Sorption of Water Vapor by B Pattern Starch

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Synopsis

Water vapor sorption isotherms of cotton cellulose and B pattern starch preparations, potato starch, corn amylose, amylomaize, and retrograded potato starch, were determined at 5 and 25°C. The crystallinity fraction of these materials equilibrated with water vapor at various partial pressures was determined by x-ray diffraction. The thermodynamic functions of adsorption were calculated, and B.E.T. constants were determined.

As has been pointed out by Macchia and Bettelheim,[1] there is surprisingly little published work on the sorption of water vapor by starch in view of potentially wide industrial interest. At the time we initiated these studies, no water adsorption data on B pattern starch had been published. Subsequently results for the B form of amylose have appeared.[1] In the present work, our previous studies on the interaction of water and pectic substances[2-4] and water and starch[5] by x-ray and isotherm methods are hereby extended to the B pattern starch preparations: potato starch, corn amylose, amylomaize, and retrograded potato starch. In addition we have made studies on cotton cellulose for the purpose of comparison.

Experimental

The samples were prepared in the manner we have recently reported.[6] For the adsorption studies, the samples were predried in vacuum at room temperature until constant weight was reached (about 1 week). After adsorption, the samples were dried in vacuum at 70°C. for a period of 7–10 days to obtain a dry weight.

The adsorption apparatus and method[2,5] and the details of determining crystallinity by x-ray diffraction[7] have been thoroughly described in previous papers from our laboratories.

Results

Adsorption isotherms at 5 and 25°C. for the various materials are shown in Figures 1–5. The treatment of the samples prior to the adsorption

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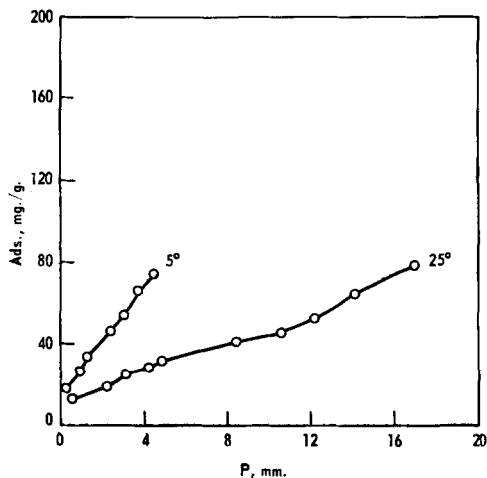* Present address: Food Technology Department, Cairo University, Giza, Cairo, Egypt, U.A.R.

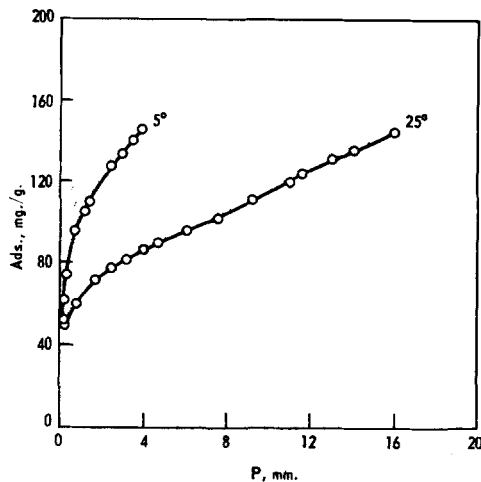Fig. 1. Adsorption isotherms of water on cotton cellulose.

Fig. 2. Adsorption isotherms of water on potato starch.

experiments did not, except for cotton cellulose, remove all of the water even though constant weight was reached by predrying at room temperature in vacuum. This residual water, the weight of which was obtained by drying in vacuum at 70°C. after adsorption was completed, is included in the isotherm data. It is, effectively, the water contained at $P/P_0 = 0$ for the B pattern starches. The values are contained in Table III which will be referred to later.

In Figures 6–10 the standard differential thermodynamic values at 25.0°C. calculated from the adsorption isotherms are given. The standard differential free energy[3] is given by
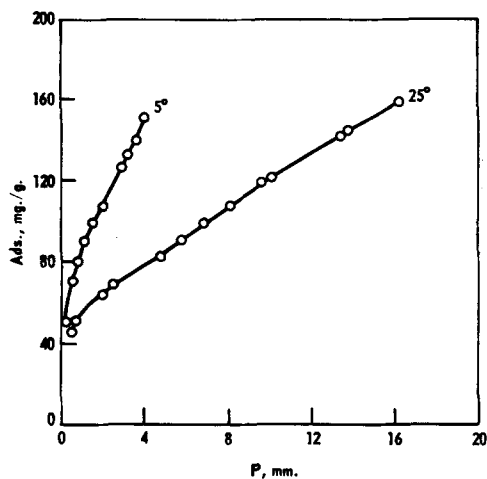
$$\Delta \bar{F}^\circ = RT \ln (P/760)$$

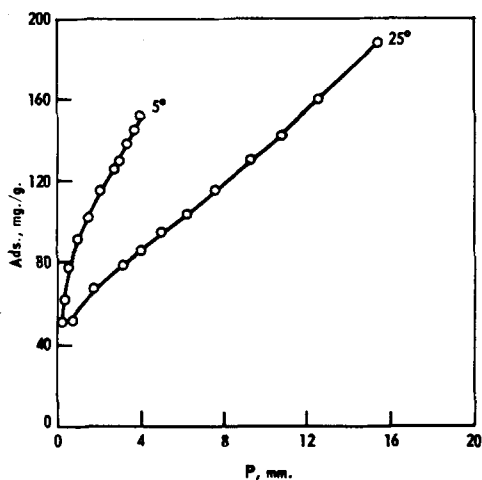Fig. 3. Adsorption isotherms of water on amylomaize.

Fig. 4. Adsorption isotherms of water on amylose.

The differential enthalpy of adsorption is given by the Clapeyron-Clausius equation applied to the adsorption isotherms at constant adsorption

$$\Delta \bar{H}^\circ = RT^2 \, (\delta \ln P / \partial T)_a$$

The standard differential entropy of adsorption is, then

$$\Delta \bar{S}^\circ = (\Delta \bar{H}^\circ - \Delta \bar{F}^\circ)/T$$

The crystallinity of the various materials at several relative pressures as determined by x-ray studies is given in Table I.

TABLE I

Crystallinity as Determined by X-Ray Diffraction at Various Relative Pressures of Water Vapor

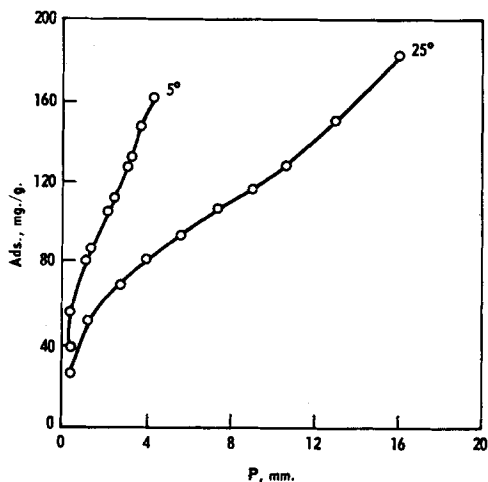| Relative pressure P/P_0	Crystallinity, fraction				
	Cotton cellulose	Potato starch	Amylomaize	Amylose	Retrograded potato starch
0	0.71	0.21	0.20	0.19	0.06
0.20	0.70	0.20	0.17	0.19	0.08
0.40	0.70	0.22	0.19	0.19	0.10
0.60	0.71	0.22	0.19	0.20	0.11
0.80	0.70	0.27	0.20	0.19	0.12

Fig. 5. Adsorption isotherms of water on retrograded potato starch.

Discussion

The crystallinity determinations indicate that adsorption of water has very little effect on the crystalline fraction. The experimental error in these determinations is about ±0.03. Therefore, the apparent increase for potato starch at $P/P_0 = 0.80$ and the trend for retrograded potato starch may not be significant. It should be emphasized that there is bound water on the starch samples at $P/P_0 = 0$ as discussed earlier and shown in Table III below. It may be concluded that water is adsorbed in the amorphous regions only and that this does not result in increased crystallinity if the starch is originally in the B pattern.

The standard differential thermodynamic values at 25.0°C. shown in the figures may be compared with those for the condensation of water vapor to liquid water at 25.0°C.: $\Delta F°_{298} = -2.06$ kcal./mole; $\Delta H°_{298} = -10.5$ kcal./mole; $\Delta S°_{298} = -28.4$ cal./deg.-mole. The thermodynamic values obtained are similar to those we have reported for several V pattern

starch preparations.[4]   The third-law entropy of gaseous water is 45.1 cal./deg.-mole at 25.0°C.[8]   The observed entropy changes in adsorption are, except for potato starch, below this value.   As we have discussed previously,[3] considerations involving water only lead to the conclusion
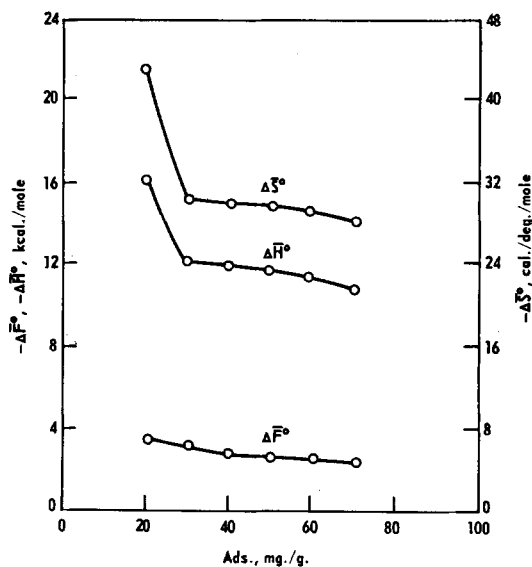

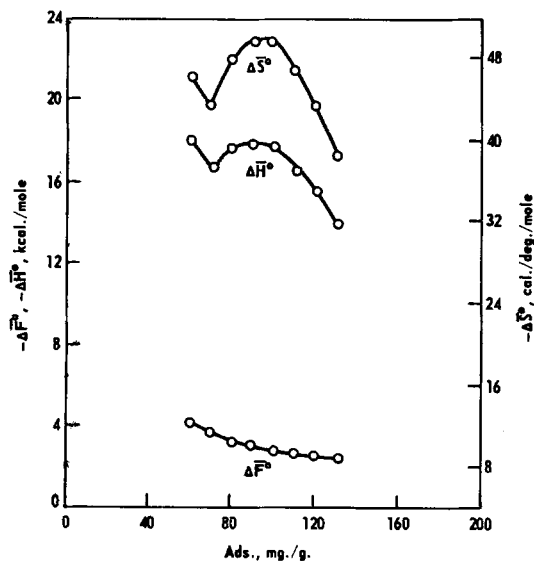Fig. 6. Standard differential thermodynamic functions for adsorption of water vapor on cotton cellulose.

Fig. 7. Standard differential thermodynamic functions for adsorption of water vapor on potato starch.

that an entropy change of 45.1 cal./deg.-mole is not likely to be obtained since it would be expected that some rotational entropy would exist for water in the adsorbed state. The translational entropy for water vapor calculated according to the Sackur-Tetrode equation is 34.6 e.u. at 25°C.,
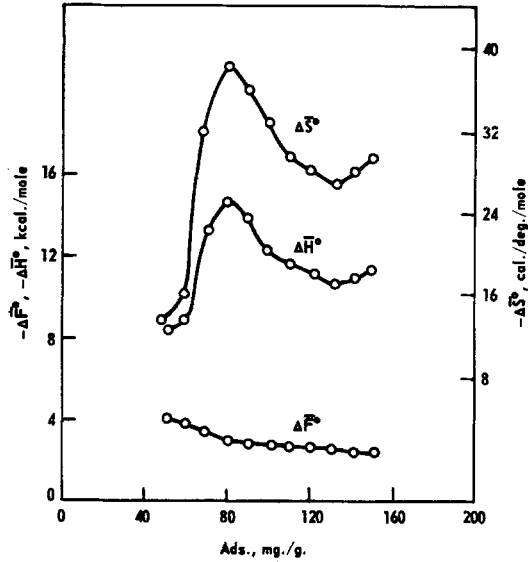

Fig. 8. Standard differential thermodynamic functions for adsorption of water vapor on amylomaize.
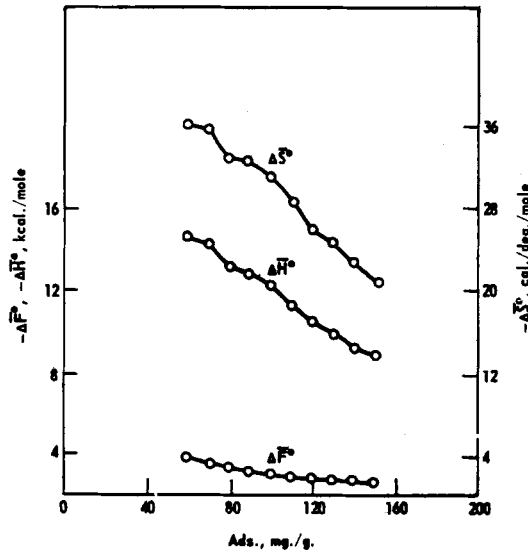

Fig. 9. Standard differential thermodynamic functions for adsorption of water vapor on amylose.
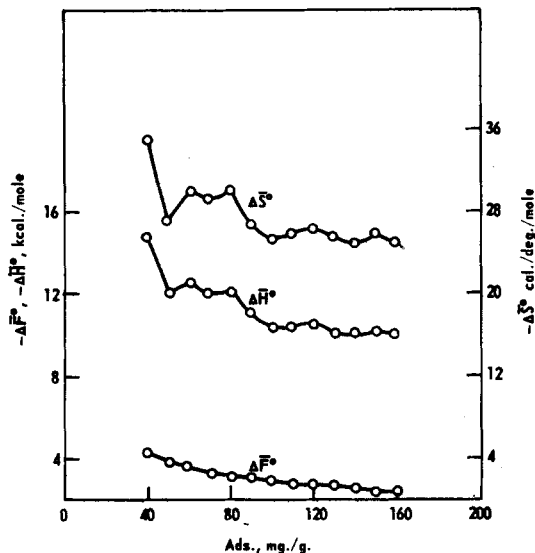
Fig. 10. Standard differential thermodynamic functions for adsorption of water vapor on retrograded potato starch.

and it would be expected that this entropy could be lost on adsorption. Except for potato starch, the maximum entropy changes do not exceed this value appreciably. Also, as we have noted previously,[3] entropy changes of greater than 45 e.u., as observed for potato starch in this work, are explicable by configurational entropy contributions from the adsorbent.

B.E.T. constants calculated from the 25.0°C. isotherms are given in Table II.

As described in the experimental part, the dry weight of the adsorbent was obtained by drying after adsorption at 70°C. in vacuum for a prolonged period. Therefore at $P/P_0 = 0$, water is contained on the surface, probably in the crystalline regions. One may assume that the additional water is adsorbed in amorphous regions. For cellulose water is not retained at $P/P_0 = 0$ indicating that there is no water in crystalline regions. The monolayer value of 0.32 mole H_2O/mole monomer, V_m from the B.E.T.

TABLE II
B.E.T. Constants at 25.0°C.

Material	V_m, mg./g.	V_m, mole H_2O/mole monomer	C	$E_A - E_L$, kcal./mole
Cotton cellulose	35.7	0.32	11.3	1.45
Potato starch	79.5	0.71	67.6	2.50
Amylomaize	75.7	0.68	43.3	2.24
Amylose	88.5	0.79	32.3	2.08
Retrograded potato starch	80.0	0.72	27.6	1.98

method, corresponds closely to one molecule of water adsorbed per molecule of monomer in the amorphous region. This result is in excellent agreement with the value found by Morrison and Dzieciuch.[9] We have previously suggested that a possible model for water adsorption in V pattern starch is that at the monolayer a molecule of water is bound by two glucose residues through a single functional group on each. On the basis of this model for starch, by using the amorphous fraction as given by the x-ray data and the values for water retained at $P/P_0 = 0$, one can calculate a value for the moles of water per mole of monomer at a monolayer. The results obtained and a comparison with the corresponding value obtained by the B.E.T. method are shown in Table III.

TABLE III
Monolayer Water

Material	$P/P_0 = 0$ H_2O, mg./g.	V_m(theory), mole $H_2O/$ mole monomer	V_m(B.E.T.), mole $H_2O/$ mole monomer
Cotton cellulose	0	0.29	0.32
Potato starch	45.7	0.79	0.71
Amylomaize	31.8	0.69	0.68
Amylose	35.7	0.73	0.79
Retrograded potato starch	17.5	0.63	0.72

On consideration of the nature of the data which enter into the calculation, the agreement between the V_m values is as good as could be expected.

As we have remarked earlier, the only other results for water adsorption on B pattern starch are those of Macchia and Bettelheim[1] for amylose. There does not appear to be substantial agreement between their results and ours. It must, however, be emphasized that although their starch was presumably B pattern, the method of preparation and treatment prior to adsorption were markedly different. Any detailed comparison of the results will have to be deferred until more comprehensive studies of the systems are made.

References

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7. C. Sterling, *Staerke*, **12**, 182 (1960).
8. *JANAF Thermochemical Tables*, The Dow Chemical Co., Midland, Mich., March 31, 1961.
9. J. L. Morrison and M. A. Dzieciuch, *Can. J. Chem.*, **37**, 1379 (1959).

Résumé

Des isothermes de sorption d'eau de la cellulose de coton et des préparations d'amidon en réseaux B, l'amidon de pomme de terre, l'amilose de grain, l'amilomais et l'amidon de pomme de terre rétrogradé, ont été déterminés à 5 et 25°C. La fraction cristalline de ces matériaux equilibrée avec la vapeur d'eau à diverses pressions partielles a été déterminée par diffraction aux rayons-X. Les fonctions thermodynamiques d'adsorption ont été calculées et les constantes B.E.T. ont été déterminées.

Zusammenfassung

Wasserdampf-Sorptionsisothermen von Baumwollcellulose und von Stärkepräparaten vom "B"-Typ, Kartoffelstärke, Maisamylose, Amylomais und retrogradierte Kartoffelstärke wurden bei 5° und 25°C bestimmt. Der kristalline Bruchteil dieser Stoffe wurde nach Einstellung des Gleichgewichts mit Wasserdampf bei verschiedenem Partialdruck durch Röntgenbeugung bestimmt. Die thermodynamischen Funktionen für die Adsorption wurden berechnet und die B.E.T-Konstanten bestimmt.