

Effect of Water Vapor Sorption on Porosity of Dehydrated Dairy Products

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Abstract

Marked structural alterations in powder granules of dehydrated dairy products were observed to occur as a result of moisture sorption. These effects were manifested in enhanced rates of gas diffusion into the interior of the powder granules after water sorption. The porosities of powders which had been exposed to various humidity conditions were assessed by determination of true and apparent densities by pycnometric techniques, using He and N₂ as the displaced media. When powders were equilibrated against water vapor at 50% relative humidity, their porosities were so altered as to essentially eliminate any molecular sieve properties. The per cent free fat was also considerably increased after equilibration of the powders against water vapor at 50% relative humidity.

The production of dehydrated dairy products which reconstitute easily to their original form has been one of the major goals of dairy research. Aside from the fat phase, milk and whey powders consist of a collection of hygroscopic substances to which the rapid addition of large quantities of water will usually result in the successful reconstitution of these products. However, from observations of numerous workers it is known that as milk powders slowly absorb increasing amounts of water, fundamental changes occur in the powder structure leading to lactose crystallization, increase in free fat, protein insolubilization, and caking of the powder bed.

Isotherms for the adsorption of water vapor by dehydrated dairy products as reported by Supplee (15), Troy and Sharp (17), Fox et al. (7), and Berlin et al. (1) have been characterized by maxima in the 50% relative humidity range. Undoubtedly, these maxima are associated with physical alterations or phase changes in the powders. Troy and Sharp (17) have attributed the observed discontinuities in the sorption isotherms to crystallization of lactose, initially present in the powder in the

form of a very hygroscopic glass. This view has been accepted by many workers and has been amply discussed by Nickerson (12) and King (9).

As the morphological changes occur, the powders become more permeable, as shown by the studies of Lampitt and Bushill (11) and Buma (5). The adsorption of water by milk powders under extremely humid conditions of 85-95% relative humidity has been shown by Buma (5) to result in a powder of increased density and gas permeability. Generally, these earlier studies have been restricted to effects of very high humidities only.

In the present study we report data on changes in the porosity of dehydrated dairy products as affected by water sorption at points along the isotherms. The points were chosen so that comparisons could be made between powders which were held in the presence of H₂O through the discontinuity in the isotherm and those which were not. In particular, data are reported pertaining to rates of diffusion of He and N₂ into various milk and whey powders allowed to equilibrate with water vapor at various relative pressures.

Materials and Methods¹

The materials studied included sweet whey, skim milk, and whole milk powders, all dried in the Dairy Products Laboratory Pilot Plant by conventional spray-drying techniques and by the foam-spray-drying technique of Hanrahan et al. (8). In addition, a sample of commercially dried sweet whey powder also was examined.

The powders were examined in their initial state upon drying and after they were allowed to adsorb equilibrium quantities of H₂O at 20 and 50% relative humidity. The adsorptions were carried out as follows:

Powder samples were put in shallow beakers and placed in glove cabinets containing atmospheres of the desired temperature and humidity conditions. Humidity control was accomplished by use of appropriate saturated

¹Reference to certain products or companies does not imply an endorsement by the Department over others not mentioned.

salt solutions (13). The glove cabinets were kept in a room maintained at 23 C. Atmospheric conditions within the glove cabinets were monitored with Bacharach recording hygrothermographs. The powders were weighed periodically and attainment of equilibrium conditions was assumed when the powder mass remained constant for several days. The equilibrium values were in close agreement with those obtained in a study of water vapor adsorption by the same materials, using an electronic recording microbalance (1).

Powder porosities were assessed through measurements of true and apparent densities by gas displacement techniques as described previously (3). Helium and nitrogen were used as the displaced media in determinations of true and apparent densities, respectively. Differences between these density values and between the corresponding penetration rates of the gases were used to assess the nature of the pore structures of the powders studied.

The helium (Southern Oxygen Company) was purified by passage through a charcoal trap maintained at -195°C with a liquid nitrogen bath. The charcoal was previously outgassed at 250-300 C for several hours to remove any adsorbed impurities. Prepurified nitrogen (Southern Oxygen Company) was passed through a liquid nitrogen cooled trap to remove any traces of moisture.

Prior to measuring the densities, the powders were degassed under high vacuum so that the densities could be measured on a dry weight basis. High vacua on the order 1.5×10^{-6} torr were consistently maintained with a mercury diffusion pump backed by a mechanical oil pump. All samples were degassed at room temperature for a minimum of 16 hours.

The crystallinity of the lactose in the powders was measured by the method of Sharp and Doob (14), using a Rudolph Model 62 polarimeter in conjunction with a Bausch and Lomb monochromator equipped with a mercury lamp as the light source.

Free fat values were obtained according to the method of Tamsma et al. (16).

The solubility of the milk powders was assessed by the method of Kontson et al. (10).

Results

The density values obtained for the various powders under the described experimental conditions are listed in Table 1. Examination of the values obtained for the powders in their initial state reveals differences in the densities as determined by He or N_2 displacement, which correspond to internal cavities within the

TABLE 1. True and apparent densities of dehydrated dairy products using helium and nitrogen as displaced media.

Powder type	Storage conditions	Nitrogen ^a	
		Helium	(g/cm ³)
Spray-dried whole milk	Original	1.297	1.230
	20% RH ^b	1.283	1.219
	50% RH	1.291	1.365
Foam-spray-dried whole milk	Original	1.292	1.211
	20% RH	1.242	1.049
	50% RH	1.262	1.341
Spray-dried skim milk	Original	1.475	1.029
	20% RH	1.417	1.010
	50% RH	1.469	1.175
Foam-spray-dried skim milk	Original	1.333	0.817
	20% RH	1.399	0.821
	50% RH	1.431	1.482
Spray-dried sweet whey	Original	1.491	1.352
	20% RH	1.479	1.313
	50% RH	1.517	1.547
Foam-spray-dried sweet whey	Original	1.492	0.768
	20% RH	1.480	0.813
	50% RH	1.509	0.527
Commercial whey	Original	1.555	1.530
	20% RH	1.505	1.469
	50% RH	1.516	1.536

^a All values are after a minimum equilibration period of 24 hours.

^b RH = Relative Humidity.

particles which are inaccessible to the larger nitrogen molecules because of the microporosity of the particle surface. The densities obtained for the powders exposed to water vapor at 50% relative humidity exhibited no microporosity effects.

Values corresponding to the pore volume, or inaccessible internal space, are presented in Table 2. These are calculated from the equation:

$$V_p = \frac{1}{\rho_a} - \frac{1}{\rho_t}$$

where ρ_a and ρ_t are the apparent and true densities, respectively, and V_p is the pore volume. In most cases this excluded particle volume was completely eliminated after exposure of the powder to moisture through the break-point in the adsorption isotherm. The powders exposed to H_2O vapor at 20% relative humidity usually did not exhibit any change in their porosity.

In cases where the pore diameters are critical in allowing entry of the gas molecules, such gas penetration occurred at a slower rate. Slow penetration of the gas molecules therefore led to a slow creep or increase in the calculated density. Once the limiting pore structure was destroyed after moisture sorption at 50% relative humidity, hindered diffusion was no longer observed and the gas molecules penetrated rapidly. These changes in diffusion rate are shown graphically in Figure 1.

TABLE 2. Restricted pore volume in dehydrated dairy products as affected by moisture adsorption.

Powder	Storage conditions		
	Original	20% RH ^a	50% RH
	(cm ³ /g)		
Spray-dried whole milk	.042	.041	0.00
Foam-spray-dried whole	.052	.148	0.00
Spray-dried skimmilk	.294	.284	.170
Foam-spray-dried skim	.474	.503	0.00
Spray-dried whey	.069	.086	0.00
Foam-spray-dried whey	.632	.554	0.00
Commercial whey	.011	.017	0.00

^a Relative Humidity.

Increased permeability of the powder particles upon moisture adsorption was also observed in the free fat values (Table 3).

Crystalline lactose values, as a function of water uptake, are presented in Table 4. Increases in crystallinity usually accompanied water sorption, as expected.

Discussion

The molecular sieve characteristics of spray-dried dairy products reported here tend to confirm earlier reports of the same phenomenon (2, 3). Our study once more demonstrates the utility of measuring true and apparent densities to study milk powder porosity. Helium was chosen to measure the true density, since helium is virtually ideal at room temperature, does not adsorb appreciably at room temperature and, furthermore, the helium molecule is

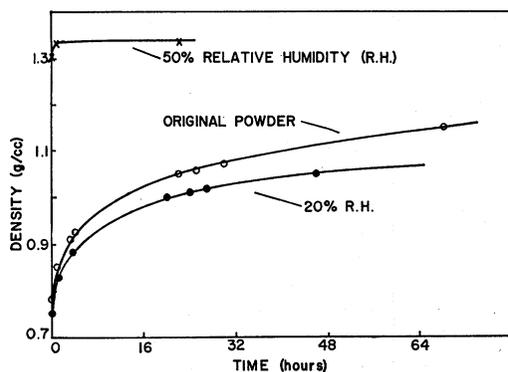


FIG. 1. Effect of moisture sorption on apparent density of foam-spray-dried whole milk powder.

TABLE 3. Per cent free fat in dried dairy products stored under various conditions of relative humidity.

Powder sample	Total fat %	% Free fat ^a		
		Original	Stored at 20% RH	Stored at 50% RH
Spray-dried whole milk	25.95	1.40	2.70	76.4
Foam-spray-dried whole	26.23	8.45	10.96	75.5
Spray-dried skimmilk	2.16	0.00	0.00	2.2
Foam-spray-dried skim	2.13	7.0	6.8	28.8
Spray-dried sweet whey	3.79	1.9	1.07	50.9
Foam-spray-dried whey	3.96	10.1	26.3	62.0
Commercial whey	1.26	3.9	10.2	56.8

^a Values are reported as percentages of total fat.

small enough to penetrate any pores, cracks, or crevices that are present on the granule surfaces. The nitrogen molecule, being somewhat larger (4 Å as opposed to 2 Å in diameter), cannot penetrate the very small pores and therefore proves useful in measuring the apparent density.

The present study is significant in showing the effects of the adsorption of critical amounts of water in destroying the molecular sieve character of spray-dried dairy products. It has been demonstrated by Fox et al. (7) that milk powders tend to become insoluble after sorbing a critical but limited amount of moisture to undergo the transformations associated with the maximum in the sorption isotherm.

TABLE 4. Per cent lactose in crystalline form in dried dairy products stored under various conditions of relative humidity.

Powder sample	% Lactose in crystalline form		
	Original	Stored at 20% RH	Stored at 50% RH
Spray-dried whole milk	6.2	7.3	9.6
Foam-spray-dried whole	2.9	4.3	8.6
Spray-dried skimmilk	5.5	5.3	16.0
Foam-spray-dried skim	4.8	5.0	15.1
Spray-dried whey	1.1	3.9	56.9
Foam-spray-dried whey	2.2	5.1	54.4
Commercial whey	43.8	42.2	53.9

We have observed similar solubility changes with the powders studied in the present investigation. The foam-spray-dried whole milk powder exhibited a solubility value of 89% initially and after exposure to moisture at 20% relative humidity; whereas, after exposure to moisture at 60% relative humidity, the solubility value decreased to 46%. There is, however, no conflict between the gas and water permeability data. The loss in solubility need not be attributed to physical changes in powder permeability, as solubility is more likely to be related to the physical state of the protein fraction rather than to the permeability of the powder granules per se.

The increased permeability of the powder granules upon water sorption is definitely associated with the transformations occurring after critical water uptake at relative humidities of 50% or higher. This is emphasized by the absence of any increase in apparent density values after H₂O sorption at 20% relative humidity. Actually, powders exposed to atmospheres of 20% relative humidity not only did not exhibit an increase in permeability but rather showed a decrement in apparent density. It is unlikely that this drop is due to any changes in molecular sieve structure, since the true density determined with He was also lowered after exposure to atmospheres of 20% relative humidity. Two possible explanations can be offered for these observations of lowered densities. Either sufficient moisture is adsorbed by the lactose glass that it becomes plastic enough to seal some pores in response to surface energy effects, or some moisture is irreversibly bound in the milk powder granules. To date, we have not resolved these alternate explanations, though limited data available at present do indicate that some water is held by the powder granules after degassing at room temperature under high vacuum.

In many cases the densities measured by N₂ displacement after H₂O sorption not only increased to reach the value obtained with He, but actually exceeded it. This was particularly evident with the foam-spray-dried whole milk. These inordinately high density values are probably due to physical adsorption of nitrogen on the internal powder surfaces. As long as these surfaces were inaccessible to N₂, because of the small pores present in the original powder, adsorption on these surfaces was negligible. However, after destruction of the molecular sieve character of the powder granules, these surfaces became exposed and available for adsorption.

The nature of physical adsorption on the wetted powders was considered further by measuring the extent of krypton adsorption at -195 C on the foam-spray-dried whole milk powder. This powder exhibited a BET (4) monolayer value of .366 cm³/g with krypton as the adsorbate, which is equivalent to 0.44 cm³/g if nitrogen were the adsorbate. The differences between helium and nitrogen determined densities for the powders exposed to atmospheres of 50% relative humidity may be attributed to physical adsorption of nitrogen. Using these density values one may calculate that .042 cm³ of N₂ are absorbed per gram of conventionally spray-dried whole milk powder and .046 cm³ of N₂ are adsorbed per gram of foam-spray-dried whole milk powder. These ambient temperature adsorption values are in excellent agreement with results of the low temperature adsorption measurements, as it is well known that many materials will adsorb one-tenth of a monolayer of nitrogen at room temperature.

Further demonstration of the destruction of the microporosity of the foam-spray-dried whole milk powder upon H₂O sorption was accomplished by measuring its density by helium displacement at 25 and -195 C. We have published data (2) showing that at low temperatures sufficient thermal contraction of milk powder occurs to prevent helium penetration. In the present case, after water sorption, the micropores were destroyed and essentially no differences in high and low temperature density values were observed.

It may be considered that the observed increase in nitrogen penetration rate is caused by the crystallization of lactose occurring in the powder granules at the breakpoint in the adsorption isotherm. While the distribution of lactose within the powder granule is not definitely known, recently presented work by Cornell and Pallansch (6) indicates that it may be only one of two continuous phases in milk powder and have even distribution throughout a continuous protein matrix. The formation of micro-crystals of lactose throughout the powder structure on water sorption may, therefore, form relatively large pores opening into the interior of the powder granule, thereby allowing the rapid penetration of gas or liquid into the interior absorption of water by milk solids must also be accompanied by swelling of the hydrated proteins. This, too, may aid in the observed destruction of microporosity within the powder structure. It is along these lines that the effect of the particle. It is fairly certain that the

cellent dispersibility of instantized skimmilk, made by a wetting and redrying process, may eventually be explained.

From the data presented in Table 4, it is apparent that conditions which lead to increased permeability of the powder particles also lead to increased levels of crystalline lactose. Nevertheless, even at the higher moisture levels we did not observe complete crystallization. Therefore, it is entirely possible that the operative mechanism in opening the pores may be a wedging effect due primarily to hydration of the proteins within the powders, which occurs simultaneously with partial crystallization of the lactose.

The open granule structure produced by sorption of critical levels of water also allows increased milk fat extraction with CCl_4 . The data of Table 3 accentuate the fact that improved penetration of the powder particles by either gas or solvent occurs extensively only after the powder has been stored under conditions which will carry it through the breakpoint in the adsorption isotherm. The increased free fat values could also be attributed to possible surface migration of the fat as a result of water sorption; however, on the basis of the data obtained in the present investigation it is more likely an effect of physical changes in pore structure.

Generally, the data reported in the present study tend to corroborate those of Buma (5) who reported increased powder permeability after water sorption. He attributed the increased permeability to the formation of cracks in the particles as a result of lactose crystallization.

In summary, the data reported here indicate that: 1) The micropore structure giving dehydrated dairy products molecular sieve properties is converted to a more open form by the adsorption of critical amounts of water by the powder particles. 2) Incomplete lactose crystallization occurs as the micropore structure is destroyed. 3) Destruction of the micropore structure of milk powders by water sorption allows increased extraction of milk fat with CCl_4 from dehydrated dairy products. This was not only observed with whole milk powders but also with whey and skimmilk powders. Upon considering the generality of the increase in free fat, it is most likely that the increase in CCl_4 extractable lipids is due to the physical alterations of the powders with increased permeability and not necessarily the dissolution of a lipoprotein membrane.

References

- (1) Berlin, E., B. A. Anderson, and M. J. Pallansch. 1967. Influence of drying method on moisture adsorption by dehydrated dairy products. 153rd Natl. Meet., Am. Chem. Soc., A 24, Miami Beach, Fla., April.
- (2) Berlin, E., E. D. DeVilbiss, and M. J. Pallansch. 1967. Effect of temperature on porosity of dried whole milk powder granules. *J. Dairy Sci.*, 50: 655.
- (3) Berlin, E., and M. J. Pallansch. 1963. Influence of drying method on density and porosity of milk powder granules. *J. Dairy Sci.*, 46: 780.
- (4) Brunauer, S., P. H. Emmett, and E. Teller. 1938. The adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.*, 60: 309.
- (5) Buma, T. J. 1966. The physical structure of spray milk powder and the changes which take place during moisture absorption. *Netherlands Milk Dairy J.*, 20: 91.
- (6) Cornell, D. G., and M. J. Pallansch. 1966. The preferential dissolution of milk powder particle constituents in ammonium sulfate solutions. 152nd Natl. Meet., Am. Chem. Soc., A 78, New York, N.Y., September.
- (7) Fox, K. K., M. J. Pallansch, and V. H. Holsinger. 1964. Phenomena associated with moisture adsorption by dried milk foams. 148th Natl. Meet., Am. Chem. Soc., A 18, Chicago, Ill., August-September.
- (8) Hanrahan, F. P., A. Tamsma, K. K. Fox, and M. J. Pallansch. 1962. Production and properties of spray-dried whole milk foam. *J. Dairy Sci.*, 45: 27.
- (9) King, N. 1965. The physical structure of dried milk. *Dairy Sci. Abstr.*, 27: 91.
- (10) Kontson, A., A. Tamsma, and M. J. Pallansch. 1965. Effect of particle size distribution on dispersibility of foam-spray-dried milk. *J. Dairy Sci.*, 48: 777.
- (11) Lampitt, L. H., and J. H. Bushill. 1931. The physico-chemical constitution of spray-dried milk powder. *Fat in spray-dried powder*. *J. Soc. Chem. Ind.*, London, 50: 45T.
- (12) Nickerson, T. A. 1965. Lactose. *In Fundamentals of Dairy Chemistry*. pp. 224-260. B. H. Webb and A. H. Johnson, eds. Avi Publishing Company, Westport, Conn.
- (13) Rockland, L. B. 1960. Saturated salt solutions for static control of relative humidity between 5 and 40 C. *Anal. Chem.*, 32: 1375.
- (14) Sharp, P. F., and H. J. Doob. 1941. Quantitative determination of α - and β -lactose in dried milk and dried whey. *J. Dairy Sci.*, 24: 589.
- (15) Supplee, G. C. 1926. Humidity equilibria of milk powders. *J. Dairy Sci.*, 9: 50.
- (16) Tamsma, A., L. F. Edmondson, and H. E. Vettel. 1959. Free fat in foam-dried whole milk. *J. Dairy Sci.*, 42: 240.
- (17) Troy, H. C., and P. F. Sharp. 1930. α - and β -lactose in some milk products. *J. Dairy Sci.*, 13: 140.