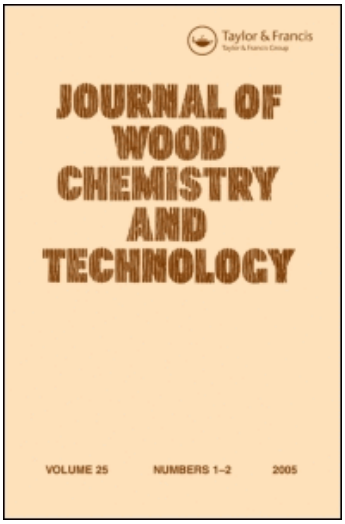

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Donnan Equilibria in Wood-Alkali Interactions. Part I. Quantitative Determination of Carboxyl-, Carboxyl Ester and Phenolic Hydroxyl Groups

Qiusheng Pu[a]; Kyosti Sarkanen[a]
[a] College of Forest Resources University of Washington, Seattle, WA

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DONNAN EQUILIBRIA IN WOOD-ALKALI INTERACTIONS. PART 1. QUANTITATIVE DETERMINATION OF CARBOXYL-, CARBOXYL ESTER AND PHENOLIC HYDROXYL GROUPS.

Qiusheng Pu and Kyosti Sarkanen
College of Forest Resources
University of Washington
Seattle WA 98195

ABSTRACT.

The functional groups in wood that may become ionized by the action of sodium hydroxide consist of carboxyl, phenolic hydroxyl and carbohydrate hydroxyl groups. The extent of ionization is dependent on the pH of the solution and causes the establishment of a Donnan equilibrium between the outer solution phase and that associated with the solid phase. Analytical techniques were developed to determine the carboxyl and phenolic hydroxyl contents of extractive-free mildly saponified hemlock and cottonwood meals using equilibration in the pH range of 12 to 12.5. The determined carboxyl contents, 0.158 and 0.127 meq/g OD wood, respectively, were confirmed by conductometric titrations of wood meal samples methylated with diazomethane prior to saponification with NaOH. Further confirmation was obtained from conductometric titrations of saponified and HCl-washed samples with $NaHCO_3$. The last-mentioned method was also applied to unsaponified hemlock and cottonwood samples to obtain their free carboxyl contents, 0.031 and 0.066 meq/g, respectively. The phenolic hydroxyl contents determined on borohydride-reduced wood samples were 0.260 and 0.147 meq/g, respectively. They were used to estimate the percentages of phenolic units present in *in situ* lignins. The results obtained suggest that hemlock lignin contains 15.0%, and cottonwood lignin, 14.2% of phenolic C_6C_3 units.

INTRODUCTION

The acidic functional groups associated with solid wood matrix consist of the following categories:

a. Carboxylic acid groups with an approximate pK value of 4.5. These groups are present in the pectic components as well as in the 4-O-methyl- glucuronic acid units of xylan hemicelluloses. In unsaponified wood, a significant part of these groups exist in esterified form.

b. Phenolic hydroxyl groups with an approximate pK of 10.2[1], associated with the lignin component.

c. Weakly acidic hydroxyl groups present in polysaccharides. It was shown by Neale[2] that, in strongly alkaline solutions, the glucose units in cellulose behave like weak acids with an approximate pK value of 13.7.

It follows from the pK values of these acidic functions that if wood material is brought to an equilibrium with an aqueous solution at pH 3 or below, all acidic groups remain unionized. On the other hand, raising the pH of the equilibrating solution to the range 6.0 to 8.5 converts all carboxylic functions to carboxylate groups, while both phenolic and carbohydrate hydroxyl groups remain unaffected. Methods based on this principle have been developed for the quantitative determination of carboxylic groups in cellulosic[3] and carbon[4,5] fibers, while few studies have been reported in the literature on the estimation of free and esterified carboxylic functions in wood[6,7].

When wood material is equilibrated with an aqueous solution at pH 12 and above, essentially all carboxylic and phenolic hydroxyl groups exist in their anionic forms. In addition, a small fraction of polysaccharide hydroxyl groups becomes ionized. In this paper, we describe a method whereby the sum of carboxylic and phenolic hydroxyl functions associated with mildly saponified wood can be estimated on the basis of titrimetric measurements in this pH range. For this purpose, wood samples are first treated with 1 N NaOH to remove acetyl groups present and to saponify carboxylic ester groups. The saponified sample is then soaked with 0.1 N HCl to

convert acidic groups to their unionized forms and washed with water. The method requires that the effects of Donnan equilibria[8,2,9] on the experimental data are evaluated quantitatively. This can be achieved by adding sodium chloride to the system and by determining the distribution of the chloride ion between the outer solution and the solution associated with the solid wood matrix, as discussed in detail in the section that follows. Also, the data must be corrected for the effects caused by the partial dissociation of the polysaccharide hydroxyl groups.

The described methodology also lends itself to the direct estimation of free phenolic groups present in wood. In this case, the saponified wood sample is washed with water to bring the prevailing pH down to approximately 8.5 with concomitant conversion of phenolate groups to their unionized state. By measuring the increase in ionized groups by raising the pH to the range 12.0 - 12.5, an estimate is obtained for the content of phenolic hydroxyl groups.

Determination of the Effects of Donnan Equilibria and of the Ionization of Polysaccharidic Components. Let us assume that W g of OD wood containing X meq/g of acidic groups is equilibrated with an aqueous solution containing V g of H_2O, c meq/g H_2O of NaOH and c' meq/g H_2O of NaCl. After equilibration, the carboxylic and phenolic hydroxyl groups are assumed to be fully ionized and a part of the water (V_i) is associated with the solid wood matrix. Likewise, the ionic species are distributed between the inner and outer solutions in the manner illustrated in Fig.1. The outer OH^- and Cl^- concentrations c_o and c_o' can now be determined titrimetrically. The following expression can be derived for X:

$$X = \frac{cV - (c_o V_o + c_i V_i)}{W} = \frac{cV - (V_o + c_i/c_o \cdot V_i)c_o}{W} \qquad (1)$$

For the chloride concentrations, we obtain:

$$c'V = c_o'V_o + c_i'V_i = (V_o + c_i'/c_o' \cdot V_i)\, c_o' \qquad (2)$$

The following equation is valid[10] for the Donnan equilibrium:

$$c_i/c_o = c_i'/c_o' \qquad (3)$$

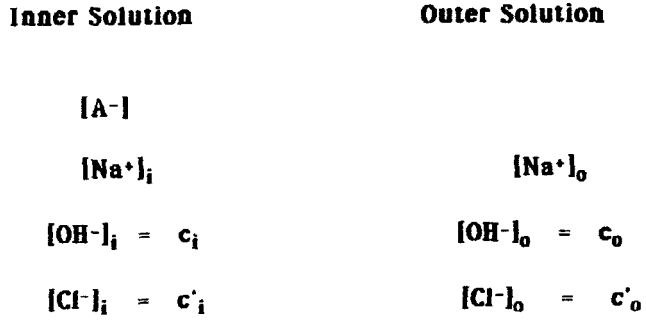

FIGURE 1. Distribution of an aqueous solution containing NaOH and NaCl between inner and outer solutions of a gel containing fully ionized acidic groups A^-. Subscripts i and o signify inner and outer solutions, respectively.

Inserting in equation (2):

$$c'V = (V_o + c_i/c_{o'}\, V_i)\, c_o' \text{ and}$$
$$c'/c_o' \cdot V = V_o + c_i/c_{o'}\, V_i \qquad (4)$$

Substituting in equation (1):

$$X = (cV - c'/c_o' \cdot c_o V)W^{-1} = (c - c'/c_o' \cdot c_o) \cdot V/W \qquad (5)$$

It should be noted that the actual consumption of alkali, A meq/g wood, expressed by Equation (6), always remains lower than X, although both values approach each other when Donnan equilibrium effects become negligible, e.g. at high NaCl concentrations.

$$A = (c - c_o) \cdot V/W \qquad (6)$$

It was mentioned earlier that if the equilibration is performed at a pH exceeding 12, the amount of ionized acidic groups includes a

significant amount of polysaccharide hydroxyl groups. On the other hand, the contribution of these groups to the total ionized groups can be readily estimated. It can be shown that the amount of these groups (X', meq/ g OD wood) is an approximately linear function of the prevailing hydroxyl ion concentration. If the wood sample contains C meq/g of accessible ionizable carbohydrate hydroxyl groups and a fraction α of these groups is ionized,

$$X' = \alpha C = K/K_w \cdot (1 - \alpha)\, C\, [OH^-] \quad (7)$$

where K and K_w are the dissociation constant of carbohydrate hydroxyl groups and the ion product of water, respectively. Since $\alpha \ll 1$, $1 - \alpha$ approximates 1, and

$$X' \approx K/K_w \cdot C[OH^-] \quad (8)$$

Thus, the contribution of dissociated carbohydrate hydroxyl groups can be eliminated by simple extrapolation of empirically determined values for X to zero hydroxyl ion concentration.

RESULTS

The determined ionized acidic groups are shown as a function of equilibrium base concentration for saponified and acid-washed hemlock meal by line 1 in Figure 2. Extrapolation to zero hydroxyl ion concentration gives the value 0.455 meq/g for the sum of carboxylic and phenolic hydroxyl groups. A similar extrapolation applied for values determined for the corresponding water-washed sample (line 2) indicates the presence of 0.290 meq/g phenolic hydroxyl groups in the wood sample. The same extrapolated value is obtained from data on hemlock sample saponified with 6 N instead of 2 N NaOH (line 5). The higher slope indicates, in this case, an increased amount of accessible polysaccharide hydroxyl groups. Subtraction of 0.290 from the previous value for total acidic groups gives the estimate 0.165 meq/g for the carboxylic acid groups.

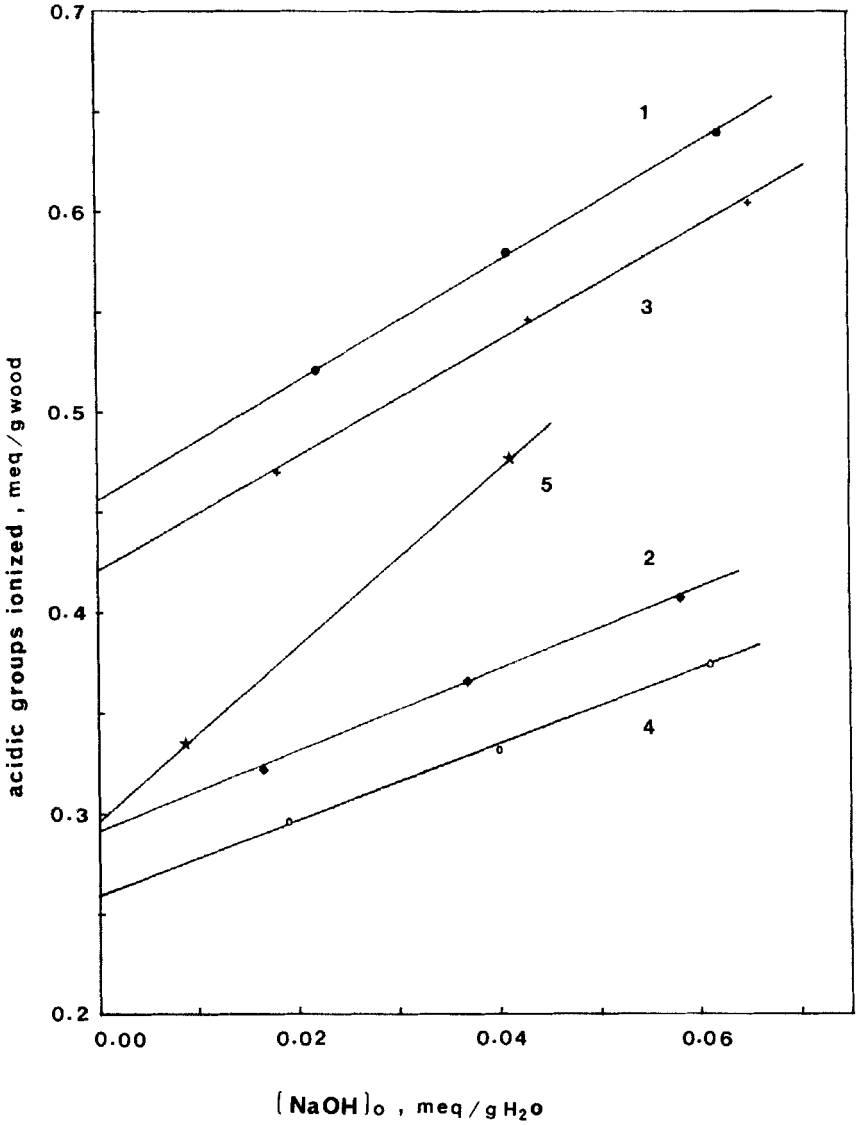

FIGURE 2. Acidic groups ionized by the action of sodium hydroxide in saponified and hemlock wood meal, expressed as a function of the hydroxide concentration of the equilibrated outer solution.- Line 1: HCl- and water- washed sample. - Line 2: Water-washed sample. - Lines 3 and 4: Corresponding lines obtained for samples which were reduced with borohydride prior to saponification. - Line 5: The same as Line 2 except the saponification of the wood meal was carried out in 6 N NaOH.

Since it was conceivable that the determined values may have included some enolized carbonyl groups, the determinations were repeated using wood samples reduced with borohydride prior to saponification. Lower values for acidic groups were indeed obtained as shown by lines 3 and 4. As expected, borohydride reduction did not change the estimate for the carboxylic acid groups, now found to be 0.160 meq/g, but reduced the estimate for phenolic hydroxyl groups down to the level of 0.260 meq/g.

Even more profound effect of borohydride reduction on the determined phenolic hydroxyl contents was observed for cottonwood samples reducing the observed value from 0.205 down to 0.147 meq/g (Fig. 3). This demonstrates that the amount of enolizable carbonyl groups in wood materials is significant requiring their reductive removal prior to phenolic hydroxyl determinations. The carboxyl content of cottonwood was found to be lower than that of hemlock, 0.133 versus 0.160 meq/g.

Effect of Variable Sodium Chloride Concentration on the Equilibrium. It was of interest to determine whether or not the increase in electrolyte concentration caused by the addition of sodium chloride to the system could influence the accessibility of ionizable acidic groups in the solid phase and thus introduce an error in the determination. For this reason, a series of experiments was carried out maintaining the initial alkali concentration c constant at the level of 0.096 meq/g H_2O and varying the sodium chloride concentration in the range 0 to 1 meq/g H_2O. The ionized acidic groups computed from equation (5) are shown as function of sodium chloride concentration in Figure 4 (line 3). It can be seen that higher sodium chloride concentrations increase slightly the amount of ionized acidic groups. This phenomenon finds a plausible explanation in the concurrent increase in the hydroxide ion concentration in the inner solution, indicated by curve 1, which, in turn causes increased ionization of the polysaccharide hydroxyl groups. On the other hand, no effect of the chloride concentration on the accessibility of the acidic groups is in evidence.

As could be expected, the curve 2 for the preferentially absorbed sodium hydroxide approaches the values computed for the ionized acidic groups as the chloride concentration is increased. When

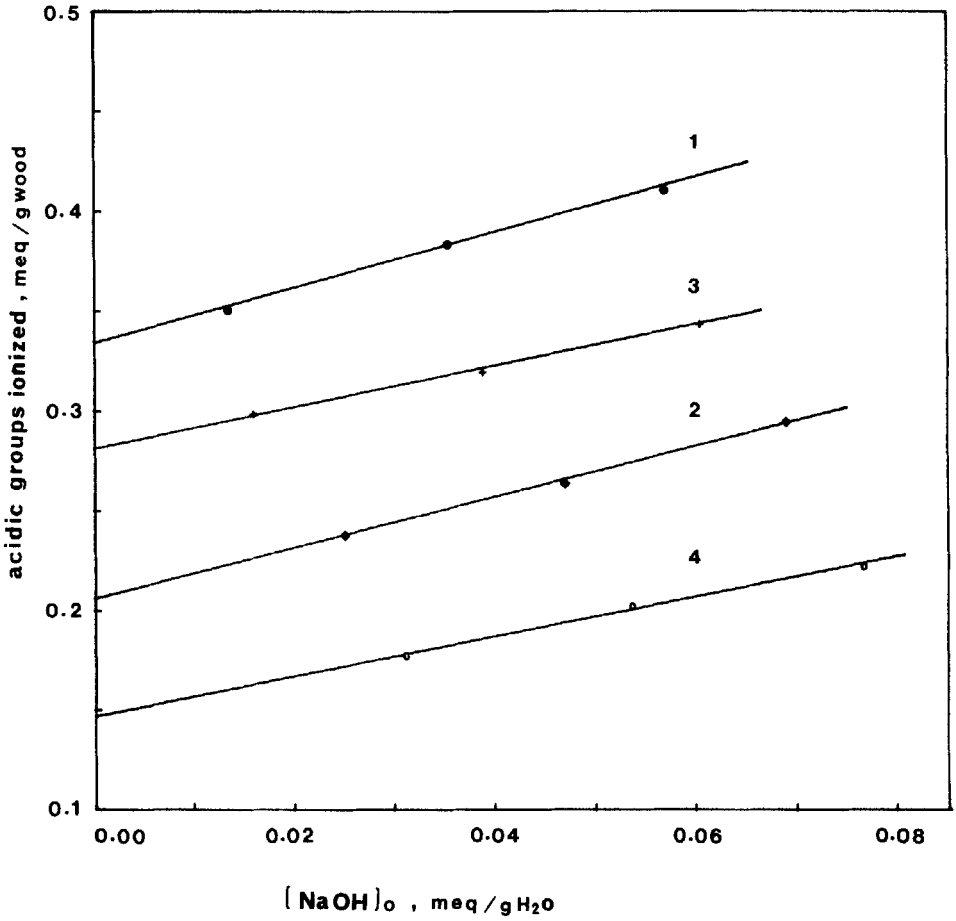

FIGURE 3. Acidic groups ionized by the action of sodium hydroxide in saponified cottonwood meal, expressed as a function of the hydroxide concentration of the equilibrated outer solution. Numbering of lines is the same as in Figure 2.

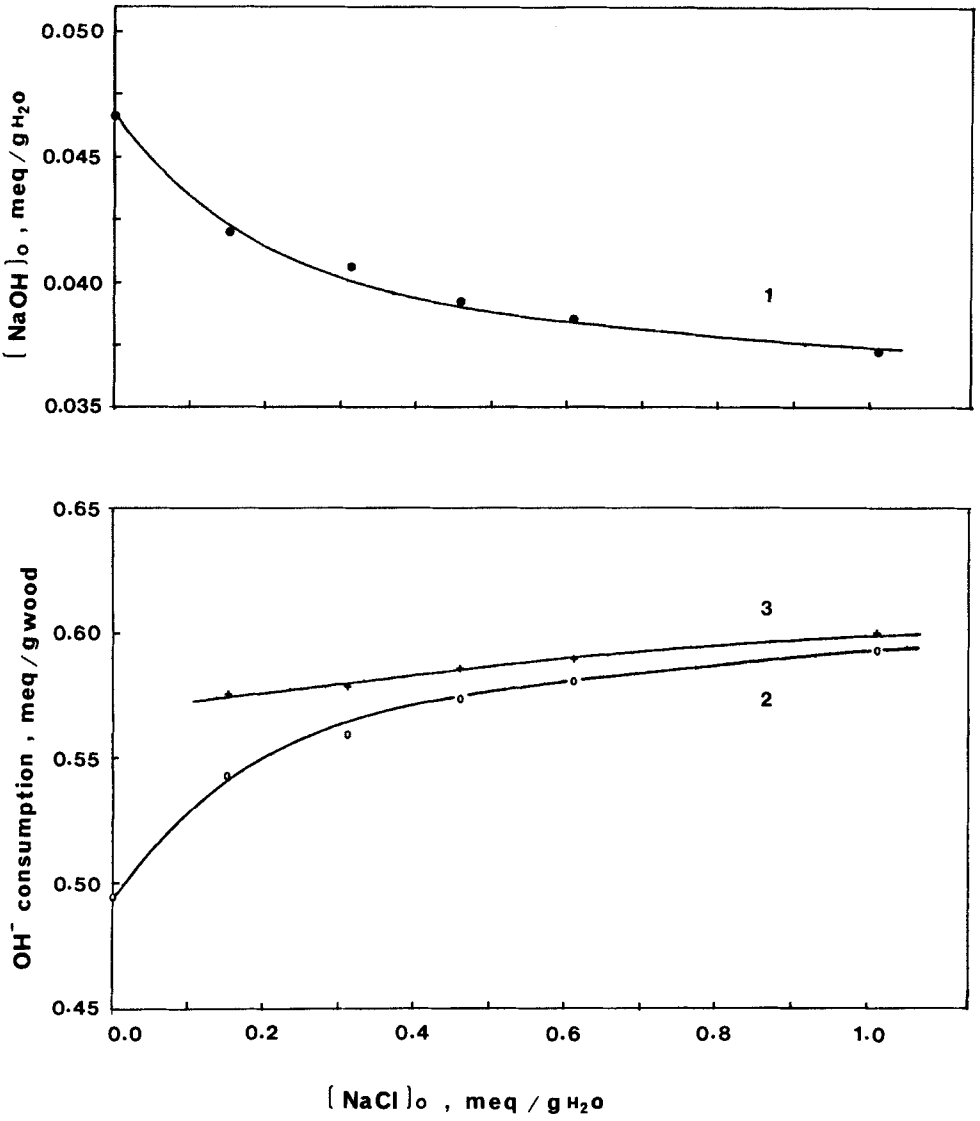

FIGURE 4. Effect of added NaCl on the ionic equilibrium established in the interaction of saponified and HCl-treated hemlock meal with aqueous sodium hydroxide. Initial concentration of NaOH: 0.096 meq/g H_2O. - Curve 1: Concentration of NaOH in the outer solution after equilibration. - Curve 2: Excess NaOH associated with the solid phase, calculated from Equation (6). Curve 3: Ionized functional groups in the solid phase, calculated from Equation (5).

the latter concentration reaches the value of 0.5 meq/g H_2O, the difference between the two values is less than 2% and the preferentially absorbed sodium hydroxide values calculated from Equation (6) may be directly used for the estimation of ionized acidic groups in the solid phase.

Conductometric Titrations of Total and Free Carboxyl Contents. It was of interest to confirm the total carboxyl values obtained on the basis of the equilibrium studies by an independent method. First, the conductometric titration method proposed by Katz, Beatson and Scallan[11] for the determination of free carboxylic acid groups in chemical pulps was applied for the determination of these groups in saponified hemlock and cottonwood samples. The method is based on the conductometric titration of HCl-washed samples with NaOH as titrant in the presence of sufficient amount of sodium chloride to eliminate Donnan equilibrium effects. It should be noted, however, that since the pH rises to approximately 10 during the titration, a fraction of phenolic hydroxyl groups may well become ionized during the procedure and thus cause a significant positive error in the estimation of the carboxylic acid content.

This anticipation was indeed confirmed experimentally. Application of the method of Katz *et al.* [11] gave values 0.220 and 0.164 meq/g for saponified hemlock and cottonwood, respectively. Since these values were more than by 35 % in excess to those obtained in equilibration, significant effect by ionized phenol groups was suspected. To eliminate this effect, separate samples of hemlock and cottonwood were methylated with diazomethane prior to saponification. Diazomethane is known to convert phenolic hydroxyls to methyl ether groups and carboxylic acid groups to the corresponding methyl esters. Alkali treatment saponifies the latter groups together with the preexisting ester groups but leaves the phenolic methyl ether groups intact. It is also probable that diazomethane converts enolizable carbonyls to ethylene oxide derivatives.

When the method of Katz *et al.* [11] was applied to methylated and saponified wood samples, the values obtained were 0.155 and 0.121 meq/g for hemlock and cottonwood, respectively, in quite satisfactory concordance with the equilibration results. Further

support for the validity of the latter values was gained from titrating saponified and HCl-washed samples conductometrically with sodium bicarbonate as titrant. In this type of system, the prevailing pH remains below the values causing ionization of phenolic hydroxyl groups. The values obtained, 0.151 and 0.126 meq/g for hemlock and cottonwood, respectively, agreed again with the equilibration results.

It was of interest to determine which fraction of the total carboxylic groups existed in a free form in the original wood. As already mentioned, the method proposed by Katz *et al.* [11] is not adequate for the purpose. For this reason, conductometric titration with bicarbonate as titrant was applied to unsaponified samples, directly treated with HCl and washed with water. Titration curves for these (curves 2) as well as earlier conductometric titrations are illustrated in Figures 5 and 6.The results indicated that hemlock contained 0.031, and cottonwood, 0.066 meq/g of free carboxylic acid groups. It should be noted that if washing with water after HCl treatment is omitted (curves 1), the sharpness of the first transition is reduced and slightly higher values are obtained. It is possible that the phenomenon is caused by calcium carbonate and/or oxalate, often occluded in wood tissues[12], which would be eliminated from the system by water-washing after the HCl treatment.

DISCUSSION

The data obtained in this study for the various acidic and ester groups present in extractive-free hemlock and cottonwood are summarized in Table 1. It is clear that a variety of methods may be used to determine the sum of carboxylic acid esters and free carboxylic acids in wood materials. Of these, conductometric titration of saponified and HCl-washed samples with sodium bicarbonate is probably the most convenient one. The same titration system, applied to unsaponified samples, appears to provide the most reliable values for free carboxylic acid functions.

It is of interest to compare the determined total carboxyl contents with those that can be estimated to be associated with the 4-O-methylglucuronic acid units of xylan hemicelluloses. It has been

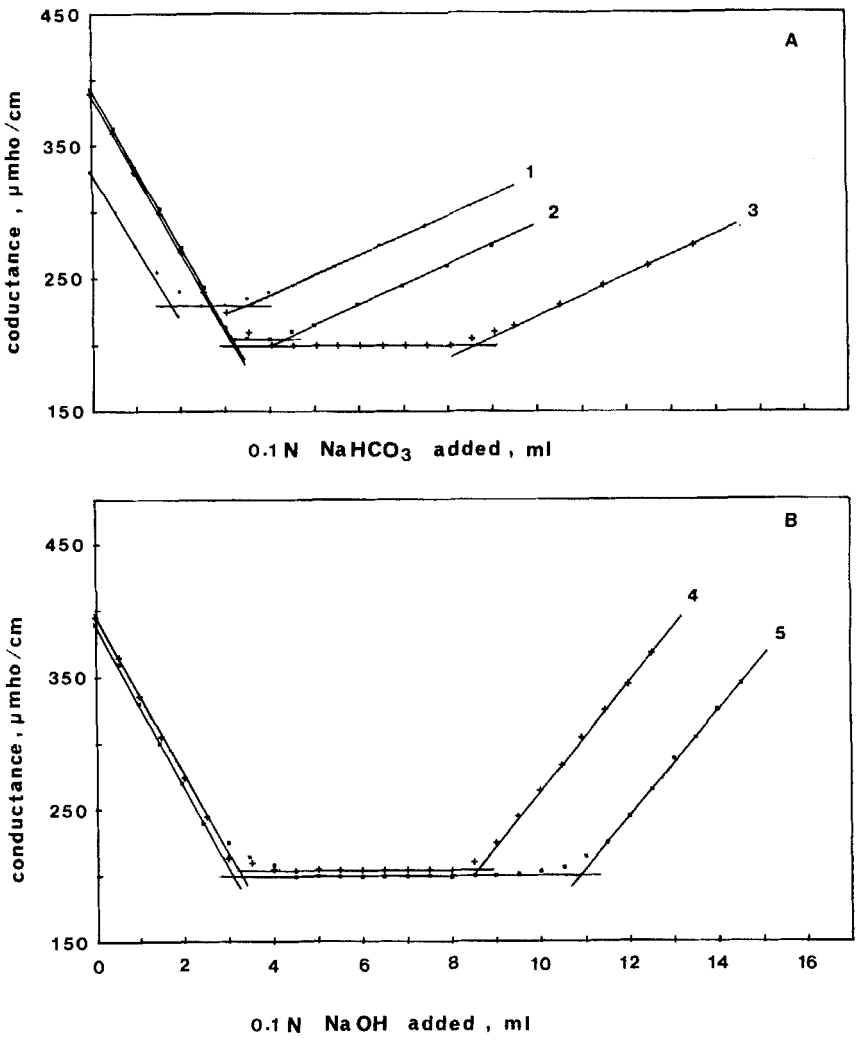

FIGURE 5. Conductometric titration curves of hemlock samples. Three ml of 0.1 N HCl added to the samples suspended in water prior to titration. - Section A: Titrations using $NaHCO_3$. Section B: Titrations using NaOH.- Curve 1: Direct titration of unsaponified sample (3.562 OD g) - Curve 2: Unsaponified HCl-washed sample (3.571 OD g). - Curve 3: Saponified and HCl-washed sample (3.551 OD g). - Curve 4: Sample methylated with diazomethane prior to saponification (3.540 OD g). - Curve 5: Saponified and HCl-washed sample (3.530 OD g).

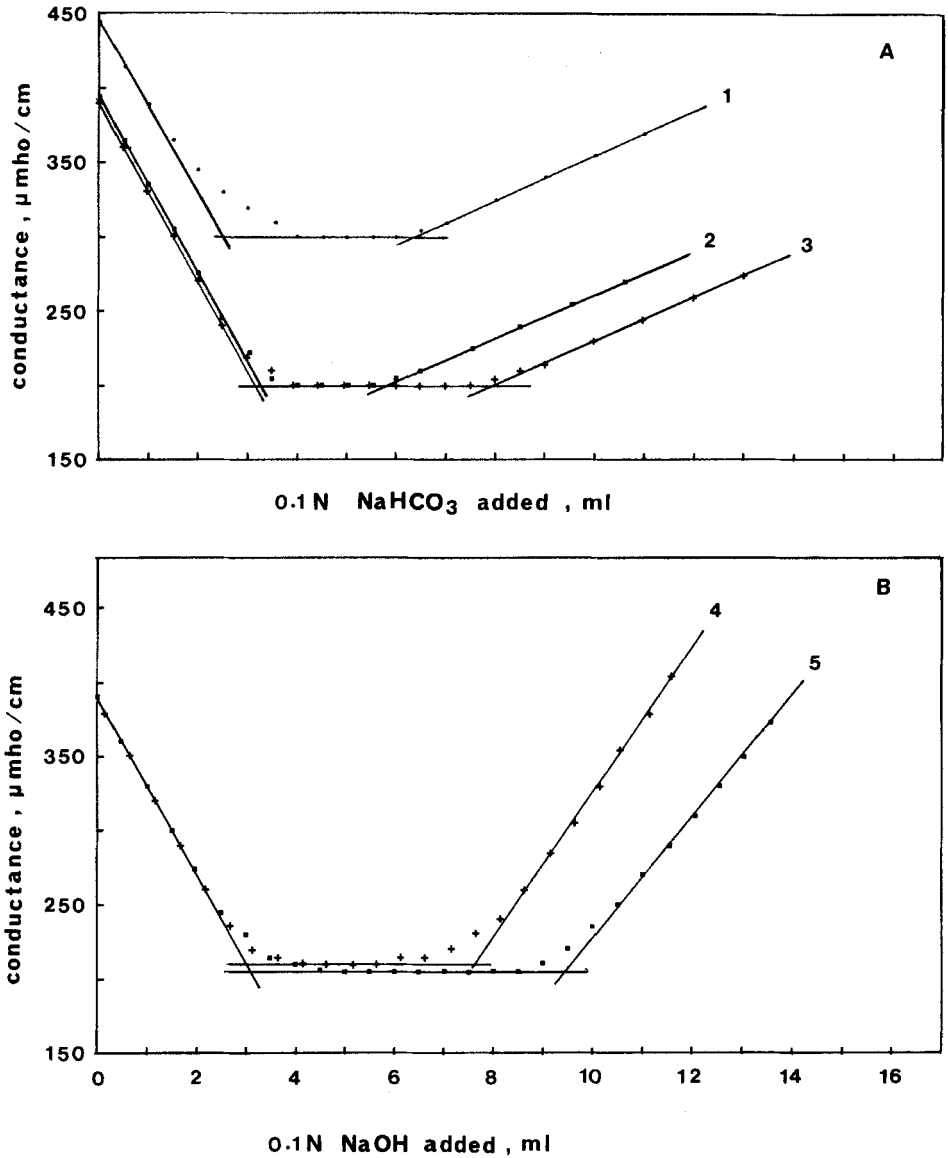

FIGURE 6. Conductometric titration curves of cottonwood samples. Sections and numbering of curves the same as in Fig. 5. In case of titration 1, 6 instead of 3 ml of 0.1 N HCl added prior to titration. OD weights of titrated samples: 3.888, 3.883, 3.878, 3.790 and 3.817 g for curves 1 to 5, respectively.

Table 1. Summary of analytical determinations on the carboxyl, carboxyl ester, and free phenolic hydroxyl contents of hemlock and cottonwood samples.

Functional group determined	Treatment of wood sample[1)]	Method of analysis	Functional group content, meq/g	
			W. Hemlock	Cottonwood
Carboxyl				
A. Sum of	SA	NaOH equilibrium[2)]	0.165	0.127
free and	RSA	- " -	0.160	0.133
esterified	MSA	Conduct. titr., NaOH	0.155	0.121
groups	SA	Conduct. titr., $NaHCO_3$	0.151	0.126
		Average of determin.	0.158	0.127
B. Free carboxyl[3)]	A	Conduct. titr., $NaHCO_3$	0.031	0.066
C. Carboxyl esters[4)]		By difference	0.127	0.061
Phenolic hydroxyl	RS	NaOH equilibrium	0.260	0.147
Enolizable carbonyl	S	NaOH equilibrium	0.030	0.058

[1)] Abbreviations used: S = Saponified; A = Acid washed; R = Reduced with borohydride; M = methylated with diazomethane.
[2)] Determined as difference in the acidic group contents of saponified samples with and without HCl wash.
[3)] Values for free carboxyl groups, determined by Sjöström *et al.* [6]: Spruce, 0.07 meq/g: birch, 0.06 meq/g.
[4)] Values for carboxyl ester groups, data by Sjöström *et al.* [6]: Spruce, 0.062 meq/g, and birch, 0.107 meq/g.

demonstrated that the Xyl:4-O-GA ratio is generally 5 for softwood xylans and 10 for hardwood xylans[13]. Western hemlock wood has been shown to contain 3.1% xylan[14]. On this basis, the 4-O-methylglucuronic acid groups would account only for 0.047 carboxylic acid milliequivalents/g of wood. This would suggest that most of the carboxylic acid functions are actually connected with other components, such as pectic materials and/or lignin.

The results suggest further that approximately 80 % of the carboxylic acid groups in hemlock wood are esterified. Since Johansson and Samuelson have demonstrated[15] that a large proportion of 4-O-methylglucuronic acid groups in birch xylan are esterified, this observation is not unexpected.

The 4-O-methylglucuronoxylan content of black cottonwood has been estimated to be approximately 18 %[16]. Accepting this value leads to the rough estimate of 0.124 meq/g wood for 4-O-methylglucuronic units. Since this value is very close to that obtained for total carboxylic functions in this study, it may be concluded that the carboxylic functions in saponified cottonwood are probably associated with xylan hemicelluloses. The value 0.066 meq/g for free carboxylic acid groups is in reasonable conformity with the value 0.087 meq/g reported by DeGroot[17] for the same species on the basis of Methylene Blue-absorption measurements.

The estimation of phenolic hydroxyl groups requires both the elimination of enolizable carbonyl groups by borohydride reduction and an extrapolation of the determined amounts of ionized groups to zero hydroxide concentration in order to cancel the effect of polysaccharide hydroxyl groups.The contents of phenolic hydroxyl groups for hemlock and cottonwood, 0.260 and 0.147 meq/g, respectively, can be used to estimate the percentage of those phenylpropane units in the respective lignins that contain a free phenolic hydroxyl group. First, the determined lignin content for saponified hemlock meal was found to be 31.7 % and that for cottonwood, 21.7 %. Secondly, the average C_9-unit weight for hemlock lignin can be estimated to be 183, and that for the cottonwood lignin, 210. Using these values, it can be calculated that hemlock lignin contains 15.0 % phenolic units, and cottonwood lignin, 14.2 %. It is of interest to compare these results with earlier analytical determinations.

Initially, milled wood lignin preparations were used to estimate the phenolic unit contents of softwood lignins. The titrimetrically obtained contents were roughly 32 %[18]. It was soon realized, however, that the milling process employed in the isolation of these preparations caused the formation of new phenolic hydroxyl groups. Attention was therefore directed to enzyme lignins whose isolation involved a less extensive milling procedure. The phenolic unit contents of these lignins, determined by periodate oxidation methods, were indeed found to be in the much lower range 19.5 to 20.5 %[19]. On the other hand, direct measurements of the phenolic hydroxyl contents of softwood samples by ultraviolet absorption and pyrolytic methods suggested an even lower range 9 to 15% for the phenolic unit content of softwood lignins[20, 21, 22]. This conclusion was supported by the recently developed aminolysis method which gave the value 13% for pine lignin[23]. This estimate is in reasonable conformity with the 15.0% content obtained in the present study.

Whether significant or not, the reported 14.4% phenolic unit content for sweetgum enzyme lignin[19], obtained by periodate oxidation, is close to the 14.2% content determined for cottonwood lignin in the present study.

The effect of borohydride reduction on the wood-alkali equilibria may be best interpreted in terms of enolizable carbonyl groups amounting to 0.030 meq/g in hemlock and to 0.058 meq/g in cottonwood. It has been demonstrated that carbonyl groups present in various cellulose preparations consume alkali[24], presumably through enol formation. In wood, however, a significant part of such carbonyl groups may reside in the lignin component since considerable amounts of enolizable carbonyl groups have been shown to be present in milled wood lignin preparations[25].

EXPERIMENTAL

Materials. W. hemlock (Tsuga heterophylla) and black cottonwood (Populus trichocarpa) meals were extracted in a soxhlet apparatus for eight hours and air-dried. Samples of the meals were subjected to the following treatments:

a. Borohydride reduction was performed as described in an earlier paper[26].

b. Methylation was carried out by suspending the wood meal sample in ethyl ether containing a roughly five-fold excess of diazomethane. The reaction was allowed to proceed overnight at below 20 °C temperature. The meal was filtered, washed thoroughly with ether and air-dried.

c. Saponification of hemlock wood meal was performed by suspending the sample in an excess of 2 N NaOH in an erlenmeyer flask. Air in the flask was displaced by nitrogen, the flask was stoppered and kept at room temperature for six hours, with continuous magnetic stirring. The suspension was filtered, the wood meal was washed repeatedly with distilled water until the filtrate remained colorless upon addition of phenolphtalein and finally, air-dried. Cottonwood meal was saponified in the same manner, except that 1 N NaOH was used.

d. HCl-washing of wood meals was conducted by stirring the sample magnetically for four hours in 0.1 N hydrochloric acid. The treated wood meal was filtered off, washed thoroughly with distilled water and air-dried.

Methods

A. Analytical Determinations. Moisture contents of wood meals were determined by conventional methods. Klason lignin contents were obtained according to TAPPI T222 om-83 and soluble lignin, using TAPPI Useful Method 250. Lignin contents were expressed as the sum of both determinations.

B. NaOH Equilibration. Twenty ml of aqueous solution containing a known concentration of NaOH and usually, 0.3 meq/g H_2O NaCl, were pipetted in a 50 ml erlenmeyer flask. In order to determine the exact weight of the added solution, the flask was weighed before and after addition. Approximately 2 g of accurately weighed wood meal sample was mixed with the solution, the flask purged with nitrogen gas, 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 solution was removed, weighed and diluted to 25 ml. The hydroxyl ion concentration in the solution was determined by titration with stadardized 0.05 N H_2SO_4 using phenolphtalein as indicator. Likewise, the chloride concentration was titrated using 0.1 N $AgNO_3$ with dichlorofluorescein as indicator. The amount of water introduced in the system as wood moisture was taken into account in calculations.

C. Conductometric Titrations. Approximately four grams of accurately weighed wood meal sample were dispersed in 400 ml of 0.001 M NaCl solution. Prior to titration, 3 ml 0.1 N HCl were added to the system. A conductivity meter of the type CDH-37 was employed in the titrations. The titrant was either 0.1 N NaOH or 0.1 N $NaHCO_3$, dispensed from a microburet while the suspension was stirred. The alkali was added at a rate of 0.5 ml per 5 min generally, but at a rate of 0.5 ml per 20 min around the end points. Since volume changes during titrations were less than 4 %, volume corrections were not necessary.

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