

COPPER(II) COMPLEXES OF AROMATIC  
POLYCARBOXYLATES

By

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COPPER(II) COMPLEXES OF AROMATIC  
POLYCARBOXYLATES

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## CHAPTER I

### INTRODUCTION

The substituted benzene polycarboxylic, which may be represented by the general formula:

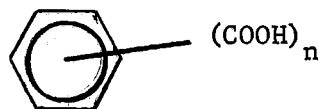


Figure 1. General Formula of Aromatic Polycarboxylic Acids

where  $n = 3-6$ , are being studied with an increasing amount of interest as ligands for the formation of metal complexes which may have varied practical applications. Two proposed applications of current interest are their ability to replace phosphates in detergents, analogous to the recent NTA (1), and in the synthesis of potentially important metallo-organic copolymers (2). Properties of the polymers which make them an interesting group of materials are their hardness and thermal stability, which has been exploited in the manufacture of durable surface coatings, and an anticipated high anisotropic electrical conductivity. The metals involved up to this time are the heavy transition and inner transition elements, e.g.  $\text{Th}^{\text{IV}}$ ,  $\text{U}^{\text{VI}}$ , and particularly those metals which by virtue of their preference for square planar coordination would enhance linear propagation (3). Most copolymers already described are unidimensional



with weak interaction between chains. To promote cross-linking higher substitutions than  $n = 4$  would be necessary.

An interesting fact from these studies is that the polymers are formed from solution at relatively low temperatures which makes their solution chemistry an interesting academic question. Apart from o-phthalic ( $n = 2$ ) for which metal complexes have been well characterized there is little evidence for quantitative studies of formation of complexes with the benzene polycarboxylic acids. One very good reason for this lack of information is the difficulty in characterizing the ionizations of the polyacids. Successive ionizations interfere which compounds the problem in the analysis by conventional methods (4). The difficulty is not in the derivation of the necessary equations but in the enormity of the arithmetic computations. With access to electronic computers this problem has been solved and ionization constants for a number of these acids are available (5).

The thermodynamics of the ionizations and how these properties are related to the position of the substituents on the ring have been described by Purdie and Tomson (6). These properties were shown to fit the electrostatic model used by Hammett (7). However, in the past most workers used only non-ionizable substituents on benzoic acid to determine the linear free energy relationships described by the Hammett equation. In the work done by Purdie and Tomson, they extended the use of the Hammett equation to the multiple ionization of the benzene polycarboxylic acids with excellent agreement for 1,2,4, and 1,3,5 benzene tricarboxylic acids but poor agreement with 1,2,3 benzene tricarboxylic acid, which contained a double ortho arrangement of COOH in the molecule. The suggestion that the Hammett relation failed was because the sigma parameter

for COOH and COO<sup>-</sup> group, which already contains a contribution from steric effects, may not be applicable when a second ortho group is present. With this extension it is possible to demonstrate that the ionization occurs in a symmetrical manner; for example, 1,2,3,4,5,6 benzene hexacarboxylic acid ionizes as 1,4,2,6,3,5.

#### Statement of Problem

Because of the rapidly expanding interest in these acids and their potential practical utility in diverse applications, it was considered important to characterize the metal complexes in solution.

This study was undertaken in order to determine the stability constants for benzene polycarboxylic acids, particularly 1,2,4,5 benzene tetra- and 1,2,3,4,5,6 benzene hexacarboxylic acids, with copper ion.

## CHAPTER II

### STABILITY CONSTANTS AND DEFINITIONS

If a species is capable of binding a proton it can also bind a metallic cation. The binding of a metallic cation in preference to a proton may be a result of many variables. These would include concentration of both proton and metal ion, the charge on the metal ion, and the geometry of the binding site, or the formation of a ring structure. If a ring structure is formed, the ligand has bound itself to more than one site on the metal ion. This process is called chelation and it adds additional stability to the complex (8).

The binding species or ligand (L) can bind the metal at one or more sites but in no case can the number of bonds exceed the coordination number of the metal. The coordination number is the number of bonds formed by each metal ion to all of its ligands.

Since the maximum possible coordination number of most metal ions exceeds the number of basic sites of most ligands, there arises a possibility of the formation of more than one complex. The complex may form in a single equilibrium step or in multi-equilibrium step reaction. If the complex forms in a single equilibrium step the reaction can be described by the equation



$$K'_F = \frac{[ML]}{[M][L]} \quad (2.2)$$

where the charges have been omitted for clarity and the equilibrium constant is  $K_f'$ .

If the thermodynamic formation constant is required then concentrations must be replaced by activities. The activity is defined as  $[ML]$  times the activity coefficient.

$$K_f' = \frac{[ML] \gamma_{ML}}{[M][L] \gamma_m \gamma_L} \quad (2.3)$$

However, if the complex forms in multi-equilibrium steps the reactions are written



where again the charges have been omitted for clarity and

$$k_1' = \frac{[ML]}{[M][L]} \quad (2.7)$$

.

.

.

$$k_n' = \frac{[ML_n]}{[M][L]^n} \quad (2.8)$$

$k_1' \dots k_n'$  are the individual conditional stability constants and the

over all conditional stability constant is defined as the product

$$K_f = k_1 k_2 \dots k_n \quad (2.9)$$

The corresponding thermodynamic equilibrium constant is therefore:

$$K_f = \frac{[ML_n]}{[M][L]^n} \cdot \frac{\gamma_{mL}}{\gamma_m \gamma_L^n} \quad (2.10)$$

Since most of the studies were done in water, it must be remembered that water is also a reasonable monodentate ligand and any other ligand must compete for coordination site with the water molecule.

#### Structure of Water

It is well known that the angle of the water molecule is approximately  $105^\circ$  and that the O-H distance is  $0.97 \text{ \AA}$ . Several descriptive models of liquid water exist, however, the better accepted models are those of Bernard and Fowler (B-F) (9) and Frank and Wen (F-W) (10). In the B-F model each water molecule has four nearest neighbors and an open tetrahedral structure held together by directed hydrogen bonds. In the F-W model the water tends to form and dissolve many hydrogen bonds forming short lived clusters surrounded by non-associated water. The water molecules in the clusters are extensively hydrogen-bonded. A rigorous statistical treatment of the F-W model by Nemethy and Seheraga (11) gives good agreement between experimental and theoretical calculations.

#### Metal Ion Hydration

When a metal ion is placed in a water solution and since water is a reasonable ligand, it is likely that the ion is hydrated with at least

the coordination number of water molecules and perhaps many more due to the alignment of the dipoles of the water molecules. Since it can be tedious to write the water part of the aquo complex they are usually omitted and are implied to be there to the maximum coordination number unless the metal ion is bound by other ligands. It is not easy to determine the number of water molecules bound to a metal ion, different experimental methods yield totally different results due to the alignment of dipoles, however, it may be assumed to be dependent on the metal ion.

#### Distribution Ratios and Definitions

When a substance is soluble in two solvents, usually water and an organic solvent, and the two solvents are in contact it is possible to have the solute in an equilibrium distribution between the two solvents.

$$D = \frac{[\text{HL}]_o}{[\text{HL}]_a} \quad (2.11)$$

D is defined as the distribution ratio, the subscript O denotes the organic phase, and [HL] denotes the concentration of the solute in each solvent. Equation (11) is, however, only an approximation because there are no perfectly immiscible solvents, so that terms like "water phase" and "organic phase" are only labels for the majority of the solvent in each phase.

If a metal (M) and a ligand (L) form a neutral species (ML) and the species is soluble in two different solvents it is then practical to use solvent extraction to study the complex in order to find the conditional stability constant. The reason being is that the charged ions will not enter the organic phase from the aqueous phase to any appreciable extent.

However, the equilibria established share all the complications of the chelation equilibria plus the fact that the neutral ligand (HL) may also be soluble in the organic phase. This complication can be overcome by finding the pH independence on the neutral ligand distribution  $(Kd)_c$ .

Figure 2 shows all possible reactions:

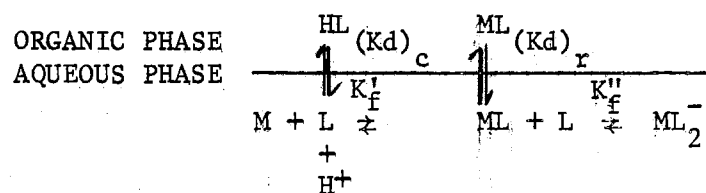


Figure 2. General Distribution Across Phase Boundary

$(Kd)_c$ , the distribution of the neutral ligand across the phase boundary, is defined by

$$(Kd)_c = \frac{[\text{HL}]_o}{[\text{HL}]_a} \quad (2.12)$$

and  $(Kd)_r$ , the distribution of the metal complex across the boundary, by

$$(Kd)_r = \frac{[\text{ML}]_o}{[\text{ML}]_a} \quad (2.13)$$

$K_{\text{HL}}$  is the association constant for the ligand

$$K_{\text{HL}} = \frac{[\text{HL}]}{[\text{H}][\text{L}]} \quad (2.14)$$

$K'_f$  is the equilibrium association constant for the complex formed.

$$K'_f = \frac{[ML]}{[M][L]} \quad (2.15)$$

The distribution ratio, D, for the entire system is

$$D = \frac{[ML]_o}{([ML] + [M])} \quad (2.16)$$

Dividing both numerator and denominator of Equation (2.16) by  $[ML]_o$ , D can be expanded in terms of equilibrium constants.

$$D = \frac{1}{\frac{1}{(Kd)_c} + \frac{[ML]_a}{[ML]_o K'_f [L]}} \quad (2.17)$$

which on rearranging gives the equation for D in its more common form.

$$\frac{1}{D} = \frac{1}{(Kd)_c} + \frac{K_{HL} (Kd)_r [H]}{K'_f (Kd)_c [HL]} \quad (2.18)$$

Since it is possible to find, by independent measurements, the values for;  $(Kd)_c$ ,  $(Kd)_r$ ,  $K_{HL}$ , and D it is possible to solve Equation (2.18) for  $K'_f$ , the conditional formation constant, of the complex.



## CHAPTER III

### EXPERIMENTAL

#### Potentiometric

All experimental emf's and pH readings were made using a Beckman 101900 Research pH Meter that has a readability of 0.05 millivolts (mv) and 0.005 pH and a standard deviation of 0.051 mv and 0.0007 pH.

#### Electrodes

The glass electrode used was a Corning 476022 with silver/silver chloride (Ag/AgCl) internal electrode element in a reference solution of 1.0 Molar HCl. The electrode was soaked in 1.0 M HCl for one week prior to use and kept in a 0.05 M potassium acid phthalate solution between titrations.

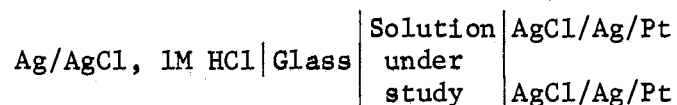
The reference electrodes used were Type III (12) electrolytic Ag/AgCl. These electrodes were found to be quite sensitive to many conditions among them mechanical shock, smoothness of platinum surface, and the presence of oxygen in the electroplating and storage solutions. It was for the last reason that all solutions were degassed with nitrogen before use. The electrodes were stored in a solution of 0.1 M KCl.

#### Solution Under Study

As was stated the solutions were degassed by bubbling  $N_2$  through them for at least 15 minutes at a rate of 20 ml/min before titrations.

and this rate was continued throughout the titration. Chloride ion (0.01 M) was added to all solutions.

The cell was set up in the following manner



this permitted two measurements to be made after each addition of base.

The solutions were maintained at  $25 \pm 0.05^\circ\text{C}$  by a Braun Thermomix II circulator-heater which circulated the temperature controlled water through a jacketed beaker. No attempt was made to keep the electrodes at the same temperature, other than placing them in the solutions.

#### Calibration of Glass Electrodes

Even though the glass electrode is reversible to hydrogen ions it is not a primary electrode and must be calibrated relative to a primary standard. To do this it is necessary to test the linear response, the Nernst slope, of the cell with pH ( $\text{pH} = -\log_{10}$  activity of hydrogen ion). Buffer solutions are used for this purpose: 0.050 M potassium acid phthalate ( $\text{pH} = 4.008$  at  $25^\circ\text{C}$ ) and 0.025 M potassium dihydrogen phosphate-0.025 M disodium hydrogen phosphate ( $\text{pH} = 6.86$  at  $25^\circ\text{C}$ ).

To evaluate the Nernst slope,  $k$ , the following equation is used

$$k = (E_{4.008} - E_{6.86}) / (6.86 - 4.008) \quad (3.1)$$

Using the calculated  $k$  the pH of an unknown solution was calculated using Equation (3.2)

$$\text{pH} = 4.008 + (E_{4.008} - E_{\text{obs}}) / k \quad (3.2)$$

where  $E_{4.008}$  and  $E_{6.86}$  are the observed emf's of the buffer solutions and  $E_{obs}$  is the measured emf of the unknown solution.

The Ag/AgCl electrodes were tested by opposing them in a buffer solution and checking the potential between them. If the potential was less than 0.2 mv the electrodes were considered useable.

#### Chemicals

1,2,4,5 benzene tetra- and 1,2,3,4,5,6 benzene hexacarboxylic acids were obtained from Aldrich Chemical Co., Inc. and were of reagent or purissima grade. The copper(II) perchlorate, reagent grade, was obtained from Frederick Smith Chemical Company and the equivalent weight of the salt was determined by cation exchange on a column prepared from Dowex 50W-X4 Resin (Baker Analyzed Reagent) and the eluant was titrated with standard potassium hydroxide.

Standard 0.2 N KOH was prepared according to Vogel (13) using analyzed reagent grade KOH (Baker Analyzed Reagent). A 10.00 ml Kimax class A automatic buret, readability 0.01 ml, equipped with an Ascarite (8-20 mesh Auther H. Thomas Co.) filled drying tube to exclude the carbon dioxide was used for titrations and to avoid exposing the KOH to the atmosphere during titrations a Teflon needle (C. R. C. Inc.) was attached to the tip of the buret. The KOH was standardized using Baker Analyzed Reagent grade potassium acid phthalate dissolved in degassed and deionized water.

The deionized water was prepared by passing distilled water through 2 meters of reagent grade Rexyn #300 (H-OH) mixed bed resin (Fisher Scientific Co., Inc.) at a rate not to exceed 1 ml/min. The water was then passed through a one meter column of activated charcoal, at the

same rate, and stored in two twelve liter flasks.

The KCl, used to maintain a constant chloride ion concentration, was Baker Analyzed Reagent. The KCN and AgCN, used in the preparation of the Ag/AgCl electrodes, were certified ACS grade (Fisher Scientific Co., Inc.).

The concentrations of the acids solutions were always about 0.01 M and were prepared daily due to the bacteria growth. One liter of 0.1 M  $\text{Cu}(\text{ClO}_4)_2$  was prepared and standardized as previously mentioned.

#### Extraction Method

The ultraviolet (uv) spectra were obtained using a Cary 14 instrument and a cell path length of 1.00 cm. The readability of this instrument is 0.005 absorbance units (au) and a standard deviation of 0.002 au. The atomic absorption (aa) instrument was a Perkin-Elmer model 290B readability of 0.005 au and a standard deviation of 0.002 au.

Extraction into the organic phase was accomplished by taking 20 ml of aqueous solution and a like amount of butanol and shaking the two together for a period of time varying from one to ten minutes at the end of which the two phases were immediately separated. The uv spectrum was taken on the organic phase to determine the amount of complex present and the aa spectrum was taken on the aqueous phase to determine the concentration of the remaining metal ion.

#### Extraction Solutions

To perform an extraction the two solvents must be mutually saturated prior to the extraction because each solvent is slightly soluble in the other and this would affect the distribution of the species.

The two solvents, water and 1-Butanol certified A.C.S. grade (Fisher Scientific Co., Inc.) were mixed and allowed to stand for at least 24 hr to let the mixture come to saturated equilibrium. Butanol was selected as the solvent because of its high solubility of the acid and dielectric constant.

## CHAPTER IV

### DISCUSSION

In order to select the most likely solvent to use in extraction the following criteria were applied: the immiscibility of the solvent with water; the solubility of the neutral ligand in the solvent; and, the dielectric constant of the solvent. Extraction of the neutral complex is enhanced in a solvent of lower dielectric constant than that of water.

Twelve organic solvents were chosen and tested for the solubility of the ligand acid. Approximately 0.1 gm of 1,2,3,4,5,6 benzene hexacarboxylic acid ( $H_6L$ ) was added to 10 ml of each dry solvent. The solutions were shaken and allowed to come to saturation by standing for several days. From a visual determination n-butanol was chosen in that all the solute had dissolved. However, the one disadvantage of butanol as an extracting medium is its considerable solubility in water, 9.1 ml/100 ml water. The remaining solvents were centrifuged and the solutions were analyzed for the acid concentration spectrophotometrically using a calculated molar absorptivity of  $H_6L$  (14). These solvents were discarded when it became apparent that the acid concentration was below  $1 \times 10^{-4}$  M, an arbitrary cutoff point.

In order to analyze an unknown solution for a certain compound by spectrophotometric measurements a calibration curve must be made. To insure that the spectrum obtained from the spectrophotometric measurements is in the reading range of the instrument certain concentrations should

be used which depend upon  $\epsilon$ , the molar absorptivity. Using the published spectrum it was possible to establish an approximate  $\epsilon$  and therefore a working range for solution concentrations.

A stock solution of  $H_6L$  was prepared using butanol saturated with water. The uv spectra were taken on solutions of concentrations  $6.0 \times 10^{-4}$  M (Figure 3),  $5.0 \times 10^{-4}$  M,  $4.5 \times 10^{-4}$  M,  $4.0 \times 10^{-4}$  M, and  $3.0 \times 10^{-4}$  M. No significant deviation from Beer's law observed and the average at 292.5 nm was calculated to be  $827.82 \pm 41.07 \text{ cm}^{-1} \text{ mole}^{-1}$ .

Since  $H_6L$  is a poly-weak acid, the first ionization of which is fairly strong  $pK_1 = 1.21$  (15), it is desirable to know what species are present in an aqueous solution containing only the free acid. Figure 4 is the alpha diagram or relative distribution of the acid species versus pH in water. Since the nature of the neutral complex is unknown and presumably changes with pH, a 1:1 complex would be favored at low pH and higher ratios of metal to acid at high pH.

#### Determination of Ligand Distribution Constant

Since the ligand is a weak electrolyte, the distribution ratio takes a more complicated form

$$D = \frac{\sum [HL]_o}{\sum [H_n L^{(6-n)-}]_a} \quad (4.1)$$

However, if it is assumed that no ionization occurs in the organic phase then Equation (4.1) assumes the form

$$D = \frac{[HL]_o}{\sum [H_n L^{(6-n)-}]_a} \quad (4.2)$$

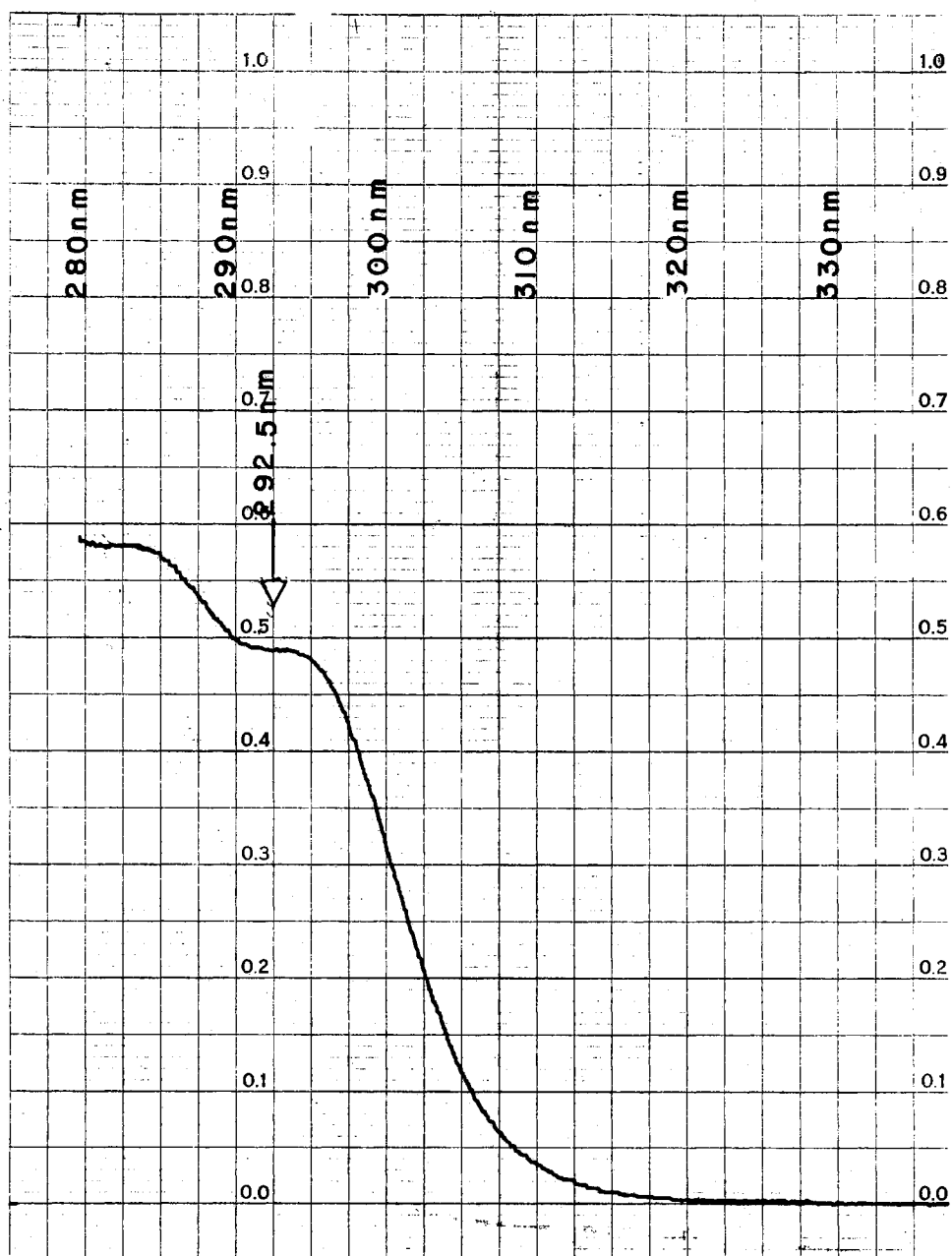


Figure 3. Ultraviolet Spectrum of Mellitic Acid in Butanol



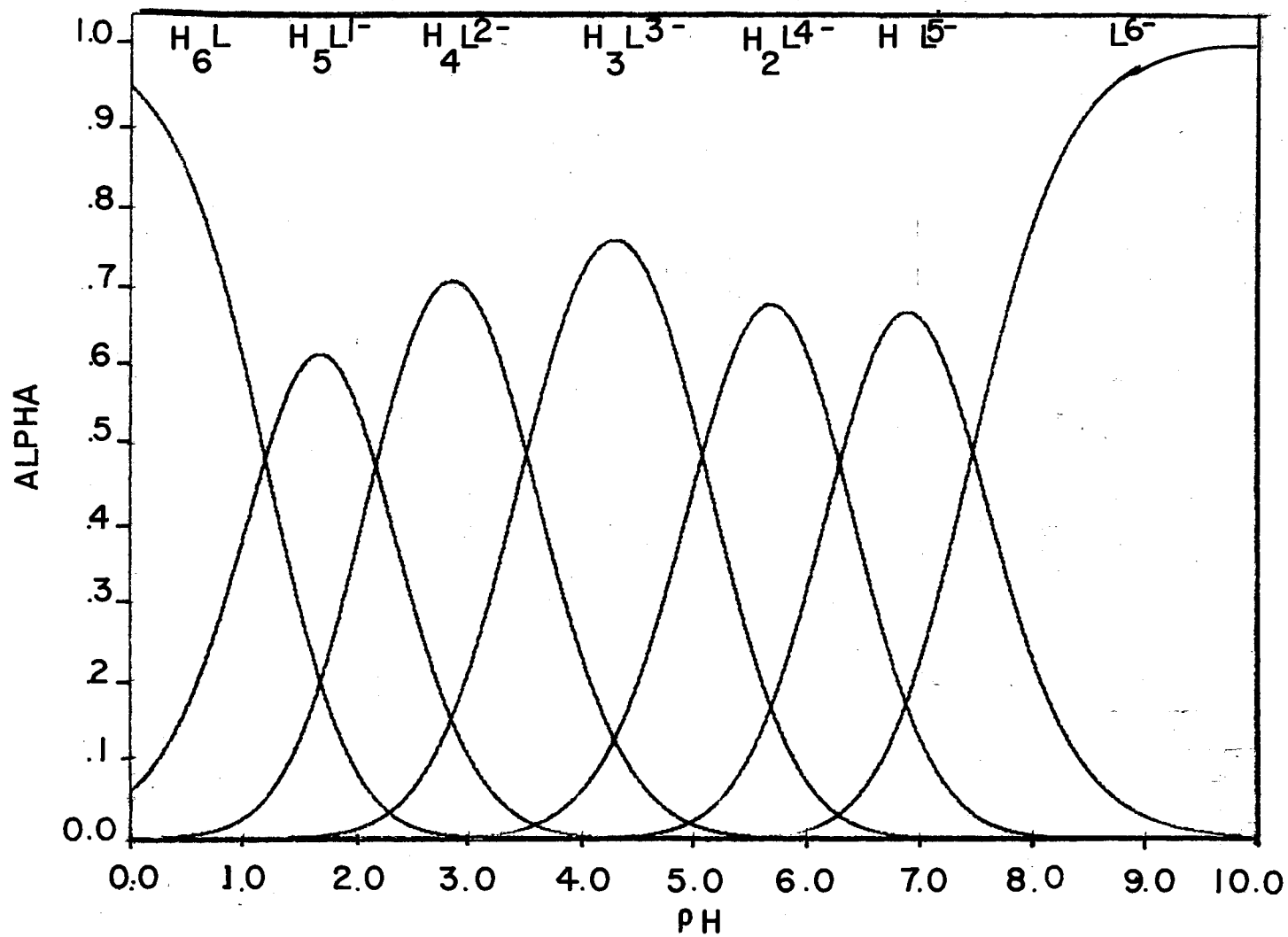


Figure 4. Alpha Diagram of Mellitic Acid

Dividing both numerator and denominator by  $[H_6L]_a$  and expanding

$$D = \frac{\frac{[H_6L]_o}{[H_6L]_a}}{1 + \frac{[H_5L^-]_a}{[H_6L]_a} + \frac{[H_4L^{-2}]_a}{[H_6L]_a} + \dots + \frac{[L^{-6}]_a}{[H_6L]_a}} \quad (4.3)$$

and simplifying and rearranging Equation (4.3), the final expression for the distribution ratio of this acid is:

$$D = \frac{(kd)_c [H^+]^3}{[H^+]^3 + K_1 [H^+]^2 + K_1 K_2 [H^+] + K_1 K_2 K_3} \quad (4.4)$$

where  $(Kd)_c$  is the distribution of the neutral ligand between solvents.

Since the total analytical concentration,  $C_a$ , of the acid is known and the amount that is transferred into the organic phase can be determined from spectrophotometric measurements then from mass balance

$$C_a = [H_n L^{(6-n)-}]_a + [H_6L]_o \quad (4.5)$$

Equation (4.2) can be rewritten as

$$D = \frac{[H_6L]_o}{C_a - [H_6L]_o} \quad (4.6)$$

D was determined over the pH range .3 to 1.3. The value of  $(Kd)_c$  is independent of  $[H^+]$  and has an average value of  $1.38 \pm 18$ . See Table I.

#### Distribution of Metal Complex

The initial attempts at sequestering metal by extracting the complex into butanol were made at high pH. The assumption was made that the

TABLE I  
pH INDEPENDENCE OF  $K_d$

| $[H_6L]_o$            | $[H_6L]_a$            | D     | pH    | $K_d$ |
|-----------------------|-----------------------|-------|-------|-------|
| $3.62 \times 10^{-4}$ | $2.71 \times 10^{-4}$ | 1.203 | 0.325 | 1.372 |
| $3.32 \times 10^{-4}$ | $2.65 \times 10^{-4}$ | 1.253 | 0.327 | 1.418 |
| $3.47 \times 10^{-4}$ | $2.57 \times 10^{-4}$ | 1.366 | 0.282 | 1.529 |
| $3.02 \times 10^{-4}$ | $2.98 \times 10^{-4}$ | 1.031 | 0.217 | 1.117 |
| $2.47 \times 10^{-4}$ | $3.22 \times 10^{-4}$ | 0.851 | 1.232 | 1.845 |
| $2.11 \times 10^{-4}$ | $3.85 \times 10^{-4}$ | 0.548 | 1.312 | 1.156 |
| $2.17 \times 10^{-4}$ | $4.05 \times 10^{-4}$ | 0.539 | 1.295 | 1.277 |

neutral complex would be  $\text{Cu}_3\text{L}$  and the solutions were prepared so that the metal ion concentration was three times that of the acid. The pH of the solutions was adjusted to approximately 7 by the addition of standard base before the metal ion was added. No evidence for metal complex being present in the organic phase was seen. It was concluded that the metal complex was present in trace amounts at this pH. On increasing the pH to 9, which should have favored the formation of more  $\text{Cu}_3\text{L}$ , there still was no evidence of the complex in the organic phase. In solutions of pH below 5 precipitation occurred in the aqueous phase. No analysis of the precipitate was done but it was assumed to be the copper mellitate,  $\text{Cu}_3\text{L}$ , or a protonated salt. The solubility products are fairly small, approximately  $10^{-10}$  for divalent mellitate salts.

The uncertainty of the complex, it was felt, was adding unknown difficulties to the extraction studies. At this time it was considered more important and perhaps more profitable to characterize the metal complex in aqueous solution.

#### Potentiometric Titrations

As a test for the potentiometric system the ionization constants of the acid in aqueous solution were calculated from replicate titrations with standard base. Excellent agreement with literature values were obtained (16). This preliminary work was considered to be useful since in the original work hydrogen rather than glass electrodes were used. The most irreproducible constant is  $K_1$ , the first ionization constant. This ionization is fairly strong and the unreliability of  $K_1$  could affect the reproducibility in a calculated formation constant.

In titrating for metal complex analyses, various amounts of stock

$\text{Cu}(\text{ClO}_4)_2$  solution (.1 M) were added to aliquots of  $10^{-2}$  M acid. What seemed to be an unusual result was observed on the addition of the metal ion in that customarily the pH of the acid solution is observed to decrease. In this instance the pH of the solution increased indicating consumption of protons on complexation. This extraordinary result caused some re-evaluation of our concepts regarding the nature of the complex.

In order to reduce the proliferations of the probable complexes in solution, the system was changed to another analogous acid, 1,2,4,5, benzene tetracarboxylic acid,  $\text{H}_4\text{L}$ . This move reduced the number of complexation sites by eliminating two carboxylic groups. Here, as in  $\text{H}_6\text{L}$ , the species present at a given pH would be helpful to determine what if any complexes would form. The alpha diagram for  $\text{H}_4\text{L}$ , pyromellitic acid, is given in Figure 5.

The sequence of proton ionization from the neutral acid has been established to be 1,4,2,5 (17). As a result pyromellitic acid might be expected to behave as a double o-phthalic acid on complexation with metals. Since the stoichiometry of the o-phthalate copper complex was determined by spectrophotometric measurements and no mention of an unusual shift in pH was reported (18). Peacock and James (19) had determined the disassociation constant for copper phthalate by potentiometric measurements but again no mention of an unusual shift in pH, since the measurements were made beyond the first equivalence point. In order to determine if o-phthalic acid behaved similarly to the other aromatic carboxylic acids, a titration was done and the same initial increase in pH on adding metal ion was again observed. This observation it turns out is more general than expected and at present there is no explanation

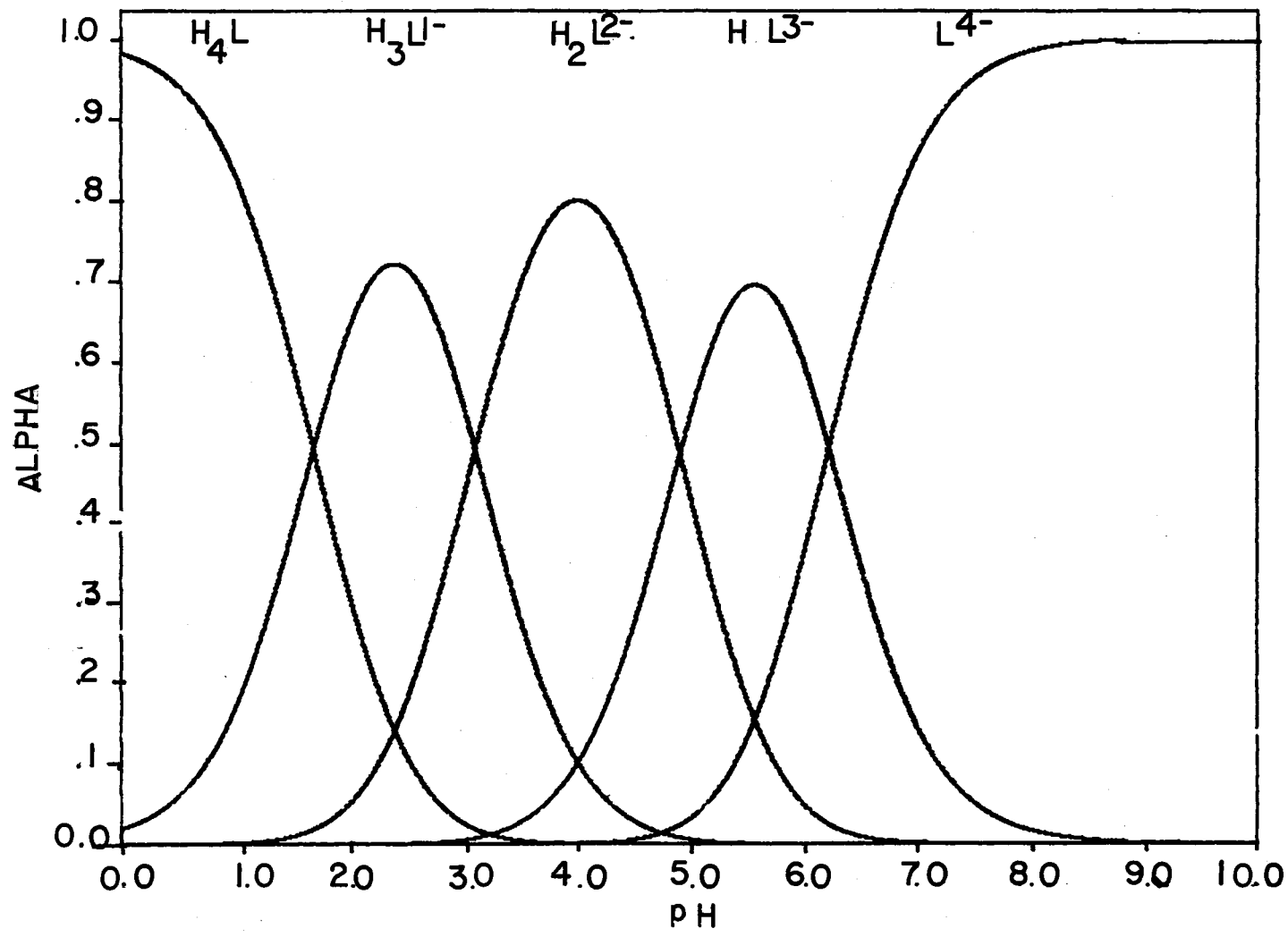


Figure 5. Alpha Diagram of Pyromellitic Acid

for it other than that a complex which involves the neutral ligand is formed.

From a pragmatic point of view our attention was turned to the titration data obtained after the first equivalence point. At this point the pH curves of the free acid and acid with metal added intersect and beyond this point there is a monotonic decrease in pH from the free acid curve as base is added to the solution containing metal ion. In this region up to the point of precipitation an attempt was made to analyze the data for a single complex using as a model the idea of a double phthalate complex. The two single complexes that were tried were  $\text{Cu}_2\text{L}$  and  $\text{Cu}_2(\text{H}_2\text{L})^{2+}$ . The latter was used because in the pH range studied  $\text{H}_3\text{L}^-$  and  $\text{H}_2\text{L}^{2-}$  are the predominate forms of the ligand and if  $\text{H}_2\text{L}^{2-}$  is removed on complexing, protons would be released as the equilibrium between  $\text{H}_3\text{L}^-$  and  $\text{H}_2\text{L}^{2-}$  is reestablished. The concentrations of the various species required to calculate the formation constants were obtained by solving the mass balance equations.

$$C_a = \sum ([\text{H}_n\text{L}^{(4-n)-}]) + [\text{Cu}_x(\text{H}_y\text{L})^{m+}] \quad (4.7)$$

$$C_m = [\text{Cu}^{2+}] + [\text{Cu}_x(\text{H}_y\text{L})^{m+}] \quad (4.8)$$

and the charge balance equation

$$\begin{aligned} [\text{K}^+] + [\text{H}^+] + 2[\text{Cu}^{++}] + m[\text{Cu}_x(\text{H}_y\text{L})^{m+}] &= [\text{H}_3\text{L}^-] + 2[\text{H}_2\text{L}^{2-}] \\ &+ 3[\text{HL}^{3-}] + 4[\text{L}^{4-}] + [\text{ClO}_4^-] \end{aligned} \quad (4.9)$$

where  $C_m$  is the analytical concentration of the metal and  $\text{Cu}_x(\text{H}_y\text{L})^m$  is a generalized formula for a 2:1 complex. The formation constant equations

are as follows:

$$K_5 = \frac{[\text{Cu}_2(\text{H}_2\text{L})^{2+}]}{[\text{Cu}^{2+}]^2[\text{H}_2\text{L}^{2-}] \gamma_{\text{Cu}^{2+}}^2} \quad (4.10)$$

$$K_6 = \frac{[\text{Cu}_2\text{L}]}{[\text{Cu}^{++}]^2[\text{L}^{4-}]} \cdot \gamma_{\text{Cu}^{++}}^{1/2} \gamma_{\text{L}^{4-}} \quad (4.11)$$

In order to obtain the activity coefficients the ionic strength, I, must be calculated from Equation (4.12)

$$I = 1/2 \sum_{i=1}^n c z_i^2 \quad (4.12)$$

where c represents the concentration of an individual ion and z its charge, and entered into the extended form of the Debye Hückel equation developed by C. W. Davies (20), accurate to I = 0.1 M.

$$\log_{10} (\gamma) = .509 (I^{1/2}/(1 + I^{1/2}) - 0.3 I) \quad (4.13)$$

Although there are three equations and three unknowns as iterative procedure was necessary to calculate the activity coefficient. Even over the restricted pH range of the second buffer region no consistent value was obtained for the formation constant of either complex.

It was noticed that on plotting the calculated formation constant for each as a function of the degree of neutralization where one constant reached a maximum the other value minimized. The analysis when carried out in terms of two competing metal complex equilibria. The equation obtained from combining the mass balance and the charge balance equations in terms of the two complexes  $\text{Cu}_2\text{H}_2\text{L}^{2+}$  and  $\text{Cu}_2\text{L}$  is cubic in  $[\text{H}_3\text{L}^-]$  and



contains the formation constant of  $\text{Cu}_2\text{H}_2\text{L}^{2+}$  as an unknown.

To solve this equation guessed values for  $K(\text{Cu}_2\text{H}_2\text{L}^{2+})$ ,  $K_5$ , were used to calculate  $K(\text{Cu}_2\text{L})$ ,  $K_6$ , and a search made for the value of  $K_5$  which gave the least deviation in the calculated  $K_6$ . Initial values of  $K_5$  were chosen which ranged from  $10^2 - 10^9$ . Low and high values were quickly eliminated since negative values for concentrations were obtained. The range wherein least deviation was found was  $5 \times 10^5 - 5 \times 10^6$  and best fit for  $K_6$  was obtained at  $K_5 = 3.8 \times 10^6$ . Calculations were successful only when metal ion was in excess over the ligand and the agreement in formation constants was good at ratios of 3:1 and 2:1. At ratios of 1:2, analytical concentrations, where statistically there is insufficient  $\text{Cu}^{2+}$  for 2:1 complex stoichiometry some other complex presumably predominates. This was not established. The formation constant for  $\text{Cu}_2\text{L}$  was calculated to be  $3.77 \pm .92 \times 10^{12}$ .

It was found that data in the latter part of the first buffer could also be treated in terms of the above two complex scheme, but not data in the first part. It was concluded that the other complex or complexes were forming in this region. Among the complexes, that were analyzed for, were  $\text{Cu}(\text{H}_3\text{L})_2$ ,  $\text{Cu}(\text{H}_3\text{L})^+$ ,  $\text{Cu}_2(\text{H}_3\text{L})^{3+}$ , and  $\text{Cu}(\text{H}_4\text{L})^{2+}$ , both separately and in combination with each other. Only the analysis for  $\text{Cu}(\text{H}_4\text{L})^{2+}$  approached anything like a satisfactory interpretation. Tables II and III show the result of this analysis.

It seems possible that there might be three or more complexes forming in the first buffer region and this generates many more arithmetical complications.

In conclusion the probable reasons that the extraction of the copper complexes were unsuccessful are; (1) The formation of a charged

TABLE II  
SINGLE COMPLEXES CONSIDERED AND RESULTS

| Complex                                | Range                                   | Ratio     |
|--|---|-----------|
| $\text{Cu}(\text{H}_4\text{L})^{++}$   | $0.97 - 3.0 \times 10^5$                | 3:1       |
| $\text{Cu}(\text{H}_4\text{L})^{++}$   | $0.34 - 1.7 \times 10^5$                | 2:1       |
| $\text{Cu}(\text{H}_4\text{L})^{++}$   | $0.29 - 1.2 \times 10^5$                | 1:1       |
| $\text{Cu}(\text{H}_4\text{L})^{++}$   | $0.15 - 1.3 \times 10^5$                | 2:1       |
| $\text{Cu}(\text{H}_3\text{L})^+$      | $0.7 - 8.6 \times 10^1$                 | 3:1       |
| $\text{Cu}(\text{H}_3\text{L})^+$      | $1.6 - 3.6 \times 10^2$                 | 2:1       |
| $\text{Cu}(\text{H}_3\text{L})^+$      | $1.5 - 5.2 \times 10^2$                 | 1:1       |
| $\text{Cu}(\text{H}_3\text{L})^+$      | no positive numbers                     |           |
| $\text{Cu}(\text{H}_2\text{L})$        | no positive numbers                     | any ratio |
| $\text{Cu}(\text{H}_3\text{L})_2$      | no positive numbers                     | any ratio |
| $\text{Cu}(\text{H}_3\text{L})_2^{++}$ | no positive numbers                     | any ratio |
| $\text{Cu}_2(\text{H}_2\text{L})_2$    | $0.84 - 4.5 \times 10^4$                | 3:1       |
| $\text{Cu}_2(\text{H}_2\text{L})_2$    | $0.8 - 3.2 \times 10^4$                 | 2:1       |
| $\text{Cu}_2(\text{H}_2\text{L})_2$    | $0.26 - 3.9 \times 10^4$                | 1:1       |
| $\text{Cu}_2(\text{H}_2\text{L})_2$    | $0.7 - 3.0 \times 10^4$                 | 1:2       |
| $\text{Cu}_2(\text{H}_2\text{L})^{++}$ | $0.32 \times 10^4 - 1.2 \times 10^9$    | 2:1       |
| $\text{Cu}_2(\text{H}_2\text{L})^{++}$ | $0.12 \times 10^5 - 5.2 \times 10^{11}$ | 1:1       |
| $\text{Cu}_2(\text{H}_2\text{L})^{++}$ | $0.11 \times 10^5 - 5.0 \times 10^9$    | 1:2       |
| $\text{CuL}$ (for polymer)             | no positive numbers                     | any ratio |
| $\text{CuL}^{--}$ (for polymer)        | no positive numbers                     | any ratio |
| $\text{Cu}_2\text{L}$                  | no positive numbers                     | any ratio |

TABLE III  
DOUBLE COMPLEXES CONSIDERED AND RESULTS

| Two Complexes  | Value for Constant of First Complex | Result                     |
|--|-------------------------------------|----------------------------|
| $\text{Cu}(\text{H}_4\text{L})^{++}; \text{Cu}(\text{H}_3\text{L})^+$      | $10^2 - 10^5$                       | no positive numbers        |
| $\text{Cu}(\text{H}_4\text{L})^{++}; \text{Cu}(\text{H}_2\text{L})$        | $10^{-1} - 10^3$                    | $4.3 - 9.2 \times 10^{-4}$ |
| $\text{Cu}(\text{H}_4\text{L})^{++}; \text{Cu}_2(\text{H}_2\text{L})^{++}$ | $10^1 - 10^5$                       | $.86 - 5.1 \times 10^5$    |
| $\text{Cu}_2(\text{H}_2\text{L})^{++}; \text{Cu}(\text{H}_3\text{L})^+$    | $10^2 - 10^6$                       | no positive numbers        |
| $\text{Cu}(\text{H}_2\text{L}); \text{Cu}(\text{H}_3\text{L})^+$           | $10^2 - 10^6$                       | no positive numbers        |
| $\text{Cu}(\text{H}_4\text{L})^{++}; \text{CuL}(\text{polymer})$           | $10^2 - 10^6$                       | no positive numbers        |
| $\text{Cu}(\text{H}_4\text{L})^{++}; \text{CuL}^{--}(\text{polymer})$      | $10^2 - 10^6$                       | no positive numbers        |

species in the first buffer region which would not be solvated in the organic phase and (2) the formation of an insoluble compound of the partially or completely neutralized acid and copper.

## CHAPTER V

### SUMMARY AND CONCLUSIONS

If it is assumed that the proliferations of complexes, particularly those carrying a net charge, observed for pyromellitic acid also applies in mellitic acid solutions it is apparent that mellitic acid is not a suitable choice for a sequestering ligand. One possibility remains, however, that if the precipitation is soluble in alkaline media the extraction may be accomplished at high pH. Stability constants are large and the insolubility of the compound may be a result of propagation of the complex to produce a metallo-organic polymer. Delicate platelets were observed in titration vessel and a profitable pursuit may be to find the best experimental conditions for isolation of copolymers.

At this time no information is available as to the preferential separation of the metal ions by mellitate. In terms of wet chemistry a number of interesting studies remain.

The possibilities for future studies would include a potentiometric and spectrophotometric study of the first buffer region to understand the complex formation of the species present. Changing to a different ion of different charge seems to be an unprofitable direction because of the uncertainty of the complex formed.

Other possibilities would be searching for a negative organic ion that would form an ion pair so that the neutral species could be extracted. Also a different organic solvent with a lower solubility in water

could be sought. Blocking of coordination sites through selective esterification could be attempted as this would give information on the complex formation.

A final possibility would include changing to  $D_2O$  or methanol and an appropriate base and doing potentiometric titration coupled with an NMR study. This particular study would provide information where the metal in the metal complex is and if a charged species is really formed.

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