[CONTRIBUTION FROM THE NORTHERN REGIONAL RESEARCH LABORATORY[1]]

Surface Area of Starch and its Role in Water Sorption

BY N. N. HELLMAN AND E. H. MELVIN

The amounts of water which starches contain when at equilibrium with atmospheres of different moisture content vary with the botanical source from which the starch is derived.[2] The following investigations were undertaken to evaluate the importance of surface area of the starch in determining its water-sorptive capacity. If starch granules be porous, the contribution of surface area to water-sorptive capacity could be a determining factor.

The surface area of starches was calculated by the methods of Brunauer, Emmett and Teller,[3] from experimentally determined sorption isotherms of nitrogen at −195°. For the purpose only of providing a surface area for comparison, the equation of Brunauer, Emmett and Teller (BET) was also applied to the interpretation of the water-sorption isotherms of the same starches whose nitrogen-sorption isotherms were measured.

Experimental

Materials.—To provide a range of water-sorptive capacities and a range of granule size, four different starches—corn, potato, tapioca and dasheen—were chosen for investigation. The corn, potato and dasheen starches were extracted from the grain or tubers at this Laboratory. Distilled water was used to separate the starch from the ground-up source material. Drying temperatures of the extracted starches in processing procedures did not exceed 45°. The tapioca starch was a first-grade commercial starch.

The pre-purified grade of nitrogen supplied by Air Reduction Company and quoted as being 99.94% pure, was used for sorption as supplied from the tank. For dead-space determinations, tank helium, $98^+\%$ pure, was used.

Apparatus and Procedures.—The nitrogen-sorption isotherms were determined by means of a volumetric gas apparatus described by Emmett.[4] Because only small amounts of nitrogen gas were adsorbed, refinements in the apparatus were necessary, such as electrical contacts to locate precisely the mercury menisci, low dead-space sample bulbs as described by Barr and Anhorn,[5] and cathetometer measurement of pressures to a precision of 0.01 mm. in a wide-bore manometer. Equilibrium between the sample and the gas pressure was apparently achieved within ten minutes of a change and no hysteresis between adsorption and desorption points was observed. Starch samples were degassed by heating at 105° for 24 hours at a pressure of 10^{-6} mm. Failure to degas in this manner resulted in lower surface areas. More prolonged heating had no effect. Sample weights varied between 7 and 9 g. Dead-space volume of the sample bulbs at −195° was equivalent to about 25 cc. of gas at room temperature.

The sorption of water by the starches was determined gravimetrically. Two-gram samples were placed over saturated solutions of various salts[6] in evacuated desiccators. The desiccators were then immersed in a large water-bath regulated at 25.10 ± 0.02°. Equilibrium water sorption was considered as reached when weights taken four days apart did not differ by more than 0.4 mg. Moisture content is expressed on the basis of weight of sample dried at 105° in a vacuum oven.

A photomicrographic technique was employed for determining apparent surface areas. Enlargements were prepared of photomicrographs of fields of the various starches mounted dry. The images of 200 to 500 granules of each starch were cut out and weighed and the average granule image weight calculated. Sections cut from similarly enlarged photomicrographs of a stage micrometer were used to provide a factor for converting the average granule image weight to average granule cross sectional area. Since the starch granules approximate spheres, four times the average cross sectional area was taken to be the average surface area of a granule.

An experimental test of the accuracy of the photomicrographic method of determining surface areas was made on a sample of corn starch whose size distribution function had been meticulously measured microscopically by M. J. Wolf of this Laboratory.[7] From his measurements it was determined that the average granule cross section was 351 μ^2. It was found by means of the photomicrographic method here employed that a count of 595 granules from four photomicrographs gave an average granule cross section of 345 μ^2. As an indication of the precision of the determination, it was found that individual photomicrographs, each containing about 150 granules, gave average values ranging from 320 to 370 μ^2.

The number of granules per gram of starch was then determined in a hemocytometer by counting the granules in a suspension of known concentration. An appropriate weight of starch was suspended and made up to a measured volume in a solution of equal parts by volume of glycerol and water. In this viscous solution, starch settling was sufficiently slow to permit removal of a representative sample for the hemocytometer. Between 250 and 500 granules were counted per field, and ten fields were counted and averaged.

The product of the average granule surface area and the number of granules per gram is reported as the apparent photomicrographic surface area of the starch.

TABLE I

SURFACE AREA OF STARCHES

	Nitrogen sorption		Photomicrographic		
	V_m,[a] cc. S. T. P. per g. starch	Surface area,[b] sq. m./g.	Surface per granule, sq. μ	Granules per gram	Surface area, sq. m./g.
Dasheen	0.603	2.62	9.9	2.67×10^{11}	2.64
Corn	.162	0.70	380	1.27×10^{9}	0.483
Tapioca	.065	.28	397	6.40×10^{8}	.254
Potato	*ca.* .026	*ca.* .11	2460	6.20×10^{7}	.152

[a] V_m is calculated from sorption data by means of the BET equation and represents the volume of gas adsorbed when the entire adsorbent surface is covered with a complete unimolecular layer. [b] The cross sectional area of an adsorbed nitrogen molecule was taken to be 16.2 sq. Å.[3]

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(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) A. Rakowski, *Kolloid Z.*, **9**, 225 (1911); **10**, 22 (1912); **11**, 269 (1912).

(3) S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309 (1938).

(4) P. H. Emmett, *Am. Soc. for Testing Materials*, Symposium on New Methods for Particle Size Determination, 1941, p. 95.

(5) W. E. Barr and V. J. Anhorn, *Instruments*, **20**, 454 (1947).

(6) N. N. Hellman and E. H. Melvin, *Cereal Chem.*, **25**, 148 (1948).

(7) M. J. Wolf, M. M. MacMasters, J. E. Hubbard and C. E. Rist, *ibid.*, **25**, 312 (1948).

TABLE II

WATER SORPTION OF STARCHES

p/p_0	Dasheen, % Absorption	Dasheen, % Desorption	Corn, % Absorption	Corn, % Desorption	Tapioca, % Absorption	Tapioca, % Desorption	Potato, % Absorption	Potato, % Desorption
0.08	5.27	6.16	5.03	5.93	5.15	6.07	4.38	5.90
.20	8.43	9.91	8.15	9.82	8.33	10.06	7.67	10.78
.31	10.31	12.22	10.13	12.16	10.35	12.54	10.01	14.00
.43	11.94	14.10	11.85	14.09	12.09	14.58	12.11	16.73
.58	14.05	16.62	14.02	16.74	14.19	17.36	14.71	20.71
.75	17.34	19.91	17.42	20.14	17.64	20.80	19.40	25.63
.85	20.63	22.90	20.68	22.89	21.12	23.55	24.12	29.50
.93	25.40	28.26	25.07	27.54	26.17	29.01	30.61	36.57

Results

The sorption of nitrogen by four typical starches —corn, potato, tapioca and dasheen—is reported in Fig. 1. It was found that the data fit the BET equation to relative pressure of 0.35, and the constants derived yield the surface area values reported in Table I.

Measurements of the average surface per granule as determined photomicrographically and the number of granules per gram of each of the four starches are reported in Table I along with the surface area per gram calculated therefrom.

Water-sorption isotherms for these four starches are given in Table II, and are in good agreement with those reported by Sair and Fetzer[8] for similar starches. These data can be fitted by the BET equation, and by employing this interpretation values are calculated for the surface areas effective in water sorption and shown in Table III.

TABLE III

SURFACE AREA OF STARCHES CALCULATED FROM WATER SORPTION

	V_m, g. H_2O/100 g. dry starch Absorption	V_m, g. H_2O/100 g. dry starch Desorption	Surface area, sq. m./g. Absorption	Surface area, sq. m./g. Desorption
Dasheen	8.01	9.41	281	330
Corn	8.00	9.51	280	334
Tapioca	8.18	9.90	287	348
Potato	8.43	12.02	296	422

Discussion

Surface areas found by nitrogen sorption (0.1 to 2.6 sq. m./g.) are in close agreement with the apparent external surface found by the photomicrographic method. It would thus appear that starch granules are relatively non-porous.

The order of water-sorptive capacities (potato > tapioca > corn = dasheen) is the inverse of that for the nitrogen-sorptive capacities (dasheen > corn > tapioca > potato). The surface areas calculated to be effective in water sorption (Table III) differ so greatly from the available surface areas of starches measured by nitrogen sorption that it must be concluded that nitrogen and water sorption differ in their location of adsorption in or on the starch granules. The objective of explaining the differing water-sorptive capacities of starches of different botanical origin on the basis of differences in nitrogen-available surface cannot be realized.

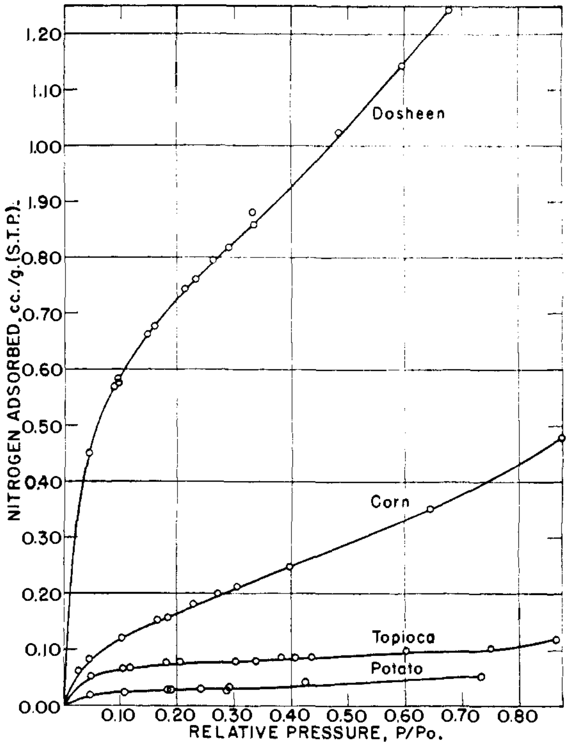

Fig. 1.—Sorption of nitrogen by starches.

Large differences between the nitrogen- and water-available surface areas have been reported previously by several investigators for cellulosic fibers and proteins, particularly by Rowen and Blaine.[9] The several explanations which these authors presented for the discrepancy in the case of textile fibers could be equally applicable to starch. It may be more useful, however, to consider that water sorption is not a surface condensation phenomenon, and thus the interpretation of the sorption data in terms of an area for sorption is incorrect. An alternative interpretation which can be applied to water sorption data is that of Cassie[10] who considered sorption to occur at sites distributed throughout a substance. The marked swelling of starch

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(8) L. Sair and W. R. Fetzer, *Ind. Eng. Chem.*, **36**, 205 (1944).

(9) J. W. Rowen and R. L. Blaine, *ibid.*, **39**, 1659 (1947).

(10) A. B. D. Cassie, *Trans. Faraday Soc.*, **41**, 458 (1945).

and the increasing clarity and intensity of the X-ray diffraction pattern as sorption occurs indicates that sorption at sites within the granule substance is a reasonable hypothesis.

The form of the Cassie equation is analogous to the BET equation and thus fits the water sorption data equally well. For its proper use, the Cassie analysis requires knowledge of swelling pressures and deformations not available for starch; however, employing the Cassie sorption equation without correcting for swelling effects yields a minimum value of 0.7 to 1.0 sorbing site per glucose unit. The logical sites for sorption would be the hydroxyl groups of the molecule, and hence of the three sites per glucose unit theoretically available one-third to one-fourth are active. Such a high proportion of the hydroxyl groups active in sorption means a relatively great exposure of all of the starch molecules and hence renders the expression of a calculated surface area for water sorption of doubtful meaning.

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Summary

The surface area of dasheen, corn, tapioca and potato starches available to nitrogen at −195° was found to be 2.62, 0.70, 0.28 and 0.11 sq. m./g., respectively. Interpretation of the water-sorption isotherms of these four starches by the BET equation requires surface areas of 330, 334, 348 and 422 sq. m./g., respectively. It was concluded that the nitrogen-available surface area of starch does not give a quantitative explanation of the water-sorptive capacity of starches of different botanical origin.

The apparent external surface area of these starches was also determined photomicrographically and found to be in close agreement with the nitrogen-available surface area.

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[Contribution from the Northern Regional Research Laboratory[1]]

A Simplified Procedure for the Characterization of Starch Fractions by Viscosity and Iodine Sorption

By Ivan A. Wolff, Laetta J. Gundrum and C. E. Rist

Increased attention has been devoted in recent years to study of the component polysaccharides of common starches—the linear or amylose fraction and the branched or amylopectin fraction. Primary characterization of these fractions includes (a) information on the relative average molecular size and (b) measurements of the proportion of linear material contained.

The intrinsic viscosity[2] is commonly considered to be a function of the molecular weight in a homologous polymer series under given conditions in the same solvent. Iodine affinity is accepted as an indication of the amount of amylose present. For this reason a study of these methods for the characterization of amyloses and amylopectins was made.

This paper reports a method for estimating accurately the intrinsic viscosity in 1 N potassium hydroxide solution of each fraction, from a measurement made at a single concentration. The iodine affinity is determined by known methods on the same alkaline solution. Thus from a single sample, information on both relative molecular size and linear content of the starch fraction may be obtained.

Viscosity Studies.—Aqueous alkali has often been suggested[3] as a suitable solvent for determination of the viscosity of starch fractions. We found that a variety of amylose and amylopectin samples dissolved completely in 1 N potassium hydroxide solution at 0° in a period of twenty-four to forty-eight hours. Storage of the dispersions at 0° for an interval of twenty-four hours after solution was complete caused a maximum decrease in the intrinsic viscosity (measured at 25°) of 0.01 unit. All values reported in this paper were obtained within such a time period. Use of a nitrogen atmosphere as recommended by Whistler and Johnson[3] was not found beneficial, although our studies included no amylose fractions with a viscosity as low as that used for illustration by those authors.

The results of viscosity determinations at 25° on a series of amyloses and amylopectins of varying molecular sizes are shown graphically in Figs. 1 and 2, where the inherent viscosity is plotted against the concentration. The viscosity of each sample was determined at six different concentrations varying from 0.1 to 0.5%.

A linear relation between inherent viscosity and concentration, with an increasing negative slope for the materials of higher molecular weight,

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(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Report of a study made under the Research and Marketing Act of 1946.

(2) The terminology recommended by L. H. Cragg, *J. Colloid Sci.*, **1**, 261 (1946), is followed in this paper.

(3) (a) Speiser and Whittenberger, *J. Chem. Phys.*, **13**, 349 (1945); (b) Whistler and Johnson, *Cereal Chem.*, **25**, 418 (1948); (c) Potter and Hassid, This Journal, **70**, 3774 (1948); (d) Lansky, Kooi and Schoch, *ibid.*, **71**, 4066 (1949).