SPECIFIC SURFACE AREAS OF MILK POWDERS PRODUCED BY DIFFERENT DRYING METHODS

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SUMMARY

Low-temperature (−195 C) adsorption of N_2 was used to study the physical surface features of whole and skimmilk powders produced by different drying techniques. Specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) multilayer adsorption theory. All the milk powders exhibited rather low surface areas ($\sim$ .1-.6 m^2/g) and abnormally low values for the energy of adsorption of N_2. Comparison of these surface areas with those obtained by permeametry yielded information on the relative porosities of the various powders. Conventional spray-dried powders were less porous than the instantized powders and the spray-dried foams.

In addition, the surface areas of several milk constituents, including lactose, α-lactalbumin, β-lactoglobulin, and Na-α-caseinate, were measured.

The further development of improved milk powders can be aided by fundamental knowledge concerning the effect of various drying techniques on the physico-chemical properties of the powder particles.

This paper presents data pertaining to the specific surface areas of milk powders produced by several drying techniques. Since measurement of the low-temperature (−195 C) adsorption of nitrogen by powder particles formed the basis of this study, the energetics of the adsorption process were analyzed for information descriptive of the chemical composition of the surfaces of the powder particles.

The specific surface areas of milk powders presented here were compared to the smoothed or streamline surface areas previously published (6) after a permeametric study of gas flow through beds of the same powders. This comparison was made to ascertain the relative surface roughness or porosity of the various types of powder particles and was found to correlate well with the relative rates of gas diffusion into these materials, as observed during a study of their true and apparent densities (2).

Wendt (22) has compared surface areas obtained with permeametry and adsorption techniques in his study of the physical features of particles of proteolyzed flour, cocoa powder, and quartz. Although he used gas adsorption to measure the surface area of spray-dried nonfat milk powders, he did not determine their areas by permeametry and made no attempt to evaluate their surface roughness.

Received for publication November 8, 1963.

During our study the adsorption of nitrogen by samples of powdered lactose, α-lactalbumin, β-lactoglobulin, and the sodium salt of α-casein was also measured.

MATERIALS AND METHODS

Milk powders used in this study were chosen to represent whole milk and nonfat products now commercially available, as well as the vacuum-dried foam and spray-dried foam powders developed during the course of recent research.

In the Dairy Products Laboratory experimental samples of vacuum-dried foam powders were made using the procedure of Sinnamon et al. (18), with minor variations as previously described (19, 20). The process entails pasteurization, condensation to 50% total solids, homogenization, incorporation of nitrogen gas, and drying the resultant foam at low temperatures in a vacuum shelf dryer.

Spray-dried foam powders were produced as described by Hanrahan et al. (9) using a 9-ft Swensen spray dryer[1] modified to inject high-pressure nitrogen gas into the feed prior to atomization.

Samples of commercial spray-dried and instantized materials were obtained through local trade channels. Table 1 lists the source and type of powders used in this study.

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

TABLE 1

Description of adsorbents and surface area data

Sample no.	Drying method and type of powder	Source	Surface area (m²/g) BET	Surface area (m²/g) Permeametry	Roughness factor	BET "C" value
	Milk powders					
1	Spray-dried skim (SDS)	DPL[a]	.21	.23	.91	15.9
2	SDS	Comm[b]	.27	.26	1.04	26.9
3	SDS	DPL	.22	....	......	10.0
4	Spray-dried whole (SDW)	DPL	.10	....	......	27.8
5	SDW	DPL	.16	....	......	10.7
6	SDW	DPL	.23	....	......	10.7
7	SDW	Comm	.21	.12	1.75	17.2
8	Vacuum foam-dried skim (VFDS)	DPL	.16	.05	3.20	14.0
9	VFDS	DPL	.18	....	......	38.9
10	Vacuum foam-dried whole (VFDW)	DPL	.35	....	......	24.9
11	VFDW	DPL	.52	....	......	25.6
12	VFDW	DPL	.24	....	......	100.2
13	VFDW	DPL	.36	....	......	20.3
14	VFDW	DPL	.51	.09	5.67	77.7
15	Foam spray-dried whole (FSPW)	DPL	.56	.11	5.09	19.2
16	FSPW	DPL	.40	....	......	13.4
17	FSPW	DPL	.64	....	......	21.3
18	Instantized skim (IS)	Comm	.24	.04	6.00	23.2
19	IS	Comm	.21	.05	4.20	46.4
20	IS	Comm	.16	.06	2.67	55.4
21	IS	Comm	.14	.04	3.50	27.7
	Milk components					
β-Lactoglobulin			.63	....	......	153.4
α-Lactalbumin			15.01	....	......	31.7
α-Casein (Na salt)			12.21	....	......	62
β-Lactose			.83	....	......	71.9
α-Lactose, monohydrate			.33	....	......	67.6

[a] DPL—Experimental powders prepared in the Dairy Products Laboratory Pilot Plant.
[b] Comm—Samples of commercial powders purchased off the supermarket shelf in Washington, D. C.

α-Lactose monohydrate was purchased from the Fisher Scientific Company[1] and β-lactose was purchased from Eastman.

Milk proteins were prepared according to published methods: β-lactoglobulin and α-lactalbumin by the method of Gordon, Semmett, and Ziegler (7) and α-casein by the method of Hipp et al. (11). All proteins were dried by lyophilization.

The helium (Southern Oxygen Company[1]) used for the free space measurements was purified by passing it through a charcoal trap maintained at −195 C with a liquid nitrogen bath. The charcoal was first degassed at 250-300 C for several hours to remove any adsorbed impurities. Prepurified nitrogen (Southern Oxygen Company[1]) was passed through a liquid nitrogen–cooled trap to remove any traces of moisture before use.

Nitrogen adsorption was measured volumetrically with an all-glass custom-made adsorption apparatus. This apparatus was of the conventional type, the construction and operation of which has been described in the literature (1, 16). Included were such refinements as a mirrored meter stick to reduce parallax errors in manometer readings and an electronic contact indicator (1, 14) to insure precision in setting the zero reference point on the manometer and to keep the dead space constant.

Prior to measuring the adsorption, the powders were degassed under high vacuum maintained by a mercury diffusion pump in series with a mechanical oil pump. All samples were degassed at room temperature while a few runs were made in which the powders were also degassed at 35-40 C. Preliminary studies indicated degassing could be considered complete when the pressure in the system remained in the 0.01 to 0.005 μ range. This could usually be accomplished by degassing 12 hr at room temperature.

The crystallinity of the lactose in finished powder particles was measured by X-ray diffraction. These results were verified with the more conventional polarimetric technique of Sharp and Doob (17).

The free fat in the whole milk powders was determined by the method of Tamsma et al. (19).

The physical dimensions of the powder particles and their surface fat globules were observed with a microscope equipped with a micrometer eyepiece, barrier filters, and a high-pressure mercury lamp as a light source. The powders were suspended in propylene glycol containing phosphine and illuminated with ultraviolet light for observations of the surface fat globules.

RESULTS

The N_2 adsorption data were used to calculate the specific surface areas presented in the fourth column of Table 1. All the milk powders exhibited rather low surface areas ranging from 0.1 to 0.6 m^2/g. The lowest values were obtained for conventional spray-dried powders and for instantized powders; hence, little fusion of the spray-dried particles occurs during the instantizing process. The more porous foam spray-dried powders exhibited somewhat higher areas.

A positive correlation was observed between the specific surface areas of the vacuum-dried whole milk foams and their free fat content (Table 2). But, increasing the free fat content of a commercial spray-dried whole milk powder of an initial free fat content of less than 1% to as much as 50% by hydration did not affect the surface area of the powder.

The areas of the instantized samples were not related to the crystallinity of the lactose in the powder particles, as X-ray diffraction indicated that Powders 19 and 20 contained no crystalline lactose, whereas Powders 18 and 21 contained 17 and 14% crystalline lactose, respectively.

Surface area values obtained by permeametry (6) are presented in the fifth column of Table 1. Since the gas adsorption technique should measure total surface area of the powder particles and permeametry yields areas of smoothed or streamlined surfaces the ratio of BET area to permeametry area should yield a value related to the surface roughness or porosity of the powders. These values are listed as roughness factors in Column 6 of Table 1. These results show that even though all powders possess relatively low specific surface areas, they vary widely in roughness. Conventional spray-dried materials derive very little of their total surface area from crevices or internal cavities. However, the agglomeration of this material by the instantizing operation produces a reduction in the permeametric specific surface area, with an increase in surface roughness or porosity. Both types of foam-dried material are characterized by roughness factors of similar magnitudes.

A calculated value related to the energy of adsorption occurring on the milk powder surface is presented in the last column of Table 1, along with similar data obtained from a study of the adsorption of nitrogen by pure milk constituents. These data indicate differences in binding energies which may be related to the surface composition of the powder particles as well as their structure.

DISCUSSION

The increase in surface area of the vacuum-dried whole milk foams with higher free fat content substantiates prior claims that the free fat is present on the surface of the particles (19). The absence of an increase in surface area of spray-dried powders with higher free fat values indicates a difference in the disposi-

TABLE 2

Effect of free fat on the surface area of foam-dried whole milk powder

Per cent free fat content of powder	△ Free fat	BET area m^2/g	Calculated area[a] m^2/g	Area BET / Area calc.
9.2	0	.24	....	......
17.0	7.8	.36	.31	1.16
26.0	16.8	.52	.39	1.33
30.0	20.8	.59	.48	1.23

[a] Area of △ free fat + .24 m^2/g.

tion or dispersion of the free fat in these powders as compared to the foam-dried materials. As observed by fluorescence microscopy, the fat in foam-dried whole milk powders exists on the surface of the powder particles in the form of small fat globules, whereas the fat was present on the surface of spray-dried powders as lakes or films.

The contribution of the free fat globules to the total surface area of vacuum-dried whole milk foam was ascertained from calculations based on observations that the fat globules on the powder surface had an average diameter of 2 μ. Assuming a fixed surface area of the base powder particle, the anticipated increase in the total surface area with increase in free fat content of the powder was determined. The agreements between calculated and observed values were good, as shown in Table 2. Therefore, we conclude that the free fat in the vacuum-dried whole milk foams exists as discrete globules contributing significantly to the total area of the powder. The mode of interaction of N_2 at -195 C with the fat is then one of adsorption rather than solubilization.

The surface areas presented in this paper were calculated using the limited form of the Brunauer-Emmett-Teller (BET) Equation (4):

$$\frac{X}{V\,(1-X)} = \frac{1}{V_m C} + \frac{(C-1)\,X}{V_m C} \qquad (1)$$

where X is the relative pressure, P/P_o, for the adsorbate; V is the volume of gas (S.T.P.) adsorbed at relative pressure X; V_m is the volume of adsorbate required to form a monolayer on the surface of the adsorbent; and C is a constant given by the equation:

$$C = \frac{a_1 b_2}{a_2 b_1} \exp \frac{(E_1 - E_L)}{RT} \qquad (2)$$

The coefficient of the exponential is considered to be approximately unity; E_1 is the heat of adsorption in the first layer; E_L is the heat of liquefaction of the adsorbate, R is the gas constant, and T is the absolute temperature. A plot of the left-hand side of Equation (1) against the relative pressure, P/P_o, yields values for V_m and the constant C. Typical BET plots for milk powders are shown in Figure 1.

This limited form of the BET equation is based on the assumption that on a free surface an infinite number of layers can be adsorbed. This is valid especially for adsorbents exhibiting Type II adsorption isotherms after the classification of Brunauer et al. (3). Since the adsorption of nitrogen on milk powder surfaces is described by Type II isotherms, use of the limited form of the BET equation is justified.

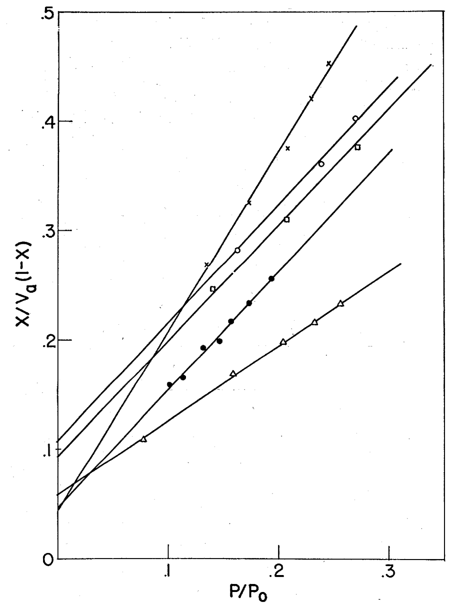

FIG. 1. BET plots for several dried milk powders. ● Foam-dried whole milk, △ Conventional spray-dried whole milk, □ Foam spray-dried whole milk, ○ Spray-dried skimmilk, × Commercial instantized skimmilk.

It has been shown that foam spray powders contain micropores or pores of molecular dimensions (2) through which nitrogen will diffuse slowly. For such materials the amount of nitrogen adsorbed on the surface of the pore walls will then depend upon the sizes of the pore openings.

BET multilayer adsorption theory yields another isotherm expression if the adsorption is not occurring on a free surface but is limited in amount by the walls of very narrow pores. When the number of layers on each pore wall is restricted to n, then the limited summation leads to the equation:

$$V = \frac{V_m C X}{1-X} \cdot \frac{1-(n+1)X^n + nX^{n+1}}{1+(C-1)X - CX^{n+1}} \qquad (3)$$

where X is the relative pressure P/P_o. Under conditions in which the surface is free and adsorption is not limited, $n = \infty$, and Equation (3) reduces to Equation (1). For foam spray powders we have found it advantageous to use the limited BET formulation (Equation 1) to obtain values of V_m and C and the more general n form to indicate the number of layers of adsorbate.

Joyner, Weiberger, and Montgomery (13) have developed a method for using the general form of the BET equation to find C, V_m, and n.

They have derived two functions $\Phi\ (n,X)$ and $\Theta\ (n,X)$ where

$$\Phi\ (n,X) = \frac{X - (n+1)\ X^{n+1} + nX^{n+2}}{(1 - X^2)} \qquad (4)$$

and

$$\Theta\ (n,X) = \frac{X - X^{n+1}}{1 - X} \qquad (5)$$

and have calculated values of these functions for different values of n and X. From the experimental data the function $\Phi\ (n,X)/V$ is calculated for different values of n and X and curves are plotted of $\Phi\ (n,X)/V$ against $\Theta\ (n,X)$ for different values of n. Proper choice of the n value will then yield a linear plot. From the Joyner, Weinberger, Montgomery plot shown in Figure 2 it is seen that the

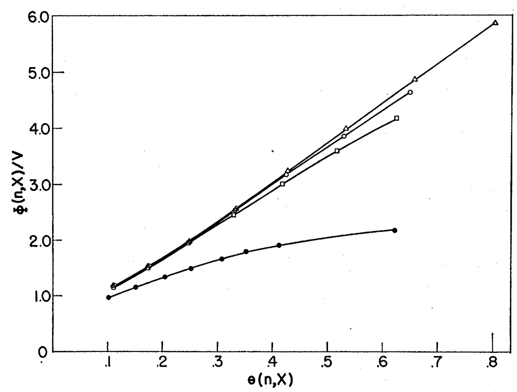

FIG. 2. Joyner, Weinberger, Montgomery plot for extended form of BET equation ● $n = 1.05$; □ $n = 3.0$; ○ $n = 4.0$; △ $n = 5.0$.

most suitable value of n is approximately 4. This means four layers of nitrogen can adsorb on the surface of the pore walls and, using the value 4.00 A for the diameter of the nitrogen molecule in the liquid state (15), one can state that the pores in foam spray-dried whole milk powders are of the order of 30 A in diameter.

Emmett and DeWitt (5) have shown that the average pore size can be estimated by assuming that all the pores are cylinders. Then, if the entire surface is attributed to the pore walls, the average pore radius is given by

$$\bar{r}_p = 2V_p/S_w \qquad (6)$$

where V_p is the pore volume. The total pore volume is obtained from the adsorption isotherm (Figure 3) because at $P/P_o = 1.0$ all the pores should be completely filled with condensed or liquefied adsorbate. We then have at the saturation pressure, $V_{ads.} = 0.97$ cm^3 (S.T.P.)/g and $V_p = (.001558)\ (.97)$ or

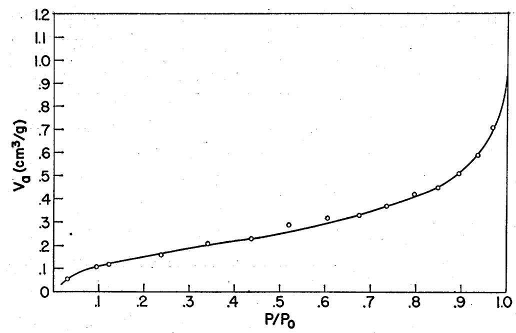

FIG. 3. Adsorption isotherm for N_2 (−195 C) on spray-dried whole milk foam.

0.00151 cm^3/g as the pore volume filled with liquid adsorbate. Employing Equation (6), $\bar{r}_p$, the average pore radius, is 47 A. This indicates a pore size larger than that obtained by the Joyner, Weinberger, Montgomery technique; however, this is only an average pore size for the powder bed and corresponds to such small pores as well as a number of larger ones including those resulting from interparticle condensation, whereas the n value corresponds to the small pores wherein the surface is restricted.

Values for the constant C of the BET equation as listed in Table 1 for most milk powders and for α-lactalbumin are abnormally low being in the range of 20 or 30, as compared to values of 100 or 200 for most other solids. The lower C values indicate lower heats of physical adsorption for nitrogen on these materials than on other solids. Recently, Hightower and Emmett (10) have reported similar C values for the physical adsorption of nitrogen on high polymers. These polymers, including polyethylene, polypropylene, and others, exhibited surface areas of about 0.5 m^2/g, which is in the same range as many of our dried milk powders.

Walker and Zettlemoyer (21) were the first to report the existence of heterogeneous surfaces with two or more C values characterizing different fractions of a surface. They developed a dual-surface BET theory and showed how their results with N_2 adsorption on MgO fit their theory.

Joy (12) has developed a means of treating heterogeneous surfaces based on a method derived from statistical mechanics. His treatment agreed with the results obtained by Walker and Zettlemoyer on MgO and with his own results on a dichlorodifluromethane-anatase surface. Joy arrived at the equation:

$$\frac{1}{C_t} = \frac{m_1}{C_1} + \frac{m_2}{C_2} = \frac{X_1}{C_1X_t} + \frac{X_2}{C_2X_t}$$

where C_1 and C_2 are the C values for Components 1 and 2, respectively, of a dual surface; X_1 and X_2 are the number of sites occupied by adsorbed molecules on the two surface components, respectively, being the same as the number of molecules adsorbed in the first layer; X_t is the sum of X_1 and X_2; and C_t is the composite C value for the total surface. We have applied his treatment to our data on foam-dried whole milk powders varying in free fat content and have arrived at a C value characteristic of the fat globules and another C value for the remainder of the surface which showed good agreement with our C values for foam-dried skimmilk powder. For our computations we used the experimentally determined C value from the conventional BET plots as C_t. Equation (7) was then used to derive a C value for the fat globules (C_2) and for the foam-dried skimmilk (C_1). The numbers X_1 and X_2 are determined by calculating the surface areas of the fat globules (using an average globule diameter of 2 μ and a fat density of 0.93 g/cm^3) and then subtracting this area from the total BET area of the powder; these surface areas are then divided by the cross-sectional area of the nitrogen molecule to get the numbers, X_1, X_2, and X_t, of N_2 molecules adsorbed. Using data for two foam-dried powders containing 9.2 and 26% free fat content we found $C_1 = 19.6 \approx 20$ and $C_2 = 50$. Substitution of these values into Equation (7) for another sample of foam-dried whole milk with 17% free fat yielded a calculated C_t of 25.7, which agrees well with the observed value of 20.3.

The results of these calculations encourage speculation that the higher energy of adsorption displayed by the fat surface for binding nitrogen may actually be observed with other gases. The free fat, when in globular form, may then serve as an efficient accumulator for the oxygen required to maintain the high rate of oxidation observed in this portion of the fat phase (8).

ACKNOWLEDGMENT

We thank D. Lutz and L. P. Witnauer of the Eastern Regional Laboratory, ARS, USDA, Wyndmoor, Pennsylvania, for the X-ray diffraction measurements.

REFERENCES

(1) Barr, W. E., and Anhorn, V. J. Scientific and Industrial Glass Blowing and Laboratory Techniques. pp. 257-283. Instruments Publishing Company, Pittsburgh, Pa. 1959.

(2) Berlin, E., and Pallansch, M. J. Influence of Drying Methods on Density and Porosity of Milk Powder Granules. J. Dairy Sci., 46: 780. 1963.

(3) Brunauer, S., Deming, L. S., Deming, W. E., and Teller, E. On a Theory of the Van der Waals Adsorption of Gases. J. Am. Chem. Soc., 62: 1723. 1940.

(4) Brunauer, S., Emmett, P. H., and Teller, E. Adsorption of Gases in Multimolecular Layers. J. Am. Chem. Soc., 60: 309. 1938.

(5) Emmett, P. H., and DeWitt, T. Determination of Surface Areas of Pigments, Carbon Blacks, Cement and Miscellaneous Finely Divided or Porous Materials. Ind. Eng. Chem., Anal. Ed., 13: 28. 1941.

(6) Fox, K. K., Holsinger, V. H., Harper, M. K., Howard, N., Pryor, L. S., and Pallansch, M. J. The Measurement of the Surface Areas of Milk Powders by a Permeability Procedure. Food Technol., 17: 127. 1963.

(7) Gordon, W. G., Semmett, W. F., and Ziegler, J. Crystalline α-Lactalbumin: An Improved Method for Its Isolation. Sulfur Distribution. J. Am. Chem. Soc., 76: 287. 1954.

(8) Greenbank, G. R., and Pallansch, M. J. The Progress of Oxidation in the Milk Powder Granule. XVIth Intern. Dairy Congr., Section V: 2, 1002. 1962.

(9) Hanrahan, F. P., Tamsma, A., Fox, K. K., and Pallansch, M. J. Production and Properties of Spray Dried Whole Milk Foam. J. Dairy Sci., 45: 27. 1962.

(10) Hightower, J. W., and Emmett, P. H. Measurement of the Surface Area of High Polymers by the Adsorption of Nitrogen at −195° C. The Johns Hopkins University, Dept. of Chemistry Annual Research Rept., p. 25. July, 1961.

(11) Hipp, N. J., Groves, M. L., Custer, J. H., and McMeekin, T. L. Separation of α-, β-, and γ-Casein. J. Dairy Sci., 35: 272. 1952.

(12) Joy, A. S. The Effect of Heterogeneity on the Shape of the Adsorption Isotherm. Second Intern. Congr. of Surface Activity II Solid-Gas Interface. 54-63. 1957.

(13) Joyner, L. G., Weinberger, E. B., and Montgomery, C. W. Surface Area Measurements of Activated Carbons, Silica Gel, and Other Adsorbents. J. Am. Chem. Soc., 67: 2182. 1945.

(14) Mills, B. A Sensitive Contact Indicator. Rev. Sci. Instr., 12: 105. 1941.

(15) Moore, W. J. Physical Chemistry. p. 179. Prentice Hall, Englewood Cliffs, N. J. 1955.

(16) Orr, C., Jr., and Dalla Valle, J. M. Fine Particle Measurement. pp. 172-188. Macmillan Company, New York. 1959.

(17) Sharp, P. F., and Doob, H. J. Quantitative Determination of α- and β-Lactose in Dried Milk and Dried Whey. J. Dairy Sci., 24: 589. 1941.

(18) SINNAMON, H. J., ACETO, N. C., ESKEW, R. K., AND SCHOPPET, E. F. Dry Whole Milk. I. A New Physical Form. J. Dairy Sci., 40: 1036. 1957.

(19) TAMSMA, A., EDMONDSON, L. F., AND VETTEL, H. E. Free Fat in Foam-Dried Whole Milk. J. Dairy Sci., 42: 240. 1959.

(20) TAMSMA, A., PALLANSCH, M. J., MUCHA, T. J., AND PATTERSON, W. I. Factors Related to the Flavor Stability of Foam-Dried Whole Milk. I. Effect of Oxygen Level. J. Dairy Sci., 44: 1644. 1961.

(21) WALKER, W. C., AND ZETTLEMOYER, A. C. A Dual Surface BET Adsorption Theory. J. Phys. Colloid Chem., 52: 47. 1958.

(22) WENDT, W. Zur Bestimmung der spezifischen Oberfläche pulverformiger Substanzen mittels Gas-Adsorption. Fette u. Seifen, 57: 910. 1955.