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RELATION OF CATION EXCHANGE TO THE ACIDIC PROPERTIES OF COTTON

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ABSTRACT

The acid-binding capacity of cotton is quantitatively determined by its content of cationic ash (the total content of the cations of inorganic bases), most of which is associated with the pectic substance. This conclusion emerges from a study of the hydrochloric-acid titration curves of dewaxed, water-washed cotton and of depectinized cotton, and from a comparison of the maxima of these curves with direct determinations, by an electro dialysis method, of the hydrogen-ion equivalence of the cationic ashes of both of these samples. The difference between the two maxima, each of which corresponds to the cationic ash, is equivalent to the carboxyl content of the pectic substance, as determined by uronic-acid analyses.

At low values of pH, the results for the acid-binding capacities were corrected for the selective sorption of water by the cotton. The nature and magnitude of this correction, and the method in which it was applied, are discussed in detail.

Measurements of the capacity of the fiber to bind hydrochloric acid were made in the absence of added salt, and in potassium-chloride solutions of 0.1 and 1.0 *M* ionic strength. The titration curves obtained in the presence of 0.1 *M* salt were slightly shifted from those obtained in the absence of salt, but no further shift was obtained by further increase in ionic strength. Subtraction at corresponding values of pH of the acid-binding capacities obtained in salt solutions with depectinized cotton from the acid-binding capacities for the dewaxed cotton yielded the titration curve for the pectic substance in the presence of salt. The curve conforms closely to the mass-action law for an acid of *pK* 3.3. This value is close to *pK* values for other polyhydroxy carboxylic acids. A titration curve for pectic substance in the absence of added salt was obtained by a similar process of subtraction. The shift in this curve from the curve for pectic substance in the presence of salt is shown to be qualitatively consistent with the predictions of the Donnan equilibrium.

The maximum acid bound by the dewaxed cotton used in this work was 0.066 M-eq/g (milliequivalent per gram). The content of pectic substance, determined directly as well as by the difference in the maxima of the titration curves, accounts for 0.056 M-eq/g. The difference between these two values, 0.010 M-eq/g, is contributed by acidic groups in the depectinized cotton. The possible source and significance of these acidic groups are discussed. It is tentatively assumed that these acidic groups are an integral part of the cellulose molecule, such as an end group. On the basis of this assumption, the cellulose has an equivalent weight of about 100,000, which corresponds to a minimum chain length of about 600 glucose residues.

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I. INTRODUCTION

Cotton and other naturally occurring cellulosic materials yield, on ignition, an ash which is alkaline in reaction. This results from the fact that the fiber normally exists as a salt, many of the anions being provided by the cellulose of the fiber and by associated materials, such as pectic substance [1, 2, 3].² The cations in water-washed cotton have been shown by Walker and Quell to consist principally of Ca^{++} , Mg^{++} , Fe^{+++} , and Al^{+++} [2]. In addition, raw cotton also contains a quantity of neutral salt, most of which is removed during washing of the fiber with water.

The manner in which cotton binds acid may be considered as an exchange process between the hydrogen ions of the acid and the cations associated with the fiber. The extent of the exchange is a function of the number and nature of the cations, the concentration of the acid, and the tendency of the hydrogen of the acidic groups in the cotton to ionize. This concept of cation exchange has been employed from time to time by earlier investigators to explain the reaction of cellulosic materials with acids and salts [1, 2, 3, 4]. The importance and wide applicability of these exchange reactions have been recognized and discussed by McLean and Wooten [3], who demonstrated that the amount of acid bound by different cellulosic materials at an arbitrary pH is proportional to their ash contents. They also suggested that the major portion of the ash is contributed by noncellulosic materials associated with the cellulose.

In the present investigation, which involved a detailed study of the acid-binding capacity of cotton fibers over a wide range of pH values, it is shown that the acid-binding capacity of cotton at any pH is determined by its cationic ash. From the complete titration curves, and the hydrogen-ion equivalence of the ash, the maximum acid bound by different samples of cotton was ascertained, which in turn permitted the quantitative allocation of the acid bound to the principal constituents of the fiber.

II. EXPERIMENTAL PROCEDURE

1. MATERIALS

Raw cotton was extracted with hot alcohol for 24 hours, and then washed thoroughly with distilled water at room temperature for several hours. Such samples will henceforth be described as *dewaxed cotton*.

A portion of the dewaxed material was further purified by extraction for 4 or 8 hours with a boiling 1-percent solution of sodium hy-

² Figures in brackets indicate the literature references at the end of this paper.

droxide, according to the method recommended for the preparation of standard cellulose. The procedure was essentially the same as that described by Corey and Gray [5], except that the apparatus of Worner and Mease [6] was used. Fibers treated in this way were shown by the method of Whistler, Martin, and Harris [7] to be free of pectic substance. In one step of this purification, the fibers were washed with a dilute solution of acetic acid. This undoubtedly removed some of the cations from the fiber and since cotton binds acid by a cation-exchange process which involves the back titration of the acid groups of the fiber by an added acid, it was necessary to make certain that all of the acidic groups were in the salt form. This was accomplished by soaking the purified samples for about 3 hours in a solution of calcium hydroxide at room temperature. They were then washed in running distilled water for about 24 hours. Cotton from which both wax and pectic substance were removed is designated *depectinized cotton*. Depectinized cotton which has been washed with a solution of calcium hydroxide is designated *lime-washed depectinized cotton*.

All samples were conditioned at 21° C and 65-percent relative humidity before weighing. The moisture contents of the fibers were determined by drying representative samples at 105° C for 2 hours in a vacuum oven.

2. METHODS

Determination of the acid-binding capacity.—Samples of cotton weighing about 5 g and containing a known amount of moisture were immersed in 100-ml portions of the acid solutions at the temperature of the experiment (0° or 25° C). Large test tubes (1½ by 8 in.) were found to be convenient for this purpose, since the samples could be easily pressed into the bottom of the tube to insure uniform wetting of the fibers or to permit squeezing the liquor from the fibers after equilibrium was reached. The amount of acid absorbed was determined by titration with sodium hydroxide of 50-ml aliquots of the original solution and of the solution in equilibrium with the sample, using bromcresol purple as the indicator. From the difference between these titers, the weight of the sample, and its content of moisture, the amount of acid taken up per gram of dry cotton was calculated. In a number of measurements, the concentrations of strongly acid solutions (in the region of pH 1) were determined by adding a weighed quantity of strong alkali to the solution, after which the titration was completed with weak acid or alkali.

Preliminary measurements at several acidities indicated that a close approximation to a final equilibrium is attained in a few hours. In most of the experiments, however, the samples were allowed to remain in contact with the solutions overnight.

Determination of pH.—Measurements of pH were made with a McInnes and Belcher-type glass electrode and a vacuum-tube potentiometer, using a cathode-ray "eye" as null indicator. The pH values were referred to potassium acid phthalate, 0.05 M, to which was assigned a pH value of 4.01 [8].

Temperature.—With the exception of one experiment at 25° ± .02° C, all of the acid solutions in contact with the cotton were kept at 0° ± .01° C to inhibit decomposition of the fibers.

Determination of cationic ash.—The hydrogen-ion equivalence of the cationic ash was determined by an electro dialysis method described elsewhere [9].

III. RESULTS AND DISCUSSION

1. SELECTIVE SORPTION OF WATER BY COTTON

The determination of the maximum acid-binding capacity of cellulose is complicated by the fact that the fibers may selectively sorb water from a solution of acid, and thus affect its titer. Since the acid-binding capacity is calculated from titer differences, a correction must be applied to compensate for this effect. At pH values below 1.5, the magnitude of the correction is appreciable compared with the acid-binding capacity of cotton, but it becomes negligible at pH values above 2.5.

If B is the amount of water selectively sorbed per gram of dry cotton, then the amount sorbed per gram from the solution by a sample which originally contains W g of water per gram is $(B-W)$. Water taken up in this manner is no longer available for dilution of the acid, and would thus tend to cause an increase in concentration of the acid solution in contact with the fiber. At the same time, however, a quantity of acid, A (M- eq/g), will be bound by the sample, and produce a decrease in concentration of the acid solution. Obviously, if any of the acid solution as such is dissolved in the sample, the titer of the solution will not be affected. From the above, it follows that if S g of dry cotton is immersed in G ml of acid solution of concentration C_0 , and the concentration of the solution after equilibrium is attained is C , the corrected acid-binding capacity of the cotton is given by the equation,

$$A = \frac{G(C_0 - C)}{S} + C(B - W), \quad (1)$$

where A is the corrected acid-binding capacity, $G(C_0 - C)/S$ is the apparent acid-binding capacity, and $C(B - W)$ is the correction for the selective sorption of water.

The actual measurement of the quality B presents considerable experimental difficulty. In the region of the maximum acid-binding capacity, measurement of titer differences in solutions of different initial acid concentrations, or in solutions of the same initial acid concentration which have been allowed to come to equilibrium with samples of different moisture contents, gives equations of the form of eq1. The solution of any two of such equations should give values for A and B , but such a procedure demands the assumption that both A and B are constant for the conditions employed. Measurements made in 0.1 and 0.2 M solutions of hydrochloric acid indicated that this assumption is not valid. The results were such as to indicate that more acid or less water was sorbed in the more concentrated of these solutions. If calculations are made from measurements of solutions for which the above assumption should be more nearly valid (0.10 and 0.11 M solutions of hydrochloric acid), the values for A and B are too sensitive to experimental error to be useful.

It was found that the following method for evaluating A and B leads to less equivocal results. A substance which is assumed not to be sorbed by the fiber was added to the solution of acid as a reference substance. The change in concentration of this substance gives a

direct measure of the amount of water ($B-W$) sorbed by the fiber. Two reference substances, sodium chloride and trehalose, were used in this work. The change in concentration of the former was determined by evaporating an aliquot of the solution and determining the dry weight of salt. In the case of the disaccharide, trehalose, the change in concentration was measured polarimetrically. The actual determinations were made as follows: Samples of cotton of known weights and moisture contents were immersed in solutions that were 0.1 M with respect to hydrochloric acid, and 3.43 M with respect to sodium chloride, and the changes in concentration of both acid and salt were determined. The acid-binding capacity, A , was then calculated, due account being taken of the water sorbed as determined by the change in salt concentration. The mean of four values, so determined, was 0.067 M -eq/g.

The value for B in solutions in the region of pH 1 was then calculated by substituting the value 0.067 for A in eq 1. The value ($C_0 - C$) is small, and therefore the determination of B by this procedure is subject to the uncertainty of this quantity. In order to improve the reliability of B , a series of 20 samples of dewaxed cotton of known weights and moisture contents was immersed in solutions of hydrochloric acid of known concentrations, the acidities of which were in the region of pH 1. The 20 equations of the form of eq 1, obtained from these measurements, were summed up and gave the equation,

$$28.63A - 3.87B = 1.489. \quad (2)$$

Substitution of the value 0.067 for A in eq 2 gave a value for B (in HCl solution) of 0.11 g of water per gram of dry cotton.

The values of A and B were also determined by a second method, in which trehalose was used as the reference substance. Samples of cotton of known weights and moisture contents were immersed in trehalose solutions that were 0.04 M with respect to hydrochloric acid. The concentration of trehalose before and after the introduction of the samples was measured polarimetrically. By this procedure, a value for B of 0.13 g of water per gram of dry cotton was obtained.

TABLE 1.—Application of the correction for the selective sorption of water to the acid-binding capacity of dewaxed cotton in 0.1 M hydrochloric acid

Initial water content	Apparent acid-binding capacity, $G(C_0 - C)/S$	Correction, $C(B - W)$	Corrected acid-binding capacity, A
<i>g/g of cotton</i>	<i>M-eq/g</i>	<i>M-eq/g</i>	<i>M-eq/g</i>
0.000	0.054	+0.012	0.066
.100	.063	+ .002	.065
.190	.075	- .007	.068
.308	.085	- .019	.066
.720	.124	- .059	.065
1.135	.164	- .097	.067
		Mean.....	0.066

The validity of this method of correction for the selective sorption of water is shown in table 1, which presents data on dewaxed fibers of widely different initial moisture contents. The measurements were

made in 0.1 *M* solutions of hydrochloric acid, and the results are corrected, using the mean value 0.12 for *B*. Each figure represents the mean of at least two determinations. In the cases of the samples of high moisture contents, some of the water was added directly to the solution with the sample. The discordant values for the apparent acid-binding capacity, $G(C_0 - C)/S$ for all of these samples are brought into close agreement by application of the correction $C(B - W)$, to give the corrected acid-binding capacity, *A*.

It is of interest to note that the values for *B*, 0.11 and 0.13 g of water per gram of dry cotton, are considerably lower than the known moisture content of cotton at relative humidities between 99 and 100 percent (about 0.3 g of water per gram of cotton) [10], which corresponds approximately to the humidity of air in equilibrium with 0.1 *M* hydrochloric acid. The result suggests that the average partition coefficient of the hydrochloric acid between the water in the external solution and the water held by the fiber is greater than unity. The average value of *B* of 0.12 g of water per gram of cotton represents the portion of the total sorbed water which is unavailable for dilution of the acid.

2. COMBINATION OF DEWAXED AND OF LIME-WASHED, DEPECTINIZED COTTON WITH HYDROCHLORIC ACID

Measurements of the combination of dewaxed and of lime-washed depectinized cotton with hydrochloric acid are given in table 2 and shown graphically in figure 1. The data were obtained in the absence

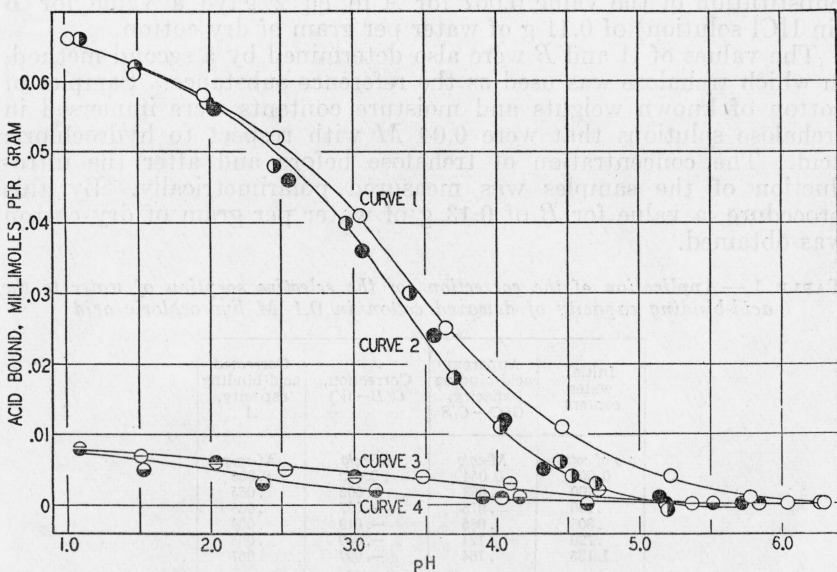


FIGURE 1.—Combination of dewaxed and of lime-washed depectinized cotton with hydrochloric acid at 0°C.

Curve 1, dewaxed cotton in the absence of added salt, ○. Curve 2, dewaxed cotton in hydrochloric acid-potassium chloride solutions of 0.1 *M* ionic strength, ⊙; and in solutions of 1.0 *M* ionic strength, ●. Curve 3, depectinized cotton in the absence of added salt, ⊖. Curve 4, depectinized cotton in solutions of 0.1 *M* ionic strength, ⊕; and in solutions of 1.0 *M* ionic strength, ⊗.

of added salt, and in solutions made up to 0.1 and 1.0 *M* ionic strengths with potassium chloride. The increase of ionic strength from 0.1 to 1.0 *M* produced no measurable effect on the titration curve of either sample, and accordingly only one curve is drawn for each sample at the two ionic strengths. The curves for dewaxed and for lime-washed depectinized cotton tended to approach maxima, at about pH 1, of 0.066 and 0.008 M-eq/g, respectively. The failure to arrive at unambiguous maxima may be due to the uncertainty in the correction for the selective sorption of water or to other secondary effects which may occur in solutions of high acid concentrations.

TABLE 2.—Combination of dewaxed and of lime-washed depectinized cotton with hydrochloric acid at 0°C, in the presence of varying amounts of potassium chloride

DEWAXED COTTON					
No added salt		0.1 <i>M</i> ionic strength		1.0 <i>M</i> ionic strength	
pH	Acid bound	pH	Acid bound	pH	Acid bound
	<i>M-eq/g</i>		<i>M-eq/g</i>		<i>M-eq/g</i>
1.08	0.066	1.08	0.066	2.03	0.056
1.47	.061	1.48	.062	2.55	.046
1.96	.058	1.98	.057	3.06	.036
2.47	.052	2.45	.048	3.56	.024
3.05	.041	2.94	.040	4.05	.012
3.64	.025	3.39	.030	4.62	.005
4.45	.011	3.70	.018	5.24	.001
5.22	.004	4.02	.011	5.72	.000
5.78	.001	4.44	.006	-----	-----
6.04	.000	4.52	.004	-----	-----
6.30	.000	4.69	.003	-----	-----
		5.20	-.001	-----	-----
LIME-WASHED DEPECTINIZED (4 HR), COTTON					
1.08	0.008	1.08	0.008	2.04	0.006
1.51	.007	1.53	.005	3.00	.004
2.04	.006	2.36	.003	4.03	.001
2.52	.005	3.15	.002	5.18	.000
3.00	.004	3.90	.001	5.84	.000
3.48	.004	4.16	.001	-----	-----
4.09	.003	4.63	.000	-----	-----
4.71	.002	5.52	.000	-----	-----
5.67	.000	-----	-----	-----	-----
6.27	.000	-----	-----	-----	-----
6.38	.000	-----	-----	-----	-----

None of the pectic substance appeared to dissolve during the titration with acid. This was indicated by sharp indicator end points, lack of frothing, exact correspondence between acid-binding capacity calculated from pH differences and from titer differences, and the pH of 0.1 *M* potassium chloride solution in contact with the sample (about 5.3). If any soluble potassium pectate had been formed, the pH value of the solution would necessarily have been appreciably higher. The pectic substance may be insoluble because it exists as an insoluble salt of polyvalent cations or as the free acid, which is insoluble in acid solutions.

The difference between the maxima of the curves indicates that about 85 percent of the acid groups of dewaxed cotton is furnished by the pectic substance. This conclusion is confirmed by direct chemical analyses presented elsewhere. The remaining acid groups appear to be associated with the depectinized cotton. Further consideration of these groups and their probable significance is given later.

The titration curves for dewaxed cotton (curves 1 and 2, fig. 1) must be considered as composites of the curves for depectinized cotton and the pectic substance. Accordingly, subtraction, at corresponding values of pH, of the ordinates of curve 3 from those of curve 1 should give a titration curve for the pectic substance in the absence of added salt. Similarly, subtraction of the ordinates of curve 4 from those of curve 3 gives the curve for pectic substance in the presence of added salt (0.1 or 1.0 *M* potassium chloride). The data thus obtained interpolated at intervals of 0.5 pH unit, are shown by the points in figure 2. The smooth curves in this figure are not drawn to fit these points, but are explained in section III-6. It should be noted that the data obtained by the subtraction process described above are not subject to errors inherent in the method of correction for the selective sorption of water by the samples, since the subtraction would presumably

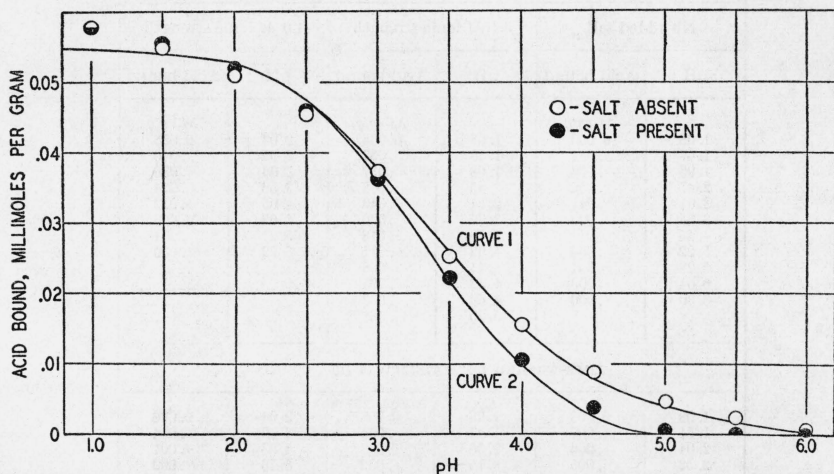


FIGURE 2.—Calculated data for the combination of pectic substance with hydrochloric acid at 0° C.

Curve 1, pectic substance in the absence of added salt, ○. Curve 2, pectic substance in solutions of 0.1 *M* or 1.0 *M* ionic strength, ●. The smooth curves are not drawn to fit the data, but are explained in the text (section III-6).

cancel any such errors. Furthermore, these results should not be susceptible to secondary effects (section III-2) for the same reason. As a result, it is not surprising that a somewhat more definite maximum is obtained. The curve approaches a maximum value of 0.058 M-eq/g.

3. HYDROGEN-ION EQUIVALENCE OF THE CATIONIC ASHES OF DEWAXED AND OF LIME-WASHED DEPECTINIZED COTTONS

The hydrogen-ion equivalence of the cationic ashes of several different samples of cotton are given in table 3. A comparison of the data for the ash determinations on dewaxed cotton with those on dewaxed cotton which had been washed with lime water and then with distilled water indicate that all of the acidic groups in the former existed in the form of salts. The data also show that if the extraction is extended from 4 to 8 hours, the cationic ashes of the lime-washed samples remain unaltered. The difference between the mean values

of the cationic ashes of dewaxed and of lime-washed depectinized cottons is 0.054 M-eq/g. This represents the cationic ash bound by the pectic substance.

TABLE 3.—Hydrogen-ion equivalence of the ashes of various cotton samples

Sample	Cationic ash
	<i>M-eq/g</i>
Dewaxed cotton.....	0.063
Lime-washed dewaxed cotton.....	.064
Lime-washed depectinized (4 hr) cotton.....	.010
Lime-washed depectinized (8 hr) cotton.....	.010

A comparison is given in table 4 of the maximum acid-binding capacities of dewaxed cotton, lime-washed depectinized cotton, and the pectic substance with their respective cationic ashes. The correspondence is very close for each sample. In addition to the excellent agreement obtained by the two methods, these values also agree well with independent determinations.³ Calculation of the data of Walker and Quell [2] for the total cationic ash as obtained by direct methods, in samples of water-washed cotton, gave a value of about 0.064 M-eq/g. Similarly, direct determinations of the uronic acid-carboxyl content, by the method of Whistler, Martin, and Harris [7] of the cotton used in this work gave a value of 0.055 M-eq/g. Since the entire uronic acid-carboxyl content of the cotton can be accounted for by titratable groups, the results suggest that the pectic substance exists on the fiber as the salts of pectic acid.

TABLE 4.—Comparison of the maximum acid-binding capacities of various samples with their contents of cationic ash

Sample	Maximum acid-binding capacity	Cationic ash
	<i>M-eq/g</i>	<i>M-eq/g</i>
Dewaxed cotton.....	0.066	0.063
Lime-washed depectinized cotton.....	.008	.010
Pectic substance (calculated).....	.058	.054

4. TEMPERATURE COEFFICIENT OF THE TITRATION CURVE OF DEWAXED COTTON

Table 5 gives the data for the titration curve at 25°C of dewaxed cotton in the absence of added salt. These data are compared with the corresponding data for dewaxed cotton at 0°C in figure 3. The results indicate that there is no measurable temperature coefficient of the equilibrium values in this range of temperature, a result in keeping with the identification of the acidic groups of the fiber as carboxyl groups [11].

³ Further investigations now in progress in this laboratory indicate that these values are also approximately verified by direct titration, with alkali, of samples of cotton freed of cationic ash by electro dialysis.

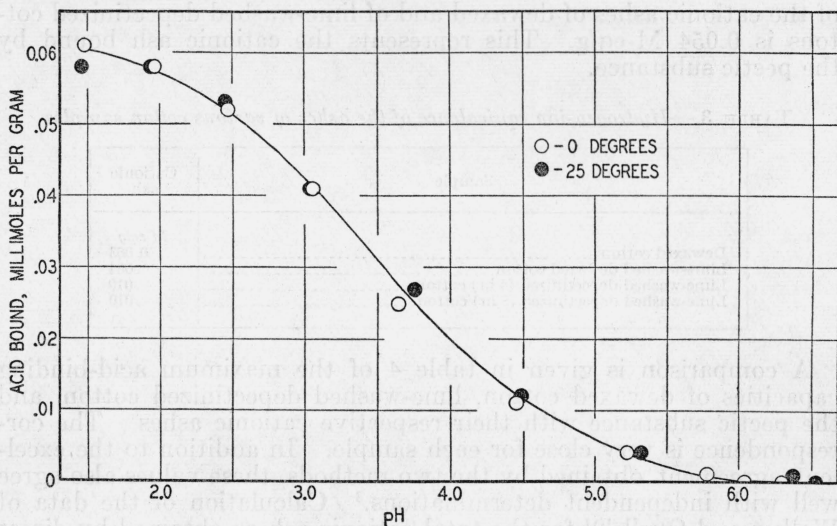


FIGURE 3.—Titration curves of dewaxed cotton at 0° and 25°C.

TABLE 5.—Combination of dewaxed cotton with hydrochloric acid at 25° C in the absence of added salt

pH	Acid bound	pH	Acid bound
	<i>M-eq/g</i>		<i>M-eq/g</i>
1.45	0.058	4.49	0.012
1.93	.058	5.32	.004
2.45	.053	6.38	.001
3.04	.041	6.54	.000
3.75	.027	-----	-----

5. SIGNIFICANCE OF THE ACIDIC GROUPS IN DEPECTINIZED COTTON

The results in the foregoing sections show that about 85 percent of the acidic groups in dewaxed cotton can be allocated to the pectic substance. The question arises, however, as to the source of the acidic groups in the depectinized cotton. The following explanations for their presence might be offered:

1. Removal of the pectic substance by the alkali may be incomplete.
2. The protein fraction of the cotton may have an appreciable acid-binding capacity.
3. The acidic groups may be present in low molecular weight degradation products of cellulose.
4. The acidic groups may be an integral part of the cellulose itself.

A comparison of the acid bound by samples of cotton which had been extracted with sodium hydroxide for 4 and 8 hours showed that both bound essentially the same maximum amount of acid. Since it has been shown by direct analyses for uronic acids that both samples were free of detectable amounts of pectic substance [12], the first of the three possibilities is immediately ruled out. Furthermore, since increasing the duration of the alkali-treatment lowered

the nitrogen content from 0.06 to <0.015 percent, and the maximum acid-binding capacities of the two samples are the same, it is difficult to see how the protein fraction could account for any substantial portion of the acid bound. The third possibility also appears unlikely because it would be expected that acidic compounds of low molecular weight would be readily removed during the treatment with alkali.

It therefore appears that the residual acidic groups in depectinized cotton may well be an integral part of the cellulose molecule, as for example, an end-group. Further work, which is necessary for establishing the validity of such a conclusion, is now in progress in this laboratory. By making the tentative assumption that these acidic groups are contained in the cellulose molecule and are present to the extent of about 0.010 M-eq/g, as determined experimentally, it is found that the cellulose has an equivalent weight of about 100,000, which corresponds to a minimum chain length of about 600 glucose residues.

6. APPLICATION OF THE DONNAN THEORY TO THE TITRATION CURVES OF THE PECTIC SUBSTANCE

As shown in figures 1 and 2, addition of salt produced shifts in the positions of the titration curves to lower pH values. The direction of this shift and the fact that it is not measurably augmented by an increase of ionic strength to 1.0 *M* suggest that the results may be explained by the Donnan equilibrium. Calculation shows that any alternative mechanism involving the competition of cations for the carboxyl groups requires a still further shift with increased concentration of these ions.⁴

The derivations of the Donnan equations for the titration curves in the absence of salt and in solutions of hydrochloric acid and potassium chloride of 0.1 *M* ionic strength are given below. Bracketed quantities are molar concentrations. The density of the phase which consists of the pectic substance is taken as unity. The subscripts "o" and "i" refer to quantities in the outside (solution) and inside (pectic substance) phases, respectively. *R* is the ratio of the activity coefficient of an ion in the inside phase to its activity coefficient in the outside phase, referred to the same standard state, and is assumed to be the same for all the ions involved. This is a reasonable assumption only when all the ions bear similar charges. *K* is the ionization constant of the acid, α is the fraction of the total acid $[A^-] + [HA]$ in the ionized form $[A^-]$, *V* represents volume, and ρ equals $[H^+]_i/[H^+]_o$. The acid groups were assumed to be present as salts of the divalent metal, *M*, [2]. The positions and shapes of the curves are not affected much by the valence of *M*, in any case. The equations follow:

⁴The titration curves for wool have been shown to be consistent with an ion-association mechanism which involves the combination of cations other than hydrogen ions with basic groups, and anions other than hydroxyl ions with acidic groups on the wool [13]. Since, according to this view, ions of unlike sign are bound by the fiber, the differences in ion concentrations inside and outside the wool phase which would be predicted by the simple application of the Donnan equations (taking into account the binding of hydrogen ions alone) would tend to be minimized, and may apparently be neglected. With cellulose, which is not amphoteric, there is no clear evidence for the existence of association of cations with carboxyl groups, and a Donnan effect is therefore to be expected.

In the absence of added salt,

$$\frac{[\text{H}^+]_i R \alpha}{1 - \alpha} = K. \quad (3)$$

$$[\text{H}^+]_o [\text{Cl}^-]_o = [\text{H}^+]_i [\text{Cl}^-]_i R^2. \quad (4)$$

$$[\text{M}^{++}]_o [\text{Cl}^-]_o^2 = [\text{M}^{++}]_i [\text{Cl}^-]_i^2 R^3. \quad (5)$$

$$2[\text{M}^{++}]_o + [\text{H}^+]_o = [\text{Cl}^-]_o. \quad (6)$$

$$[\text{A}^-] + [\text{Cl}^-]_i = [\text{H}^+]_i + 2[\text{M}^{++}]_i. \quad (7)$$

$$2 \frac{V_o}{V_i} [\text{M}^{++}]_o + 2[\text{M}^{++}]_i = [\text{A}^-] + [\text{HA}] = 0.055. \quad (8)$$

These reduce to

$$\{[\text{A}^-] + [\text{HA}]\} \rho R^2 \alpha^2 - \frac{\{[\text{A}^-] + [\text{HA}]\} (\rho^3 R^3 - 1)}{\rho^2 R + \frac{V_o}{V_i}} \alpha + \frac{(\rho^2 R^2 - 1) K}{\rho R} (\alpha - 1) = 0. \quad (9)$$

$$\text{pH} = pK + \log \frac{\rho R \alpha}{1 - \alpha} \quad (10)$$

In hydrochloric acid-potassium chloride solutions of 0.1 *M* ionic strength

$$\frac{[\text{H}^+]_i R \alpha}{(1 - \alpha)} = K. \quad (11)$$

$$[\text{H}^+]_o [\text{Cl}^-]_o = [\text{H}^+]_i [\text{Cl}^-]_i R^2. \quad (12)$$

$$[\text{M}^{++}]_o [\text{Cl}^-]_o^2 = [\text{M}^{++}]_i [\text{Cl}^-]_i^2 R^3. \quad (13)$$

$$[\text{K}^+]_o [\text{Cl}^-]_o = [\text{K}^+]_i [\text{Cl}^-]_i R^2. \quad (14)$$

$$[\text{K}^+]_o + 2[\text{M}^{++}]_o + [\text{H}^+]_o = [\text{Cl}^-]_o = 0.1. \quad (15)$$

$$[\text{A}^-] + [\text{Cl}^-]_i = [\text{H}^+]_i + [\text{K}^+]_i + 2[\text{M}^{++}]_i. \quad (16)$$

$$2 \frac{V_o}{V_i} [\text{M}^{++}]_o + 2[\text{M}^{++}]_i = [\text{A}^-] + [\text{HA}] = 0.055. \quad (17)$$

These reduce to the following equations, neglecting $2[\text{M}^{++}]_o$ in eq 15:

$$\alpha = \frac{0.1 (\rho^2 R^2 - 1)}{\{[\text{A}^-] + [\text{HA}]\} \rho R^2} + \frac{\rho^2 R}{\rho^2 R + \frac{V_o}{V_i}}. \quad (18)$$

$$\text{pH} = pK + \log \frac{\rho R \alpha}{1 - \alpha}. \quad (19)$$

Figure 4 shows the calculated acid titration curves for the salt of a carboxylic acid of pK 3.3 present to the extent of 0.055 M-eq/ml.⁵ These curves were calculated by varying the parameter, ρ , and taking R as unity. Curve 1 was calculated from eq 9 and 10 and curve 2 from eq 18 and 19. The latter curve is only very slightly altered by increasing the ionic strength from 0.1 to 1.0 M . From the shape of the curves and the direction of the pH shift (fig. 4), it is seen that the titration data for the pectic substance (fig. 2) are qualitatively consistent with the Donnan equilibrium, but the shift produced by the addition of salt is considerably smaller in the experimental curves than in the theoretical. It is interesting to note that the experimental data (circles) of figure 2 can be fitted very closely with calculated curves (solid lines) obtained by taking R equal to 0.05. It should be noted that R is present in each term of eq 9, 10, 18, and

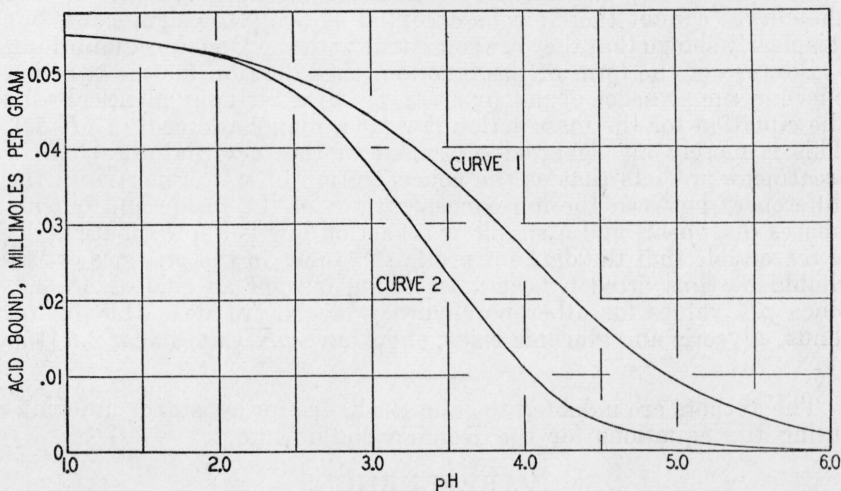


FIGURE 4.—Theoretical Donnan titration curves for an insoluble acid of pK 3.3.

Curve 1, in the absence of added salt. Curve 2, in solutions of 0.1 M ionic strength. The assumptions and conditions used are described in the text (section III-6).

19 in the relationship R/V_1 . Therefore, the adjustment of either R or V_1 can eliminate the discrepancy between the theoretical curves of figure 4 and the experimental data of figure 2. However, V_1 has been fixed at the highest reasonable value by taking a value of unity for the specific volume, and the rather improbable value of R equals 0.05 is therefore required to make the calculated curves conform with the data.

Aside from the a priori unlikelihood of this value of R , the agreement of the calculated curves with the data is subject to question on the following grounds: The solid lines of figures 2 and 4 represent the calculated amounts of acid fixed by the fiber by exchange with cations held by carboxyl groups. Experimentally determined acid-binding capacities are a measure of the total amount of acid adsorbed by the solid phase. If the value for R were 0.05, it would have as a consequence the presence within the solid phase of large quantities of dis-

⁵ The value 0.055 M-eq/g is the mean of the values for the maximum acid-binding capacity, cationic ash, and uronic acid-carboxyl content of the pectic substance (section III-3).

solved acid at low values of pH, with resulting large discrepancies between the calculated and experimental values for the total amount of acid adsorbed. If the pectic substance is thought of as being dispersed throughout the fiber, which is rather unlikely [14], the circles of figure 2 would represent only the acid fixed by the carboxyl groups, since they were calculated by a subtraction process that should cancel the effect of any acid dissolved in the fiber. For such a case, however, calculations show that there would be a sharp rise, not found by experiment, in the total amount of acid adsorbed by both the dewaxed and depectinized cotton at low values of pH (fig. 1). If, on the other hand, the pectic substance is thought of as existing in a shell around the fiber, the subtraction process should not cancel the effect of the acid dissolved in the shell, and the circles of figure 2 should show a sharp rise at low values of pH, which was also not found experimentally. The quantitative agreement of the data of figure 2 with the curves cannot therefore be accepted as being too significant, but it is clearly shown that they are consistent with the Donnan equilibrium.

Because of the form of the function, the equation for the titration curve in the presence of salt (curve 2, fig. 2) is virtually identical with the equation for the mass-action law for a monobasic acid of pK 3.3. This is merely an algebraic statement of the fact that the Donnan treatment predicts that as the concentration of salt is increased, the differences between the ion concentrations of the inside and outside phases disappear, and a simple mass-action law is approximated. It is reasonable that the data for pectic substance in the presence of salt should be thus fitted by the mass-action law for an acid of pK 3.3, since pK values for other polyhydroxy acids are near this figure. Thus, glyceric and gluconic acids, e. g., have pK values near 3.5 [15].

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