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A COMPARISON OF THE MOISTURE ADSORPTION-DESORPTION PROPERTIES OF CORN STARCH, U.S.P., AND DIRECTLY COMPRESSIBLE STARCH

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ABSTRACT

The moisture adsorption and desorption properties of corn starch, U.S.P., and a directly compressible corn starch were studied. Both systems exhibited Type II adsorption behavior with hysteresis observed in both cases. The B.E.T. method was used to determine monolayer coverage and surface area for both the adsorption and desorption isotherms. It was calculated that the average corn starch granule increased in volume by approximately 9.2% due to swelling in the presence of moisture.

INTRODUCTION

Corn starch is widely used in the tablet dosage form, finding use as a diluent, binder, disintegrant, glidant, and antiadherent. Most important among these uses has been the ability of starch to rapidly and reliably cause disintegration of a tablet.

Several authors have determined the adsorption-desorption isotherms for water vapor on corn starch. The isotherms obtained by Sair and Fetzer[1] did exhibit hysteresis but the authors did not perform any surface area determinations. Gupta and Bhatia[2] also observed hysteresis in their adsorption-desorption data. A B.E.T. analysis of the data yielded a monolayer capacity of 0.33 mole of water per 100 grams of corn starch. Treatment of the adsorption-desorption data obtained from the corn starch-water system was also performed by Das, Sethi and Chopra[3]. These authors calculated a surface area of 298 m^2/g for corn starch.

Recently, articles[4-6] have been published which claim improved processing qualities as well as improved tablet performance characteristics for a modified corn starch which was suitable for direct compression. Since this modified starch was said to be identical chemically to corn starch, U.S.P., it is reasonable to assume that differences in its surface properties may account for its altered behavior in the tablet. The objective of this study was to evaluate the surface properties of corn starch U.S.P., and the directly compressible starch as related to their moisture adsorption and desorption properties.

EXPERIMENTAL

All statements of procedure referring to "starch" apply equally to corn starch, U.S.P. (A. E. Staley) and to a modified, directly compressible corn starch, STA-Rx 1500 unless otherwise noted.

Small quantities of starch, approximately 1 to 3 grams, were weighed into 10 cm petri dish bottoms and then placed, along with the petri dish tops, into a vacuum oven. These samples were then dried at 70°C and 0.02 mm Hg for 5 days. Temperature and time studies of the amount of moisture removed indicated that neither higher drying temperatures nor longer drying periods were necessary.

Upon completion of the drying process the samples were weighed in order to determine the amount of moisture lost and, by difference, the amount of dry starch remaining. A knowledge of the amount of dry starch present was necessary for subsequent calculations.

An analytical balance with a sensitivity of 0.1 mg was used for all weighings performed during the course of this study.

Adsorption-Desorption Study

Relative humidity chambers were prepared by filling desiccating jars with appropriate salt solutions. The range in relative humidity encompassed in the various chambers was from 7.1% to 100% at $25^{o}C$. These relative humidity chambers were maintained at $25.0^{o}C \pm 0.05^{o}C$ in a constant temperature oven of original design.

The adsorption isotherm was constructed by placing samples of previously dried starch in the various chambers and then weighing these samples at 2 day intervals until constand weight was exhibited.

The desorption isotherms was determined using an almost identical procedure. In this case, however, the dried starch samples were equilibrated in a 100% relative humidity chamber prior to being placed in the other relative humidity chambers.

Scanning Electron Microscopy

Dried and undried starch samples were mounted on sample holders by placing a thin film of glue on the holder and then sprinkling the starch on top. Excess starch was removed by gently tapping the holder.

When the glue had thoroughly dried, the samples were sputter coated with gold to increase their conductance.

The samples were then placed in the electron microscope (Mini-Som) for observation. The images formed on the cathode ray tube were photographed with a Polaroid camera.

RESULTS AND DISCUSSION

Adsorption and Desorption of Water Vapor

Adsorption-desorption isotherms for corn starch, U.S.P. and STA-Rx 1500 are presented in Figures 1 and 2, respectively. Both systems are seen to

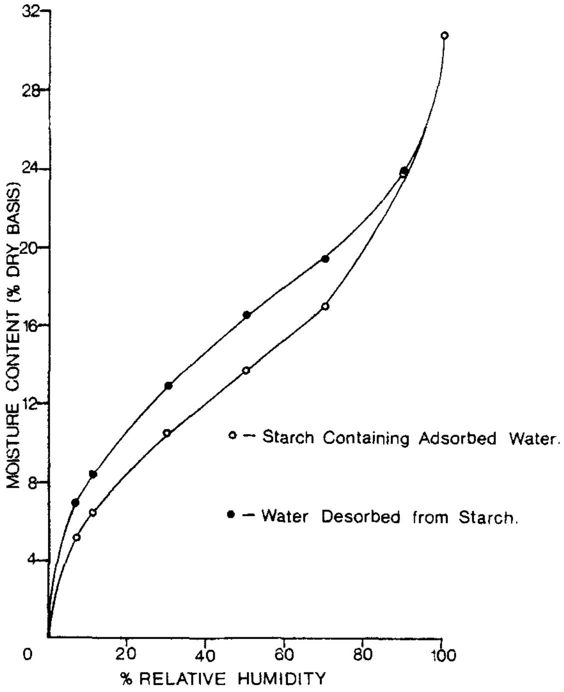

FIGURE 1

Adsorption and desorption isotherms for water vapor on corn starch, U.S.P., at 25^{o}C.

exhibit Type II adsorption as classified by Brunauer[7]. Hysteresis is evident in both systems and this hysteresis was shown to be reversible.

The maximum amount of water bound by corn starch, U.S.P. at 25^{o}C was found to be 30.9% by weight (dry basis). This compares favorably with the value of 30.7% by weight (dry basis) at 22^{o}C obtained by Mousseri, et al., with an NMR method[8].

The maximum amount of water bound by STA-Rx 1500 was determined to be 39.4% by weight (dry basis) at 25.0^{o}C.

The low moisture content regions of both adsorption isotherms were analyzed by the B.E.T. method. The equation representing the generalized B.E.T. theory[9] is:

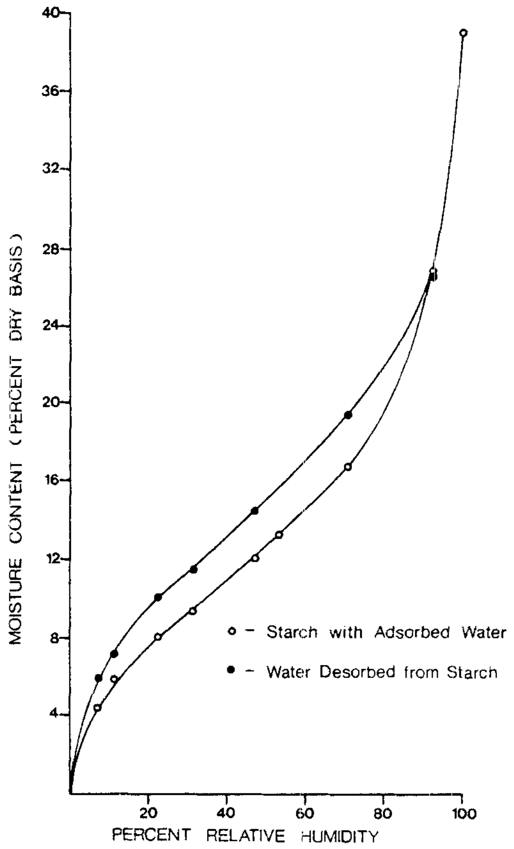

FIGURE 2

Adsorption and desorption isotherms for water vapor on STA-RX 1500 at 25°C.

$$\frac{P/P_o}{V(1-P/P_o)} = \frac{1}{CVm} + \frac{(C-1)P/P_o}{CV_m} \qquad (1),$$

where

P = the pressure of the water vapor,

P_o = the pressure of the water vapor in an atmosphere saturated with water vapor,

V = the STP volume of gas adsorbed at pressure p,

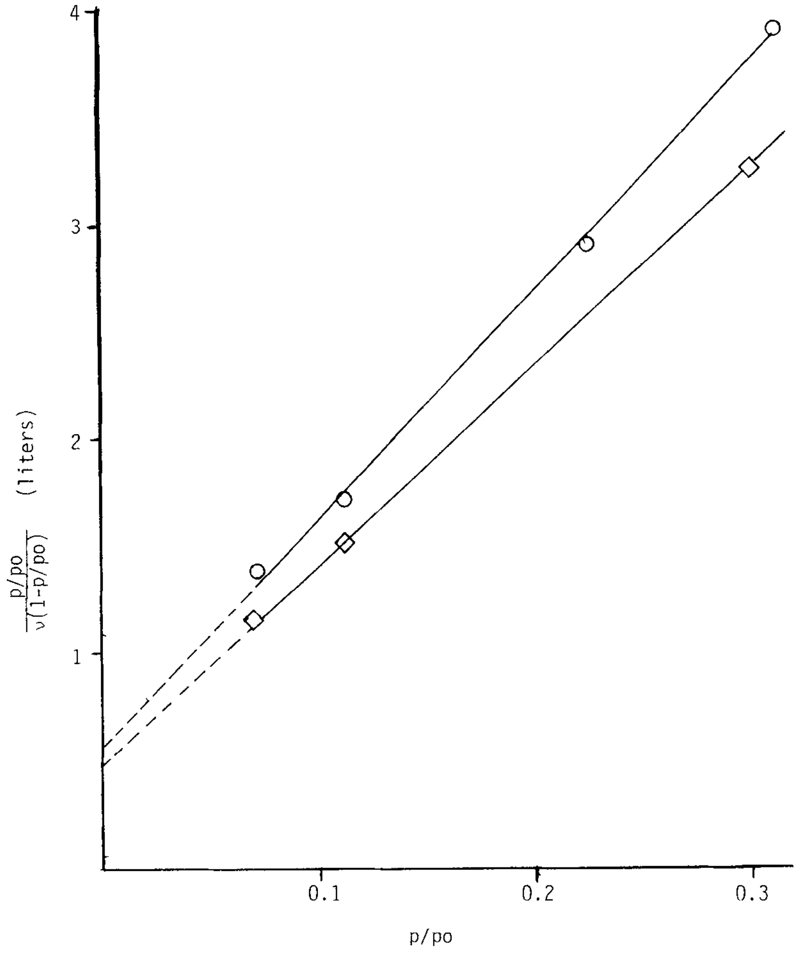

FIGURE 3

B. E. T. treatment of the adsorption of water vapor by Starch, ○ , and STA-RX 1500, ◇ , at 25°C.

V_m = the STP volume of gas adsorbed when the surface is covered with a monomolecular film of gas,

c = the B.E.T. constant.

Since equation 1 is a linear equation, a plot of $\frac{P/P_o}{V(1-P/P_o)}$ vs. P/P_o

(Figure 3) can be used to determine V_m. Once V_m is known, the calculation of the surface area is straight forward.

Monolayer coverage (V_m) for corn starch, U.S.P. occurred at 0.46 mole of H_2O/100 g of starch, yielding a surface area estimate of 348 m^2g. This compares reasonably well with the surface area estimate of 290 m^2g obtained by Das, Sethi, and Chopra[10] using water vapor adsorption.

V_m equalled 0.40 mole of H_2O/100 g of starch for STA-Rx 1500 and resulted in a surface area estimate of 305 m^2/g.

In theory, any small molecule that is relatively inert can be used as the absorbate in a B.E.T. analysis; water and nitrogen are, however, the most common. A problem arises in that water vapor adsorption and nitrogen vapor adsorption seldom yield the same results. Young and Healey[11] attribute this discrepancy to residual water. This residual water freezes at the temperature employed in nitrogen adsorption (77^oK) and occludes many of the pores and surface irregularities of the solid. The area thus obtained is an estimate of the external surface area of the solid, which may be relatively small compared to the total surface area.

For materials which have a high affinity for water, such as starch, water vapor adsorption would appear to be more appropriate than nitrogen vapor adsorption for surface area analysis.

Scanning Electron Microscopy

Scanning electron micrographs were taken of corn starch, U.S.P. and STA-Rx 1500 (Figures 4 and 5).

Granules of corn starch, U.S.P. (Figure 4) were found to be round in shape with very few surface imperfections. No pores were observed, even at magnifications of 10,000X. This does not preclude the existence of pores since a pore with a diameter of $100A^o$, when magnified 10,000X would have appeared to be 0.1 mm. An image 0.1 mm in size would have been relatively difficult to accurately discern on the cathode ray tube display. The lack of observable pores does mean that any pores that were present were very small.

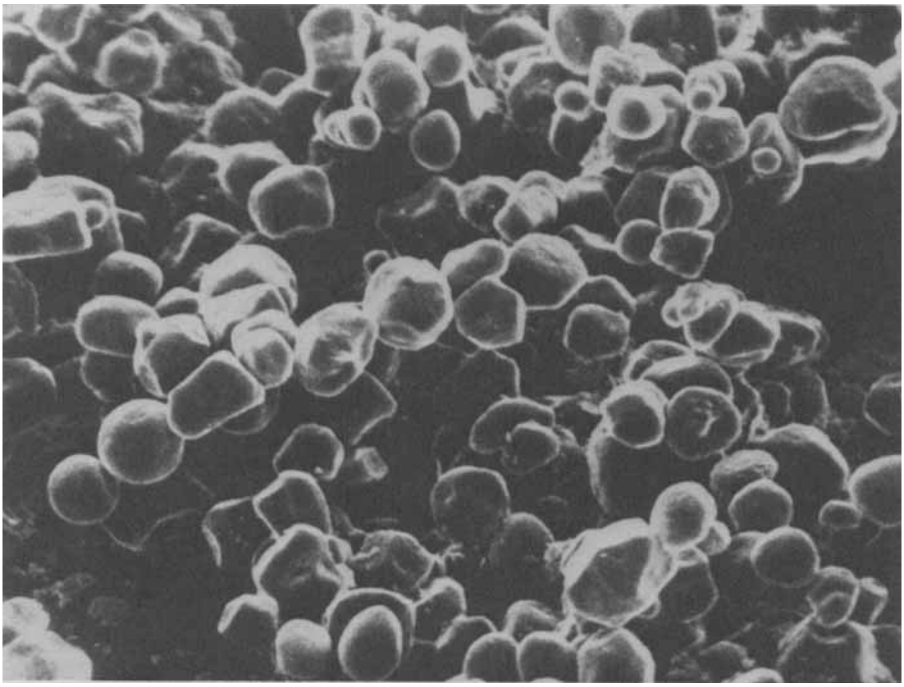

FIGURE 4

Scanning electron micrograph of corn starch, U.S.P., after drying treatment. Magnification = 1000x.

Granules of STA-Rx 1500 (Figure 5) showed extremely varied shapes and sizes. In fact, it appeared as if corn starch granules had been compressed under heavy pressure and the resulting agglomerates broken apart. The granule surface appeared to be free of pores; however, the statements regarding experimental uncertainty made for corn starch, U.S.P. also hold for STA-Rx 1500.

The average granule size of corn starch, U.S.P., as determined from Figure 4, was found to be 7.6 μ with a standard deviation of 2.1 μ. An average granule size was not determined for STA-Rx 1500. The range of granule sizes was so large and the granule shapes were so varied that such a determination was deemed meaningless.

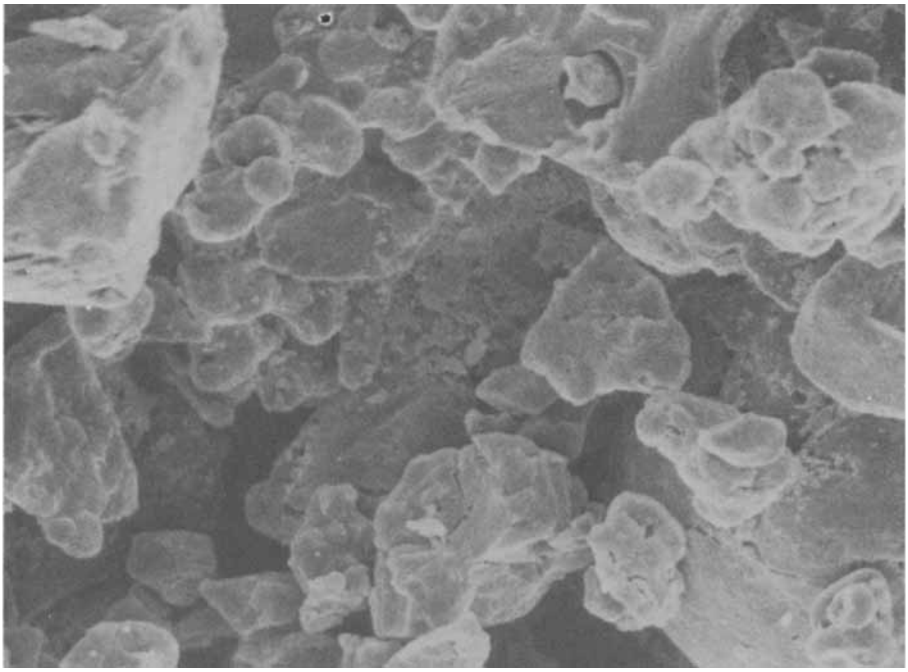

FIGURE 5

Scanning electron micrograph of STA-RX 1500 after drying treatment.
Magnification = 1000x.

The etiology of the adsorption-desorption hysteresis exhibited by corn starch has long been a matter of debate. The classical explanation attributes this phenomenon to the presence of "ink bottle" pores and capillary condensation. Another explanation, which has remained relatively obscure, attributes the hysteresis to reversible hydrogen bond breakage. This postulation is intriguing in that it also accounts for the ability of starch to swell. According to this explanation, the drying of starch results in hydrogen bonds being formed between some of the hydroxyls which had just been vacated by the removal of water. Subsequent adsorption of water vapor occurs first on those hydroxyls which had remained free. As the adsorption process proceeds, however, the inter-hydroxyl hydrogen bonds formed during drying would be broken and replaced with hydroxyl-water hydrogen bonds. Thus, for a given relative humidity of adsorbate vapor, more sites are available for solid-vapor interaction during the desorption process than during the adsorption process. If this latter hypothesis is correct, and the adsorption-desorption hysteresis is indeed the result of an increased surface available for binding water, the desorption isotherm may be related to the surface area of the swollen material in the same manner that the adsorption isotherm can be related to the surface of the unswollen material. Furthermore, the degree of swelling obtained from such an analysis should correlate with microscopic observations made by other investigators[12].

B.E.T. analysis of the desorption isotherm of corn starch, U.S.P. (Figure 1) yielded a value of 0.55 mole of H_2O/100 g of starch for V_m and a surface area estimate of 415 $m^2 g$. Since the average dry granule size of corn starch, U.S.P. had been determined by S.E.M., the change in surface area could also be related to the change in granule diameter and granule volume if 3 assumptions were made.

These assumptions were:

1. The granules are spherical,
2. the granules swell isotropically,
3. most of the surface area is close enough to the outside of the granule that it can be considered to lie on the outside of the sphere.

The diameters, surface areas, and volumes of unswollen and swollen corn starch, U.S.P. are compared in Table 1.

Hellman, Boesch, and Melvin[12] determined microscopically that the diameter of an average corn starch granule increased by 9.1% when going from the vacuum dry state to the state in equilibrium with a 100% relative humidity environment. The value of 9.2% found in this study is in excellent agreement with their value and would seem to validate the reversible hydrogen bond hypothesis.

Table 1

Geometric Comparison of Unswollen and Swollen Corn Starch, U.S.P.

Dimension	Unswollen	Swollen	% Increase
Surface Area (m^2/g)	348	415	19.3
Diameter (μ/granule)	7.6	8.3	9.2
Volume (μ^3/granule)	1839	2395	30.2

Analysis of the desorption isotherm of STA-Rx 1500 (Figure 2) was performed in the same manner as was previously described for corn starch, U.S.P. A value of 0.49 mole of H_2O/100 g of starch was obtained for V_m which yielded a surface area estimate of 367 m^2/g. The surface area of STA-Rx 1500 increased by 20.3% (the unswollen surface area was 305 m^2/g) upon swelling. Since it was not feasible to calculate an average granule diameter for STA-Rx 1500 and since the assumption of a fixed granule geometry was not valid for STA-Rx 1500, the change in average granule diameter and average granule volume could not be calculated.

French[13] has indicated that, for reversible swelling, it is the amorphous regions within the starch granules which swell upon the adsorption of water. The larger increase in surface area upon swelling exhibited by STA-Rx 1500 (20.3% for STA-Rx 1500 versus 19.3% for corn starch, U.S.P.) probably indicates that granules of STA-Rx 1500 contain a higher percentage of amorphous material than do granules of corn starch, U.S.P.

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