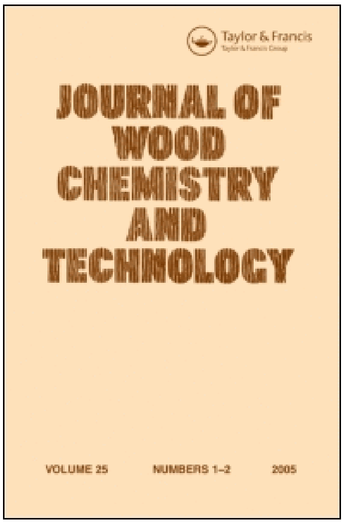

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DONNAN EQUILIBRIA IN WOOD-ALKALI INTERACTIONS

PART 3. THEORETICAL MODELING

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ABSTRACT

Wood-alkali interactions in aqueous solution were described with Donnan equilibrium and ionic dissociation equilibrium theories. Theoretical models of three systems, NaOH-H_2O-wood, NaOH-NaCl-H_2O-wood, and NaOH-Na_2CO_3-H_2O-wood, were developed. Theoretical predictions fit experimental data well. The theoretical modeling also shows good agreement with experimental results reported in the literature when applied to NaOH-H_2O-cotton system. Theoretical simulations indicate that carbohydrate hydroxyl groups can be considered as mono-basic weak acids at alkali concentrations lower than 3 M. At higher alkalinities (> 3 M), however, further hydroxyl groups are also significantly ionizable.

INTRODUCTION

In the previous papers of this series[1,2], the strong acid group contents (carboxyl, phenolic and enolic hydroxyl groups) in softwood and hardwood meal samples were determined in situ with a newly developed method. The primary dissociation constant and the total amount of ionized carbohydrate hydroxyl groups in alkali solutions were also measured. It was concluded that the ionization of all strong acid groups and partial ionization of carbohydrate hydroxyls in alkali solution causes the establishment of an ion electric potential equilibrium, i.e. Donnan equilibrium, between the inside and outside of wood fibers. Thus, an unequal OH^- concentration distribution between the two phases can be expected. The Donnan equilibrium effect on the alkali concentration distribution was well characterized by measuring the bulk liquor concentration change of sodium chloride in the NaOH-NaCl-H_2O-wood system. It is necessary to apply a theoretical model, however, to completely elucidate the Donnan equilibrium in wood-alkali interactions. The objective of this research is to develop such a theoretical model.

MODEL DERIVATION

The following describes the theoretical model of wood-alkali interactions in solution. The apparent alkali consumption, an important characteristic of the wood-alkali interactions, is expressed as a function of the dissociated carbohydrate hydroxyl amount and the alkali concentration distribution between the inside and outside of wood fibers. The equation calculating the dissociated carbohydrate hydroxyl amount is derived with the ionic dissociation equilibrium theory. The prediction of the alkali concentration distribution is based on the Donnan equilibrium theory.

Apparent alkali consumption.

The measured alkali consumption by wood is usually quantified with the bulk liquor alkali concentrations before and after adding a wood sample into an alkali solution. That is,

$$N = \frac{V \cdot (C - C_o)}{W} \qquad (1)$$

Where, N is the measured alkali consumption by wood, mole/mole polysaccharide (monosaccharide unit); W is the amount of wood, expressed as moles of polysaccharides; V is the weight of water in the original solution, kg; C is the initial alkali concentration of the solution, mole/kg H_2O; and C_o is the bulk liquor alkali concentration after adding wood sample into the solution, mole/kg H_2O.

To compare with the results of cotton cellulose, the apparent alkali consumption by the polysaccharides of saponified wood meal is defined as the difference of the measured alkali consumption and the amount of phenolic and enolic hydroxyl groups.

$$P = N - \Theta = \frac{V \cdot (C - C_o)}{W} - \Theta \qquad (2)$$

Where, P is the apparent alkali consumption, mole/mole polysaccharide; Θ is the amount of phenolic and enolic hydroxyl groups, mole/kg H_2O, $\Theta = 0.07$ for W.hemlock wood[1].

It should be noted that the carboxyl groups in original wood have been converted to carboxylate after saponification and washing with water[1]. Eq. 2, therefore, expresses the measured alkali consumption by polysaccharide hydroxyls only.

Eq. 2 is based on the experimentally measured values of the initial alkali concentration, C, and the bulk liquor alkali concentration after equilibrium, C_o. To theoretically predict the apparent alkali consumption, P, for a given equilibrium alkali concentration, C_o, the variable C in Eq. 2 must be eliminated. Therefore, the total alkali mass balance in the experimental system has to be employed.

The total amount of alkali is equal to the sum of alkali moles in bulk liquor, inner solution of wood fibers, and associated with strong acid groups plus partial carbohydrate hydroxyls. That is,

$$C \cdot V = C_o \cdot (V - V_i \cdot W) + C_i \cdot V_i \cdot W + (\Theta + \alpha) \cdot W \qquad (3)$$

Substituting this equation into Eq. 2 we get the simple result,

$$P = \alpha - (C_o - C_i) \cdot V_i \qquad (4)$$

Where, V_i is the inner solution volume of wood fibers, expressed as the weight of water, kg/mole polysaccharide; C_i is the inner solution alkali concentration, mole/kg H_2O; α is the total amount of ionized carbohydrate hydroxyls, eq/mole polysaccharide.

As shown in Eq. 4, the values of the ionized carbohydrate hydroxyl amount, α, the inner solution alkali concentration, C_i, and the inner solution volume, V_i, are needed to calculate the apparent alkali consumption, P, for a given value of the outside alkali concentration, C_o. The values of V_i are experimentally measured. α and C_i are functions of C_o, which can be derived with the ionic dissociation equilibrium and Donnan equilibrium theories. The derivations of α and C_i are described as follows.

Dissociation of carbohydrate hydroxyl groups.

Strong acid groups (carboxyl, phenolic and enolic hydroxyl groups) in wood fibers have low pK values $(< 10)^1$. Therefore, they can be completely ionized at pH values greater than 10. Carbohydrate hydroxyl groups, however, are only partially ionizable in alkali solution because of their weak acidity[3,4,5]. The reactivities of the carbohydrate hydroxyls are sufficiently different that they can be approximately classified into two groups[6]; primary and secondary. Ionization of these two hydroxyl groups will occur simultaneously in alkaline solutions. Based on the ionic dissociation equilibrium theory[7], the dissociation equilibrium of carbohydrate hydroxyls in alkali solution is expressed as follows.

$$AH_2 \overset{K_1}{\longleftrightarrow} H^+ + AH^- \overset{K_2}{\longleftrightarrow} 2H^+ + A^= \tag{5}$$

$$K_1 = \frac{[AH^-]\cdot[H^+]_i}{A_f\cdot[AH_2]'-[AH^-]-[A^=]} = \frac{K_w\cdot[AH^-]}{[OH^-]_i\cdot\{A_f\cdot[AH_2]'-[AH^-]-[A^=]\}} \tag{6}$$

$$K_2 = \frac{[A^=]\cdot[H^+]_i}{[AH^-]} = \frac{K_w\cdot[A^=]}{[OH^-]_i\cdot[AH^-]} \tag{7}$$

Let, $\alpha_1 = [AH^-] / [AH_2]'$; $\alpha_2 = [A^=] / [AH_2]'$

$\beta_1 = K_1 / K_w$; $\beta_2 = K_2 / K_w$ (8)

$C_i = [OH^-]_i$

Substituting Eq. 8 into Eqs. 5-6 we get,

$$\alpha_1 = \frac{A_f\cdot K_1\cdot[H^+]_i}{[H^+]_i^{\,2} + K_1\cdot[H^+]_i + K_1\cdot K_2} \tag{9}$$

$$\alpha_2 = \frac{A_f\cdot K_1\cdot K_2}{[H^+]_i^{\,2} + K_1\cdot[H^+]_i + K_1\cdot K_2} \tag{10}$$

The total amount of ionized carbohydrate hydroxyl groups (eq/mole polysaccharide) is then,

$$\alpha = \alpha_1 + 2\cdot\alpha_2 = \frac{A_f\cdot\{K_1\cdot[H^+]_i + 2\cdot K_1\cdot K_2\}}{[H^+]_i^2 + K_1\cdot[H^+]_i + K_1\cdot K_2}$$

$$= \frac{A_f\cdot(1 + 2\cdot\beta_2\cdot C_i)\cdot\beta_1\cdot C_i}{1 + \beta_1\cdot C_i + \beta_1\cdot\beta_2\cdot C_i^2} \qquad (11)$$

Where, $[AH_2]'$ is the total amount of polysaccharides, expressed as monomer units per kilogram water (mole/kg H_2O); $[AH^-]$ is the concentration of the polysaccharides with one dissociated hydroxyl in each monomer unit, mole/kg H_2O; $[A^=]$ is the concentration of the polysaccharides with two dissociated hydroxyls in each monomer unit, mole/kg H_2O; A_f is the accessibility of polysaccharides to alkali, $0 < A_f < 1$; K_1 and K_2 are the primary and secondary dissociation constants; $K_w = [H^+]_i\cdot[OH^-]_i = 10^{-14}$ is the water ionic product; $[H^+]_i$ and $[OH^-]_i$ are concentrations of hydrogen cation and hydroxide anion in the inner solution of wood fibers, mole/kg H_2O.

Donnan equilibrium effect.

Donnan equilibrium theory[8] is applied to predict the inner solution alkali concentration, C_i, for a given outside alkali concentration, C_o. The equations calculating C_i in several experimental systems are separately derived.

1. NaOH-H_2O-wood system.

The unequal ionic distribution in this system is shown in Fig. 1.

	fiber inside			fiber outside	
ions	ionizable groups	Na^+	OH^-	Na^+	OH^-
conc.	$A+\varphi$	$C_i+A+\varphi$	C_i	C_o	C_o

FIGURE 1. Ionic distribution in NaOH-H_2O-wood system.

In Fig. 1, $\varphi = \varphi' / V_i$, where φ' is the amount of carboxyl, phenolic and enolic hydroxyl groups in wood fibers, mole/mole polysaccharide, $\varphi' = 0.11$ for W. hemlock wood[1]; and A is the concentration of dissociated hydroxyl groups, eq/kg H_2O.

Based on Donnan equilibrium theory[8], the ionic products of Na^+ and OH^- ion pair in the inside and outside solutions must be equal. Thus the ionic equilibrium is expressed with the following equation.

$$(C_i + A + \varphi) \cdot C_i = C_o^2 \qquad (12)$$

By solving Eq. 12, the inner solution alkali concentration, C_i, can be predicted for a given outside alkali concentration, C_o.

$$C_i = \left[\left(\frac{\alpha + \varphi'}{2 \cdot V_i}\right)^2 + C_o^2 \right]^{0.5} - \frac{\alpha + \varphi'}{2 \cdot V_i} \qquad (13)$$

2. NaOH-NaCl-H_2O-wood system.

If a neutral electrolyte, such as NaCl, is added to the NaOH-H_2O-wood system, the original ionic distribution would be changed, as shown in Fig. 2.

	fiber inside				fiber outside		
ions	ionizable groups	Cl^-	Na^+	OH^-	Cl^-	Na^+	OH^-
conc.	$A+\varphi$	C_i'	$C_i+C_i'+A+\varphi$	C_i	C_o'	C_o+C_o'	C_o

FIGURE 2. Ionic distribution in $NaOH-NaCl-H_2O$-wood system.

In Fig. 2, C_i' and C_o' are Cl^- concentrations in the inside and outside solutions respectively, mole/kg H_2O. The following equations can be derived to describe the ionic equilibria between the inside and outside solutions.

For Na^+ and OH^-,

$$(C_i + C_i' + A + \varphi)\cdot C_i = (C_o + C_o')\cdot C_o \tag{14}$$

For Na^+ and Cl^-,

$$(C_i + C_i' + A + \varphi)\cdot C_i' = (C_o + C_o')\cdot C_o' \tag{15}$$

The inner solution alkali concentration C_i can then be derived from Eqs. 14-15, as shown in Eq. 16.

$$C_i = \{[\frac{\alpha + \varphi'}{2\cdot V_i\cdot(1+C_o'/C_o)}]^2+C_o^2\}^{0.5} - \frac{\alpha + \varphi'}{2\cdot V_i\cdot(1+C_o'/C_o)} \tag{16}$$

Eq. 16 simplifies to Eq. 13 for Co'= 0.

3. $NaOH-Na_2CO_3-H_2O$-wood system.

Fig. 3 shows the ionic distribution after adding Na_2CO_3 instead of NaCl to the $NaOH-H_2O$-wood system.

	fiber inside				fiber outside		
ions	ionizable groups	$CO_3^=$	Na^+	OH^-	$CO_3^=$	Na^+	OH^-
conc.	$A+\varphi$	C_i'	$C_i+2C_i'+A+\varphi$	C_i	C_o'	C_o+2C_o'	C_o

FIGURE 3. Ionic distribution in $NaOH$-Na_2CO_3-H_2O-wood system.

Where C_i' and C_o' are $CO_3^=$ concentrations in the inside and outside solutions respectively, mole/kg H_2O.

The ionic equilibrium equations between the inside and outside of wood fibers are shown for each ion pair as follows.

For Na^+ and OH^-,

$$(C_i + 2\cdot C_i' + A + \varphi)\cdot C_i = (C_o + 2\cdot C_o')\cdot C_o \qquad (17)$$

For Na^+ and $CO_3^=$, the Na^+ concentration in the equilibrium equation is squared because its counterpart anion $CO_3^=$ is divalent.

$$(C_i + 2\cdot C_i' + A + \varphi)^2\cdot C_i' = (C_o + 2\cdot C_o')^2\cdot C_o' \qquad (18)$$

The inner solution alkali concentration C_i can be calculated by solving Eqs. 17-18.

RESULTS AND DISCUSSION

As shown in Eqs. 4, 8, 11, 13 and 16, the accessibility of carbohydrate to alkali, A_f, the primary and secondary dissociation constants of carbohydrate hydroxyls,

K_1 and K_2, and the inner solution volume of wood (or cotton), V_i, are required to predict the apparent alkali consumption, P, for a given outside alkali concentration, C_o. The primary dissociation constant, K_1, was determined to be $0.93*10^{-14}$ with wood meal[2]. Experimental data of accessibility, A_f, for both wood and cotton, and inner solution volume, V_i, for cellophane and cotton cellulose have been reported[2,3]. However, the secondary dissociation constant, K_2, and the inner solution volume, V_i, of wood fibers need to be determined with literature data.

The following presents the calculations of the secondary dissociation constant and the inner solution volume of wood fibers, as well as the theoretical modeling results of the apparent alkali consumption by wood polysaccharides and cotton cellulose.

Secondary dissociation constant (K_2) of carbohydrate hydroxyl groups.

Philipp's et al. data[9] of alkali consumption by cotton cellulose, generated with high alkalinities (>3M), are used to calculate the secondary dissociation constant (K_2) of carbohydrate hydroxyl groups. Use of these high alkalinity data is necessary to determine K_2 because the secondary ionization will be negligible at lower alkalinities (<3M). The significance of secondary ionization as a function of alkali concentration is shown with theoretical simulations and will be discussed later in this paper.

Philipp et al. measured the alkali consumption of cotton cellulose in the alkali concentration range of 1.5 to 7 M. Sodium chloride was used to correct for the so-called "non-solvent water" effect on the alkali consumption. The indirect method of measuring the alkali consumption by cotton cellulose used by Philipp et al. is essentially same as that used in our previous publication[2]. The experimental procedure includes: 1) add cotton cellulose sample to a solution of NaOH and NaCl with concentrations C and C' respectively; 2) take an aliquot of the solution from the mixture after equilibrium and titrate to determine the concentrations of NaOH and NaCl, C_o and C_o'. The amount of the ionized carbohydrate hydroxyls can then be calculated with the following equation developed in Ref. 1.

$$\alpha = \left(C - \frac{C'}{C_o'} \cdot C_o\right) \cdot \frac{V}{W} \tag{19}$$

Where, C' and C_o' are the bulk liquor concentrations of NaCl before and after the equilibrium, mole/kg H_2O.

As shown in Eqs. 8 (for β_2) and 11, Parameters A_f, β_1,and C_i must be known to calculate K_2 for a given C_o and the measured α. The accessibility (A_f) data of cotton cellulose to alkali has been reported[2]. β_1 was calculated to be 0.93 using the K_1 value determined in previous literature[2]. The inner solution alkali concentration, C_i, can be calculated with Eq. 16 for measured equilibrium concentrations of NaOH and NaCl in bulk liquor, C_o and C_o'.

Table I. Secondary dissociation constant K_2 calculated with Philipp's data[9] (cotton cellulose)

$[OH^-]_o$	4.347	5.089	6.222	average
$K_2 \cdot 10^{14}$	0.068	0.062	0.039	0.056

The inner solution volume, V_i, for cotton cellulose is given in Ref. 3. The calculated values of K_2 are shown in Table I.

Inner solution volume (V_i) of wood fibers.

The ionized carbohydrate hydroxyl amount (α) and the apparent alkali consumption (P) have been measured by the indirect method for the wood-NaOH-NaCl-H_2O experimental system[2]. The data are used to estimate the inner solution volume (V_i) of wood fibers at different bulk liquor alkali concentrations (C_o). The calculation procedure is briefly described as follows: 1) substitute the primary and secondary dissociation constants ($K_1=0.93*10^{-14}$, $K_2=0.056*10^{-14}$) into Eq. 8 to calculate β_1 and β_2 ; 2) substitute β_1, β_2, and the measured α into Eq. 11 to calculate the inner solution alkali concentration, C_i; 3) Substitute α, P, C_i, and C_o, into Eq. 4 to calculate the inner solution volume, V_i.

The calculated results of V_i are converted to the regularly used unit, g H_2O/g polysaccharide, and plotted in

Fig. 4. As shown by curves 2 and 3 in the figure, the mercerized wood has higher V_i values than the unmercerized sample. This difference is presumably due to the higher accessibility (100 %) of the mercerized wood[2] to alkali.

The V_i values of cellophane and cotton cellulose from the literature[3] are also plotted in Fig. 4 for comparison. It is shown that wood inner solution volume, V_i, is between that of cellophane and cotton. A comparison of the crystalline region percentage in these materials anticipates this result. Cellophane has no crystalline region and can swell easily. Accessibility values at low alkalinities, reported in Ref. 2, can be used to estimate that softwood and cotton cellulose have crystalline regions of about 37 % and 64 % respectively. Fig. 4 shows that the order of the inner solution volume V_i values is consistent with that of crystalline region percentages for cellophane, wood, and cotton cellulose.

Theoretical modeling.

By using the previously determined values of the carbohydrate accessibility (A_f), carbohydrate hydroxyl dissociation constants (K_1 and K_2), and the inner solution volume (V_i) for wood and cotton, the apparent alkali consumptions (P) for the systems NaOH-H_2O-wood, NaOH-NaCl-H_2O-wood, NaOH-Na_2CO_3-H_2O-wood, and NaOH-H_2O-cotton, were simulated with the developed model. All the simulations are a priori. The detailed experimental procedure and some data used for the model verification have been reported[2,3].

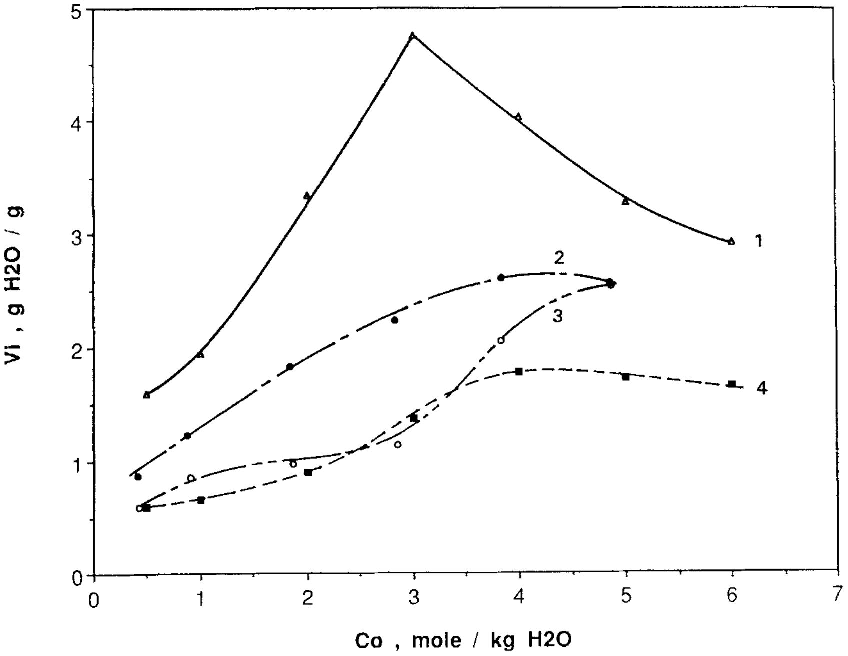

FIGURE 4. Inner solution volume, V_i, as a function of outside OH^- concentration, C_o, for cellophane[3] (curve 1), mercerized and unmercerized wood meal (curves 2 and 3, respectively), as well as unmercerized cotton[3] (curve 4) samples.

Fig. 5 shows the theoretical predictions of the apparent alkali consumption, P, changing with outside alkali concentration, C_o, for the $NaOH$-H_2O-wood system. It can be seen that the model predictions (solid lines) fit experimental results well. On the other hand, it is indicated that the two solid lines are quite different in value and shape. The mercerized wood line is smooth and above the unmercerized one. The later has a "S" shape and approaches the former at the outside alkali concentration of 5 M. This result is attributable to the different accessibilities of the samples. The mercerized wood is totally accessible. The unmercerized wood, however, is only partially accessible at low alkalinities. Its accessibility increases with solution alkalinity and reaches 100 % at about 5 M of the alkali concentration[2].

The simulations without considering the secondary ionization of carbohydrate hydroxyls are also plotted in Fig. 5 (dashed lines), to show the contribution of the secondary ionization on the apparent alkali consumption, P. It can be seen that theoretical curves with and without considering the secondary ionization are almost identical at alkali concentrations lower than 3 M. At higher alkalinities (> 3 M), however, the difference between the two curves are significant. This means that the secondary ionization of carbohydrate hydroxyl groups become significant when the alkali concentration increases to 3 M and higher.

Fig. 6 shows good agreement between the model predictions and reported experimental data[3] of the apparent alkali consumption (P) by cotton cellulose at different outside alkali concentrations, C_o. Comparison of the two curves, with and without considering the secondary ionization, also shows that the secondary ionization is unimportant below C_o of 3 M. Furthermore, it was found that a value of the secondary dissociation constant (K_2) of

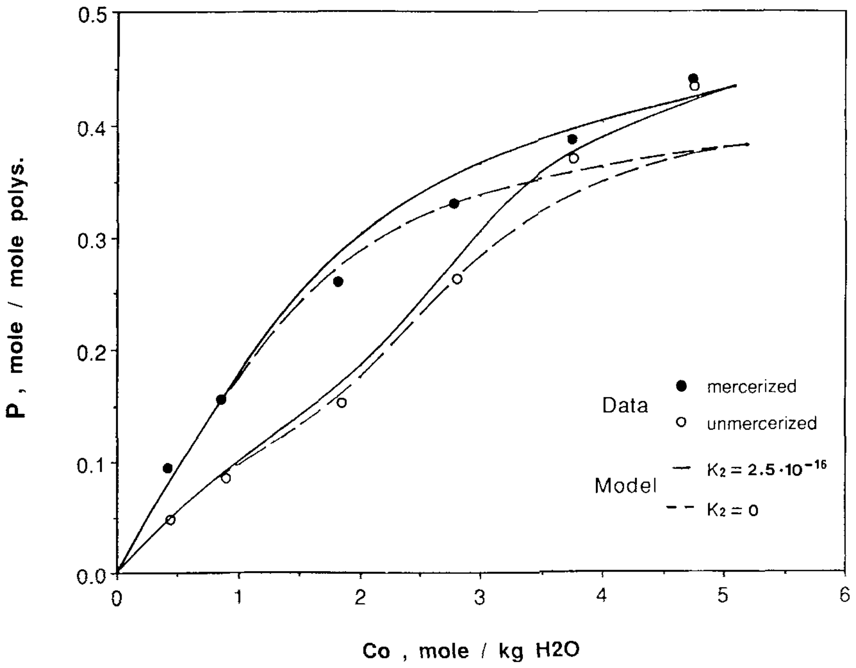

FIGURE 5. Model predictions and experimental data of the apparent alkali consumption, P, as a function of outside OH^- concentration, C_o, for wood meal samples.

$0.025*10^{-14}$ instead of $0.056*10^{-14}$, estimated with Philipp's data, predicts the experimental data for both NaOH-H_2O-wood (Fig. 5) and NaOH-H_2O-cotton (Fig. 6) systems. The improved fit with a lower K_2 value may be explained by NaOH hydration that becomes significant at high concentrations and reduces the effective alkali concentration[10]. A K_2 less than the true value will compensate for the alkali hydration effect and improve the model predictions.

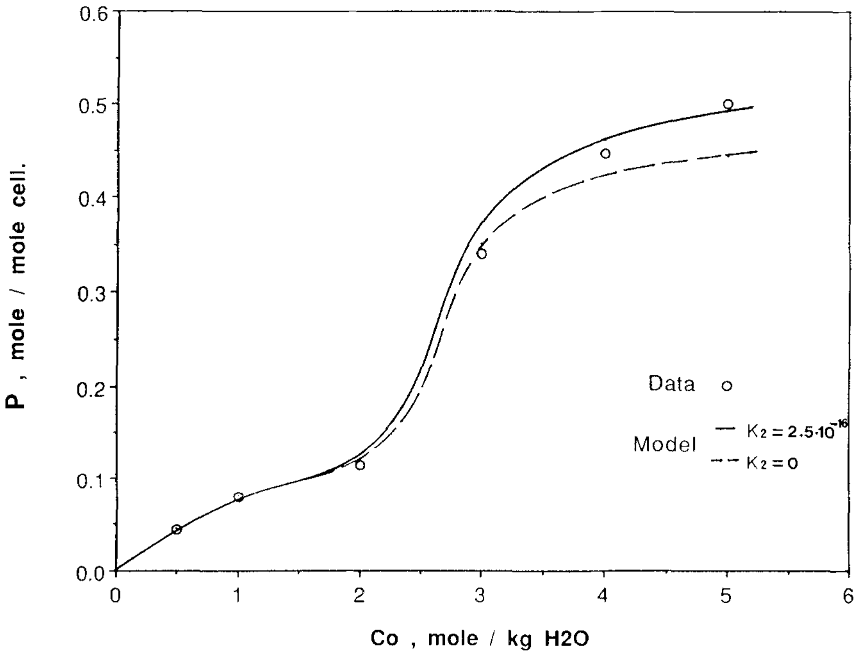

FIGURE 6. Model predictions and experimental data[3] of the apparent alkali consumption, P, as a function of outside OH^- concentration, C_O, for unmercerized cotton cellulose.

In Fig. 7, the apparent alkali consumption (P) curves for unmercerized wood meal and cotton cellulose are compared. It is shown that wood meal consumes more alkali than cotton at low alkalinities (< 3 M) but less at higher alkalinities. This result may be explained by the accessibility change with alkali concentration for wood and cotton. As discussed in Ref. 2, wood meal has higher accessibility at low alkalinities (< 3 M) due to its totally accessible hemicellulose. However, the accessibility of

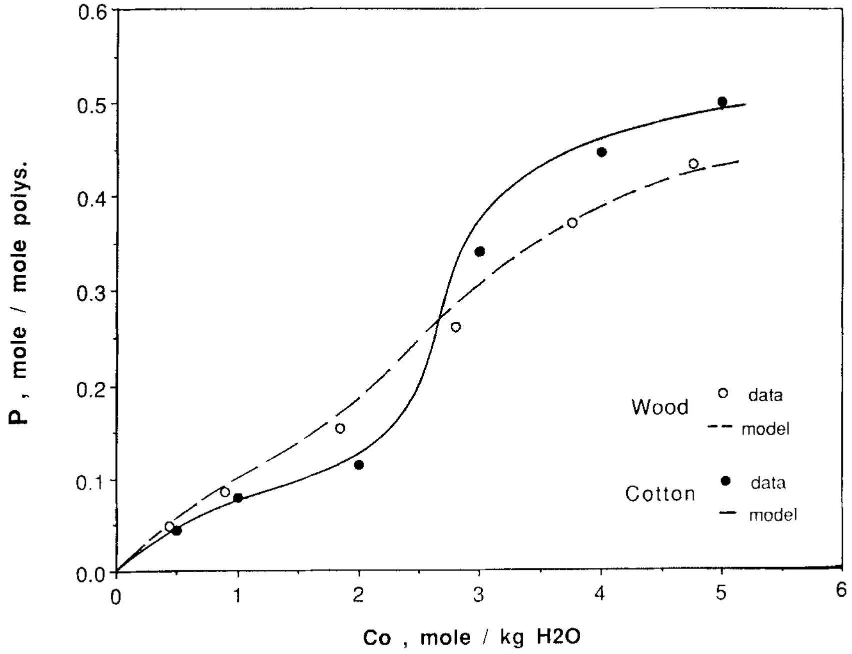

FIGURE 7. Comparison of the apparent alkali consumption, P, as a function of outside OH^- concentration, C_o, for unmercerized wood meal and cotton cellulose.

wood increases slowly with alkali concentration because of lignin retarding the swelling of wood fibers. Consequently, cotton cellulose has higher accessibility after the alkali concentration reaches 3 M.

Accessibility differences cannot explain the higher apparent alkali consumption by cotton at alkali concentrations approaching 5 M. At this concentration the accessibilities of cotton and wood are both 100%. The Donnan equilibrium effect is more significant in the wood-alkali interactions, however, due to the complete ionization of the acidic groups associated with wood fibers. This results in a larger difference between the inside and outside hydroxide concentration in wood than in cotton. According to Eq. 4, the consequence of this larger difference is a less apparent alkali consumption, P.

Theoretical modeling of NaOH-NaCl-H_2O-wood and NaOH-Na_2CO_3-H_2O-wood systems was also conducted. It was assumed that the accessibility, A_f, and the inner solution volume, V_i, are independent on the addition of neutral electrolytes. Fig. 8 shows good agreement between the model predictions and data. It is clear that for the same initial NaOH concentration (0.5 mole/kg H_2O) and added neutral electrolyte, the mercerized wood sample (curves 1 and 2) consumes more alkali than unmercerized sample (curves 3 and 4) because the former has higher accessibility ($A_f = 1$). From Eq. 12, it is obvious that the inside alkali concentration, C_i, is always less than the outside alkali concentration, C_o. However, the addition of neutral electrolyte will reduce the Donnan equilibrium effect and increase C_i. The added electrolyte thus results in more carbohydrate hydroxyl dissociation and more apparent alkali consumption. The increase in the apparent alkali consumption with the electrolyte concentration in the solution for all the curves is a result of reducing the Donnan equilibrium effect by the addition of neutral electrolyte. In addition, it can be found from Fig. 8 that

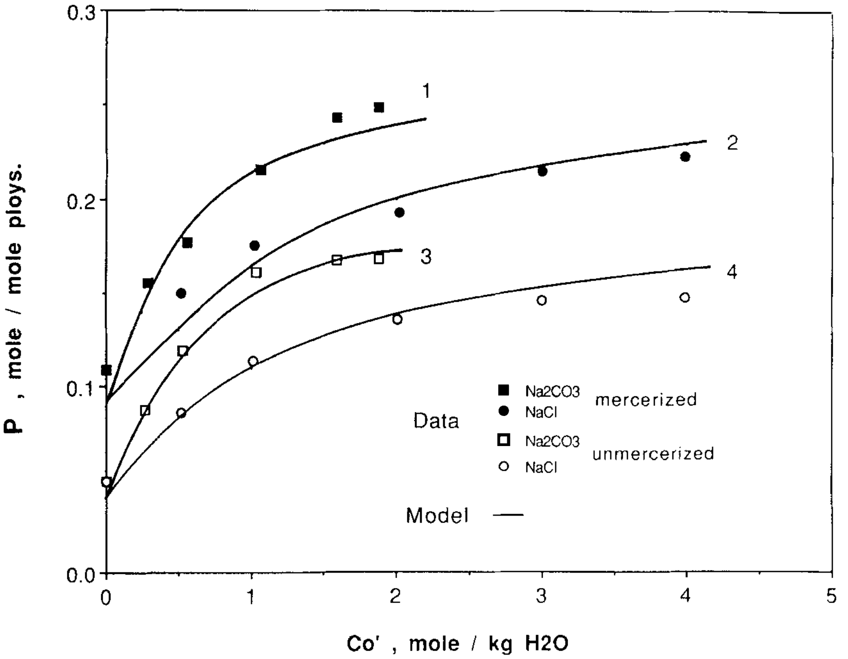

FIGURE 8. Model predictions and experimental data of the apparent alkali consumption, P, as a function of outer neutral electrolyte concentration, C_0', at a constant initial OH^- concentration (0.5 mole/kg H_2O) for wood meal samples.

Na_2CO_3 (curves 1 and 3) can reduce Donnan equilibrium effect more effectively than NaCl (curve 2 and 4). The stronger effect of Na_2CO_3 over NaCl on the Donnan equilibrium is because of its divalent nature. All the curves in Fig. 8 tend to level off after the neutral electrolyte concentration increases to a given value. The origin of this limitation is shown in Eq. 16. For a constant outside alkali concentration, C_0, the inner solution alkali concentration, C_i, approaches to C_o as the electrolyte concentration (C_o') becomes large. The Donnan equilibrium effect is thus eliminated.

SUMMARY

A theoretical model of wood-alkali interactions was proposed, based on theories of Donnan equilibrium and ionic dissociation equilibrium. Theoretical modeling of the apparent alkali consumption in three systems, NaOH-H_2O-wood, NaOH-NaCl-H_2O-wood and NaOH-Na_2CO_3-H_2O-wood, fit experimental results well. Model simulations for the NaOH-H_2O-cotton system also show good agreement with experimental data from the literature. The theoretical model is now being combined into an existing pulping model[11] to improve the accuracy of the effective alkali concentration prediction. This has special importance for the theoretical simulations of extended pulping schemes, such as RDH (Rapid Displacement Heating) and MCC (Modified Continuous Cooking) which have complex alkali profiles throughout the cooking.

NOMENCLATURE

A: total amount of dissociated polysaccharide hydroxyls, eq/kg H_2O.

A_f: accessibility factor of polysaccharide to alkali, $0 < A_f < 1$.

$[AH_2]'$: total amount of polysaccharides, mole/kg H_2O.

$[AH^-]$: concentration of the polysaccharides having one dissociated hydroxyl in each monomer unit, mole/kg H_2O.

$[A^=]$: concentration of the polysaccharides having two dissociated hydroxyls in each monomer unit, mole/kg H_2O.

C , C': NaOH and NaCl concentrations in the original solution, mole/kg H_2O.

C_i , C_o: equilibrium OH^- concentrations in inside and outside of fibers, mole/kg H_2O.

C_i' , C_o': neutral electrolyte concentrations in inside and outside of wood fibers, mole/kg H_2O.

K_1 , K_2: primary and secondary dissociation constants of polysaccharide hydroxyl groups.

K_w: water ionic product at 25°C, 10^{-14}.

P: apparent alkali consumption by polysaccharides, mole/mole polysaccharide.

V: weight of water in original solution, kg.

V_i: inner solution volume of wood fibers, expressed as the weight of water, kg/mole polysaccharide.

W: polysaccharide amount, mole.

Greek Letters :

α: total amount of dissociated polysaccharide hydroxyl groups, eq/mole polysaccharide.

$\alpha 1$: fraction of the polysaccharides having one dissociated hydroxyl in each monomer unit.

$\alpha 2$: fraction of the polysaccharides having two dissociated hydroxyls in each monomer unit.

$\beta 1$, $\beta 2$: ratios of dissociation constants to water ionic product.

ϕ , ϕ': strong acid groups (carboxyl, phenolic and enolic hydroxyl groups) in wood fibers, mole/kg H2O and mole/mole polysaccharide.

θ: amount of phenolic and enolic hydroxyl groups in wood fibers, mole/kg H2O.

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