (Lim and Nickerson, 1973).

In addition to ethanol, various alcohols affect the solubility of lactose and the mutarotation equilibrium between the α- and β-forms. Majd and Nickerson (1976), reported that the solubility of lactose in alcohol-water mixtures decreased with increasing alcohol concentration and alcohol chain length. The crystallization of lactose in alcohol solutions is extensive. The solubility and crystallization of lactose in alcohol solutions are type of alcohol and agitation (Majd and Nickerson, 1976), salts (Herrington, 1934b), temperature and pH (Singh et al., 1991), organic solvents and alcohol concentration (Nickerson and Lim, 1974), and initial lactose form (Singh et al., 1991; Nickerson and Lim, 1974).

Since the 1970's, the preferred methods for sizing small particles have been laser diffraction or laser light-scattering. The major advantage of laser diffraction is the relationship between scattering angle and particle size is a fundamental one, requiring no calibration. The popularity of the technique also stems from the fact that it is rapid, highly reproducible, applicable to a broad range of sample types, and covers a wide range of particle size. Samples can be presented to the instrument as dry powders, in suspensions using a wide range of suitable liquids, in emulsions, and in sprays (Parsons, 1992; Allen, 1981).

The sizing of milk powders, particularly dry whole milk (DWM), by laser diffraction is best accomplished in a liquid suspension, since the stickiness of these powders prevents efficient dispersal as individual dry particles. Octanol and isobutanol have been recommended as suitable suspending media (“Choice of liquid suspension media for particle size analysis of powders”, Tech. Bull., Malvern Instruments Ltd., Spring Lane, Malvern, England, p. 19). However, lactose recrystallization in the presence of alcohols could alter size and morphology during sizing.

This study reports the changes in the size and microstructure of spray-dried milk powders suspended in isobutanol during particle size measurement by laser light-scattering. Comparisons are made with 1-octanol as a suspension medium.

Materials and Methods

Spray drying

Spray-dried whole milk powders with modified lactose concentrations were prepared as outlined in Fig. 1. Homogenized, pasteurized whole milk (230 kg) was obtained from the Pennsylvania State University Creamery. The milk was ultrafiltered (55°C) using a sanitary pilot plant unit (Model S-1, Abcor, Inc., Wilmington, MA) equipped with a 5.6 m² spiral-wound membrane (nominal molecular weight cut-off 10,000 daltons) at a mean transmembrane pressure of 45 psi (concentration volume ratio = 5.3). The retentate was then diafiltered with two volumes (2 X 187 kg) of chlorinated (20 ppm free chlorine) reverse osmosis-treated water. Approximately 29 kg of the final retentate (35.8% total solids, 0.06% lactose) was collected and stored at 4°C prior to spray-drying.

Lactose concentration of the spray-dryer feed was adjusted to yield dry powders with nominal lactose concentrations of 0, 30, 40, 50 and 70% by weight. Food grade lactose monohydrate (Land O’ Lakes, Minneapolis, MN) was dissolved in water at 55°C; the concentration varying from 28-39% depending on the desired lactose content of the final powder. Lactose solution and retentate were mixed (30 minutes at 55°C) to achieve the final desired lactose concentration at a constant feed concentration of 30% total solids by weight.

Approximately 1.2 kg of each powder was produced using a portable spray dryer (Niro Atomizer, Hudson, WI): inlet air temperature 160-170°C, outlet air temperature 70-80°C, feed temperature 55°C, feed rate 30 ml/min, and centrifugal atomizer operated at 27,000 r.p.m. Powders were stored in sealed plastic containers at 22-25°C until analyzed.

Particle size distribution

Particle size distribution was measured using the "MasterSizer" laser light-scattering particle size analyzer equipped with an MS 15 sample presentation unit and 100 mm lens (Malvern Instruments Ltd., Malvern, England). Milk powders were dispersed in isobutanol or 1-octanol (Fisher Scientific, Pittsburgh, PA) at room temperature (20-22°C) until an obscuration value of 0.2, corresponding to a volume concentration of 0.03-0.05%, was obtained (40-60 seconds). Particle size distributions were recorded at 1, 2, 3, 4, 5, 10, 20, and 30 minutes after this initial dispersion time. Ultrasonic dispersion (50 W at 27 kHz), for the first five minutes, and mechanical stirring were applied to ensure that particles were independently dispersed.

Scanning electron microscopy (SEM)

Isobutanol-milk powder dispersion (3 ml) was collected from the particle size analyzer at 5 minutes using a disposable syringe, and filtered through 0.2 μm polycarbonate filters (Poretics Corp., Livermore, CA). The filters with retained particles were dried overnight in a desiccator at room temperature, attached to aluminum stubs (10 mm diameter) with double sticky tape, and sputter coated with gold using an argon plasma operating at 10 mA and 1.4 kV for 8 minutes. A drop of silver paint was applied to the edge of the coated filter to improve grounding. Samples not exposed to isobutanol were picked up directly onto double sticky tape and prepared as described above. The samples were viewed with either an International Scientific Instruments Model ISI-60 (Topcon, Pleasanton, CA) or a JEOL 5400 (JEOL USA, Peabody, MA) scanning electron microscope operated at an accelerating voltage of 10 or 5 kV.

X-ray diffraction

The X-ray diffraction pattern of the milk powders was determined between 10° and 30° using an automated
Lactose crystallization in spray-dried milk powders

Figure 1. Schematic for the preparation of spray-dried milk powder with modified lactose concentration.

Table 1. Composition of Milk Powders

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lactose (g/100 g)</th>
<th>Moisture (g/100 g)</th>
<th>Protein (g/100 g)</th>
<th>Fat (g/100 g)</th>
<th>Ash (g/100 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.04 ± 0.01</td>
<td>2.92 ± 0.031</td>
<td>42.3 ± 0.85</td>
<td>51.2 ± 0.44</td>
<td>3.75 ± 0.015</td>
</tr>
<tr>
<td>B</td>
<td>27.1 ± 0.57</td>
<td>2.92 ± 0.027</td>
<td>29.9 ± 0.79</td>
<td>36.7 ± 0.55</td>
<td>2.71 ± 0.019</td>
</tr>
<tr>
<td>C</td>
<td>36.8 ± 1.27</td>
<td>2.50 ± 0.021</td>
<td>25.9 ± 0.77</td>
<td>34.6 ± 0.37</td>
<td>2.55 ± 0.021</td>
</tr>
<tr>
<td>D</td>
<td>47.5 ± 0.71</td>
<td>3.04 ± 0.018</td>
<td>20.2 ± 0.80</td>
<td>29.6 ± 0.61</td>
<td>1.98 ± 0.020</td>
</tr>
<tr>
<td>E</td>
<td>67.1 ± 1.27</td>
<td>2.08 ± 0.015</td>
<td>13.5 ± 0.71</td>
<td>15.2 ± 0.21</td>
<td>1.23 ± 0.015</td>
</tr>
</tbody>
</table>

Table 1 presents the composition of the milk powders. All powders were prepared from the same dialyzed ultrafiltration retentate and spray-dried under

Compositional analyses

Lactose concentration was determined by AOAC method 984.15, protein by method 930.29, fat by method 932.06, moisture by method 927.05 and ash by method 930.30 (Association of Official Analytical Chemists, 1990).

Results and Discussion

Table 1 presents the composition of the milk powders. All powders were prepared from the same dialyzed ultrafiltration retentate and spray-dried under
Lactose content | d\(_{\text{v}, 0.5}\) (\(\mu\text{m}\)) | d\(_{\text{v}, 0.5}\) (\(\mu\text{m}\))
--- | --- | ---
0 | 25.4\(^a\) | 25.3
27 | 14.9\(^b\) | 13.6
37 | 16.1\(^b\) | 15.2
48 | 17.4\(^b\) | 19.0
67 | 16.9\(^b\) | 21.7

\(^1\)Treatment means followed by the same lower case letter are not significantly different (\(p > 0.05\)).

Table 2. Median volume-based diameter, d\(_{\text{v}, 0.5}\), of milk powders obtained from laser light-scattering particle size analysis.

According to Saito (1985), peaks at angles of 10.5 and 12.4° are characteristic of the \(\beta\)-form and \(\alpha\)-form of lactose, respectively. Both peaks were observed in the diffraction patterns of milk samples containing lactose, indicating that during exposure to isobutanol both \(\alpha\)- and \(\beta\)-lactose were formed. Other peaks characteristic of \(\alpha\)-lactose (16.4, 19.6 and 20°) and \(\beta\)-lactose (19.1 and 20.9°) were also observed. Several studies have reported the transformation of amorphous or solubilized lactose into the different crystal forms when treated with alcohols (Lim and Nickerson, 1973; Majd and Nickerson, 1976; Nickerson and Lim, 1974; Singh et al., 1991). Nickerson and Lim (1974) reported that both the \(\alpha\)- and \(\beta\)-forms of lactose can be obtained on crystallization from alcohols, and that the rate of conversion of \(\alpha\)-lactose monohydrate to anhydrous \(\alpha\)-lactose was slower in isobutanol compared to methanol, ethanol or propanol.

Figures 6-10 are scanning electron micrographs of the spray-dried milk powders before and after exposure to isobutanol. The general morphology of the fresh milk powders is similar to results obtained in other studies (Kalab, 1979; Caric and Kalab, 1987; Mistry et al., 1992). The particles are almost spherical with dents, have a smooth surface, and there is no evidence of lactose crystallization. The absence of characteristic peaks in the X-ray diffraction patterns confirms the absence of crystalline lactose. Spray drying retentate produced some “hollow” particles (Fig. 6) not observed for those powders containing lactose. The surface of fresh powders with 67% lactose (Fig. 10A) displayed fracture lines.

Micrographs of the milk powders after isobutanol treatment revealed crystal growth that was proportional to the original amount of amorphous lactose in the sample. The manner in which lactose crystals emanate from the surface of discrete particles (Fig. 8B-10B) suggests that they were formed while the particles were in suspension, and not during the subsequent drying period. Studies in this laboratory (unpublished data) and by others (e.g., Saltmarch and Labuza, 1980) have consistently shown particle accretion when lactose crystallization occurs during drying or upon storage at high relative humidity. The shape of \(\alpha\)-lactose crystals is controlled by the rate of growth. According to Herrington (1934a), prism-shaped crystals of \(\alpha\)-lactose are formed when the velocity of growth is very high; at least 9 different shapes of \(\alpha\)-lactose crystals including prisms, diamond shaped plates, pyramids, and fully developed tomahawks at slower crystallization rates were observed. When lactose is precipitated quickly by alcohol, it separates first in the form of prisms, but as crystallization slows down, the prisms widen to the tomahawk form (Herrington, 1934a). \(\beta\)-Lactose may also form prisms when crystallization is sufficiently rapid (Herrington,
Lactose crystallization in spray-dried milk powders

Figure 2. Particle size distribution of milk powders containing 0 and 67% lactose by weight obtained from laser light-scattering size analysis of suspensions of powders in isobutanol (t = 5 minutes).

Figure 3. Changes in d[v, 0.5] as a function of time of exposure to isobutanol (% lactose indicated).

Figure 4. X-ray diffraction pattern for milk powder containing 0% lactose (bottom), and 67% lactose (top) prior to exposure to isobutanol.

Figure 5. X-ray diffraction pattern for milk powder containing 67% lactose after exposure to isobutanol.

Conclusions

The median diameter of lactose containing spray-dried milk powders suspended in isobutanol changes over time as a result of the solubilization and/or recrystallization of lactose on the surface of the milk particles. Both α- and β-lactose were formed during contact with isobutanol as indicated by X-ray diffraction and SEM. No changes in median diameter were observed when powders were exposed to 1-octanol. If isobutanol is used as a suspension medium for sizing of milk powders containing lactose, contact time should be reduced to a minimum (less than five minutes) and kept constant for all samples. 1-Octanol was determined to be the a suitable suspension medium for sizing of milk powders containing lactose. These results may also be relevant to the sizing of whey and whey permeate powders.

References

Lactose crystallization in spray-dried milk powders

Figures 6-10. Scanning electron micrographs of milk powders with:

- 0% lactose (Figure 6);
- 27% lactose (Figure 7);
- 37% lactose (Figure 8);
- 48% lactose (Figure 9); and
- 67% lactose (Figure 10);

before (Figures 6A, 7A, 8A, 9A, and 10A) and after (Figures 6B, 7B, 8B, 9B, and 10B) exposure to isobutanol. Arrow in Figure 10 indicates the particle magnified in Figure 11.

Figure 11. Scanning electron micrograph of milk powder with 67% lactose after exposure to isobutanol. Details of particle identified by arrow in Fig. 10.


Editor’s Note: All of the reviewer’s concerns were appropriately addressed by text changes, hence there is no Discussion with Reviewers.