

AN ABSTRACT OF THE THESIS OF

CHI-SOON CHANG for the degree of Master of Science  
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Title: THE USE OF pH MEASUREMENTS FOR THE DETERMINATION  
OF FORMATION CONSTANTS OF METAL-ORGANIC COMPLEXES IN  
KRAFT PULP BLACK LIQUOR.

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Abstract approved: \_\_\_\_\_

Murray L. Laver

A study of the complexation reaction of two organic compounds known to be present in kraft black liquor with four metal ions (Al, Ca, Fe, Mg) has been carried out by pH measurements. Results indicate that a degraded carbohydrate acid [2-hydroxybutanoic acid (L)] forms complexes with aluminum, ferric, calcium and magnesium ions under acidic conditions ( pH: 2 - 5 ). The logarithm of the apparent formation constants ( $\log K_i$ ) of complexes under 1.5 M ionic strength for  $AlL_1$ ,  $AlL_2$  and  $AlL_3$  are 3.03, 2.51 and 1.49 respectively. The  $\log K_3$  of  $FeL_3$  is 2.69. Formation constants of  $CaL$  and  $MgL$  were not determined from this study.

Indulin AT, a lignin material isolated from kraft pulp black liquor, was investigated in complexation reactions. Titration results showed that only calcium and magnesium formed complexes with Indulin AT under basic conditions

(pH: 9 - 11). Their average formation constants ( $\log \bar{\beta}$ ) under 1.5 M ionic strength are 2.31 for CaL and 2.20 for MgL. The formation of hydroxide complexes of aluminum, and ferric ions were probably much stronger than those with Indulin AT in basic medium. Therefore, no complexes were found under the conditions used in this work.

The results suggests that lignin and related materials can form complexes under the conditions of kraft pulp black liquor production, and therefore they may enhance the formation of scale in kraft pulp mills.

THE USE OF pH MEASUREMENTS FOR THE DETERMINATION  
OF FORMATION CONSTANTS OF METAL-ORGANIC COMPLEXES  
IN KRAFT PULP BLACK LIQUOR

by

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Thank God -- no matter what form you are.

Thank my parents --- whose money.

Thank Dr. Murray L. Laver -- my advisor.

Thank all of you, your opinions, tolerance  
and whatever ..., ....., .. ..., .....

Who else's been left ?

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THE USE OF pH MEASUREMENTS FOR THE DETERMINATION OF  
FORMATION CONSTANTS OF METAL-ORGANIC COMPLEXES IN  
KRAFT PULP BLACK LIQUOR

I. INTRODUCTION

The depositions of inorganic salts on the inside surfaces of black liquor evaporator tubes and other flowlines cause serious and persistent problems in the operation of alkaline pulp mills. The buildup of these scales not only causes a continual loss of energy input, but also creates blockouts in the flowlines; then the whole mill is required to be shut down for cleaning. Since many types of metal ions are brought into the pulping process through raw materials, water systems, and added chemicals, different types of scales have been found (8).

Results from studies conducted by Frederick and Grace (8, 9) showed empirical evidence that the organic constituents of the black liquor played an important role in the formation of these scales. They found that using black liquor entirely composed of inorganic constituents did not form scales when heated in a bench sized scaling evaporator. However, the addition of lignin components or related model compounds did generate significant scaling. Therefore, they postulated that some of the organic compounds degraded from the wood structure could be effectively solubilized with some metal ions in

the system and form some type of organometallic complexes. These complexes might be unstable under high temperature, and break down, releasing the metal ions which would probably combine with inorganic anions to form scales.

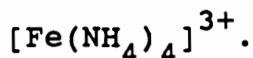
The objectives of the present study was to determine the formation constants of the organometallic complexes which are formed by using organic components known to be present in kraft pulp black liquor.

## II. HISTORICAL REVIEW

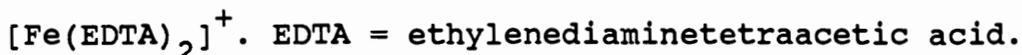
### A. Structures of Chemical Complexes

Rossotti in Ramette's book (24) has defined a complex as " a species formed by the association of two or more simple species each of which is capable of independent existence." There are three basic types of complexes:

A. inorganic combines with inorganic, example:



B. organic combines with inorganic, example :



C. organic combines with organic as molecular complex,



In the following paragraphs, because of the conditions in kraft pulp black liquor, we only discuss complexes of the second type.

The formation of a complex can be explained by the molecular orbital theory. Simply, formation of a complex can be considered as an overlap of filled orbitals of an organic molecule with empty orbitals of metal ions(15). In general, the greater the difference between the electronegativities of the metal ion and the atoms of the organic molecule, the less the character of a covalent bond exists, then the weaker of the possible bonds. Inczedy (17) used the Lewis acid-base theory to treat the formation of complexes. For most complexes with transition

metal ions, their stabilities are higher than those of the alkali and alkaline-earth metal ions, because transition metal ions have more d-orbitals available for bonding. It has also been shown from many studies that transition metal ions can coordinate with more organic molecules. Those molecules which have electron donor abilities are called ligands.

Although a great variety of organic compounds and metal ions exist in alkaline black liquor, only a few organic compounds are suspected of forming stable complexes with metal ions. Polysaccharides have hydroxyl groups on their structures, but their chelating ability with metal ions is weak in aqueous systems; the complexes are only found in dry conditions (3). In the alkaline pulping process, most polysaccharides will have been peeled off into monomeric carbohydrate molecules (26) and chemically converted to different types of organic acids (27). Theoretically, these acids are good ligands in the formation of complexes with metal ions.

The major organic acids degraded from polysaccharides are 2-hydroxycarboxylic acid with back bone from  $C_2$  to  $C_6$ . Among them, lactic acid, 2-hydroxybutanoic acid and isosaccharinic acid have been determined to be present in the largest amounts (19). With a hydroxyl group adjacent to a carboxylic group, these acids have greater ability to chelate with some metal ions.

The main complex structure is proposed as a five-membered ring composed of a carboxylic group and adjacent hydroxyl groups (22) (Figure 1).

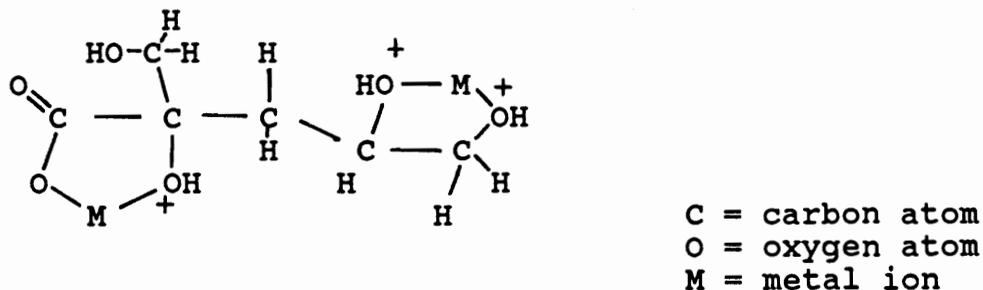


Figure 1. Complex of metal-hydroxycarboxylate

Since 2-hydroxybutanoic acid and isosaccharinic acid have structures similar to Figure 1, they are expected to form complexes with some metal ions, specially with trivalent ions.

Lignin and lignin related compounds are the type of organic compounds suspected of forming stable complexes in the black liquor from kraft pulping. Studies by Westervelt (28) showed that catechol-4-sulfonate formed strong complexes with calcium in alkaline aqueous media. Catechol can form stable complexes with most metal ions due to its adjacent hydroxyl groups. With an ultraviolet experiment, Imsgard et al (16) found that catechol and related compounds have greater molar absorptivities than those of other phenolic compounds in the presence of  $\text{Fe}^{3+}$ . Hon and Chang (14) also proposed from their experiments that the stability of lignin-metal complexes on wood surfaces prevented the photodeterioration of the wood

surfaces.

Lignin does not have a well defined, uniform structure, and the only structure of a lignin-metal complex has been proposed by Hayashi (11) around 1960. This is shown in Figure 2. Due to extensive demethylation by sulfite during the pulping process, catechol structures could form in the lignin polymer which provide good chelating sites with  $\text{Cr}^{3+}$  (Figure 2). Later Hayashi verified his assumption using gas chromatography (12) and conductometric titration (11). This evidence was later supported by the work of

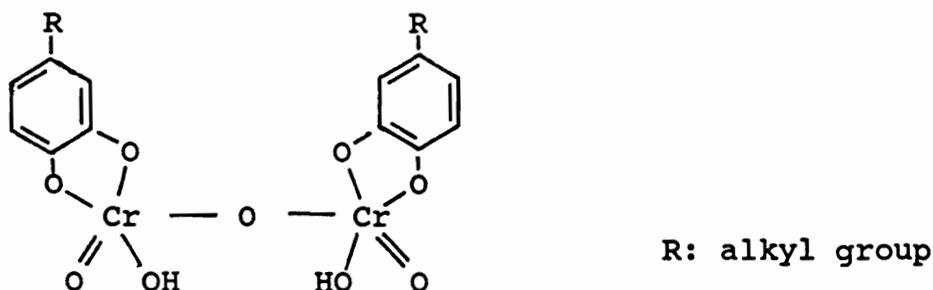


Figure 2. Complex structure of liginosulfonate-Cr(III)

Falkehag et al (7). Hayashi (13) also determined the stability constants of liginosulfonate with some metal ions. However, in the kraft pulping process, the demethylation reaction is not so pronounced, only 6% catechol structure (based on 100  $\text{C}_6\text{-C}_3$  structure) were found (21). This fact does not seem to explain the vast scale forming phenomena in the kraft process. In some organic compounds, two adjacent oxygen atoms can also

provide chelating reactions. Since 70% of the lignin structure has 3-methoxy-4-hydroxyl phenylpropane units, it is possible that the adjacent methoxy and hydroxy group on the phenylpropane units is the major binding site for the complexation.

### B. Equilibrium Analysis

The formation of a metal-organic complex can be expressed by the following general reaction :



the thermodynamic tendency of the reaction to go to the right can be quantitatively expressed by the equilibrium constant ( $\beta$ ), it is also called the formation constant.

$$\beta = \frac{a_{M_m L_l}}{a_M^m a_L^l}$$

where "a" stands for the activities of each species present in the system. However, in most studies, these terms have been replaced by their concentrations while introducing a third kind of neutral ion which can keep the ionic strength of the system constant, so that the activity coefficients of the species become unity.

In order to determine the equilibrium constant, the concentration of either species in the reaction has to be measured. Since there are some property changes between

species, their concentration can be measured by many physical methods such as spectrophotometric, potentiometric, conductometric or chromatographic and so on.

Most complex formations between metal ions and organic compounds involve some spectral changes or proton displacements, so that spectrophotometry and potentiometry have been adopted for a majority of the cases. In the present work, due to the inherent character of the lignin samples, spectrophotometry can not be used because no light passes through the dark samples. Thus potentiometry is the most practical method for this study.

Although the recent rapid development of ion-selective electrodes can provides considerable convenience in the direct measurement of the free metal ions, few ion-selective electrodes are currently commercially available for the specific metal ions that are suspected to form complexes in kraft pulping black liquor. Therefore, a traditional glass electrode for measuring the proton concentration was used.

Since the proton of the ligand is released during the formation of the complex, there is a relationship between the free metal ion, the ligand, and the proton. The degree of complex formation on the position of the equilibrium can be established through the relationship of these components in the system. The details of these

relationships and the mathematics for determination of the constants will be discussed later.

### III. EXPERIMENTAL

#### A. Preparation of Ligands

##### 1. Solution of 2-Hydroxybutanoic Acid

Sodium 2-hydroxybutyrate(1.26 g), (reagent grade 98%, Aldrich Chemical Co.) was dissolved in distilled deionized water and the solution was diluted to 100.0 ml in a volumetric flask. Since the free acid form was necessary as the ligand, this sodium salt solution was passed through a column of Dowex 50W-X4 (50-100 mesh), a strong cation exchange resin, at a flow rate of 4-5 ml/min, and washed with distilled deionized water until the pH of the effluent was that of the distilled deionized water (pH = 5.6-5.8). The effluent was collected in a round-bottomed flask, concentrated on a rotary evaporator to 20-30 ml, then transferred with washing to a 100.0 ml volumetric flask, and diluted to volume with distilled deionized water. This resulted in a 0.1 M solution of 2-hydroxybutanoic acid.

The Dowex 50W-X4 column was prepared by slurring 20-30 g of the polystyrenesulfonic acid form of the cation exchange resin (68.2% moisture content) in distilled deionized water. After the resin was completely swelled, the slurry was poured into a 1.5 cm diameter by 15.0 cm long glass column. The resin was washed with distilled deionized water, first at a rate of 7-10 ml/min, then at a

rate of 3-5 ml/min until the effluent showed the same pH as the distilled deionized water (pH = 5.6-5.8).

## 2. Suspension of Indulin AT

The Indulin AT kraft pine lignin (Westvaco Inc., Chemical Division, Charleston Heights, SC) is a purified form of kraft lignin supplied as a free flowing brown powder containing 97 % lignin on a dry weight basis. In calculations concerning the concentrations of the Indulin AT suspensions, the average molecular weight of each phenylpropane unit was considered to be 185. A 2% w/w (0.1 M) suspension of Indulin AT was prepared by adding 2.0 g of Indulin AT into 98.0 ml of water with stirring. In order to prepare a stable suspension of Indulin AT, this mixture was mixed with 250.0 ml of 3 M potassium chloride and 50.0 ml of distilled deionized water to yield a final "concentration" of 0.027 M in Indulin AT. The suspension was shaken each time before aliquots were removed for titration.

## B. Preparation of 0.1 M Metal Salt Solutions

### 1. Calcium.

$\text{CaCO}_3$  (1.00 g) was slurried with ca 10 ml of water and a minimum amount of concentrated hydrochloric acid (ca 1.0 ml) was added to dissolve the  $\text{CaCO}_3$ . The resulting

solution was boiled to remove carbon dioxide gas, cooled and diluted to 100.0 ml in a volumetric flask with distilled deionized water (pH = 3.24).

## 2. Magnesium.

MgO (0.40 g) was slurried with ca 10 ml of water and a minimum amount of concentrated hydrochloric acid (ca 1.0 ml) was added to dissolve the MgO. The resulting solution was diluted to 100.0 ml in a volumetric flask with distilled deionized water (pH = 2.73).

## 3. Aluminum.

$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (3.75 g) was dissolved in distilled deionized water and diluted it to 100.0 ml in a volumetric flask with distilled deionized water (pH = 3.04).

## 4. Iron(III).

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (2.70 g) was dissolved in distilled deionized water and diluted to 100.0 ml in a volumetric flask (pH = 1.59). Fresh solution was prepared each month.

### C. Preparation of Titrant

The standard potassium hydroxide titrant was prepared by dissolving 6.601 g of potassium hydroxide pellets (reagent grade) in 100.0 ml of distilled deionized water

followed by dilution to 1 liter in a volumetric flask with distilled deionized water.

A primary standard solution of potassium acid phthalate was prepared by dissolving 0.73582 g of dried potassium acid phthalate ( $\text{KHC}_8\text{H}_4\text{O}_4$ ) in 70 ml of water. The primary standard was titrated with the potassium hydroxide solution to a phenolphthalein end point. Calculation was done according to the equation:

$$M (\text{KOH}) = \frac{\text{grams of } \text{KHC}_8\text{H}_4\text{O}_4}{\text{mol wt of } \text{KHC}_8\text{H}_4\text{O}_4 * \text{vol of KOH titer in liters}}$$

The KOH solution was 0.0991 M. The solution was used to titrate all solution of metal ligand complexes.

#### D. Preparation of Neutral Salt Solution

Potassium chloride solution of 1 M and 3 M were prepared separately by dissolving 37.3 g and 111.8 g respectively of potassium chloride in 500.0 ml of distilled deionized water.

#### E. pH Measurements

All pH measurements were made with a Beckmann Expandomatic SS-2 pH meter with a saturated KCl calomel electrode (Corning Cat. No. 476002) as a reference electrode and a glass electrode (Corning Cat. No. 476022) for pH determination. A Corning 140 pH meter (digital)

with a combination electrode (Corning Cat. No. 476183) was also used for some pH determinations.

Prior to the pH measurements, the glass electrode was calibrated with standard pH buffers 7.00, 4.00, or 10.00. The electrodes were calibrated routinely every two weeks, but in some titrations, electrodes were calibrated before each titration. The reference electrode was checked visually for a clog on a routine basis. If any clog was found, the electrode tip was connected with a vacuum for 15 minutes and soaked in a 5% w/w NaOH solution. This procedure was repeated several times until the clog had disappeared.

All glassware used in the pH measurements including the electrodes, were soaked in 4 M HCl for 1 min and rinsed with distilled deionized water after each measurement.

The pH measurements were made in a 100.0 ml, 3 necked round-bottomed flask. Glass could be used rather than polyethylene because the experimental conditions included a high concentration of neutral salt (KCl), so that the small amount of Na ions that might dissolve from the glass would have a negligible effect on ionic strength. The apparatus is shown in Figure 3.

The flask was fitted with a lid with inlets for a buret, a tube for nitrogen gas, and the electrodes. A carbon dioxide-free atmosphere above the solution in the titration flask was provided by continuous flushing with

nitrogen gas which was first purified by bubbling through a 0.1 M NaOH solution then through deionized water.

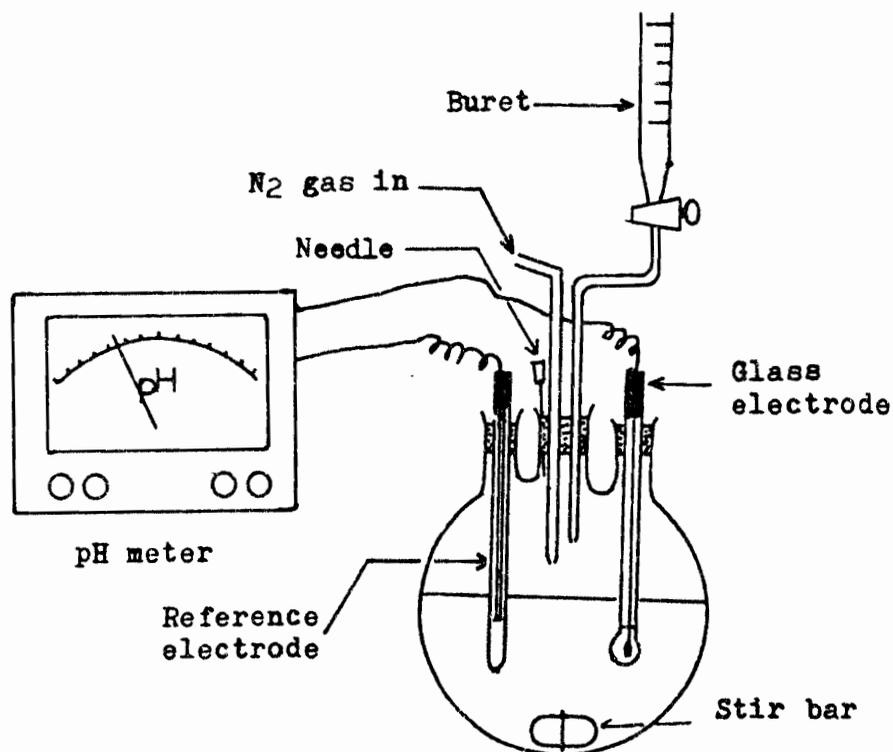


Figure 3. Titration Equipment

A 50.0 ml ( $\pm 0.1$  ml) buret was used to titrate the solution of 2-hydroxybutanoic acid. A 10.0 ml ( $\pm 0.05$  ml) buret was used to titrate the Indulin AT suspensions.

A representative titration of 2-hydroxybutanoic acid solution involved the transfer 10.0 ml of 0.1 M 2-hydroxybutanoic acid solution to the reaction flask (Figure 3) along with 25.0 ml of 3.0 M KCl solution, 1.0 ml of 0.1 M selected metal salt solution and 14.0 ml of distilled deionized water to yield a final solution of 50.0 ml. This provided a solution 0.02 M in 2-hydroxybutanoic acid and

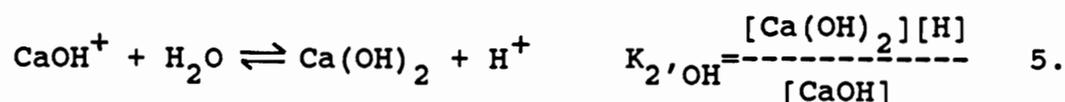
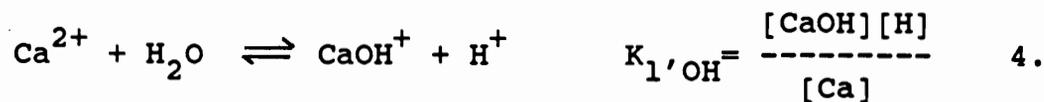
0.002 M metal ion at a ligand:metal ion ratio of 10:1. The solution was titrated with 0.0991 M potassium hydroxide solution at  $25.0 \pm 0.1$  C. The pH was read at equilibrium after selected additions of the potassium hydroxide titer.

A representative titration of Indulin AT suspension involved the transfer of 40.0 ml of Indulin AT suspension 0.027 M (the density of the Indulin AT suspension was assumed to be 1.0) to the reaction flask (Figure 3) along with 1.0 ml of the selected metal salt solution (0.1 M) and 9.0 ml of distilled deionized water to yield a final volume of 50.0 ml. The "concentration" of Indulin AT in the final mixture was therefore 0.0216 M with 0.002 M metal ion. The resulting suspension was titrated with 0.0991 M potassium hydroxide solution and the pH was recorded at equilibrium after selected additions of the potassium hydroxide titer.

## IV. RESULTS AND DISCUSSION

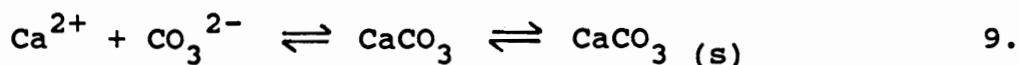
## A. Theoretical Analysis

In a system containing Ca (or Mg) ion and organic acid (HL), several reaction steps between each component are possible as shown: (for simplicity, the charges are not shown except for specific cases)



Where  $K_1$ ,  $K_2$  and  $K_{1,\text{OH}}$ ,  $K_{2,\text{OH}}$  are the formation constants for steps 1, 2, 4 and 5, and  $K_{\text{HL}}$  is the dissociation constant of the acid. In an aqueous system, dissolved  $\text{CO}_2$  may also cause some side reactions such as:





However if the experiment is well designed, the side reactions can be prevented or ignored because they are minor. In systems with Ca ions and Mg ions, the metal hydrolyses reactions can also be ignored under pH's below 12. Thus, several mass laws can be written based on equations 1, 2 and 3 as:

$$\text{Total Ca} = [\text{Ca}^{2+}] + [\text{CaL}^+] + [\text{CaL}_2] \quad 11.$$

$$\text{Total HL} = [\text{L}^-] + [\text{HL}] + [\text{CaL}^+] + 2[\text{CaL}_2] \quad 12.$$

$$\text{Total H} = [\text{H}^+] - [\text{OH}^-] + [\text{HL}] \quad 13.$$

There is also a charge balance in the system,

$$[\text{H}^+] + [\text{K}^+] + 2[\text{Ca}^{2+}] + [\text{CaL}^+] = [\text{OH}^-] + [\text{L}^-] + [\text{Cl}^-] \quad 14.$$

(the concentration of  $[\text{K}^+]$  and  $[\text{Cl}^-]$  from the ionic strength medium have been canceled out because of  $[\text{K}^+] = [\text{Cl}^-] = 1.5 \text{ M}$ )

From equations 11 and 12, we have

$$[\text{Ca}^{2+}] = \text{Tot Ca} - [\text{CaL}^+] - [\text{CaL}_2] \quad 15.$$

$$[\text{L}^-] = \text{Tot HL} - [\text{HL}] - [\text{CaL}^+] - 2[\text{CaL}_2] \quad 16.$$

Substituting  $[\text{Ca}^{2+}]$  and  $[\text{L}^-]$  in eq. 14 with eq. 15 and 16

and rearranging, we obtain the following relationship:

$$[K^+] + [H^+] + 2 \text{ Tot Ca} = [\text{OH}^-] + \text{Tot HL} - [\text{HL}] + [\text{Cl}^-] \quad 17a.$$

or 
$$[\text{HL}] = [\text{OH}^-] - [H^+] + \text{Tot HL} - [K^+] + [\text{Cl}^-] - 2\text{Tot Ca} \quad 17b.$$

in which  $[K^+]$  is the base added and  $[\text{Cl}^-]$  came from the addition of the Ca ion. Thus  $[\text{HL}]$  is the only unknown in eq. 17b which needs to be determined.  $[K^+]$  can be substituted with  $b \cdot \text{Tot HL}$ , where "b" is called degree of neutralization, and is defined as:

$$b = \frac{\text{total amount of titrant added}}{\text{total amount of the titrant}} = \frac{\text{KOH (M)} * \text{ml}}{2\text{-HBA added}} \quad 17c.$$

Because  $[\text{Cl}^-]$  came with the preparation of the Ca ion, so its total charge amount equals the  $2\text{Tot Ca}$ . Thus eq. 17b becomes:

$$[\text{HL}] = [\text{OH}^-] - [H^+] + (1-b) \cdot \text{Tot HL} \quad 17d.$$

In order to determine the formation constant of eq. 1 and eq. 2, N. Bjerrum(1) defined the average ligand number ( $\bar{n}$ ), which is

$$\begin{aligned} \bar{n} &= \frac{\text{Total complexed ligand}}{\text{Total metal ion}} = \frac{[\text{CaL}] + 2[\text{CaL}_2]}{[\text{Ca}] + [\text{CaL}] + [\text{CaL}_2]} \\ &= \frac{\beta_1[\text{Ca}][\text{L}] + 2\beta_2[\text{Ca}][\text{L}]^2}{\text{Ca} + \beta_1[\text{Ca}][\text{L}] + \beta_2[\text{Ca}][\text{L}]^2} = \frac{\beta_1[\text{L}] + 2\beta_2[\text{L}]^2}{1 + \beta_1[\text{L}] + \beta_2[\text{L}]^2} \quad 18. \end{aligned}$$

$$\text{where } \beta_1 = K_1 = \frac{[\text{CaL}]}{[\text{Ca}][\text{L}]} \quad 19.$$

$$\beta_2 = K_1 K_2 = \frac{[\text{CaL}_2]}{[\text{Ca}][\text{L}]^2} = \frac{[\text{CaL}_2]}{[\text{CaL}][\text{L}]} * \frac{[\text{CaL}]}{[\text{Ca}][\text{L}]} \quad 20.$$

$\beta_1$  and  $\beta_2$  are called overall formation constants.

$$\text{According to eq 12 and eq 18, } \bar{n} = \frac{\text{Tot HL} - [\text{HL}] - [\text{L}]}{\text{Tot Ca}} \quad 21.$$

Thus  $\bar{n}$  can be determined from the known tot Ca, the tot HL and the [HL], and  $[\text{L}^-]$  which can be calculated from eq. 17d and eq. 3. The  $\beta$  can be determined from the relationship between  $\bar{n}$  and  $[\text{L}^-]$ . Generally, the relationship of  $\bar{n}$  and  $[\text{L}^-]$  is shown by plotting  $\bar{n}$  vs.  $-\log[\text{L}]$ . The estimated stepwise constants ( $K_{\bar{n}}$ ) can be obtained from this plot at the corresponding  $-\log[\text{L}]$  value of the point  $\bar{n}-0.5$ . This half- $\bar{n}$  method was first used by Bjerrum (1), and within a section of  $\bar{n}$ , there is a relationship as:

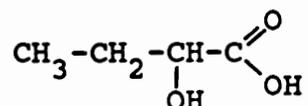
$$\log K_{\bar{n}} = \log \frac{[\text{ML}_{\bar{n}}]}{[\text{ML}_{\bar{n}-1}][\text{L}]} = \log \frac{[\text{ML}_{\bar{n}}]}{[\text{ML}_{\bar{n}-1}]} + \log \frac{1}{[\text{L}]} \quad 22.$$

if the  $K_{\bar{n}}/K_{\bar{n}-1}$  is greater than 100, then there are only two successive complex species present. Thus, at  $\bar{n}-0.5$  the  $[\text{ML}_{\bar{n}}] = [\text{ML}_{\bar{n}-1}]$ , and eq. 22 becomes

$$\log K_{\bar{n}} = -\log[\text{L}]_{\bar{n}-0.5} \quad 23.$$

### B. 2-Hydroxybutanoic Acid

The structure of 2-hydroxybutanoic acid (2-HBA) is :



The dissociation of the proton of the alcohol group is far weaker than that of the carboxyl group. The titration curves show no change at higher pH range ( pH > 5 ), confirming that the complex formation model discussed in equations 1 and 2 are suitable.

Figure 4 shows the pH-titrations of 2-HBA with 0.01 M and 0.001 M Ca ions. It is hard to see a significant difference between the curves a, b and c at low pH ( < 5 ), where hydrolysis of Ca can be ignored (eq. 4, 5), although this is the pH range where complexation between 2-HBA and Ca ions would be expected to occur.

A typical set of data resulting from eq. 3, eq. 17d and 21 and Figure 4 (volume of KOH added, pH) is presented in Table 1. The  $\bar{n}$  vs.  $-\log[L]$  of 2-HBA-Ca are shown in Figure 5 from the data in Table 1. It shows that the average 2-HBA anion on the Ca ion is quite low and appears to be a constant in spite of the increase of  $[L^-]$ . Apparently, these values have no meaning for the real situation in this system. It seems no reasonable explanation for the case of 0.001 M Ca ion + 0.02 M 2-HBA either (Figure 5).

Figures 6 and 7 are the pH-titration curves and degree

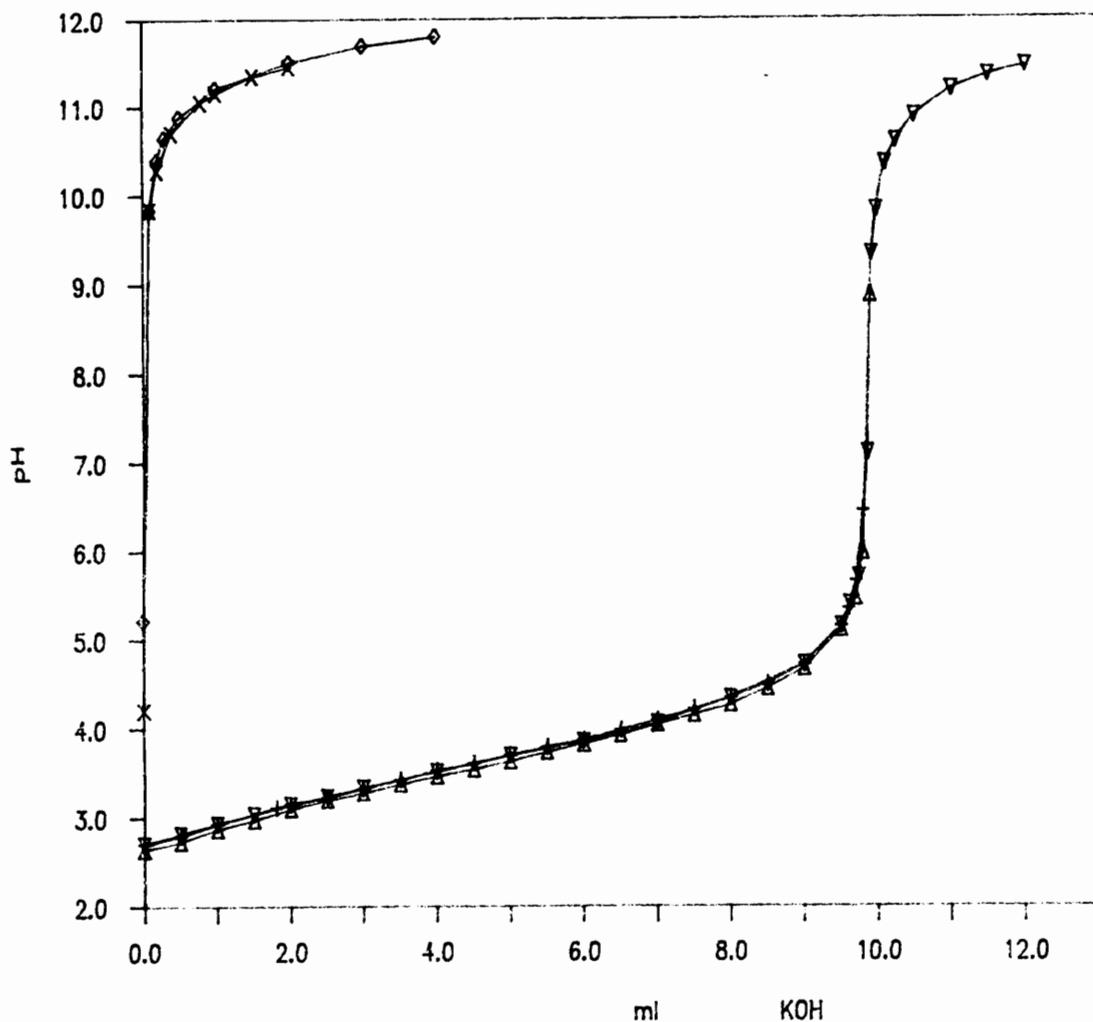


Figure 4. pH-titrations of (a) 0.02 M 2-hydroxybutanoic acid (2-HBA) ( $\nabla$ ); (b) 0.02 M 2-HBA + 0.01 M Ca ion ( $\Delta$ ); (c) 0.02 M 2-HBA + 0.001 M Ca ion (+); (d) 0.01 M Ca ion (x); (e) 0.001 M Ca ion ( $\diamond$ ) with 0.0991 M KOH at  $\mu = 1.5$  M and 25 C.

Table 1. Determination of the formation degree,  $\bar{n}$ , of the complex between calcium and 2-hydroxybutanoic acid at 1.5 M ionic strength and 25 C.

0.01 M Ca ion 50.0 ml		0.02 M 2-HBA + 0.01 M Ca ion 50.0 ml			$b^c$	$[HL]^d$	$[L]^e$	$-\text{Log}[L]$	$\bar{n}^f$
OH ml(d) <sup>a</sup>	pH(d)	OH ml(b) <sup>b</sup>	OH ml(b-d)	pH(b)					
0.00	4.20	0.00	0.00	2.64					
0.10	9.84	0.50	0.50	2.73	0.05	0.0170	0.00195	2.71	0.091
0.20	10.28	1.00	1.00	2.87	0.10	0.0163	0.00259	2.59	0.072
0.40	10.70	1.50	1.50	2.98	0.15	0.0155	0.00316	2.50	0.080
0.80	11.05	2.00	2.00	3.10	0.20	0.0146	0.00394	2.40	0.070
1.00	11.15	2.50	2.50	3.20	0.25	0.0137	0.00464	2.33	0.074
1.50	11.34	3.00	3.00	3.28	0.30	0.0127	0.00519	2.29	0.100
2.00	11.45	3.50	3.50	3.38	0.35	0.0118	0.00605	2.22	0.091
3.00	11.62	4.00	4.00	3.47	0.40	0.0108	0.00684	2.17	0.091
5.00	11.84	4.50	4.50	3.55	0.45	0.00988	0.00750	2.13	0.105
		5.00	5.00	3.64	0.50	0.00894	0.00835	2.08	0.098
		5.50	5.50	3.74	0.55	0.00802	0.00942	2.03	0.065
		6.00	6.00	3.83	0.59	0.00709	0.0103	1.99	0.058
		6.50	6.50	3.93	0.64	0.00618	0.0112	1.95	0.031

- a. Titration-pH curve (d) in Figure 4.  
 b. Titration-pH curve (b) in Figure 4.  
 c. Calculated from eq. 17c.  
 d. Calculated from eq. 17b.  
 e. Calculated from eq. eq. 3;  $pK_{HL} = 3.67$ .  
 f. Calculated from eq. 21.

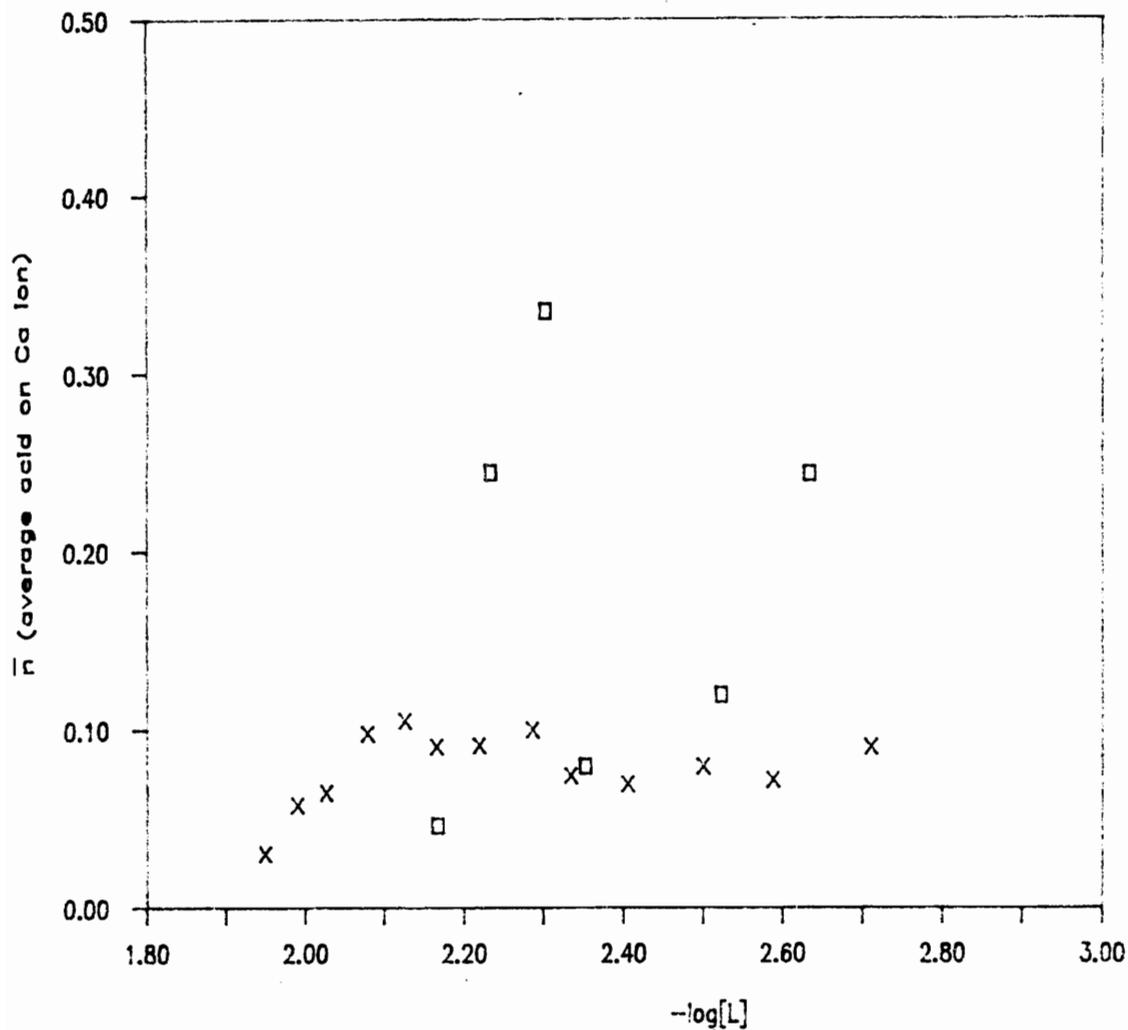


Figure 5. Degree of complex formation of (a) 0.02 M 2-HBA + 0.01 M Ca ion (x); (b) 0.02 M 2-HBA + 0.001 M Ca ion (□) at 1.5 M KCl and 25 C.

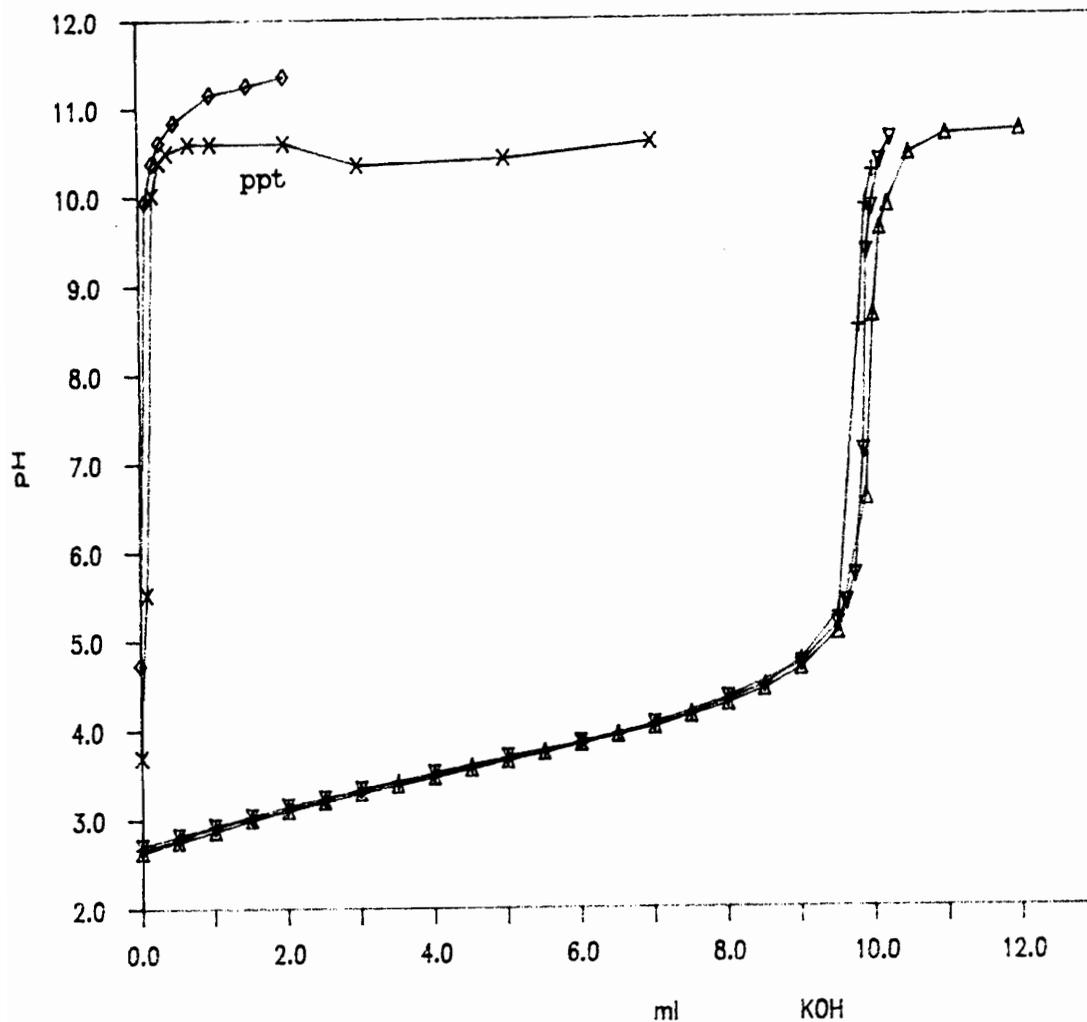


Figure 6. pH-titrations of (a) 0.02 M 2-HBA ( $\nabla$ ); (b) 0.02 M 2-HBA + 0.01 M Mg ion ( $\Delta$ ); (c) 0.02 M 2-HBA + 0.001 M Mg ion (+); (d) 0.01 M Mg ion (x); (e) 0.001 M Mg ion ( $\diamond$ ) with 0.0991 M KOH at  $\mu = 1.5$  M and 25 C.

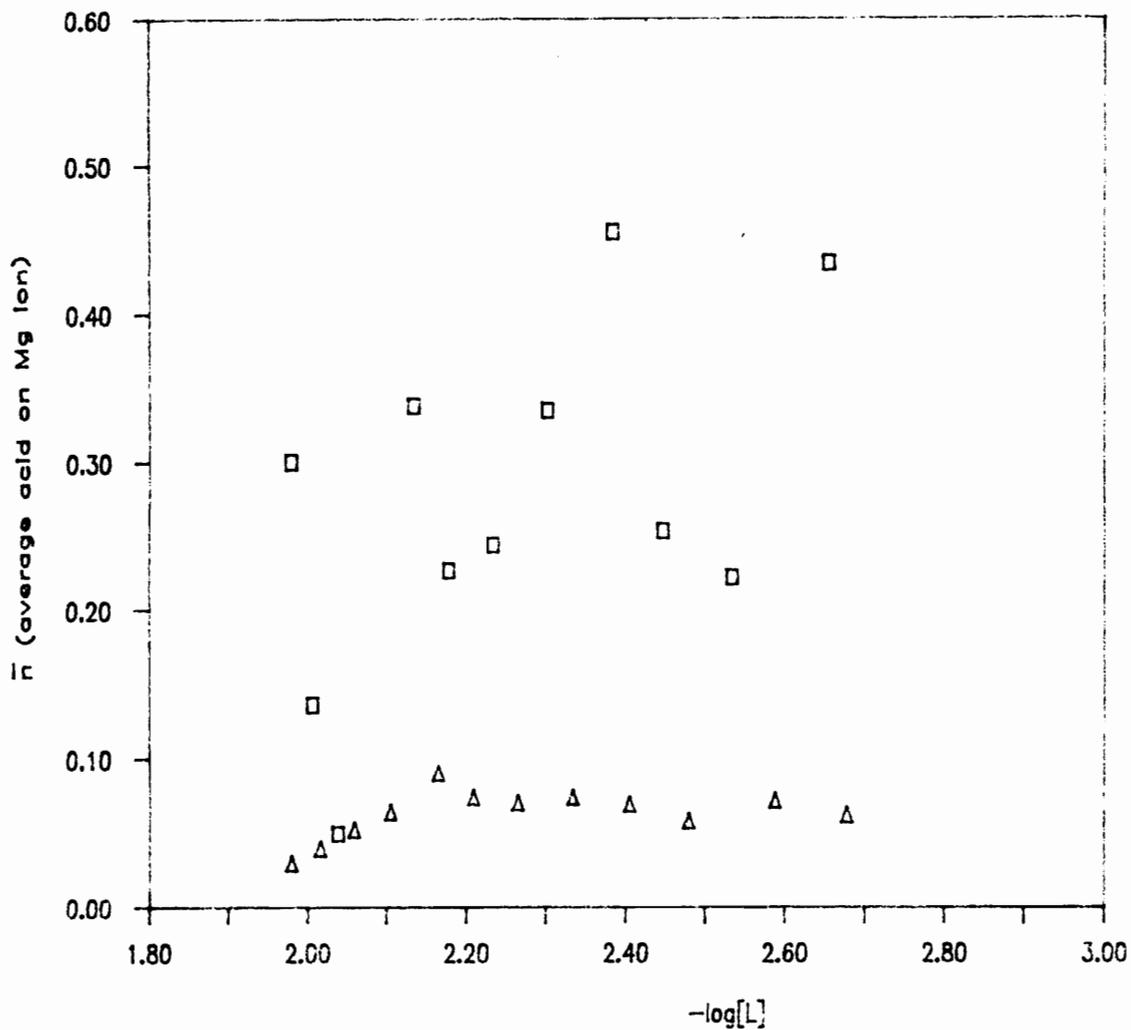


Figure 7. Degree of complex formation of (a) 0.02 M 2-HBA + 0.01 M Mg ion ( $\Delta$ ); (b) 0.02 M 2-HBA + 0.001 M Mg ion ( $\square$ ), at 1.5 M KCl and 25 C.

of complex formation curves of 0.02 M 2-HBA with 0.01 M and 0.001 M Mg ion. These data show similar phenomena to the Ca ion.

Figure 8 shows the pH-titrations of 2-HBA with 0.01 M and 0.001 M Al ion. The curves show the differences between the titration of solutions containing Al ions and without Al ions. Although, the Al ion could cause hydrolysis even at low pH, the (c) curve gives the net difference due to the complexation at  $\text{pH} < 4$  [comparing the base volume at the same pH of (c) and (e)]. Curve (a) shows more shift, but it hydrolyzes more severely at low pH and produces white precipitates around  $\text{pH} = 5$ . In this study, we did not investigate what the precipitate is.

The  $\bar{n}$  vs.  $-\log[L]$  plots of 2-HBA-Al are shown in Figure 9. A typical relationship of  $\bar{n}$  vs.  $-\log[L]$  is shown (a). An estimated  $K_1$ ,  $K_2$ ,  $K_3$  can be obtained from eq. 23, in which  $\log K_1$  is the corresponding  $-\log[L]_{0.5}$ ,  $\log K_2$  is  $-\log[L]_{1.5}$ , and  $\log K_3$  is  $\log[L]_{2.5}$ . Because the values, which stand for the successive constants of the species, differ a little from each other, there is a possible overlap from the third species within a section; so a refinement is necessary. From figure 9, we can use  $\bar{n} = 0.5, 1.5, 2.5$  and the corresponding  $[L^-]$  to set up simultaneous equations with eq. 18, then to solve the  $\beta_1, \beta_2, \beta_3$  by iteration method (17) or any other mathematical method.

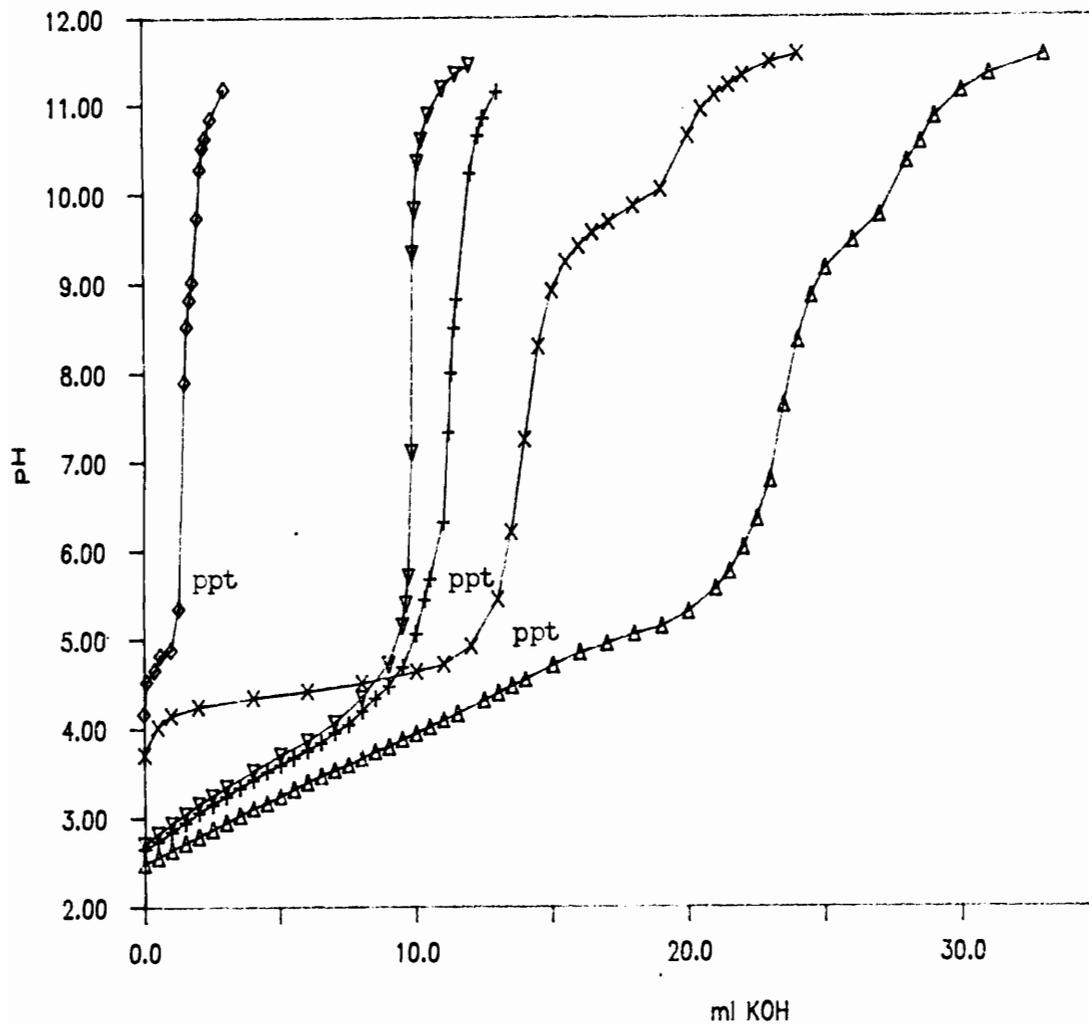


Figure 8. pH-titrations of (a) 0.02 M 2-HBA ( $\nabla$ ); (b) 0.02 M 2-HBA + 0.01 M Al(III) ion ( $\Delta$ ); (c) 0.02 M 2-HBA + 0.001 M Al(III) ion (+); (d) 0.01 M Al(III) ion (x); (e) 0.001 M Al(III) ion ( $\diamond$ ) with 0.0991 M KOH at  $\mu = 1.5$  M and 25 C.

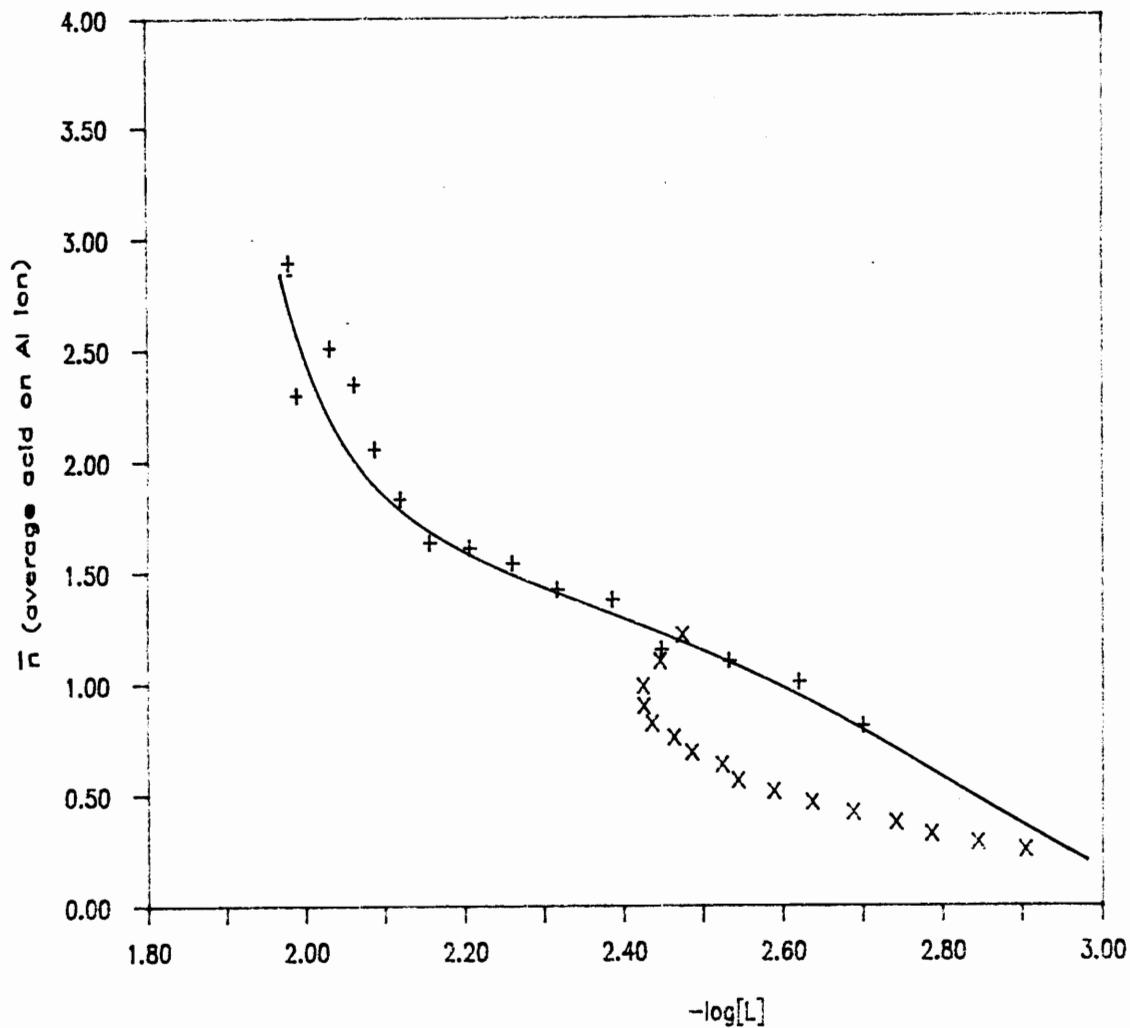


Figure 9. Degree of complex formation of (a) 0.02 M 2-HBA + 0.01 M Al(III) ion (x); (b) 0.02 M 2-HBA + 0.001 M Al(III) ion (+), at 1.5 M KCl and 25 C.



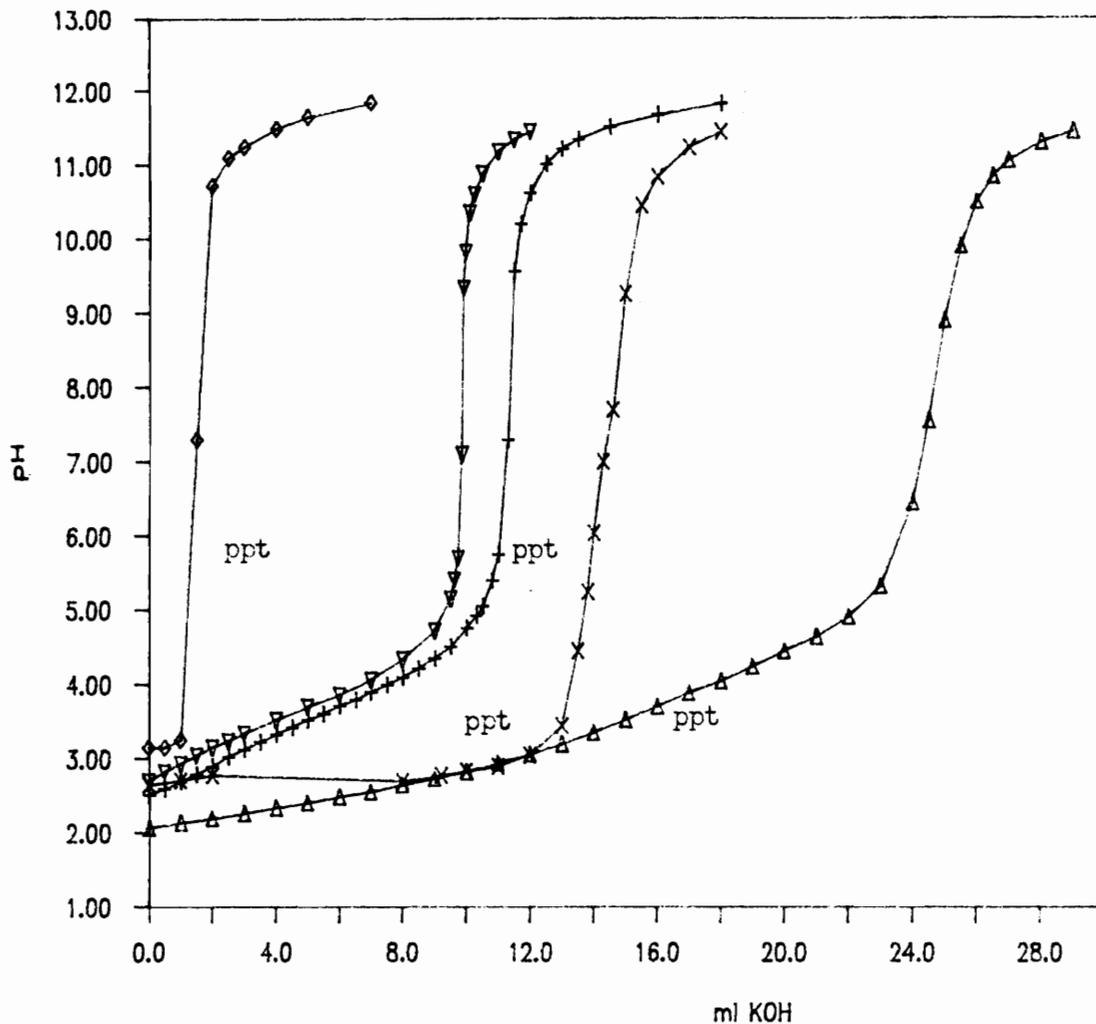


Figure 10. pH-titrations of (a) 0.02 M 2-HBA ( $\nabla$ ); (b) 0.02 M 2-HBA + 0.01 M Fe(III) ion ( $\Delta$ ); (c) 0.02 M 2-HBA + 0.001 M Fe(III) ion (+); (d) 0.01 M Fe(III) ion (x); (e) 0.001 M Fe(III) ion ( $\diamond$ ) with 0.0991 M KOH at  $\mu = 1.5$  M and 25 C.

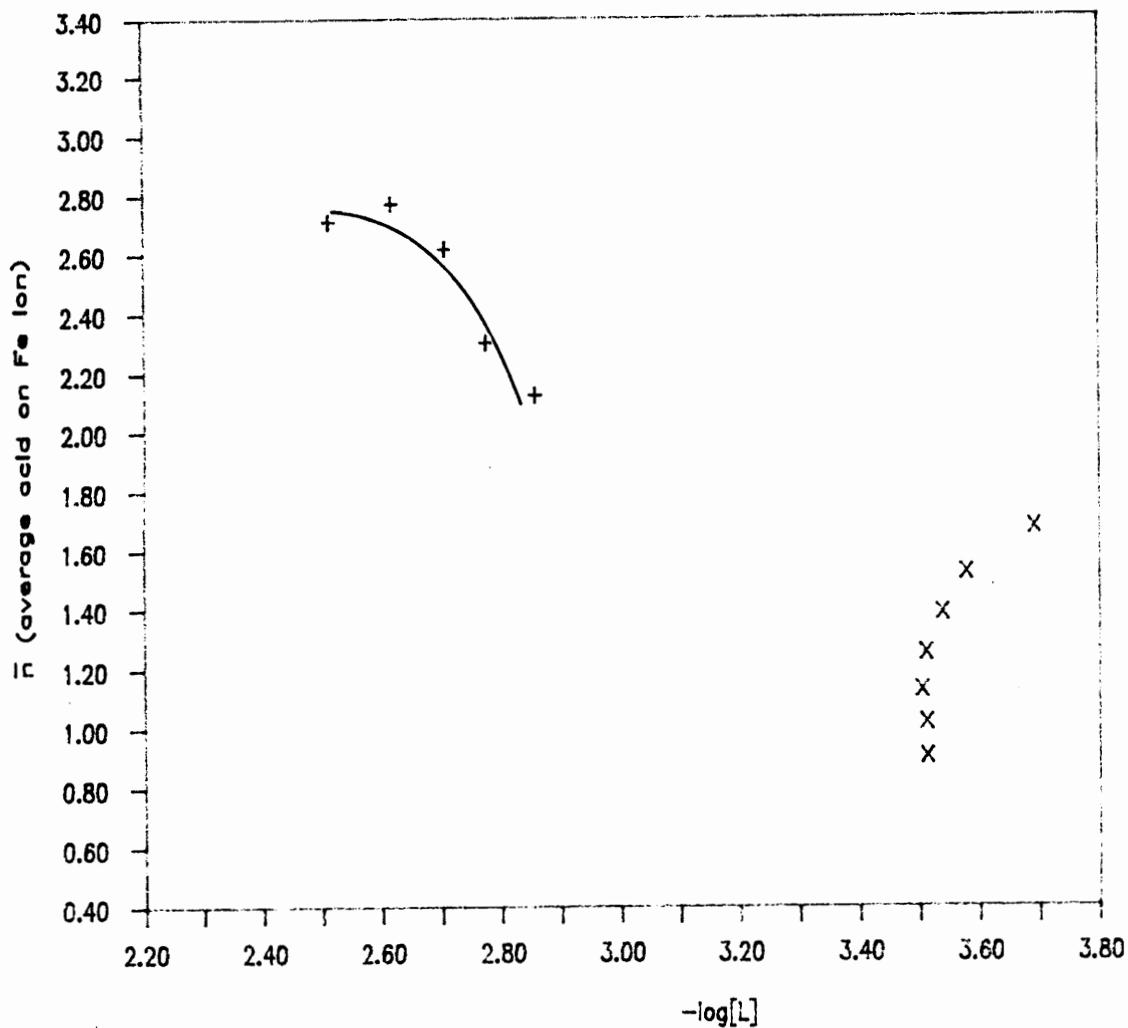


Figure 11. Degree of complex formation of (a) 0.02 M 2-HBA + 0.01 M Fe(III) ion (x); (b) 0.02 M 2-HBA + 0.001 M Fe(III) ion (+), at 1.5 M KCl and 25 C.

Table 2 Formation constants of 2-hydroxybutyrate(L)-metal complexes at 1.5 M ionic strength and 25.0 C.

Metal	$\log K_1$	$\log K_2$	$\log K_3$	$\log \beta_3$	method
Al	$2.98 \pm 0.1$ $3.03$	$2.3 \pm 0.03$ $2.51$	$1.99 \pm 0.04$ $1.49$	7.27 7.43	eq. 23 iteration(17)
Fe			$2.69 \pm 0.1$		eq. 23

The meanings of  $K_1$  and  $\beta_3$  have been defined in the Results and Discussion Section.

### C. Indulin AT (Lignin)

Because Indulin AT is a polyelectrolyte ligand, it's behavior is different than that of a simple ligand in an ionic medium. The charge built-up during the dissociation of it's hydrogen ions could cause not only a change of the conformation but also a new energy barrier which affects the hydrogen ion dissociation on the other functional sites.

In the polyelectrolyte area, the dissociation constant is a function of the free energy ( $\Delta G$ ). The Henderson-Hasselbalch equation generally is used to express the apparent dissociation constant ( $pK_{app}$ ) at the specific stage.

$$pK_{app} = pH + m \log \frac{1-\alpha}{\alpha} \quad 25.$$

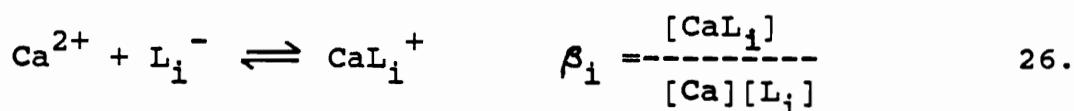
where  $\alpha$  is the degree of dissociation of the acid site and "m" is a constant for a given set of conditions.

Similarly, for the association between a binding site of the polyelectrolyte and a metallic cation, such as Ca, the measured formation constant ( $\beta_1$ ) also varies with the  $\alpha$  of the polyelectrolyte.

Although several mathematical models have been developed for the study of the formation constants between metal ions and polyelectrolytes (23, 10), each model has it's restrictions for a given application. Both discrete and continuous models can be applied on those metallic-

organic system in which metal ions can be measured separately by an ion-selective electrode. Gregor's method works on well ordered polymers in which all binding sites act independently in complexation, but the constants will vary with the dissociation stages (29). It is actually an average constant of all binding sites. However, for a polymer with great variation like lignin, this model may be a practical one for application.

The formation equilibrium for each site is



where  $\text{L}_i$  is the  $i$ th binding site. When in terms of a whole polymer, which has different types of binding sites, an average formation constant is defined as

$$\bar{\beta} = \frac{\sum[\text{CaL}_i]/n}{[\text{Ca}]\sum[\text{L}_i]/n} = \frac{[\text{CaL}]}{[\text{Ca}][\text{L}]} \quad 27.$$

where  $[\text{CaL}]$  and  $[\text{L}]$  stand for the binding unit in a polymer. Then they also can be assigned as the concentration of function groups of the polymer.

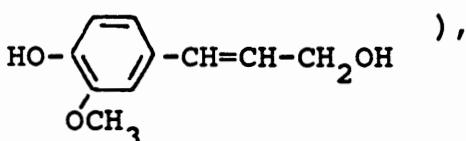
For this application, it was found that Calvin and Melchior's method (2) is more feasible. It is assumed that when only L and HL are only measured in a certain range of pH, then due to the complexation, the horizontal shift of the titration curve at the same pH value will be

equal to the hydrogen ion liberated. If the degree of neutralization of an acid is denoted as  $a'$  and in the presence of the metal ion by  $a$ , then the concentration of the bound ligand is given by  $(a-a')HL_{tot}$  and the average ligand number ( $\bar{n}$ ) by the following equation

$$\bar{n} = \frac{\text{bound L}}{M_{tot}} = \frac{(a-a')HL_{tot}}{M_{tot}} \quad 28.$$

The free ligand  $[L]$  concentration can be calculated according to eq. 12 and the definition above.

$$[L] = \frac{HL_{tot} - (a-a')HL_{tot}}{1 + H \cdot K_{app}} \quad 29.$$

Because Indulin AT is an alkaline type of polyconiferyl alcohol ( monomer as  ),

the adjacent oxygens on the hydroxy and methoxy groups provide the only binding site for complexation.

Figures 12 and 13 give the pH-titrations of Indulin AT with different amounts of Ca and Mg ions separately. Although it is reported (25) that this kind lignin has approximated 15%  $-COOH$  on the structure, the horizontal change (base volume difference) due to the complexation is seen at  $pH > 9$ , where all  $COOH$ s should have already dissociated. Therefore, in my calculation, only the amount of phenol was counted, which is reported to be 70% of the

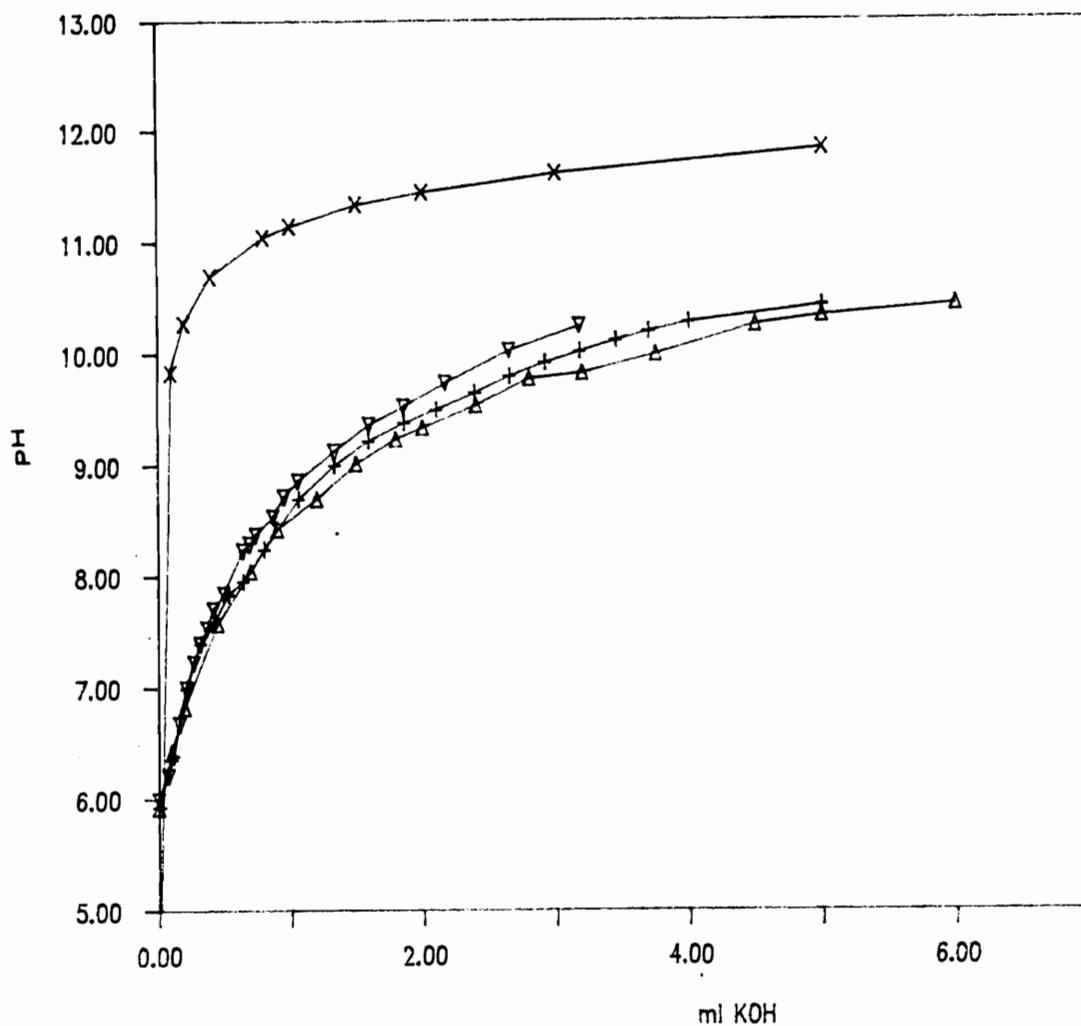


Figure 12. pH-titrations of (a) 0.0216 M Indulin AT ( $\nabla$ ); (b) 0.0216 M Indulin AT + 0.01 M Ca ion ( $\Delta$ ); (c) 0.0216 M Indulin AT + 0.002 M Ca ion (+); (d) 0.02 M Ca ion (x) with 0.0997 M KOH at  $\mu = 1.5$  M and 25 C.

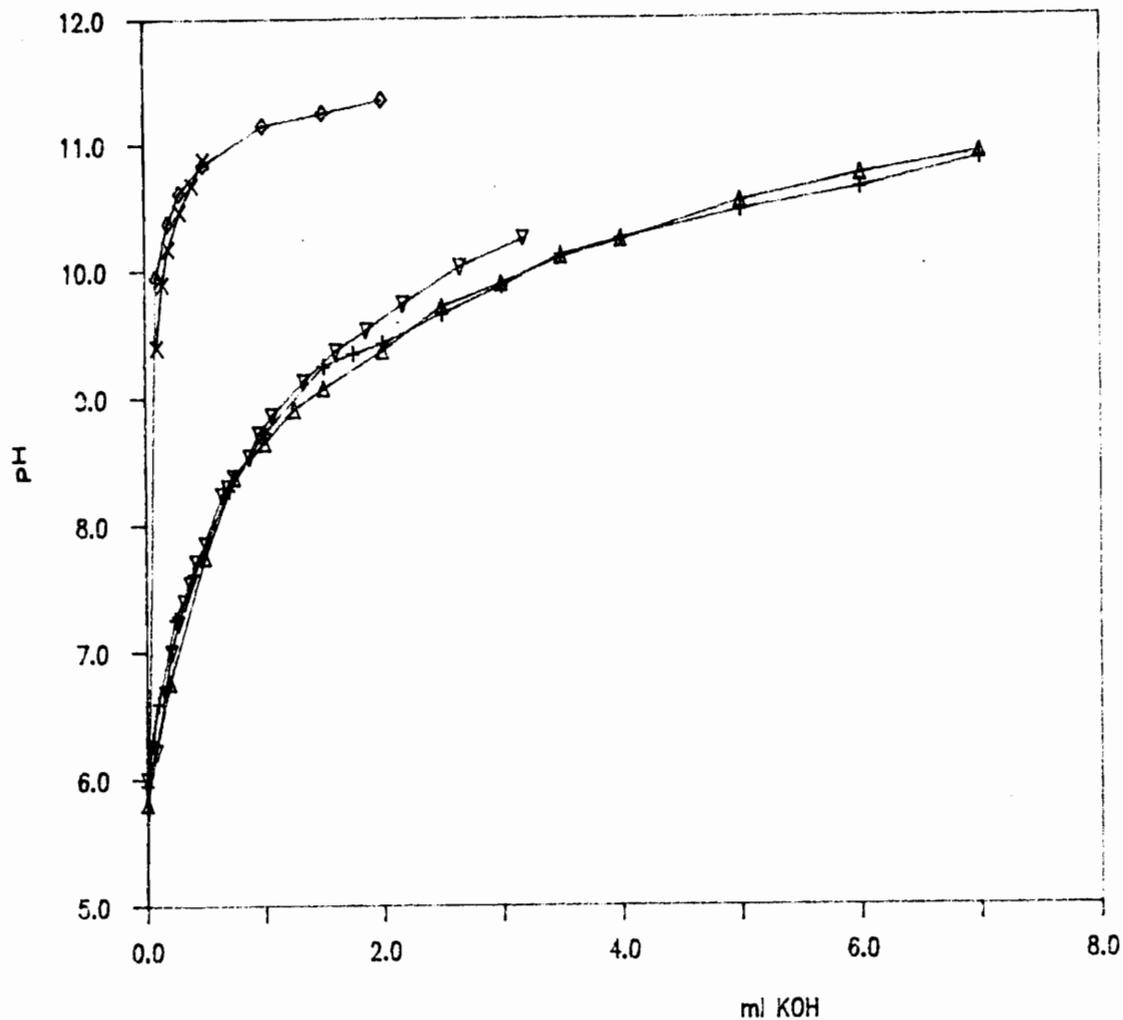
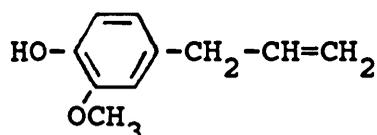


Figure 13. pH-titrations of (a) 0.0216 M Indulin AT (▽); (b) 0.0216 M Indulin AT + 0.002 M Mg ion (Δ); (c) 0.0216 M Indulin AT + 0.001 M Mg ion (+); (d) 0.002 M Mg ion (x); (e) 0.001 M Mg ion (◇) with 0.0997 M KOH at  $\mu = 1.5$  M and 25 C.

monomer (25).

The  $\bar{n}$  vs  $-\log[L]$  of Indulin AT with 0.01 M and 0.002 M Ca ion are given in Figure 14. Based on eq. 27, it is reasonable that when the amounts of Ca ions increase, relatively there will be less lignin monomer averaging on each Ca ion. Both curves do not show the same trend as the case of Ca + 2-HBA. The less movable polyelectrolyte in solution might trap the bivalent ion more easily for balancing the charge.

The  $\log \bar{\beta}$  ( $2.31 \pm 0.14$ ) from this report is larger than that of eugenol (



) ( $\log K_1 = 1.48$ )

(6), which is assumed to be the repeating unit of this Indulin AT structure. Actually, it is difficult to compare the constant of even the same polyelectrolyte from different sources (4), because there are always some variations of structure and the conditions under which measurements were made.

Figure 15 is the plots of  $\bar{n}$  vs  $-\log[L]$  of Indulin AT with 0.002 M and 0.001 M Mg ion. Again, they show the similar trend as the Ca ion. The  $\log \bar{\beta}$  can be directly read from the curves:  $2.40 \pm 0.16$  for the case of 0.001 Mg ion, and  $2.20 \pm 0.18$  for the 0.002 M Mg ion.

The binding properties of metal-lignin are not well known, but the value shows that physical absorption

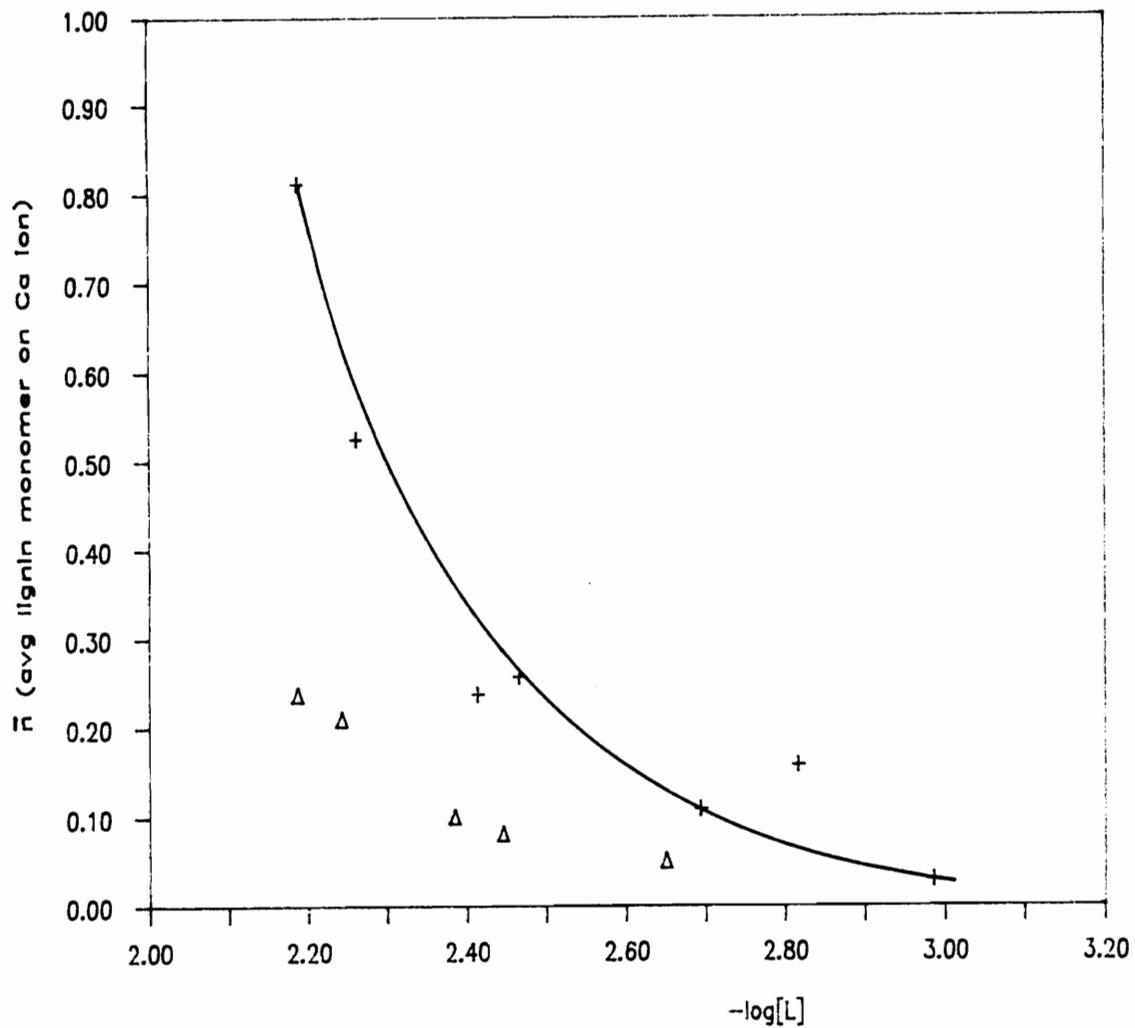


Figure 14. Degree of complex formation of (a) 0.0216 M Indulin AT + 0.01 M Ca ion ( $\Delta$ ); (b) 0.0216 M Indulin AT + 0.002 M Ca ion (x), at 1.5 M KCl and 25 C.

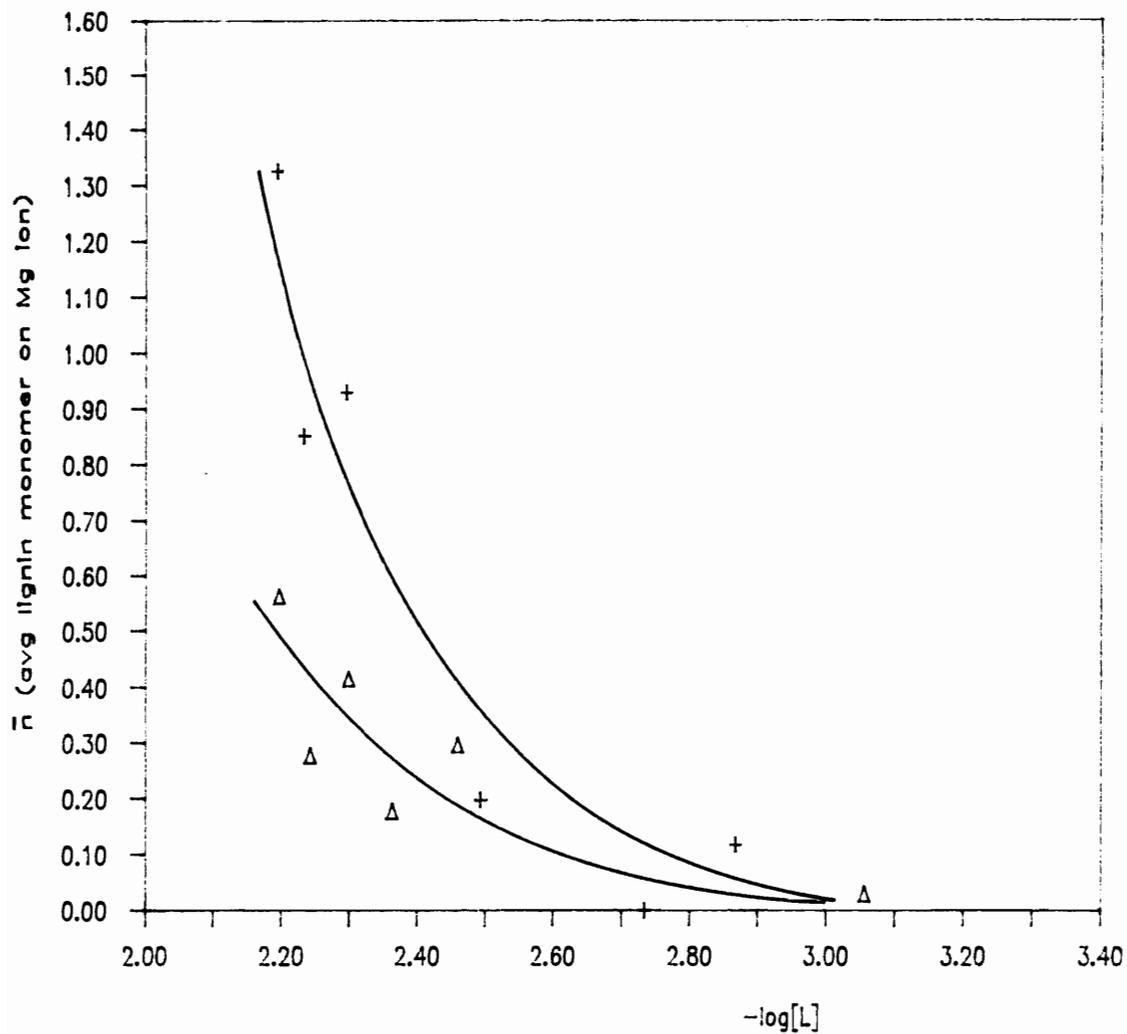


Figure 15. Degree of complex formation of (a) 0.0216 M Indulin AT + 0.002 M Mg ion ( $\Delta$ ); (b) 0.0216 M Indulin AT + 0.001 M Mg ion (+); at 1.5 M KCl and 25 C.

probably contributes much more than chemical binding, if chemical binding is the cause of Ca-eugenol complex (6).

This value also means that lignin can absorb large amounts of Ca ions and Mg ions despite the release of a proton being weakened by the para alkyl substituent and the steric effects on the phenol unit of this large polymer (5), especially under conditions where the metal ion will be heavily solvated.

Formation constants of Al and Fe with Indulin AT were not determined by this method. It does not mean that they do not exist, but based on the observation (Figures 16 and 17), almost all difference between (b)-(d), (c)-(e) are caused by metal hydrolysis. The lignin-metal complexes are present in very small amounts in the intended region. Studies from humic acid, a stronger complex ligand than lignin, concludes that most of the Al and Fe-humate complexes can only be investigated under pH < 8 and 9 respectively (18).

Figure 18 is the net pH-titration of Al, Ca, Fe and Mg ions with Indulin AT in a 0.5 M ionic strength system. All metal-lignin curves show no shift over that of lignin alone. Checking with the Marinsky equations (20): any polyelectrolyte has a following thermodynamic relation in solution

$$\text{pH} - \log \frac{\alpha}{1-\alpha} = \text{p}\bar{\text{H}} - \text{p}\bar{\text{Na}} + \text{pNa} - \log \frac{\alpha}{1-\alpha} = \text{pKapp} \quad 30.$$

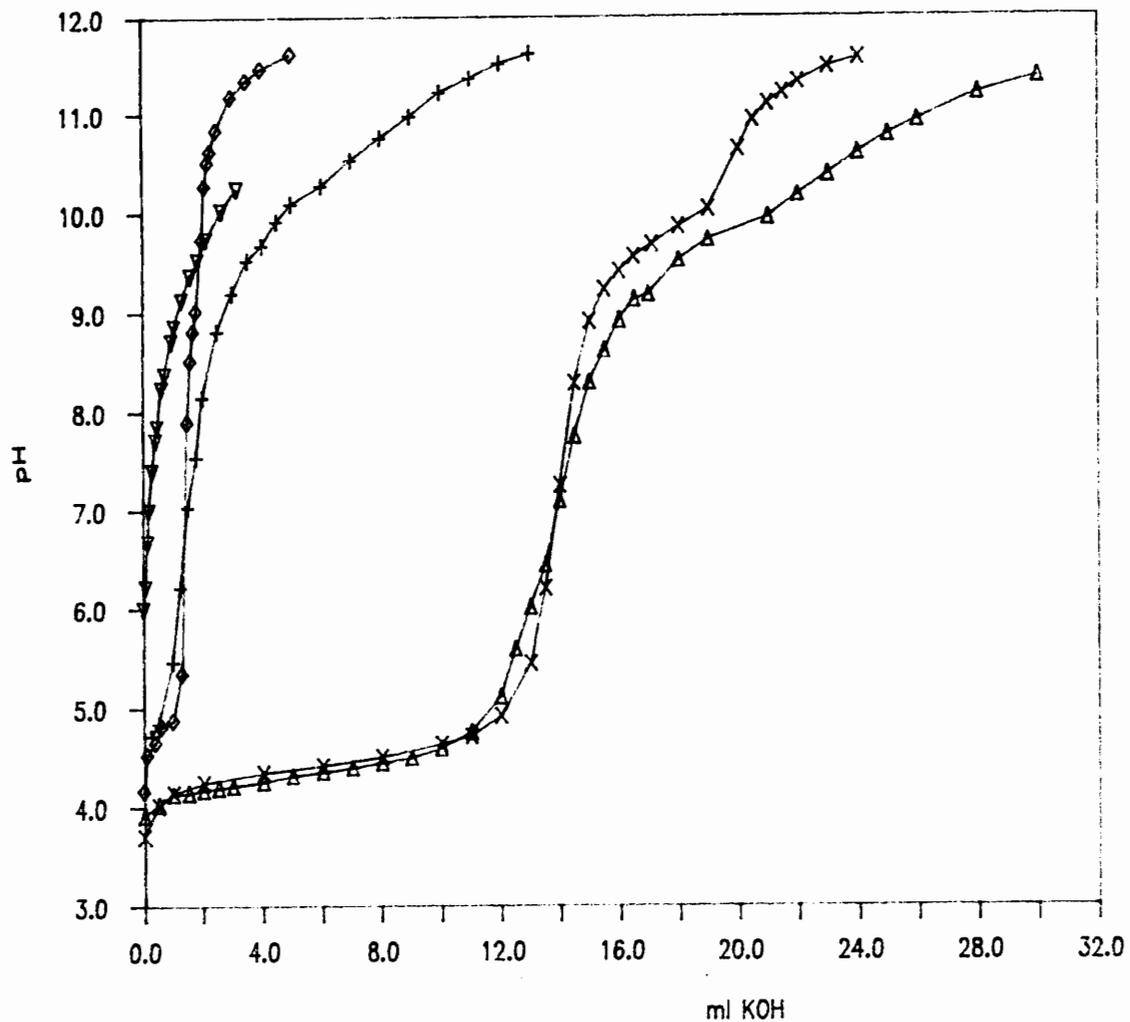


Figure 16. pH-titrations of (a) 0.0216 M Indulin AT ( $\nabla$ ); (b) 0.0216 M Indulin AT + 0.01 M Al(III) ion ( $\Delta$ ); (c) 0.0216 M Indulin AT + 0.001 M Al(III) ion (+); (d) 0.01 M Al(III) ion (x); (e) 0.001 M Al(III) ion ( $\diamond$ ) with 0.0997 M KOH at  $\mu = 1.5$  M and 25 C.

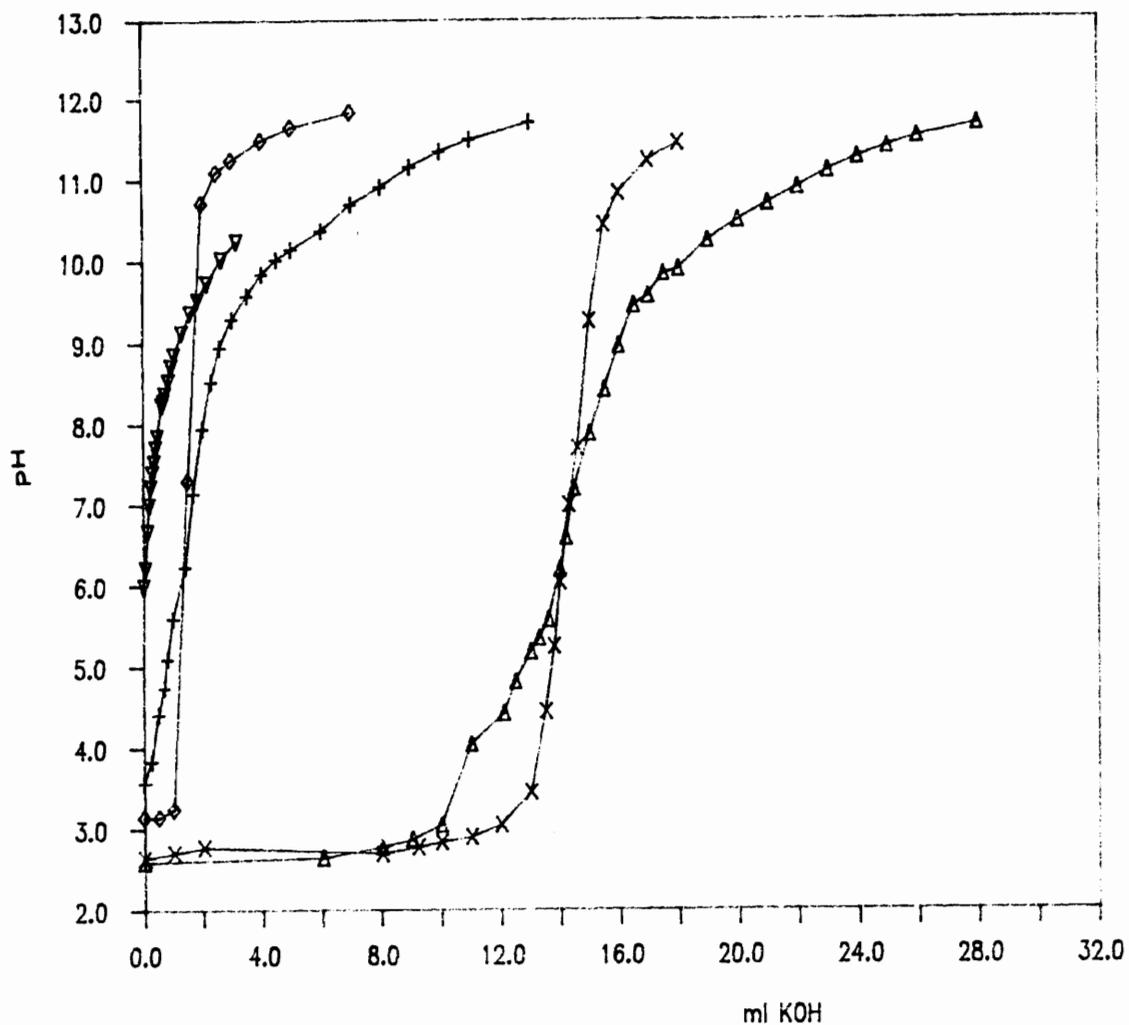


Figure 17. pH-titrations of (a) 0.0216 M Indulin AT ( $\nabla$ ); (b) 0.0216 M Indulin AT + 0.01 M Fe(III) ion ( $\Delta$ ); (c) 0.0216 M Indulin AT + 0.001 M Fe(III) ion (+); (d) 0.01 M Fe(III) ion (x); (e) 0.001 M Fe(III) ion ( $\diamond$ ) with 0.0997 M KOH at  $\mu = 1.5$  M and 25 C.

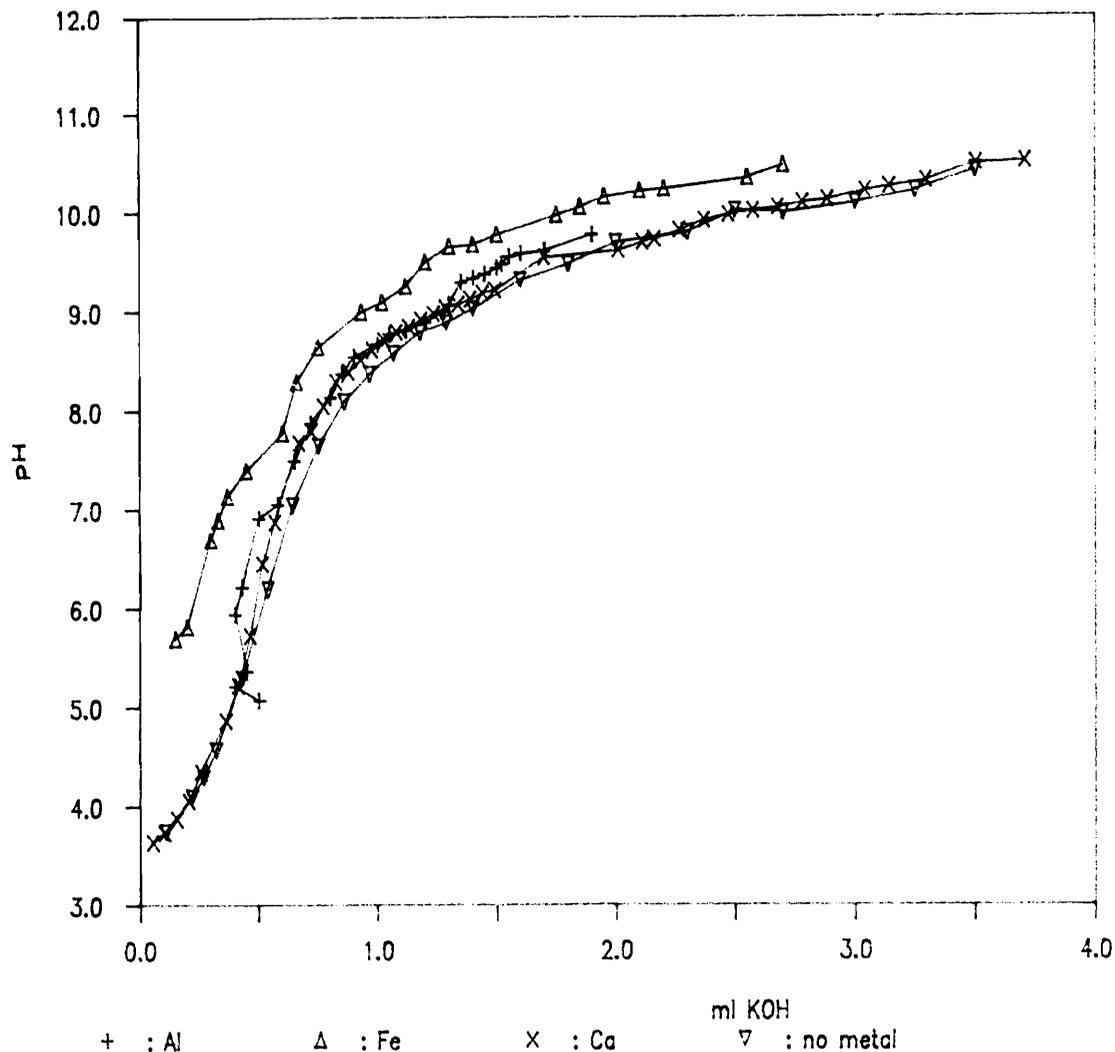


Figure 18. Net pH-titrations\* of (a) 0.0216 M Indulin AT (▽); 0.0216 M Indulin AT + (b) 0.01 M Ca ion (x); (c) 0.01 M Al(III) ion (+); (d) 0.01 M Fe(III) ion (Δ), at 0.5 M KCl and 25 C.

\* Net pH-titration means that the base volume of the curves have already been subtracted from the base volume needed for the titration of metal ion solution alone at the same pH value.

where  $\bar{p}H$  and  $\bar{p}Na$  denote the logarithm concentration of  $H^+$  and  $Na^+$  species in the gel phase. If the polymer is impermeable and inflexible, the plot of  $\bar{p}H$  vs  $\bar{p}Kapp$  should be unique at any ionic strength. Applying this relationship to Indulin AT at 0.5 M and 1.5 M KCl ionic strengths, we find that the result\* (Figure 19) suggests that Indulin AT shows some flexible properties. Comparing this result and the titrations of metal-Indulin AT at 0.5 M ionic strength, it is postulated that most of the binding must occur inside the structure. They are available only after the polyelectrolyte begins to expand due to the penetration of mass neutral ions(K , Cl ) which increase the repulsion of  $L^-$  and then provide more binding sites.

\* Linear regression analysis technique shows that the t-test of the slopes of curves (b) and (c) in figure 19 are significant at a level of  $\alpha = 0.05$ .

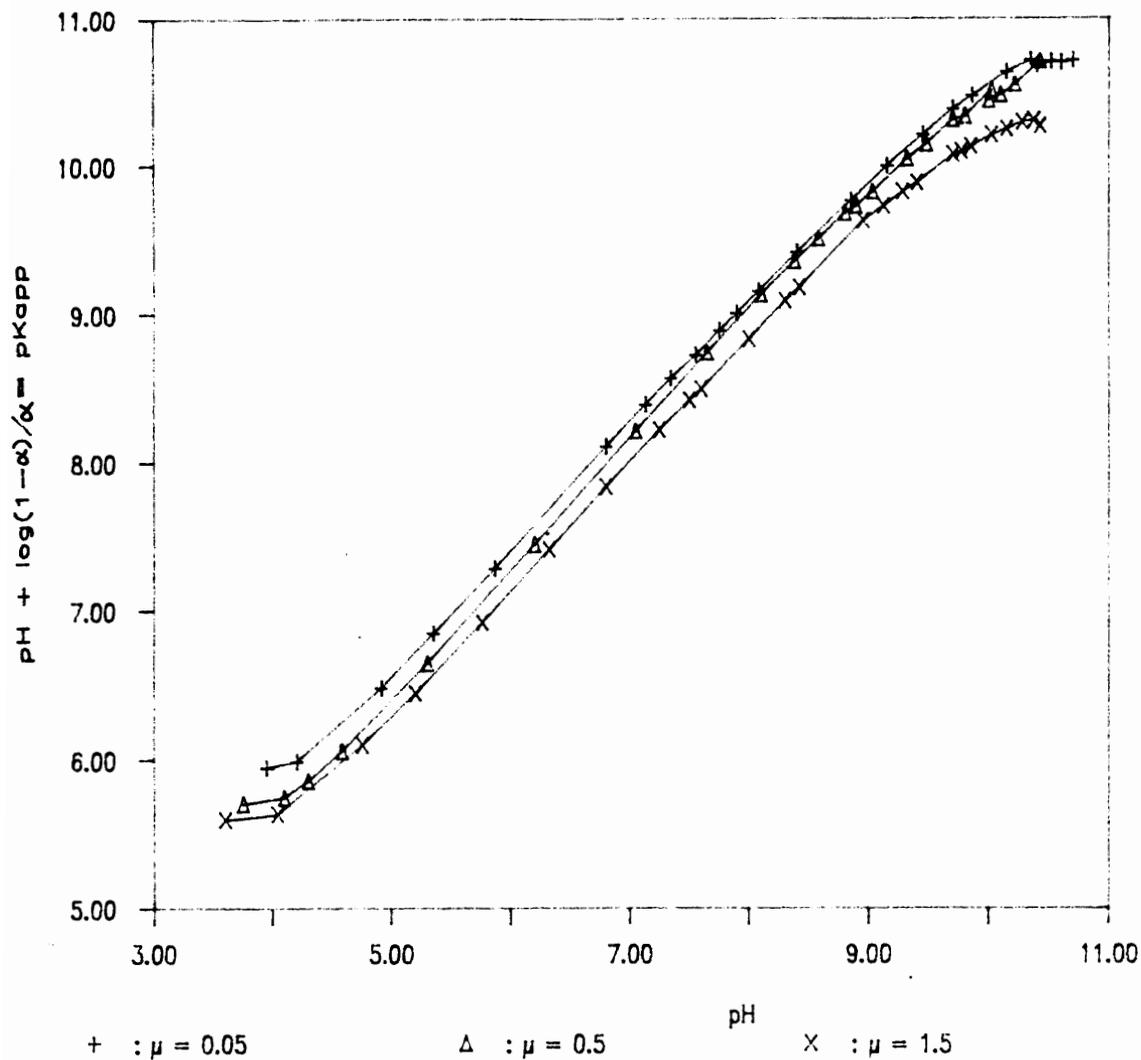


Figure 19. The pKapp function vs. pH of Indulin AT, 0.0216 M at (a) 0.05 M (+); (b) 0.5 M ( $\Delta$ ) and (c) 1.5 M (x) KCl at 25 C.

## V. CONCLUSIONS

1. Several complexes of 2-hydroxybutanoic acid (2-HBA) with aluminum, calcium, ferric and magnesium ions were shown based on pH measurements in the acidic range.
2. Formation constants ( $\log K_i$ ) of  $AlL_1$ ,  $AlL_2$ ,  $AlL_3$  are 3.03, 2.51 and 1.49. Only a third step formation constant of  $FeL_3$  ( $\log K_3$ ) was found which had a constant of 2.69 (L = 2-HBA anion).
3. Stable complexes of heavy metal ions with acid were found only when the concentration of metal ions were low and the pH of the medium was below 3.
4. Formation constants ( $\log K_1$ ) of calcium and magnesium ions were not determined from this study.
5. Indulin AT forms complexes probably only with calcium and magnesium ion under basic condition. Aluminum and ferric ions tend to form hydroxide precipitates under these conditions.
6. The average formation constants ( $\log \bar{\beta}$ ) of  $CaL$  and  $MgL$  are 2.31 and 2.40 under the condition of 1.5 M ionic strength (L = Indulin AT monomer).
7. Indulin AT behaves as a flexible and permeable polymer in a 1.5 M ionic strength medium.
8. Results from this study give strong evidence to support the conclusion of the previous study in which lignin and its fractions in kraft pulping black liquor may form complexes with calcium or magnesium ions,

which probably enhance the formation of scale in kraft pulp mills.

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