

## Reversibility of Water Vapor Sorption by Cottage Cheese Whey Solids

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### Abstract

Desorption isotherms for water vapor from cottage cheese whey solids vary with the way water is first sorbed by the whey solids. When water is sorbed progressively in small increments between zero pressure and saturation pressure, the powder becomes more porous during lactose crystallization. Subsequent desorption data follow a sigmoid pattern as a function of relative pressure. More water is desorbed from the powder than could be removed by evacuation before exposure to water vapor. Lactic acid also is desorbed from the whey solids under these conditions.

A sigmoid desorption isotherm representing higher moisture contents at all relative pressures is obtained when moisture sorption is accomplished in a single step at or near the saturation pressure. The latter type of desorption is considered more representative of the dehydration process in powder manufacture as moisture versus vapor pressure data for whey concentrates adhere closely to this isotherm. Cottage cheese whey concentrates contained more moisture than Cheddar cheese whey concentrates at the same relative pressure.

### Introduction

Extensive use has been made of water vapor sorption data in the development of dehydrated foods (7, 10) with the sorption isotherm considered (12) as the key to understanding water sorption properties of the food. Accordingly, both adsorption and desorption isotherms have been used to interpret phenomena during food dehydration and to predict the hygroscopicity and/or storage stability of the dried food product. Therefore, we measured the water sorption properties of whey solids to determine if it is possible to predict from such data whether a whey powder will be nonhygroscopic and free flowing or easily wetted and subject to rapid caking. More fundamentally, we tried to determine why it is more difficult to spray dry cottage cheese whey than Cheddar cheese whey (9).

Adsorption and desorption isotherms for water on Cheddar cheese whey solids have been reported (2), but only the adsorption isotherm was determined with the cottage cheese whey solids. When we extended our studies to determine the relationship between moisture content and vapor pressure in fluid or semi-solid whey concentrates, we found that the data were not in complete agreement with values expected from the adsorption isotherms. Therefore, we completed a detailed study of the reversibility of the water vapor sorption isotherms characteristic of cottage cheese whey solids.

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### Experimental Methods

*Water sorption measurements.* Water vapor sorption on cottage cheese whey solids was measured gravimetrically at 24 C. A Cahn Model RG recording electrobalance<sup>4</sup>, incorporated into a custom made glass adsorption apparatus was used as described (2). Reversibility in water sorption was studied by first measuring water uptake at relative pressures  $P$  ranging from .02 to .97 in increments of .05  $P_0$  (where  $P_0$  is the vapor pressure of  $H_2O$  at 24 C.) and then measuring water vapor desorption over the same  $P/P_0$  range. At the end of the desorption cycle the system was evacu-

ated to  $10^{-5}$  torr to determine if any water is irreversibly held by the powder under these conditions. A second series of measurements were then taken in the same fashion to compare consecutive adsorption-desorption cycles and thus to determine the influence of prior moisture uptake on subsequent sorptive capacity of cottage cheese whey powder. Alternatively, samples of whey powders were exposed initially to high humidities at or near the saturation pressure rather than sorbing water gradually through shifts in the pressure in increments of  $.05 P_0$ . After achieving equilibrium conditions near  $P_0$ , complete desorption isotherms were determined. In this manner we determined a desorption isotherm under conditions which are more relevant to the dehydration process.

Two lots of cottage cheese whey powder, foam spray dried in the Dairy Products Laboratory Pilot Plant, were in this study. In the manufacture of one lot, the whey concentrate ( $\sim 54\%$  total solids) was held overnight to allow for  $\alpha$ -lactose crystallization before spray-drying. The second lot was dried immediately after concentration to yield an experimental powder sample in which almost all of the lactose was in the amorphous state. Sorption measurements were also made with freeze-dried cottage cheese whey. The liquid whey was lyophilized in a laboratory freeze dryer, yielding a material with little crystalline  $\alpha$ -lactose. Lactose crystallinity was determined, after dissolution of the powder, by the polarimetric technique of Sharp and Doob (11). Optical rotation was read with a Perkin-Elmer Model 141 automatic polarimeter with digital read-out.

**Vapor pressure measurements.** Cottage and Cheddar cheese whey concentrates containing 40 to 70% total solids were prepared by dispersing commercial powders in distilled water. The concentrates were stored overnight at 5 C to allow any lactose mutarotation and/or changes in crystallinity. The fluid concentrates were placed in sample tubes suitably equipped with high vacuum stopcocks and connectors to permit attachment to a vacuum apparatus, which was designed for preliminary outgassing of samples and subsequent vapor pressure measurements. Dissolved air was removed from the concentrates by outgassing through several freeze-thaw cycles with liquid nitrogen to freeze the concentrates. After the stopcock leading to the pump was shut, the samples were thermostated at 21.6 C, and the equilibrium vapor pressures were read with an Octoil-S filled U-tube manometer. After these

measurements, the total solids contents of the concentrates were determined to account for any water evaporation during these operations.

Lactic acid was determined by the method of Lawrence (8).

## Results and Discussion

Sorption and desorption isotherms with a cottage cheese whey powder which initially contained 56.3% crystalline  $\alpha$ -lactose are in Fig. 1. A series of discontinuities appear in the initial sorption isotherm between relative pres-

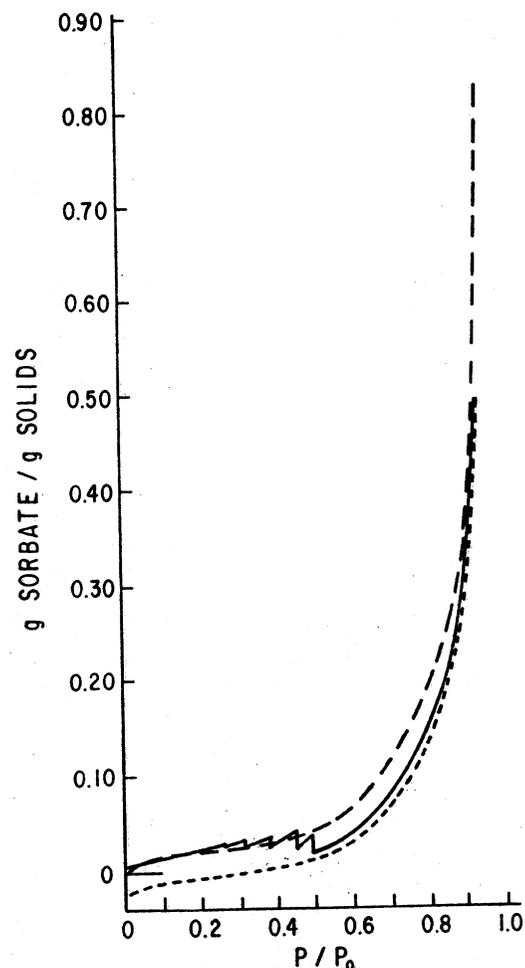


FIG. 1. Sorption and desorption isotherms (24 C) for foam spray dried cottage cheese whey powder (56.3% crystalline lactose). Solid curve: initial sorption isotherm. (---): first desorption isotherm and subsequent sorption-desorption cycle. (—): desorption isotherm for powder which sorbed  $H_2O$  at saturation pressure only. The experimental points followed the indicated curves but are omitted for clarity.

tures of .26 and .49. These are probably the effects of further lactose crystallization (2). Equilibration was slow at each of these points, requiring approximately 5 days for the mass of sorbed water to become constant. The relative pressure was maintained at each of these pressures until the mass of powder plus sorbed water remained constant for a minimum of 24 h. The subsequent desorption isotherm was a sigmoid type II (3) isotherm, which was almost perfectly coincident with the sorption isotherm above  $P/P_0 = .5$ . During desorption more vapor was removed from the powder than in the initial outgassing as the desorption isotherm crossed the original zero moisture axis at  $P/P_0 = .3$ . Zero moisture in the figure corresponds to the powder mass reached after outgassing ( $10^{-6}$  torr) 1 wk at ambient temperature prior to sorption measurements. We have chosen to present the sorption data based on this dry mass rather than the lowest mass after desorption to demonstrate more clearly the experimental observations.

Data with freeze-dried whey (Fig. 2) also demonstrate that more vapor is desorbed from powder following exposure to moisture through a complete sorption-desorption cycle. An earlier report (2) only showed adsorption isotherms for cottage cheese whey powders. Although desorption measurements were not over the entire range in relative pressure values  $0 \leq P/P_0 \leq 1.0$ , the samples were outgassed after the sorption measurements. Each of these powders displayed a greater weight loss during the final outgassing than in the original treatment before the sorption measurements.

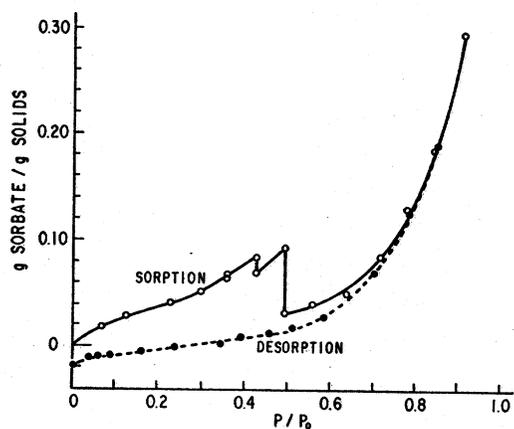


FIG. 2. Sorption and desorption isotherms (24 C) for freeze-dried cottage cheese whey. One cycle only.

The desorption data reported here for cottage cheese whey solids contrast sharply with results with Cheddar cheese whey and whole milk powders (2). Desorption measurements showed that .02 g sorbed water per g whole milk powder, and .03 g sorbed water per g Cheddar cheese whey powder remained irreversibly sorbed and could not be removed by outgassing ( $10^{-5}$  torr) at 25 C.

Further crystallization of lactose in whey powder during water sorption probably leads to changes in powder porosity which permit the escape into the vapor phase of material trapped in occlusions within the powder particles. We have reported increased permeability to  $N_2$  and  $CCl_4$  in dehydrated dairy products after lactose crystallization (1). Flink and Karel (4, 5) have reported that a number of volatile organic compounds are trapped in microregions in amorphous sugars (including lactose), when aqueous solutions of these sugars are combined with the organic compounds and freeze-dried. The organic volatiles are released upon crystallization of the sugar. Apparently, a similar mechanism operates during water sorption by whey solids. Their studies with the carbohydrates and small organic molecules suggested to us that lactic acid might become volatile upon lactose crystallization. Analysis of the whey sample used to obtain the sequential sorption-desorption data in Fig. 1 showed that it contained .5% lactic acid after the final desorption and outgassing whereas originally the powder contained 9.1% lactic acid. Admittedly, some lactic acid might have been lost during the original degassing as well as during the water vapor sorption-desorption cycle. The desorption data may represent both lactic acid and water vapor desorptions while some water remains irreversibly sorbed as with Cheddar cheese whey and milk powders (2). We presently are investigating the water sorption process in cottage cheese whey powders further to determine when lactic acid is released from the powder. The sorption data in this paper are reported as grams sorbate/grams solids since it is not possible as yet to distinguish between masses of water and lactic acid desorbed.

Isotherms (Fig. 1) representing the second sorption-desorption cycle on the same powder sample were almost perfectly superimposable upon the first desorption isotherm, indicating no further structural changes in the whey solids. Similar results were obtained with sequential isotherms with sweet whey and milk powders (2).

The desorption isotherm (Fig. 1), obtained when another sample of the same powder was immediately saturated with water vapor upon outgassing, was a type II isotherm lying above the other desorption isotherms at all  $P/P_0$ . The dry mass of the powder obtained at the end of the desorption measurements was identical with the mass reached during the initial outgassing. Apparently no further lactose crystallization occurred during this type of desorption experiment.

A similar set of data is in Fig. 3 for sorption and desorption measurements with two samples of cottage cheese whey powder contain-

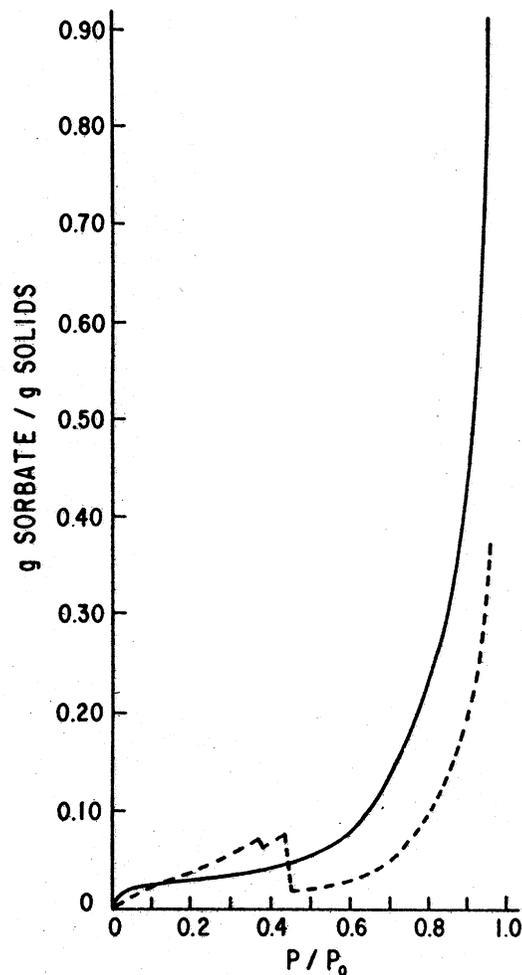


FIG. 3. Sorption and desorption isotherms (24 C) for foam-spray dried cottage cheese whey (8.8% crystalline lactose). Broken curve: initial sorption isotherm and subsequent desorption to  $.5P_0$ . Solid curve: desorption isotherm for powder exposed to  $H_2O$  vapor at saturation pressure only.

ing 8.8% crystalline lactose. One sample was allowed to sorb water in small increments over the range  $0 \leq P/P_0 \leq 1.0$  before desorbing water over the range  $.52 \leq P/P_0 \leq 1.0$ . The sample was accidentally lost at this point, and no further desorption measurements could be made; however, the nature of the desorption isotherm is evident from the available data. A second sample was initially exposed to water vapor near the saturation pressure and desorption then measured over the entire range  $0 \leq P/P_0 \leq 1.0$ . The differences between the two types of desorption isotherms are more pronounced here because of the low crystalline lactose. Some crystallization of lactose probably did occur during desorption from the rapidly water-saturated sample as there is an apparent shift in the desorption isotherm at  $P/P_0 = .62$ .

Results of the vapor pressure measurements with the whey concentrates are shown graphically in Fig. 4 as moisture content (g  $H_2O$ /g solids) vs water activity. Cottage cheese whey concentrates contained more

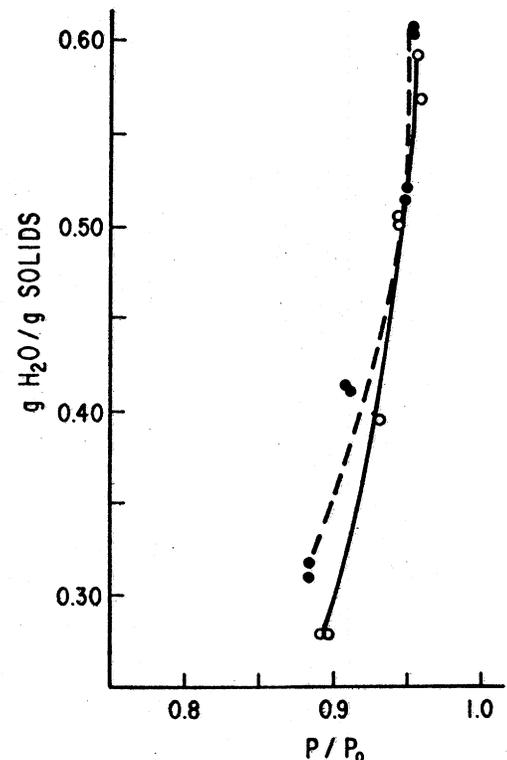


FIG. 4. Relationship of water content to vapor pressure in whey concentrates; ● cottage cheese whey, ○ Cheddar cheese whey.

moisture than Cheddar cheese whey concentrates at each  $P/P_0$ . These differences in water holding by the concentrates may be associated with the difficulties in spray drying cottage cheese whey (9). The moisture content vs activity data of Fig. 4 follow more closely the desorption isotherm with whey powder rapidly saturated with water than the desorption isotherm after first sorbing water in small increments over the entire sorption isotherm. Apparently, desorption measurements after such rapid water uptake correspond more closely to the dehydration process and might, therefore, be more useful in understanding dehydration phenomena.

#### Conclusion

Comparison of the desorption isotherms (Fig. 1 and 3) following rapid saturation of the sample with water to the initial sorption isotherms (Fig. 1 and 3) suggests that these desorption curves may correspond closely to the form the sorption isotherms might have taken were it not for lactose crystallization. This notion may be useful in predicting the maximum amount of water that may be sorbed before lactose crystallizes as  $\alpha$ -lactose $\cdot$ H<sub>2</sub>O and excess moisture is desorbed. It is suggested that when a whey powder containing lactose glass is exposed to water vapor at any relative pressure high enough for lactose crystallization, moisture will be sorbed up to the moisture content at that  $P/P_0$  on the desorption isotherm after rapid saturation. Upon taking up this maximum quantity of water, the powder will lose moisture as the lactose crystallizes and finally reach a minimum moisture content for that  $P/P_0$  as predicted from a desorption isotherm determined after first allowing the powder to sorb water in increments over the entire sorption isotherm. This hypothesis was tested with several whey powders containing 10 to 50% crystalline lactose. The powders were outgassed under high vacuum and then exposed to water vapor at  $P/P_0$  between .6 and .75. Indeed, the maximum and minimum moisture reached by the powders closely followed the two types of desorption isotherms described above.

The data demonstrate the significance of sample history and prior exposure to water in attempting to anticipate the hygroscopicity of

a dried food product such as cottage cheese whey. Similarly, Hagerdal and Lofqvist (6) have recognized the importance of considering an adsorption isotherm as a sample pretreatment which might affect subsequent adsorption and desorption measurement. Actually, all the materials examined in our study had once been dried, and it is possible that irreversible changes may have been introduced through the drying procedure. Further studies of water sorption phenomena might include desorption measurements with fluid whey.

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