Effect of pH and Neutral Salts upon the Swelling of Cellulose Gels

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Synopsis

The swelling of cellulose gel is considered to be caused by an osmotic pressure differential resulting from a difference in concentration of mobile ions between the interior of the gel and the exterior solution. The fundamental feature within the gel, bringing about the unequal distribution, is the presence of ionizing acidic groups attached to the macromolecular network. Using the Donnan theory to describe the distribution of ions, it is shown that the experimentally observed decreases in swelling brought about by extremes of pH and by salt addition may be explained in a semiquantitative way. The swelling behavior of superabsorbent gels appears to be almost completely governed by the proposed mechanism. For conventional wood pulps, the mechanism describes the smaller variations in swelling caused by pH and salt addition. For these gels, electrolytic effects are only responsible for a fraction of the total swelling—the remainder being associated with the macromolecular network itself. The unequal distribution of hydrogen ions between a gel and an exterior solution is described briefly, along with the effect that this has on the potentiometric titration of the gel.

INTRODUCTION

In a recent article, we have reviewed some of the extensive literature on the observed effects of electrolytes upon the swelling of cellulosic gels. In accompanying experimental studies, we confirmed the important role played by the acidic groups in the gels and the nature of their counter ions.[1] Most particularly, we showed that if the mixture of counter ions normally present in a wood pulp was removed and replaced by a single species, the pulp was increasingly swollen in the order $Al^{3+} < H^+ < Mg^{2+} < Ca^{2+} < Li^+ < Na^+$. In the present article, we examine the effect of pH upon the swelling of cellulose gels. Among other phenomena, a change in pH can bring about the conversion of the acidic groups from the free acid to salt form (and vice versa) with accompanying changes in swelling. In addition, because of the important role it plays during pH changes, we study the simultaneous presence of a neutral salt.

The most systematic study of the effect of pH and added neutral salt on the swelling of wood pulps was recently carried out by Lindstrom and Carlsson[2]: these authors showed clearly that the swelling of wood pulps is maximum at about neutrality and is depressed at both low and high pH values. At all pH values, swelling was further reduced by the presence of salt. The effects are considerably more exaggerated in the superabsorbent pulps.[3,4] Lepoutre, Hui, and Robertson[3] increased the degree of swelling of a bleached kraft pulp some thirtyfold by grafting onto the fibers a polymer rich in acid groups. They noted that while the swelling remained constantly high in the pH range of 9–5, it dropped drastically when pH was lowered further, reaching the swelling level of the unmodified pulp at pH 3.5. The swelling was also reduced to about half when the neutral product was placed in 1% sodium chloride solution rather than water.

A detailed explanation of this is possible, we feel, using the concepts on the mechanism of swelling of gels originally proposed by Proctor.[5] He suggested that the important characteristic of many gels is the presence of ionizable groups attached to the macromolecular network. When such a gel is placed in an ionic solution, an exchange of mobile ions takes place between the gel and the solution, but because of the presence of the bound groups, the mobile ions are unevenly distributed—the gel contains the higher concentration. Proctor suggested that the gel swells as a result of the entry of water in an attempt to reduce the osmotic pressure differential resulting from the difference in concentration. Swelling, he proposed, continues until the osmotic pressure differential is equal to the resistance to further expansion brought about by the cohesive forces of the macromolecular network. Using the theory of Donnan[6,7] to describe the distribution of ions, Proctor and Wilson[8] explained the swelling behavior of gelation as a function of pH, accurately pinpointing the pH of maximum swelling.

Application of Proctor's theory to cellulose is largely confined to the work of Neale.[9,10] To explain the swelling of cellulose in sodium hydroxide solution, Neale considered the hydroxyl groups as very weak acids capable of forming sodium salts. In this way, he was able to account for the swelling behavior on a semiquantitative basis. Because of the very low dissociation constant of the hydroxyl groups, conversion to the sodium salt and subsequent swelling necessarily takes place at very high alkalinities. Farrar and Neale[10] also observed variations in the swelling of cellophane and cotton placed in ionic solutions of different concentrations at near neutral pH. Here they considered the carboxylic acid groups to be the active species. Farrar and Neale, however, only tested their hypothesis so far as to confirm that in dilute solutions, the distribution of ions between the gel and external solution was in accord with the Donnan theory for the number of carboxylic acid groups present.

In the present article, we extend the early work of Proctor and Neale using essentially their type of approach. As a result of the concentrated effort that has more recently been put into the field of synthetic polymers, more sophisticated treatments of the swelling of polyelectrolyte gels now exist. However, as stated by Pennings and Prins in a recent critical appraisal of Neale's work, the older approach does bring out the salient features of swelling behavior without a great loss of rigor.[11] In addition, the approach is susceptible to easy comprehension and relates to readily measured parameters. In the absence of previous theoretical studies of the swelling of cellulose in the pH range where the ionizing groups are provided by the acid groups rather than the hydroxyl groups, we thus feel this further application of the technique is justifiable.

THEORY

Our theoretical treatment follows the manner of those of Donnan, Proctor, and subsequent workers. In brief, we consider a gel containing bound acidic groups that has swollen to equilibrium in an aqueous solution of given pH and neutral salt concentration. As the acidic groups cannot move out of the gel, the solution within the gel is regarded as separated from the external solution by a semipermeable membrane which confines the acidic groups but gives free passage to water and all simple ions. All mobile ions are assumed to be present to some extent on either side of the membrane and, by taking into account the various

chemical equilibriums that must exist on either side and between the two sides, the interrelationships of concentration are derived. From these, the excess concentration of mobile ions within the gel is calculated. This excess of concentration E is directly proportional to the osmotic pressure differential between the two sides of the membrane, which, in turn, we assume is directly proportional to the degree of swelling achieved. Thus, the net result of the theoretical calculations is E as a function of pH and neutral salt concentration; and this will subsequently be compared with experimental data of swelling as a function of the same parameters.

Model

The treatment will be restricted to the case where any given set of conditions is achieved by an acid, base, and salt derived from a particular monovalent cation and a particular monovalent anion. As the ions used in experimental work were sodium and chloride, these ions will be used in the theory. In Figure 1, the hypothetical membrane is represented as a broken line separating the solution within the gel from the external solution; and expressions have been given to the concentrations of the various ions in the following sequence. Inside the gel, the acid groups are assumed to have a concentration c and a degree of dissociation α, thus yielding a concentration $c(1 - \alpha)$ in undissociated form (RH) and $c\alpha$ in dissociated form (R⁻). Symbols have arbitrarily been chosen to represent the concentration of H⁺ and Cl⁻ on either side of the membrane. Having defined the concentrations of hydrogen ions, the hydroxyl-ion concentrations immediately follow from the hydrolytic constant of water. Electrical neutrality must exist in each solution and in order to satisfy this condition, the concentration term given the sodium ion is that necessary to ensure that there are equal concentrations of positive and negative ions in each solution.

We will now suppose that the acid groups behave similarly to a soluble acid and that their degree of dissociation is governed by a dissociation constant defined in the usual way:

$$K_a = \frac{[R^-][H^+]}{[RH]}$$

Introducing the appropriate concentration terms from Figure 1 and rearranging, we obtain the concentration of ionized groups:

$$c\alpha = \frac{K_a c}{K_a + y} \tag{1}$$

	GEL PHASE		EXTERNAL SOLUTION	
RH	$c(1-\alpha)$			
R⁻	$c\alpha$			
H⁺	y		H⁺	x
OH⁻	K_w/y		OH⁻	K_w/x
Na⁺	$K_w/y + n + c\alpha - y$		Na⁺	$K_w/x + m - x$
Cl⁻	n		Cl⁻	m

Fig. 1. Representation of the equilibriums existing when a gel is placed in contact with a solution. RH and R⁻ refer to the undissociated and dissociated acid groups, respectively.

Having thus satisfied in the model the various equilibriums which must exist on either side of the membrane, we may now consider the equilibriums between the two sides.

Distribution of Ions

According to the Donnan theory, the presence of a nondiffusible ion on one side of a membrane affects the partition of all diffusible ions.   This is effectively the case with an electrolytic gel and an exterior solution.   Using as an approximation the concentrations of the various ions rather than the activities, the appropriate Donnan equilibrium for the model is:

$$\lambda = \frac{[H^+]_g}{[H^+]_s} = \frac{[Na^+]_g}{[Na^+]_s} = \frac{[OH^-]_s}{[OH^-]_g} = \frac{[Cl^-]_s}{[Cl^-]_g}$$

where g and s refer to the gel and the external solution, respectively. λ is a distribution constant defined by the ratios.   Substituting from Figure 1:

$$\lambda = \frac{y}{x} = \frac{K_w/y + n + c\alpha - y}{K_w/x + m - x} = \frac{K_w/x}{K_w/y} = \frac{m}{n} \tag{2}$$

Adding the first two ratios:

$$\lambda = \frac{K_w/y + n + c\alpha}{K_w/x + m}$$

and substituting λx for y, and λn for m, we have

$$\lambda = \sqrt{1 + \frac{c\alpha}{K_w/y + n}} \tag{3}$$

This equation, in conjunction with the expression for $c\alpha$ [eq. (1)], gives the distribution constant in terms of the hydrogen-ion and chloride-ion concentrations within the gel.   The derivation is in the manner used by Hitchcock in his considerations of membrane equilibrium in general[12]; and for $n = 0$, eq. (3) reduces to his equation for the equilibrium between a nondiffusible acid and a base in the absence of added salt.

It will be noted that, in the absence of chloride ions ($n = 0$), λ decreases with increasing hydroxyl concentration (K_w/y) tending from an initially very high value to unity in the limit.   At any hydroxyl concentration, concentrations of chloride approaching the hydroxyl concentration bring about a drastic reduction in λ.

Since λ is always greater than unity, positive ions are more concentrated in the gel and negative ions more concentrated in the exterior solution.   This of course also applies to the hydrogen-ion concentration and we have by taking logarithms of the relationship $\lambda = y/x$:

$$pH_s = pH_g + \log_{10} \lambda \tag{4}$$

That is, the pH in the solution is always greater than that in the gel and as λ can be very large, the difference in pH can be several units.

Calculation of the Degree of Swelling

The difference in concentration of all *diffusible* ions E between the gel and the external solution is given by:

$$E = [H^+]_g + [OH^-]_g + [Na^+]_g + [Cl^-]_g$$
$$- [H^+]_s - [OH^-]_s - [Na^+]_s - [Cl^-]_s$$

From this, by introducing terms from Figure 1 and using λ to convert external concentrations, we obtain

$$E = c\alpha + 2(Kw/y + n)(1 - \lambda)$$

which by use of eq. (3) to eliminate $(Kw/y + n)$ reduces to

$$E = \left(\frac{\lambda - 1}{\lambda + 1}\right) c\alpha \tag{5}$$

Our research has shown that this simple relationship has not been previously reported. E is directly proportional to the osmotic pressure differential as stated in van't Hoff equation; and, following Proctor's original proposal, we will also accept E as in turn proportional to the degree of swelling. It will be noted that E approximates to $c\alpha$ when λ is high.

Swelling due to electrolytic effects is a manifestation primarily brought about by the concentration of nondiffusible ions within the gel which, in turn, is a function of the internal pH. The equations governing swelling, therefore, most naturally relate to the conditions within the gel. In using the equations, we specified the concentration of acid groups, the acid dissociation constant, and the concentration of chloride ions within the gel, and then for a series of postulated internal pH values calculated successively α, λ, and E. External concentrations yielding the set internal concentrations were calculated once λ was known. The equations may be rearranged to express swelling directly in terms of conditions external to the gel; but the resultant equations are quite complex. Table I shows sets of calculations for the absence and presence of the chloride ion. The chloride-ion concentration can be taken as a measure of the sodium chloride concentration at all but the lowest pH values where a small part of the chloride is associated with the hydrochloric acid necessary to achieve the set pH. A concentration of acid groups of 0.1 equiv/l. was chosen for the calculations as this corresponds to the experimental values for the swollen pulps.

Swelling in the Absence of Salt

Figures 2 and 3 shows the variation in swelling with pH for gels containing the same concentration of acid groups but different dissociation constants. The shapes of the curves may be understood by considering the principal ions present under any given conditions.

First, consider a gel in free-acid form allowed to equilibrate with water. The most abundant ions in the system are the hydrogen ions dissociated by the acid groups and these will remain in the gel to preserve electrical neutrality. There being no ions in the external 'solution' other than hydrogen and hydroxyl resulting from the dissociation of water, the external solution will exhibit a pH of 7.0, and its total ion concentration will be very low. The concentration of ions within the gel in excess of the external concentration E will thus approximate

TABLE I

Sample Calculations of the Degree of Swelling of a Gel Containing Weak Acid Groups in the Absence and Presence of Salt[a]

pH_g	$c\alpha$ [eq. (1)]	$[Na]_g$ (Fig. 1)	λ [eq. (3)]	pH_s [eq. (4)]	$[Cl^-]_s$ (λn)	$[Na^+]_s$ (Fig. 1)	E [eq. (5)]
			$c = 0.1000$, $K_a = 1 \times 10^{-4}$, $[Cl^-]_g = 0$ (no salt case)				
2.5	0.0031	0.0000	31343.00	7.0	0.0000	0.0000	0.0030
3.0	0.0091	0.0081	30151.00	7.5	0.0000	10^{-7}	0.0091
4.0	0.0500	0.0499	22360.00	8.3	0.0000	10^{-6}	0.0500
5.0	0.0909	0.0910	9534.00	9.0	0.0000	10^{-5}	0.0909
6.0	0.0990	0.0990	3147.00	9.5	0.0000	10^{-5}	0.0989
7.0	0.0999	0.0999	999.00	10.0	0.0000	0.0001	0.0997
8.0	0.1000	0.1000	316.00	10.5	0.0000	0.0003	0.0994
9.0	0.1000	0.1000	100.00	11.0	0.0000	0.0010	0.0980
10.0	0.1000	0.1001	31.64	11.5	0.0000	0.0032	0.0939
11.0	0.1000	0.1010	10.04	12.0	0.0000	0.0101	0.0819
12.0	0.1000	0.1100	3.32	13.0	0.0000	0.0332	0.0537
13.0	0.1000	0.2000	1.41	13.2	0.0000	0.1414	0.0172
			$c = 0.1000$, $K_a = 1 \times 10^{-4}$, $[Cl^-]_g = 0.01$ (salt case)				
2.5	0.0031	0.0099	1.14	2.6	0.0114	0.0087	0.0002
3.0	0.0500	0.0181	1.38	3.1	0.0138	0.0131	0.0015
4.0	0.0909	0.0599	2.45	4.4	0.0245	0.0245	0.0210
5.0	0.0990	0.1008	3.18	5.5	0.0318	0.0318	0.0474
6.0	0.0999	0.1090	3.30	6.5	0.0330	0.0330	0.0530
7.0	0.1000	0.1099	3.31	7.5	0.0332	0.0331	0.0536
8.0	0.1000	0.1100	3.32	8.5	0.0332	0.0332	0.0536
9.0	0.1000	0.1100	3.31	9.5	0.0332	0.0332	0.0536
10.0	0.1000	0.1100	3.30	10.5	0.0330	0.0333	0.0535
11.0	0.1000	0.1110	3.18	11.5	0.0318	0.0349	0.0521
12.0	0.1000	0.1200	2.45	12.4	0.0245	0.0490	0.0420
13.0	0.1000	0.2100	1.38	13.1	0.0138	0.1520	0.0160

[a] Numbers rounded off from computer calculations.

to $c\alpha$ or $[H^+]_g$, which in turn will be determined by the acid dissociation constant. Thus, if the acid groups are strong, the gel will exhibit high swelling at low pH_g. If the acid groups are weak, the gel will have a low degree of swelling at high pH_g.

With the progressive neutralization of the acid groups, it can be seen, from eq. (3) and the example given in Table I, that λ is reduced but still remains high. Most of the sodium of the added caustic soda, therefore, enters the gel and E continues to approximate to $c\alpha$, the only appreciable quantity of ions affecting swelling are the sodium and hydrogen counter ions of the dissociated acid groups. Maximum swelling is achieved upon complete ionization.

Beyond a pH_s of 10, λ is reduced rapidly. There is an increasingly even distribution of ions with an appreciable quantity of ions accumulating outside the gel. Swelling is, therefore, reduced and, as all acid groups are now dissociated, the decrease is independent of the dissociation constant.

Swelling in the Presence of Salt

Figures 2 and 3 also show the degree of swelling as a function of pH_s in solutions of different concentrations of salt.

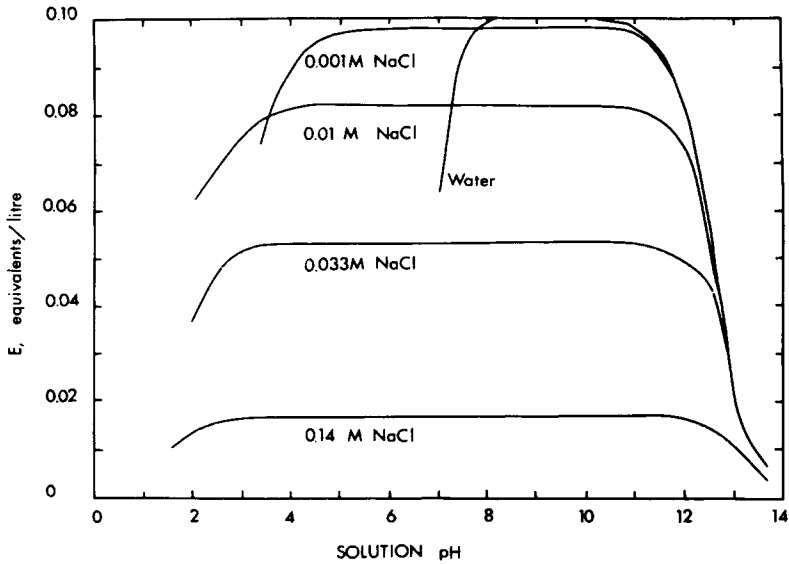In the presence of small concentrations of salt, the rising section of the swelling

Fig. 2. Theoretical plots of E (which is taken as proportional to the degree of swelling) as a function of pH and external salt concentration. The gel contains 0.1 equiv/l. of strong acid groups (K_a = 0.1 mol/l.).

curve, as the gel is neutralized, is displaced to lower external pH values; however, swelling rises to almost the same maximum. As can be seen from eq. (3), the internal concentration of chloride ions need only be of the order of the hydroxyl concentration (K_w/y) to bring about an appreciable reduction in λ. The distribution constant at low chloride concentrations, however, remains sufficiently high that E still approximates $c\alpha$. Thus, the swelling for a given internal pH
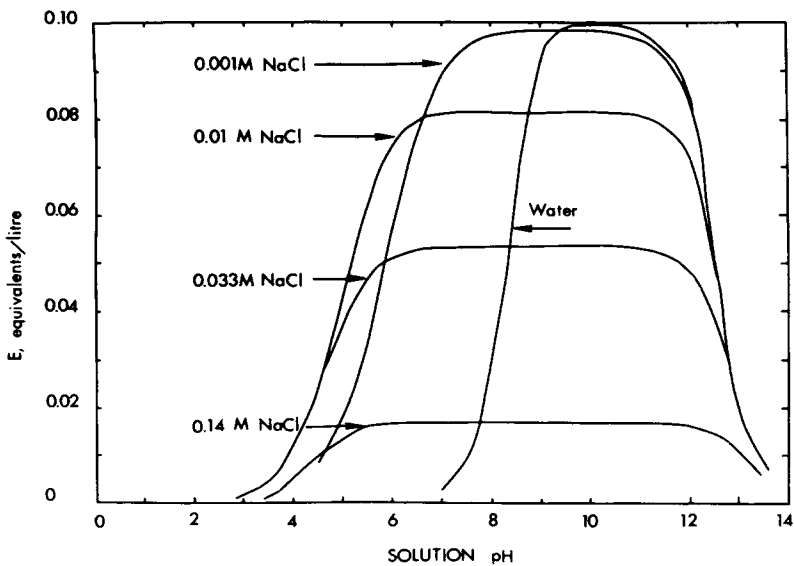

Fig. 3. Theoretical plot as for Figure 2 but for a gel containing weak acid groups (K_a = 1 $\times$ 10^{-4} mol/l.).

is still close to that in the absence of chloride, however, the external pH at which the swelling is observed is reduced considerably [eq. (4)].   In qualitative terms, the salt may be regarded as permitting the transport of hydrogen ions out of the gel.

The addition of high concentrations of salt causes λ to approach unity and, in addition to the internal and external pH values approaching equality, swelling is much reduced.   At a certain level of salt addition, the chloride ions actually have more control on swelling than pH.   Thus from eq. (3):

$$\lambda = \sqrt{1 + \frac{c\alpha}{n}} \qquad (6)$$

where $n \gg K_w/y$.   The condition where the chloride concentration exceeds the hydroxyl concentration is readily achieved in practice with salt solutions which are close to neutrality and quite dilute.

Titration of Gels

That the pH within a gel is not necessarily equal to that of the external solution is an interesting manifestation of the Donnan theory.   The effect that the phenomenon has on the potentiometric titration of a gel comes directly from the calculations of swelling as a function of pH.   Figure 4 shows the theoretical curves for the titration of a weak acid in the presence of various concentrations of salt. Taking logarithms of eq. (1), we have the usual relationship between pH of a soluble acid of low molecular weight and its degree of neutralization

$$pH_g = pK_a + \log_{10}\left(\frac{\alpha}{1 - \alpha}\right) \qquad (7)$$

However, the pH which would be measured in the titration of a gel would be that of exterior solution.   Introducing this expression into eq. (4):
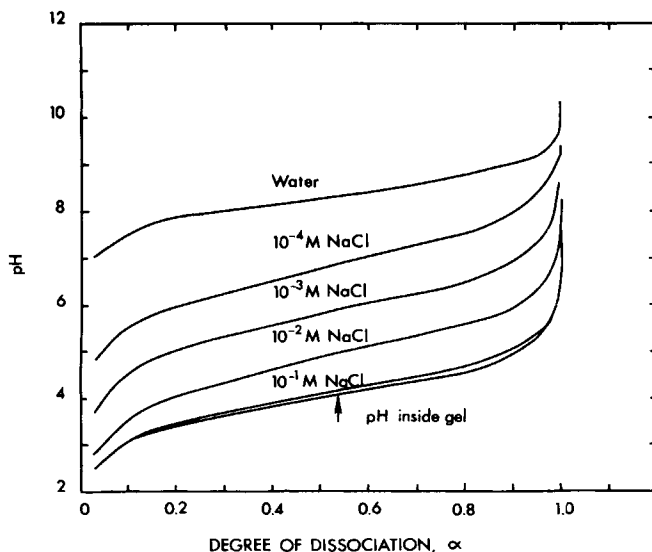

Fig. 4. Theoretical plot of the internal pH and the accompanying external pH values in salt solutions of different concentrations as a gel is progressively neutralized.   The curves are for a gel containing weakly acidic groups ($K_a = 10^{-4}$).

$$pH_s = pK_a + \log_{10}\left(\frac{\alpha}{1-\alpha}\right) + \log_{10}\lambda \qquad (8)$$

Thus, if the pK_a of a cellulose gel is estimated (as is usual for a soluble acid) from the pH of half neutralization, the pK_a would be too high by an amount $\log_{10}\lambda$—an appreciable amount in the absence of salt.

EXPERIMENTAL

Materials

The superabsorbent pulp was a carboxymethylated cotton crosslinked in the wet state with epichlorohydrin.[4] It was received in dry sodium form from Buckeye Cellulose Corp. Wood pulps were prepared from red sprucewood (*Picea rubens*) by conventional pulping procedures; variations in pulp yield being obtained by varying the cooking time. The pulps reported in this study were kraft pulp of 49% yield and sulfite pulp of 77% yield. The high yield in the latter case was adopted to obtain a pulp which contained a high concentration of acid groups. Wood pulps were kept in a "never-dried" condition prior to treatment.

Chemicals used throughout were of reagent grade and all water used was deionized to a conductivity of less than 0.3×10^{-6} mho cm^{-1}.

Swelling Procedures

The "as-received" superabsorbent pulp was soaked at 0.5% consistency in either water or a salt solution of the set concentration, and the pH was adjusted with either sodium hydroxide or hydrochloric acid.

Wood pulps were first freed of their usual mixture of cations and converted to the acid form by repeated washing with $0.1M$ hydrochloric acid and were then washed with deionized water until free of the chloride ion.[1] The pulps were then made to 0.5% consistency in water or salt solution and the pH adjusted by the addition of sodium hydroxide or hydrochloric acid.

All pulps were allowed to equilibrate overnight in sealed containers and the final pH values noted before the measurement of swelling.

Measurement of Swelling

The degrees of swelling reported are the water retention values determined in the swelling medium. The technique used and its validity as a measure of swelling has been previously reported.[13]

For a number of samples the degree of swelling was also determined by the more absolute solute-exclusion technique.[14]. This procedure was also carried out in the swelling medium using a solution of dextran of molecular weight 2×10^6 adjusted to the same pH and salt concentration as the swelling medium. Changes in dextran concentration were monitored by precision polarimetry. The degrees of swelling thus obtained agreed well with the water retention values.

Both techniques give the degree of the swelling of a pulp expressed as the ratio by weight of water to solid material in the swollen gel.

Titration of Pulps

Pulp, 2.0 g converted to its acid form, as described earlier, was dispersed in 200 ml of water or salt solution. The suspension was then titrated slowly under a nitrogen atmosphere using standardized sodium hydroxide solution. The titration was followed potentiometrically.

The acid contents of the pulps were: superabsorbent 3.8 mequiv/g, sulfite pulp 0.30 mequiv/g, kraft pulp 0.09 mequiv/g.

RESULTS AND DISCUSSION

Swelling Behavior of Pulps

The cellulosic fibers most clearly demonstrating the effects discussed are the superabsorbent pulps. The high swelling potential of these pulps appears attributable to their augmented content of acid groups.

Figure 5 shows the swelling behavior of a carboxymethylated cotton as a function of pH and added salt. The results follow closely predicted trends. The rise in swelling occurs at the pH values expected of weakly acidic groups, a plateau region occurs around neutrality and the decrease in swelling commences at pH 10, as predicted for acid groups of any strength. A lowering of the whole curve occurs with added salt. Not coinciding with expectation is the curve for swelling in the nominal absence of salt which appears to correspond to a theoretical curve for the presence of a small amount of salt. It is probable that this is caused by the experimental difficulty of reducing salt concentrations to the very low levels required by the theory.

The data that we have gathered on wood pulps together with that published by Lindstrom and Carlsson[2] show that these pulps behave as expected in the theory (Fig. 6). However, the effects are slighter than those observed on the
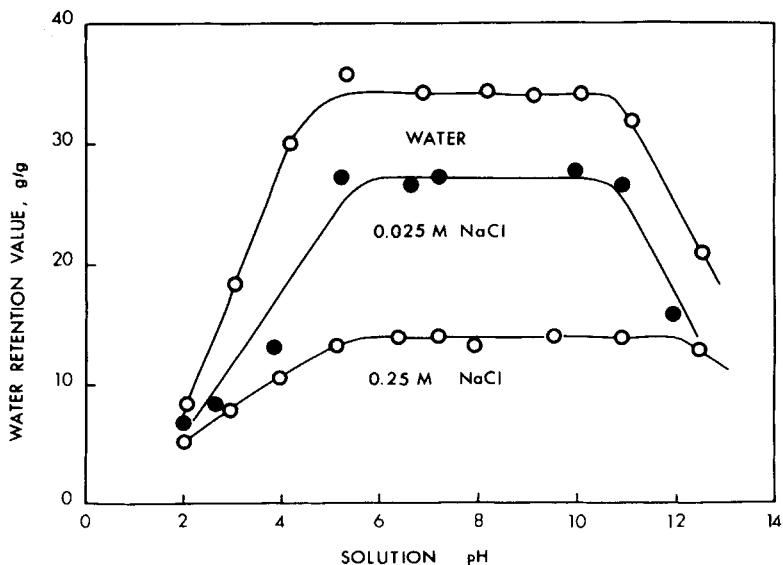

Fig. 5. Experimentally determined degree of swelling of a superabsorbent pulp as a function of the pH and salt concentration of the external solution.
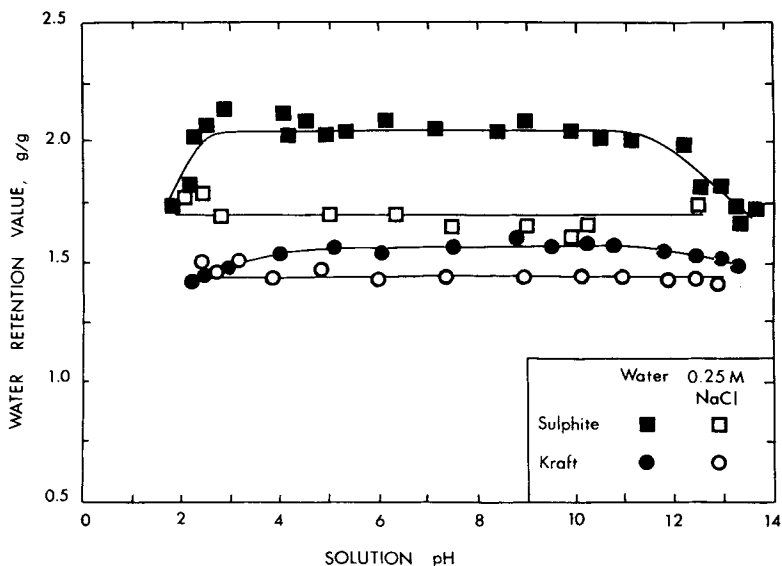
Fig. 6. Experimentally determined degrees of swelling of sulfite and kraft wood pulps as a function of pH in the presence and absence of salt. (●) Kraft with water; (○) kraft with 0.25M NaCl; (■) sulfite with water; (□) sulfite with 0.25M NaCl.

superabsorbents and appear superimposed upon a basic degree of swelling which is independent of electrolytic conditions. It is possible that such a basic swelling exists in the case of the superabsorbents but is only a small fraction of the total swelling. In considerations of the swelling of ion-exchange resins, Gregor has found that these too appear to have a "rest volume" when the osmotic differential due to electrolytic effects is zero.[15,16] The volume may be interpretated as the intrinsic swelling ability of the macromolecular network itself once free of acidic groups.[16]

At neutral pH and in the nominal absence of salt, the swelling of the super-absorbent pulp is 34×10^{-3} l./g and, as the pulp contains 4×10^{-3} equiv/g of acid groups, $c\alpha$ is of the order 0.1 equiv/l. Conventional pulps swell to a lesser extent, and have fewer acid groups, but $c\alpha$ is of the same order. Since, for neutral pH and the absence of salt, we have equated $c\alpha$ with the degree of swelling, clearly there is some other property which must be taken into account when comparing different gels. This has been termed the elastic modulus of the gel.[16] The first water entering a dry gel placed in water may be imagined as forming an extremely concentrated solution of the available ions; and hence, a high driving pressure for swelling. However, as the gel swells, the interior solution will become more dilute and the osmotic pressure less. At the same time, if we consider the gel matrix to behave elastically in the manner of Hooke's law, the resistance of the gel to further expansion will increase with swelling. The position of equilibrium between the two forces will then depend upon the elastic modulus. For ion-exchange resins, Gregor and Frederick equated the elastic modulus with the degree of crosslinking; the less the crosslinking, the greater the swelling of a gel under a given osmotic pressure.[16] A difference in modulus due to crosslinking might well be responsible for the difference in swelling behavior between the conventional and superabsorbent pulps. The volume of the swollen cell walls

of pulp fibers is close to that of the original wood fibers,[17] and it is possible that much of the original cohesive strength remains, the source of this strength being undisturbed intermicrofibrillar contacts.[18] On the other hand, during the preparation of the superabsorbent pulps, a forceful expansion could take place such that many of these crosslinks could be irreversibly broken and the fibers henceforth be more deformable structures. The lack of cohesive strength in the superabsorbents is apparent in the ease with which the fibers disintegrate under mechanical action.[19]

While the theoretical plots bring out the main features of swelling behavior, the predicted reductions in swelling for the extremes of pH or added salt are somewhat more drastic than experimentally observed. This is apparent in the quantitative comparison of theory and experiment in Figure 7. The major cause of this discrepancy is probably that, in common with Neale in his studies at high pH, we have assumed that the concentration $c\alpha$ remains constant throughout all swelling and contraction. The fixed value we have chosen is that of the swollen gel. However, $c\alpha$ is itself a function of the degree of swelling and may be expected to increase with contraction of the gel. The effect will be to increase both λ and E over what we have calculated. While realizing this, we have not yet found it possible to introduce the necessary correction into usable equations.

Titration Curves of Pulps

In Figures 8 and 9, the experimental titration curves of a superabsorbent pulp and a wood pulp carried out in the presence and nominal absence of salt are given. Similar curves also have been reported with synthetic ion-exchange resins where the ideal case for no salt is not observed.[20] With the superabsorbent, the ap-
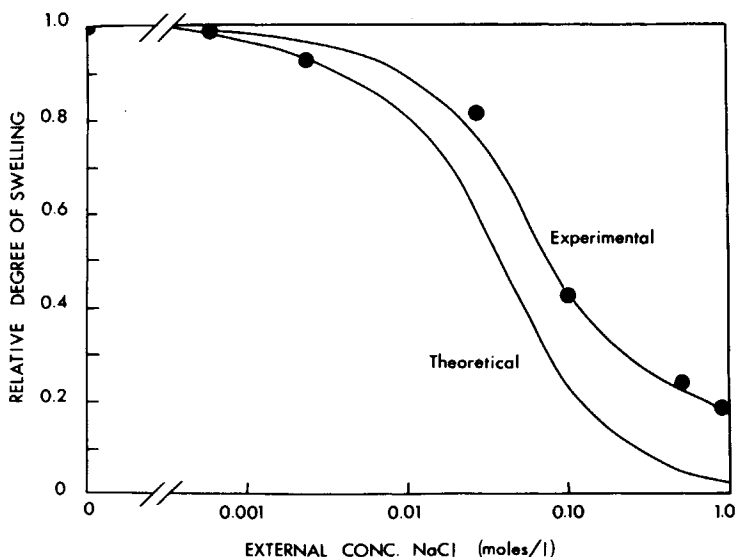

Fig. 7. A comparison of theory and experiment for the fractional reduction in swelling of the superabsorbent pulp brought about by increasing concentrations of salt at near neutral pH. The fractional reductions are expressed as E/E_0 and WRV/WRV_0 where E_0 (theoretical) and WRV_0 (experimental) refer to the degrees of swelling in water.
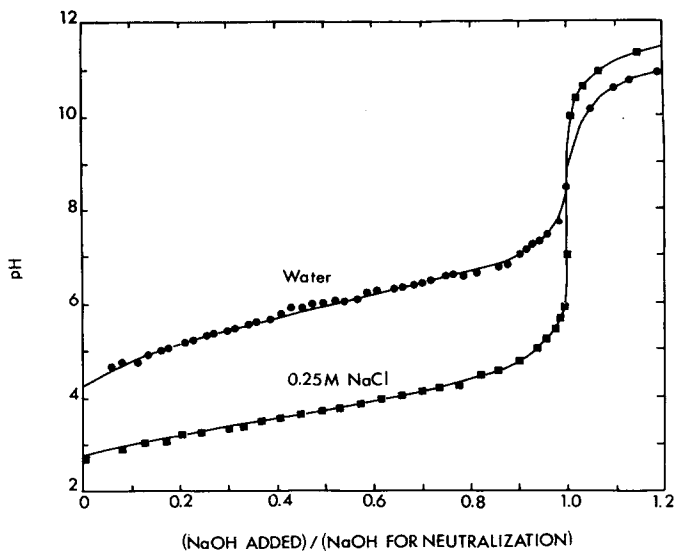
Fig. 8. The potentiometric titration curves of the superabsorbent pulp in the presence and absence of salt.

parent pK_a drops from over 6.0 to 3.75 with the addition of $0.25M$ NaCl; 3.75 being a more reasonable value for acidic groups of carboxymethylated cellulose.[21] Chowdhury and Neale have reported a value of 3.42 for the soluble material.[21] Kraft pulps in which the acid groups are also carboxylic exhibit a similar pK_a in the presence of sufficient salt, while high-yield sulfite pulps have a lower pK_a in keeping with the greater strength of the sulfonic acid groups present.

More rigorous treatments of the potentiometric titration curves of polyelectrolytes exist[22] and continue to be refined[23,24] but it has been shown that taking into account the Donnan effects explains a large fraction of the anomalous behavior of these gels.[22]
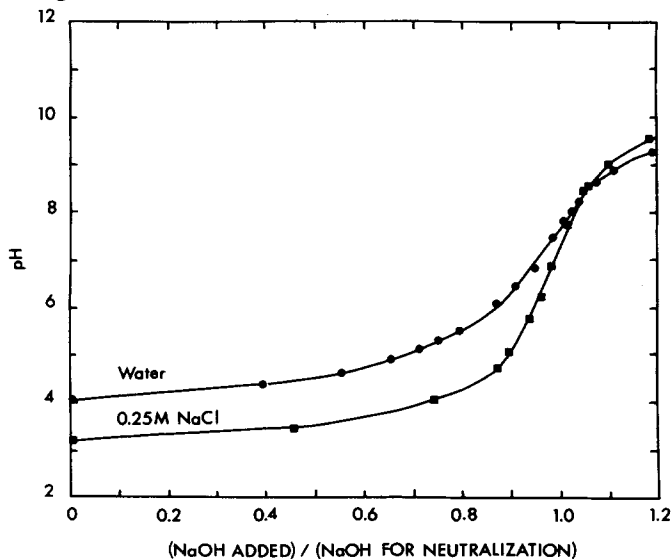

Fig. 9. The potentiometric titration curve of the sulfite pulp in the presence and absence of salt.

Implications of These Studies

The results presented in this article compliment existing studies in showing the profound effect of pH and salt upon the swelling of the superabsorbent pulps. It has been known for some time that such pulps must be in neutralized form for maximum absorption, and the reduced absorption at low pH has recently been exploited to produce an economical drying process.[25] That the absorption of these pulps for 1% sodium chloride solution is a fraction of that for water was probably a surprising and somewhat disappointing initial finding, since such a solution simulates the physiological fluids to which certain absorbency products are exposed. All these effects are, however, completely in keeping with the mechanism we have proposed.

Although conventional wood pulps show less response to the effects of pH and added salt, the small changes observed are of industrial significance. Small increases in swelling bring about appreciable increases in the plasticity of the fibers and their ability to bond extensively during sheet formation. We have already shown that converting the acid groups of sulfite and kraft pulps from the free acid to the sodium salt results in 20–30% increase in the tensile strength of the paper made from them. Conversion to salts of divalent and trivalent metals, however, bring about less swelling and lower paper strength. Part of the raison d'être for the current work was to investigate what additional effects we may expect if, after neutralization, the pH is raised even further. While most paper is prepared at about a pH of 5.0, there are reported advantages to using higher and even alkaline pH values. If the proportionality between swelling and papermaking properties is accepted, our results suggest that no further change in paper properties should be expected for a wide range of pH following neutralization of the acid groups. This is by no means clear from studies of pH in the literature where no attention is given to the nature of the cations present in the pulp or in the aqueous medium. Thus, a pulp in the commonly occurring calcium form may lose strength if it is made acid by the addition of alum and gain strength if it is made alkaline by the use of sodium hydroxide. However, where the pH is not greatly removed from neutrality, these are the effects of counter-ion exchange rather than the effect of pH. In our study, we have deliberately involved only one cation to isolate the effects of pH from those of ion exchange.

A trend in papermaking is towards increased recycling of drainage waters, hence there is growing interest in knowing what effects the higher electrolyte concentrations have upon paper properties. For a salt of a monovalent cation, our studies show the order of concentration which will bring about a reduction of swelling. Again, however, in extrapolating the effects we have found to mill situations, the nature as well as the concentration of recycled cations needs to be considered.

If the concepts put forward are to be accepted, it is apparent that the concentration of ions in a pulp suspension is not necessarily that inside the fiber wall in the absence of appreciable ionic strength. This is not generally taken into account in studies of the kinetics of cellulose reactions. However, if λ is high, any cationic reactant will be more concentrated at the location of the reaction inside the cell wall than in the external solution. On the other hand, anionic reactants will be largely confined to the external solution. These phenomena are of increased importance in laboratory studies where, unlike most industrial processes, there is a tendency to use pure reagents and deionized water.

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