

Water Vapor Sorption Properties of Various Dried Milks and Wheys

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Abstract

An electronic recording microbalance was incorporated into a gravimetric adsorption apparatus for precise study of adsorption and desorption phenomena on dehydrated dairy products. Data are reported for water sorption by spray-dried whey, skim milk, and whole milk powders as well as foam-spray-dried whey and milk powders. During the sorption measurements a weight maximum was observed in the area of $P/P_0 \approx 0.5$. The maxima in the adsorption curves are attributed to the occurrence of morphological changes in the sorbent. Evidence for the irreversibility of these morphological effects was obtained from repeated adsorption-desorption studies. The physical changes occurring in the powders may be associated with lactose crystallization, as the magnitude of the weight maxima with their concomitant distortion of the normal sigmoid sorption isotherm was inversely related to the lactose crystallinity in the powders.

Dehydrated milk products absorb sufficient water at moderate and high relative humidities to promote reactions leading to protein insolubility (7), increased free fat (11, 12), accelerated flavor deterioration (5, 15), and rapid caking of the powder bed (17). Since consideration of these effects is of prime importance in the development of stable dehydrated milk products, the moisture sorption properties of such materials have been extensively studied by many workers.

Due to the complex nature of the systems under investigation, these studies have resulted in the publication of much conflicting data. The isotherms for water adsorption on milk powder published by Supplee (14), Troy and Sharp (17), and Fox et al. (7) exhibited a discontinuity in the region of fifty per cent relative humidity. Reports of other investigators (10), however, showed only smooth isotherms with no breaks or discontinuities.

Much of this earlier work was carried out by

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the weighing bottle and desiccator method or by the dynamic method of Fox et al. (7). These methods are restricted by several experimental limitations. Individual powder samples cannot usually be carried through a complete adsorption-desorption cycle; the choice of humidity conditions is limited to that available with sulfuric acid or saturated salt solutions; and relatively large samples, one gram or more, are required, rendering the vapor sorption by the powder granules subject to the effects of diffusion through the powder bed.

The commercial development of reliable microbalances has made it convenient to design equipment to conduct sorption studies on very small samples, ca. 10 mg, with greater accuracy and increased flexibility in choice of pressure and temperature conditions. The present communication presents data so obtained for the sorption of water vapor by a variety of dehydrated dairy products prepared with different drying techniques.

Materials and Methods¹

Powders studied included dehydrated sweet whey, Cottage cheese whey, skim milk, and whole milk spray-dried in the Dairy Products Laboratory Pilot Plant, using either conventional methods or the foam-spray-drying method of Hanrahan et al. (9), as well as samples of commercially dried sweet whey and Cottage cheese whey.

Water vapor sorption was measured gravimetrically using the Cahn RG recording electrobalance coupled with a Houston Omnigraph Model 6520 potentiometric recorder. The balance was mounted in the vacuum bottle supplied by the Cahn Instrument Company so that measurements could be carried out in atmospheres of controlled humidity. The bottle was incorporated into an all glass custom-made adsorption apparatus equipped with pumps for outgassing the powders and with suitable devices for controlling and monitoring temperature and humidity.

High vacuum for powder degassing was

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

maintained with a mercury diffusion pump backed by a mechanical oil pump. Pressure in the system during the degassing operations was monitored with an Alphatron model 530 ionization type vacuum gauge.

The source of water vapor for the sorption experiments was a flask of triply distilled water connected to the balance chamber and maintained at a temperature lower than that of the powder sample. Initially the water was held through three cycles of freezing, pumping, and thawing to remove any dissolved gases. Variations in relative pressure were effected simply by varying the temperature of the bath surrounding the water vapor source. Pressure in the system during the course of the sorption experiments was monitored with an Octoil-S filled manometer.

Aluminum sample pans and nichrome stirrups were used as supplied by the balance manufacturer. They were suspended with a nichrome wire from the balance beam into a tube thermostated at 25.5 C with a constant temperature water bath. A chromel-alumel thermocouple was placed inside the tube in the vicinity of the sample pan and was wired through the balance control unit with temperature readout obtained with a Leeds and Northrup millivolt potentiometer.

A schematic diagram of the apparatus is shown in Figure 1.

In a typical experiment, a powder sample weighing 10-12 mg was spread out in a thin layer on the balance pan and degassed at room

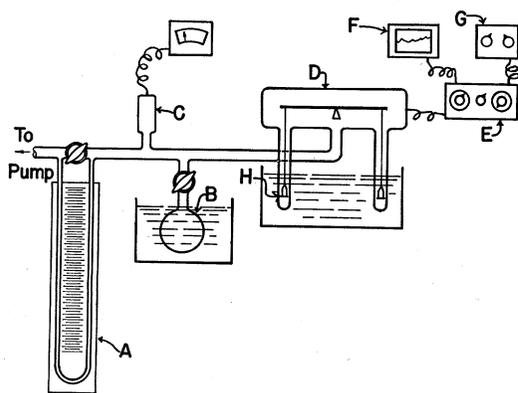


FIG. 1. Schematic diagram of the sorption apparatus. A, manometer; B, temperature controlled water as source of water vapor; C, alphatron vacuum gauge; D, Cahn RG electrobalance enclosed in vacuum bottle; E, balance control unit; F, potentiometric recorder for mass readout; G, millivolt potentiometer for temperature readout from thermocouple placed near sample pan, H.

temperature to remove adsorbed gases and vapors. Outgassing was considered complete when the powder mass remained constant for several hours at 10^{-4} torr. After degassing, the powder was exposed to water vapor at a relative pressure, P/P_0 , of .025 and allowed to sorb moisture until an equilibrium value was obtained. The relative pressure was then increased by raising the temperature an appropriate increment to obtain the desired increment in relative pressure. This procedure was repeated until the complete adsorption isotherm was obtained with adsorption points taken at increments of .05 P/P_0 units. Desorption measurements were obtained in analogous fashion by lowering the temperature of the water vapor source. It was thus possible to establish complete adsorption-desorption isotherms for the materials studied.

In these determinations the powders were considered to be at their equilibrium moisture contents only after the powder mass remained constant for at least several hours. The equilibration periods required varied with the relative humidity; however, in the moderate to high relative humidity range these periods were often several days.

Prior to measuring the adsorption of water by the powders similar procedures were carried out in the absence of any powder to obtain appropriate correction factors for adsorption on the balance pans and other components.

The crystallinity of the lactose present in several of the powders was assessed by the polarimetric method of Sharp and Doob (13).

Results

The isotherms obtained for water adsorption on and desorption from foam-spray-dried whole milk powder are shown in Figure 2. There are obvious deviations from a sigmoid isotherm as well as the appearance of hysteresis in the lower relative pressure segment of the isotherm.

The first half of the adsorption leg of the isotherm is very similar to a Type II isotherm with the point B break of Emmett and Brunauer (6) occurring in the vicinity of 0.1 relative pressure. There is, however, a sharp break in the isotherm at $P/P_0 \approx 0.6$, where the powder undergoes desorption at constant water vapor pressure. At relative pressures beyond the maximum the shape of the isotherm corresponds well with that of a Type II isotherm according to the classification of Brunauer et al. (4).

The desorption leg of the isotherm follows a smooth, sigmoid curve; however, there remains some absorbed water which is apparently irreversibly bound and cannot be removed

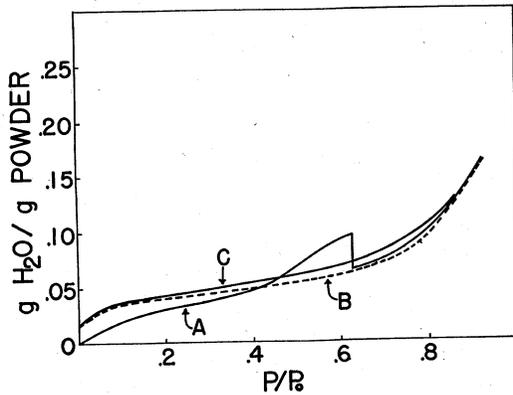


FIG. 2. Water sorption isotherm for foam-spray-dried whole milk at 24.5 C. Curve A, adsorption; Curve B, desorption; Curve C, readsorption. In the interests of clarity, no experimental points are shown in this and the following figures. Points were measured at intervals of .05 P/P₀.

even under high vacuum at 25 C. Subsequent adsorption data, obtained after the first complete adsorption-desorption cycle, yield smooth, reversible, sigmoid curves and are almost exactly superimposable upon the initial desorption isotherm.

Data for water adsorption on foam-spray-dried sweet whey are presented in similar fashion in Figure 3. The forms of the adsorption-desorption curves are the same as obtained for whole milk powder except that in the lower humidity ranges the magnitude of initial water sorption is somewhat lower on the whey powder. The data shown in Figure 3 are for foam-spray-dried whey powder prepared by injecting N₂ into the concentrate feed prior to atomization. Similar results were obtained for water sorption on foam-spray-dried whey powder

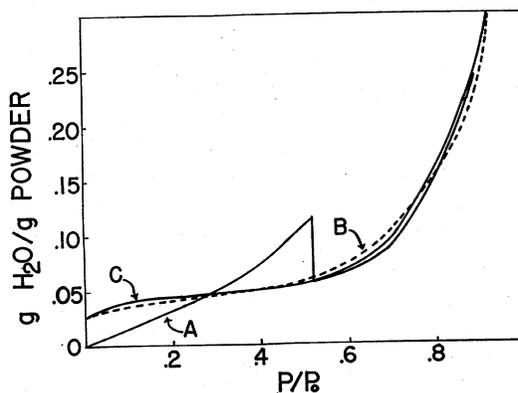


FIG. 3. Sorption isotherms for foam-spray-dried sweet whey. A, adsorption; B, desorption; C, readsorption.

when CO₂ was used in place of N₂ and on conventionally spray-dried whey powder (Fig. 6).

Comparative data for H₂O sorption on spray-dried whole milk and skimmilk powders are presented in Figure 4. Apparently the fat is less hygroscopic, hence the whole milk powder adsorbs less water. When the water sorption on the whole milk powder was calculated on a solids-not-fat basis, there was, however, very little difference between such a corrected isotherm and that observed for the skimmilk powder.

The adsorption isotherms obtained for conventionally spray-dried whole milk and foam-spray-dried whole milk are compared in Figure 5. There is apparently no difference in the equilibrium moisture contents of the powders, as the two isotherms are almost superimposable and differ only in the positions of the maxima on the two isotherms. Though the equilibrium values were essentially identical, there were differences in the adsorption rates with the foam-spray-dried powder exhibiting a faster rate of adsorption.

Data obtained for several types of whey powders are shown in Figure 6. The samples of commercial whey powders adsorbed less moisture than the Dairy Products Laboratory Pilot Plant experimental powders, and the breaks in the isotherms were also smaller in these cases. Both acid wheys showed a break in their respective isotherms at 0.35 P/P₀, which is substantially lower than that observed with all the other powders, i.e., 0.52 < P/P₀ < 0.625. The isotherm obtained for the foam-spray-dried Cottage cheese whey powder displayed a break at 0.35 P/P₀ and another at 0.45 P/P₀, after which the shape of the curve was that of a type II isotherm. The commercial

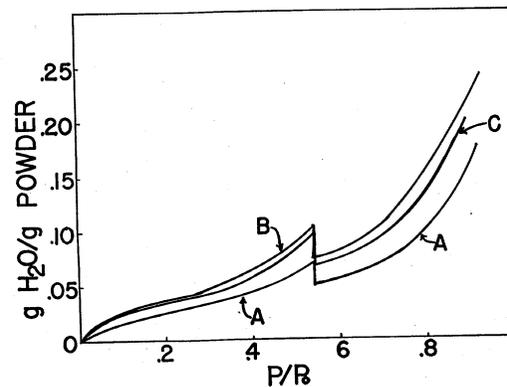


FIG. 4. Effect of fat content on water adsorption isotherms. A, spray-dried whole milk; B, spray-dried skimmilk; C, whole milk data corrected to a solids-not-fat basis.

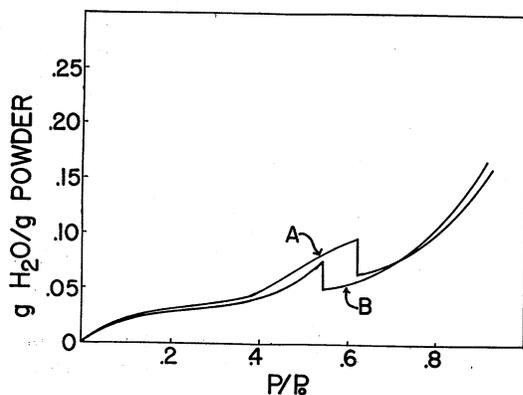


Fig. 5. Influence of drying method on water adsorption isotherm. A, foam-spray-dried whole milk; B, conventional spray-dried whole milk.

acid whey, though showing only one discontinuity at 0.35 P/P_0 , continued to desorb water over the entire range $0.35 < P/P_0 < 0.45$ when the isotherm assumed the shape of a type II isotherm.

The Cottage cheese whey powders differed from all the other powders studied in that they could not be completely degassed under the same conditions of 10^{-3} torr at 25 C. After these powders were held through the maximum in the isotherm they desorbed more H_2O ; and upon final degassing, after completing the adsorption measurements, sufficient water was removed so that the total mass of desorbed water, i.e., before and after adsorption, accounted for the total moisture content as determined by the standard toluene distillation method.

Discussion

The maxima observed in the sorption isotherms of the present study substantiate results

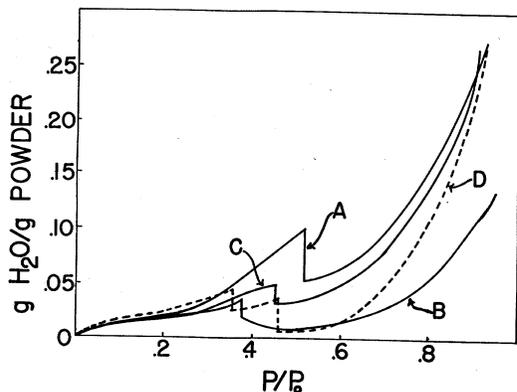


Fig. 6. Water adsorption isotherms for various whey powders. A, spray-dried sweet whey; B, commercial acid whey; C, commercial sweet whey; D, foam-spray-dried Cottage cheese whey.

published by Supplee (14), Troy and Sharp (17), and Fox et al. (7). However, they conflict with data published by Heldman et al. (10), who reported only smooth sigmoid isotherms with no discontinuities.

Weight maxima of the type reported here are often ascribed to artifacts or thermomolecular flow influences, and lastly, when the data cannot be discounted for such reasons, they are associated with phase changes occurring in the sorbent as a result of the sorption.

Thermomolecular flow effects, in the form of spurious weight changes, due to temperature gradients along the hangdown wire in such micro-weighing techniques are often encountered in the pressure range of 10^{-3} to 10 torr; however, Thomas and Williams (16) have reported thermomolecular flow effects at high pressures as well. These were manifested in the form of a maximum in the adsorption isotherm for krypton on charcoal held at -78 C. Thermomolecular flow effects can be eliminated as a source of error in our results because we have conducted additional experiments (1) using other procedures where thermomolecular flow could not occur, and we still observed weight maxima in the isotherms.

Another source of error, leading to maxima in adsorption isotherms and reported by Gordon (8) in a study of the sorption of organic vapors by high polymers, involved pressure changes in the system due to adsorption on the balance and other parts of the experimental set up. In our experiments the water vapor pressure in the system was carefully monitored and we can exclude this source of error.

We are thus convinced that the isotherms reported in the present communication are correct. The absence of any breaks in the isotherms reported by some workers may be attributed to their failure to measure the mass sorbed at sufficiently close intervals on the relative pressure scale. For example in the work reported by Heldman et al. (10) equilibrium moisture values were only determined at relative humidities of approximately 20, 40, 60, and 90%. Upon examining the isotherms reported in the present paper it becomes obvious that determinations made only at the four stated intervals could lead to erroneous results in the basic shape of the isotherm. Furthermore, the technique used by Heldman et al. (10) was actually a desorption method, hence leading to different results.

Obviously the discontinuity in the isotherm is associated with some phase change occurring in the sorbent. Supplee (14) associated this

behavior with a change taking place in the protein fraction. However, Troy and Sharp (17) and most later workers have associated the discontinuity with lactose crystallization. Initially the lactose in milk powder is present in the form of an amorphous glass which is very hygroscopic. However, once it absorbs sufficient water, the lactose crystallizes as the α -monohydrate, which is a relatively nonhygroscopic form, thus losing water upon the completion of the crystallization process. This latter view may be substantiated with the data reported in the present study by comparing the adsorption isotherms obtained for conventionally spray-dried sweet whey and the commercial sweet whey (Figure 6). The spray-dried whey powder was an experimental powder manufactured in the Dairy Products Laboratory Pilot Plant and contained 1.7% crystalline lactose, while the commercial powder contained 69.0% crystalline lactose. Clearly the amount of water sorbed at the maximum and the magnitude of the drop in the isotherm are inversely related to the amount of lactose present in the powder in crystalline form. A similar relationship between lactose crystallinity and adsorption behavior was noted in a series of skim milk powders, though not reported here in detail.

The most significant difference between the adsorption data obtained for milk and whey powders was that the initial sorption in the lower portion of the isotherm is much greater on milk powder than on the whey powders. These whey powders were approximately 70% lactose. Hence it is apparent that the initial site of sorption in milk powder is not the lactose glass nor is it the whey proteins, but more likely a water-protein binding involving casein is the initial interaction.

Heldman et al. (10) suggested a mechanism for water adsorption by milk powder, first involving adsorption on the external surface of the particles, followed by sorption by the lactose glass, and finally, water diffusion into the particles and protein swelling. Several arguments can be presented in support of our hypothesis that the initial interactions at lower relative humidities involve a water-bulk protein interaction. The fact that the equilibrium moisture values for whole milk powder (Fig. 5) are identical for foam-spray-dried and spray-dried powders indicates that the initial sorption is not restricted to the external surface but rather there is immediate binding of water by some identical bulk phase component. The observed differences in adsorption rates between the powders may, however, be readily understood in terms of their physical structure and

permeability. Foam-spray-dried materials consist of hollow porous granules which are readily penetrated by gases, while conventionally spray-dried powder granules are dense and relatively impervious to gases (3). Hence adsorption may initially occur more rapidly on the foam-dried materials since the bulk phase interaction sites are initially more accessible in these powders; however, the equilibrium values should be independent of the drying method, as was observed.

On the basis of fluorescence microscopy observations and from calculations based on the energy of adsorption of N_2 , we have demonstrated in an earlier publication (2) that the fat in conventionally spray-dried whole milk powder is present in the form of surface films. If the adsorption of water at lower relative humidities is restricted to the external surfaces of the powder, the presence of such a hydrophobic film on the surface should limit the amount of water sorbed in the initial portion of the isotherm for whole milk, even when the data are corrected to a non-fat basis. The data in Figure 4 clearly show that in the first half of the isotherm the amount of water sorbed by the skim milk powder and the solids-not-fat portion of the whole milk powder are almost identical. These results are however quite reasonable if the sorption at lower relative humidities involves water-protein binding followed by swelling of the protein matrix.

Of all the powders studied, outgassing difficulties were encountered only with the Cottage cheese wheys. Apparently these whey powders must differ structurally from the other powders studied. It is possible that the hindrance in degassing is related to a molecular sieve structure which is destroyed as the powder undergoes the phase transformation at the break point, thus permitting more complete degassing after this sorption point. This behavior is analogous to observations previously reported (1) concerning the effects of moisture sorption on the permeability of other dehydrated dairy products.

Observations have been made (18) that foam-spray-drying produces a powder which has superior free-flowing characteristics, with less of a tendency to cake in humid environments than comparable spray-dried materials. It was therefore suggested that foam-spray-dried powders are less hygroscopic than those spray-dried in conventional fashion. From the data reported in this paper for sorption by both types of powders it is apparent that there is no simple and straightforward relation between hygroscopicity and milk powder caking. The de-

termination of the causative factors in the caking of such powders thus remains an unsolved problem which is presently being studied.

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