

TRANSITION METAL COMPLEXES OF ETHYLENE-
MALEIC ACID COPOLYMER

By

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MALEIC ACID COPOLYMER

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CHAPTER I

INTRODUCTION

Historical

In 1871 Hlasiwetz and Habermann¹ proposed that some naturally occurring substances, e.g., rubber, proteins, and gums were polymeric in nature. However, at this time acceptable organic research consisted of synthesizing and isolating pure compounds of known molecular weight which could be defined by a simple molecular formula. Herein lay much of the trouble which led to the early confusion in polymer chemistry. Chemists had believed for years that rubber, proteins, and gums were made from colloidal aggregates of small molecules held together by some undefined binding force. The belief grew that all substances could under proper conditions be transformed to a colloidal state, and conversely that all colloidal substances were physical aggregates of simpler molecules. This belief retarded the developments in the field of polymer chemistry for nearly half a century.

In 1929, W. H. Carothers² started a series of investigations in which polymeric molecules were prepared by established organic reactions and the properties of the products were correlated with polymer structure. The first "supermolecules" synthesized by Carothers had molecular weights on the order of 2500 to 5000. They were waxy materials incapable of being formed in fibers. It was not until he synthesized macromolecular materials with molecular weights greater than 15,000 to 25,000 that

distinctly new products were achieved. This work was particularly effective in breaking the last resistance to the new theories, opening up the field of polymer chemistry to the synthesis of polymers, and establishing polymer chemistry on a firm chemical footing. Even then the fundamental concept that high polymers are actually high molecular weight compounds with covalent bonds as the force binding atoms together was not generally accepted until after 1930.

In 1948 Fouss³ proposed the suitably fitting name polyelectrolytes for the group of substances which from the molecular point of view were polymers but whose electrochemical and solution properties bring them into the realm of electrolytes. Polymers of this kind differ from non-electrolyte polymers in the same way that low-molecular-weight electrolytes differ from non-electrolytes. They are soluble in polar solvents, conduct electricity, and are affected by Coulombic forces between the charges they possess. The configuration of the polyelectrolyte molecule in dilute solution may be greatly expanded by the electrostatic repulsion between its charged groups, and this effect manifests itself in some of the solution properties such as the intrinsic viscosity.

Types of Polyelectrolytes

Much of the early work was carried out on proteins⁴ and on synthetic organic ionizable polymers polyacrylic acid (PAA)⁵, polymethacrylic acid (PMA)⁵, and polyvinylamine (PVA).⁶ The ionizable groups on these polyelectrolytes are weakly acidic or weakly basic. Strongly acidic and basic polymers such polyvinylsulfonic acid (PVSA),⁷ polystyrenesulfonic acid (PSSA)⁸, and the quaternized form of PVA⁹ are also known and find an application as ion exchange resins. Polyphosphates¹⁰ are examples of

another class, the inorganic polyelectrolytes.

An interesting group of organic macromolecules from the point of view of electrolyte behavior are copolymers, and especially the hydrolyzed copolymers of maleic anhydride because the maleic anhydride residues are separated by at least one comonomer unit. Examples of these compounds are styrene-maleic anhydride (ST-MA)¹¹, vinyl ether-maleic anhydride (VEE-MA)¹¹ and ethylene-maleic anhydride (EMA)¹². Hydrolysis of these copolymers leads to macromolecules containing spaced pairs of carboxyls. The titration curves of such macroions have led them to be called "polydibasic acids."¹³

Solution Behavior of Polyelectrolytes

The behavior of these electrically charged polymers in solution is largely accounted for by a rather general picture in which the dominant concept is the electrostatic interaction between ionized groups in which the solvent serves as the continuous dielectric medium. Although this picture has provided useful models for the interpretation of typical phenomena, such as counterion binding and many transport properties, it should be considered a rather drastic oversimplification. In fact, in the rapidly developing field of solution properties of globular proteins, the structure of water surrounding the polyelectrolyte has been recognized as a factor of paramount importance in controlling conformational stability of the molecule.^{4,14}

In most cases though the study of polyelectrolytes is regarded as an extension of the studies on simple electrolytes. If the polyion has a well-defined shape, then the main distinction from simple electrolytes can be considered to be the high charge of the polyion. With flexible

chain polyions, the fixed charges may be separated from each other, to some extent, as the chain expands when the system is diluted. Nevertheless, effects produced by the interaction of ionic charges will not vanish in the limit of infinite dilution--as they do in solutions of simple electrolytes. The electrochemical behavior of polyions in solution also reflects the effect of the macroion on counterion binding,⁵ ionic activity coefficient,^{15,16} ion-pair formation,¹⁷ ionization equilibrium,^{18,19} and conductance.²⁰ Thus, it is clear that the problems of electrostatic repulsion of fixed charges and the electrochemistry cannot be strictly separated. It is this interdependence which contributes to the complexities and the fascination in this field.

A theoretical treatment which would incorporate all the characteristics of polyions in solution would be very difficult so a number of investigations have attempted partial solutions. Two of the prominent solution models were reported by Fuoss²¹ and Morawetz et al.²²--the rigid rod model--and Hermans and Overbeek²³ and Wall²⁴--the spherical model. The spherical model has been extended to resins and gels by Harris and Rice.²⁵

In dilute polymer solution Kirkwood and Westheimer¹⁹ were instrumental in separating polyelectrolytes from simple electrolytes with respect to ionization equilibria. Katchalsky and Spitnik¹⁸ derived an empirical approximation to describe the titration curve of polymeric acids. Activity coefficient corrections were applied to macromolecular solutions,^{16,26} but the most concentrated efforts to interpreting polyion activities was done by Nagasawa and coworkers.¹⁵

Kuhn,²⁷ in 1934, developed the theory that changes in the shape of polyelectrolytes in solution were not accompanied by any appreciable changes in the energy of the solution. The theories derived by Flory²⁸

and Huggins²⁹ were based on the same approach. These theories were supported by the so called θ solvent technique proposed by Flory.³⁰ In this theory the primary goal was the elimination of interactions between solute molecules so as not to contribute to the deviation from solution ideality. These solvation theories as applied to unionized polyelectrolytes are associated with ΔS° .

When a polyelectrolyte is ionized, the interactions between solute and solvent are identical to those of small ions only a larger contribution to the energy of the solution is made. For simple electrolytes the binding of a water molecule by an ion will lead to a decrease in entropy, negative ΔS ; and this decrease may be expected to be most marked with small ions and those of high charge such as an ionized macroion.³¹ The structure-breaking effect accompanying ionic solvation will result in a reduction of the number of hydrogen bonds as compared with the number in pure water.³² Shoolery and Alder³³ concluded that the principal effect of the large univalent electrolytes was to break down the water structure while multivalent ions predominantly polarized the water.

As an example, when alkali is added to VEE-MA, the coiled molecule begins to expand because of electrostatic repulsion between the charged groups.¹¹ This has marked effects on the properties, such as viscosity, of the solution. In the absence of added salts the chain of the neutralized acid appears to be almost fully extended which in turn rearranges the water molecules causing ΔH° to change. Thus, ΔH° and ΔS° are of potential value to a better understanding of polyionic processes in solution; and when the role that the solvent plays is better understood, significant new advances can be expected.

Current Applications

Even though the solution properties of macroions are not thoroughly understood, successful industrial applications for them are numerous. One of the most successful is the use of EMA copolymers as carriers for immobilizing enzymes.³⁴ Insolubilized enzymes bound to EMA have application in most industries using microbial or enzymatic processes. They also have application in analytical and clinical chemistry as well as remedial medicine. The cost of insolubilizing enzymes on carriers such as EMA can be minimized by the ability to recover and recycle the EMA and the enzymes.

Polyelectrolytes have also been used in the pollution abatement of heavy metal ions from industrial waste streams.³⁵ Natural systems--alginic acid with gelatine and polygalacturonic acid--as well as synthetic systems--PMA and polyethylen-imine--are examples of polyions which have effectively removed transition metal ions from waste streams by forming the appropriate complexes. In this process both the metal ions and the polymer can be recycled thus lowering costs for this recovery method. Although EMA--the copolymer chosen for this study--has not been applied to this particular recovery method, the possibility does exist that it could be, and the knowledge gained by this investigation will be valuable when considering new systems for pollution control.

Statement of the Problem

The first requirement was to find a polymer which was well-defined but most well-behaved. A polymer is considered to be well-behaved if the polymer with complexing capabilities has the groups of ligands sufficiently separated from one another along the polymer chain so as to behave independently of one another in an analogous manner to a low molecular weight

chelating agent. Hydrolyzed ethylene-maleic acid (HEMA) was the polymer chosen for the study. It has several advantages. The monomeric unit--2,3-dimethyl succinic acid--is available for study; the absence of hydrophobic bonding in the copolymer backbone. This characteristic contributes to the well-behaved requisite. The well-defined requirement has been outlined in Technical Bulletin I-261 of the Monsanto Chemical Co., and from kinetic and infrared studies.¹² Another advantage for having chosen HEMA is that succinic acid, which is structurally related to the copolymer, and the transition metal complexes of succinic acid have been extensively studied.^{32,36,37}

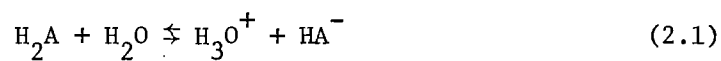
Previous studies of metal ion-polymer complexation have led to conflicting results. Some of the stabilities reported have been low^{38,39,40,41} (~100) while other stabilities reported are high (> 10⁵).^{42,43} As a result, this study was initiated to bring to light some of the complications encountered in polymer system complexation.

CHAPTER II

THEORY AND BACKGROUND

Dibasic Acid General Equations

The thermodynamic ionization constants (K_i^0) of a dibasic acid defined for the equilibrium reactions



are given by

$$K_1^0 = (a_{\text{H}^+})(a_{\text{HA}^-}) / (a_{\text{H}_2\text{A}}) \quad (2.3)$$

and

$$K_2^0 = (a_{\text{H}^+})(a_{\text{A}^-}) / (a_{\text{HA}^-}) \quad (2.4)$$

To calculate the respective K_i 's the following equations are used: the ionization constant of water

$$K_w = (a_{\text{H}^+})(a_{\text{OH}^-}) \quad (2.5)$$

the mass balance condition for the total acid concentration, a

$$a = [\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^-] \quad (2.6)$$

the electroneutrality condition

$$b + [H^+] = [HA^-] + 2[A^{2-}] + [OH^-] \quad (2.7)$$

where b represents the concentration of base added in the titration of H_2A the definition of the ionic strength, μ

$$\mu = \frac{1}{2} \sum_i z_i^2 C_i \quad (2.8)$$

where z_i is the charge on the ion and C_i is the concentration of the ion and the activity of an ion X , a_x , is defined as the concentration of X , $[X]$, times the activity coefficient of X , f_x . One of the functional forms derived for the activity coefficient is

$$-\log f_i = 0.509 z_i^2 \{ \mu^{1/2} / (1 + Ba) \mu^{1/2} - C\mu \} \quad (2.9)$$

where $i = 1$ or 2 for a dibasic acid, $Ba = 1$ and $C = 0.3$. This is the extended form of the Debye Hückel equation developed by C. W. Davies³¹ accurate to $\mu = 0.1M$.

To satisfy Equation (2.7), the hydrogen ion concentration must be introduced. The procedure used to calculate the ionization constants is usually a standard reiteration around the above equations terminated by convergence on a particular parameter, e.g., f_x . After determining the hydrogen ion concentration, the concentration of the other acid species in solution can be determined.

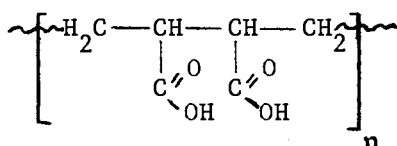
The total acid concentration Equation (2.6) can be rewritten in terms of H_2A and the cooperative product of dissociation constants by appropriate substitution in the dissociation constant expressions to yield a form of the equation suitable for reiteration

$$a = \left[1 + \frac{K_1}{\{H^+\}f_1} + \frac{K_1K_2}{\{H^+\}^2f_2} \right] [H_2A] \quad (2.10)$$

Which in turn allows one to calculate the thermodynamic dissociation constants using concentrations and activity coefficient corrections for acids with two distinct buffer regions and whose first ionization occurs from a neutral molecule.

Polymeric Dibasic Acid Equations

In contrast to simple dicarboxylic acids, polymeric acid systems treated as dibasic acids



cannot be described completely from the equations for simple dibasic acids. For as pointed out in Chapter I, the interactions of ionic charges of polyelectrolytes do not vanish at infinite dilution as they do for simple electrolytes; therefore, the possibility of calculating constant K_i 's is eliminated. In an attempt to correct for the inability to obtain a constant K_i , several parameters were introduced. One of the parameters which helps to describe a polymer system is the degree of dissociation, α . For a system such as the example given above, α is given by

$$\alpha_1 = [HA^-]/(1 - [HA^-]) \quad (2.11)$$

for the first buffer region and

$$\alpha_2 = [A^{=}] / (1 - [A^{=}]) \quad (2.12)$$

for the second buffer region where the concentrations of the polymer ions are given in monomoles/liter. (One monomole consists of one residue of maleic anhydride and one of ethylene for EMA). This definition which is convenient because each polyacid carries two different classes of carboxyl groups leads to $\alpha = 2$ at complete ionization.

The Henderson-Hasselbalch equation

$$\text{pH} = \text{pK} + \log[\alpha/(1 - \alpha)] \quad (2.13)$$

uses α as a parameter. If the pH values of simple acids are plotted against $\log[\alpha/(1 - \alpha)]$, straight lines with a slope of 1 are obtained. However, for polymeric acids the slope is greater than 1 for the first dissociation of "polydibasic" acids and for PMA the slope approaches 2.¹⁸ As a result of this variance, Katchalsky¹⁸ introduced the parameter n into the empirical Henderson-Hasselbalch equation. The Katchalsky form corrected for activity coefficients is given by

$$\text{pH} = \text{pK}_i + n \log[\alpha/(1 - \alpha)] - A\mu^{1/2} \quad (2.14)$$

where $i = 1$ or 2 and A is the Debye Hückel constant.

To determine n for the copolymer under study one plots pH against $\log[\alpha/(1 - \alpha)]$ for both buffer regions. For substituted ethylene-maleic acid copolymers, as a rule n is slightly greater than 1 for the widely spaced first carboxyl groups and is greater than 2 for the ionization of the second carboxyl groups.¹¹ After determining the value of n for each buffer region, the correction is combined with the appropriate pK to obtain $\text{pK}_{i,\text{app}}$ --the apparent dissociation constant--which is related to pH by the equations

$$\text{pH} = \text{pK}_{1,\text{app}} + \log[\alpha/(1 - \alpha)] - 0.509 \mu^{1/2} \quad (2.15)$$

for the first buffer region and

$$\text{pH} = \text{pK}_{2,\text{app}} + \log[\alpha/(1 - \alpha)] - 1.527 \mu^{1/2} \quad (2.16)$$

for the second buffer region.

These two equations were used during this study to determine apparent association constants between the transition metal ions and HEMA.

Another method of treating polyacids is to make a correction for electrostatic effects. If the polymer is treated as a rodlike model and if it is assumed that the only reason successive ionizations in the polymer differ is a statistical effect, an electrostatic correction is added to Equations 2.15 and 2.16. The general form is

$$\text{pH} = \text{pK}_{i,\text{app}} + \log[\alpha/(1 - \alpha)] + 0.434 e\psi_{e1}/kT \quad (2.17)$$

where $e\psi_{e1}$ is the electrostatic potential necessary to remove H^+ against the strong forces of the charges already present in the molecule. Since the magnitude of ψ_{e1} should be dependent on the effects of nearest charged groups, the potentiometric titration curves should reflect the differences in the conformations of the polyions because the charge separations of the carboxyls are not far enough apart to be considered noninteracting. Nagasawa and coworkers^{44,45} and Gregor and Kagawa⁴⁶ have studied this electrostatic influence in atactic, isotactic, and syndiotactic PAA and PMA. These authors concluded that to verify unambiguously that the observed differences between the titration curves of the three conformational forms is very difficult and, as a result, the differences have been attributed to the flexibility of the polymer chain (i.e., the polymer is not rodlike). It would be desirable then to take into account the flexibility of the polymer backbone in the theory. Until the theory is extended the application of the rodlike model should be restricted to

relatively stiff polyelectrolytes or to data at a high degree of neutralization.

Electrostatics of Ionization

In discussions of strengths of dicarboxylic acids, the main interest has usually been around the relative magnitudes of the first and second dissociation constants. In the general case the ratio of successive constants K_1/K_j ⁴⁷ is given by

$$K_1/K_j = (j(n - i + 1))/(i(n - j + 1)) \quad (2.18)$$

which for a dibasic carboxylic acid with noninteracting carboxyl groups reduces to

$$K_1/K_2 = 4 \quad (2.19)$$

A measure of the electrostatic influence of the carboxylate group on the carboxyl group is generally described as the deviation of the ratio K_1/K_2 from the statistical factor of 4. Bjerrum⁴⁸ was one of the first to attempt to correlate ionization constants and molecular structure. He developed an electrostatic model for dibasic acids to predict the ratio of K_1/K_2

$$K_1/K_2 = 4 \exp \left(\frac{-ze^2}{rkT\epsilon} \right) \quad (2.20)$$

where z is the net charge left by the first ionization (-1 for dicarboxylic acids), e is the charge on the proton (4.80×10^{-10} esu), r is the distance in cm of the proton to be ionized from the charge already present, k is the Boltzmann constant (1.38×10^{-16} erg/deg-molecule), ϵ is the bulk dielectric constant of water (79 at 25°C), and 4 is the statistical factor for a

dibasic acid derived from Equation (2.18). In the model proposed by Bjerrum the acid is treated as a molecule without structure and without volume in a continuous dielectric medium with ϵ equal to that of the bulk dielectric constant of the solvent. In reality the leaving H^+ must pass through the solvent. The dielectric constant must be affected and therefore less than the bulk value.

Kirkwood and Westheimer⁴⁹ (K-W) later developed a model to account for this reduced dielectric constant. In this model the dielectric constant is treated as essentially an adjustable parameter. Even this treatment is an oversimplification because the K-W theory provides an algorithm based upon electrostatics for the calculation of the effective dielectric constant. These models establish that electrostatic effects are undeniably important, but other effects such as stereochemical effects also contribute to the ionization constants.

Stereochemical Influence on Ionization Constants

In recent years chemists have become increasingly aware of the stereochemical effects on the ionization constants of diastereoisomeric acids. Disubstituted succinic acid are among the group of acids which have been studied extensively; two of the more interesting ones are 2,3-dimethylsuccinic acid (2,3-DMSA) and tartaric acid. These two dicarboxylic acids exist in three forms---two optically active forms (d and l) and one optically inactive form (meso). Several investigators^{50,51,52,53,54} have unambiguously determined the dissociation constants for several disubstituted succinic acids. Until the work by these authors, precise conductivity and potentiometry determinations of the 2,3-disubstituted succinic acids were rare. Since diastereoisomers of 2,3-DMSA and tartaric acid contain identical atoms and bonds, the internal elec-

tronic displacement must be the same. It is therefore reasonable to suggest that the observed differences in strengths arise from the interactions between groups and atoms in space.⁵⁰

A study has been performed⁵³ which demonstrates the effects on the acid dissociation constants of mixing the diastereoisomers. Mixtures of the isomers would be expected to give weighted averages of K_1^O and K_2^O as a function of both the molar ratio of d,l/meso and the degree of ionization. This expected relationship has been established for 2,3-DMSA and tartaric acid.

If a polymer has the ability to statistically arrange itself in the optically active form and the optically inactive form in the backbone, then the presence of these isomeric forms influence the acid dissociation constants of the polymer just as it occurs in the mixed monomers of 2,3-DMSA and tartaric acid. This possibility certainly does exist for EMA which is polymerized by a radical mechanism, since the group at the active end of the growing chain is almost certainly planer and the steric configuration has not been fixed until another monomer unit has been added.⁵⁵

This is not to imply that these stereochemical interactions extend ad infinitum. Gane and Ingold⁵⁶ have concluded that the internally transmitted effects become negligibly small after propagation through two or at the most three saturated carbon atoms. However, as in the case of some polymers (e.g., PAA and PMA), separation of carboxyl groups does not occur over two or three carbon atoms so interference in determining dissociation constants must be prevalent from internally transmitted effects (i.e., all carboxyl groups are equidistant thus no distinct buffer regions exist in the titration curves). For copolymers of the type HEMA, ST-MA, and VEE-MA, the carboxyls are arranged in dibasic groups and can be assigned two different dissociation constants.¹³ The stereochemical effect cannot

be disregarded in these "polydibasic acids"; even though, it should not be as prevalent as in PAA. By employing Equations (2.15) and (2.16) when determining the dissociation constants, one can approach a constant number, but the ability to use weighted averages of K_1 and K_2 as a molar ratio of d,l/meso and α should allow one to attain a "complete" dissociation constant. Without the thermodynamic constants one can only determine the apparent association constants between metal ions and polyions as opposed to the feasibility of determining thermodynamic constants for the monomeric counterparts.

Ligand-Metal Ion Interactions

For succinic acid and divalent transition metals, Nancollas and coworkers^{36,37} have determined that two complex species exist in solution. The formulation of the complexes are given by



and



where HA^- and $A^{=}$ correspond to monomeric residues at different stages of ionization. However, for polymeric acids in which each monomeric unit is treated as a dibasic acid the data conform to an analysis in which only one complex (MA) is formed. The thermodynamic stability constant expression for this complex is given by

$$K_{MA}^0 = [MA]/[M^{2+}][A^{=}]f_2^2 \quad (2.23)$$

where the concentrations are given in moles/liter and f_2 is the mean activity

coefficient of the divalent ions. The ionic species concentrations may be calculated from the following equations: the total metal ion concentration, m

$$m = [M^{2+}] + [MA] \quad (2.24)$$

the total polymer concentration in terms of moles of monomer, a

$$a = [H_2A] + [HA^-] + [A^{=}] + [MA] \quad (2.25)$$

the electroneutrality

$$b + [H^+] + 2[M^{2+}] = [HA^-] + 2[A^{=}] + 2m \quad (2.26)$$

where b is the concentration of base added in the titration the ionic strength, μ

$$\mu = b + [H^+] + 3[M^{2+}] + [A^{=}] \quad (2.27)$$

The method chosen to evaluate Equation 2.23 was reiteration around Equations 2.24, 2.25, 2.26, and 2.27 to a convergence of f_i , the activity coefficient (Equation 2.9).

Influence of Counterion Binding and Neutral Salts

While the titration behavior of low molecular weight acids and bases is independent of the nature of the base or acid used as a titrant, this is not the case with polymeric acids and bases. Gregor and Kagawa⁴⁶ observed that the titration behavior of polymers was dependent in part on the specific acid or base used indicating that polyelectrolytes further complicate the titration curve by binding the counterions of the titrant. This is considered one of the more important characteristics of macroions.²⁴

Katchalsky and Spitnik¹⁸ studied the effect of CaCl_2 and NaCl on PMA at half-neutralization. The pH decreased in the presence of the salts and continued to decrease with increasing concentration of the salts. This result is indicative of ion binding and demonstrates the futility of titrating polyelectrolytes in the presence of varying concentrations of neutral salts.

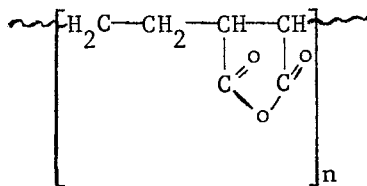
All these interactions 1) the degree of ionization, 2) the electrostatic effect, 3) the stereochemical effect, 4) counterion binding, and 5) the salt effect must be considered to gain an appreciation for the difficulties encountered in determining the thermodynamic constants of polyelectrolytes and metal complexes in which the polyelectrolytes participate as ligands.

CHAPTER III

EXPERIMENTAL

Description of the Polymer

The alternating 1:1 copolymer of ethylene and maleic anhydride was synthesized by Hanford⁵⁷ in 1945. Machi, et al.¹² also synthesized and studied EMA. The infrared spectrum had the characteristic peaks which indicated that the copolymer was composed of the methylene group of the ethylene monomer and the cyclic anhydride of the maleic anhydride monomer. From the spectrum Machi and his coworkers determined that the extent of sequence addition was negligible. Later the research personnel of the Monsanto Chemical Company under the supervision of Johnson⁵⁸ synthesized the copolymer and made extensive studies of the chemical and physical properties of EMA. The linear derivatives commercially available have molecular weight ranges of 2 - 3,000, 20 - 30,000, and 60 - 70,000. The scope of this study involves the 20 - 30,000 derivative which has the structure



where $n = 170$.

Preparation of Solutions

Deionized H₂O

The deionized water used in all experiments was prepared by passing distilled water through about 3 ft. of reagent grade Rexyn #300 (H-OH) mixed bed resin (Fisher Scientific Co., Inc.). The water was then passed over a 3 ft. column of activated charcoal and stored in two twelve liter flasks, which were vented to the atmosphere through Ascarite (8 - 20 mesh) (Arthur H. Thomas Co.) to remove CO₂.

Standard Base

The standard tetramethylammonium hydroxide (QOH) was prepared from a 10% by volume stock solution of tetramethylammonium hydroxide supplied by Eastman Organic Chemicals. 100 ml of the stock QOH was added to 900 ml deionized water which had been swept free of CO₂ and stored under a nitrogen atmosphere for approximately two hours at room temperature prior to the addition of QOH. The resulting solution was standardized potentiometrically against approximately 2.5×10^{-3} moles of dry, chemically pure potassium acid phthalate (Baker) dissolved in deionized H₂O free of CO₂. In all instances the concentration of the base was approximately 0.1M.

Ethylene-Maleic Acid

In order to prepare the acid with a concentration of 0.01M--based on monomer molecular weight, about 0.5 grams of the copolymer, EMA, was hydrolyzed to the acid (HEMA) by warming approximately 400 ml of deionized water with the anhydride at 70 - 80° for a period of 2 hours. The solution was cooled, filtered and made up to 1 liter. Solutions were stored in

Pyrex containers at 5° because bacteria and mold readily consumed the polymer at room temperature.

Metal Perchlorates

Chemically pure transition metal perchlorates as the hexahydrates were purchased from G. Frederick Smith Chemical Company. The solutions were approximately 0.05M in metal ion. Standardization of the solutions was done by passing two ml aliquots through a column loaded with acidic Dowex 50-W-X8 20 - 50 mesh exchange resin. The column was then washed with 100 ml of deionized water. The eluted acid was titrated potentiometrically with standardized QOH. Solutions were stored at room temperature in Pyrex containers.

Apparatus

Glassware

The titration cell used in this study was a 200 ml round-bottom flask modified to allow access to the solution for two calomel electrodes, two glass electrodes, and delivery tubes for nitrogen and the titrant, QOH. (Figure 1)

A 50.00 ml Kimax class A automatic buret with a readability of 0.01 ml equipped with a drying tube filled with Ascarite to exclude CO₂ and indicating silica gel to exclude atmospheric water was used to dispense the QOH.

Potentiometer

A Beckman research pH meter Model 1019 with a readability of 0.05 mV. and a standard deviation of 0.051 mV. was used for all experimental emf measurements.

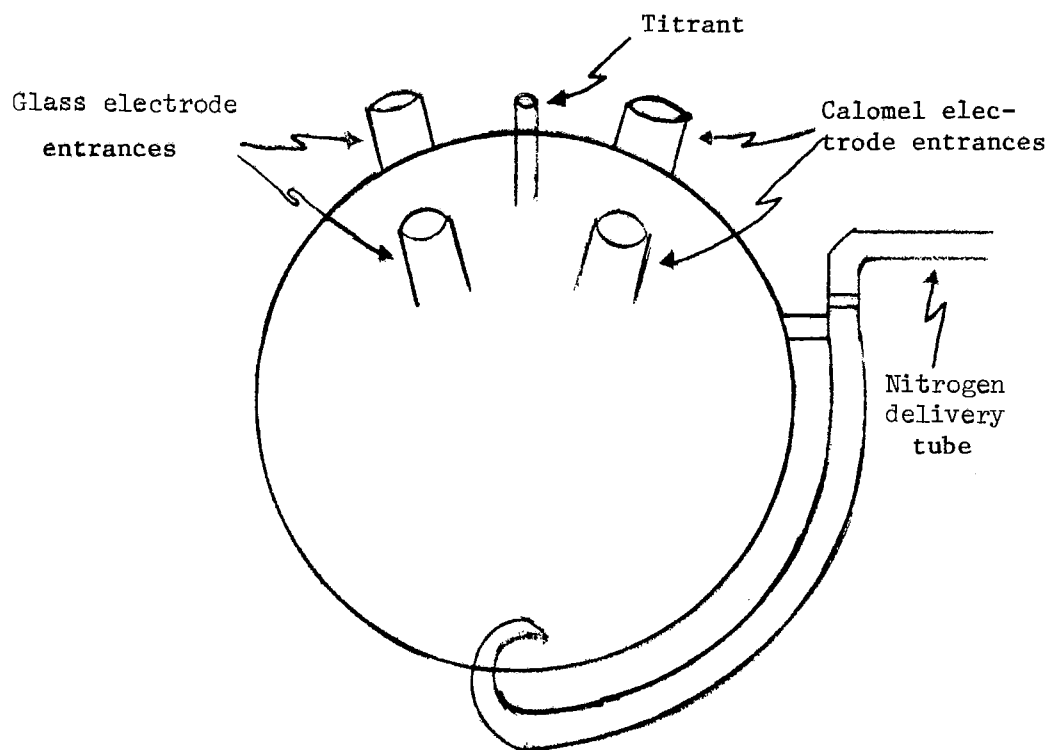


Figure 1. Titration Vessel

Electrodes

The electrode system consisted of commercial glass electrodes (Beckman 39301) with Ag/AgCl internal elements in reference solutions of 1.0M HCl as indicator electrodes and calomel electrodes prepared in this laboratory as reference electrodes. The glass electrodes were allowed to equilibrate approximately one week in a buffer solution of pH 4.008 prior to use and between titrations.

Commercial reference electrodes, Beckman 39071 Frit Junction Calomel Reference Electrodes, were found to be unsatisfactory when adequate reproducibility could not be achieved with time in standard buffer solutions. The inconsistency was attributed to the nonreproducible liquid junction across the frit.

In an attempt to achieve reproducibility, the reference calomel electrodes were prepared by the method described by Vogel⁵⁹ and consisted of aqueous saturated potassium chloride solution and calomel paste (Figure 2). Junction with the solution under study was made via an aperture (0.01 mm) which proved to be reproducible. After the calomel electrodes were prepared, they were allowed to equilibrate for at least eight hours before use. Before using the electrodes, a few drops of fresh salt solution were drained from the side-arm and the stopcock closed prior to immersing the tip in the solution under study. A cell constructed with these components would typically produce the same emf in a buffer solution of 4.008 pH to within 0.2 mV. over an extended period of normal use. Because the only electrical contact made was around the closed stopcock, this reduced the chance of a change in the ionic strength of the 0.01M solution under study from excessive leakage of the saturated KCl solution of the calomel electrode. If 0.01 ml of the saturated KCl solution (about 4.5 M at 25^o) were to leak into the solution under study which consisted of a perchlorate

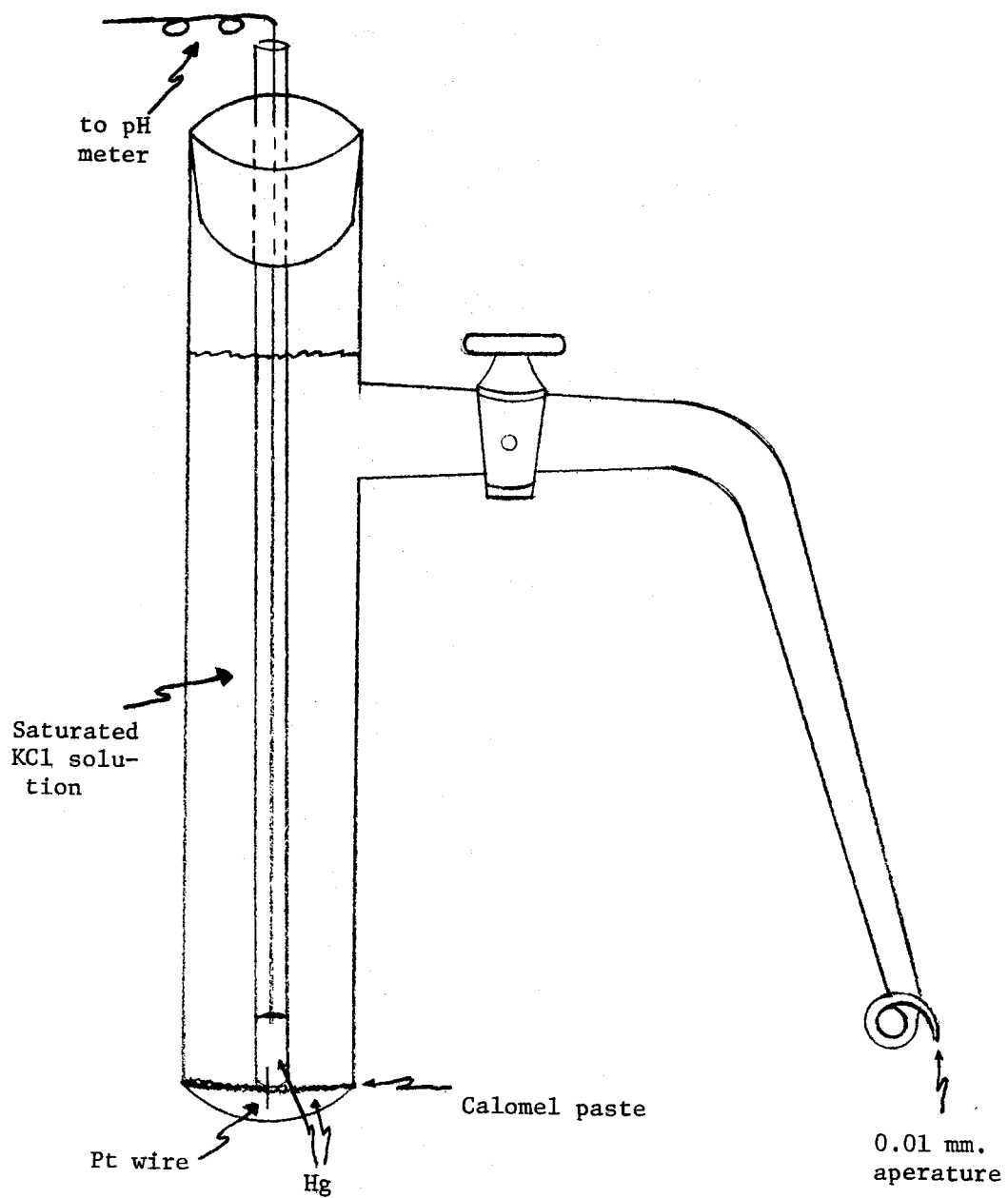
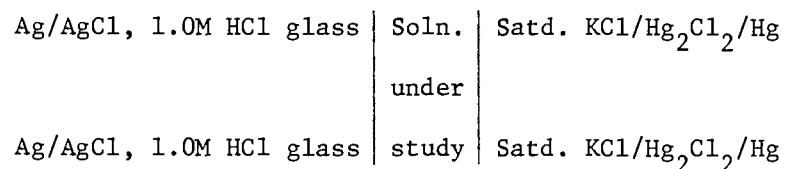


Figure 2. Calomel Reference Electrode

concentration of 2.7×10^{-3} , the solubility product constant of KClO_4 would be exceeded. This particular complication was not encountered during this study.

Emf measurements were made at $25 \pm 0.05^\circ$ with a cell of the type



This cell allowed four measurements of emf to be made at each point during the titration and served as an internal check on the electrode system. If the differences in the emf between each calomel and a single glass electrode were greater than 0.3 mV., the measurements were discarded from further calculations. If no mechanical or electrical failure could be found for the discrepancy, the calomel electrodes were remade.

To compensate for differences in the emf's measured between two glass electrodes and one calomel, a calibration procedure was devised to correct for the deviation of asymmetry potentials, e_a , of the glass electrodes. When these variations attributed to e_a exceeded 4 mV., the glass electrode was replaced.

Procedure

Calibration of Glass Electrodes

Glass electrodes are reversible to hydrogen ions but are not primary electrodes and must be calibrated relative to primary standards. This is done by testing the linear response of the cell emf with pH ($\text{pH} = -\log a_{\text{H}^+}$). The two buffer solutions normally used to calibrate the system were NBS standard potassium acid phthalate ($\text{pH} = 4.008$ at 25°C , 0.0500M) and borax

(pH = 9.18 at 25° C, 0.0100M). The system was calibrated before and after the titration experiment. From the observed emf's the Nernst slope k --the linear response--was calculated using the equation

$$k = (E_{4.008} - E_{9.180}) / (9.180 - 4.008) \quad (3.1)$$

where $E_{4.008}$ and $E_{9.180}$ are the emf's in the respective buffer solutions. The glass electrodes were replaced if the value of k varied from the theoretical value, 0.0592 V at 25° C by more than 0.3 mV. Using k , the pH of an unknown solution was calculated from

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

where E_{obs} was the measured emf of the solution under study at each point in the titration. The assumption of a linear response to pH was checked occasionally by the measurement on a 0.02500 M KH_2PO_4 - 0.0250 M Na_2HPO_4 solution which has been defined by NBS to have a pH of 6.86 at 25°C. The results were always within experimental error.

Titration of Solutions

The titration cell was immersed in a water bath in which the temperature was controlled to $25 \pm 0.05^\circ \text{C}$ with a Braun Thermomix II circulator-heater. All emf measurements, electrode calibrations and titration experiments, were made in a solution purged of carbon dioxide by a stream of nitrogen gas. Nitrogen was bubbled through the solution under study for approximately 30 minutes prior to the potentiometric measurements and continued during the experiment by forcing nitrogen through the solution at a slow rate. The nitrogen also served as a means of stirring the solution.

After the system was calibrated, a 50.00 ml aliquot of HEMA was added

to the empty titration vessel. If a metal complex were being analyzed, the appropriate divalent transition metal perchlorate solution was added to the cell in the ratios of analytical concentrations of metal to polymer of approximately 2:1, 1:1, and 1:2. Thermal equilibrium with the bath was rapidly attained. With the exception of the HEMA neutralization curves, this work consisted of a study of the first buffer region principally because precipitation of the metal ion-polymer complex prevented the analysis of the second buffer region.

CHAPTER IV

EXPERIMENTAL RESULTS AND DISCUSSION

Acid Dissociation Constants

As discussed in Chapter III, the measurements were made with a glass electrode-calomel electrode assembly. HEMA, the acid selected for study, is a substituted polymeric succinic acid, but, unlike succinic acid or 2,3-DMSA, the buffer regions are quite distinct. Since $K_1 > 10^3 K_2$, two separate buffer regions are developed and essentially two equivalents of base are required to neutralize each repeating dicarboxylic acid unit of the polymer.

Table I contains a sample set of experimental data. All of the data necessary to calculate K_1 and K_2 is contained in Table I. Five to twelve measurements of pH were made in each buffer region to calculate the ionization constants. About three minutes were required to obtain each data point; the total titration took approximately $1\frac{1}{4}$ hours, and the emf's of the buffer solutions, $E_{4.008}$ and $E_{9.180}$, agreed to within 0.2 mV. before and after the titration.

It has been inferred that one carboxylic acid group from each adjacent pair is preferentially dissociated, leading to the first inflection in the titration curve (Figure 3a). At 50% of the total neutralization the electrical charge density might be considered to be uniformly distributed throughout the molecule. The data were treated using the Katchalsky¹⁸ form of the Henderson equation corrected for activity coefficients (Equations

TABLE I
TYPICAL TITRATION DATA OF HYDROLYZED ETHYLENE-MALEIC ACID

Base Vol. ml	EMF mV x 100	Base Vol. ml	EMF mV x 100
0.0	2.332	4.5	-0.057
1.0	1.759	5.1	-0.522
1.6	1.488	5.6	-0.806
1.8	1.406	5.8	-0.904
2.0	1.329	6.0	-1.036
2.2	1.269	6.2	-1.126
2.4	1.190	6.4	-1.238
2.6	1.116	6.6	-1.340
2.8	1.029	7.0	-1.562
3.0	0.968	7.5	-1.846
3.5	0.735	8.0	-2.121
4.0	0.377	9.0	-2.472

Acid concentration = 9.945×10^{-3} M; Base concentration = 0.1103M;
Initial volume of acid = 50.00 ml; T = 25°C; $E_{4.008} = 0.1788$ V.;
 $E_{9.180} = -0.1256$ V; $pK_W = 14.00$.

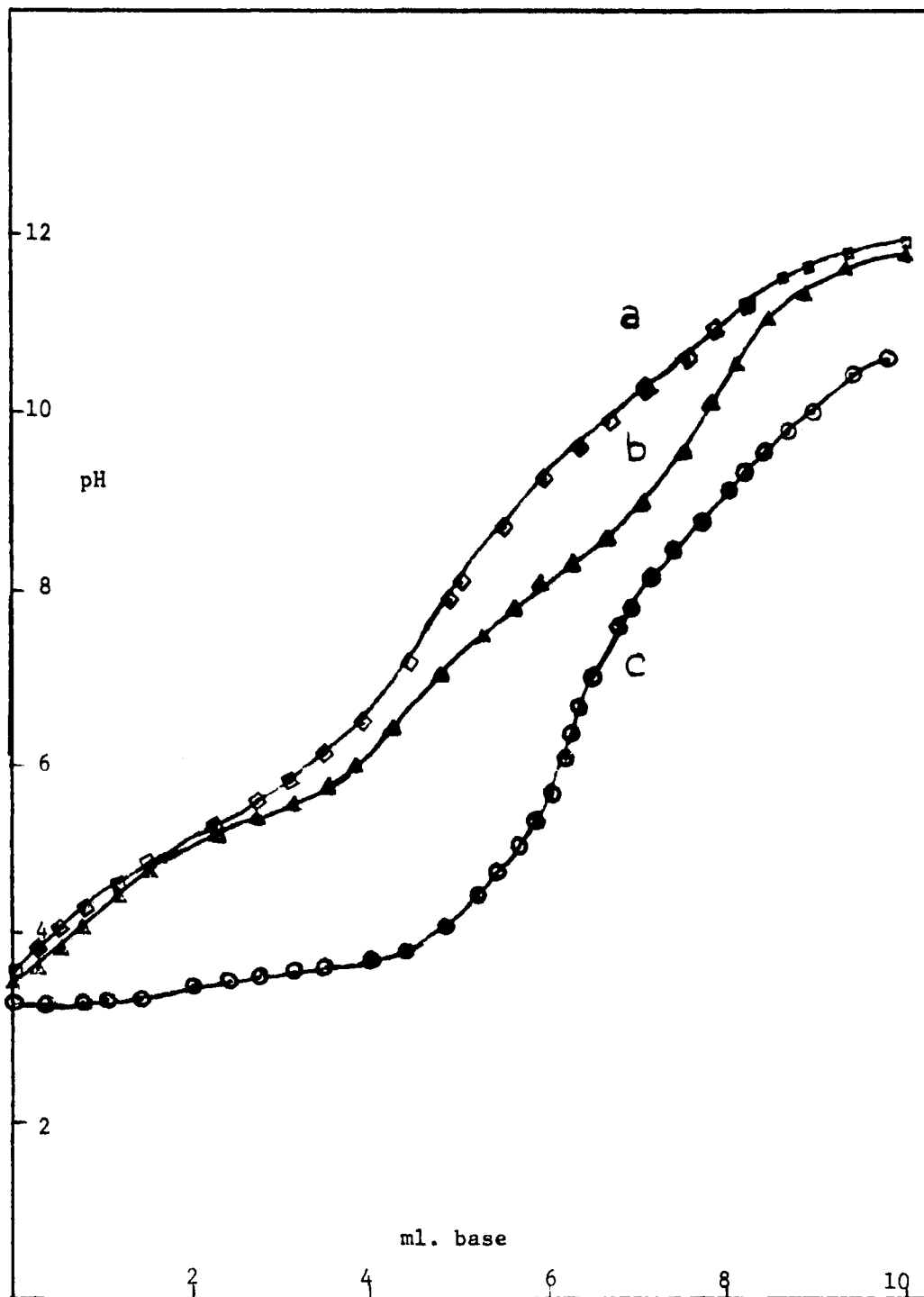


Figure 3. Typical HEMA Titration Curves Plot of pH Versus ml. Base for HEMA-QOH, HEMA-KOH, and HEMA-Cu²⁺ Titrated With QOH

2.15, 2.16, and 2.9). Values for n in the Katchalsky equations determined from the slopes of the plots of pH versus $\log[\alpha/(1 - \alpha)]$ for both buffer regions were 1.5 and 2.2 respectively. The pK values from Equations 2.15 and 2.16 relate to the ionization constants at the midpoints of the respective buffer regions. The manner in which the dissociation constant, pK_1 , apparently varies with α is illustrated in Figure 4a, where $\alpha = 1$ corresponds to the half-neutralization point. The apparent dissociation constant, $pK_{1,app}$, is related to pH by Equation 2.15. The smooth curve is an indication that the elongation of the polyion on neutralization is not complicated by an additional configuration transition; consequently, the treatment of the data is simplified. For comparison, the variation of pK_1 with α for hydrolyzed n-butyl vinyl ether-maleic acid copolymer is included (Figure 4b). This curve is typical of the dependence of $pK_{1,app}$ on α when a compact coil to random coil transition is induced by ionization.⁶⁰ The curves are for analogous copolymers differing only in the side-chain substituents and should coincide at values of α greater than 0.7. They do not because activity coefficient corrections have been made only for HEMA.

The results in Table II were obtained from the data presented in Table I. The carboxylic oxygen atoms are more basic in HEMA than in succinic acid and 2,3-DMSA, owing in part to the inductive effect of the ethylene moiety of the polymer. For the second dissociation in particular, the large difference in basicity also reflects the increased difficulty in removing a proton from the highly charged polyion.

Since the analytical method is potentiometry, a complication may arise from competitive ion binding by the cation of the base used. Alkali metal ions are generally poor participants in ion association unless the ligand is highly charged. This phenomenon is not, however, unknown for lithium

TABLE II
HYDROLYZED ETHYLENE-MALEIC ACID IONIZATION CONSTANTS

Base Vol ml	1st ioniza- tion, %	$pK_{1,app}^a$	$K_{1,app}$ $\times 10^{+5}$	Base Vol ml	2nd ioniza- tion, %	$pK_{2,app}^b$	$K_{2,app}$ $\times 10^{+10}$
1.80	42.5	4.847	1.42	5.80	36.8	9.119	7.60
2.00	47.2	4.913	1.22	6.00	41.6	9.234	5.83
2.20	52.0	4.971	1.07	6.20	46.3	9.318	4.81
2.40	56.7	4.998	1.01	6.40	51.0	9.415	3.85
2.60	61.4	5.044	0.90	6.60	55.7	9.515	3.06

^a Mean $pK_{1,app}$ = 4.956; Mean $K_{1,app}$ = 1.11×10^{-5} ; Mean pK_1 = 4.965; Mean K_1 = 1.08×10^{-5} .

^b Mean $pK_{2,app}$ = 9.320; Mean $K_{2,app}$ = 4.79×10^{-10} ; Mean pK_2 = 9.602; Mean K_2 = 2.50×10^{-10} .

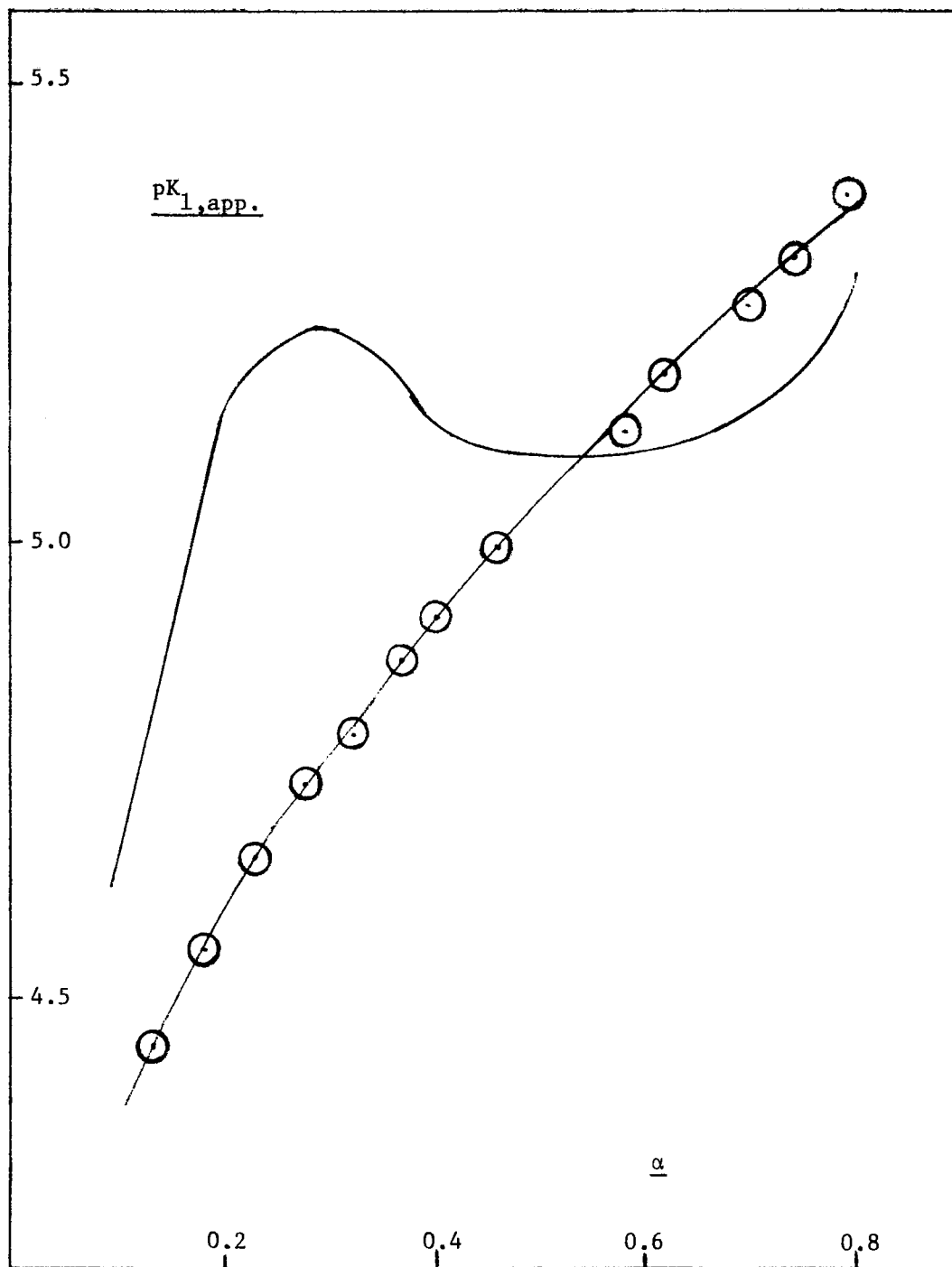


Figure 4. Plot of $pK_{1,app}$ Versus α for HEMA and n-Butyl Vinyl Ether-Maleic Acid

and sodium ions with acetic acid at relatively high alkali ion concentrations.⁶¹ In PAA, low concentrations of lithium, sodium, and potassium have been observed to depress the pH titration curve. This depression has been attributed to cation-polyion interactions rather than to specific salt effects.⁶²

Metal Complexes

The interaction of polyelectrolytes with their counterions is particularly interesting, since polymers constitute a unique type of chelating agent--intermediate between monomeric ligands and ion-exchange resins. The counterions studied were the divalent ions of the transition metals manganese, cobalt, nickel, copper, zinc, and cadmium. In Figure 3c, a typical potentiometric curve is shown with the copper (II) ion present. By analogy with the divalent transition metal succinates^{36,37} at similar analytical concentrations of reagents, one might anticipate the two complex species MHA^+ and MA to exist in solution for at least some of the metal ions. However, analysis of the emf data from experiments in which the ratio of the analytical concentrations of metal and polymer were approximately 2:1, 1:1, and 1:2 indicated that the system could be satisfactorily interpreted in all cases by the consideration of only one complex (MA) (Equation 2.22). The thermodynamic stability constant expression is given by Equation 2.23. The concentration of ionic species in the stability constant expression may be calculated as discussed in Chapter II.

Because the acid dissociation constants are known to be concentration dependent⁴⁶, the initial acid analytical concentration was kept constant in all titrations with metal ion present. At higher concentrations of A^- , as would be obtained in the second buffer region, higher complexation is possible



Analysis of the data was not always possible because of precipitation especially when the metal ion was in excess.

It has been proposed¹³ that the concept of ionic strength has meaning in polymer solutions only if the product $e\psi_{e1}$ in the extended Henderson-Hasselbalch equation is less than kT (Equation 2.17). In the present case the maximum value of $e\psi_{e1}$ calculated from the last point used in the first buffer region is $0.7 kT$. Therefore, some confidence is gained for the ability to apply the interionic-attraction theory to this system, and it is encouraging that even in its present form, without elaborating on the solution model, constant values for stabilities of metal complexes can be approached. Furthermore, when no activity corrections are made, the "stabilities" calculated are not by any means constant. It should be possible to vary the model by examining the dependence of K_{MA} on changing the parameters Ba and C in the Davies equation, but this has not been attempted in the light of more serious approximations made--for example, the use of the macroscopic dielectric constant for H_2O in the vicinity of the polymer.

Dissociation constants K_1 and K_2 derived from Equations 2.3 and 2.4 were used to calculate K_{MA} , but this presumes that their dependence on α is determined by only a change in ionic strength, which is not the case. A considerable improvement was obtained if instead $K_{1,app}$ from Equation 2.15 was used. In this way a correction was made for the dependence of the first dissociation constant on α in the complex-formation reaction. This

was done by selecting data points from the first buffer region when metal was present to correspond with the points used in determining the apparent dissociation constant. A similar correction could not be made for K_2 in this part of the titration curve, and the average $K_{2,app}$ value was used. This probably contributes to the relatively large error in K_{MA} compared to the very precise succinate data of Nancollas, et al.^{36,37}

Stability constants are given in Tables III through VIII. Compared to the corresponding divalent metal monosuccinates, the stabilities of the mono-HEMA complexes are greater by at least six orders of magnitude. With the exception of manganese and cobalt the association constants for all the dicarboxylate complexes follow the Irving-Williams order of stability. This result is consistent with the metal monosuccinate data. No data is available for metal-2,3-DMSA complexes. Copper-mono-HEMA as expected is again considerably more stable than the others, which is attributed to the contribution to the crystal field-stabilization energy from tetragonal distortion of the octahedral symmetry as a result of the Jahn-Teller effect.

The increase in stability in going to HEMA complexes is in part a result of the increased basicity of the coordinating oxygen atoms. This is directly related to the heat of formation of the complexes and indirectly, through ΔG , to the entropy of formation. It is difficult to predict what effect an increase in basicity will have upon the heat term. For example, the metal-dicarboxylate complexes are formed with an unfavorable positive enthalpy. The complexes are therefore stabilized by a relatively large positive entropy, reflecting the liberation of coordinated water molecules from the interacting ions. As the basicity increases in going from oxalate to succinate, the enthalpy becomes progressively more positive. If

TABLE III
MANGANESE - HEMA FORMATION CONSTANT

10^3 M _a	10^3 M _m	10^{-8} K _{MA}	$-\Delta G^\circ$ Kcal/mole	Mean 10^{-8} K _{MA}	Mean $-\Delta G^\circ$
9.364	5.277	6.45	11.01		
9.364	5.277	6.46	11.01		
8.860	9.988	6.63	11.02		
8.860	9.988	6.10	10.98	6.41 ± 0.2	11.01 ± 0.01

Base concentration = 0.1103M; Initial volume of acid = 50.00 ml.; T = 25°C

TABLE IV
COBALT - HEMA FORMATION CONSTANT

$10^3 a$ M	$10^3 m$ M	10^{-8} K_{MA}	$-\Delta G^\circ$ Kcal/mole	Mean $10^{-8} K_{MA}$	Mean $-\Delta G^\circ$
9.382	4.782	4.19	10.77		
9.382	4.782	4.28	10.78		
9.364	4.782	4.54	10.82		
8.880	9.052	4.21	10.78		
8.880	9.052	4.15	10.77		
8.262	9.052	4.73	10.84		
8.287	14.08	3.98	10.74		
8.287	14.08	3.81	10.72		
8.272	14.08	4.69	10.83	4.29 ± 0.3	10.79 ± 0.03

Base concentration = 0.1103M; Initial volume of acid = 50.00 ml.; T = 25°C

TABLE V
NICKEL - HEMA FORMATION CONSTANT

$10^3 a$ M	$10^3 m$ M	10^{-8} K_{MA}	$-\Delta G^\circ$ Kcal/mole	Mean $10^{-8} K_{MA}$	Mean $-\Delta G^\circ$
9.382	4.973	3.38	10.66		
9.382	4.973	3.65	10.70		
9.361	4.973	3.45	10.67		
9.361	4.973	3.71	10.71		
8.880	9.412	4.08	10.76		
8.880	9.412	4.07	10.76		
8.860	9.412	3.77	10.72		
8.860	9.412	3.63	10.69		
8.287	14.64	4.02	10.75		
8.287	14.64	3.86	10.73	3.76 ± 0.2	10.72 ± 0.03

Base concentration = 0.1103M; Initial volume of acid = 50.00 ml.; T = 25°C

TABLE VI

COPPER - HEMA FORMATION CONSTANT

10^3 a M	10^3 m M	10^{-10} K_{MA}	$-\Delta G^\circ$ Kcal/mole	Mean 10^{-10} K_{MA}	Mean $-\Delta G^\circ$
9.382	4.975	4.22	13.28		
9.382	4.975	4.32	13.29		
9.364	4.975	4.99	13.37		
9.364	4.975	4.76	13.34		
8.880	9.417	4.53	13.31		
8.880	9.417	4.86	13.35		
8.860	9.417	3.91	13.23		
8.860	9.417	3.77	13.21		
8.287	14.65	4.86	13.35		
8.287	14.65	4.75	13.34		
8.269	14.65	3.99	13.25		
8.269	14.65	3.72	13.21		
8.272	14.65	5.12	13.38	4.45 ± 4.2	13.31 ± 0.05

Base concentration = 0.1103M; Initial volume of acid = 50.00 ml.; T = 25°C

TABLE VII
ZINC - HEMA FORMATION CONSTANT

10^3 M _a	10^3 M _m	10^{-8} K _{MA}	$-\Delta G^\circ$ Kcal/mole	Mean 10^{-8} K _{MA}	Mean $-\Delta G^\circ$
9.361	5.024	5.23	10.89		
9.361	5.024	5.33	10.90		
8.860	9.056	5.07	10.88		
8.860	9.056	5.08	10.88		
8.860	9.056	5.07	10.88		
8.269	14.80	4.67	10.83		
8.269	14.80	4.24	10.78		
8.269	14.80	5.07	10.88	4.97 ± 0.3	10.87 ± 0.03

Base concentration = 0.1103M; Initial volume of acid = 50.00 ml.; T = 25°C

TABLE VIII
 CADMIUM - HEMA FORMATION CONSTANT

10^3 M	10^3 M	10^{-8} K_{MA}	$-\Delta G^\circ$ Kcal/mole	Mean 10^{-8} K_{MA}	Mean $-\Delta G^\circ$
9.361	4.966	19.4	11.55		
9.361	4.966	19.8	11.62		
9.364	4.966	20.5	11.63		
8.860	9.396	22.4	11.68		
8.860	9.396	22.5	11.68		
8.862	9.396	23.0	11.70		
8.269	14.71	ppt	-----	21.3 ± 1.4	11.67 ± 0.06

Base concentration = 0.1103M; Initial volume of acid = 50.00 ml.; T = 25°C

this trend were to continue to HEMA, the entropy contribution would be considerable. On the other hand for the corresponding metal-glycinate complexes, where the nitrogen atom has a basicity almost equal to the second oxygen in HEMA, the enthalpy is negative and reinforces a smaller entropy term to produce much more stable complexes. It becomes necessary, therefore, to consider both possibilities. Compare as an example copper-succinate ($K_{MA} = 1.82 \times 10^3$) and copper-HEMA ($K_{MA} = 4.45 \times 10^{10}$). The literature values for the formation of copper-succinate are $\Delta H = 4.56$ Kcal/mol and $\Delta S = 30.1$ eu at 25° . A similar ΔH for copper-HEMA would mean an entropy contribution of 64 eu/monomer. If, however, it is assumed that the entropy is unchanged (the chelate effect is small for a seven-membered ring), the calculated ΔH for copper-HEMA is -5.5 Kcal/mol. The real situation is perhaps intermediate between these two extremes. Some credence to this conclusion is indicated by the observed heat of formation of CuPAA,⁶³ $\Delta H = 1.6$ Kcal/mol. A change in enthalpy would not explain exclusively the increase in stability over the succinates, and it is better to think of it in terms of an additional favorable entropy factor. This might indicate an additional configuration transition in going from an ordered hydrogen-bonded ligand species to a complex.

As expected, the stability constants are indeed much longer than any others previously reported for analogous systems. This is in part due to the difference in ionic strength, but perhaps more so to the fact that previously competitive ion binding by the added salt has been ignored.

CHAPTER V

SUGGESTIONS FOR FUTURE WORK

Since the association constants of the transition metal-HEMA complexes are very large, it seems that the natural reference to future work should involve the measurement of the heats of association of the complexes. By measuring the heats of complex formation, one can then determine if the association reaction is heat or entropy driven.

To provide an insight into the binding of metals other than the transition metals, the association constants and the heats of formation for Group I and Group II metal ions with HEMA should be determined. The heats of formation measurements will determine if the reaction is enthalpy or entropy driven. If the HEMA-alkali and HEMA-alkaline earth complexes are strong enough, this extension of the study opens up the potential for using polyelectrolytes in a desalination process analogous to the pollution abatement process proposed for transition metals.

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