On the Water Sorption of Starch Granules

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Introduction

It is generally recognized that the physical and chemical properties of starch are different in variety and that the variety of starch is classified by the sources from root, tuber and cereal. Starch granules are hydrophilic and crystalline polymer. The hydrophilic and crystalline properties are considered to be correlative with the physical properties such as the gelatinization temperature and the viscosity in viscogram. Potato starch has low gelatinization temperature and high viscosity in a viscogram, while it has lower crystallinity and higher swelling power than those of other starches. The viscosity increased with an increase of swelling power because of a small amount of micelle of starch according to the report by Meyer[1]. But the viscosity and swelling power are effected with the experimental condition. It is characteristics of starch that the crystallinity of starch seemed to increase with an increment of sorption water. It is considered that the highly crystalline starch have large sorption water and starch granules have some crystalline water[2]. The properties of starch are different from cellusose in the respects that the highly crystalline cellulose have a small amount of sorption water and crystalline portion have scarcely sorption water. But lowly crystalline potato starch have higher moisture content than those of other starches which were kept in equilibration state at the same vapor pressure. The relationship between hydrophylia and crystallinity in starch are not clear. The author described about the relationship between the water sorption[3] and the crystallinity by means of X-ray diffractometer[4], moisture regain[5] and specific volume[6], and also heat of sorption[7] in this paper.

1. On the sorption of water

Water sorption in starch is destined with relative humidity and moisture content and it depended on the hydrophilic character of starch. The water which was adsorbed on the surface and absorbed into the starch granules is so called sorption water. Sorption water was considered to form hydrogen bond between OH group in a glucose residue. By this consideration, adsorption of water was used for glucose residue and sorption of water did for starch granuels in this paper. The extent of water sorption in starch were determined as the moisture conntent equilibrated under the various humidity[3].

The figure 1 showed that the relationship between the relative humidity and equibrated moisture content of potato starch at 25° and 40°C. The curve in the figure showed the difference between sorption and desorption processes giving so called hysteresis. The hysteresis phenomena in starch were as like as that in the report by Hellman[8] and that in gas sorption.[10] Determination of the contents of hydrogen bond between starch and sorbed moisture by PMR (Proton Magnetic Resonance)[9] showed no hysteresis in sorption and desorption process similar to the fact in the experiment of heat of sorption[7]. These results suggested that the bounding state of the sorbed water molecule to OH group of glucose residue in sorption was almost the same state as in desorption.

These were some equations of Henry, Langumuir, Freundlich and BET (Brunauer Emmett Teller) for sorption phenomena.[10,11] The curve in the figure 1 was shown a typical sigmoid
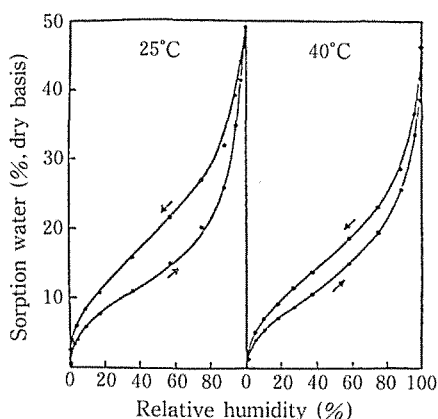
Fig. 1. Hysteresis loop of sorption and des-
orption of water in potato starch.

which was the same as that in BET of multilayer sorption, and sorption phenomena in starch
was able to be interpreted with the BET theory.   The curve line was separated to the three
portions, first convex, second linear and third concave portions which were called as the portions
of bound, semi-bound and free water, respectively.   The moisture content in the portion of
bound water was obtained from the BET equation as that of monolayer sorption.   The content
of monolayer sorption water was 7–8% for starch by Hellman[12] and the author[3].   The area
of surface of starch granule was calculated from the content of monolayer sorption water and
cross area of sorption water molecule.   The area of sorption water was estimated 3.6×10^3 m²
per gram and 288 m² for 0.08 gram which was content of monolayer sorption water per gram of
starch granule on the basis of one water molecule having 10.8 Å² area by Livingston[13].   The
surface area estimated by microscopic method was 0.28 m² per gram of starch granules.   It was
almost the same value as that of 0.11 to 0.28 m² obtained with nitrogen gas adsorption method
by Hellman[12], and this value was very smaller than the value obtained by sorption water
method.   The difference of value between nitrogen gas method and water sorption method may
be attributed that the nonpolar nitrogen molecule is adsorbed only on surface of starch granules
and do not absorbed inner, although water molecule may be adsorbed on both outside and
inside of starch granules.   It was understood that a starch granule has larger amount of glucose
residue inside than those on surface.   If one molar water per a glucose residue, the moisture
content of starch may be 0.11, therefore the moisture content of 0.08 suggests that the 30%
glucose residue is not accessible for sorption.   The value of 30% was almost the same as that
of crystallinity of moistened potato starch by means of X-ray diffraction method and crystalline
portion may scarcely have accessible glucose residue in starch granules.   The monolayer sortion
water meant generally the monomolecular sorption water on both outside and inside of starch
granules and did not sorption moisture in a glucose residue.   But it is considered that the
monolayer sorption water meant moisture content per a glucose residue.   This is the same
consideration that the surface area of polar polymer meant the number of polar rather than
the amount of area[14),15].   Moreover this view was supported with the relationship between
the crystallinity and accessibility in moisture regain.[5]   Assuming that the water molecule
bound to OH group in glucose residue, monolayer water was adsorbed at the OH group at the
position of C_6 which was most easy to form hydrogen bond in the all OH groups of glucose
residue acording to the report by Leach[16].   The bounding between water molecule and OH
group in the positions of C_2 and C_3 were very little known.   If the sorption rule in stareh is fol-
lowed by the BET theory, the multilayer sorption may cause in OH group at the position of C_6.

The starch granules swelled with absorbing water and these specific volume increased with an increase of sorption water. The figure 2 showed the relationship between the moisture content and density or volume which were measured by floating method using the mixture solvent of carbon tetrachloride and nitrobenzene. The density of starch granule became maximum when it contained about 5% moisture and decreased with an increase of amount of sorption water. These phenomena in starch was almost the same as those in cellulose[18]. The relationship between the density and moisture content for starch granules were shown in the table 1 where the equations decreasing about 1/3 degree of density of containing moisture were given. The specific volume, a reciprocal of density, increased with an increase of the sorption water. These results showed that the sorption water influenced directly the swelling of moistened starch granules. The increased specific volume of various starch granules by absorbing water were as follows; 0.90 for potato, 0.865 for sweet potato, 0.891 for tapioca, 0.905 for corn and 0.893 for waxy rice starches. The range of increased volume was 0.87 to 0.90 cc/g for starch and 1 to 0.95 for cellulose[19]. The specific volume of sorption water 0.895 cc/g which was calculated from the cross area (10.8 Å²) of absorbing water molecule according to the report by Livingston was almost the same as those described above. The increment of starch granules by absorbing water was the same as that of absorbing water molecule.
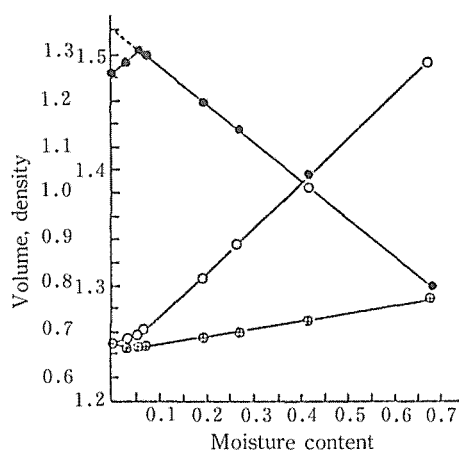

Fig. 2. Density of moistened potato starch. ●, density; ⊕, specific volume, 1/density; ○, volume of moistened starch, specific volume × (1 + moisture content).

Table 1. The relationship between density and moisture content of starch.

Potato	$1.519 - (1/3) R$
Sweet potato	$1.518 - (1.04/3) R$
Tapioca	$1.520 - (1.03/3) R$
Wheat	$1.515 - (0.91/3) R$
Corn	$1.514 - (0.995/3) R$
Waxy corn	$1.515 - (1/3) R$
Waxy rice	$1.518 - (0.95/3) R$

R = moisture content (dry basis).

To elucidate the density of starch granules was important for starch industry and the density was ordinary value of 1.5 which was measured by means of replacing of xylene and air in dry starch by the picnometer method[20]. But the density was 1.6 by means of replacing of water instead of xylene. The difference of the density between the water and xylene replacing methods was considered to be attributed from the volume of 0.9 cc/g of sorption water in starch granules. The density of starch granules when immersed in water was 1.36 to 1.38. The value was calculated from the saturated moisture content measured by the vapor and centrifugal methods[21].

2. On the crystallinity

The measurement of crystallinity was very important to study the sorption character, the physical property and water of crystallization. The crystallinity of a hydrophilic cellulose

was measured by means of X-ray diffractometer, moisture regain and specific volume.[22]   The crystallinity was measured generally by X-ray diffractometer.   The crystallinity of potato starch by this method was reported by Sterling[23].   But the reports as to the crystallinity of starch by a X-ray diffractometer were a few and the reports by other methods were scarcely known.   The author reported the crystallinity of starch by means of X-ray diffractometer[4], moisture regain[5] and specific volume[6].

2–1   X-ray diffractometer method

The measurement of crystallinity of cellulose was carried out by Hermans[24] and Wakelin[25] methods. · To determine the crystallinity by these methods were necessary to know the 100% crystalline and 100% amorphous or various crystalline materials.   But these various crystalline starch were not known generally and the crystallinity of starch was effected by sorption water in starch granules.   By these matter, assuming that the Hermans and Wakelin methods were able to be adapted for the measurement of crystallinity of starch, the relative crystallinity was estimated from integral intensity in X-ray diffractogram using the symmetrical reflection techhnique.[4]

The figure 3 showed the result of X-ray diffractogram by the Hermans technique.   The upper area which was separated with smooth curve corresponded to crystalline portion and the lower area did to the back ground.   The upper area was assumed to be proportional to the crystallinity of starch granules.   As shown in the figure 4, the different of area between the intensity of crystalline and ball milled starches in the X-ray diffractogram, the shadowed portions, was considered to correspond to crystalline portion based on the Wakelin theory.   The results were almost the same as the values reported by Zobel[1] and Sterling[23].   The table 6 showed the crystallinity of various starches when the crystallinity of air dry potato starch was assumed to be 24%.
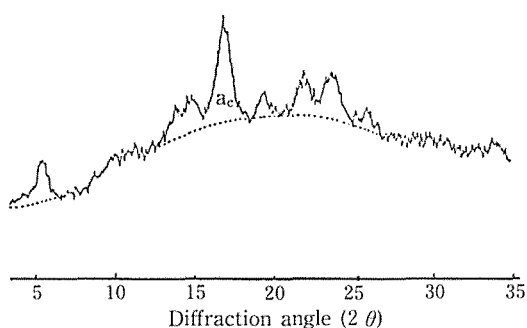

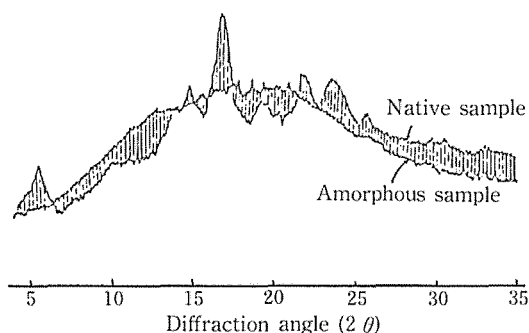Fig. 3.   X-Ray diffractogram of potato starch (Hermans' method).

Fig. 4.   X-Ray diffractograms of native and amorphous potato starch (Wakelin's method).

2–2   Moisture regain method

Crystallinity of starch which were measured by X-ray diffractometer were almost the same as those reported by Zobel, and the potato starch which had large equilibrated moisture content was less crystallinity than that of others.   When the starch had large equilibrated moisture content, it showed a small crystallinity.   The same was the in the case of cellulose.   From these results, it was considered that the water sorption in starch granules caused in the inner side of amorphous portion and on the surface of crystalline portion, not in the inner side of crystalline portion.   The moisture regain method of starch was described as follows.

The relationship between accessibility (A) and crystallinity (x) was shown in the following

equation, $A=\sigma x+(1-x)$. The σ was accessibility of crystalline portion. When the accessibility of amorphous portion was 1, that of the crystalline portion was 0.18 which was very near to the value of 0.17 to 0.19 for cellulose[28,29]. The accessiblity of starch granules was not known. In the case of cellulose, the accessibility of a cotton cellulose was measured by means of the deuterium oxide replacement method and then the accessibility of various fiber was derived from the ratio of their moisture content per the moisture content of the cotton cellulose[22,28-30]. It was considered that the relationship between the equilibrated moisture content, which was moisture regain (R), and accessibility (A) was shown in the following equation, $R=rA$. The constant (r) was calculated from the saturated moisture content and the crystallinity of starch, whose value of 0.667 was estimated from the equation, $R=r(\sigma x+1-x)$. The value of 0.667 indicated that the six mole water bound to the hydroxy group in a glucose residue. The saturated moisture of amylopectin was reported six mole water per a glucose residue by Tomita[31], and adsorbed water molecules corresponded to almost six mole layer on a anatase when the heat of evaporation was zero according to report by Harkins and Jura[32].

The accessibility in crystalline portion of starch granules was calculated with the same manner as that for cellulose when crystalline portion of starch took a square form or a cylindrical one. The accessibility measurement technique in the square form was depended on the report by Mark[33]. The dimension of crystallite was 130 Å for starch and 100 Å for cellulose. The each value of unit cell for starch was reported by Rundle[36], Kreger[37] and French[38], and that for cellulose done by Meyer[39]. The accessibility of crystalline portion (σ) was calculated from the ratio of unit cell per dimension of crystallite as shown in the table 2. The σ value was estimated to be 0.18 or 0.15 for starch and cellulose. The method in cylindrical form was depended on the report by Kast[29] and then it was assumed that the half of glucose residue on the surface of crystalline portion was accessible. The calculation on diameter of cylindrical crystalline portion for a Å was shown in the table 3. The values of 43 and 50 Å in dimension of crystalline

Table 2. The accessibility of crystalline portion of starch and cellulose by Mark's method.

| | Unit cell | Dimension of crystallite | Number of glucose unit | | σ |
	($\overset{\circ}{A}{}^2$)	(Å)	Total	Edge	
Rundle[a]	8×4.6	130	$493(17\times29)$	88	0.18
Kreger[b]	18×18	130	$322(\ 7\times\ 7)$	56	0.18
French[c]	12×16.25	130	$392(12\times\ 9)$	76	0.19
Meyer (cellulose)	8.35×7.9	100	$338(13\times14)$	50	0.15

[a] The 4 glucose units in 16×9.2 correspond to a glucose unit each corner of $8\times4.6\overset{\circ}{A}{}^2$
[b] Total, $(7\times8)2G+(7+8)\times7\times2G=322$; edge, $7\times4\times2G=56$.
[c] Total, $(12\times9+11\times8)\times2G=392$; edge, $(11+8)\times2\times2G=76$.

Table 3. The accessibility of crystalline portion on various dimension of crystallite in starch and cellulose by Kast's method.

| | Area of unit cell ($\overset{\circ}{A}{}^2$) | Glucose | Number of glucose units and α at a A | | | σ for a Å |
			Total	Edge	σ	
Rundle	$8\times4.6=37$	1	$1\pi a^2/4\times37$	$1\pi a/6$	$12.33/a$	0.18 for 70
Kreger	$18\times18\times\sin120=281$	6	$6\pi a^2/4\times281$	$2\pi a/17$	$11.02/a$	0.18 for 60
French	$12\times16.25\times\sin96.5=194$	4	$4\pi a^2/4\times194$	$2\pi a/14$	$13.86/a$	0.17 for 80
Meyer	$8.35\times7.9\times\sin84=66$	2	$2\pi a^2/4\times66$	$1\pi a/8$	$8.25/a$	0.19 for 43
						0.18 for 45
						0.17 for 50

a = diameter of cylindrical crystalline portion.

portion of cellulose were calculated from each value of σ by Howsmon[28] and Kast[29], respectively. The dimension of crystalline portion in starch was reported with the various values of 77[23] and less than 100 Å[2] except 130 Å and these values were almost the same as those of 70 and 80 Å which were calculated from the σ value of 0.18. · The assumption that the half glucoe residue on the surface of cylindrical crystalline portion was accessible, was understood from the β-1, 4 glucoside linkage in cellulose. In starch, it was not understood from the α-1, 4 glucoside linkage, but was done from the double helix structure according to report by French[38].

The crystallinity was calculated from the moisture content under saturated state. In this case, there was six mole water binding to a glucose residue. Moreover, the moisture content of the crystalline starch whose a glucose residue bound with 1, 2 and 3 mole water were shown in the table 4. The moisture content of starch which had the glucose residue binding with one mole water was almost same value as content of monolayer sorption water calculated from BET equation. The moisture content of starch which had the glucose residue binding with two or three mole water was as like as that of air dry starch. From these results, it was considered that the content of monolayer sorption water was one molar adsorbing water in a glucose residue as described in the section 1, "On the sorption of water". The water sorption in starch did not occur in the inner side of crystalline portion as in the case of cellulose. This supported the report by French that there was no water in the crystalline portion of starch.

Table 4. Equilibrium moisture contents at various crystallinities.

	x	σ	$6\,H_2O$	$3\,H_2O$	$2\,H_2O$	$1\,H_2O$
Potato	0.32	0.18	0.492	0.246	0.164	0.082
Sweet potato	0.42	0.18	0.437	0.218	0.146	0.073
Corn and Wheat	0.45	0.18	0.421	0.210	0.140	0.070
Cellulose	0.71	0.18	0.279	0.139	0.093	0.046

x = crystallinity; σ = accessibility of crystalline portion.

2-3   On the specific volume method

The starch had no water in the inner side of the crystalline portion, and sorption water was mainly sorbed in the amorphous portion. The swelling volume of starch granules increased with an increase of sorption water. This phenomenon occured at the amorphous portion and did not at the crystalline portion. The relationship between the specific volume of crystalline and amorphous portions and the crystallinity was reported in cellulose[22,29]. The relationship in cellulose was shown in the similar way as that in starch as follows[6]:

The relationship between the specific volume of material (V_o), crystalline (V_c) and amorphous (V_a) portions, and the crystallinity (x) was shown in the following equation, $V_o = xV_c + (1-x)V_a$. The value of specific volume was 0.629 for V_c and 0.680 for V_a in cellulose[29]. The values of V_a in starch was calculated to be 0.673 for potato, waxy corn and waxy rice starches, and to be 0.684 for sweet potato, tapioca, wheat and corn starches[6]. The specific volume of crystalline portion (V_c) was calculated from the each unit cell reported by Rundle[36], Kreger[37], Frech[38] and Meyer[39] as shown in the table 5. The unit cell which was reported by Rundle and Kreger contained the moisture and the density was calculated from value of the unit cell. The both values of density were so much larger than those of dry starch and cellulose. From the results of that the crystalline portion did not have the moisture and the high density, the specific volume of crystalline portion of starch corresponded to the value from the unit cell reported by French and moreover it was almost the same as that of cellulose. The specific volume of starch with the moisture of zero % was derived from the specific gravity which was calculated from the equation shown in the table 1. The crystallinity calculated from the

Table 5. The specific volume and density of crystalline portion of starch and cellulose.

	Volume of unit cell (ml)	Glucose	H_2O	Volume	Density
Rundle	$16 \times 9.2 \times 10.6 \times N = 939.6$	8	2	0.593	1.686
Kreger	$18 \times 18 \times \sin 120 \times 10.6 \times N = 1791.1$	18	1	0.553	1.808
French	$12 \times \sin 96.5 \times 16.25 \times 10.48 \times N = 1222.7$	12	0	0.629	1.590
Meyer	$8.35 \times \sin 84 \times 7.9 \times 10.3 \times N = 406.9$	4	0	0.628	1.592

N = avogadro's number, 6.022×10^{23}

Table 6. The crystallinity of starch and cellulose estimated by various methods.

	X-ray			Regain	Specific volume
	1	2	3		
Potato	0.24	0.24	0.25	0.32	0.34
Sweet potato	0.32	0.31	0.37	0.42	0.45
Tapioca	0.33	0.31	0.39	0.45	0.47
Wheat			0.36	0.45	0.44
Corn	0.32	0.36	0.39	0.45	0.42
Rice	0.35	0.46	0.38		
Waxy corn			0.39	0.31	0.30
Waxy rice				0.32	0.32
Cellulose		0.71		0.70	0.69

1, Hermans' method; 2, Wakelin's method; 3, Zobel's report.

specific volume was shown in the table 6. Moreover, each crystallinity by the X-ray diffracto-meter, moisture regain and that reported by Zobel[1] were given in the table. The crystallinity by X-ray method was lower than those by other methods, but the values in air state were lower than those in moistened state by X-ray method. The crystallinity of moistened potato starch was 1.33 times and 1.5 times more than that of air dry state reported by Sterling[23] and by the author[4], respectively. It was considered that the crystallinity of moistened starch by X-ray method became to be almost the same as those by the moisture regain and the specific volume methods.

3. On the heat of sorption

The heat of sorption was generated when a material sorbed water, and it was found to be related to crystallinity. There were two kinds of heat of sorption. One was integral heat and other was differential heat which was generally called heat of sorption. The heat of wetting was generated by immersion of water. The integral (q_{Int}) and differential (q_d) heat of sorption were calculated with the heat of wetting from the following equations.

$$Q_{Int} = (Q_{I_0} - Q_I) - N(hv - RT) \qquad \text{cal (g. starch)}^{-1}$$

$$q_{Int} = (Q_{I_0} - Q_I)/N - (hv - RT) \qquad \text{kcal (mol. } H_2O)^{-1}$$

$$q_d = \partial(Q_{I_0} - Q_I)/\partial N - (hv - RT) \qquad \text{kcal (mol. } H_2O)^{-1}$$

where Q_{Int} was integral heat of sorption per g of starch; N was mole of sorption water; Q_I and Q_{I_0} were heat of wetting in the material contained some and no moisture, respectively; h_v was heat of evaporation; R was gas constant; T was absolute temperature and $h_v - RT = 10.52 - 0.59 = 9.93$ Kcal (mol. $H_2O)^{-1}$.

The heat of wetting for starch was measured by means of microthermomater.   The integral and differential heat of sorption were calculated from the values of heat of wetting.   These results were described as follows[7]:

3-1   Heat of wetting

The relationship between heat of wetting and moisture content in potato starch was shown in the figure 5 and there were no hysteresis between sorption moisture and desroption one. This phenomenon was similar to the relationship between the half height width in PMR and the moisture content of starch[9].   The heat of wetting increased with a decrease of moisture content and the logarithmic heat of wetting gave essentially straight line agaist sorption moisture.   These results were similar to those by Schierbaum[41].   The heat of wetting in the starch containing no moisture (Q_{I_0}) was gave by extraporation to zero in the half logarithmic graph of heat of wetting against moisture content.
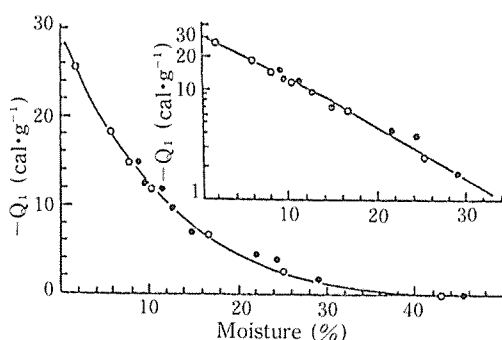

Fig. 5.   The heat of wetting of potato starch.
○, adsorption;   ●, desorption.

The heat of crystallization in cellulose was reported in the following equation by Hermans[42], $(Q'_{I_0} - Q_{I_0}) \times 0.62 \times X^{-1}$.   The Q'_{I_0} and Q_{I_0} were heat of wetting of amorphous and crystalline materials, respectively, when the both materials contained no moisture, and X was crystallinity. The heat of crystallization in cellulose was reported to the 4.1 ± 0.2 Kcal per mole of glucose residue by Hermans[43].   The heat of crystallization was calculated from the above equation with Q'_{I_0} in ball milled and Q_{I_0} in crystalline materials, and the crystallinity was estimated by the moisture regain method.   These results were as follows; 4.17 for cellulose, 0.5 for potato, 0.4 for sweet potato and tapioca, 1.8 for wheat and 2.2 Kcal per mole of glucose residue for corn starches.   The heat of crystallization in cereal starch was higher than that of root and tuber starches.   The same was the true in such phenomena that the temperature and absorbed heat on gelatinization in starch were differed by the variety of starch[44], and also that the temperature of gelatinization increased with an increase of temperature in the maturation period[45].

3-2   Integral heat of sorption

The integral heat of sorption was heat per sorption mole water which was generated when the material containing no moisture sorbed water.   The integral heat of sorption decreased with an increase of sorption water and it was considered to become the heat of evapolation of 9.93 Kcal (mol. H_2O)$^{-1}$ on the saturated moisture state.   Wahba reported that the integral net heat of sorption per gram of cellulose, $(Q_{I_0} - Q_I)$, was in proportion to the amorphous region.   These heat were calculated from the heat of wetting of moistened starches which were equilibrated in various relative humidity.   The heat for sweet potato was almost the same

as that of tapioca and was 1.2 times more than that of corn and wheat starches.   It was considered that the amorphous region in sweet potato and tapioca was 1.2 times more than that in wheat and corn starches.

3-3   Differential heat of sorption

The differential heat of sorption (q_d) were calculated from the equation described above and decreased with an increase of sorption water.   It was considered to become constant at the moisture content more than 20%.   The phenomena in the differential heat of sorption were almost the same as those in the isosteric heat of sorption as shown in the figure 6.   The isosteric heat of sorption (q_{st}) was $q_{st}=q_d-RT$, and was calculated from the equation of Clausius Clapayron[10,11,40].   The figure 6 showed the isosteric heat which was calculated from the

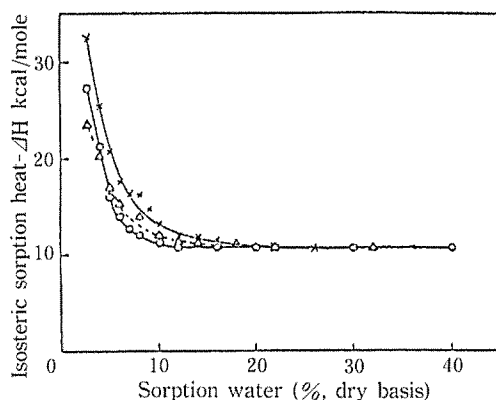Fig. 6.   Relation of isosteric sorption heat and sorption
water.
○—○,potato;   △⋯△,sweet potato;   ×—×,rice.
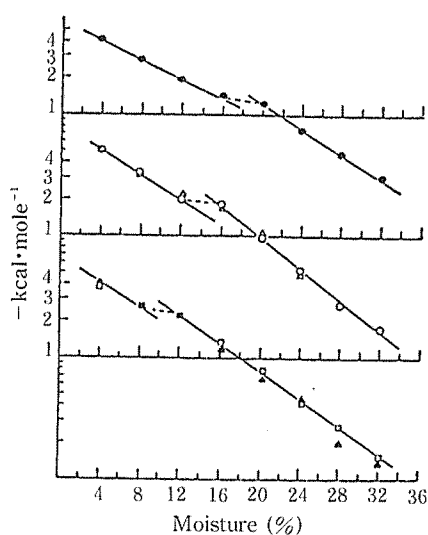

Fig. 7.   The differential net heat of sorption
of starches.

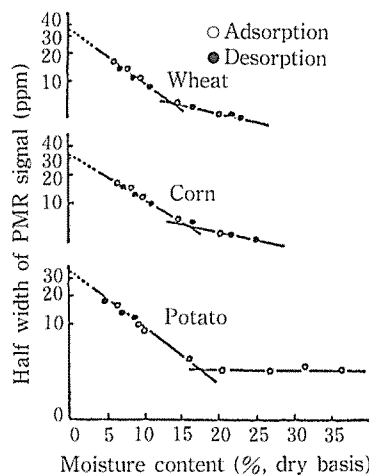●, potato;   ○, sweet potato;
△, tapioca;   □, wheat;   ▲, corn.

Fig. 8.   Relation between half width
of PMR signals and moisture
content.

experimental results at 25° and 40°C [7]. The figure 7 was the graph of logarithmic value of differential net heat of sorption $(q_d + h_v - RT)$ protted against the moisture content. The graph showed the two straight lines in each starches. It was considered that heat of sorption for potato starch changed at $18 \pm 2\%$ of moisture content, $14 \pm 2\%$ for sweet potato and $10 \pm 2\%$ for wheat and corn starches. These phenomena corresponded to the relationship between the moisture content and half height width in PMR where the half height width changed at 14 to 15% of moisture content for cereal and 17 to 18% for tuber and root starches as shown in the figure 8.

Harkins and Jura reported that the heat of water vaporization on desorption of moistened anatase was 6.55 Kcal (mol. H_2O)$^{-1}$ at first molecular layer, 1.64 at second, 0.4 at third, 0.1 at fourth, 0.025 at fifth and almost zero at over sixth and decreasing ratio was 0.25 [32]. The differential net heat of sorption in starch contained the moisture of monolayer sorption water was 2.75 Kcal (mol. H_2O)$^{-1}$ for potato, 3.2 for sweet potato, 3.3 for tapioca and 2.7 for wheat and corn starches. Assuming that the second sorption layer corresponded the moisture content which was two times more than that of monolayer sorption in starch, the net heat of second sorption layer was 0.45 times more than that in first layer. The decreasing ratio of starch was larger than that of anatase.

Conclusion

The author described the sorption phenomena, the crystallinity and heat of sorption on the starch. The sorption phenomena in starch was explainable with gas sorption theory. The theory of the relationship between the crystallinity and sorption water in cellulose was able to be adapted to elucidate the same relationship in starch. The experimental studies on these matter in starch were no so much, it was necessary to study more.

Summary

The author described the relationship between the amount of sorption water and crystallinity or heat of sorption in starch granules.

The values of the monolayer sorption water in starch were 7–8% of starch and saturated sorption water would be six molecules for each glucose residue and the crystallinity of starch were found to be from 31 to 45% by means of moisture regain method. The crystallinity measured by means of X-ray method increased with increasing sorption water and seemed to become the values by means of the moisture regain and specific volume methods. The heat of crystallization of starch were as follows: 0.4–0.5 Kcal (mol. glucose residue)$^{-1}$ for potato, sweet potato and tapioca starches, and 1.9–2.2 Kcal (mol. glucose residue)$^{-1}$ for corn and wheat starches. The amorphous portion in sweet potato and tapioca starches were 1.2 times as much as that of wheat and corn starches according to the results as to integral net sorption heat.

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要　　約

澱粉粒の水分収着について

奈　良　省　三

　澱粉粒における水分収着や結晶化度と収着水分量あるいは収着熱について述べた。澱粉での単分子収着水分量は7～8％であって，飽和水分状態ではグルコース残基あたり6分子の水分収着と思われる。澱粉の結晶化度はリゲイン法で31～45％である。X線回折法による澱粉の結晶化度は収着水分量の増加にともなって増大し，飽和水分状態ではリゲイン法や比容積法による値と同程度になると思われる。澱粉の結晶化熱はジャガイモ，カンシヨ，タピオカでグルコース残基あたり0.4～0.5 kcal で，トウモロコシ，コムギでは1.9～2.2 kcal であった。正味積分収着熱からサツマイモ，タピオカ澱粉の非晶部分はトウモロコシ，コムギの1.2倍であった。