Sorption of Water, Sodium Sulfate, and Water-Soluble Alcohols by Starch Granules in Aqueous Suspension[1]

J. N. BEMILLER and G. W. PRATT, Department of Chemistry and Biochemistry, Southern Illinois University at Carbondale, 62901

ABSTRACT

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A method using blue dextran 2000 to measure the amount of water sorbed by starch granules in suspension is reported. The dextran is too large to penetrate starch granules; therefore, as granules sorb water, the concentration of the dextran increases in the free solution. The concentration change is followed spectrophotometrically. The method was used to determine the sorption of water by various starches and starch derivatives; however, because the chromophore is anionic, the method does not work with cationic starches that adsorb blue dextran. Potato starch and corn starch had water contents of 33 and 28%, respectively, in suspension at neutral pH. Water uptake increased only slightly with increasing pH. Sodium sulfate went into granules with water but did not mix with the tightly bound moisture of the granule. Dimethoxyethane, a hydrophobic molecule, did not penetrate the granules to a significant extent. Methanol, ethanol, 1-propanol, and 1-butanol were preferentially sorbed in comparison to water. They appeared to penetrate the granules with the water and to mix freely with the moisture of the granule. Under conditions of industrial derivatization (high pH, Na_2SO_4, NaOH), the alcohols were taken up in even larger amounts.

The least known aspect of starch chemistry is the nature of the raw material, the starch granule. In typical starch derivatizations, alkali is added to a starch-salt water slurry, followed by addition of the organic reagent. The reaction is usually conducted at an elevated temperature. The external environment of a starch granule in a starch derivatization reaction can be described in terms of the temperature and the amounts of water, salt, alkali, and organic reagent. However, little is known of the nature of the internal environment in which the reaction takes place. This investigation was conducted to examine the nature of the internal environment of the starch granule under typical derivatization conditions. Specifically, we determined the amount of water taken up by derivatized and underivatized starch granules, the effect of pH and sodium sulfate on this uptake, and the effect of the size and polarity of certain organic molecules on their uptake.

Measures of the sorption and desorption of water vapor by "dry" starch have been reported (Bushuk and Winkler 1957, Dumanskii and Nekryach 1960, Hellman and Melvin 1950, Sair and Fetzer 1944, Taylor et al 1961, Ubertis and Roversi 1953, Zhuravleva 1948), but the relationship between sorption of water vapor and sorption of water by starches in aqueous suspension has not been established.

Leach (1965) introduced the use of high molecular weight solutes that were assumed not to penetrate the granules, a concept also employed in this work, to measure the water sorbed by starch in suspension. By measurements of the heat capacity of starch suspensions, Freeman (1942) determined the amount of water sorbed or bound to starch as a function of temperature.

Leach et al (1961) measured the sorption of alkalis by suspended granular starches by titrating the amount of alkali remaining after an equilibrium had been obtained. Lancaster and Conway (1968) obtained the sorption isotherm for NaOH at various amounts of starch and temperatures. Leach et al (1961), Samec (1927), and de Willigen and de Groot (1971) found that sorption of NaOH was markedly increased in the presence of Na_2SO_4 and NaCl.

Kurilenko and Yakovkina (1960) determined the amounts of water and ethanol sorbed by starch at equilibrium conditions in aqueous ethanolic solutions.

In the present work, a blue dextran with a high molecular weight (2,000,000) was used to determine the uptake of water by unswollen

granules. The basic procedure used was as follows: Starch was added to an aqueous solution of the blue dextran, and the water was allowed to equilibrate between the aqueous phase and the starch phase. Then the starch was removed, and the concentration of blue dextran was determined spectrophotometrically. As the starch granules took up water, the concentration of blue dextran in the aqueous phase showed a corresponding increase. By a simple calculation, the amount of water lost to the starch phase was determined. Since the procedure using blue dextran was first described (BeMiller and Pratt 1973), it has been applied by Brown and French (1977) and Dengate et al (1978).

Potato starch was chosen for this investigation because it did not absorb blue dextran at any pH. A 2% concentration of organic solvent was chosen as approximating the reagent level used in commercial starch derivatization. Only water-soluble organic solvents were used so that the change in the aqueous phase could be determined accurately.

MATERIALS AND METHODS

Materials

A commercial corn starch, a low-substituted hydroxyethyl corn starch (Penford Gum 300, 3% by weight hydroxyethyl groups), a carboxymethyl corn starch (Astrogum 21, 1.5% by weight sodium carboxymethyl groups), and a commercial potato starch were obtained from Penick and Ford, Ltd. A commercial corn starch sulfosuccinate half-ester (sodium salt), a cationic (diethylaminoethyl ether) corn starch, high-amylose corn starches, and a commercial corn starch of more than 95% amylopectin (waxy maize) were obtained from National Starch and Chemical Co. A corn starch and a epichlorohydrin cross-linked corn starch (0.04% by weight epichlorohydrin) were obtained from A. E. Staley Mfg. Co. Blue dextran 2000 was obtained from Pharmacia Fine Chemicals.

Determination of Water Uptake

Starch (5.000 g) of known moisture content was placed into 25-ml flasks. Distilled water (10.00 ml) was added to half the flasks and 10.00 ml of a solution of blue dextran 2000 of known concentration to the other half. Two concentrations of blue dextran were used: 1.4000 g/l and 0.2000 g/l. Alternatively, solutions of specified pH and/or salt concentration, with and without blue dextran, were added to the flasks, which were placed in a water bath with a reciprocal shaker controlled to 25° C and shaken vigorously for exactly 1 hr.

The solutions were filtered through Whatman No. 1 filter paper in a Buchner funnel, and the filtrates were placed in cuvettes in a double-beam spectrophotometer. Absorbances were determined at 640 nm with 20-fold amplification. A solution without blue dextran

was used as the blank, against which the absorbance of the blue dextran solution was read. The amount of water lost to the starch phase was determined from the increase in concentration of the blue dextran solution according to the following formula: grams of water lost to the starch phase = $5.0000 (1 - A_i/A_f)$.[2] Using the original amount of water in the starch phase (percent moisture),[3] the new total amount of water in the system and in the starch phase was calculated.

Determination of Uptake of Sodium Sulfate

A solution of approximately 18% Na_2SO_4 containing approximately 1.4 g of blue dextran per liter was prepared. Aliquots (10.00 ml) of this stock solution were placed in tared, covered crucibles and evaporated to dryness on a steam bath. The crucibles were then heated in a gas flame until they glowed red for 30 min, cooled in a dessicator, and weighed. The exact concentration of the Na_2SO_4 solution was then calculated as percent by weight.

Stock solution (10.00 ml) was mixed with 5.0000 g of starch and shaken in a 25° C water bath. A blank of 18% sodium sulfate solution without blue dextran was treated similarly and used in the reference beam of the spectrophotometer. Following filtration and determination of the absorbances, the solutions were placed in crucibles and ashed as described for the stock solution.

In other investigations, the stock 18% Na_2SO_4-blue dextran solution (10.00 ml) was added to 5.0000 g of starch and the mixture titrated to pH 11.0 with dilute NaOH, using an automatic titrator. A blank of 18% Na_2SO_4 was treated similarly and used in the reference beam of the spectrophotometer. Following filtration and determination of the absorbances, the solutions were analyzed for sodium sulfate by ashing as described.

Determination of Uptake of Organic Reagents

Starch (5.0000 g) was mixed with 10.00 ml of an aqueous solution containing 2% (v/v) of an organic solvent and blue dextran. (A blank without blue dextran was similarly prepared.) These mixtures were shaken for 1 hr and filtered through a Buchner funnel as before; the absorbance was then measured to obtain the change in concentration of the blue dextran solution. A portion of the supernatant, usually 2.00 ml, was mixed with a small amount of the internal standard (bismethoxyethyl ether). Aliquots were then injected into a gas chromatograph under conditions previously determined to give a clean, sharp peak of the organic solvent used, and the change in concentration of the organic solvent was calculated from the relative peak areas.

Determination of Uptake of Organic Reagents at High pH in the Presence of Sodium Sulfate

The following procedure was used to measure water uptake at higher pH values. A 2% (v/v) solution of the aqueous solution of the organic reagent (10.00 ml) containing approximately 15% Na_2SO_4 was added to 5.0000 g of starch in a 25-ml flask. Using an automatic titrator, the pH of the mixture was adjusted to 11.0 with 0.33 M NaOH. Absorbance at 640 nm was read against a blank that had been treated identically, including the pH adjustment, but that contained no blue dextran. Absorbances were also determined for blue dextran solution adjusted to pH 11.0 and for the final solution obtained by shaking for 1 hr in a water bath and removing the starch by filtration. Absorbances were corrected for the known dilution of the solution, and the organic solvent content was determined by gas-liquid chromatography as described.

RESULTS AND DISCUSSION

Preliminary work revealed seven facts: 1) the absorbance of blue dextran solutions changes linearly with concentration; 2) an immediate increase in A_{640} resulted when starch was added to a blue dextran solution; 3) A_{640} of a starch-water slurry increased more slowly with time because of leaching of soluble starch molecules

TABLE I
Uptake of Water[a] by Various Starches as a Function of pH and Blue Dextran Concentration

| | Blue Dextran Concentration (g/L) | | | | | |
| | 0.2 at pH | | | 1.4 at pH | | |
Starch	7.0	9.5	11.0	7.0	9.5	11.0
Potato	33.1	34.4	33.0	33.2	33.7	33.6
Corn						
Underivatized	20.0[b]	28.5	30.1	27.2[b]	28.7	28.3
	18.1[b]	26.8	30.8	25.7[b]	28.1	28.9
Hydroxyethyl	40.9	45.7	44.1	42.3	45.0	43.9
Carboxymethyl, sodium salt	35.3	35.6	36.2	34.0	34.7	35.1
Sulfosuccinate half-ester,						
sodium salt	40.5	42.9	45.7	41.1	42.2	43.7
Epichlorohydrin cross-linked	28.1	28.7	28.1	26.6	28.1	28.3
High-amylose						
~50%	22.1	35.4	35.3	30.7	34.1	34.9
~70%	⋯	30.2	33.4	26.9[b]	31.9	33.0
Waxy maize	28.9[b]	31.1	33.9	32.8[b]	32.5	34.6

[a] Percent water in the final starch phase.
[b] Value appears to be low, perhaps from adsorption of blue dextran by the starch granules.

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[2] A_i and A_f are the initial and final absorbances at 640 nm.
[3] The moisture content was determined by heating five samples to 100° C in a vacuum oven for 12 hr.

from the granules; 4) this latter increase was dependent on the rate of stirring; 5) equilibrium was complete in less than 1 hr; 6) blue dextran did not absorb on filter paper; and 7) the method could not be used with cationic starches because of absorption of the blue dextran onto the starch (Pratt 1975). Because the values obtained for the uptake of water by various starches using low concentrations of blue dextran were in close agreement (Table I), we could assume that no significant absorption of blue dextran onto other starches took place; an exception was underivatized corn starches at pH 7 (Table I).

Water Uptake By Starch

A reciprocal shaker gave a lower value for water uptake than did a rotary shaker for otherwise approximately identical conditions for all starches examined (Pratt 1975). Among the underivatized starches, potato starch, which is easily gelatinized, sorbed the most water. The water content of suspended potato starch was 33–34% and of corn starch 26–27%, the exact value depending upon the conditions. Data from a similar experiment reported by Leach (1965) give values of 36.2% for potato starch and 30.0% for corn starch. Dumanskii and Nekryach (1960) determined 33.6% water in potato starch from water vapor sorption and heat of wetting experiments.

The presence of base (high pH) is very important in industrial reactions of starch. One might expect that, as the pH is raised, alkoxide ions could be formed and would repel one another, thus causing an expansion of the granule. The expanded structure would then be expected to take up more water because of the increased space and the hydration of the negative charges. The presence of salt would reduce the interaction of like charges. The data in Table I do not support this idea. Surprisingly, very little if any increase in water content was found with increasing pH. The starch evidently accomodates the increase in pH with very little structural change, except when granules are swollen by rapid addition of the base, leading to localized high concentrations.

Hydroxyethyl starch prepared from corn starch, when equilibrated with water at pH 11, contained 44% water as compared to 28–29% for underivatized corn starch (Table I). One may easily imagine that ethylene oxide is taken up by the starch and goes into areas that are normally somewhat hydrophobic because of extensive hydrogen bonding. Then, upon reaction, which generates hydroxyethyl groups, this area becomes more hydrophilic and more open.

Epichlorohydrin cross-linked corn starch was similar to corn starch in its ability to sorb water. Although the addition of ethylene oxide produced an increase in water sorption, addition of epichlorohydrin, which might be predicted to go into the same areas, gave an essentially unchanged ability to sorb water. This may indicate that starch chains must be free to move in order to take up water.

The high-amylose corn starches also appeared to sorb more water than did ordinary corn starch. The 100% amylopectin corn starch (waxy maize) showed about the same degree of water uptake as did the high-amylose starch. Neither these values, nor any of the others, can be correlated with gelatinization temperatures.

Both the anionic starches, carboxymethyl starch and the starch sulfosuccinate half-ester, showed an increase in water uptake, perhaps owing to the introduction of the charged anion, which makes the starch more hydrophilic.

The information given by the blue dextran method of water uptake analysis is the amount of water sorbed by the starch. Where this water is located is not revealed. It could be either on the surface of the granules or inside them. Neither does the method indicate whether the water inside the granules is free or bound.

Role of Salt

Sodium sulfate prevented leaching of starch molecules from the granules while they were in suspension at 25–45°C (Pratt 1975). One mechanism by which sodium sulfate may act as a gelatinization inhibitor is by preventing dissolution of starch polysaccharides, particularly amylose, by somehow stabilizing intermolecular associations.

As the temperature of the starch suspension was raised, the concentration of sodium sulfate in the extragranular solution increased (Pratt 1975). This is evidence that starch granules preferentially take up water over salt. As the temperature increased, the granules probably expanded and, in so doing, sorbed more water. Another possibility is that, initially, sodium sulfate adsorbed onto the starch. Physical adsorption usually decreases with increasing temperature; thus the starch could have released salt back to the solution as the temperature increased. However, if this were true, the salt concentration of the solution would have dropped when starch was added to it, an occurrence that was not observed. Therefore, the best interpretation of the data is that the starch granules prefer water as the temperature increases. Probably very little starch-salt interaction exists; instead, the competition between salt and starch for the water is of primary importance.

Potato starch had an apparent final salt-water content of 33.4% in 18.7% sodium sulfate at pH 7 (Pratt 1975). This value is equivalent to that found using water alone (Table I). Thus, water in the potato starch was less according to the amount of salt present. In the case of hydroxyethyl corn starch, the amount of salt water sorbed was reduced, in comparison to the amount of pure water sorbed (28.0% salt-water in the final starch phase as compared to 42.3% water), to a value close to that for underivatized corn starch. With corn starch, salt at pH 7 apparently enhanced the adsorption of blue dextran because a value of 14.5% salt-water in the final

TABLE II
Amount of Water (and Salt) Taken Up by Various Starches at pH 11.0

Starch	Percent Moisture in Original Starch	Na$_2$SO$_4$ Concentration		A_i[a]	A_f[b]	Percent Salt Water in Starch
		Initial	Final			
Potato	15.52	17.18	18.05	1.201	1.348	33.6
Corn						
Hydroxyethyl	9.94	17.43	18.63	1.218	1.446	35.3
Underivatized	10.98	16.85	17.68	1.194	1.320	28.5

[a] Initial absorbance at 640 nm.
[b] Final absorbance at 640 nm.

TABLE III
Uptake of Organic Solvent at Neutral pH[a]

	Methanol	Ethanol	1-Propanol	1-Butanol	1,2-Dimethoxy-ethane
Water and solvent					
Transferred from blue dextran phase to starch phase, ml	1.345	1.264	1.326	1.309	1.315
In final starch phase, %	33.43	32.57	33.23	33.05	33.11
Solvent					
In final blue dextran phase, %	1.86	1.84	1.92	1.89	2.15
Transferred to final starch phase, ml	0.039	0.039	0.034	0.035	0.013
Water					
Transferred to final starch phase, ml	1.307	1.225	1.292	1.274	1.302
Solvent					
In the solvent-water portion of final starch phase, %	1.85	1.93	1.60	1.70	0.65

[a] 5.0000 g of a 15.52% moisture commercial potato starch in 10.00 ml of a 2% aqueous solution of the organic solvent.

	Ethanol	1-Propanol	1-Butanol
Water and alcohol			
Transferred from blue dextran phase to starch phase, ml	0.5918	1.616	2.393
In final starch phase, %	26.75	32.15	42.86
Alcohol			
In final blue dextran phase, %	1.52	1.51	1.17
Transferred to final starch phase, ml	0.045	0.040	0.102
Water transferred to the final starch phase, ml	0.547	1.531	2.291
Alcohol in the alcohol-water portion of final starch phase, %	3.34	1.99	3.22

[a] 5.0000 g of a 15.52% moisture commercial potato starch in Na₂SO₄.

starch phase was indicated (Pratt 1975; the apparently low value may result from adsorption of blue dextran by the starch granules). However, in all three cases, the concentration of salt in the final blue dextran solution was about the same, ie, 19.2–19.7% (Pratt 1975).

At pH 11 (Table II), the presence of sodium sulfate had little effect on the uptake of the aqueous phase by potato and corn starch, although less water was present in the final starch phase by the amount of salt present. However, again the presence of salt greatly reduced the uptake of the aqueous phase by hydroxyethyl corn starch.

Uptake of Organic Solvent

With the exception of ethanol-water, all mixtures of organic solvents and water were sorbed to about the same extent (Table III). However, a large difference was found in the amount of organic solvent transferred to the starch phase. 1,2-Dimethoxyethane (DME) was transferred only to a very small degree and probably does not penetrate the granule; however, the granules still took up about the same amount of water as they normally did. Alcohols were sorbed to a greater extent (17–20% more) than was water.

Calculation of the percent alcohol content of the alcohol-water portion of the starch phase was done to determine whether the alcohol simply partioned itself between the total available water. The ratios for the solvent concentration in the bulk solution divided by the alcohol concentration in the bound solution at pH 7 were as follows: methanol, 1.005; ethanol, 0.955; 1-propanol, 1.200; 1-butanol, 1.105; DME, 3.308. Because DME does not appear to penetrate the granule, it was concentrated, as water was taken up, in the extragranular solution. Methanol, on the other hand, appeared to be equally present in the external and internal solutions, indicating that it can mix freely with the tightly bound water of the starch. This is a good indication that, wherever water was bound within or on the granule, methanol was also bound there. Ethanol, however, slightly preferred the starch phase. 1-Propanol and 1-butanol were in higher concentration in the bulk solution, but the granules took up a greater proportion of all the alcohols studied than they did water.

At pH 11 in the presence of salt and alcohol, the percent water-alcohol in the starch phase increased with increasing length of the

carbon chain (Table IV). The amount of ethanol and 1-propanol sorbed by starch at pH 11 increased by approximately 16% over the amount sorbed at pH 7. Butanol showed a more dramatic increase (almost 200%) in the amount taken up in the presence of NaOH and Na₂SO₄; about half of the 1-butanol present in the initial blue dextran solution was transferred to the final starch phase.

The ratios for the alcohol concentration in the bulk solution divided by the alcohol concentration in the starch phase at pH 11 were as follows: ethanol, 0.455; 1-propanol, 0.759; 1-butanol, 0.314. Comparison of these values to the ratios obtained at neutral pH with no salt shows that, at high pH in the presence of sodium sulfate, the alcohol went preferentially into the starch phase and that the uptake of alcohol in general and 1-butanol in particular was increased.

The conclusions are that some polarity is required for sorption of organic molecules by starch granules, that alcohols prefer the starch phase to bulk water, and that preference for the starch phase is enhanced by alkali and salt, particularly as the length of the carbon chain increases.

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