Donnan Equilibria in Wood-Alkali Interactions. Part II. Effect of Polysaccharide Ionization at High Alkalinities

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DONNAN EQUILIBRIA IN WOOD-ALKALI INTERACTIONS. PART 2. EFFECT OF POLYSACCHARIDE IONIZATION AT HIGH ALKALINITIES.

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ABSTRACT.

The equilibria of mildly saponified W. hemlock wood meal with aqueous sodium hydroxide were studied in the concentration range 0.5 to 5.0 N, using added sodium chloride to characterize the Donnan effects involved in the equilibria. With increasing alkali concentration, the alkali reversibly consumed by the wood meal increases, reaching the value of 1.7 eq/kg dry wood. Quantitative determinations of the accompanying increase in anionic groups associated with the wood matrix suggest that these groups are formed predominantly through the ionization of monomeric units in polysaccharides, behaving as very weak monobasic acids. Comparison of results obtained for mercerized and unmercerized wood indicate that 63 % of the polysaccharides in the latter case are accessible to equilibration at alkali concentrations of 2 N and below. Elimination of Donnan effects by sufficiently high added sodium salt concentrations can be used to determine the average acidic dissociation constant of polysaccharides in mercerized wood. The value found for ambient temperature, $0.93 \cdot 10^{-14}$, declines slowly with increasing temperature. Water associated with the inner solution was found to

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increase from 0.6 to 1.3 g/g wood with increasing hydroxyl ion
concentration from 0.5 to 2.0 N. In the same alkalinity range, the
ratio of inner to outer hydroxyl ion concentration was shown to
increase from 0.55 to 0.70 when the measurements were carried out
in the presence of 0.5 M NaCl. The importance of polysaccharide
ionization and accompanying Donnan effects in the interpretation of
kinetic kraft pulping studies is demonstrated.

Introduction.

In the previous paper of this series[1] quantitative interpretation of
data on saponified hemlock wood meal in equilibrium with very
dilute NaOH solutions was used to estimate the amounts of
carboxylic, phenolic hydroxyl and enol groups in this material. The
results obtained are summarized in Table 1.

When the pH in equilibrated systems is raised above 12, gradual
ionization of the hydroxyl groups of wood polysaccharides takes
place contributing to the resulting Donnan equilibria. Neale[3] has
studied analogous equilibria in cellophane-aqueous NaOH systems
and demonstrated that the glucose units of cellulose can be dealt
with as weak monobasic acids with an approximate pK_a value of 14.
Similar behaviour may be ascribed to wood cellulose as well as to
hexose and pentose units in hemicelluloses. On this basis, the sugar
units of the total polysaccharide components in hemlock wood
represent together 4.26 weakly acidic equivalents/ kg of dry wood,
as shown in Table 1.

As in the previous study[1], hemlock wood meal, after removal of
extractives, was treated with 1 N NaOH at ambient temperature to
remove acetyl groups and to saponify ester functions to carboxylate
groups. After saponification, the wood meal was thoroughly washed
with water, bringing the pH of the filtrate down to the range 8 to 9.
Simultaneously, the alcoholate groups of polysaccharides and the
phenolate and enolate groups of lignin are hydrolyzed. Consquently,
only carboxylate functions remain in the solid matrix as their sodium
salts.

Table 1. Acidic groups present in extractive-free, saponified Western hemlock wood meal[1], containing 39.4% cellulose, 31.7 % lignin and 4.0 % pentosan (xylan+arabinan[2], unit weight 132). Estimated percentage for galactoglucomannan (by difference): 24.9%. Consequently, total hexosans (unit weight 162): 64.3%.

Acidic functions.	Mol/kg dry wood
A. Groups with pK < 11[1]:	
Carboxylic acids	0.158
Phenolic hydroxyls	0.260
Enolic hydroxyls	0.030
Total	0.448
B. Monosaccharide units in:	
Hexosans	3.96
Pentosans	0.30
Total	4.26

As pointed out in the previous paper, the Donnan condition applied to wood-alkali equilibria can be expressed by the following equation where subscripts i and o refer to inner and outer solutions, respectively:

$$[Na^+]_i[OH^-]_i = [Na^+]_o[OH^-]_o = [OH^-]_o^2 \tag{1}$$

If $[A^-]_i$ represents the sum of anionic groups (carboxylate, phenolate, enolate and alcoholate functions of carbohydrate hydroxyls) associated with the solid wood matrix:

$$[Na^+]_i = [A^-]_i + [OH^-]_i \quad \text{and}$$

$$\{[OH^-]_i + [A^-]_i\} \cdot [OH^-]_i = [OH^-]_o^2$$

It follows that the following relationship is valid for all equilibria:

$$[OH^-]_i < [OH^-]_o < [Na^+]_i \qquad\qquad (2)$$

The goal of this study was to determine what amount of NaOH becomes reversibly associated with the wood matrix, to derive an average acidic dissociation constant for wood polysaccharides, and to estimate the hydroxyl ion concentration and the amount of water in the inner solution as a function of the OH$^-$ concentration in the outer solution. It should be noted that all concentrations in this paper are expressed as molalities (mol/kg water) rather than molarities (mol/l).

Results and Discussion

<u>Effect of Donnan Equilibrium on the Amount of NaOH Consumed in the Ionization of Wood Polysaccharides.</u> The reversible consumption of alkali (AC, eq/kg wood) in equilibration can be determined readily from the following equation:

$$AC = \{[OH^-] - [OH^-]_o\} \, V/W \qquad\qquad (3)$$

where [OH] and [OH]$_o$ are the titrimetrically determined hydroxyl ion concentrations before and after equilibration, respectively, and V, the total weight of water and W, the weight of wood in the system. The alkali consumption in equilibration increases with increasing hydroxyl ion concentration as shown by Curve 1 in Figure 1. It should be noted, however, that the consumption values are always lower than the amount of anionic groups present in the solid matrix (A$^-$, meq/g wood) due to the fact that the hydroxyl ion concentration is lower in the inner compared with the outer solution, as shown in Equation 2. In this case, no method is available for the determination of the matrix-bound anionic groups.

The previous paper[1] outlined a method whereby the difficulty in the determination of anionic groups can be eliminated by adding a neutral electrolyte, such as NaCl, in the system. As a consequence, the alkali consumption in equilibration increases, as shown by Curve 2 in Fig. 1. The reason for this increase is due to a reduction in the
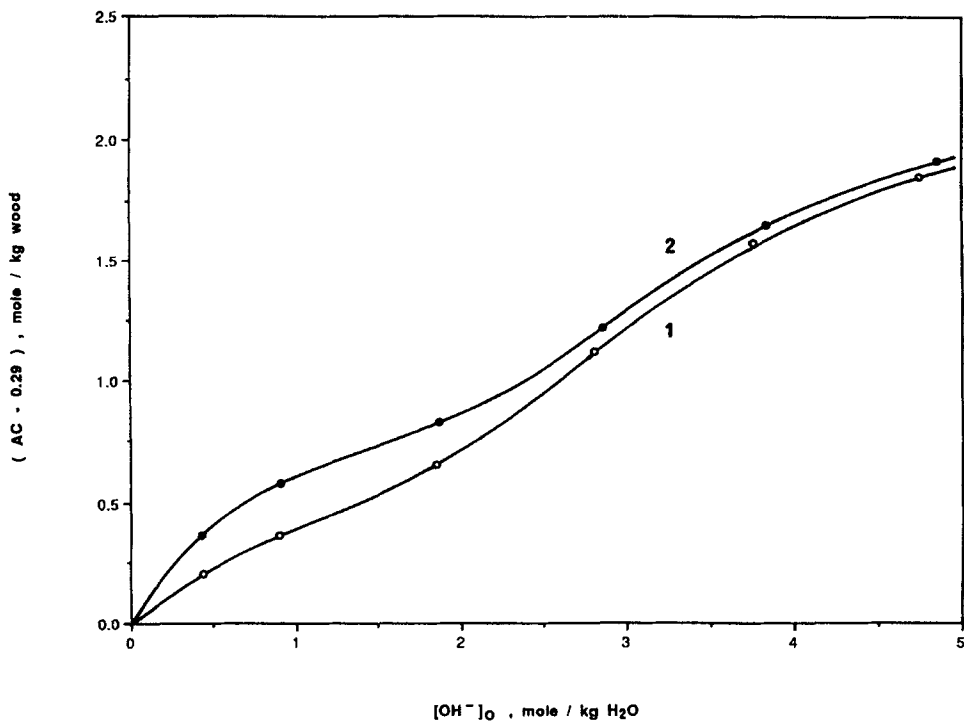
FIGURE 1. Alkali consumption (AC - 0.29, eq/kg wood) in the equilibration of mildly saponified extractive-free hemlock wood as a function of outer hydroxyl ion concentration $[OH^-]_0$ (Curve 1). - Curve 2 gives the same values in the presence of 0.5 M NaCl.

difference between inner and outer hydroxyl ion concentrations. By determining the chloride ion concentrations before and after equilibration, the total amount of anionic groups can now be calculated from the following equation:

$$A^- = \{[OH^-] - \frac{[Cl^-]}{[Cl^-]_o} \cdot [OH^-]_o\} \cdot V/W \tag{4}$$

When saponified hemlock wood meal is equilibrated with chloride containing alkali, the determined anionic groups include, in addition to ionized polysaccharide hydroxyl groups, phenolate and enolate groups associated with the lignin component (0.29 eq/kg wood, Table 1). Correcting for the latter groups, the fraction of ionized monomeric units in wood polysaccharides, f_i, can be calculated from the following equation, taking into account that hemlock wood contains a total of 4.26 moles of these groups in one kg of wood (Table 1):

$$f_i = \frac{A^- - 0.29}{4.26} \tag{5}$$

The dependence of f_i on outer hydroxyl ion concentration was determined by performing a series of equilibration experiments using solutions containing varying amounts of NaOH and 0.5 mole NaCl/kg H_2O . The results are shown as Curve 1 in Figure 2. It can be seen that at 5 M outer NaOH concentration, the ionized groups correspond to approximately one equivalent per polysaccharide monomer unit.

At 5 M alkali concentration, the crystalline regions of the cellulose component have been converted to alkali cellulose and thus participate in the equilibration. This is not the case at lower alkali concentrations where native cellulose lattices are resistant to penetration by alkali and are therefore inaccessible to equilibration. On the other hand, it has been shown in mercerized cotton cellulose studies that cellulose II lattices equilibrate with aqueous alkali and are presumed to be completely accessible[4]. Mercerized wood meal was therefore prepared by performing the saponification in 6 instead of 1 N NaOH. The values obtained for the ionization of this preparation are recorded by Curve 2 in Figure 2. As could be
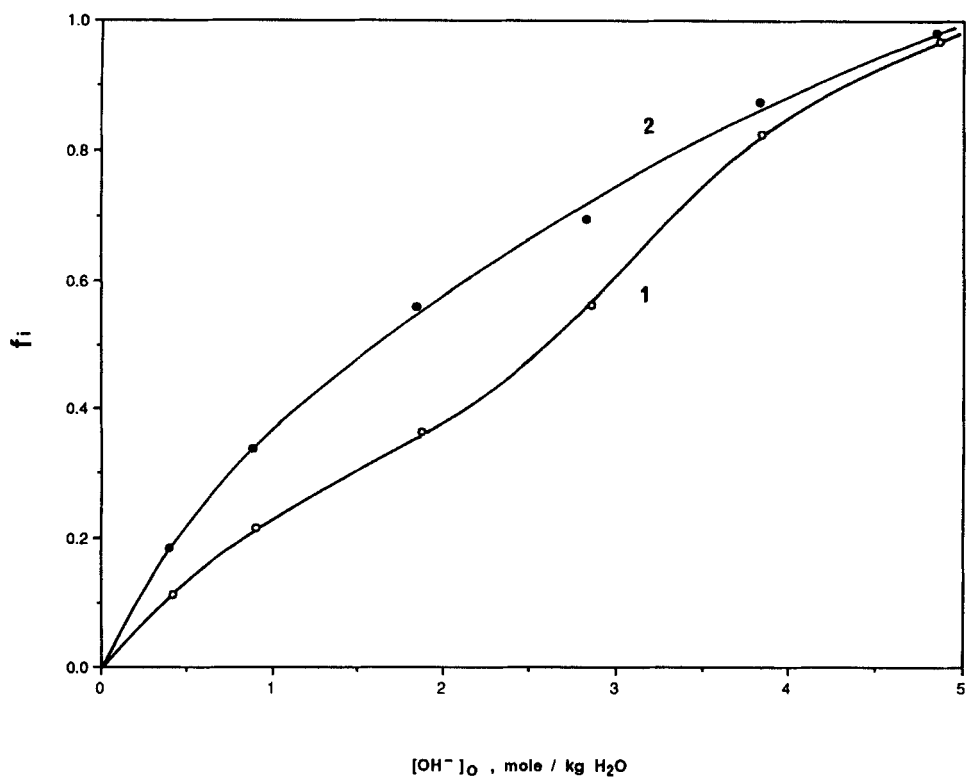
FIGURE 2. Curve 1: Fraction of ionized polysaccharide units f_i as a function of $[OH^-]_0$, determined for saponified hemlock wood from Donnan equilibrium measurements. - Curve 2: Fraction of ionized polysaccharide units in mercerized wood.

anticipated, curves 1 and 2 approach each other at high alkali concentrations.

Accessibility of Hemlock Polysaccharides. The accessibilities of the polysaccharide components of the saponified wood meal could be calculated based on the assumption that those present in the mercerised sample were completely accessible. The accessibility values obtained are presented as a function of outer NaOH concentration in Figure 3. For comparison, the corresponding accessibility curve for cotton cellulose[4] is included in the figure. It may be assumed that the accessibilities of wood and cotton celluloses are likely to be equal and that the hemicellulose components are completely accessible to the action of alkali. Taking into account that saponified hemlock wood contains approximately 39.4 % cellulose and 28.9% hemicelluloses, a theoretical accessibility curve for wood polysaccharides can be derived, also included in Figure 3. It can be seen that the derived and experimental curves are close to each other at alkali concentrations lower than 2 M, but the derived curve reaches complete accessibility faster than the experimental one. These results suggest that wood and cotton celluloses possess approximately equal accessibilities, but the former requires higher alkalinities for complete mercerization, probably because of the restrictive influence of the lignin component. On the other hand, the total accessibility of wood polysaccharides, 63 %, is substantially higher that of cotton cellulose (36 %) as a consequence of the presence of fully accessible hemicelluloses in the former. Consequently, wood polysaccharides bind reversibly larger amounts of below-mercerizing strength alkali than cotton.

Effect of Donnan Equilibria on the Determination of Residual Alkali in Kraft Pulping. It is an accepted practice to determine the residual alkali as well as the effective alkali consumed in the pulping process, from titrimetrically determined NaOH concentrations of the pulping liquors[5], assuming that the observed reduction in alkali concentration is equivalent to additional carboxylic and phenolic hydroxyl functions generated by the pulping process. This assumption overlooks, however, the effect of the ionized polysaccharide units present in the pulp component and, also, the effects caused by the modified Donnan equilibrium.

$[OH^-]_0$, mole / kg H_2O
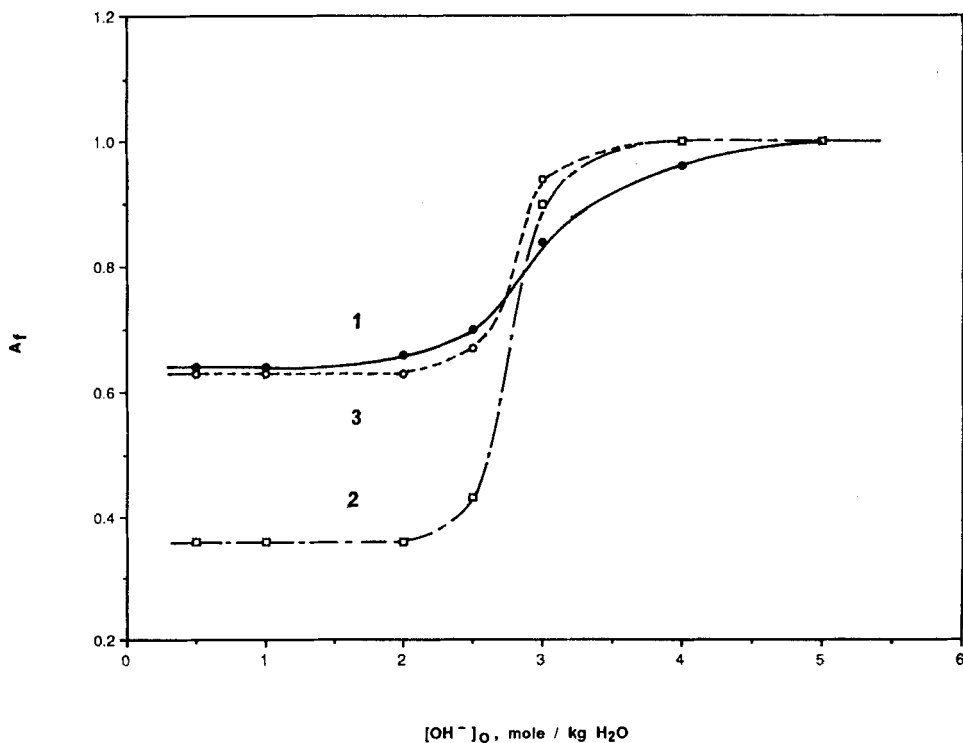
FIGURE 3. Accessibilities of unmercerized wood and cotton polysaccharides as a function of outer hydroxide concentration. Curve1: Fraction of accessible polysaccharide units A_f in mildly saponified hemlock wood, calculated from the difference between ionized saccharide units in mildly saponified and mercerized samples. - Curve 2: Fraction of accessible glucose units in unmercerized cotton cellulose. - Curve 3: Expected accessibility of hemlock polysaccharides, assuming the hemicellulose components to be completely accessible and the cellulose component to have the same accessibility as cotton cellulose.

In order to estimate the magnitude of error in conventional residual
alkali determinations, hemlock wood meal was treated with a typical
kraft liquor (EA 20% Na_2O of dry wood, sulfidity 25%) for various
periods of time at 90°C. In the first series of experiments, the
residual alkali was determined titrimetrically using an aliquot of the
liquor. In the second series of experiments, the treated wood was
separated by filtration and washed thoroughly with water. An
aliquot of combined filtrate and washings was, in this case, used for
residual alkali determination.

Figure 4 presents the apparent residual alkali values observed in
both series of experiments. It can be seen that conventional residual
alkali determination indicates higher alkali consumption, because the
consumed amount includes, in this case, NaOH reversibly bound to
wood polysaccharides. In the second method, washing the treated
wood with water releases the bound sodium hydroxide not only from
polysaccharides, but also from lignin phenolate groups. The
contribution of the latter groups is relatively small, as demonstrated
by Curve 3, corrected for the hydrolyzed phenolate groups. Overall,
the results demonstrate that the conventional residual alkali
determination, when applied to initial stages of kraft pulping,
provides estimates for consumed effective alkali that can be as much
as 58% higher than the real consumption. It is also clear that the
residual alkali determination after completed pulping must likewise
afford results that are grossly misleading. On the other hand, reliable
values can be obtained by aquiring a representative sample of pulp
suspended in the liquor and by applying a method similar to that
employed in the second series of experiments.

Estimation of Average Acidic Dissociation Constant for Wood
Polysaccharides. The data aquired for the amounts of dissociated
polysaccharide hydroxyl groups were, as such, insufficient for the
calculation of the average acidic dissociation constant, for the simple
reason that the volume of the inner solution V_i and its hydroxide
concentration were unknown and could be expected to have variable
values depending on the alkali- and overall electrolyte concentration.
On the other hand, as already mentioned, adding inorganic sodium
salts to the system reduces the Donnan effect. Thus, at sufficiently
high added electrolyte concentrations, the hydroxide concentrations
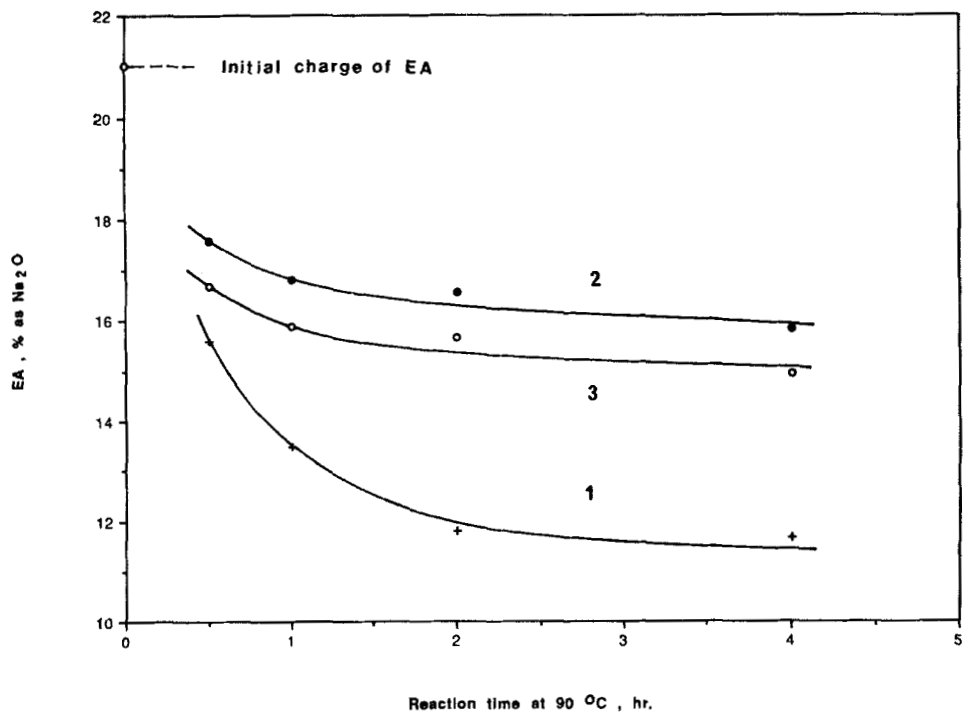
FIGURE 4.   Residual alkali determinations in the treatment of hemlock wood meal with kraft liquor (EA 21% Na_2O of OD wood, sulfidity 27%, L/W=5) at 90°C. Curve 1: Direct titration of liquor. Curve 2: Titration of filtrate and washings. - Curve 3: Curve 2 corrected for alkali released in the hydrolysis of lignin phenolate groups.

of the inner and outer solutions may become virtually identical.
Under such conditions, the measured alkali consumption by
polysaccharides (AC - 0.29) becomes equivalent to the ionized
polysaccharide hydroxyl groups, greatly simplifying the estimation of
their effective acidic dissociation constant. It was therefore of
interest to study the effect of increasing concentrations of added
inorganic sodium salts on the values of alkali consumption, measured
for the mercerized wood sample. If virtually complete elimination of
the Donnan effect could be achieved at sufficiently high salt
concentration, AC and A$^-$ would become nearly identical. Under these
circumstances, α, the degree of dissociation, of polysaccharide units
could be estimated from the following equation, analogous to Eq. 5:

$$\alpha \ = \ f_i \ = \frac{AC - 0.29}{4.26} \qquad\qquad (6)$$

The polysaccharide dissociation constant K_a can then be estimated
from the following equation:

$$K_a \ = \ \frac{K_w}{[OH^-]_o} \cdot \frac{\alpha}{(1 - \alpha)} \qquad\qquad (7)$$

where K_w is the ion product of water.

As electrolytes added to 0.5 molal NaOH, both NaCl and Na_2CO_3 were
tested using the saponified as well as mercerized wood meal
samples. The results are summarized in Figure 5. It is clearly
indicated that sodium chloride, even at high concentrations, is not
able to cancel Donnan effects. In contrast, the measured AC values
appear to level off at 2 M concentrations of the divalent electrolyte
Na_2CO_3, suggesting that virtual elimination of Donnan effects has
been achieved at this point, making the estimation of K_a possible.
Using the α-value obtained for mercerized wood meal in the
presence of 1.9 M Na_2CO_3, provides the magnitude $0.93 \cdot 10^{-14}$ for K_a.

To confirm this result, the determinations were repeated using
another divalent electrolyte $Na_2S_2O_3$. The results obtained are
summarized in Table 2 and conform well with the average K_a value
of $0.93 \cdot 10^{-14}$.
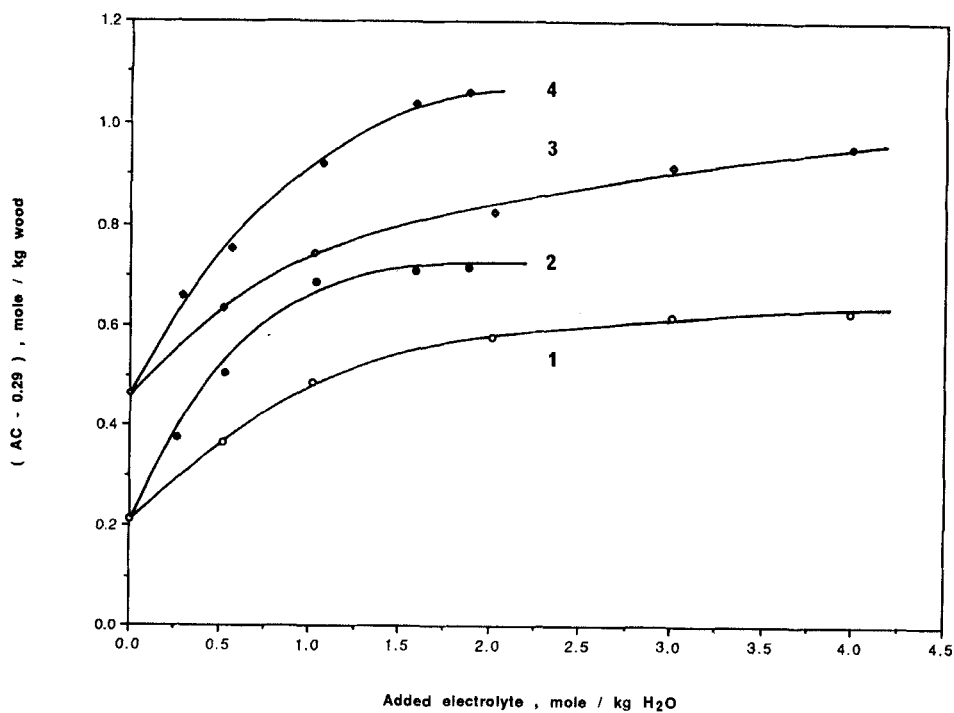
FIGURE 5.   Effect of added electrolytes on the excess alkali con-
sumption at constant original hydroxyl ion concentration [OH⁻] (0.5
eq/kg H_2O). Curve 1: Saponified hemlock meal with NaCl as added
electrolyte.   - Curve 2: Saponified sample with Na_2CO_3 as electrolyte.
-   Curve 3: Mercerized sample with NaCl electrolyte.   -   Curve 4:
Mercerized sample with Na_2CO_3 electrolyte.

Table 2. Dissociation constants K_a estimated for mercerized hemlock polysaccharides from alkali consumption (AC) values obtained using 0.1 - 0.5 M NaOH solutions containing 1.6 - 2.5 moles/l of divalent electrolytes.

Added Electrolyte	Moles/l	$[OH^-]_o$	α	$K_a \cdot 10^{14}$
Na_2CO_3	1.600	0.349	0.243	0.92
- " -	1.900	0.346	0.244	0.93
$Na_2S_2O_3$	2.000	0.308	0.223	0.93
- " -	2.500	0.053	0.046	0.91
- " -	2.500	0.150	0.122	0.93
			Average	0.93

Effect of Temperature on the magnitude of K_a. In order to determine the effect of temperature on K_a, measurements on mercerized wood were repeated at 0 and 40°C and the $\ln(K_a/K_w)$ values were plotted against inverse absolute temperature, as illustrated in Figure 6. A linear relationship was obtained which demonstrates that K_a declines with increasing temperature.

Estimation of the Hydroxyl Ion Concentration $[OH^-]_i$ and the Amount of Water, V_i, in the Inner Solution. Once the magnitude of K_a is known, the data shown in Figures 2 and 3 can be utilized to calculate the hydroxyl ion concentration of the inner solution in systems containing NaCl from the following equation:

$$[OH^-]_i = \frac{K_w}{K_a} \cdot \frac{\alpha}{(1 - \alpha)} = 1.08 \cdot \frac{\alpha}{(1 - \alpha)} = 1.08 \frac{f_i}{A_f - f_i} \quad (8)$$

The utility of this equation is, however, limited to alkali concentrations below 2 M. The reason for this circumstance is that the amount of ionized groups associated with the wood matrix at higher alkali concentrations turned out to be larger than could be expected from the ionization of polysaccharide units. The
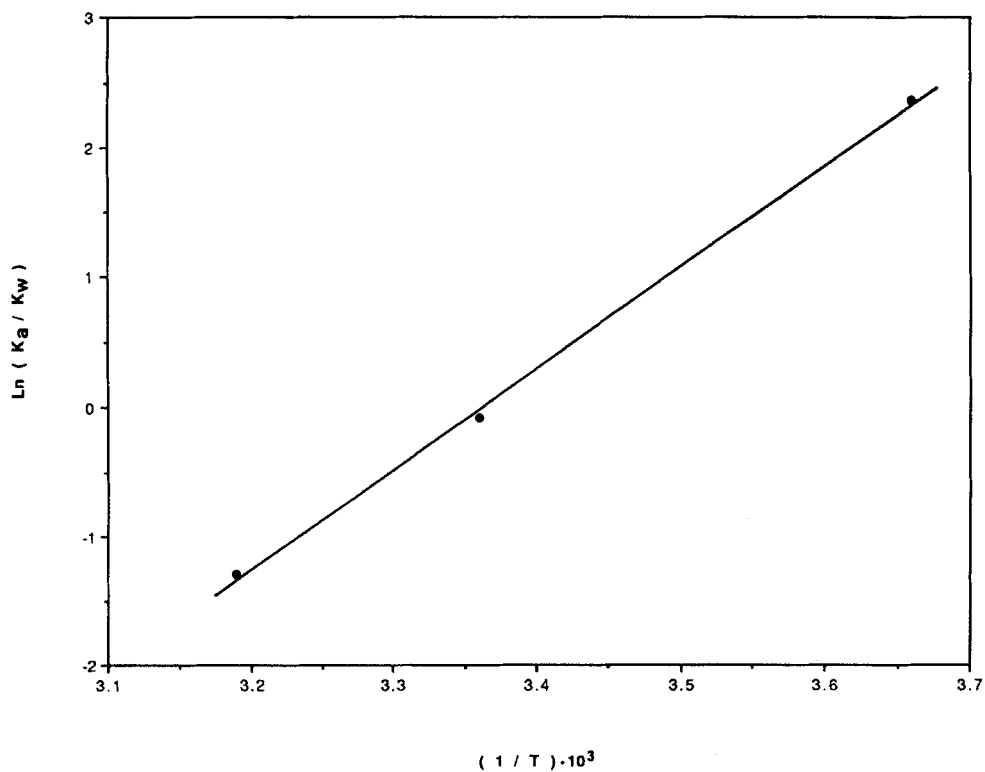
FIGURE 6.   Relationship between polysaccharide dissociation constant K_a and temperature. Ln (K_a/K_w) as a function of inverse absolute temperature.

FIGURE 7. The ratio of inner and outer hydroxyl ion concentrations $[OH^-]_i/[OH^-]_o$ as a function of $[OH^-]_o$ with 0.5 M NaCl as added electrolyte.

FIGURE 8.   Estimated approximate inner solution volumes V_i as a function of $[OH^-]_o$ for saponified (Curve 1) and mercerized (Curve 2) hemlock wood meal samples.

phenomenon may be caused by incipient ionization of hydroxyl groups in the lignin component, for example.
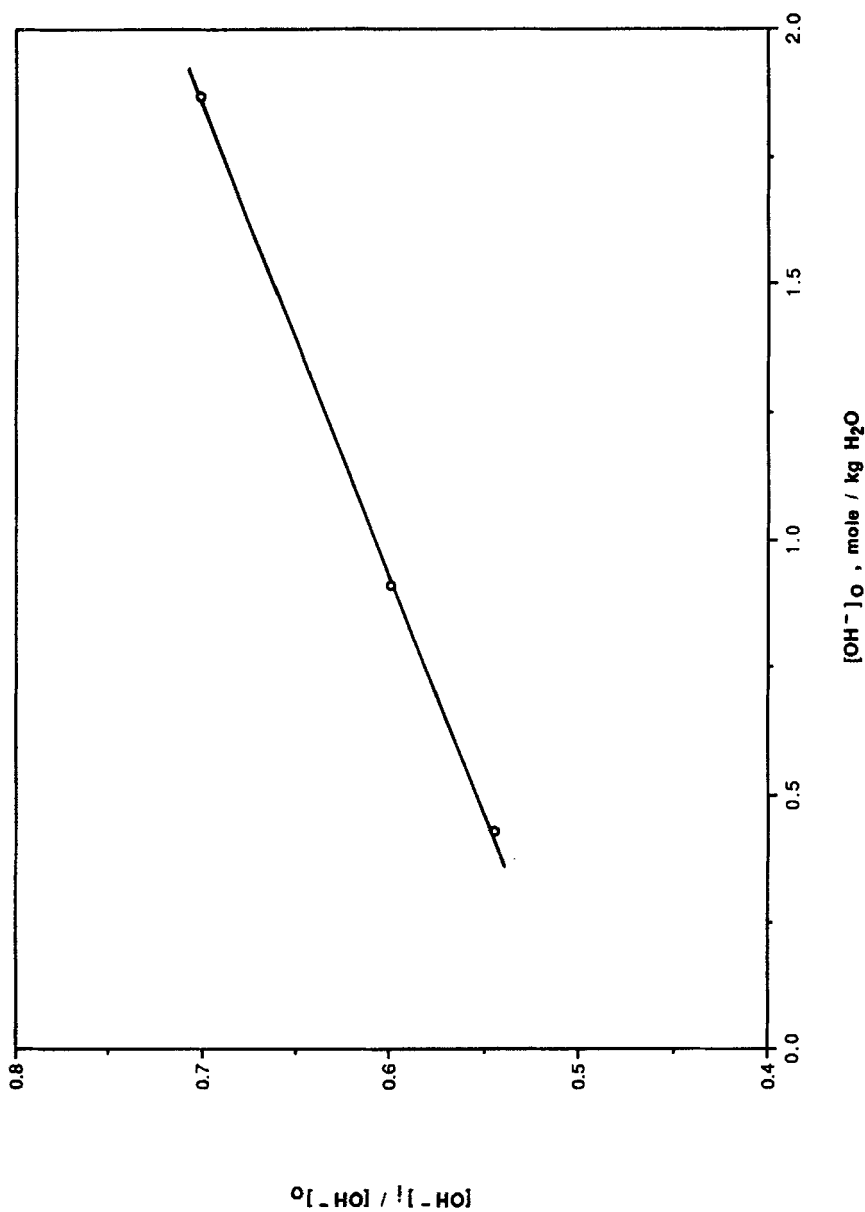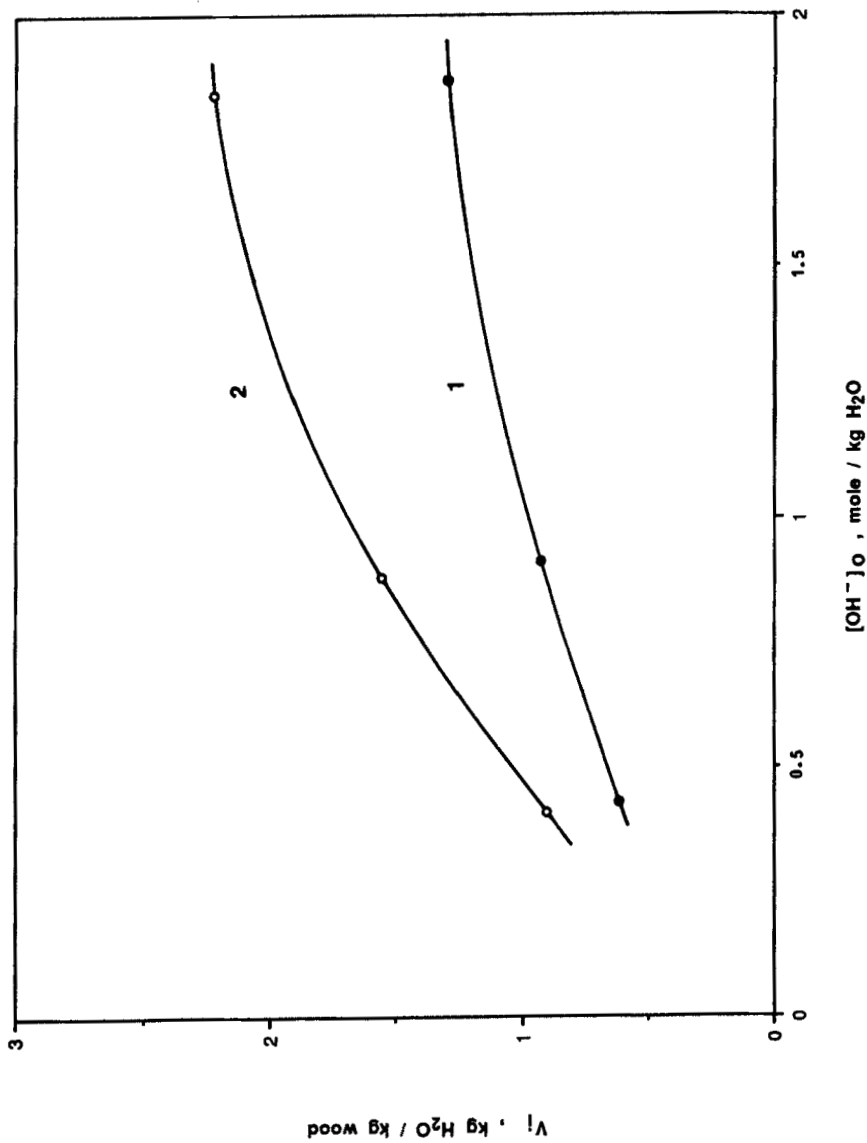
The calculated $[OH^-]_i/[OH^-]_o$ ratios for systems containing 0.5 M NaCl are shown as a function $[OH^-]_o$ in figure 7. It can be seen that this ratio increases from 0.55 to 0.7 when the alkalinity is increased from 0.5 to 2.0 M.

The inner solution volume is then obtained from the following equation:

$$V_i = \frac{4.26 \cdot A_f \cdot \alpha - (AC - 0.29)}{[OH^-]_o - [OH^-]_i} \tag{9}$$

The calculated values for V_i in chloride containing systems are shown in Figure 8 as functions of 0 to 2 M outer hydroxide ion concentrations. The values obtained are, however, highly sensitive to minor variations in AC values and are to be considered as rough estimations only.

It should noted that the presence of sodium chloride in the equilibrated systems reduces the Donnan effect. Consequently, the $[OH^-]_i/[OH^-]_o$ ratio in systems devoid of added electrolyte will be lower. An effort was made to derive approximate values for inner hydroxyl ion concentrations in these systems from experimental data and the K_a value of polysaccharides. It turned out, however, that the accumulation of error factors in the calculations prevented the derivation of reasonable estimates for the inner hydroxyl ion concentrations in these systems.

Conclusion

In the past, the ability of wood polysaccharides to bind alkali from aqueous solutions has not been recognized, although the analogous interaction between cellulose and sodium hydroxide has been known for a long time. The phenomenon exerts a significant effect on the course of of alkaline pulping processes, such as kraft pulping. The alkali reversibly bound to the wood or pulp matrix reduces the

hydroxyl ion concentration in the liquor and direct effective alkali determinations on the liquor provide therefore an exaggerated estimate of the extent of irreversible chemical processes that have occurred during the pulping. As the pH is lowered during the pulping process, the matrix-bound alkali acts as a buffer, releasing gradually additional alkali to the liquor.

It appears also that the hydroxyl ion concentration prevailing in the liquor does not directly influence the rates of delignification and polysaccharide degradation. Rather, these processes ought to be controlled by the alkalinity of the inner solution which is lower than that of the liquor as a consequence of Donnan effects. The presence of inert electrolytes, such as salts of organic acids, sodium carbonate etc., increases the alkalinity of the inner solution. It is therefore not correct to assume that the addition of black liquor or sodium carbonate to white liquor should have no effect on the rate of pulping.

Since it was found that the magnitude of the acidic dissociation constant of wood polysaccharides declines with increasing temperature, it is not possible, on the basis of results reported herein, to evaluate the magnitude and kinetic influence of Donnan equilibria at 170°C, the commonly used pulping temperature.

Ionization of polysaccharides must also have an effect on the filtration and washing of alkaline pulp suspensions, retarding the release and removal of alkali from the pulp.

<div align="center">EXPERIMENTAL</div>

Materials.

Acetone-extracted W. hemlock (Tsuga hetterophylla) wood meal was suspended in 0.1 N HCl, stirred magnetically for four hours, filtered, washed with distilled water and air-dried, in order to remove mineral constituents. Samples of the wood meal were then subjected to the following treatments.

a. Saponification was performed by suspending the sample in an excess of 1 N NaOH in an Erlenmeyer flask, purging air from the flask by nitrogen and stirring the contents magnetically for six hours at ambient temperature. The saponified wood meal was filtered, washed with distilled water until the filtrate remained colorless upon addition of phenolphthalein and air-dried.

b. Mercerization of wood meal was carried out by the same procedure, except that 6 M NaOH was used.

Methods.

All concentrations were determined as moles/kg H_2O. For this purpose, pipetted aliquots for titrations were weighed using an analytical balance.

A. NaOH Equilibration Experiments.

a. For the determination of Actual Consumption (AC) of alkali, 20 ml of a solution containing a known concentration of NaOH was added to 2 g of accurately weighed wood meal in a 50 ml erlenmeyer flask. The amount of the added solution was determined by weighing. The flask was purged by nitrogen, stoppered and immersed for equilibration in a constant temperature bath adjusted to 25 °C for two hours, with occasional magnetic stirring. After equilibration, a 5 ml aliquot of clear supernatant solution was removed, weighed and diluted to 25 ml. The OH$^-$ concentration in the solution was determined by titration with 0.5 N H_2SO_4 using phenolphthalein as indicator. The amount of water introduced to the system as wood moisture was taken into account in calculations.

b. In the determination of matrix-bound anionic groups (A$^-$) formed in the equilibration, the same procedure as under "a" was used, except that the NaOH solution contained in this case 0.5 mole NaCl/kg H_2O. After equilibration, the chloride concentration was titrated using 0.1 N $AgNO_3$ with dichlorofluorescein as indicator.

c. Effect of added electrolyte concentration. In this series of experiments, the original NaOH concentration was kept constant at

Table 3. Experimental data for a chloride-free equilibration (Curve 1 in Fig. 1). W = weight of wood meal sample in OD grams. V = g of total water in the system. [OH$^-$] = Initial hydroxyl ion concentration, mole/kg H$_2$O. [OH$^-$]$_0$ = Hydroxyl ion concentration of outer solution after equilibration. AC = Alkali consumption, mole/kg wood.

W	V	[OH$^-$]	[OH$^-$]$_0$	AC
2.065	20.139	0.4844	0.4333	0.498
2.071	20.144	0.9640	0.8966	0.656
2.015	20.140	1.9438	1.8494	0.944
2.063	20.050	2.9462	2.8016	1.405
2.070	20.058	3.9460	3.7534	1.866
2.063	19.823	4.9731	4.7507	2.137

Table 4. Experimental data for a chloride-containing system (Curve 2 in Fig. 1 and Curve 1 in Fig.2). [Cl$^-$] and [Cl$^-$]$_0$ = Initial and outer chloride concentration after equilibration, mole/kg H$_2$O, respectively. A$^-$ = Matrix-bound anionic groups, mole/kg wood. f$_i$ = Calculated fraction of ionized polysaccharide units.

W	1.960	1.962	1.962	1.963	1.966	1.953
V	20.129	20.134	20.079	20.070	19.914	19.760
[OH$^-$]	0.4913	0.9935	1.9773	3.0024	4.0272	5.0755
[OH$^-$]$_0$	0.4273	0.9090	1.8684	2.8551	3.8356	4.8576
[Cl$^-$]	0.5064	0.5066	0.5060	0.5092	0.5115	0.5173
[Cl$^-$]$_0$	0.5204	0.5258	0.5258	0.5306	0.5372	0.5417
AC	0.657	0.867	1.115	1.506	1.940	2.205
A$^-$	0.775	1.208	1.835	2.683	3.799	4.418
f$_i$	0.114	0.215	0.363	0.562	0.824	0.969

0.5 eq/kg H_2O and the concentrations of added electrolytes were varied. The NaCl concentrations were varied in the range 0.5 to 4.0 M, and those of Na_2CO_3 and $Na_2S_2O_3$, in the range 0.25 to 2.0 M. The actual alkali concentration was determined according to procedure under "a".

Experimental data obtained in chloride-free and chloride containing systems are illustrated in Tables 3 and 4, respectively.

B. Treatment of Wood Meal with Kraft Liquor.

Samples of untreated hemlock wood meal were mixed in 5:1 volume-to-weight ratio with kraft liquor containing 20% effective alkali as Na_2O and 25% sulfidity and placed in small autoclaves. The autoclaves were inserted in tightly fitting pockets of a rocking cylindrical aluminum block preheated to 90°C and kept at that temperature for various periods of time. The autoclaves were cooled and the contents filtered. In the first series of experiments, 5 ml aliquots of the filtrate were titrated with 0.2 N HCl with phenolphtalein as indicator. In the second series of experiments, the filtered wood meal was washed with several portions of distilled water. The combined filtrate and washings were diluted to 250 ml, and a 50 ml aliquot titrated with 0.2 N HCl.

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