SOLUTION-STABILITY RELATIONSHIPS
OF METAL 8-HYDROXYQUINOLINATES

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By

HENRY FRANK STEGER, B.Sc.

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AUTHOR: Henry Frank Steger, B.Sc. (McMaster University)

SUPERVISOR: Dr. A. Corsini

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The solution stability of chelates formed between several metal-ions and 5-substituted-8-hydroxyquinolines has been determined. The dependence of solution stability on (a) the solvent composition, and (b) the basicity of the ligand donor sites has been examined.

It was found that the effect of solvent composition on metal chelate stability is essentially independent of the metal-ion. A mathematical description of the relationship between metal-chelate stability and ligand basicity has been derived and gives excellent agreement with the experimental data. The relative contributions of the N-M and the O-M bond to chelate stability are evaluated and shown to vary slightly with the metal-ion. Also, the character of the bonding in the metal chelates is implied.

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GENERAL INTRODUCTION

The importance of metal chelates in biological, physiological and chemical systems is now recognized(1-4). In biological and physiological systems, the biuret reaction, the amino acid salts of the heavy metals and the medicinals of the pyrocatechol series are illustrations of useful chelate compounds. Other chelates such as chlorophyll, haemoglobin, cytochrome and vitamin B_{12} are indispensable for life processes.

In chemistry, the study of metal chelates has added widely to knowledge in inorganic and analytical chemistry. The interest in metal chelates ranges from structural chemistry to applied chemical problems such as exist in analytical chemistry.

In analytical chemistry, chelating agents have been used extensively in qualitative(5), gravimetric(6), titrimetric(7) and spectrophotometric analysis(8), and in ion-exchange(9), solvent extraction(10) and "in situ" separations(11). Dimethylglyoxime, cupferron, EDTA and 8-hydroxyquinoline are examples of important reagents in analytical methods.

One disadvantage of chelating agents in chemical analysis is the lack of selectivity in their reactions with metal-ions. Feigl(12) has defined the term "selective" in relation to analytical reagents. A selective reagent gives an analytical reaction with a limited number of metal-ions under specified experimental conditions. Some examples of specific chelating agents are dimethylglyoxime, which precipitates only Pt(II), Pd(II) and Ni(II) quantitatively; 2,9-dimethyl-1,10-phenanthroline, which permits the spectrophotometric determination of copper as Cu(I) without interference from other metal-ions; and calcichrome, which forms a chelate with Ca(II) only.

Selectivity often results from differences in the solution stability of the chelates formed between a given ligand* and a series of metal-ions. Considerable research has been done in this area, particularly in determining the factors that govern the solution stability of metal complexes.

Important factors that affect metal-chelate stability are (a) steric effects which influence the formation of the chelate, (b) the nature of the donor atom(s), (c) the basicity of the donor atom(s), (d) properties of the metal-ion such as charge, size and preferred stereochemistry, and (e) the nature of the solvent. Factors (a) to (d) are closely interrelated.

This work is concerned primarily with the effect of the solvent medium and the effect of the basicity of the ligand donor atom(s) on the stability† of the metal chelates of several 5-substituted-8-hydroxyquinolines.

The 8-hydroxyquinoline family of ligands was chosen for study for two reasons: first, since substitution in the quinoline ring is readily made, many derivatives are synthetically available; second, 8-hydroxyquinoline is an important reagent, with applications in gravimetric, titrimetric, spectrophotometric, fluorimetric, polarographic and amperometric analysis, and in solvent extraction and chromatography(13).

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*The terms "ligand" and "reagent" are used interchangeably throughout.

†The term "stability" here refers to the solution stability of the metal chelate, as defined by the concentration equilibrium constant. The terms "stability constant" and "formation constant" are used interchangeably throughout.

HISTORICAL INTRODUCTION

For a metal-chelate reaction of the type

$$M^{z+} + nH_JL \rightleftharpoons ML_n^{(z-nJ)+} + nJH^+,$$

the solution stability has been defined by

$$^{c}K' = \frac{[ML_n^{(z-nJ)+}][H^+]^{nJ}}{[M^{z+}][H_JL]^n}, \quad (1)$$

and also by

$$^{c}K'' = \frac{[ML_n^{(z-nJ)+}]}{[M^{z+}][L^{-J}]^n}. \quad (2)$$

$^{c}K'$ and $^{c}K''$ are simply related by the protonation constants of the ligand, L^{J-}. Thus,

$$^{c}K'' = {}^{c}K' \prod_{j=1}^{J} {}^{c}K_j^H \quad (3)$$

where $^{c}K_j^H$ is the jth protonation constant.

All three constants, $^{c}K'$, $^{c}K''$ and $^{c}K_j^H$, are concentration equilibrium constants; i.e., the species are expressed in moles/liter, for example.

The solution stability is defined more correctly by the thermodynamic equilibrium constant in which concentration terms are replaced by the unitless activity terms. Thus,

$$^{T}K'' = \frac{[ML_n^{(z-nJ)+}]}{[M^{z+}][L^{J-}]^n} \cdot \frac{\gamma_{ML}}{\gamma_M \gamma_L{}^n} \quad (4)$$

where γ_S is the activity coefficient of species, S. Only occasionally have thermodynamic constants been evaluated in studies relating to metal-complex stability. Most often in such studies, the equilibrium values obtained in an experiment are used for comparative purposes, so that thermodynamic values are not necessary. Provided that all equilibrium constants required for a particular study are determined under identical experimental conditions (i.e., solvent, temperature, ionic strength*), concentration equilibrium constants suffice in most studies. It is necessary in these determinations to maintain the ionic strength constant at a level appreciably higher than the concentration of the reacting species in order to minimize changes in the activity coefficients of the species(14).

The solution stability of metal complexes is an important parameter in analytical chemistry. For example, for a complex to be analytically useful, the free energy change for its formation must be large; i.e., the reaction must be essentially quantitative. Thus a stable complex is required, and, consequently, for any potentially useful analytical complex, the determination of its solution stability is a requisite.

The solution stability of metal complexes is also related to the selectivity of the reagent, since often selectivity merely reflects differences in stability of the complexes of groups of metal-ions. Thus, studies on factors that affect ligand selectivity must include those factors that affect complex stability.

In the past two decades, many stability constants of complexes formed between metal-ions and ligands (particularly organic) have been

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*Hereafter, ionic strength will often be denoted by the symbol I.

measured. Several relationships between the stability of the complex and the properties of the metal-ion and of the ligand have been discussed(15). For example, correlations with the ionization potential, ionic radius, electronic structure and electronegativity of the metal-ion and with structural changes in the ligand have been made.

Two interesting correlations that have not been fully examined are (a) the effect on proton-ligand and metal-ligand stability on replacement of water by aqueous-organic binary solvents, and (b) the effect of donor-atom basicity on the stability of complexes formed by the same metal-ion with various ligands. This thesis is concerned mainly with the investigation of these two factors in greater detail.

A theoretical derivation applicable to both solvent and basicity correlations has been suggested by Duncan(16) and developed by Irving and Rossotti(17,18). For the protonation of a ligand having one donor atom,

$$\mathrm{H} + \mathrm{L} \xrightleftharpoons{{}^{c}K_{HL}} \mathrm{HL}\ ,$$

and for the 1:1 metal-ligand complex formation,

$$\mathrm{M} + \mathrm{L} \xrightleftharpoons{{}^{c}K_{ML}} \mathrm{ML},$$

the protonation constant, ${}^{c}K_{HL}$, and the complex formation constant, ${}^{c}K_{ML}$, are related by

$$\log {}^{c}K_{ML} = \log {}^{c}K_{HL} + \frac{1}{2.303RT}(\mu^{o}_{M}-\mu^{o}_{ML}-\mu^{o}_{H}+\mu^{o}_{HL})$$

$$+ \frac{1}{2.303RT}(\mu^{t}_{M}-\mu^{t}_{ML}-\mu^{t}_{H}+\mu^{t}_{HL}) + \log \frac{\gamma_{M}\gamma_{HL}}{\gamma_{ML}\gamma_{H}} \qquad (5)$$

where μ^{o}_{S} is the chemical potential or the partial molar free energy of species S at infinite dilution in water, μ_S^t is the free energy of transfer of species S, at infinite dilution, from water to the solvent in which complexation occurs, and γ_S is the activity coefficient of species S in the reaction medium. All charges are omitted for simplicity. Equation (5) is exact.

Effect of Solvent Composition on Metal-Complex Stability

Previous investigators have shown that the stability, $\log {}^cK_{HL}$, of many proton-ligand complexes containing either an N-H or O-H group^(19-21)^ and the stability, $\log {}^cK_{ML}$, of metal complexes of N or O donor ligands^(22, 23)^ are approximately linear functions of the molar fraction, n, of the organic component of the solvent, at least for small values of n.

Irving and Rossotti^(18)^ have shown that the relationship between the stability, $\log {}^cK_{CL}$, of the complex CL* in dioxane-water and the corresponding stability, $\log {}^cK^w_{CL}$, in water is given by

$$\log {}^cK_{CL} - \log {}^cK^w_{CL} = A + B \qquad (6)$$

where

$$A = \frac{1}{2.303RT}\,(\mu_C^t - \mu_{CL}^t + \mu_L^t) \;,$$

and

$$B = \log \frac{\gamma_C \gamma_L}{\gamma_{CL}} - \log \frac{\gamma_C^w \gamma_L^w}{\gamma_{CL}^w} \;.$$

For $(\log {}^cK_{CL} - \log {}^cK^w_{CL})$ to be a linear function of the molar fraction of the organic component, A must be proportional to n. The term B must be either proportional to n or negligible compared to A. It has been shown

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*C denotes either a proton or a metal-ion.

that A is proportional to n for some methanol and ethanol-water mixtures(24-26).

In general, the stability of complexes containing either an O-H or an O-M link increases with increasing organic content of the solvent(18), due to a decrease in the dielectric constant of the solvent. The approximate constancy of the Walden-Stokes product of the limiting conductivity and the viscosity in several "water-rich" solvents(27-31) indicates that the effective radii of the free ions (i.e., the radius of the solvated ions) remain essentially constant in solutions ranging from 0 to 60% v/v dioxane-water. Thus, the increase in the attractive forces between ions with increasing organic content is not due to changes in the size of the ions but to the decrease in the dielectric constant of the bulk solvent. Furthermore, according to Irving and Rossotti(18), as the dielectric constant decreases, the ion-ion interaction involving the proton (or metal-ion) and the anionic oxygen atom of the ligand increases to a greater extent than the ion-dipole interaction between the proton (or metal-ion) and the solvent molecules.

The stability of complexes containing an $(N-H)^+$ link initially decreases and then increases with increasing organic content of the solvent. This behavior has been explained on the basis of the protonating ability of the solvent. Braude and Stern(32) studied the effect of the solvent composition on the Hammett acidity function, H, for solutions of hydrogen chloride in several organic-aqueous media. They found that H decreased until the molar fraction of organic component reached approximately 0.5, and then increased. The change in H was explained in terms of the quasi-crystalline tetrahedral structure of water(33), in which aqueous solvates

($4H_2O$, H^+) are formed. The protons are accommodated in the interstices of the lattice and are bonded equally to four neighbouring water molecules. On the addition of organic solvent, the tetrahedral structure is gradually disrupted through the interposition of organic molecules. As the organic content increases, the aqueous solvation shell is gradually dispersed and the aqueous solvates (nH_2O, H^+)($n < 4$) are replaced by H_3O^+. This corresponds to the minimum of the acidity function value. At higher organic content, H_3O^+-ions are replaced by lyonium-ions (i.e., protonated solvent molecules) which are strongly protonating. The stability of $(N-H)^+$ complexes in aqueous solvents of increasing organic content should, of course, parallel the protonating ability of the solvent. Irving and Rossotti(18) suggested that an increase in the organic content up to that corresponding to the minimum value of H would be expected to increase the ion-dipole forces between a proton and a nitrogen donor to a lesser extent than the ion-dipole forces between a proton and the more electronegative oxygen donor. (Beyond the minimum, the interaction between the proton and nitrogen would be greater than that between the proton and the oxygen atom of the organic solvent component.)

No simple relationship appears to exist between the solvent composition and the stability of complexes containing a N-M link. An increase in the organic content of the solvent has little influence on the stability of certain complexes of ammonia(34), ethylenediamine(35-37) and imidazole(38).

The effect of solvent composition on the stability of complexes that contain both an O-M and N-M link has not been investigated. By analogy with simpler complexes, an increase in the organic content of the solvent is expected to increase the stability of complexes in which the O-M bond is of predominant importance, but to have a lesser effect on the stability of complexes containing a strong N-M bond. Rossotti(39) found that the slope of the plot of $\log^{T}K_{ML}$ against the reciprocal of the dielectric constant decreases in the order Mg > Ni for complexes of 8-hydroxyquinoline-5-sulfonic acid.

Thus, the variation in stability of a bidentate complex with solvent composition (i.e., dielectric constant) may allow assessment of the relative importance of the two donor-metal bonds. Furthermore, since the magnitude of the solvent effect on chelate stability is expected to vary among different groups of cations (e.g., class (a) and class (b) ions), improvements in selectivity may be achieved in chemical analysis by the selection of a suitable solvent composition. Finally, with the increasing use of mixed solvent systems in analytical processes, further knowledge of the effect of solvent composition on proton-ligand and metal-ligand complexes is important. Accordingly, studies relating to solvent composition and complex stability were made in the present work.

Effect of Ligand Basicity on Metal-Complex Stability

Several studies have shown that the stability of metal complexes increases with increasing basicity of the donor atom(s). In most instances, an approximately linear relationship exists between the stability, $\log^{c}K_{ML}$, of the metal complex and the stability, $\log^{c}K_{HL}$, of the corresponding proton complex, for a family of closely related ligands. This correlation has the form

$$\log^{c}K_{ML} = a\cdot\log^{c}K_{HL} + b \qquad (7)$$

where a and b are constants. Table I summarizes the complexation reactions that satisfy equation (7).

For ligands with more than one donor atom, correlations have usually been made with the protonation constant of the most basic center(17,22,40). Some correlations have been made, however, with the sum of the protonation constants of all basic centers involved in chelate formation(41).

Equation (5) can be written(18) as

$$\log {}^{c}K_{ML} = \log {}^{c}K_{HL} + C + D \tag{8}$$

where

$$C = \frac{1}{2.303RT}\,(\mu^{o}_{HL}-\mu^{o}_{ML}+\mu^{t}_{HL}-\mu^{t}_{ML}) + \log \frac{\gamma_{HL}}{\gamma_{ML}}$$

and

$$D = \frac{1}{2.303RT}\,(\mu^{o}_{M}-\mu^{o}_{H}+\mu^{t}_{M}-\mu^{t}_{H}) + \log \frac{\gamma_{M}}{\gamma_{H}} \quad .$$

The term D is independent of the nature of the ligand, and is constant for all complexes of a given metal-ion provided that the solvent, temperature and ionic strength are kept constant. For the relationship between $\log {}^{c}K_{ML}$ and $\log {}^{c}K_{HL}$ to be linear, C must itself be a linear function of $\log {}^{c}K_{HL}$. For the special case of unit slope, the term C must be constant or negligible compared to $\log {}^{c}K_{HL}$. The value of C is largely determined by the difference between μ^{o}_{ML} and μ^{o}_{HL} (18). Thus, for C to be constant, the changes in μ^{o}_{ML} and μ^{o}_{HL} with the ligand must be similar. For C to be negligible compared to $\log {}^{c}K_{HL}$, μ^{o}_{ML} and μ^{o}_{HL} must be approximately equal. If the changes in μ^{o}_{ML} and μ^{o}_{HL} are not similar, C varies with the ligand, and the relationship between $\log {}^{c}K_{ML}$ and $\log {}^{c}K_{HL}$ is non-

TABLE I

Correlation of Metal-Complex Stability with Ligand Basicity

System	Reference
Ag(I) complexes of substituted amines	(42,43)
Ag(I), Cu(II), Ni(II), Zn(II), Cd(II) complexes of substituted pyridines	(42,43,44,45)
Alkaline earth complexes of substituted iminodiacetates	(46,47)
Transition metal complexes of substituted 1,10-phenanthrolines	(48,49)
Mg(II), Ba(II), Ni(II), Cu(II), Ce(III) complexes of substituted β-diketones	(22,40)
Fe(III) complexes of substituted phenols	(50,51)
Cu(II), Pb(II) complexes of carboxylic acids	(52,53)
Metal-ion complexes of substituted 8-hydroxyquinolines	(17,18,41,54)
Mg(II), Ni(II), Zn(II) complexes of substituted tropolones	(55,56)
Ni(II), Cu(II) complexes of substituted phthalic acids	(57)
Cu(II) complexes of substituted salicylaldehydes	(58)

linear. For a linear relationship of non-unit slope, the changes in μ^o_{ML} and μ^o_{HL} with the ligand must be dissimilar but linear functions of $\log{}^cK_{HL}$.

The difference between μ^o_{ML} and μ^o_{HL} depends on (a) the difference in the electrostatic interactions between the metal-ion and ligand and the proton and ligand, (b) the difference in the σ-acceptor strength of the metal-ion and the proton, (c) the extent to which the metal-ion participates in π-bonding, and (d) the difference in the entropy of formation between ML and HL.

Two groups of workers(41,59) have found that even with closely related ligands, a linear relationship between $\log{}^cK_{ML}$ and $\log{}^cK_{HL}$ may not be obtained. Beimer and Fernando(59) were unable to find a linear relationship for several 5-halo-8-hydroxyquinolines. These workers concluded that, in general, a linear relationship between $\log{}^cK_{ML}$ and $\log{}^cK_{HL}$ should not be expected because the relationships between measured parameters are complex.

Williams et al.(41) found a non-linear relationship between $\log{}^cK_{ML}$ and $\log{}^cK_{HL}$ for the Fe(II) complexes of several halo derivatives of 8-hydroxyquinoline and also for the Cu(II) complexes of substituted salicylaldehydes. These workers have suggested that equation (8) is not universally applicable because changes in μ^o_{ML} and μ^o_{HL} are not necessarily similar. Also, should the relationship between $\log{}^cK_{ML}$ and $\log{}^cK_{HL}$ be linear, unit slope should not be expected. The similarity in μ^o_{ML} and μ^o_{HL} cannot be deduced from thermodynamic arguments(18) but requires a discussion of the bonding in ML and HL.

Several workers have commented on the slope of the $\log{}^cK_{ML}$-$\log{}^cK_{HL}$

relationship. Williams(41) suggested that both μ^{o}_{ML} and μ^{o}_{HL} are similarly dependent on the σ-donor (acceptor) property of the ligand, but are differently dependent on its π-donor (acceptor) property. Most σ-donor substituents are also π-donors (e.g., methyl) and most σ-acceptor substituents are also π-acceptors (e.g., nitro). Thus, a change in substituent in a ligand causes changes in the σ- and π-electron densities which are usually in the same direction, i.e., electron-acceptor substituents reduce the σ-donor property but increase the π-acceptor property of the ligand. Hence, complexes of π-donor metal-ions with a series of ligands having electron-acceptor substituents should be stabilized with respect to the corresponding proton complexes by metal to ligand π-bonding. Therefore, the slope of the plot of $\log {}^{c}K_{ML}$ against $\log {}^{c}K_{HL}$ should be less than unity.

Recently, Da Silva(60,61) and Sun and Brewer(44) provided experimental evidence that deviations from unit slope in plots of $\log {}^{c}K_{ML}$ against $\log {}^{c}K_{HL}$ are due solely to π-bonding. Both Da Silva and Brewer assumed that the σ-acceptor property of the metal-ion and proton are similar. Furthermore, they neglected differences in the electrostatic interaction between the ligand and the metal-ion or proton. Da Silva's work is particularly open to criticism because it predicts metal to ligand π-bonding in metal complexes where none is possible, e.g., in the saturated aliphatic amine complexes of Ag(I) and in the α-substituted acetate complexes of Ca(II). Nieboer and McBryde(62) have concluded that there is no a priori basis for selecting a single factor such as metal to ligand π-bonding to explain a less than unit slope. Rather, a thorough understanding of how complex stability depends on electrostatic and covalent bonding is required.

In recent studies$^{(63,64)}$, attempts were made to determine the relative extent of covalent and electrostatic bonding in metal 8-hydroxyquinolinates.

In an infrared study (600-250 cm^{-1} region) of the tris(8-hydroxyquinolinato) complexes of Aℓ(III), Fe(III) and Co(III), Larsson and Eskilsson$^{(63)}$ found that the intensities of the absorption bands assigned to the O-M vibrations indicated a donation of charge from ligand to metal increasing in the order Aℓ < Fe < Co. They concluded that this was the order of increasing covalent and decreasing electrostatic character in the O-M bond.

In an NMR study of the 8-hydroxyquinoline complexes of Mg(II), Zn(II), Sn(II), Pb(II), Pt(II), Aℓ(III), Co(III) and Rh(III), Baker and Sawyer$^{(64)}$ attempted to show whether the N-M and O-M bonds were primarily electrostatic or covalent. They compared the chemical shifts of the ligand protons in the metal chelates with the corresponding shifts in the anionic, neutral and protonated forms of the ligand, which served as approximate models for O-M electrostatic, O-M covalent and N-M interactions, respectively. Electrostatic or covalent character was attributed to those chelates which were found to be "labile" or "inert", respectively. The results are summarized in Table II.

To date, no attempt has been made to correlate the slope of the $\log {}^{c}K_{ML}$-$\log {}^{c}K_{HL}$ plot with properties of the metal-ion (or metal) for the complexes formed between a given metal-ion and a series of closely related ligands. Such an attempt is made in this thesis, for the complexes of several 5-substituted-8-hydroxyquinolines. The ligands used were

TABLE II

Bonding in Metal 8-Hydroxyquinolinates

Ion	N-M	O-M
Mg(II)	labile*	labile*
Zn(II)	labile	labile
Sn(II), Pb(II)	labile	inert
Pt(II)	inert	inert
Aℓ(III), Co(III), Rh(III)	inert*	labile

*These bonding interactions were found to be weak compared to the others.

8-hydroxyquinoline, 5-chloro-8-hydroxyquinoline, 8-hydroxyquinoline-5-sulfonic acid, 5-acetyl-8-hydroxyquinoline and 5-nitro-8-hydroxyquinoline. The metal-ions taken were (a) the alkaline-earth ions Mg(II) and Ca(II), (b) the first-row transition-metal ions Mn(II), Fe(II), Fe(III) and Ni(II), (c) the Group III ions Aℓ(III), Sc(III) and Ce(III), and (d) Ag(I), Zn(II) and Pb(II). The nature of the bonding in these complexes is indicated.

Other Correlations of Metal-Complex Stability

Several correlations of metal complex stability with metal-ion properties have been made. In general, these correlations have been for a given ligand and a series of metal-ions and have involved $\log {}^{c}K_{ML}$ and either a function of the metal-ion charge and radius, or the ionization potential of the metal. For example, correlations of $\log {}^{c}K_{ML}$ with $1/r_M$ or the ionic potential, z_M/r_M, have been made for complexes of the alkaline earth metals(65-67), and of the lanthanides(68). Other workers have suggested that the function, z_M/r_M, is not a suitable parameter for correlations involving complexes of metal-ions of different charges. Instead, z_M^2/r_M (65,69), which is justified by the Born Equation(70), and $z_M/(r_M+r_L)$ (71) have been used. Also, correlations have been made with the highest stepwise(72-79) and the overall ionization potential of the metal(80-82), where the ionization potential has been taken as a measure of the tendency of the metal-ion to bond covalently(83).

Qualitative correlations between metal complex stability and the nature of the ligand donor atom has been advanced by Ahrland, Chatt and Davies(84), and by Edwards and Pearson(85). In these correlations, metal-ions in the periodic table have been designated as class (a) (or "hard"), class (b) (or "soft), or borderline between the two classes. Class (a) metal-ions are those whose coordination to donor atoms is governed mainly by electrostatic interactions. Thus, the higher the charge and the smaller the radius of the metal-ion and donor atom, the more stable the complex formed. Such metal-ions include members of the alkali metals, alkaline earth metals, lanthanides, actinides, the early transition metals, and Aℓ(III) and Ga(III); i.e., the more electropositive ions, which form their most stable complexes with ligands containing the more electronegative donor atoms such as nitrogen and oxygen.

Class (b) metal-ions are found within the triangle described by lines joining copper to tungsten to polonium, i.e., those ions whose complexes have considerable covalent character. The coordinating ability of class (b) metal-ions does not regularly increase with increasing charge or decreasing radius. All class (b) metal-ions have a large number of d-electrons in their outer shell, which are potentially available for π-donation to the ligand. Class (b) metal-ions generally form their most stable complexes with ligands having "soft" donors such as sulfur and phosphorus.

Bjerrum(86) and Manning(87-89) have suggested a method whereby the nature of the bonding in a metal complex could be determined. The ratio of successive stability constants may be represented by

$$P = \frac{{}^{c}K_{n-1}}{{}^{c}K_{n}} = S \times T \times R. \qquad (9)$$

S is a statistical factor calculable from the number of available binding sites of the metal-ion and ligand. T is a measure of the electrostatic work done against the repulsion of the (already) bound ligand, and should be independent of the nature of the metal-ion and ligand. R is the "rest effect" and covers those effects which are neither statistical nor electrostatic. Bjerrum defined R as the influence of the bound ligand(s) on the binding power of the metal-ion. If the metal-ligand bond is predominantly electrostatic, R is approximately unity. If the metal-ligand bond is sufficiently covalent to transfer considerable charge to the metal-ion, the electrostatic attractive force between the 1:(n-1) metal-ligand complex and the incoming ligand is reduced, and the value of R is increased. The greater the covalency of the metal-ligand bond, the greater the value of R.

A detailed summary of correlations between complex stability and metal-ion properties has been given by Rossotti$^{(14)}$.

Measurement of Proton-Ligand and Metal-Ligand Complex Stability in Dioxane-Water Media

The determination of equilibrium constants has long been used as a means of assessing the structural effects of ligands on metal chelate stability. The concentration formation constant, ${}^{c}K_n$, for the stepwise reaction,

$$ML_{n-1} + L \rightleftharpoons ML_n ,$$

is given by

$${}^{c}K_n = \frac{[ML_n]}{[ML_{n-1}][L]} . \qquad (10)$$

For a system in which the highest complex formed is ML_N, there are N stepwise formation constants, ${}^{c}K_1$, ${}^{c}K_2$,....., ${}^{c}K_N$. L is the chelating form of the ligand. For some ligands (e.g., ethylenediamine), L is neutral;

for others containing acidic protons (e.g., 8-hydroxyquinoline), L is anionic.

In the present work, formation constants were determined by a modified form of Bjerrum's "batch" or "one-point" method. This method, applicable to ligands whose chelating form is basic, involves the potentiometric measurement of the hydrogen-ion concentration in solutions containing metal-ion, ligand and hydrogen-ion. Protonation of the ligand provides a means of varying the concentration of free ligand, L, over a wide range.

Bjerrum introduced the use of the quantity, $\bar{n}$, the average number of ligands bound to a metal-ion at a particular concentration of L. In the Bjerrum method, measurements are made over a wide range of concentrations of L, such that $\bar{n}$ varies from 0 to N. Bjerrum developed general equations and methods for the calculation of the N formation constants from the data ($\bar{n}$, [L]). These equations have found widespread use in the study of metal complexes.

The modifications to the Bjerrum method used in this study were introduced by Calvin and Wilson(40). These workers used a potentiometric titration technique in which an acidified solution of ligand and metal-ion is titrated with a solution of standard base. They also introduced the use of the mixed solvent, dioxane-water, to overcome difficulties associated with the limited aqueous solubility of many metal chelates. The determination of complex stability is complicated, however, by difficulties encountered in mixed solvent (e.g., the measurement of pH, and ion association).

Although the potentiometric method is widely applicable, it has a number of limitations. The upper pH limit of the method is determined by the pH of hydrolysis of the metal-ion. In general, this limit is about pH 6-7 for divalent transition metal-ions. The lower limit is about pH 2.5. In solutions of high acidity, the concentration of hydrogen-ion released on chelation is virtually undetectable. A further limitation is that valid measurements cannot be made in the presence of a solid phase containing either metal-ion or ligand. Thus, systems that involve ligands or chelates of very low solubility even in organic-water media cannot be studied by this method and another method must be chosen. Other methods available for the determination of formation constants are based on spectrophotometric, polarographic, solvent extraction, ion-exchange and solubility techniques(90), some of which make use of radioactive tracers.

In the potentiometric determination of metal chelate formation constants, the measurement of hydrogen-ion concentration in dioxane-water solution is required. This measurement is made with a pH meter, for which the glass and calomel electrode assembly has been calibrated to allow the conversion of the pH reading to $-\log [H^+]$.

The calibration is necessary for two reasons. The first arises from differences between the activity coefficients of species in water and in dioxane-water media. The pH* values of the standard buffer solutions used for calibrating the pH meter are evaluated for aqueous solution. Because the activity coefficient of a species depends on the solvent composition, significance cannot be attached to pH measured in organic-water solution when the pH meter has been previously calibrated with an aqueous

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*The pH defined by the National Bureau of Standards is given by $\mathrm{pH} = -\log [C_{H^+} \cdot \gamma_{\pm}]$, where $\gamma_{\pm}$ is the mean activity coefficient for the electrolyte, $HC\ell$.

standard buffer solution.

The second reason for calibration arises from the effect of solvent composition on the liquid-junction potential of the saturated calomel electrode.

Van Uitert and Haas(91) compared the behavior of the glass electrode to the hydrogen electrode in dioxane-water media containing up to 75% v/v dioxane-water, and showed that the glass electrode functioned linearly with respect to the hydrogen electrode over the pH range of 1.5 to 11. This showed that the glass electrode can be used as a hydrogen-ion activity or concentration probe in dioxane-water media. These workers then obtained a "correction factor" to convert the pH-meter reading into $-\log [H^+]$. Solutions of hydrochloric acid in dioxane-water solvent* were prepared and their pH-meter reading, R, was determined, where

$$R = -\log [H^+] - \log U_{H^+} . \qquad (11)$$

The term, $\log U_{H^+}$, is the "correction factor" and was found to be a function of the molar fraction of dioxane** and the ionic strength***, but is independent of the hydrogen-ion concentration, at least in strong acid solutions. Because $\log U_{H^+}$ is constant for a given solvent composition and ionic strength, the glass-calomel electrode assembly can be used as a hydrogen-ion concentration probe.

In this present study, 20, 40, 60 and 75% v/v dioxane-water solvents

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*It was assumed that the hydrochloric acid was completely dissociated in each solvent mixture used.

**Primary medium effect of Harned and Owen(92).

***Secondary medium effect of Harned and Owen(92).

were used, with 0.1M sodium perchlorate as the background electrolyte. The Van Uitert correction factor was determined for each solvent. Similarly, the concentration ion-product of water, p_cK_w, was determined in each dioxane-water solvent, since this quantity is required for the calculation of formation constants.

Recently, during the course of this study, Irving and Mahnot(93) determined values of log U_{H^+} for solutions of hydrochloric acid in several solvents of varying dioxane content. The ionic strength was maintained at 0.1 by the addition of sodium chloride. The results of Irving and Mahnot and of this study are in good agreement.

A Synopsis of Work in this Thesis

1. The Van Uitert correction factor and the concentration ion-product of water have been determined for 20, 40, 60 and 75% v/v dioxane-water. The pH range in which the Van Uitert correction factor is constant has been widened by using an 8-hydroxyquinoline buffer system.
2. The solution stability of the proton complexes of several 5-substituted-8-hydroxyquinolines and of a few sulfur-donor ligands has been determined in dioxane-water solvents ranging from 0-75% v/v dioxane. The behaviors of the S-H and O-H complexes are compared and explained.
3. The solution stability of the chelates formed between several metal-ions and 5-substituted-8-hydroxyquinolines has been determined in several dioxane-water solvents. The variation in stability is compared to the variations obtained for the O-H and $(N\text{-}H)^+$ complexes. The value of this comparison in assessment of (a) the relative importance of the O-M and N-M bonds in the complex, and (b) the relative importance of N-M bonds in complexes with different metal-ions, is demonstrated. The effect of the

solvent composition on the stability of bidentate chelates has not been previously investigated in detail.

4. A calorimetric study of some metal complexes of 8-hydroxyquinoline-5-sulfonic acid was undertaken to determine whether the variation in the stability of metal-ligand and proton-ligand complexes with solvent composition is due to enthalpy or entropy effects.
5. The stability of several metal complexes of 5-substituted-8-hydroxyquinolines is correlated with the stability of the corresponding proton complexes in 60% v/v dioxane-water. The stability of the proton-ligand complexes and z_M/r_M, the effective electrostatic potential field, of the metal-ion are used to derive a mathematical description which predicts the slope of this correlation. This mathematical description permits evaluation of the relative importance of the N-M and O-M bond to chelate stability. The description is correlated with the half-wave potentials determined in this work for Fe(III) complexes, and also is used to explain stability data(17,41,59) and redox potential data(94) of previous workers.

EXPERIMENTAL AND RESULTS

Apparatus

Calibrated volumetric ware was used throughout this work whenever this was appropriate.

Infrared spectra were recorded with a Beckman IR-5 infrared spectrometer (Beckman Instruments Inc., Fullerton, California). Spectra in the visible region were recorded with a Cary Model 14 Spectrophotometer (Applied Physics Corp., Monrovia, California). Other spectrophotometric measurements in the visible region were made using a Hitachi Perkin-Elmer Model 139 Spectrophotometer (Perkin-Elmer Corp., Norwalk, Connecticut), the cell compartment of which was maintained at 25°C.

The potentiometric titration apparatus for the determination of protonation constants and chelate formation constants consisted of a titration cell, a pH meter, two ten-millimeter microburets and a constant-temperature water bath. The pH meter was a Radiometer Model PHM4c (Radiometer, Copenhagen, Denmark) equipped with a Beckman saturated calomel electrode and a Radiometer G202B (low sodium-ion error), or with a saturated calomel and E-1 glass electrode supplied by the Fisher Scientific Company. A sodium perchlorate-agar salt bridge was used in the determination of chelate formation constants of Ag(I).

The apparatus for the calorimetric determination of ΔH values consisted of a 500-ml silvered Dewar flask and a suitable rubber stopper with sufficient holes to hold a Beckmann thermometer (Jenaer Normalglas, West Germany), a teflon stirrer attached to a stirring motor, and a piece of 6 mm tubing at the bottom of which was a glass bulb equipped with a ground glass tip and an inside ground glass stopper. The stopper was released by pressing downwards on a section of 2-mm glass rod inside the glass tubing and bulb. A file mark was placed on the stem and the bulb was calibrated as a delivery pipet. It was found to deliver 9.80±0.01 ml (average of four attempts).

The polarograms of the Fe(III) complexes of 8-hydroxyquinoline derivatives were recorded on a Polarecord E261 polarograph (Metrohm, Switzerland). A dropping mercury electrode and silver-silver chloride reference electrode were used. The capillary characteristics of the dropping mercury electrode were not determined.

Reagents

All common laboratory chemicals were either analyzed grade or sufficiently pure for the purpose intended.

Reagent-grade 1,4-dioxane was purified by refluxing over sodium for at least 24 hours, followed by fractional distillation through a 1-meter column packed with glass helices. The fraction boiling in the range 100.5-101.0°C was collected as required and used within 24 hours. The dioxane used in the potentiometric titration of 8-mercaptoquinoline and of Fe(II) complexes was collected under a stream of nitrogen gas previously passed through a solution of pyrogallic acid and then through a calcium chloride drying tube.

Carbonate-free sodium hydroxide for use in potentiometric titrations was prepared as given by Kolthoff and Sandell (95). The sodium hydroxide solution (~0.1M) was standardized by titration against 20-ml portions of a standard potassium hydrogen phthalate solution using phenolphthalein indicator. Another sodium hydroxide solution (~1M) was prepared and similarly standardized for use in the calorimetric determination of ΔH values of chelate formation.

Solutions of perchloric acid (~0.03M) containing sodium perchlorate (0.50M) were used in the potentiometric titrations. The hydrogen-ion concentrations of these solutions were determined by potentiometric titration with standard sodium hydroxide solution (0.1M).

Solutions of hydrochloric acid (1.5M and 0.25M) were prepared and standardized potentiometrically for use in the calorimetric determination of ΔH values.

Metal-ion solutions (~0.1M) for potentiometric titrations were prepared from the perchlorate salts (G. F. Smith Chemical Co., Columbus, Ohio). These solutions were standardized by accepted EDTA methods(96). The EDTA solution was standardized by titration against a standard Zn(II) solution. Dilute solutions (~0.01M) of the metal perchlorates were prepared by tenfold dilution of the corresponding 0.1M solutions.

A standard silver nitrate solution (~0.01M) was prepared by dissolving the required weight of the dried salt in deionized water.

An ammonium ferrous sulfate solution (~0.01M) was standardized by titration of 20-ml portions of the Fe(II) solution with a standard potassium dichromate solution using sodium diphenylamine sulfonate indicator.

A scandium chloride (Alfa Inorganics, Beverly, Mass.) solution (~0.01M) was prepared and standardized with EDTA.

The organic reagents used in this work were either purchased or synthesized, as pointed out below.

8-Hydroxyquinoline (oxine, 8-quinolinol)*. 8-Hydroxyquinoline (Eastern

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*The name oxine for 8-hydroxyquinoline is sometimes used in this thesis, particularly in diagrams.

Chemical Corp., Pequannock, New Jersey) was twice steam-distilled and then recrystallized from 50% v/v ethanol-water to give white needles, mp, 75-76°C.

5-Chloro-8-hydroxyquinoline. 5-Chloro-8-hydroxyquinoline (Aldrich Chemical Co., Milwaukee, Wisconsin) was steam-distilled and then recrystallized from 50% v/v ethanol-water to give white needles, mp, 124.5-125.5°C.

8-Hydroxyquinoline-5-sulfonic acid. 8-Hydroxyquinoline-5-sulfonic acid (Eastman Organic Chemicals, Rochester, New York) was twice recrystallized from 5% v/v hydrochloric acid-water and heated at 130°C for 24 hours to give the anhydrous reagent.

5-Acetyl-8-hydroxyquinoline. 5-Acetyl-8-hydroxyquinoline was prepared by the method of Matsumura(97). The product was recrystallized twice from hot water to give cream-coloured needles, mp, 110.5-111.5°C.

5-Nitro-8-hydroxyquinoline. 5-Nitroso-8-hydroxyquinoline was prepared by the method of Albert and McGrath(98). It was then oxidized to 5-nitro-8-hydroxyquinoline by the procedure described by Petrow and Sturgeon(99). The 5-nitro-8-hydroxyquinoline was recrystallized from hot water to give yellow needles, mp, 176-177°C.

8-Mercaptoquinoline. The sodium salt of 8-mercaptoquinoline was prepared by the procedure of Kealey and Freiser(100), and twice recrystallized from ethanol-water.

Sebacic acid. Sebacic acid (Fisher Scientific Co.) was twice recrystallized from hot water to give colourless needles, mp, 133-134°C.

2-2'-Di-(thioethyl)sulfide. 2-2'-Di-(thioethyl)sulfide (Aldrich Chemical Co., Milwaukee, Wisconsin) was distilled under reduced pressure, bp, 135-136°C at 10 mm(101).

Calibration of the Glass Electrode in Dioxane-Water Media

The glass electrode was calibrated to read $-\log[H^+]$ in a dioxane-water medium by comparing the pH-meter reading, R, given by a standard solution of a strong acid, to the calculated hydrogen-ion concentration. The strong acid was assumed to be completely dissociated in the dioxane-water medium. The correction factor, $\log U_{H^+}$, is the difference between R and the calculated hydrogen-ion concentration. This value was then applied to other pH-meter readings obtained in the same solvent system.

Correction factors were obtained for dioxane-water media of various composition at I (ionic strength) = 0.1.

The titration cell used for obtaining the correction factors was a 250-ml jacketted beaker; water at 25.0±0.1°C was circulated through the outer jacket. The cell was fitted with a lucite cover with holes for the glass and calomel electrodes, a nitrogen gas inlet tube, a thermometer and two 10-ml burets.

The procedure was as follows. Purified-grade nitrogen gas was bubbled through the solution which was to be titrated. The contents of the cell were stirred magnetically. The tip of the sodium hydroxide buret, drawn out into a fine capillary, was placed below the surface of the solution during a titration. The buret was gravity filled from a 4-l polyethylene bottle. The contents of both the buret and the bottle were protected from atmospheric carbon dioxide by absorption tubes filled with Ascarite.

The pH meter was standardized before use with Beckman standard buffer solutions of pH 4.01 and 7.00.

The titration procedure was as follows: 20 ml of a standard perchloric acid solution (~0.03) 0.50M in sodium perchlorate were pipetted into the cell, followed by the appropriate volumes of dioxane and water to give a final volume of 100 ml and a solution composition of 0, 20, 40, 60 or 75% v/v dioxane-water. The electrodes were inserted into the solution, and nitrogen gas passed through the solution for 5-10 minutes while the contents of the cell reached 25.0±0.1°C.

Then small increments of standard sodium hydroxide were added. With each addition of base, a small volume of dioxane was added to keep the solution composition constant, and the R value was measured. A minimum of three titrations for each solution composition were performed.

At each point on the titration curve, the R value was compared with $-\log[H^+]$ calculated from the molarities and volumes of acid and base and the total volume of solution.

The Van Uitert and Haas correction factor$^{(91)}$, $\log U_{H+}$, is given by

$$\log U_{H+} = p_cH - R \qquad (11)$$

where $p_cH = -\log[H^+]$. Log U_{H+} was found to remain constant only in a narrow pH range for a strong-acid solution. Table III gives the calculated correction factors and the pH ranges in which they are constant. The ionic strength (0.1) was calculated assuming complete dissociation of the sodium perchlorate electrolyte.

The narrowness of the pH range in which the correction factor is constant results from unreliable pH readings after about 80% neutralization

TABLE III

Glass Electrode Correction Factors

% v/v Dioxane-Water	Log U_{H^+}	pH Range
0	-0.095	1.97-2.89
20	-0.087	2.37-2.56
40	-0.075	2.40-2.68
50	-0.067*	-
60	0.037	2.29-2.83
75	0.363	1.97-2.52

*This value calculated from the data in reference (102).

of the strong acid.

Figure 1 shows the correction factor as a function of molar fraction dioxane in the solvent. This plot is similar to several plots obtained by Van Uitert (91) and by Irving and Mahnot (93).

An 8-hydroxyquinoline buffer system was used in an attempt to widen the pH range over which the correction factor is constant. First, the $\log{}^{c}K_{NH}$ value of the ligand in the solvent medium was determined (see Potentiometric Determination of Protonation Constants) without a correction factor. From the $\log{}^{c}K_{NH}$ value, a correction factor was calculated and the latter used to obtain a new value for the $\log{}^{c}K_{NH}$. The re-iterative procedure resulted in a convergence of the values of the correction factor and $\log{}^{c}K_{NH}$. For 60 and 75% v/v dioxane-water solution, the pH ranges of constant correction factors were expanded from 2.29-2.83 and 1.97-2.52 to 2.29-4.2 and 1.97-4.3, respectively.

Unfortunately, in 20 and 40% v/v dioxane-water solutions, the weak and strong acid buffer zones did not overlap because of the high $\log{}^{c}K_{NH}$ values. Hence, the pH range of constant correction factors could not be expanded in these solvent media by the above procedure, but the correction factors determined at pH values close to the $\log{}^{c}K_{NH}$ values agreed well with those found in the strong acid region.

Since the glass electrode responds linearly with hydrogen-ion concentration up to $R \approx 11.5$, previous authors assumed that the correction factor determined in strong acid solution was valid at least up to $R \approx 11.5$. The expansion of the pH range in which the correction factor is constant as shown in the present study strengthens the justification of this assumption.

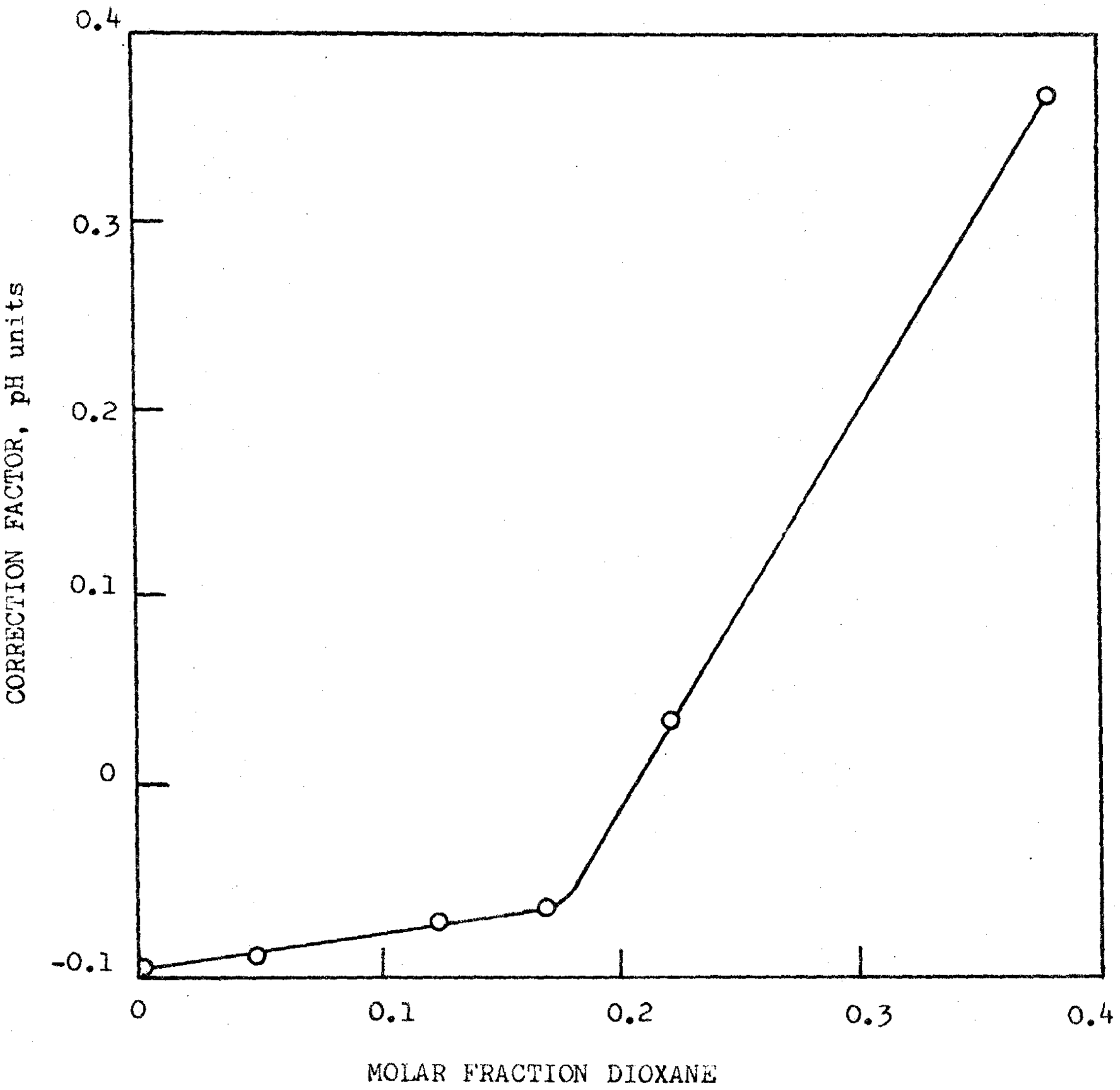

Figure 1. Glass electrode correction factor *versus* molar fraction dioxane in the solvent. The circles are experimental points.

Determination of p_cK_w

Values of p_cK_w in dioxane-water media were determined from data given by the titrations in which the correction factors were determined.

At each point on the titration curve past the equivalence point, the pH reading was corrected for sodium-ion error, using the data available for aqueous systems(103). The sodium-ion corrections applied were small, the maximum being less than 0.05pH units. Application of the correction factor to each point yielded p_cH.

From the volume of base added, and from corrections for the incomplete dissociation of sodium hydroxide in dioxane-water solutions(104), the values of p_cOH were calculated. Then, p_cK_w was calculated for each point from

$$p_cK_w = p_cH + p_cOH. \qquad (12)$$

Table IV summarizes the calculated values of p_cK_w.

The value of p_cK_w in 50% v/v dioxane-water is larger than that obtained by Takamoto et al. (15.38)(105) and by E. J. Billo (15.33)(102). These workers, however, did not correct for the incomplete dissociation of sodium hydroxide in 50% v/v dioxane. A value of 15.35 is obtained in the present work if this incomplete dissociation is ignored.

This work has shown that pH readings in dioxane-water media are reproducible and can be related to such concentration quantities as p_cH, p_cOH and p_cK_w by simple algebraic correction terms. The correction terms and the values of p_cK_w were necessary for the calculation of proton and metal-chelate formation constants in the various solvent media used.

TABLE IV

Concentration Dissociation Constant of Water

% v/v Dioxane-Water	p_cK_w	pH Range
20	14.38	10.5-12.2
40	15.12	11.2-12.8
50	15.60*	-
60	16.34	13.2-13.6
75	18.24	13.1-14.1

*This value was calculated from the data in reference (102).

Potentiometric Determination of Protonation Constants

The apparatus used for the potentiometric determination of protonation constants was the same as that used for the calibration of the glass electrode. For the titrations of 8-mercaptoquinoline, a #14 rubber stopper equipped with holes as in the lucite cover, was used to ensure tight closure of the cell to the atmosphere. The rubber stopper was fitted with a glass-spoon assembly that could be lowered into the solution. The sodium salt of 8-mercaptoquinoline was held in the spoon above the solution. De-oxygenated nitrogen gas was bubbled through the solution for one hour. The spoon was lowered into the solution and the titration was begun.

The titration procedure was as follows: 5 ml of a standard solution of the ligand in dioxane were pipetted into the titration cell (8-hydroxyquinoline-5-sulfonic acid was prepared in aqueous solution as the monosodium salt). Next, 20 ml of the perchloric acid solution were added, followed by appropriate volumes of dioxane and water to give a volume of 100 ml and solution compositions of 0, 20, 40, 60 and 75% v/v dioxane-water. Small increments of standard sodium hydroxide solution were then added as described before, and the pH recorded. Attainment of equilibrium was rapid in every titration.

The pH readings were converted to hydrogen-ion concentrations as previously described. The protonation constants were calculated as discussed below.

The variable $\bar{p}$, the average number of protons bound to each ligand molecule, is given by

$$\bar{p} = \frac{[\text{total available protons}]-[\text{free hydrogen-ion}]}{[\text{total ligand}]} . \qquad (13)$$

This variable was calculated for each point on the titration curve. At any point in a titration, the stoichiometric concentration of available protons is equal to $J \cdot C_L + [C\ell O_4^-] + [OH^-] - [Na^+]$, where C_L is the analytical concentration of the ligand H_JL which has J dissociable protons, $[Na^+]$ and $[C\ell O_4^-]$ are the analytical concentrations of sodium-ion and perchloric acid respectively, and $[OH^-]$ is the equilibrium concentration of hydroxide-ion.

Then,

$$\bar{p} = \frac{J \cdot C_L + [C\ell O_4^-] + [OH^-] - [Na^+] - [H^+]}{C_L} \tag{14}$$

where $[H^+]$ is the concentration of free hydrogen-ion. All concentrations are in moles/liter.

For all ligands used in this work, J was 2. The two protonation constants of each ligand were obtained from the $(\bar{p}, \text{pH})$ data as given below.

Equation (13) can be rewritten as

$$\bar{p} = \frac{[HL] + 2[H_2L^+]}{[L^-] + [HL] + [H_2L^+]} , \tag{15}$$

which on appropriate substitution yields

$$\bar{p} = \frac{{}^cK_{OH}[H^+] + 2\,{}^cK_{OH}\,{}^cK_{NH}[H^+]^2}{1 + {}^cK_{OH}[H^+] + {}^cK_{OH}\,{}^cK_{NH}[H^+]^2} . \tag{16}$$

Equation (16) may be rearranged to give

$$\frac{\bar{p}}{(\bar{p}-1)[H^+]} = {}^cK_{OH}\,{}^cK_{NH}\,\frac{(2-\bar{p})[H^+]}{(\bar{p}-1)} - {}^cK_{OH} \tag{17}$$

or

$$Y = {}^cK_{OH}\,{}^cK_{NH}X - {}^cK_{OH} \tag{18}$$

where

$$Y = \frac{\bar{p}}{(\bar{p}-1)[H^+]}$$

and

$$X = \frac{(2-\bar{p})[H^+]}{(\bar{p}-1)} .$$

The values of ${}^{c}K_{OH}$ and ${}^{c}K_{NH}$ were obtained from the intercept and slope of a linear least-squares fit of the data to equation (18). An IBM 7040 or a CDC 6400 computer was used. Only values of $\bar{p}$ in the range 0.2-0.8 and 1.2-1.8 were used in the calculations. The remaining data were rejected because the coefficients X and Y are very sensitive to experimental errors at values of $\bar{p}$ near 0, 1 and 2. Some representative titration data are shown in Appendix 1.

The protonation constants are given in Table V. The constants are the results of at least two determinations. The precision is expressed as the average of the standard deviation, σ, where

$$\sigma = \sqrt{\frac{\Sigma\ (\bar{p}_{exp} - \bar{p}_{calc})^2}{(N-1)}} \tag{19}$$

and $\bar{p}_{exp}$ represents the experimental $\bar{p}$ values,

$\bar{p}_{calc}$ represents the $\bar{p}$ values calculated from the determined protonation constants, and

N is the number of data points.

The sulfonate group in 8-hydroxyquinoline-5-sulfonic acid is too acidic for potentiometric determination of its protonation constant. This is not important, however, since the sulfonate group is completely dissociated in the pH range in which metal chelation occurs.

TABLE V

Ligand Protonation Constants

(25.0°C, I = 0.1)

Ligand	% v/v Dioxane	$\mathrm{Log}\,{}^{c}K_{NH}$	$\mathrm{Log}\,{}^{c}K_{OH}$	σ
8-Hydroxyquinoline	20	4.70	10.26	0.02
	40	4.36	10.88	0.02
	60	3.97	11.48 11.53*	0.01
	75	3.73	12.01 12.38*	0.01
5-Chloro-8-hydroxyquinoline	20	3.35	9.49	0.02
	40	2.94	10.04	0.02
	60	2.55	10.64	0.01
	75	2.39	11.12	0.01
8-Hydroxyquinoline-5-sulfonic acid	0	3.96	8.42	0.02
	20	3.76	9.03	0.01
	40	3.69	9.71	0.01
	60	3.56	10.32	0.03
	75	3.56	10.86	0.03
5-Acetyl-8-hydroxyquinoline	20	3.65	8.01	0.01
	40	3.33	8.44	0.02
	60	2.93	9.05	0.01

TABLE V (Cont'd.)

Ligand	% v/v Dioxane	$\log {}^{c}K_{NH}$	$\log {}^{c}K_{OH}$	σ
	75	2.79	9.65	0.01
5-Nitro-8-hydroxyquinoline	20	2.23 2.25*	6.24	0.02
	40	1.96*	6.59	0.03
	60	1.61*	7.19	0.01
	75	1.43*	7.92	0.02
8-Mercaptoquinoline	20	2.04	8.50	0.02
	40	1.91†	8.90	0.02
	60	1.76†	9.45	0.02
	75	1.65†	10.35	0.02
Sebacic acid	20	5.05	5.92	0.01
	40	6.00	6.77	0.01
	60	7.27	7.90	0.01
2,2'-Di-(thioethyl)-sulfide	20	9.10	10.41	0.04
	40	9.91	11.02	0.02
	60	11.04	12.10	0.03

*Determined spectrophotometrically.

†Values extrapolated from data in reference (100).

Potentiometric Determination of Metal Chelate Formation Constants

The titration procedure was similar to that used in the potentiometric determination of protonation constants. The standard metal-ion solution was added in 2-, 5- and 5-ml portions in place of the corresponding volume of water for titrations in 40, 60 and 75% v/v dioxane-water, respectively. In titrations with 8-hydroxyquinoline-5-sulfonic acid, a 5-ml portion of the metal-ion solution was used each time.

In titrations of Fe(II) and Ag(I), the ligands were added as solids. The solutions containing Fe(II) were de-aerated for one hour before addition of the ligand and titration. This procedure was used because the Fe(II) complexes are readily oxidized to the Fe(III) complexes. No oxidation was observed in the titrations.

In order to prevent precipitation of silver chloride during the titrations involving Ag(I), contact between the saturated calomel electrode and the Ag(I) solution was made through a sodium perchlorate-agar salt bridge. The correction factor of the glass electrode was re-determined and found to be -0.58±0.01 in 60% v/v dioxane-water at 25.0°C and $I = 0.1$.

To test the reliability of pH readings obtained with the salt bridge, the $\log {}^{c}K_{NH}$ value of 8-hydroxyquinoline was determined and found to be 3.92 (compared to 3.97 without the salt bridge).

Typical chelate formation curves are shown in Figures 7 and 8. Both figures show that the pH at which chelation occurs increases in the series Ni < Zn < Mn < Mg < Ca, i.e., the reverse order of chelate stability.

Formation constants could not be determined in 20% v/v dioxane-water because of precipitation of the metal chelates.

The general equations of Hearon and Gilbert(106) for the calculation

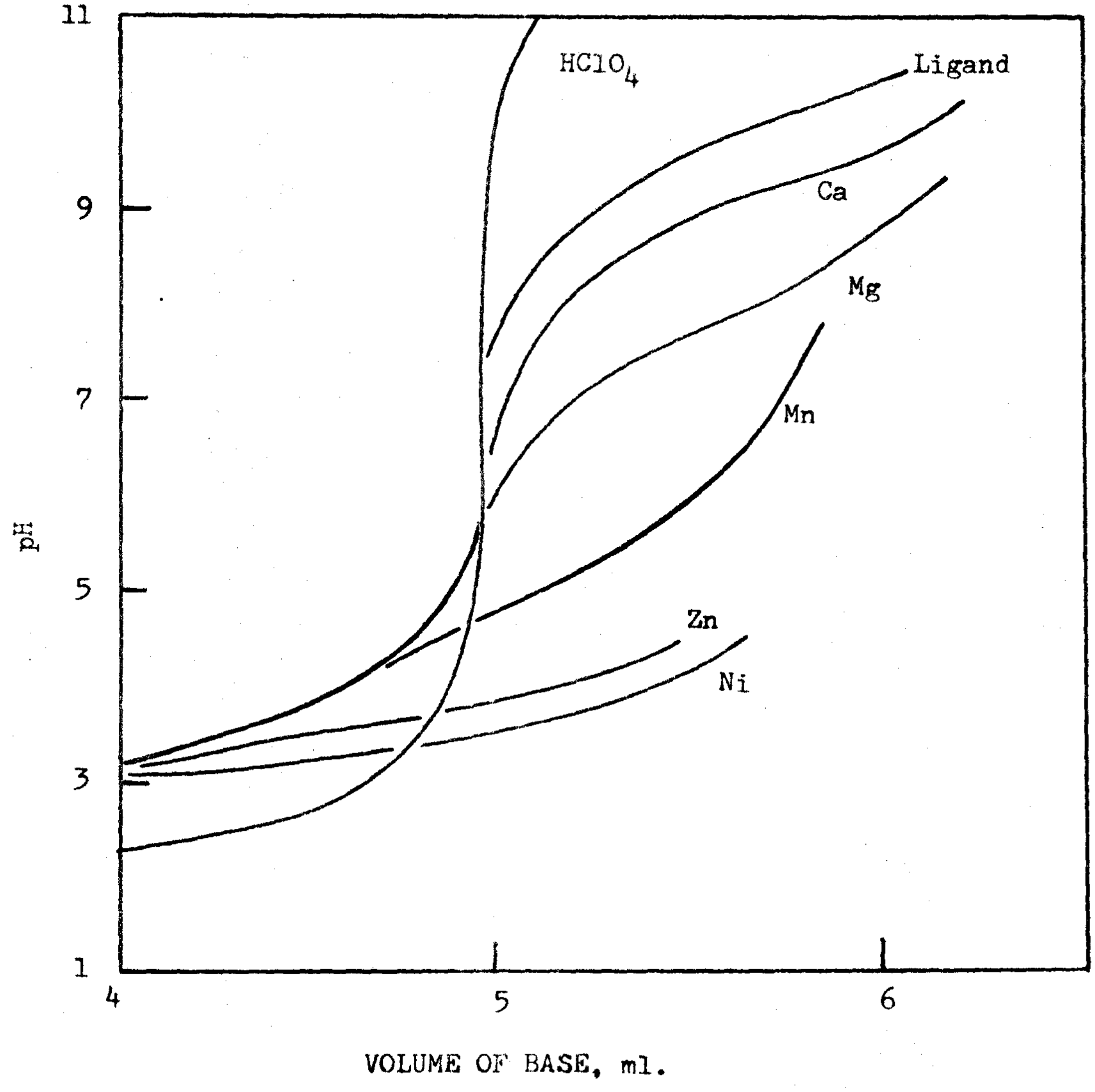

Figure 2. Titration curves of metal chelates of 8-hydroxyquinoline in 60% v/v dioxane-water, 25°C, I = 0.1.

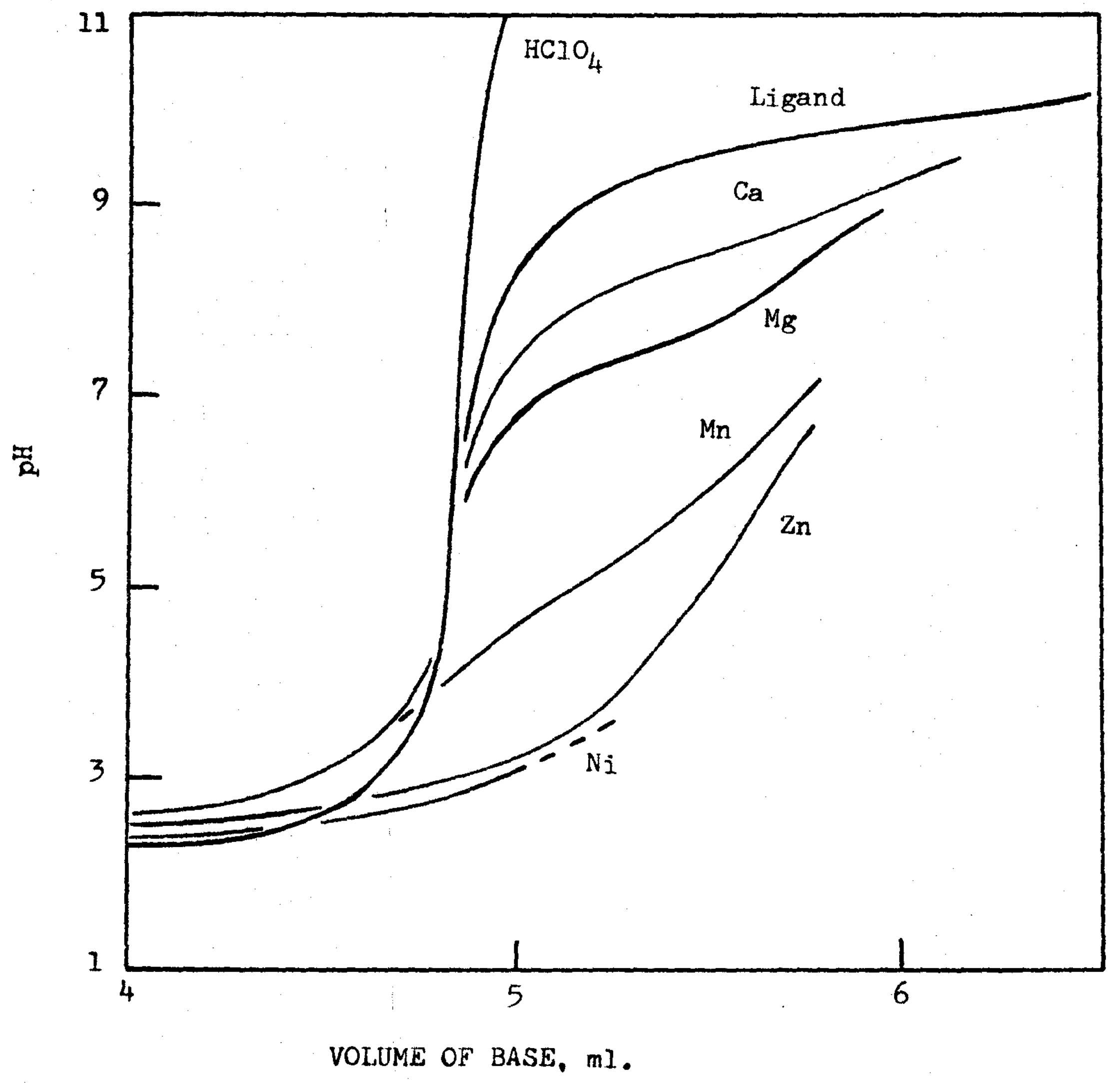

Figure 3. Titration curves of metal chelates of 5-chloro-8-hydroxyquinoline in 60% v/v dioxane-water, 25°C, I = 0.1.

of metal-chelate formation constants from potentiometric data are

$$[L] = \frac{-z_L\ C_L - z_M C_M - \Sigma z_S [S_S]}{\sum_{j=0}^{J} j\, {}^{c}\beta_j^H [H^+]^j} \tag{20}$$

and

$$\overline{n} = \frac{C_L - [L] \sum_{j=0}^{J} {}^{c}\beta_j^H [H^+]^j}{C_M} \tag{21}$$

where C_M and C_L are the analytical concentrations of the metal-ion and ligand, respectively, in moles per liter; z_M and z_L are the charges of the metal-ion and the chelating form of the ligand, respectively, and z_S and $[S_S]$ are the charge and concentration of the S^{th} ion which contains neither metal-ion nor ligand. This quantity is known; it contains the anions of metal-salt and strong acid, the cation of the base, and $[H^+]$ and $[OH^-]$. $[L]$ is the molar concentration of the chelating form (charge omitted) of the ligand; $\overline{n}$ is the average number of ligands bound to a metal-ion at a particular value of $[L]$, and is given by

$$\overline{n} = \frac{\text{total concentration of ligand bound to metal-ion}}{\text{total concentration of metal-ion}} . \tag{22}$$

${}^{c}\beta_J^H$ is the overall protonation constant.

Values of $[L]$ and $\overline{n}$ for all systems studied were calculated from the appropriate form of equations (20) and (21), i.e.,

$$[L] = \frac{C_L - [H^+] - [Na^+] + [C\ell O_4^-] + [OH^-]}{{}^{c}K_{OH}[H^+] + 2\,{}^{c}K_{OH}\,{}^{c}K_{NH}[H^+]^2} \tag{23}$$

and

$$\bar{n} = \frac{C_L - [L](1 + {}^cK_{OH}[H^+] + {}^cK_{OH}{}^cK_{NH}[H^+]^2)}{C_M} . \qquad (24)$$

The derivation of equation (23) and (24) from (20) and (21) are given fully in references (102) and (106).

Calculation of values of $\bar{n}$ and corresponding values of [L] from the experimental quantities provides the data from which formation constants may be calculated.

For systems in which the highest chelate formed is ML , equation (22) becomes

$$\bar{n} = \frac{[ML] + 2[ML_2]}{[M] + [ML] + [ML_2]} \qquad (25)$$

where charges are omitted for simplicity. The stepwise formation constants are given by

$${}^cK_1 = \frac{[ML]}{[M][L]} \qquad (26)$$

and

$${}^cK_2 = \frac{[ML_2]}{[ML][L]} \qquad (27)$$

Substitution of equations (26) and (27) into (25) gives

$$\bar{n} = \frac{{}^cK_1[L] + 2{}^cK_1{}^cK_2[L]^2}{1 + K_1[L] + K_1K_2[L]^2} \qquad (28)$$

or

$$\bar{n} = \frac{{}^c\beta_1[L] + 2{}^c\beta_2[L]^2}{1 + {}^c\beta_1[L] + {}^c\beta_2[L]^2} \qquad (29)$$

where ${}^c\beta_1 = {}^cK_1$,

and ${}^{c}\beta_2 = {}^{c}K_1{}^{c}K_2$.

Equation (29) can be rearranged to give

$$\frac{\bar{n}}{(1-\bar{n})[L]} = \frac{(2-\bar{n})[L]}{(1-\bar{n})}\,{}^{c}\beta_2 + {}^{c}\beta_1 \tag{30}$$

or

$$Y = {}^{c}\beta_2 X + {}^{c}\beta_1 \tag{31}$$

where
$$Y = \frac{\bar{n}}{(1-\bar{n})[L]}$$

and
$$X = \frac{(2-\bar{n})[L]}{(1-\bar{n})} .$$

A graph of X against Y yields a straight line of intercept ${}^{c}\beta_1$ and slope ${}^{c}\beta_2$. In the present work, the slope and intercept were obtained by a least-squares fit to data. This method avoids subjective factors and utilizes a large amount of the available data(107). Values of $\bar{n}$ near 0, 1 and 2 were rejected since X and Y are sensitive to experimental errors in $\bar{n}$ at such values.

For a system in which the highest chelate is ML_3,

$$\bar{n} = \frac{{}^{c}\beta_1[L] + 2{}^{c}\beta_2[L]^2 + 3{}^{c}\beta_3[L]^3}{1 + {}^{c}\beta_1[L] + {}^{c}\beta_2[L]^2 + {}^{c}\beta_3[L]^3} \tag{32}$$

where ${}^{c}\beta_3 = {}^{c}K_1{}^{c}K_2{}^{c}K_3$. Rearrangement of equation (32) gives

$$\frac{\bar{n}}{(1-\bar{n})[L]} = \frac{(2-\bar{n})[L]}{(1-\bar{n})}\,{}^{c}\beta_2 + \frac{(3-\bar{n})[L]^2}{(1-\bar{n})}\,{}^{c}\beta_3 + {}^{c}\beta_1 \tag{33}$$

or

$$Y = {}^{c}\beta_2 X + {}^{c}\beta_3 Z + {}^{c}\beta_1 \tag{34}$$

where
$$X = \frac{(2-\bar{n})[L]}{(1-\bar{n})} ,$$

$$Y = \frac{\bar{n}}{(1-\bar{n})[L]},$$

and

$$Z = \frac{(3-\bar{n})[L]^2}{(1-\bar{n})}.$$

Substitution of three sets of $(\bar{n},[L])$ data into equation (34) yields three simultaneous linear equations in the unknowns, ${}^c\beta_1$, ${}^c\beta_2$ and ${}^c\beta_3$. Only $\bar{n}$ values in the ranges 0.15-0.85, 1.15-1.85 and 2.15-2.85, were used. All titrations were carried out at a ligand:metal molar ratio of at least 8:1 (usually greater).

The experimental stepwise formation constants are given in Tables VI to XI. The average constants, $\frac{1}{z}\log{}^c\beta_z$, where z is the charge on the metal-ion, are given in Table XII. The stepwise constants of trivalent metal-ions are not reported. The solution to the three simultaneous linear equations is very sensitive to errors in the experimental data. To obtain reproducible values of the stepwise constants requires personal judgement(107) of the data. The value of the average constant, however, is easily reproduced. No data need be rejected.

The precision of the data is expressed as the average of the standard deviation, σ, where

$$\sigma = \sqrt{\frac{\Sigma(\bar{n}_{exp} - \bar{n}_{calc})^2}{(N-1)}} \tag{35}$$

and $\bar{n}_{exp}$ is the experimental $\bar{n}$ value,

$\bar{n}_{calc}$ is the $\bar{n}$ value calculated from the determined formation constants,

and N is the number of data points.

All formation constants are the average of at least two determina-

TABLE VI

Formation Constants of Metal Chelates of 8-Hydroxyquinoline in Dioxane-Water Solvents

(25.0°C, I = 0.1)

Ion	% v/v Dioxane	$\log {}^cK_1$	$\log {}^cK_2$	σ
Ag(I)	60	6.06	4.64	0.01
Mg(II)	40	5.26	5.01	0.05
	60	5.79	5.23	0.02
	75	6.38	5.86	0.03
Ca(II)	60	4.40	3.61	0.01
	75	5.22	4.37	0.03
Mn(II)	40	6.97	6.45	0.02
	60	7.62	6.70	0.01
	75	8.35	7.32	0.02
Fe(II)	60	9.59	8.58	0.05
Ni(II)	40	10.26	9.75	0.09
	60	11.08	10.68	0.07
	75	11.79	11.29	0.02
Zn(II)	40	9.35	8.81	0.02
	60	9.96	9.02	0.04
	75	10.60	9.16	0.03
Pb(II)	40	9.90	7.30	0.02
	60	10.82	7.59	0.08
	75	11.36	9.08	0.06

TABLE VII

Formation Constants of Metal Chelates of 5-Chloro-8-hydroxyquinoline in Dioxane-Water Solvents

(25.0°C, I = 0.1)

Ion	% v/v Dioxane	$\log^c K_1$	$\log^c K_2$	σ
Mg(II)	40	5.08	4.85	0.04
	60	5.38	5.05	0.03
	75	5.66	5.23	0.03
Ca(II)	60	4.02	3.15	0.02
	75	4.28	3.51	0.02
Mn(II)	40	6.20	6.09	0.02
	60	7.13	6.43	0.01
	75	7.40	6.65	0.02
Fe(II)	60	8.61	8.01	0.06
Ni(II)	40	9.71	8.82	0.01
	60	10.34	9.55	0.04
	75	10.91	9.59	0.03
Zn(II)	40	8.81	8.57	0.05
	60	9.00	8.85	0.01
	75	9.61	8.92	0.02
Pb(II)	60	10.26	7.56	0.05

TABLE VIII

Formation Constants of Metal Chelates of 8-Hydroxyquinoline-5-sulfonic acid in Dioxane-water Solvents

(25.0°C, I = 0.1)

Ion	% v/v Dioxane	Log^cK_1	Log^cK_2	σ
Mg(II)	0	4.28	3.59	0.09
	20	4.67	3.91	0.05
	40	5.17	4.38	0.04
	60	5.70	4.79	0.02
Ca(II)	0	3.66	2.26	0.08
	20	3.95	2.68	0.08
	40	4.16	2.99	0.04
	60	4.53	3.48	0.06
Mn(II)	0	5.99	4.96	0.05
	20	6.23	5.46	0.02
	40	6.85	5.86	0.02
	60	7.43	6.31	0.01
Ni(II)	0	9.40	8.31	0.02
	20	9.73	8.46	0.02
	40	10.12	8.93	0.01
	60	10.60	9.27	0.02
Zn(II)	0	8.40	7.10	0.02
	20	8.63	7.42	0.01
	40	9.11	7.99	0.01
	60	9.66	8.40	0.01

TABLE IX

Formation Constants of Metal Chelates of 5-Acetyl-8-hydroxyquinoline in Dioxane-water Solvents

(25.0°C, I = 0.1)

Ion	% v/v Dioxane	$\log {}^{c}K_1$	$\log {}^{c}K_2$	σ
Ag(I)	60	5.35		0.02
Mg(II)	40	4.30	4.27	0.01
	60	4.91	4.48	0.02
	75	5.34	4.71	0.04
Ca(II)	60	3.71	3.04	0.03
	75	4.10	3.40	0.04
Mn(II)	40	6.21	5.80	0.02
	60	6.78	6.30	0.02
	75	7.32	6.54	0.04
Fe(II)	60	8.56	7.62	0.08
Ni(II)	40	9.15	8.78	0.04
	60	9.91	9.24	0.03
	75	10.31	9.84	0.01
Zn(II)	40	8.20	7.72	0.03
	60	8.57	8.13	0.04
	75	9.27	8.64	0.05
Pb(II)	60	9.04	6.45	0.03

TABLE X

Formation Constants of Metal Chelates of 5-Nitro-8-hydroxyquinoline in Dioxane-water Solvents

(25.0°C, I = 0.1)

Ion	% v/v Dioxane	$\mathrm{Log}\,^{c}K_1$	$\mathrm{Log}\,^{c}K_2$	σ
Ag(I)	60	4.82	4.26	0.01
Mg(II)	40	3.80	3.52	0.09
	60	4.27	3.90	0.04
	75	4.80	4.41	0.04
Ca(II)	60	3.24	2.52	0.02
	75	3.74	2.99	0.05
Mn(II)	40	5.47	4.78	0.04
	60	6.15	5.11	0.03
	75	6.45	5.70	0.04
Fe(II)	60	7.16	6.41	0.05
Ni(II)	60	8.81*		
	75	9.44*		
Zn(II)	40	7.20	6.50	0.04
	60	7.73	6.69	0.03
	75	8.43	7.23	0.06
Pb(II)	60	7.63	5.53	0.04

*Determined spectrophotometrically.

TABLE XI

Formation Constants of Metal Chelates of 8-Mercaptoquinoline in Dioxane-water Solvents (25.0°C, I = 0.1)

Ion	% v/v Dioxane	$\mathrm{Log}^{c}K_1$	$\mathrm{Log}^{c}K_2$	$\frac{1}{2}\mathrm{Log}^{c}\beta_2$
Mg(II)	60	3.56	3.19	3.37
	75	4.55	3.11	3.83
Mn(II)	60	7.75	5.71	6.73
	75	7.70	7.00	7.35

TABLE XII

Average Formation Constants,

$\frac{1}{z}\log{}^{c}\beta_z$ of Metal Chelates of (1) 8-Hydroxyquinoline, (2) 5-Chloro-8-hydroxyquinoline, (3) 5-Acetyl-8-hydroxyquinoline, (4) 5-Nitro-8-hydroxyquinoline, (5) 8-Hydroxyquinoline-5-sulfonic acid.

Ion	% v/v Dioxane	1	2	3	4	5
Ag(I)	60	6.06			4.82	
Mg(II)	0					3.94
	20					4.29
	40	5.14	4.97	4.29	3.66	4.78
	60	5.51	5.22	4.70	4.09	5.25
	75	6.12	5.45	5.03	4.61	
Ca(II)	0					2.96
	20					3.32
	40					3.57
	60	4.01	3.59	3.38	2.88	4.00
	75	4.80	3.90	3.75	3.37	
Mn(II)	0					5.48
	20					5.85
	40	6.71	6.15	6.01	5.13	6.36
	60	7.16	6.78	6.54	5.75	6.87
	75	7.84	7.03	6.93	6.08	
Fe(II)	60	9.09	8.31	8.09	6.79	

TABLE XII (Cont'd.)

Ion	% v/v Dioxane	1	2	3	4	5
Ni(II)	0					8.85
	20					9.09
	40	10.00	9.27	8.97		9.52
	60	10.88	9.95	9.58		9.94
	75	11.54	10.25	10.08		
Zn(II)	0					7.75
	20					8.03
	40	8.98	8.69	7.96	6.65	8.55
	60	9.49	8.93	8.35	7.21	9.07
	75	10.08	9.27	8.96	7.83	
Pb(II)	60	9.20	8.91	7.75	6.53	
Aℓ(III)	40	10.65				
	60	11.25	10.61	8.88	7.14	
	75	12.15				
Sc(III)	60	10.18	9.47	8.81	7.19	
Fe(III)	60	12.58	11.46	10.46	8.63	
Ce(III)	60	7.66	7.23	6.61	5.65	

tions. Representative metal-chelate formation data are given in Appendix II.

Spectrophotometric Determination of Protonation Constants

The second protonation constant, $\log {}^{c}K_{NH}$, of 5-nitro-8-hydroxyquinoline was determined spectrophotometrically in 20, 40, 60 and 75% v/v dioxane-water because the pH range of protonation is beyond the lower limit of the potentiometric method.

The first protonation constant, $\log {}^{c}K_{OH}$, of 8-hydroxyquinoline in 60 and 75% v/v dioxane-water was also determined spectrophocometrically. In the range of protonation (pH 12-13), the sodium-ion errors are appreciably large (>0.05 pH units). Also, reproducible behavior of the glass electrode at high pH values in solvents of large % v/v dioxane-water has not been demonstrated.

Preliminary spectra of the ligands at various pH values were recorded in the visible range in order to find suitable wavelengths for measurement. Solutions of the ligand (10^{-3} - 10^{-4} M) were prepared in the appropriate solvent compositions. The pH of these solutions was adjusted with either perchloric acid or sodium hydroxide solution to give solutions containing only one form of the ligand.

Figure 4 shows the spectra of the neutral and the protonated forms of 5-nitro-8-hydroxyquinoline in 20% v/v dioxane-water. At 453 mμ, the neutral form has a strong absorption band; the protonated form does not absorb at this wavelength.

The spectra of the neutral and anionic forms of 8-hydroxyquinoline in 60 and 75% v/v dioxane-water are shown in Figure 5. At 386 mμ, the absorbance of the anionic form is strong; the neutral form absorbs negligibly. Table XIII summarizes the pertinent spectral data. The wave-

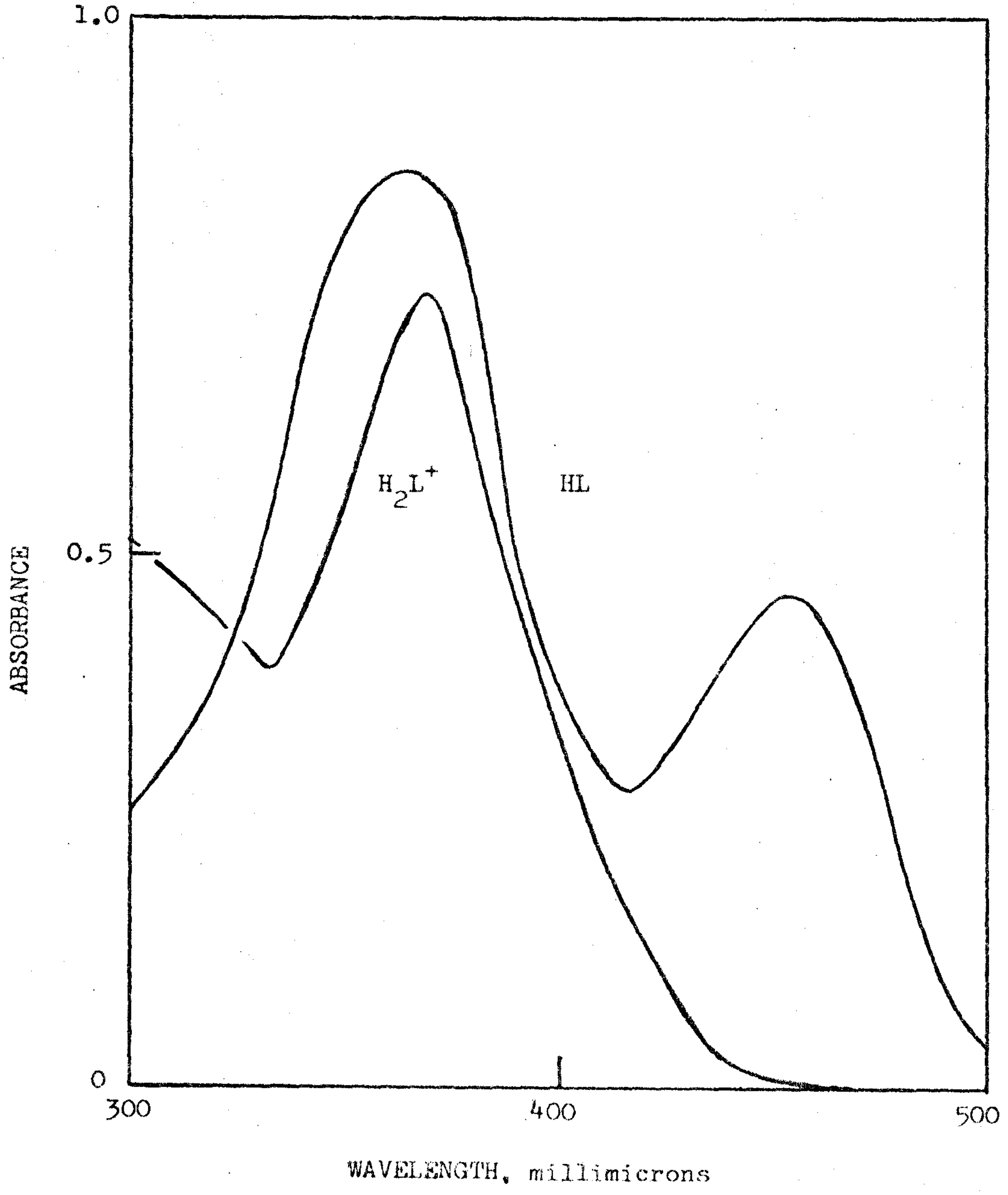

Figure 4. Absorption spectra of the neutral (pH = 4.6) and the protonated (pH ≈ 0) forms of 5-nitro-8-hydroxyquinoline in 60% v/v dioxane-water, 25°C, I = 0.1.

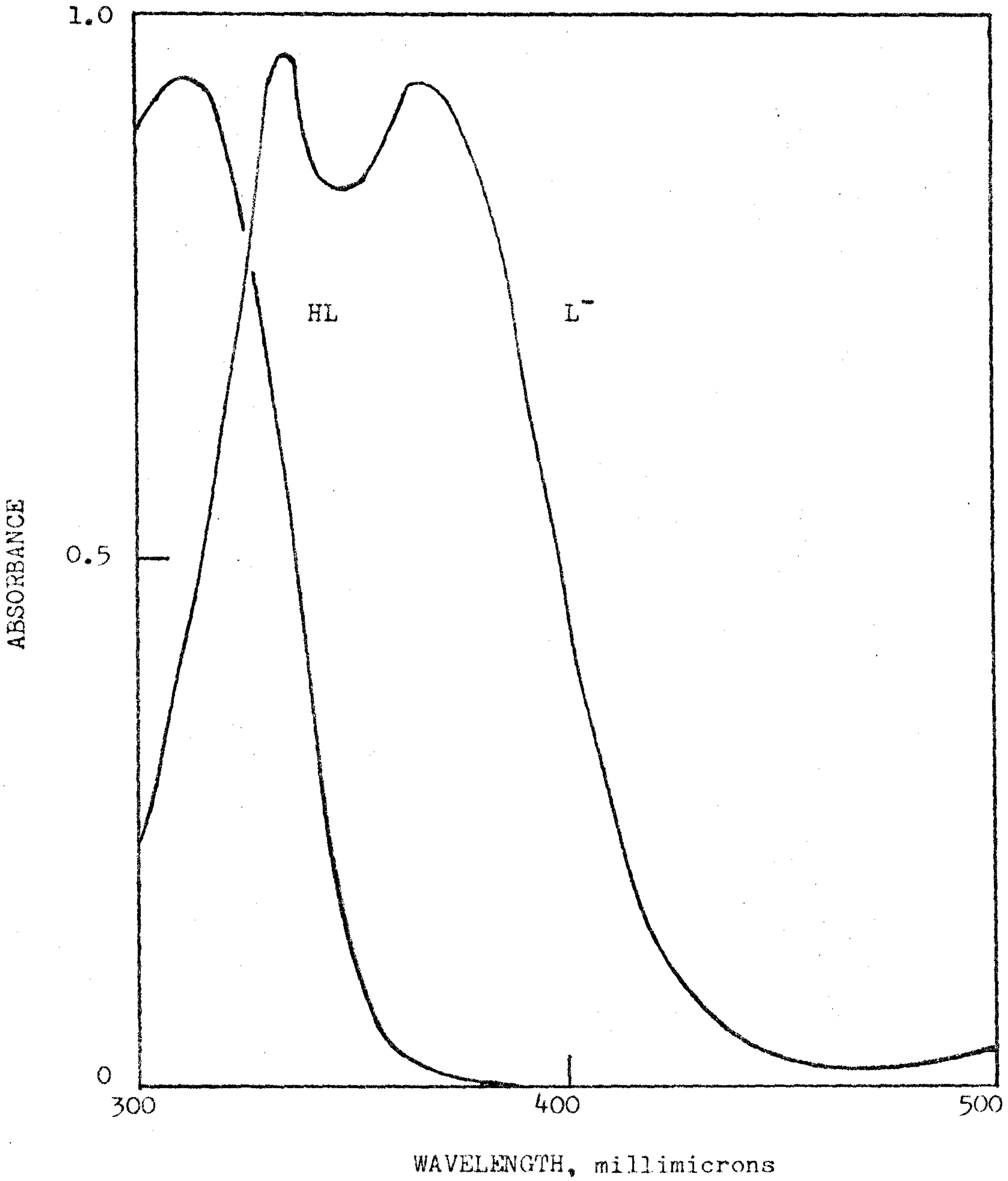

Figure 5. Absorption spectra of the neutral (pH ≈ 6) and anionic (pH = 14) forms of 8-hydroxyquinoline in 60% v/v dioxane-water, 25°C, I = 0.1.

TABLE XIII

Spectral Data for Ligands

(25°C, 1-cm fused silica cells)

Ligand	% v/v Dioxane	pH	λ(mμ)	Log ε
5-Nitro-8-hydroxyquinoline (neutral form)	20	5.2	453	3.48
	40	5.3	453	3.30
	60	4.6	453	3.04
	75	4.5	453	2.85
8-Hydroxyquinoline (anionic form)	60	~14	386	4.59
	75	~15	386	4.59

lengths 453 and 386 mμ were used for determining the protonation constants.

Solutions for the determination of the protonation constants were prepared as follows. 10-ml portions of a standard solution of the ligand in dioxane were diluted to the mark in 50-ml volumetric flasks with appropriate volumes of dioxane and aqueous solutions to give solvent compositions of 20, 40, 60 or 75% v/v dioxane-water. The pH of these solutions was maintained either by perchloric acid or sodium hydroxide. The ionic strength was adjusted to 0.1 with sodium perchlorate*. The flasks were equilibrated at 25.0°C and the volumes adjusted to 50.0 ml with a few drops of a dioxane-water mixture of appropriate composition. Fused silica absorption cells (1.00 cm) were used.

A plot of absorbance (at 453 mμ) against pH is shown in Figure 6 for 5-nitro-8-hydroxyquinoline in 20% v/v dioxane-water. The data for 40, 60 and 75% v/v dioxane-water give similar plots.

A Beer's law plot was made for the anionic form of 8-hydroxyquinoline in 60 and 75% v/v dioxane-water. All solutions were prepared essentially as previously described except that the volume of standard ligand solution added ranged from 2 to 10 ml. A volume of dioxane necessary to give 10 ml was then added. The Beer's law plot was the same for 60 and 75% v/v dioxane-water solution and is shown in Figure 7. The pH was calculated to be 14 and 15 for the two solutions.

The second protonation constant of 5-nitro-8-hydroxyquinoline was calculated using the equation

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*In solutions of pH 1 or less, the ionic strength was not controlled.

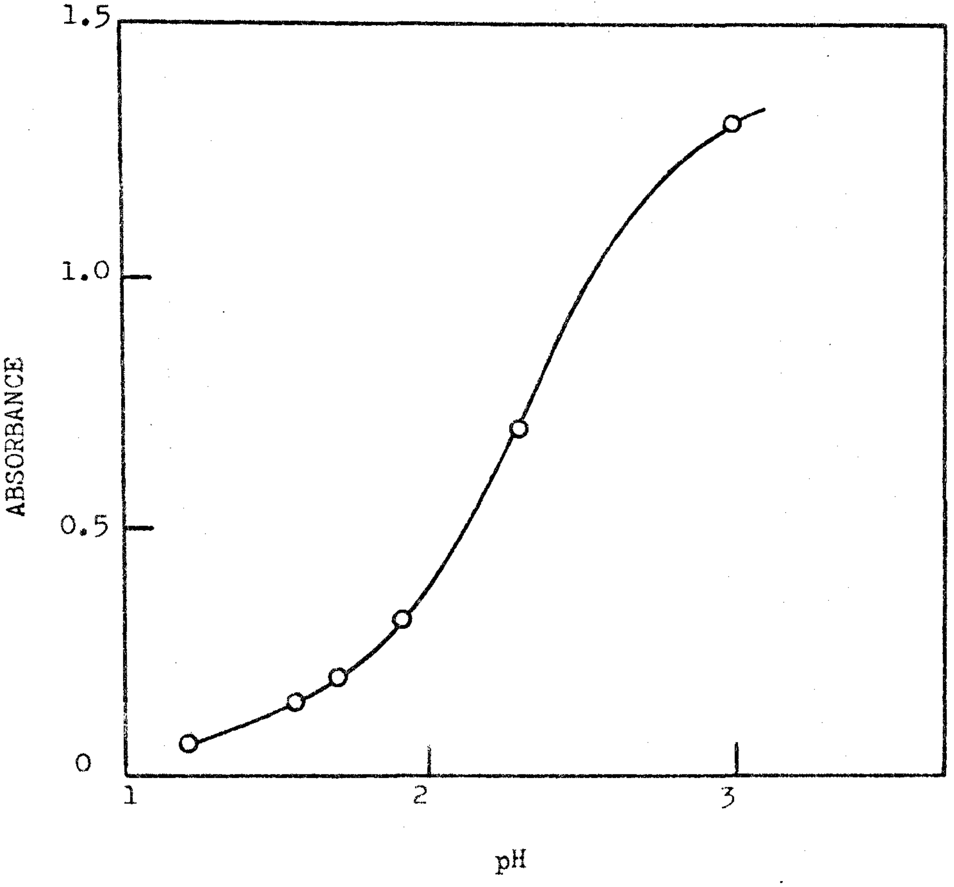

Figure 6. Absorbance versus pH for 5-nitro-8-hydroxyquinoline in 20% v/v dioxane-water, 25°C, I = 0.1, λ = 453 mμ.

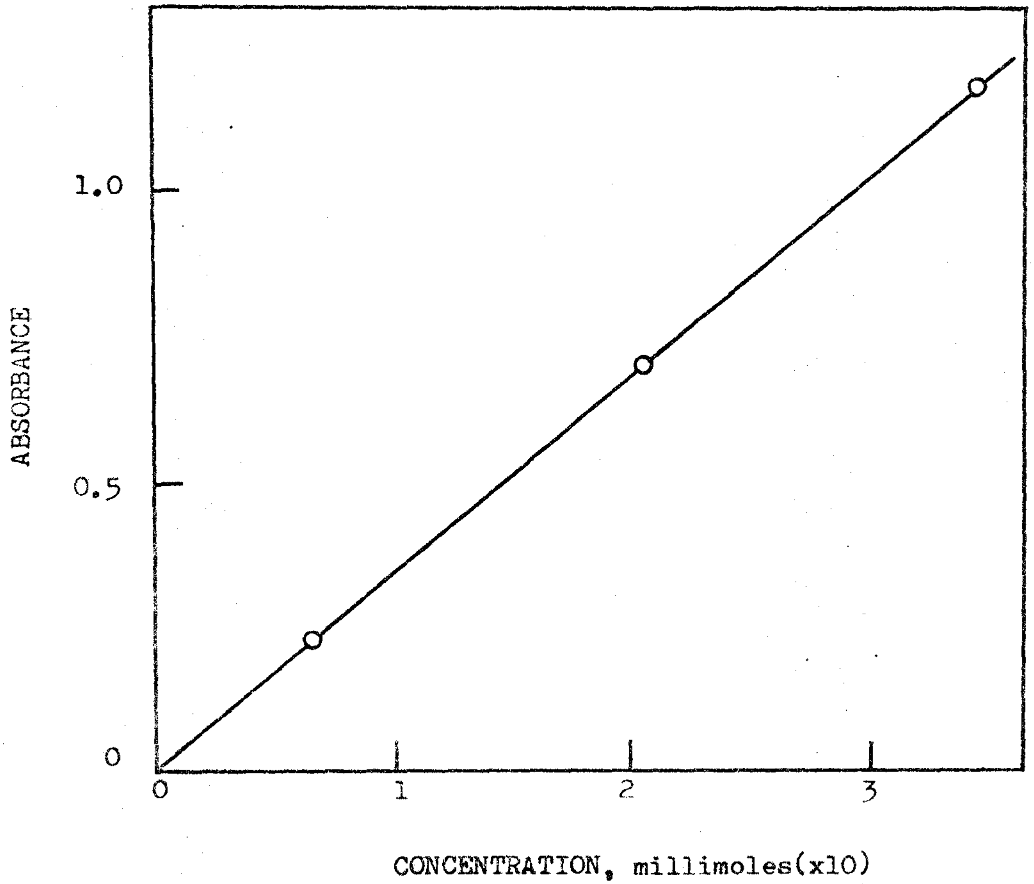

Figure 7. Beer's law plot of absorbance *versus* concentration for the anionic form (pH ≈ 14) of 8-hydroxyquinoline in 60% v/v dioxane-water, 25°C, I = 0.1, λ = 386 mμ.

$$\log {}^{c}K_{NH} = p_{c}H + \log \frac{A_{HL}-A}{A-A_{H_2L}} \qquad (36)$$

where A_{HL}, A_{H_2L} represent the absorbance of the neutral and protonated forms of the ligand and A represents the absorbance of the mixture of HL and H_2L^+. The pH of the solutions of the ligand was measured.

The first protonation constant of 8-hydroxyquinoline was calculated as follows. The concentration of the anionic form of the ligand was determined from the Beer's law plot. The concentration of the neutral form of the ligand was obtained from the difference between the analytical ligand concentration and the concentration of the anionic form. The concentration of free base (p_cOH) was obtained from the difference between the analytical concentration of NaOH added and the concentration of the anionic form of the ligand. The pH of the solutions was then calculated from

$$p_cH = p_cK_w - p_cOH\ . \qquad (12)$$

The protonation constant was calculated from

$$\log {}^{c}K_{OH} = p_{c}H + \log \frac{[HL]}{[L^-]}\ . \qquad (37)$$

The values of the protonation constants are given in Table V.

Spectrophotometric Determination of Metal-Chelate Formation Constants

The first stepwise formation constant of Ni(II) 5-nitro-8-hydroxyquinolinate* was determined spectrophotometrically in 60 and 75%

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*To be consistent with the nomenclature in the literature of 8-hydroxyquinoline complexes, the above name is used instead of the proper name, bis(8-hydroxyquinolinato) Ni(II).

v/v dioxane-water. The pH range of chelation is below the lower method of the potentiometric method. The latter method showed that the Ni(II) chelate was completely formed at pH 2.3.

Preliminary spectra showed that the Ni(II) chelate absorbs strongly at 439 mμ (log $\varepsilon = 4.19$), and that the protonated form of the ligand does not absorb in this region but the neutral form does (log $\varepsilon = 3.00$ at 439 mμ). The appreciable difference in the extinction coefficients, however, enabled the determination of the formation constant.

Solutions containing Ni(II)(10^{-5} M) and the ligand (10^{-5} M) were prepared as previously described for the potentiometric determination of formation constants. Measured portions of standard perchloric acid solution (0.159M) were added to these solutions. The portion of acid added was different for each solution to give different degrees of chelate formation. The pH of these solutions was measured and their absorbance at 439 mμ recorded.

The concentration of the anionic form of 5-nitro-8-hydroxyquinoline was calculated from equation (23). The first stepwise stability constant, ${}^{c}K_1$, was calculated from the equation

$$\frac{\varepsilon - \varepsilon_0}{[L]} = {}^{c}K_1(\varepsilon_1 - \varepsilon) \tag{38}$$

where ε_0, ε_1 and ε are the extinction coefficients of the solution in the absence of the ligand, of the neutral form of the ligand, and of the solution containing both the ligand and the metal chelate[(108)], respectively. For 1.00 cm absorption cells, ε is given by

$$\varepsilon = \frac{A - \varepsilon_1[L]}{C_M} \tag{39}$$

where A is the absorbance of the solution. The absorbance of the Ni(II) chelate versus pH in 75% v/v dioxane-water is shown in Figure 8.

The values of the first stepwise formation constant are given in Table X.

Calorimetric Determination of ΔH

The heats of reaction, ΔH, for the formation of several metal complexes of 8-hydroxyquinoline-5-sulfonic acid were determined. The apparatus used was described earlier. The procedure used in all determinations was as follows. A 50-ml portion of one of the reactants was pipetted into the Dewar flask and was diluted with measured volumes of dioxane and/or water, to give a volume of 100.0, 102.5 and 106.5 ml for solution compositions of 0, 20 and 40% v/v dioxane-water, respectively (Solution A). The glass bulb was filled to the mark with the other reactant (Solution B), and the rubber stopper holding the bulb, stirrer and thermometer was placed securely in the Dewar flask. The flask was immersed in a constant temperature bath (25.0°C), and the stirrer started. The contents of the flask were allowed to equilibrate for one hour.

The temperature inside the flask was recorded every 30 seconds for at least three minutes or until the rate of change of temperature with time became constant. The stopper on the tip of the glass bulb was removed with the glass rod, allowing Solutions A and B to mix. Time was recorded at this point and the temperature was measured every 30 seconds until the rate of change of temperature with time was constant. The pH of the contents of the flask was determined for determination of ΔH for protonation and metal chelation.

The heat of dilution of Solution A was determined by the given

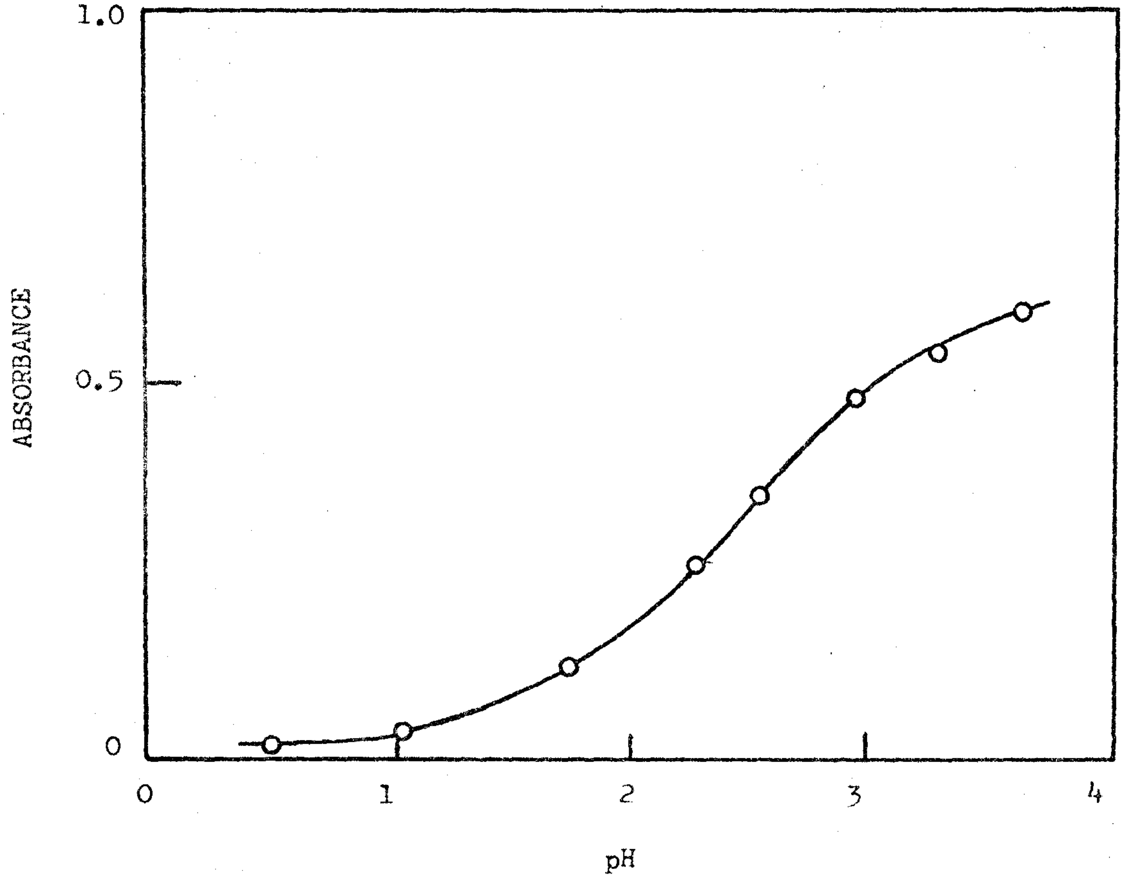


Figure 8. Absorbance *versus* pH for Ni(II) 5-nitro-8-hydroxyquinolinate in 60% v/v dioxane-water, 25°C, I = 0.1, λ = 439 mμ.

procedure except that distilled water was used as Solution B. The heat of dilution of Solution B was determined similarly. If Solution A was a dioxane-water mixture, its heat of mixing with the completely aqueous Solution B was determined.

Table XIV summarizes the physical quantities determined and the corresponding compositions of Solutions A and B.

The concentration ratio of metal: di-sodium 8-hydroxyquinolinate-5-sulfonate was 1:2. The 1:1 metal-ligand complex precipitated at the concentration (0.01M) necessary to obtain suitably large temperature changes. The experimentally determined values of ΔH_c of metal chelation are the sums of the values of ΔH_c for each stepwise addition.

The temperature change associated with the reactions under study was determined as follows. The Beckmann thermometer was set such that 1.660° Beckmann corresponded to 24.87°C. All Beckmann thermometer readings were changed to degrees centigrade and were corrected for temperature differences between the stem and bulb of the thermometer, according to

$$T = T_1 + [0.00016 \cdot T_2(T_1 - T_A)] \qquad (40)$$

where T is the corrected temperature in degrees centigrade, T_1 is the Beckmann thermometer reading in degrees centigrate, T_2 is the Beckmann thermometer reading and T_A is the air (i.e., thermometer stem) temperature.

Figure 9 is the time-temperature curve for a calorimetric experiment for rapid processes such as acid-base neutralization and chelate formation. The reaction corresponding to the curve is exothermic. The observations are divided into three ranges: t_1 to t_2 (fore period); t_2 to t_3 (reaction period); t_3 to t_4 (after period). Because of the short reaction times

TABLE XIV

Calorimetric Quantities

Determination	Solution A	Solution B
Calibration of calorimeter	50 ml 1.5N HCℓ 50 ml H_2O	9.8 ml 1N NaOH
ΔH_p, ligand protonation	(i) 50 ml 0.05M 8-HQ-5-SO_3H*, Na salt (mono) 50 ml H_2O	9.8 ml 0.1N NaOH
	(ii) 50 ml 0.05M 8-HQ-5-SO_3H, Na salt (di) Dioxane and H_2O	9.8 ml 0.25M HCL
ΔH_c, chelate formation	50 ml 0.05M 8-HQ-5-SO_3H, Na salt (di) 50 ml H_2O	9.8 ml 0.1M metal-ion solution

*8-HQ-5-SO_3H = 8-hydroxyquinoline-5-sulfonic acid.

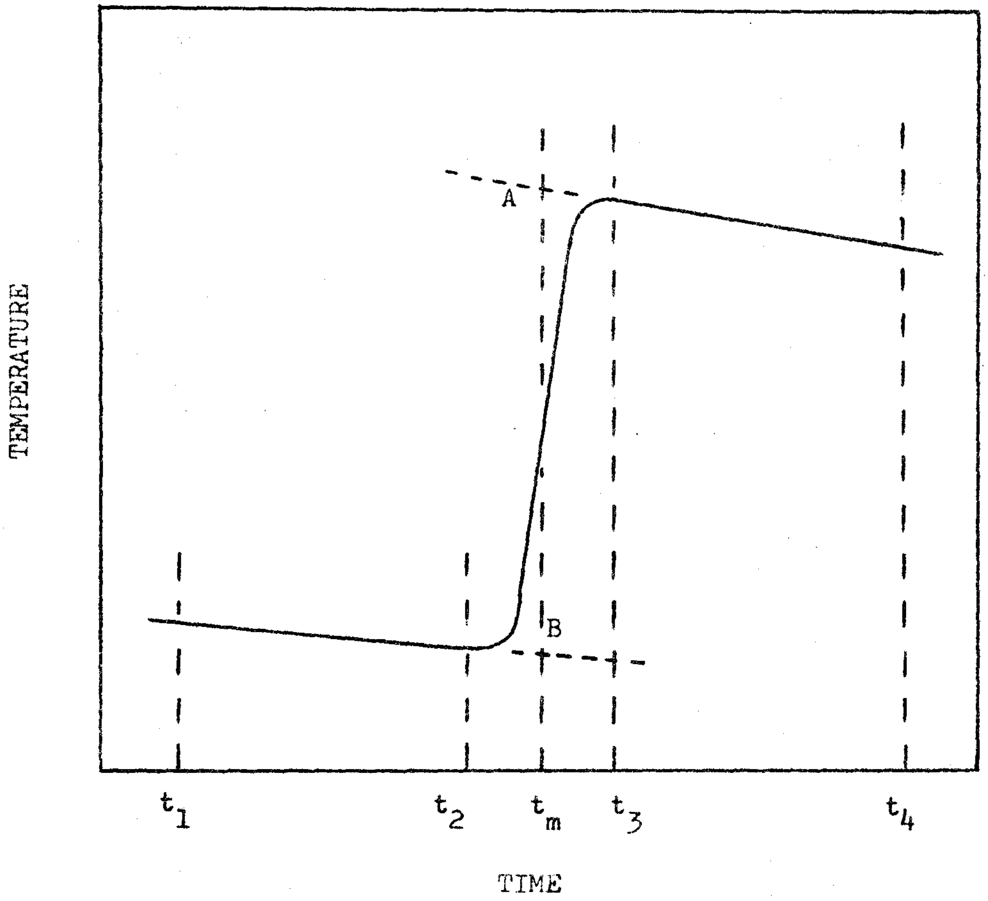


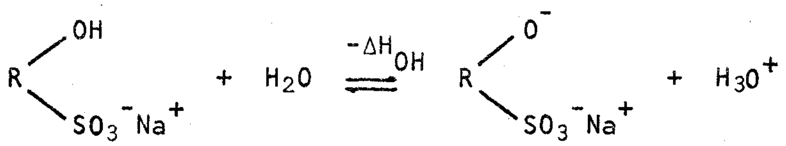
Figure 9. Typical Time-Temperature curve for a rapid exothermic reaction.

involved, the temperature change in the fore and after periods may be approximated as a linear function of time. The temperature rise, $T_A - T_B$, may be obtained by linear extrapolation as shown in Figure 9(107).

The heat capacity of the calorimeter was determined by calibration using the heat of the reaction between $HC\ell$ and NaOH(110). The result was corrected for the heats of dilution of the reactants. The heat capacity of the calorimeter was calculated to be 15.4±0.8 cal/deg (6 determinations).

In the experimental determination of the heats of protonation and metal chelation, the heat released is the difference between the heat of reaction and the heat content of the calorimeter and the solvent (dioxane-water mixture). Corrections for the heats of dilution of the reactants and for the heat of mixing of dioxane-water solvent with pure aqueous solution were made.

Heat of Ligand Protonation. The heat of reaction, ΔH_L, between NaOH and the mono-sodium salt of the reagent is the sum of the heats of reaction of the equilibria,



and

$$H_3O^+ + OH^- \overset{\Delta H_w}{\rightleftharpoons} 2H_2O$$

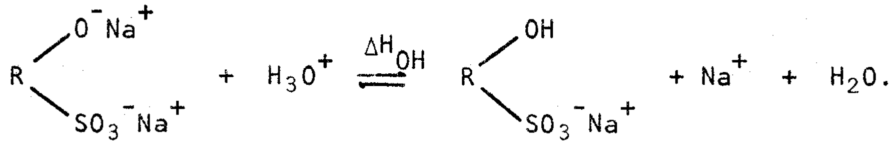
where ΔH_{OH} is the heat of phenolic proton association. Thus

$$\Delta H_L = \Delta h_w - \Delta H_{OH}. \tag{41}$$

Measurement of the pH of the reaction solution allowed the calculation of

$\overline{p}$. These calculations showed that the reaction was quantitative.

The heat of reaction between HCℓ and the di-sodium salt of the reagent gives directly the heat of phenolic proton association; i.e.,



Calculation of $\overline{p}$ showed that this reaction was quantitative.

The heat of phenolic proton association was determined in this way for 0, 20 and 40% v/v dioxane-water. The reactions between NaOH and the mono-sodium salt and between HCℓ and the di-sodium salt of the ligand gave values of the heat of phenolic proton association in excellent agreement. The average of these values of ΔH_{OH} are given in Table XV.

Heat of Chelate Formation. The heats of chelate formation of Mg(II), Mn(II), Ni(II) and Zn(II) with the di-sodium salt of 8-hydroxyquinoline-5-sulfonic acid in water were determined by the above method. Measurement of pH allowed calculation of $\overline{n}$ for these solutions. These calculations showed that metal chelation was quantitative.

The heat of chelate formation, ΔH_{12}, is the sum of the heats of metal chelation of the stepwise reactions,

$$M + L \xrightleftharpoons{\Delta H_1} ML,$$

and

$$ML + L \xrightleftharpoons{\Delta H_2} ML_2,$$

and is given by

$$\Delta H_{12} = \Delta H_1 + \Delta H_2. \qquad (42)$$

TABLE XV

Thermodynamic Functions for Reactions of 8-Hydroxyquinoline-5-sulfonic acid and Metal-ions (25°C, I = 0.1)

Reaction Product	% v/v Dioxane	-ΔG Kcal/mole	-ΔH Kcal/mole	ΔS e.u.
HL	0	11.90	5.5	22
	20	12.78	5.8	23
	40	13.86	6.2	26
MgL_2	0	11.04	2.8	26
MnL_2	0	15.50	5.6	32
	50*	17.98	6.8	46
NiL_2	0	24.16	13.2	36
	50*	26.26	14.8	34
ZnL_2	0	21.28	9.6	36
	50*	23.96	10.4	36

*Reference (111).

Entropy of Complex Formation. The entropy change was calculated from

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{43}$$

where T is the average temperature of the reaction and ΔG is the free energy change given by

$$\Delta G = -1.364 \log {}^{T}K_{OH} \tag{44}$$

for ligand protonation, and

$$\Delta G = -1.364 \log {}^{T}K_1 {}^{T}K_2 \tag{45}$$

for metal chelation at 25.0°C.

The results are tabulated in Table XV.

Polarographic Half-Wave Potentials

The procedure used was: a solution of perchloric acid was prepared as in the calibration of the glass electrode. Solutions of 8-hydroxyquinoline and also of the 5-chloro, 5-acetyl and 5-nitro derivatives (all 5×10^{-3} M) in 60% v/v dioxane-water were prepared as in the potentiometric determination of protonation constants. Solutions of the Fe(III) complexes of these ligands in 60% v/v dioxane-water were prepared as in the potentiometric determination of metal-chelate formation constants. The pH of all solutions was adjusted to 5.0-5.5.

Figure 10 shows the polarogram of the Fe(III) complex of 8-hydroxyquinoline at pH 5.3 in 60% v/v dioxane-water at ionic strength 0.1 (sodium perchlorate). The catalytic wave for the free ligand (-1.48v) is not shown.

The method used to calculate the half-wave potential, $E_{1/2}$, was as described by Meites(112), and is shown in Figure 10. The values of the

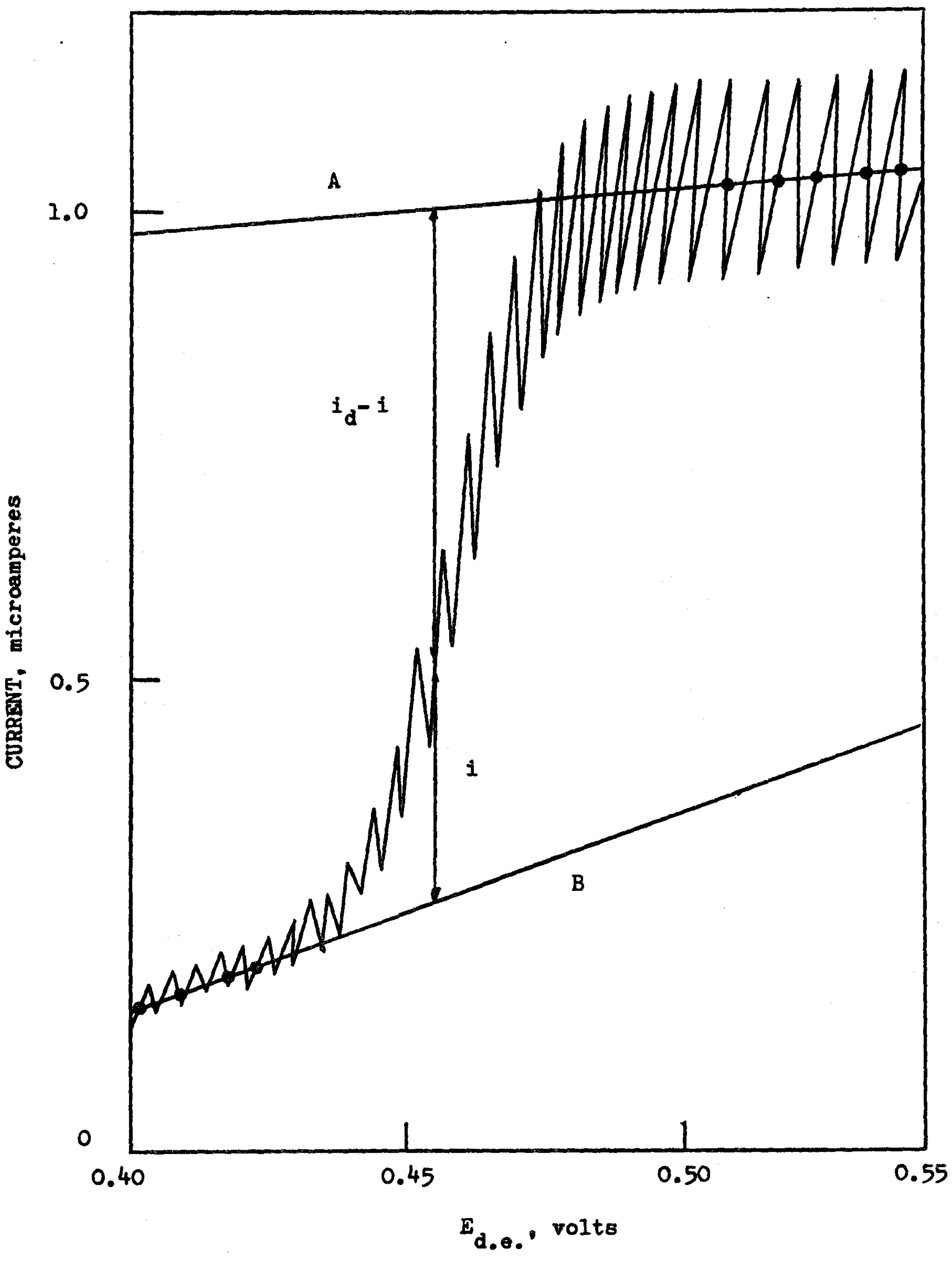


Figure 10. Polarogram of Fe(III) 8-hydroxyquinolinate in 60% v/v dioxane-water, 25°C, I = 0.1 (sodium perchlorate).

potential of the dropping mercury electrode, $E_{d.e.}$, and of the corresponding current, i, and of $(i_d - i)$ where i_d is the diffusion current, were determined from Figure 10.

The term $\log(i/i_d - i)$ was plotted against $E_{d.e.}$. The slope of this plot was evaluated by linear least-squares. The half-wave potential is given by the value of $E_{d.e.}$ at $\log(i/i_d - i) = 0$. No correction was made for the IR drop through the polarographic cell. Table XVI summarizes the values of $E_{1/2}$ for the Fe(III) complexes.

TABLE XVI

Half-wave Potentials of Fe(III) Complexes of 8-Hydroxyquinoline Derivatives in 60% v/v Dioxane-water

Fe(III) Complex	Slope	$E_{1/2}$ (volts)
8-Hydroxyquinolinate	0.059	-0.50
5-Chloro-8-hydroxyquinolinate	0.052	-0.37
5-Acetyl-8-hydroxyquinolinate	0.057	-0.24
5-Nitro-8-hydroxyquinolinate	0.063	-0.02

DISCUSSION

Effect of the Solvent

Figures 11 to 17 show the stability of the $(N\text{-}H)^+$ and O-H complexes and the average stabilities of several metal complexes of 8-hydroxyquinoline derivatives in dioxane-water media as a function of the stability of these complexes in 60% v/v dioxane-water. Figure 11 shows that the $(N\text{-}H)^+$ protonation constants decrease and Figure 12 shows that the O-H protonation constants increase with increasing dioxane content of the solvent. The ligands in Figures 11 and 12 are (1) 5-nitro-8-hydroxyquinoline, (2) 5-acetyl-8-hydroxyquinoline, (3) 8-hydroxyquinoline-5-sulfonic acid, (4) 5-chloro-8-hydroxyquinoline and (5) 8-hydroxyquinoline. The numbers of these ligands are encircled in Figures 11 and 12. Figures 13 to 17 demonstrate that the average stabilities of the metal complexes vary with solvent composition in a manner similar to the stability of the O-H complex and opposite to that of the $(N\text{-}H)^+$ complex. This behavior is observed regardless of the metal-ion.

Figures 19 and 20 show the variation in the stability of S-H and S-M complexes with molar fraction dioxane. The similarity of the solvent effect on O-H (and O-M) and S-H (and S-M) complexes is discussed later.

The increase in stability with increasing dioxane content is due primarily to enthalpy rather than entropy changes. Figure 18 shows the ΔH values determined in this work and by Freiser and Gutnikov(111) for some metal complexes of 8-hydroxyquinoline-5-sulfonic acid. The increase in the average heats of reaction with dioxane content is similar to the increase in the average stabilities of the metal complexes. The calculated

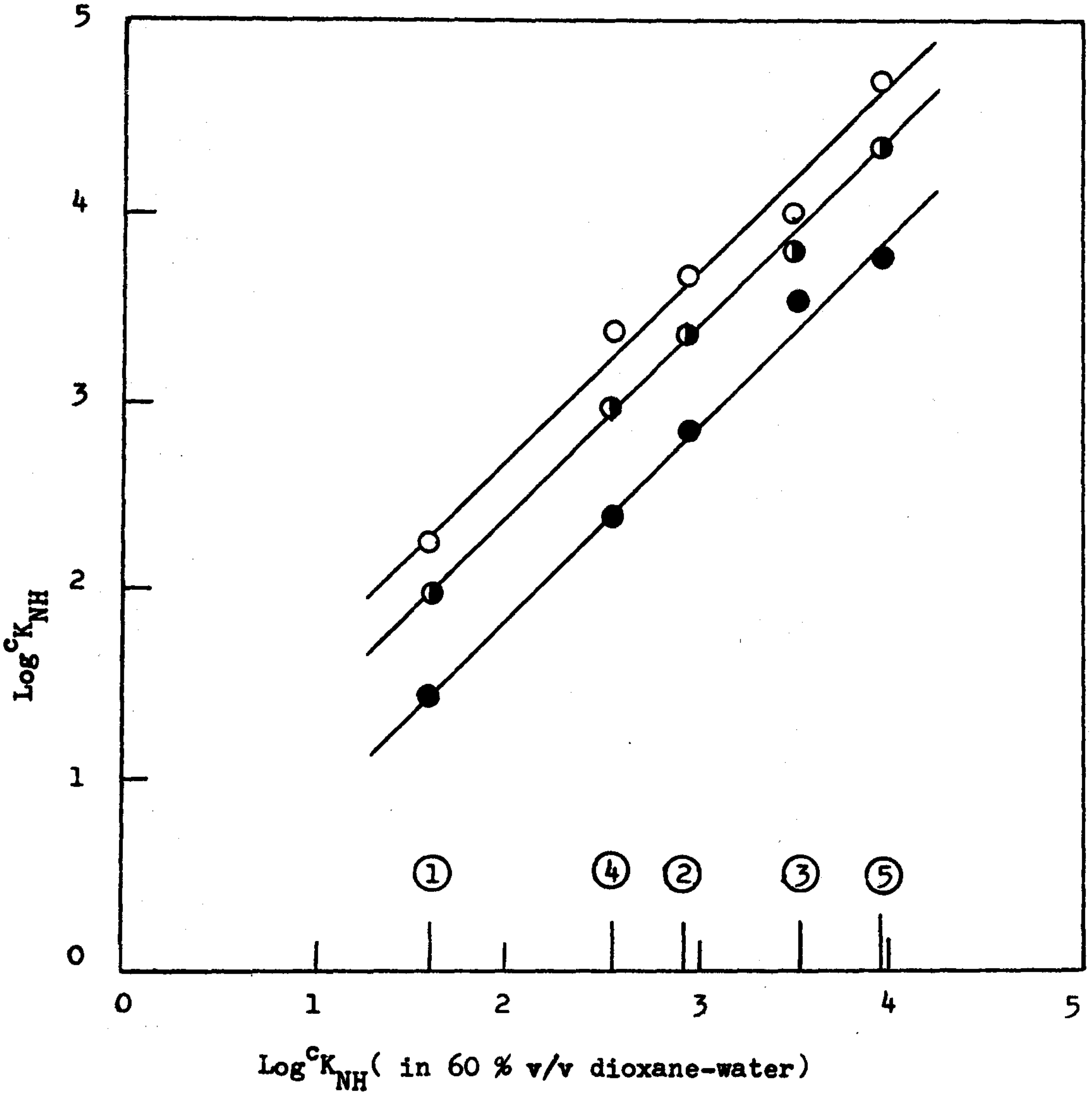


Figure 11. Log^{c}K$_{NH}$ of 8-hydroxyquinoline derivatives in 20 (○), 40 (◑) and 75 (●) % v/v dioxane-water versus log^{c}K$_{NH}$ in 60% v/v dioxane-water (25.0°C, I = 0.1).

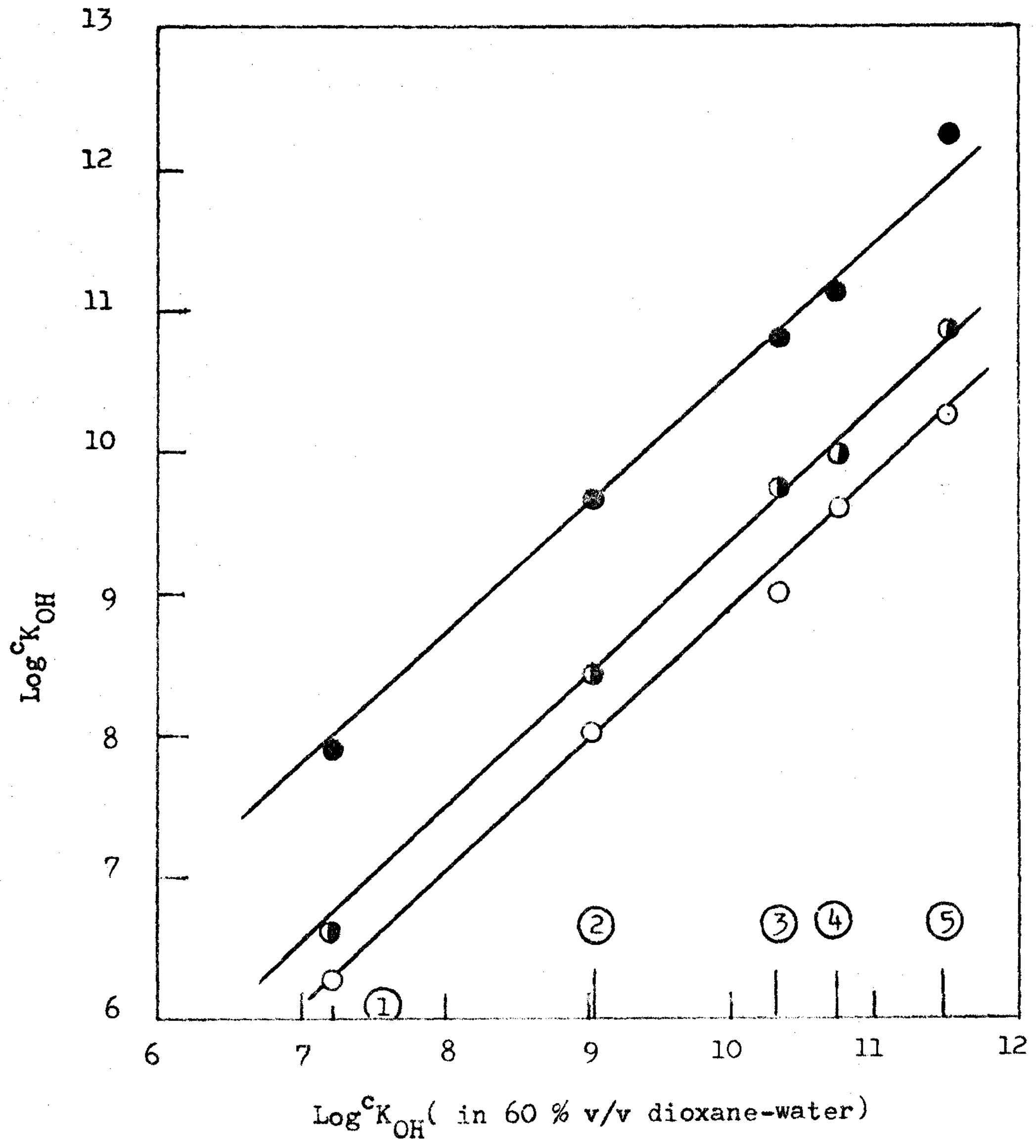


Figure 12. Log$^{c}K_{OH}$ of 8-hydroxyquinoline derivatives in 20 (○), 40 (◐) and 75 (●) % v/v dioxane-water versus log$^{c}K_{OH}$ in 60% v/v dioxane-water (25.0°C, I = 0.1).

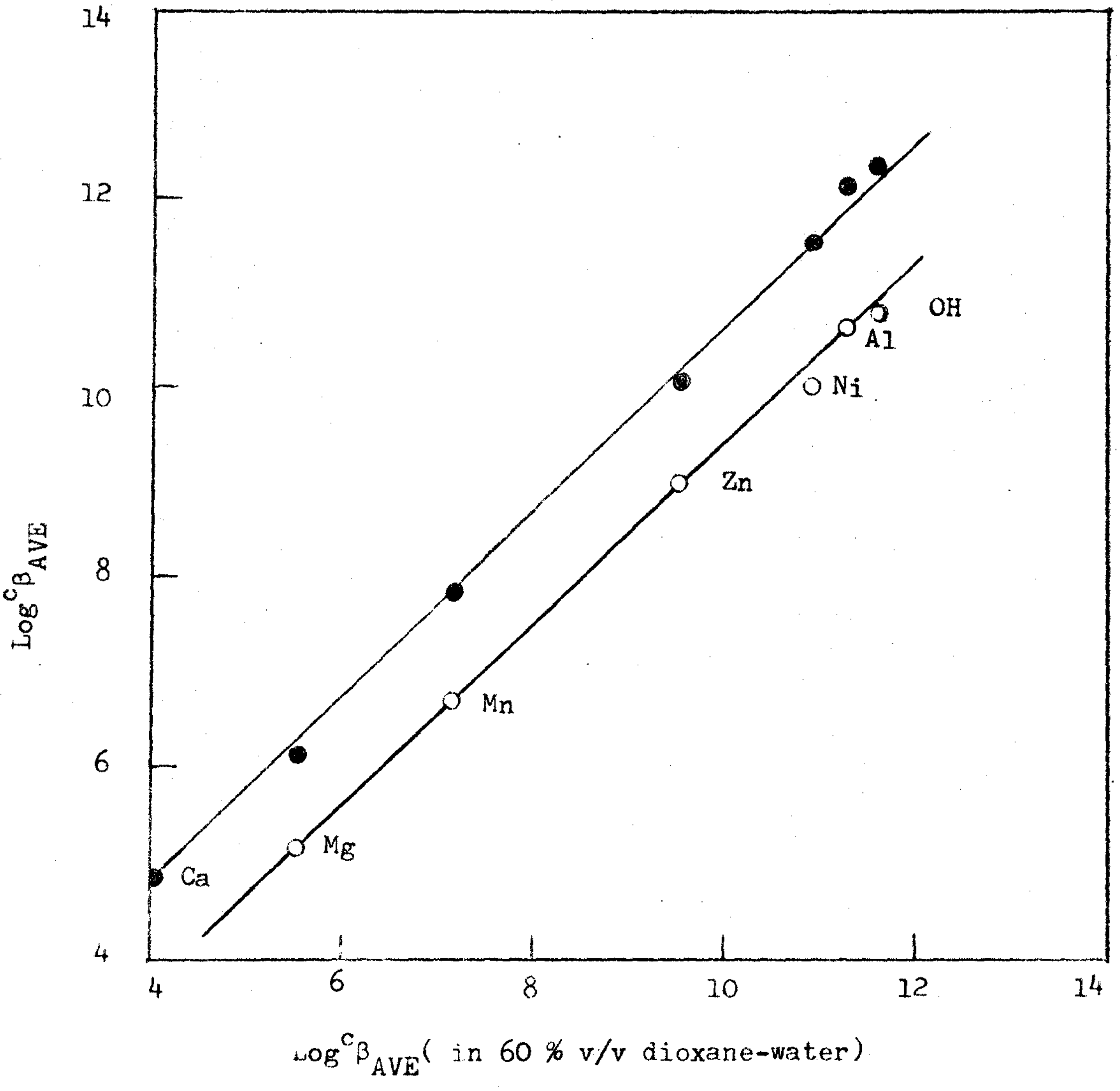


Figure 13. $Log^c\beta_{AVE}$ of metal complexes of 8-hydroxyquinoline in 40 (○) and 75 (●) % v/v dioxane-water as a function of $log^c\beta_{AVE}$ in 60% v/v dioxane-water (25.0°C, I = 0.1).

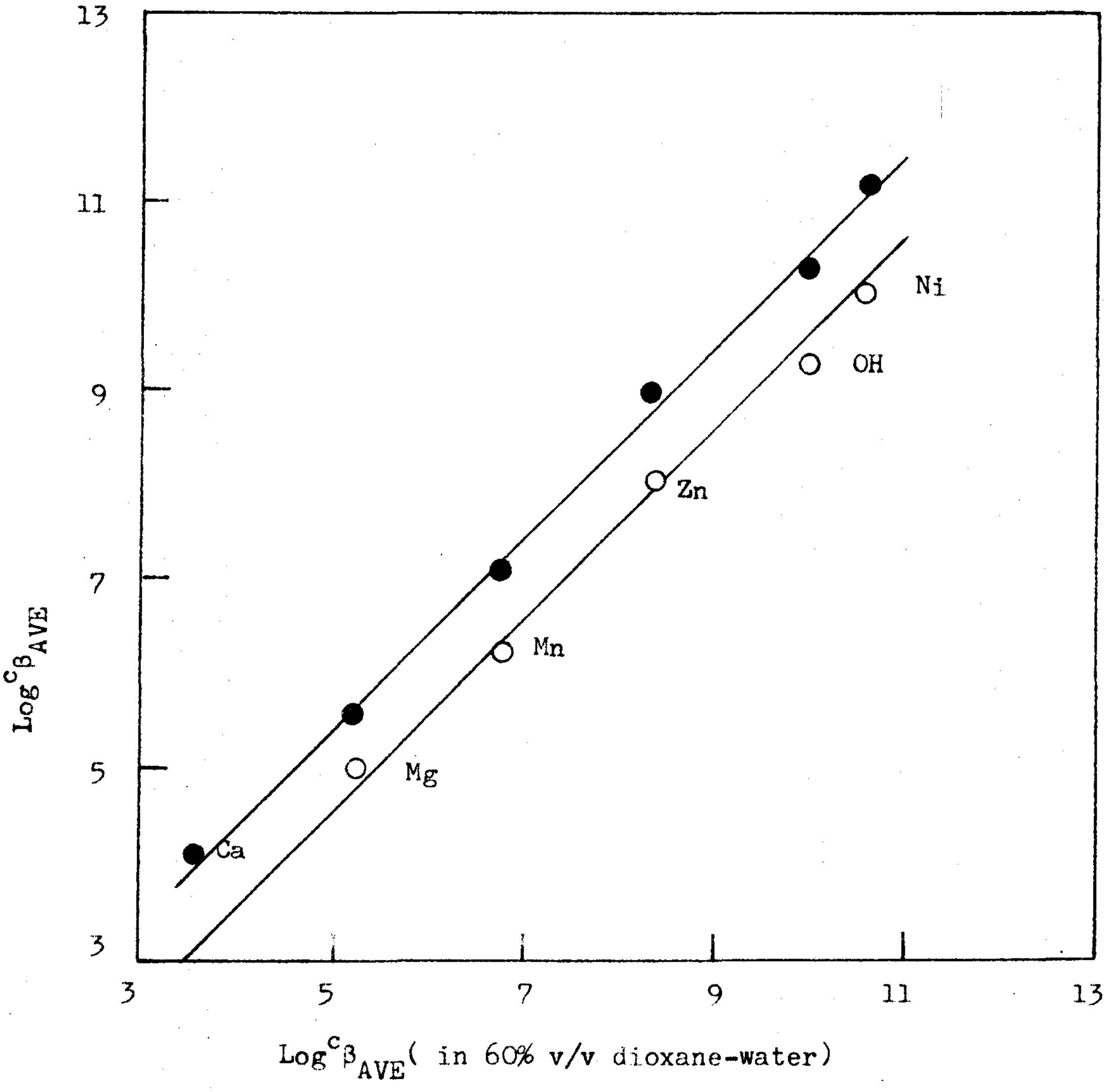


Figure 14. $\text{Log}^c\beta_{AVE}$ of metal complexes of 5-chloro-8-hydroxyquinoline in 40 (○) and 75 (●) % v/v dioxane-water as a function of $\log^c\beta_{AVE}$ in 60% v/v dioxane-water (25.0°C, I = 0.1).

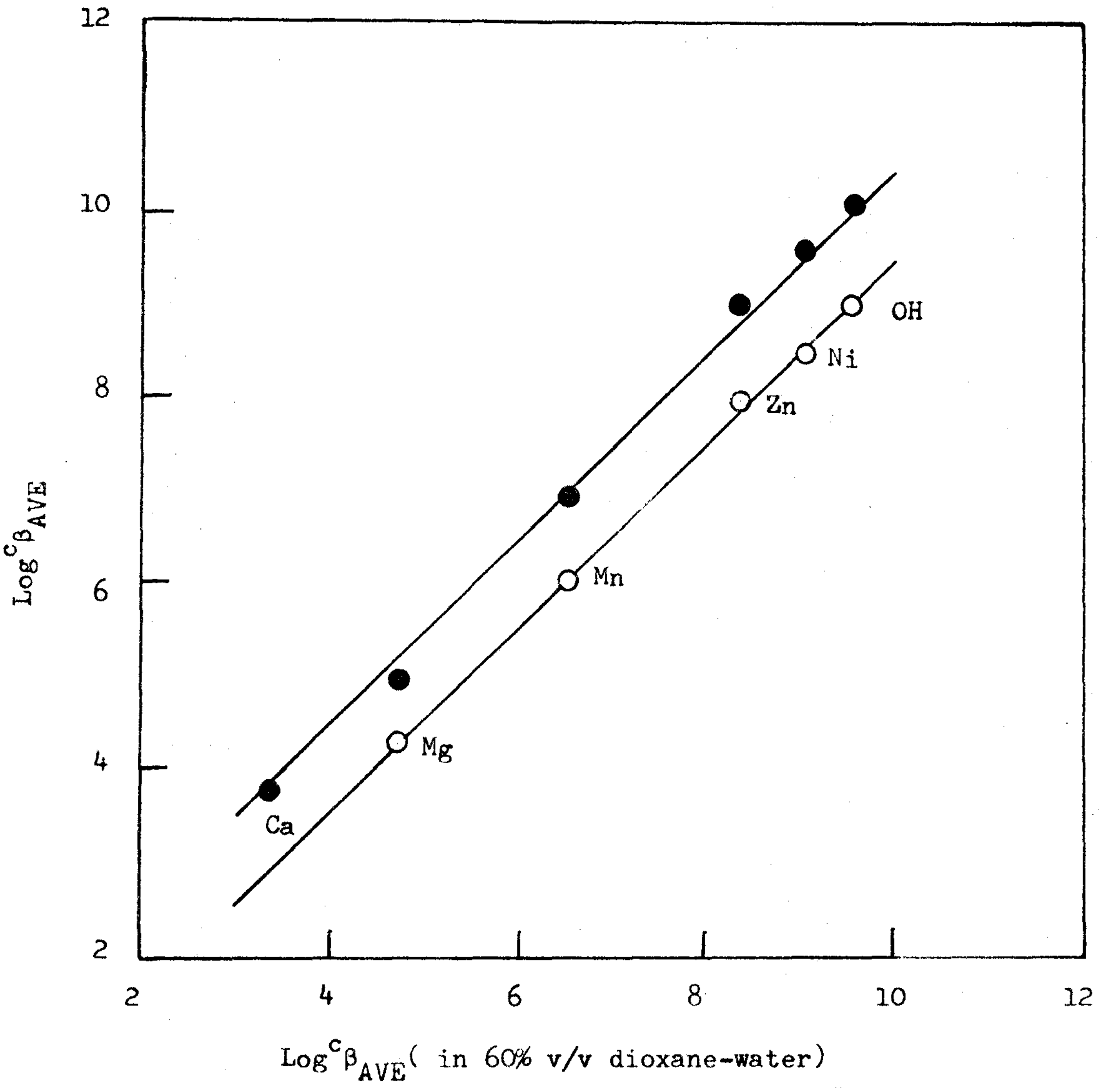


Figure 15. $\mathrm{Log}^{c}\beta_{AVE}$ of metal complexes of 5-acetyl-8-hydroxyquinoline in 40 (○) and 75 (●) % v/v dioxane-water as a function of $\log^{c}\beta_{AVE}$ in 60% v/v dioxane-water (25.0°C, I = 0.1).

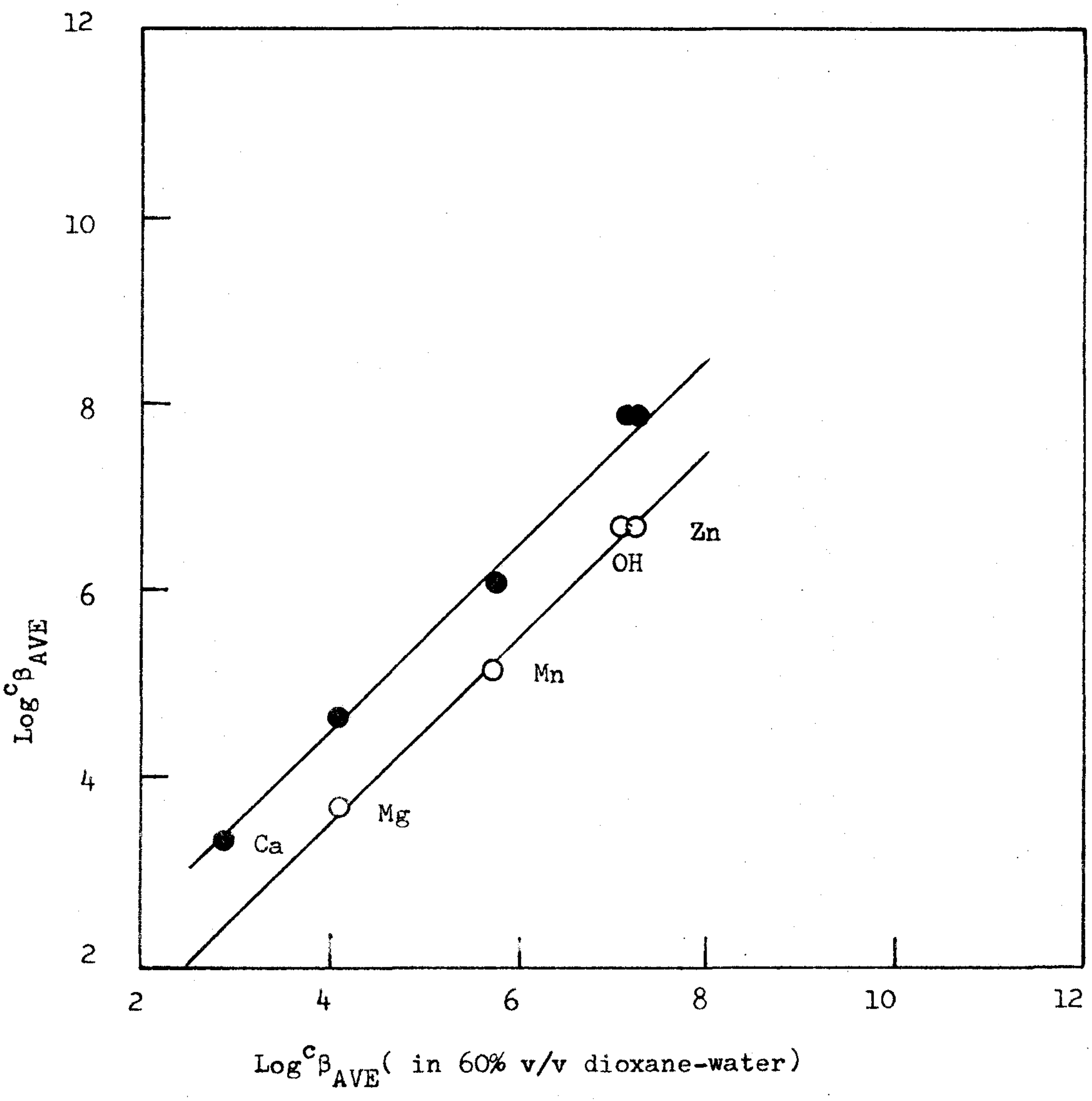


Figure 16. $\mathrm{Log}^{c}\beta_{AVE}$ of metal complexes of 5-nitro-8-hydroxyquinoline in 40 (○) and 75 (●) % v/v dioxane-water as a function of $\log^{c}\beta_{AVE}$ in 60% v/v dioxane-water (25.0°C, I = 0.1).

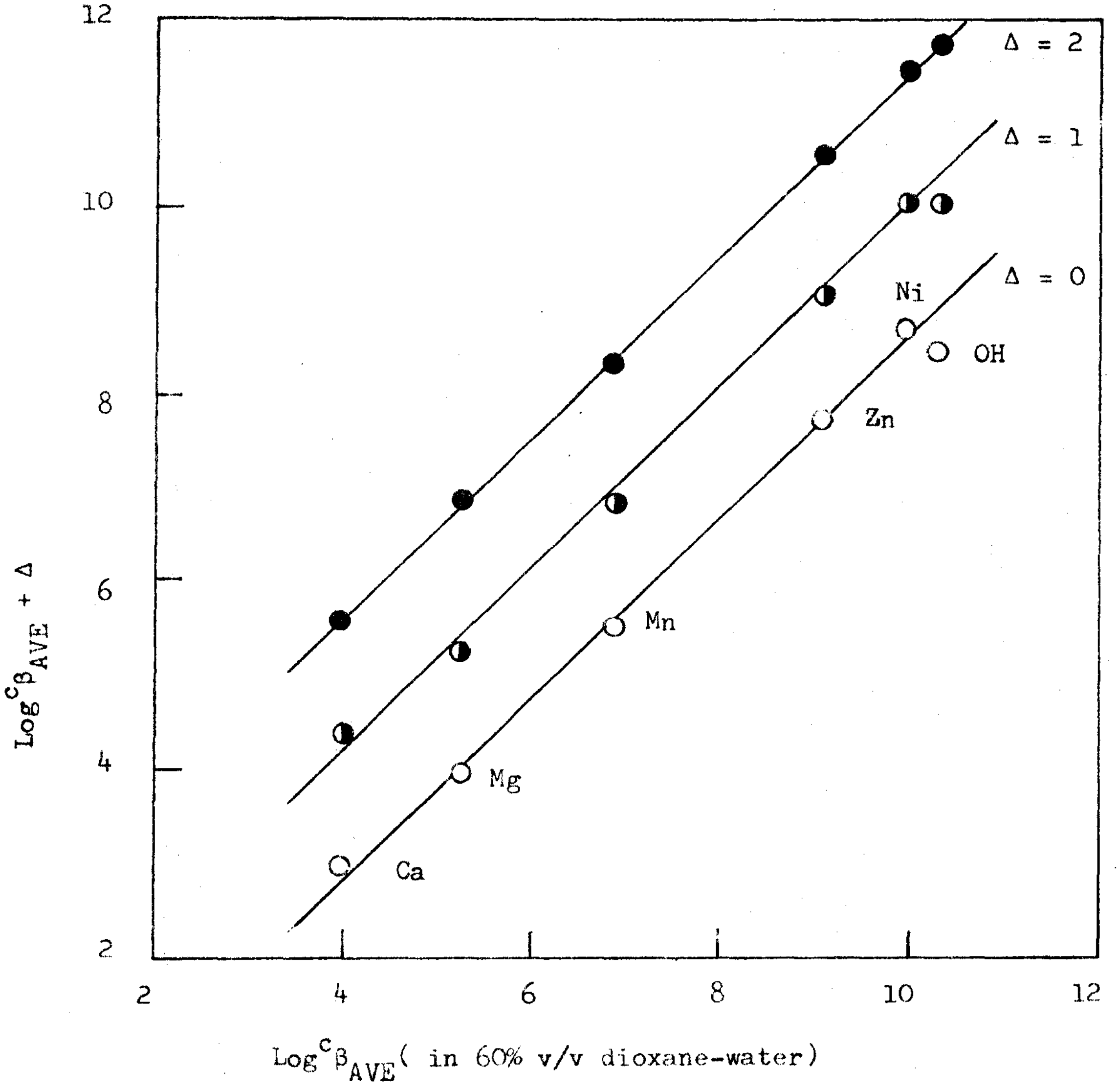


Figure 17. $\mathrm{Log}^c\beta_{AVE}$ of metal complexes of 8-hydroxyquinoline-5-sulfonic acid in 0 (○), 20 (◑) and 40 (●) % v/v dioxane-water as a function of $\log^c\beta_{AVE}$ in 60% v/v dioxane-water (25.0°C, I = 0.1).

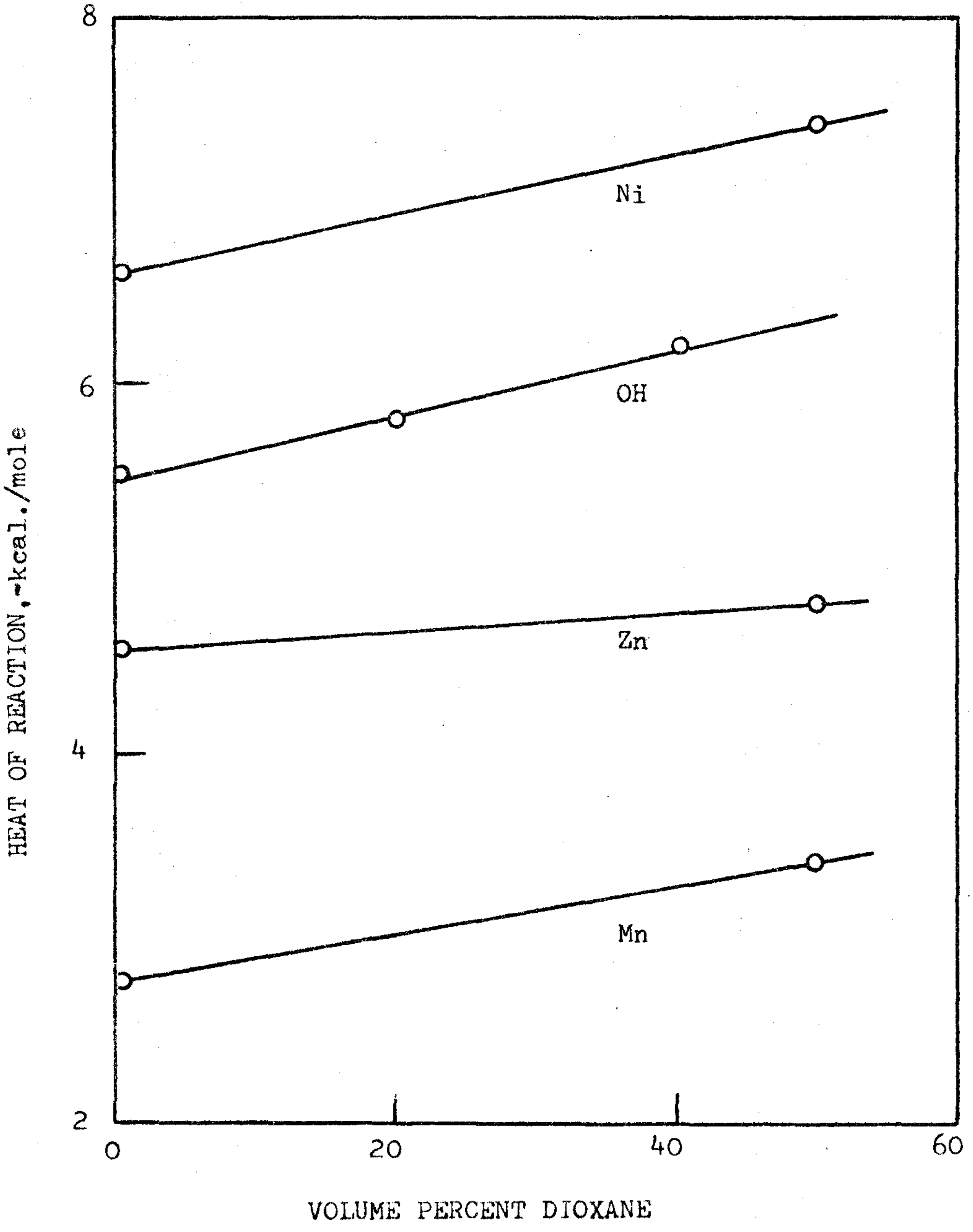


Figure 18. Average heat of reaction of metal-ion and proton complexes of 8-hydroxyquinoline-5-sulfonic acid *versus* volume percent dioxane.

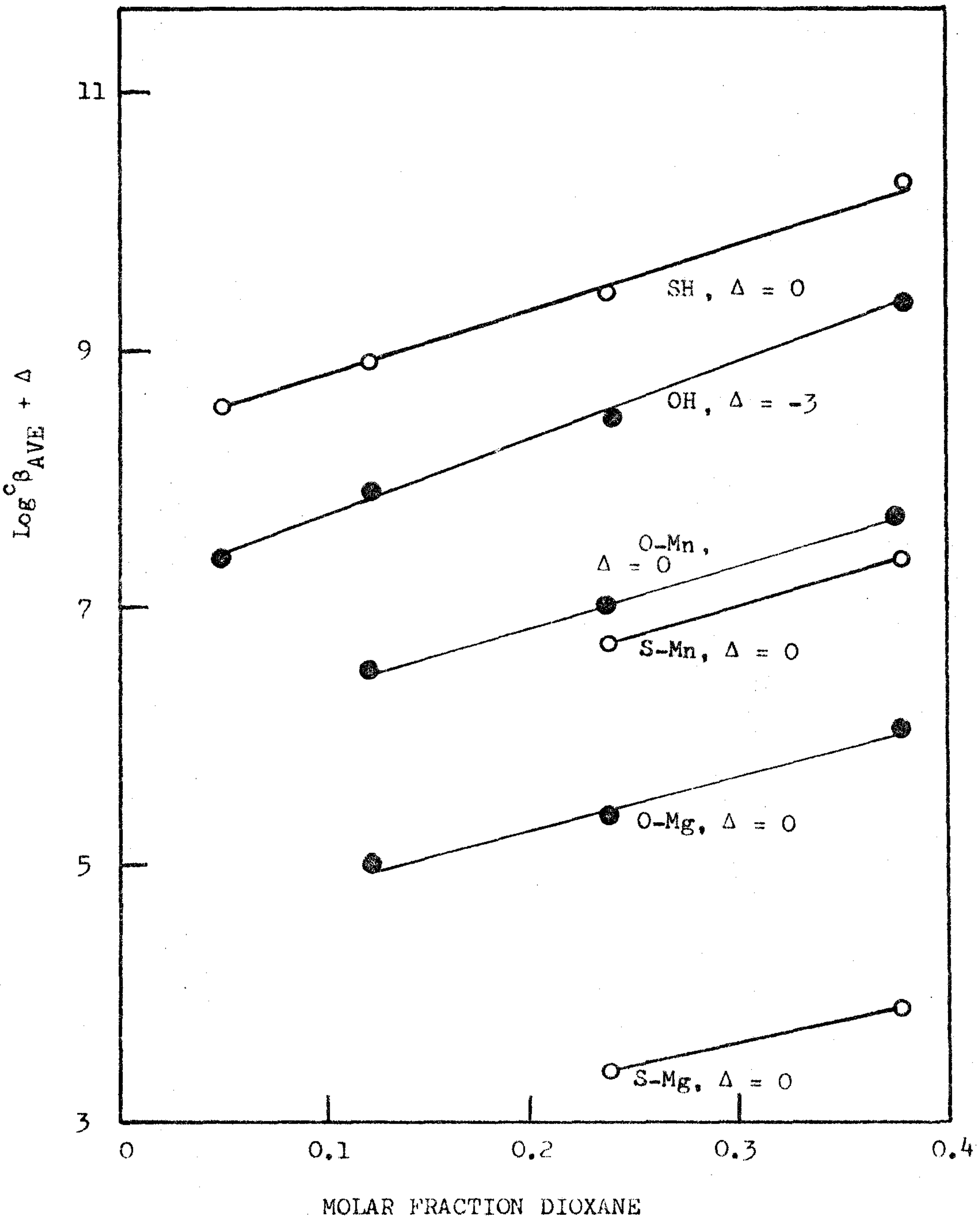


Figure 19. $\text{Log}^{c}\beta_{\text{AVE}} + \Delta$ of the complexes of 8-mercaptoquinoline (○) and 8-hydroxyquinoline (●) *versus* molar fraction dioxane (25.0°C, $I = 0.1$).

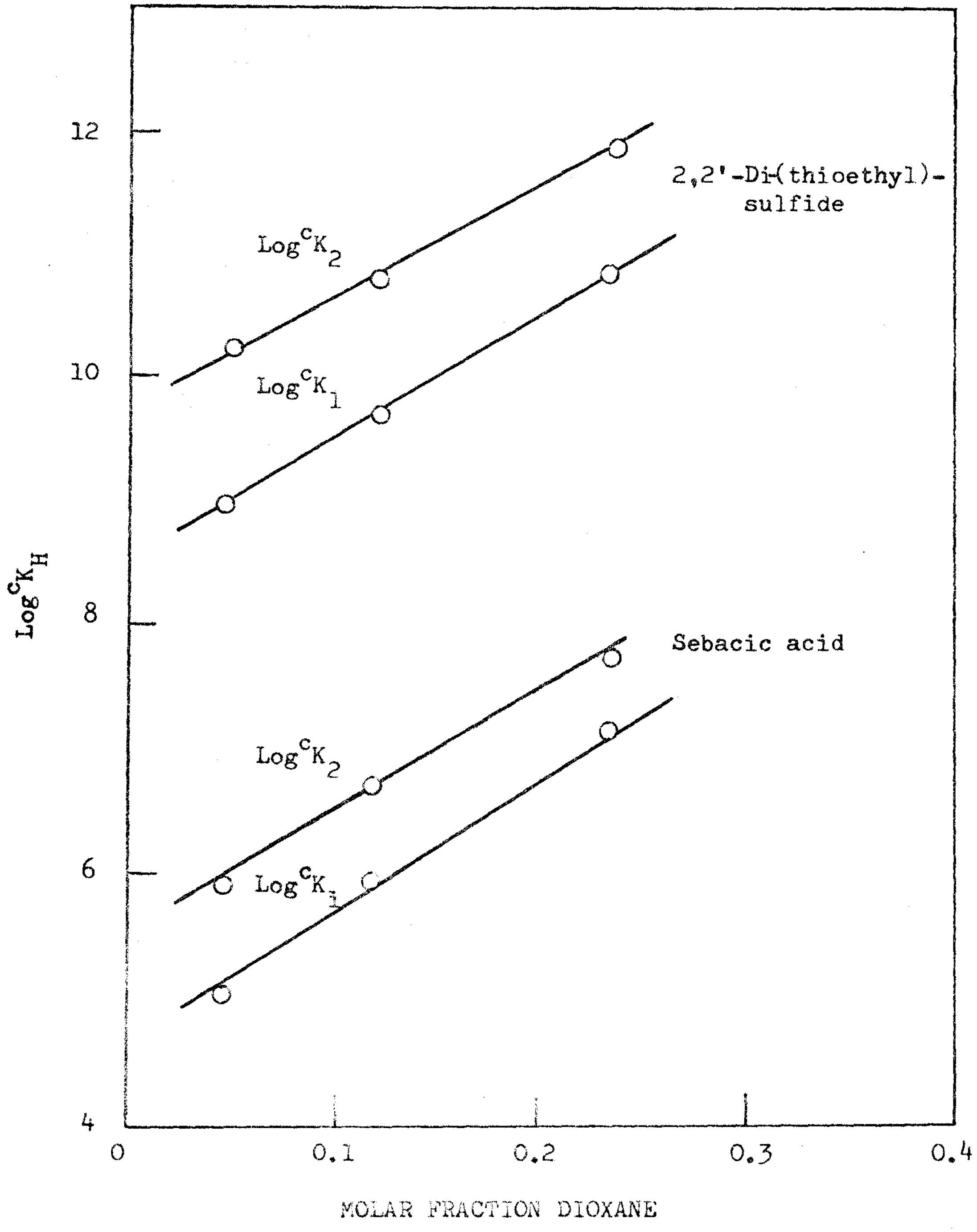


Figure 20. Protonation constants of 2,2'-di-(thioethyl)sulfide and sebacic acid *versus* molar fraction dioxane (25.0°C, I = 0.1).

entropy change between pure water and 50% v/v dioxane-water for ligand protonation and for metal chelation is approximately 3 and 0 e.u., respectively.

The equilibria involved are of the form

$$H^{+} + L^{-} \overset{{}^{c}K_{OH}}{\rightleftharpoons} HL \tag{I}$$

$$M^{2+} + 2L^{-} \overset{{}^{c}\beta_{2}}{\rightleftharpoons} ML_{2} \tag{II}$$

$$M^{3+} + 3L^{-} \overset{{}^{c}\beta_{3}}{\rightleftharpoons} ML_{3} \tag{III}$$

Surprisingly, the increase in equilibrium constants with increasing organic content of the solvent was similar for all reactions. It was anticipated that with decreasing dielectric constant, the stability of the trivalent metal complexes would increase more rapidly than the stability of the divalent metal complexes which, in turn would increase more rapidly than the stability of the O-H proton complexes.

The observed behavior can be explained, however, as follows. Reactions (II) and (III) can be written as stepwise reactions:

$$M^{2+} + L^{-} \overset{{}^{c}K_{1}}{\rightleftharpoons} ML^{+} \tag{IIa}$$

$$ML^{+} + L^{-} \overset{{}^{c}K_{2}}{\rightleftharpoons} ML_{2} \tag{IIb}$$

where ${}^{c}\beta_{2} = {}^{c}K_{1}{}^{c}K_{2}$, and

$$M^{3+} + L^{-} \overset{{}^{c}K_{1}}{\rightleftharpoons} ML^{2+} \tag{IIIa}$$

$$ML^{2+} + L^{-} \overset{{}^{c}K_{2}}{\rightleftharpoons} ML_{2}^{+} \tag{IIIb}$$

$$ML_2^+ + L^- \overset{^cK_3}{\rightleftharpoons} ML_3 \qquad (IIIc)$$

where ${}^c\beta_3 = {}^cK_1{}^cK_2{}^cK_3$. In the five reactions above and in reaction (I), one unit of positive and negative charge is neutralized. Indeed, for reactions (IIb) and (IIIc), not only is the charge neutralization equivalent to that of reaction (I) but also the charges of the corresponding species are the same. Therefore, stability changes for these stepwise reactions are expected to be similar to that of the O-H complex with increasing dioxane content.

The charges of the species in reactions (IIa), (IIIa) and (IIIb) differ from those of the corresponding species in reaction (I); however, these reactions also involve the neutralization of one unit of positive and negative charge. The increase in the average stability constants of these reactions parallel to that of the O-H complex (Figures 13 to 17) indicates that the increases in the free energy change with increasing dioxane content are similar to that of the O-H complex. Thus, the important consideration is the amount of charge neutralization in the reaction and not the absolute charges of the reactant and product species.

The results of the present study show that the solvent effect is essentially independent of the charge and the chemical nature of the reactant cations. As a result of this behavior, no conclusions regarding the relative importance of the O-M and N-M bond in the complexes of the various metal-ions can be drawn from the available data. Irving and Rossotti(18) had suggested that the magnitude of the solvent effect could give information on the relative O-M and N-M bond strengths in the metal complexes of bidentate ligands containing both an oxygen and nitrogen donor. The present work shows that such is not the case.

The variation in the stability of the metal 5-substituted-8-hydroxyquinolinates with dioxane content of the solvent essentially parallels that of the O-H complex. This same behavior has also been observed for the complexes of several metal acetylacetonates, in which there is no N-M bond, but two O-M bonds(113). The influence of the solvent on the strength of the N-M bond must be relatively small; the relative solvent effect on the O-M and N-M bond stability is likely in proportion to ion-ion:ion-dipole effects.

Since the solvent effect is essentially independent of the particular metal-ion in the complex, no advantage in analytical selectivity of the ligands can be obtained by changing the solvent composition.

The data obtained for the effect of the solvent on the stability of S-H and S-M complexes are sparse. This is due primarily to experimental difficulties arising from the ease of oxidation of thiols to disulfides and the tendency of the corresponding metal complexes to polymerize and precipitate. In some cases, the metal complexes were too stable to be studied potentiometrically. Only the Mg(II) and Mn(II) complexes of 8-mercaptoquinoline were sufficiently soluble and unstable to be studied potentiometrically.

The data for 8-mercaptoquinoline (Figure 19) and for 2-2'-di-(thioethyl)sulfide and sebacic acid (Figure 20) are sufficient to show that stability of S-H and S-M complexes varies similarly to that for the corresponding oxygen complexes. This shows that the effect of primary importance is charge neutralization, i.e.,

$$O^- + M^{n+} \rightleftharpoons OM^{(n-1)+}$$

$$S^- + M^{n+} \rightleftharpoons SM^{(n-1)+}.$$

Differences in the nature of the donor atoms such as polarizability (i.e., hardness) are of only secondary importance.

Effect of Ligand Basicity

As mentioned in the HISTORICAL INTRODUCTION, several workers have shown that the slope of the relationship between $\log{}^cK_{ML}$ and $\log{}^cK_{HL}$ for the complexes of a given metal-ion with a series of closely related ligands is dependent on the metal-ion. The purpose of this section is to show that the property of the metal-ion which governs the slope is the ionic potential, z_M/r_M, where z_M amd r_M are the charge and radius of the metal-ion. A theoretical function composed of the ionic potential and ligand basicity is derived in order to evaluate the contributions of the N-M and O-M bonds to chelate stability. This function is used to explain the data of previous workers(17,41,59).

The first and second successive stability and the average stability of the complexes of Ag(I), Mg(II), Ca(II), Mn(II), Fe(II), Ni(II), Zn(II) and Pb(II), and the average stability of the complexes of Aℓ(III), Sc(III), Fe(III) and Ce(III) with

(1) 8-hydroxyquinoline
(2) 5-chloro-8-hydroxyquinoline
(3) 8-hydroxyquinoline-5-sulfonic acid
(4) 5-acetyl-8-hydroxyquinoline and
(5) 5-nitro-8-hydroxyquinoline

were plotted against the stability of the corresponding O-H complexes for 60% v/v dioxane-water. The plots of the average stability of the metal complexes against the stability of the O-H complexes are shown in Figures 21 and 22. The plots of $\log{}^{c}K_1$ or of $\log{}^{c}K_2$ versus $\log{}^{c}K_{OH}$ were very similar.

The relationship

$$\log{}^{c}S = a\cdot\log{}^{c}K_{OH} + b \qquad (46)$$

where S is K_1, K_2 or β_{AVE} was determined for each metal-ion by a linear least-squares fit to data. The calculated slopes and intercepts are summarized in Table XVII.

For each divalent metal-ion except Pb(II), Table XVII shows that the slope of the plot of $\log{}^{c}K_1$ against $\log{}^{c}K_{OH}$ is approximately equal to the slope of $\log{}^{c}K_2$ against $\log{}^{c}K_{OH}$ (and, therefore, to that of the $\log{}^{c}\beta_{AVE}$ plot). Experimentally, values of ${}^{c}K_1$, ${}^{c}K_2$ and ${}^{c}K_3$ were not obtained for the trivalent metal-ions. It was assumed that the slope of the $\log{}^{c}\beta_{AVE}$ plot was representative of the slope of each stepwise stability for these metal-ions. The case of Pb(II) is discussed later.

Examination of Figures 21 and 22 shows a general trend in the scattering of the experimental $\log{}^{c}\beta_{AVE}$ values about the best straight line for the complexes of Mn(II), Fe(II), Ni(II), Zn(II), Sc(III), Fe(III) and Ce(III). This trend does not exist for Ag(I), Mg(II), Ca(II), Pb(II) and Aℓ(III). The values of $\log{}^{c}\beta_{AVE}$ for 8-hydroxyquinoline, 8-hydroxyquinoline-5-sulfonic acid and 5-acetyl-8-hydroxyquinoline tend to lie on or slightly above the line. The values of $\log{}^{c}\beta_{AVE}$ for 5-chloro-8-hydroxyquinoline and 5-nitro-8-hydroxyquinoline tend to lie slightly below the line. The Student t test(115) shows that the scattering for 5-chloro-8-hydroxyquinoline and 5-nitro-8-hydroxyquinoline is significant. The

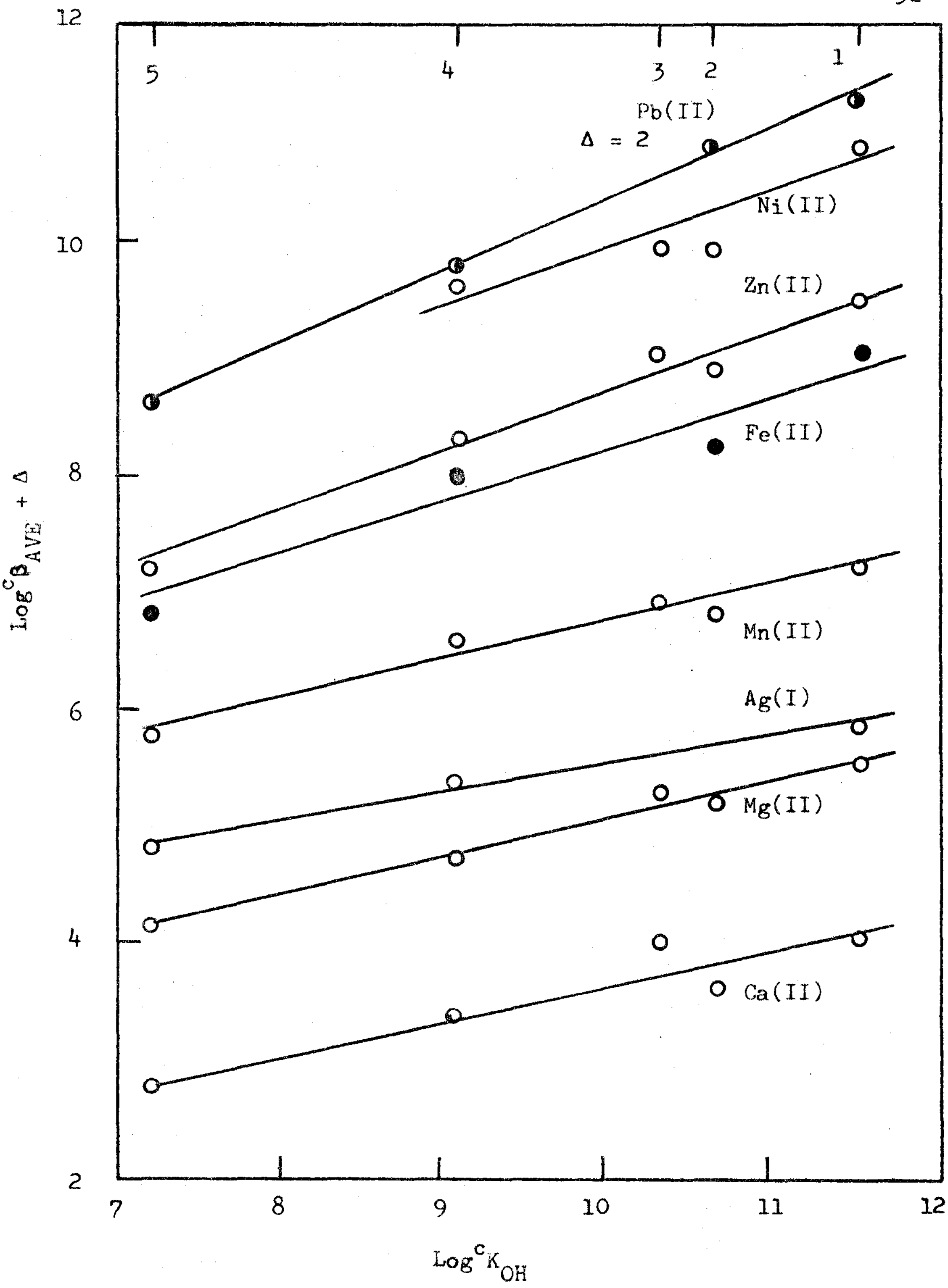


Figure 21. $\log{}^c\beta_{AVE}+\Delta$ as a function of $\log{}^cK_{OH}$ for the complexes of 8-hydroxyquinoline derivatives in 60% v/v dioxane-water at 25.0°C and I = 0.1. Δ = 0 unless specified.

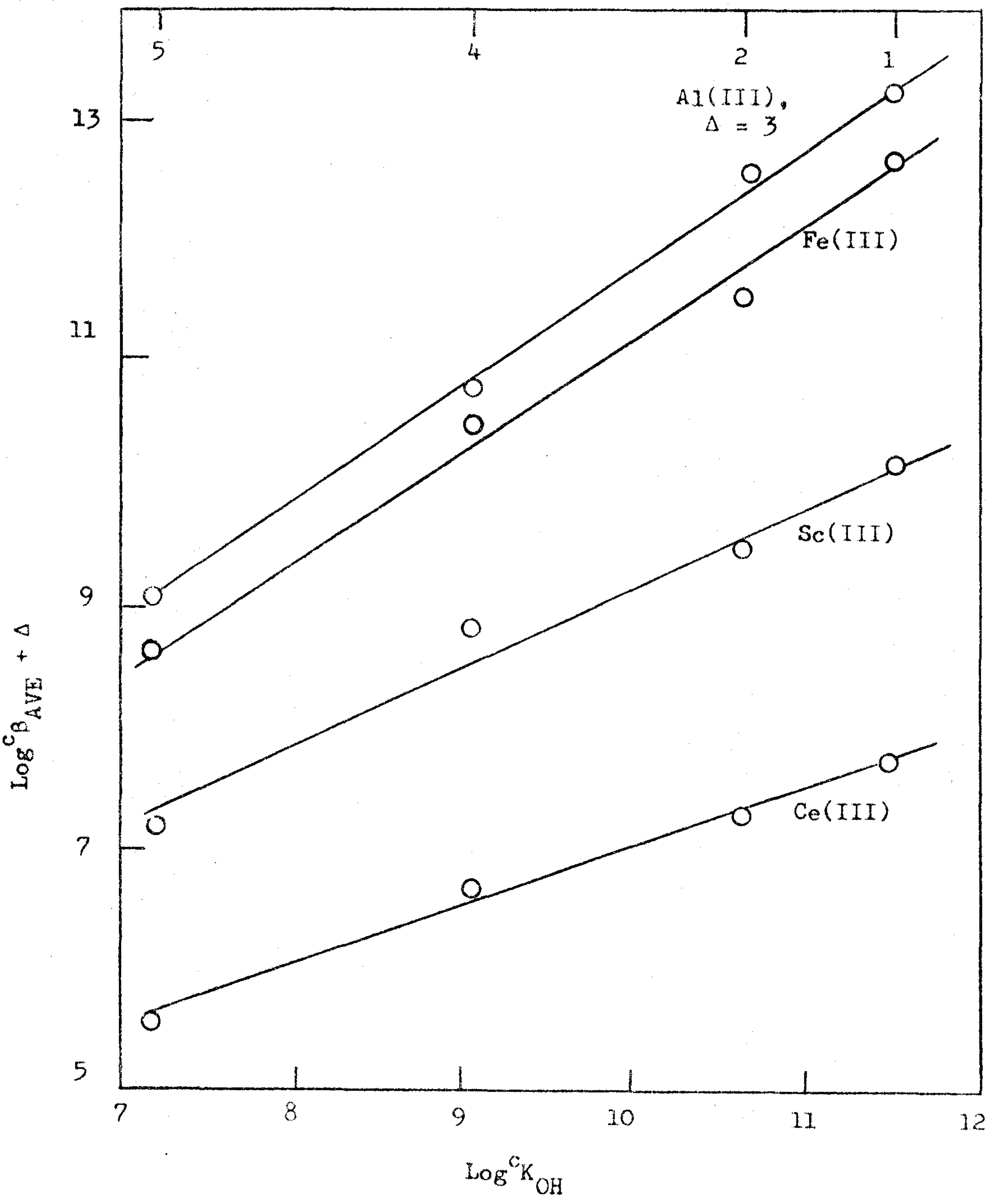


Figure 22. $\mathrm{Log}^{c}\beta_{AVE} + \Delta$ as a function of $\log^{c}K_{OH}$ for the complexes of 8-hydroxyquinoline derivatives in 60% v/v dioxane-water at 25.0°C and $I = 0.1$. $\Delta = 0$ unless specified.

TABLE XVII

Slope and Intercept Values in 60% v/v Dioxane-Water

$\mathrm{Log}^{c}S = a \log {}^{c}K_{OH} + b$

(25.0°C, I = 0.1)

Ion	S	a	b
Ag(I)	$K_1(\beta_{AVE})$	0.29	2.74
	K_2	0.09*	2.62
Mg(II)	K_1	0.34	1.81
	K_2	0.31	1.63
	β_{AVE}	0.33	1.70
Ca(II)	K_1	0.25	1.55
	K_2	0.26	1.20
	β_{AVE}	0.25	1.36
Mn(II)	K_1	0.35	3.53
	K_2	0.32	3.19
	β_{AVE}	0.33	3.35
Fe(II)	K_1	0.49	3.71
	K_2	0.46	3.25
	β_{AVE}	0.48	3.42
Ni(II)	K_1	0.49	5.33
	K_2	0.50	4.51
	β_{AVE}	0.49	4.75
Zn(II)	K_1	0.49	3.80
	K_2	0.54	3.22
	β_{AVE}	0.52	3.56

TABLE XVII (Cont'd.)

Ion	S	a	b
Pb(II)	K_1	0.74	2.13
	K_2	0.51	1.90
	β_{AVE}	0.64	2.00
Aℓ(III)	β_{AVE}	0.97	0.19
Sc(III)	β_{AVE}	0.66	2.56
Fe(III)	β_{AVE}	0.87	2.40
Ce(III)	β_{AVE}	0.51	1.93

*Experimental evidence(114) indicates the formation of the 1:2 complex of Ag(I) with 8-hydroxyquinoline in solution.

scattering for each ligand is in the same direction as the deviation of the calculated value of $\log{}^{c}K_{NH}/\log{}^{c}K_{OH}$ for the ligand from the average value of this ratio for all ligands. The values of $\log{}^{c}K_{NH}/\log{}^{c}K_{OH}$ are tabulated in Table XVIII. The average value is 0.30±0.08. This indicates that the correlation of $\log{}^{c}\beta_{AVE}$ with $\log{}^{c}K_{OH}$ is only approximate, and that $\log{}^{c}\beta_{AVE}$ should be more properly correlated with both $\log{}^{c}K_{NH}$ and $\log{}^{c}K_{OH}$, as in the relationship

$$\log{}^{c}\beta_{AVE} = d\cdot\log{}^{c}K_{NH} + e\cdot\log{}^{c}K_{OH} + b. \tag{47}$$

The parameters, d and e, are measures of the sensitivity of metal-complex stability to nitrogen donor atom and oxygen donor atom basicity.

Equation (47) was solved for the sensitivity parameters, d and e and for b by substitution of three sets of ($\log{}^{c}\beta_{AVE}$, $\log{}^{c}K_{NH}$, $\log{}^{c}K_{OH}$) data for each metal-ion. The large precision errors in the data of Table XIX illustrate that this method fails. Because of the approximate constant value of the ratio, $\log{}^{c}K_{NH}/\log{}^{c}K_{OH}$, the value of the determinant used to solve equation (47) is small and, therefore, the experimental error in the data is magnified. Hence, reproducible values of d and e were difficult to obtain. A new approach was used to solve for d and e. This new approach is developed in the next section, Theoretical Development.

Theoretical Development

In this section, the relationship between the sensitivity parameters, d and e, and the bonding properties of both the metal-ion and the proton is determined. From this relationship, values of d and e for a given metal-ion are calculated and stability data of its complexes are explained.

TABLE XVIII

Ratio of Ligand Protonation Constants in 60% v/v Dioxane-Water (25.0°C, I = 0.1)

Ligand	$\text{Log}\,^{c}K_{NH}$	$\text{Log}\,^{c}K_{OH}$	$\dfrac{\text{Log}\,^{c}K_{NH}}{\text{Log}\,^{c}K_{OH}}$
8-Hydroxyquinoline	3.97	11.53	0.344
5-Chloro-8-hydroxyquinoline	2.55	10.64	0.242
8-Hydroxyquinoline-5-sulfonic acid	3.56	10.32	0.345
5-Acetyl-8-hydroxyquinoline	2.93	9.05	0.324
5-Nitro-8-hydroxyquinoline	1.61	7.19	0.224
		Average:	0.30±0.08

TABLE XIX

Values of d, e and b in 60% v/v Dioxane-Water

$$\mathrm{Log}^{c}\beta_{AVE} = d\cdot\log^{c}K_{NH} + e\cdot\log^{c}K_{OH} + b$$

(25.0°C, I = 0.1)

Ion	d	e	b
Ag(I)	0.7±0.3	-0.1±0.7	2±1
Mg(II)	9±22	-4±8	4±5
Ca(II)	1±1	1±2	2±3
Mn(II)	-79±227	-19±47	-7±15
Fe(II)	200±600	-32±93	9±20
Ni(II)	1.3±0.7	0.2±0.8	2±2
Zn(II)	11±25	-4±11	4±6
Pb(II)	2±2	3±3	2±3
Aℓ(III)	7±20	-3±9	2±8
Sc(III)	3±4	1±2	3±3
Fe(III)	2±4	-1±3	3±3
Ce(III)	-12±39	6±15	-3±8

The two major factors that influence the strength of a chemical bond are the electrostatic interaction, E, and the covalent interaction, J, between the components of the bond. In the gaseous state, the energy of formation, ΔH^g, of a bond having both electrostatic and covalent character is given by

$$\Delta H^g = E + J. \tag{48}$$

For a predominantly electrostatic bond, equation (48) reduces to

$$\Delta H^g = E. \tag{49}$$

According to several authors$^{(65-83,116-124)}$, ΔH^g is related to ΔH^s, the energy of formation of the bond in solution, as follows:

$$\Delta H^s = \Delta H^g + B \tag{50}$$

where B is a constant.

For the equilibrium in solution

$$C + L \underset{25.0°C}{\overset{{}^{T}K_{CL}}{\rightleftharpoons}} CL,$$

the free energy change, ΔG^s_{CL}, is given by

$$\Delta G^s_{CL} = -1.36 \log {}^{T}K_{CL} \tag{51}$$

$$= \Delta H^s_{CL} - T\Delta S^s_{CL}. \tag{52}$$

Therefore,

$$-1.36 \log {}^{T}K_{CL} = \Delta H^g_{CL} + B - T\Delta S^s_{CL}. \tag{53}$$

Writing equation (53) for the O-H and O-M bond gives

$$\Delta H^g_{OH} = -1.36 \log {}^{T}K_{OH} - B_{OH} + T\Delta S^s_{OH} \tag{54}$$

and

$$\Delta H^g_{OM} = -1.36 \log{}^T K_{OM} - B_{OM} + T\Delta S^s_{OM}. \tag{55}$$

Combining equations (54) and (55) yields

$$\log{}^T K_{OM} = \frac{\Delta H^g_{OM}}{\Delta H^g_{OH}} \log{}^T K_{OH} + A \tag{56}$$

where

$$A = \left[\frac{\Delta H^g_{OM}}{\Delta H^g_{OH}} (B_{OH} - T\Delta S^s_{OH}) - B_{OM} + T\Delta S^s_{OM} \right] / 1.36.$$

For a given metal-ion with a series of closely related ligands in one solvent composition, A is approximately constant$^{(18)}$.

A similar derivation for the N-H and N-M bond gives

$$\log{}^T K_{NM} = \frac{\Delta H^g_{NM}}{\Delta H^g_{NH}} \log{}^T K_{NH} + D \tag{57}$$

where

$$D = \left[\frac{\Delta H^g_{NM}}{\Delta H^g_{NH}} (B_{NH} - T\Delta S^s_{NH}) - B_{NM} + T\Delta S^s_{NM} \right] / 1.36.$$

D is approximately constant for a given metal-ion with a series of closely related ligands in one solvent composition$^{(18)}$.

If the heats of formation of the N-M and O-M bonds in a metal chelate are assumed to be independent and additive, then equations (56) and (57) can be combined to give the following expression for the concentration constant:

$$\log{}^c K_{NMO} = \frac{\Delta H^g_{NM}}{\Delta H^g_{NH}} \log{}^c K_{NH} + \frac{\Delta H^g_{OM}}{\Delta H^g_{OH}} \log{}^c K_{OH} + b \tag{58}$$

where b = A + D + a logarithmic term composed of the activity coefficients of the species involved in the equilibrium. The entropies, ΔS^{s}_{NM} and ΔS^{s}_{OM}, are not additive. In term b, they are combined, however, to give $\Delta S^{s}_{NMO} + U$. The difference between $\Delta S^{s}_{NMO} + U$ and the sum of the entropies of the $(N\text{-}H)^+$ and O-H complexes is essentially constant for closely related ligands.

In the ensuing development, the behavior of the metal-ions is compared to that of the proton. Hence, ΔH^{g}_{NH} and ΔH^{g}_{OH} can be treated as constants and are denoted by $1/\theta$ and $1/\tau$, respectively. Also, the average stability, $\log{}^{c}\beta_{AVE}$, is used for the stability of the metal chelate, rather than $\log{}^{c}K_{NMO}$, which represents the stability of the 1:1 complex. Equation (58) can now be rewritten as

$$\log{}^{c}\beta_{AVE} = \theta\cdot\Delta H^{AVE}_{NM}\ \log{}^{c}K_{NH} + \tau\cdot\Delta H^{AVE}_{OM}\ \log{}^{c}K_{OH} + b \tag{59}$$

where ΔH^{AVE}_{NM} and ΔH^{AVE}_{OM} are the average energies of formation of the N-M and O-M bonds, respectively.

Because the ratio, $\log{}^{c}K_{NH}/\log{}^{c}K_{OH}$ is approximately constant, equation (59) can be written as

$$\log{}^{c}\beta_{AVE} = (0.30\ \theta\cdot\Delta H^{AVE}_{NM} + \tau\cdot\Delta H^{AVE}_{OM})\log{}^{c}K_{OH} + b. \tag{60}$$

The slope of equation (60) is given by

$$a = 0.30\ \theta\cdot\Delta H^{AVE}_{NM} + \tau\cdot\Delta H^{AVE}_{OM}. \tag{61}$$

In order to solve equation (61), ΔH^{AVE}_{NM} and ΔH^{AVE}_{OM} must be related to the bonding properties of the metal-ion. If the nature of metal-ligand bonding is known, the most appropriate bonding property of the metal-ion may be chosen.

The Bjerrum(86) and Manning(87-89) equation,

$$P = \frac{{}^{c}K_1}{{}^{c}K_2} = S \times T \times R, \tag{9}$$

gives an insight into the nature of the bonding in metal complexes. For a singly charged bidentate ligand bonding to a hexahydrated metal-ion, $S = 4.8$ and $T = 1.6$(87-89). For a predominantly electrostatic metal complex, the following holds:

$$\begin{aligned} P &= 4.8 \times 1.6 \times 1.0 \\ &= 7.7 \end{aligned}$$

i.e., $\log P = 0.87$.

The values of log P for the complexes of the divalent metal-ions used in this study are summarized in Table XX. The low value of log P for Zn(II) 5-chloro-8-hydroxyquinolinate is likely due to an inaccurate value of $\log{}^{c}K_2$ caused by the precipitation of the complex at $\bar{n}$ values less than unity. This value was not used to determine the average value of log P for Zn(II). The average value of log P is 0.8 for Ca(II), Mn(II), Fe(II) and Ni(II) and 0.9 for Zn(II). Therefore, predominantly electrostatic bonding is indicated for the complexes of these metal-ions.

The log P values for the Mg(II) complexes are indicative of predominantly electrostatic bonding in the complexes. The value of log P for Mg(II) 8-hydroxyquinolinate-5-sulfonate, however, indicates a predominantly electrostatic chelate, whereas the log P value (~0.4) for the other complexes indicates predominantly electrostatic bonding in which the Mg(II) ion is bound only to the oxygen donor atom(87-89).

The values of log P for Pb(II) are considerably greater than 0.87.

TABLE XX

Values of Log P in 60% v/v Dioxane-Water

(25.0°C, I = 0.1)

Ion	Oxine	5-Chloro-oxine	5-Acetyl-oxine	5-Nitro-oxine	Oxine-5-sulfonic acid
Mg(II)	0.56	0.33	0.43	0.37	0.91
Ca(II)	0.79	0.87	0.67	0.72	1.05
Mn(II)	0.92	0.70	0.48	1.04	1.12
Fe(II)	1.00	0.60	0.94	0.75	-
Ni(II)	0.40	0.79	0.67	-	1.19
Zn(II)	0.94	0.15	0.44	1.04	1.22
Pb(II)	3.23	2.70	2.59	2.10	-
R[Pb(II)]	3.7	3.1	3.0	2.4	-

The calculated values of R for the Pb(II) complexes are given in Table XX. The large values of R indicate appreciable covalent character in the Pb-ligand bonds (R = 1.0 for electrostatic bonding).

The variation in log P for Pb(II) is expected. The greater the acidity of the donor atom of the ligand, the less is its polarizability, i.e., the tendency to bond covalently decreases. Hence, the Pb-ligand bonds are expected to have greater covalent character in the 8-hydroxyquinoline complex than in the 5-chloro-8-hydroxyquinoline complex, for example. The variation in log P for Pb(II) shows that $\log{}^cK_1$ and $\log{}^cK_2$ do not change similarly with the ligand. This explains the fact that the slope (0.74) for $\log{}^cK_1$ versus $\log{}^cK_{OH}$ is different from that (0.51) for $\log{}^cK_2$ versus $\log{}^cK_{OH}$.

The Bjerrum-Manning method suggests that the N-M and O-M bonds are predominantly electrostatic in character. Other workers have concluded that metal-ligand bonding is predominantly electrostatic in the 8-hydroxyquinoline complexes of Ni(II) and Zn(II)(64), Aℓ(III) and Fe(III)(63), Mg(II) and Ca(II)(125,126) and Ce(III)(127). Thus, equation (61) can be written as

$$a = 0.30\ \theta \cdot E_{NM}^{AVE} + \tau \cdot E_{OM}^{AVE}. \qquad (62)$$

Since all covalent interactions are neglected, this treatment is approximate. The approximation is particularly large for the Pb(II) complexes.

An important parameter that determines the electrostatic energy of a metal-ligand bond is z_M/r_M, the effective electrostatic potential field of the metal-ion (i.e., the ionic potential). This parameter determines the potential field experienced by the ligand donor atoms. The use of this parameter allows the electrostatic interaction of the N-M and O-M bond to be written as

$$E_{NM}^{AVE} = \rho \frac{z_M}{r_M} \quad (63)$$

and

$$E_{OM}^{AVE} = \rho' \frac{z_M}{r_M}, \quad (64)$$

respectively. Substitution of equations (63) and (64) into (62) yields

$$a = \frac{z_M}{r_M} (0.30\ \theta \cdot \rho + \tau \cdot \rho') \quad (65)$$

or

$$a = \frac{z_M}{r_M} (\alpha' + \beta) \quad (66)$$

where $\alpha' = 0.30\ \theta \cdot \rho$ and $\beta = \tau \cdot \rho'$. The quantity a is a sensitivity parameter and is determined by the ionic potential of the metal-ion relative to that of the proton.

Equation (66) was solved using the values of a (Table XVII) and z_M/r_M (128) for Fe(II) and Ce(III) to give $\underline{\alpha' = 0.0532}$ and $\underline{\beta = 0.123}$.

Substitution of equation (66) into (59) gives

$$\log{}^c\beta_{AVE} = \frac{z_M}{r_M} (\alpha \cdot \log{}^cK_{NH} + \beta \cdot \log{}^cK_{OH}) + b \quad (67)$$

where $\alpha = \alpha'/0.30$. Equation (67) predicts that the plot of $\log{}^c\beta_{AVE}$ versus $(\alpha \cdot \log{}^cK_{NH} + \beta \cdot \log{}^cK_{OH})$ has slope $= z_M/r_M$. Table XXI illustrates that the slope of the plot of $\log{}^c\beta_{AVE}$ against $(\alpha \cdot \log{}^cK_{NH} + \beta \cdot \log{}^cK_{OH})$ is in good agreement with z_M/r_M for Fe(II), Ni(II), Zn(II), Aℓ(III), Sc(III), Fe(III) and Ce(III), but not for Ag(I), Mg(II), Ca(II), Mn(II) and Pb(II).

TABLE XXI

Slope Values in 60% v/v Dioxane-Water

$$\mathrm{Log}^{c}\beta_{AVE} = m(\alpha \cdot \log^{c}K_{NH} + \beta \cdot \log^{c}K_{OH}) + b$$

(25.0°C, I = 0.1)

Ion	z_M/r_M	m
Ag(I)	0.794	1.63
Mg(II)	3.03	1.89
Ca(II)	2.02	1.49
Mn(II)	2.50	1.90
Fe(II)	2.70	2.72
Ni(II)	2.91	2.91
Zn(II)	2.70	2.89
Pb(II)	1.67	3.61
Aℓ(III)	5.89	5.49
Sc(III)	4.21	3.97
Fe(III)	4.79	4.91
Ce(III)	2.91	2.92

These plots are shown in Figures 23 and 24.

The calculated slopes for Mg(II), Ca(II) and Mn(II) are less than z_M/r_M. If, however, $\log{}^c\beta_{AVE}$ is plotted against $\beta \cdot \log{}^cK_{OH}$, the slope agrees with z_M/r_M for these metal-ions (Table XXII).

TABLE XXII

Slope Values

$$\text{Log}{}^c\beta_{AVE} = s(\beta \cdot \log{}^cK_{OH}) + b$$

Ion	z_M/r_M	s
Mg(II)	3.03	2.92
Ca(II)	2.02	2.12
Mn(II)	2.50	2.61

The data of Table XXII suggest that the slopes for Mg(II), Ca(II) and Mn(II) are determined solely by the O-M bond, i.e., changes in the contribution of the N-M bond to chelate stability with the ligand are negligible compared to those of the O-M bond, suggesting that the N-M interaction is weak. This behavior is consistent with the low affinity displayed by these ions for nitrogen donors(4,129,130). Hence, the stability of the complexes of these ions may be properly correlated only with $\log{}^cK_{OH}$, as is done in equation (46).

The calculated slopes for Pb(II) and Ag(I) are greater than z_M/r_M. Hence, z_M/r_M is too small to account for the metal-complex stability change as the ligand is varied, i.e., z_M/r_M is not representative of the

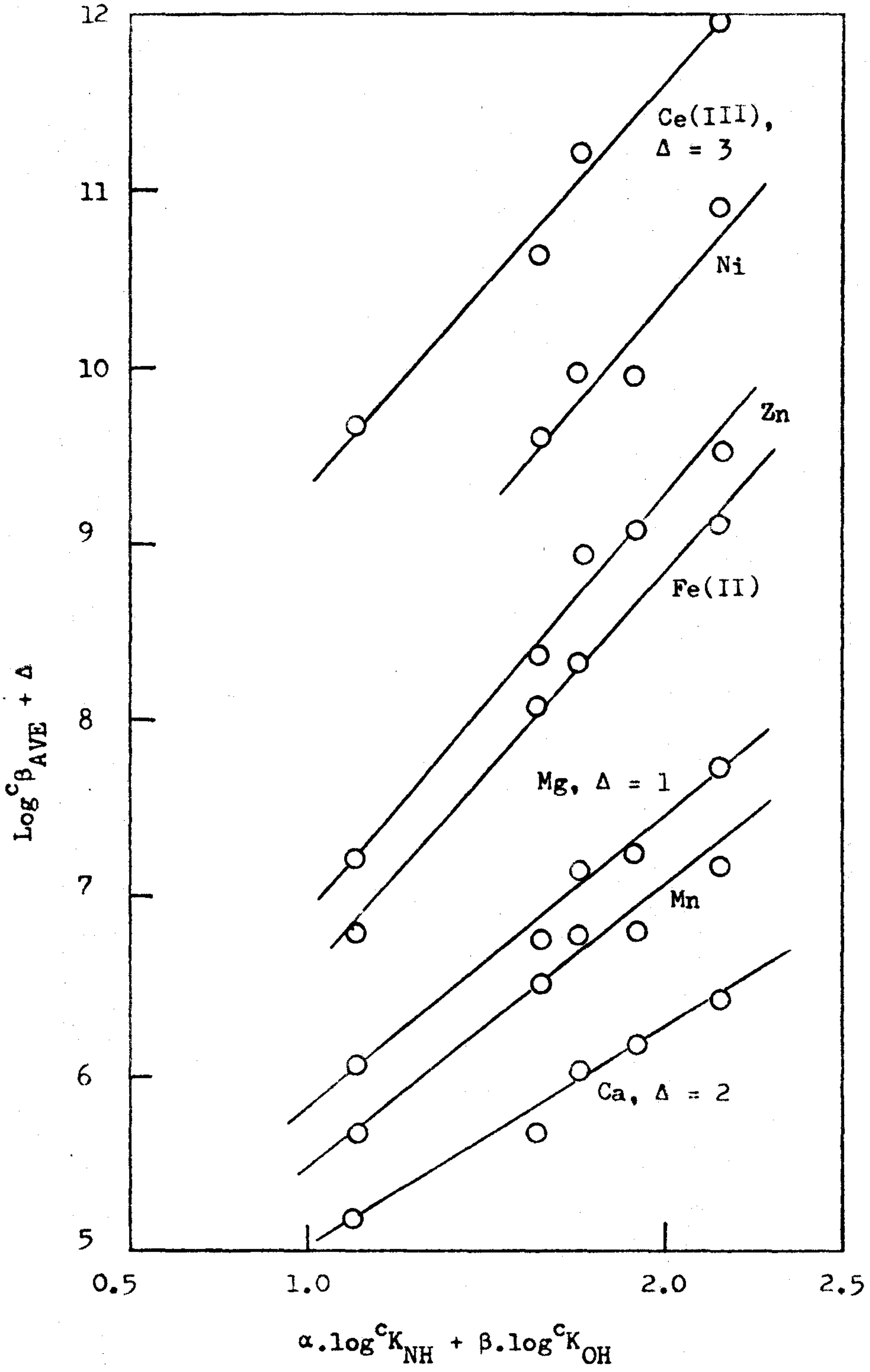


Figure 23. $\text{Log}^c\beta_{AVE} + \Delta$ as a function of $(\alpha\cdot\log^cK_{NH} + \beta\cdot\log^cK_{OH})$ for the complexes of several 8-hydroxyquinoline derivatives in 60% v/v dioxane-water at 25.0°C and I = 0.1. Δ = 0 unless specified.

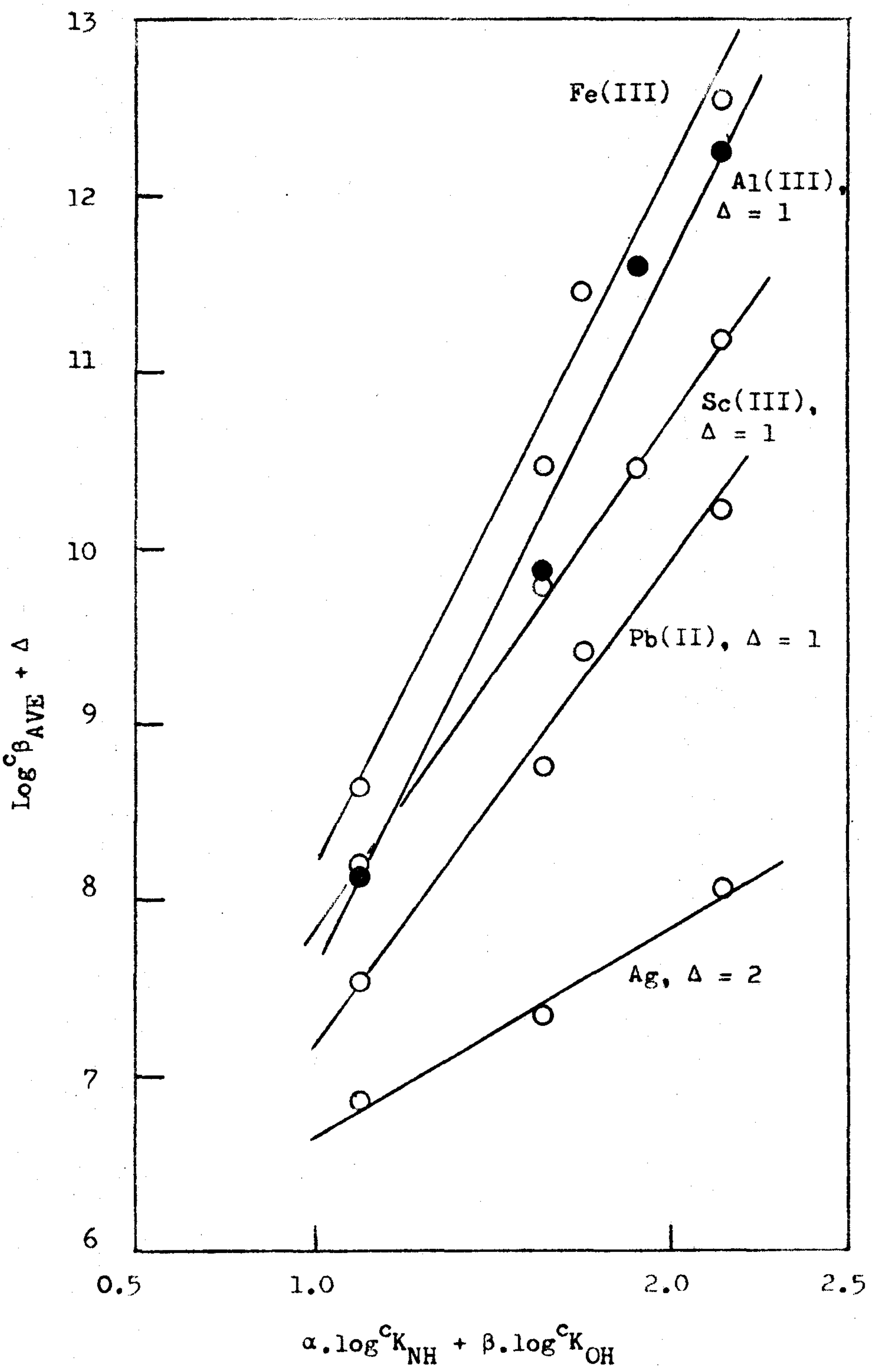


Figure 24. $\mathrm{Log}^{c}\beta_{AVE} + \Delta$ as a function of $(\alpha\cdot\log^{c}K_{NH} + \beta\cdot\log^{c}K_{OH})$ for the complexes of several 8-hydroxyquinoline derivatives in 60% v/v dioxane-water at 25.0°C and $I = 0.1$. $\Delta = 0$ unless specified.

total force between metal-ion and ligand. The Bjerrum-Manning method has suggested that the Pb-ligand bond has appreciable covalent character. Baker and Sawyer(64) also have concluded that the O-Pb bond in 8-hydroxyquinoline complexes is covalent. Therefore, the electrostatic model of metal-ligand bonding should be expected to fail.

Because of its strong class (b) character, Ag(I)(84) is not expected to form predominantly electrostatic bonds. The covalent character of the Ag-ligand bonds is indicated by the plots of $\log {}^cK_1$ versus $\log {}^cK_{OH}$ and of $\log {}^cK_2$ versus $\log {}^cK_{OH}$, in which the slope of the former plot (0.29) is greater than that of the latter (0.09).

From the foregoing discussion, it is concluded that the metal-ligand bonding in the Ag(I), Pb(II) complexes has appreciable covalent character. As stated in the HISTORICAL INTRODUCTION, the ionization potential of the metal has been used to represent the tendency of the metal-ion to bond covalently. No attempt, however, was made in the present study to obtain a correlation of ionization potential with the stability of the complexes of Pb(II) and Ag(I).

A comparison of equations (47) and (67) shows that for predominantly electrostatic metal complexes, the sensitivity parameters, d and e, are given by

$$d = \frac{z_M}{r_M} \cdot \alpha \tag{68}$$

and

$$e = \frac{z_M}{r_M} \cdot \beta . \tag{69}$$

The values of d and e for the metal-ions used in this study (except for Ag(I) and Pb(II) are tabulated in Table XXIII.

TABLE XXIII

Values of Sensitivity Parameters, d and e

Ion	d	e
Mg(II)	0	0.373
Ca(II)	0	0.248
Mn(II)	0	0.308
Fe(II)	0.507	0.332
Ni(II)	0.527	0.358
Zn(II)	0.507	0.332
Aℓ(III)	1.07	0.724
Sc(III)	0.762	0.518
Fe(III)	0.867	0.589
Ce(III)	0.527	0.358

From equation (47)

$$\log^{c}\beta_{AVE} = d\cdot\log^{c}K_{NH} + e\cdot\log^{c}K_{OH} + b \qquad (47)$$

unit slope is predicted for the plot of $\log^{c}\beta_{AVE}$ versus ($d\cdot\log^{c}K_{NH}$ + $e\cdot\log^{c}K_{OH}$). Unit slope was found for all metal-ions except Ag(I) and Pb(II), as is shown in Table XXIV. The value of the intercept b appears to have no simple chemical interpretation(41).

Application to Previous Work

Correlations with Metal-Complex Stability

Irving and Rossotti(17,18) determined the stabilities of the Mg(II), Ni(II) and Zn(II) complexes with several 8-hydroxyquinoline derivatives (Table XXV, ligands 2-8) in 50% v/v dioxane-water. These workers calculated slopes of 0.95, 1.40 and 1.17 for the plot of $\log^{c}\beta_{AVE}$ versus $\log^{c}K_{OH}$ for Mg(II), Ni(II) and Zn(II), respectively. These results are discussed below.

Williams et al.(41) found that the complexes of Ni(II) and Zn(II) with 5-formyl-8-hydroxyquinoline (Table XXV, ligand 1) were more stable than predicted by the data of Irving and Rossotti. Figure 25 illustrates that the data points of the Ni(II) and Zn(II) 5-formyl-8-hydroxyquinolinates lie considerably above the best line through the data of Irving and Rossotti. This enhanced stability was attributed to increased metal to ligand π-bonding caused by the strong π-electron attracting formyl group(41).

The plot of $\log^{c}\beta_{AVE}$ against ($d\cdot\log^{c}K_{NH}$ + $e\cdot\log^{c}K_{OH}$) for the data of both Irving and Rossotti and Williams et al. has a slope of 0.95, 1.03

TABLE XXIV

Slope and Intercept Values in 60% v/v Dioxane-Water

$$\mathrm{Log}\,^{c}\beta_{AVE} = (d \cdot \log {}^{c}K_{NH} + e \cdot \log {}^{c}K_{OH}) + b$$

(25.0°C, I = 0.1)

Ion	Slope	b
Ag(I)	2.05	2.76
Mg(II)	0.94	1.70
Ca(II)	1.04	1.36
Mn(II)	1.05	3.33
Fe(II)	1.01	3.42
Ni(II)	0.93	4.78
Zn(II)	1.06	3.56
Pb(II)	2.16	2.00
Aℓ(III)	0.94	0.19
Sc(III)	0.93	2.56
Fe(III)	1.04	2.40
Ce(III)	1.00	1.93

TABLE XXV

Protonation Constants of 8-Hydroxyquinoline Derivatives
in 50% v/v Dioxane-Water
(20°C, I = 0.3)

	Ligand	$\text{Log}^{c}K_{NH}$	$\text{Log}^{c}K_{OH}$
1.	5-Formyl-8-hydroxyquinoline	2.51	7.43
2.	8-Hydroxycinnoline	1.77	8.84
3.	4-Methyl-8-hydroxycinnoline	2.59	9.00
4.	5-Hydroxyquinoxaline	<1	9.29
5.	8-Hydroxyquinazoline	3.30	9.59
6.	6-Methyl-8-hydroxyquinoline	4.76	10.71
7.	8-Hydroxyquinoline	4.48	10.80
8.	5-Methyl-8-hydroxyquinoline	4.71	11.11

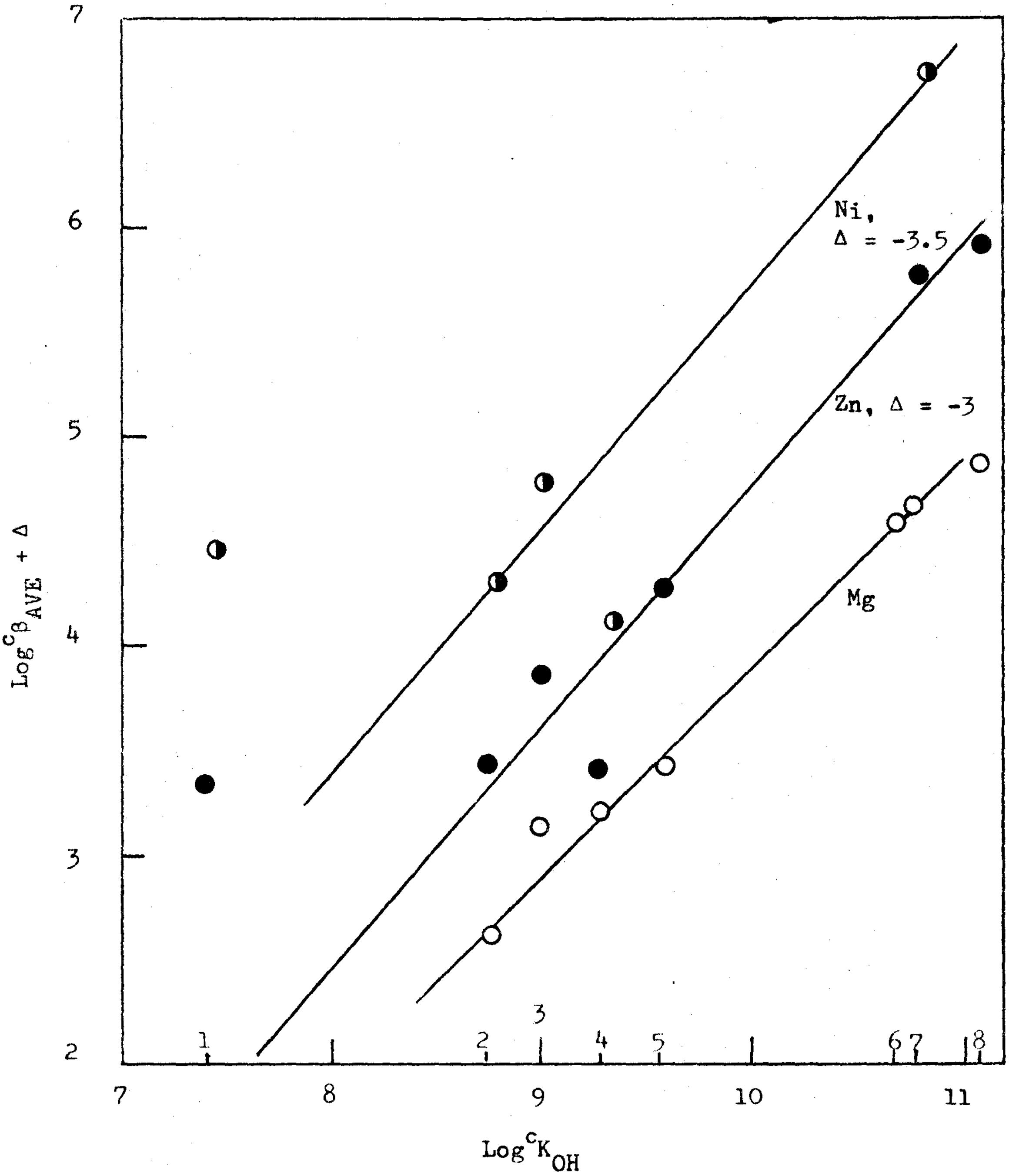


Figure 25. Log$^c\beta_{AVE}$ + Δ *versus* log$^cK_{OH}$ for the complexes of several 8-hydroxyquinoline derivatives in 50% v/v dioxane-water at 20.0°C and I = 0.3. Data is from references (17) and (41). Δ = 0 unless specified.

and 0.99 for Mg(II), Ni(II) and Zn(II), respectively. The values of $\alpha = 0.181$ rather than 0 was required in order to obtain unit slope for Mg(II). This indicates that a portion of the Mg-chelate stability is due to the formation of a N-Mg bond, and is in contrast to the result presented earlier in this thesis, namely, that the contribution of the N-Mg (and N-Ca and N-Mn) bond to chelate stability is negligible with respect to the corresponding O-metal bond. The results of the present study are at least consistent in that a contribution by the N-Ca bond to chelate stability is not expected if none is found for the N-Mg bond. There appears to be no simple reason for the discrepancy between this study and that of Irving and Rossotti concerning the N-Mg bond.

The enhanced stability of the Ni(II) and Zn(II) 5-formyl-8-hydroxyquinolinates is not apparent in the plot of $\log {}^c\beta_{AVE}$ versus $(d \cdot \log {}^cK_{NH} + e \cdot \log {}^cK_{OH})$, as shown in Figure 26. Thus, there is no need to consider increased metal to ligand π-bonding as discussed by Williams et al. Rather, the apparent enhanced stability observed in the plot of $\log {}^c\beta_{AVE}$ against $\log {}^cK_{OH}$ arises because the treatment neglected the N-metal interaction.

Tomkinson and Williams(94) determined the stability of the Fe(III) complexes of several 5-substituted-8-hydroxyquinolines. These workers reported a slope of 0.88 for the plot of $\log {}^c\beta_{AVE}$ versus $\log {}^cK_{OH}$. This value is in good agreement with that of 0.87 found for Fe(III) in this thesis in which similar 5-substituted-8-hydroxyquinolines were used. The plot of $\log {}^c\beta_{AVE}$ against $(d \cdot \log {}^cK_{NH} + e \cdot \log {}^cK_{OH})$ has unit slope (0.96) for the Fe(III) data of Tomkinson and Williams.

Beimer and Fernando(59) found a non-linear relationship between

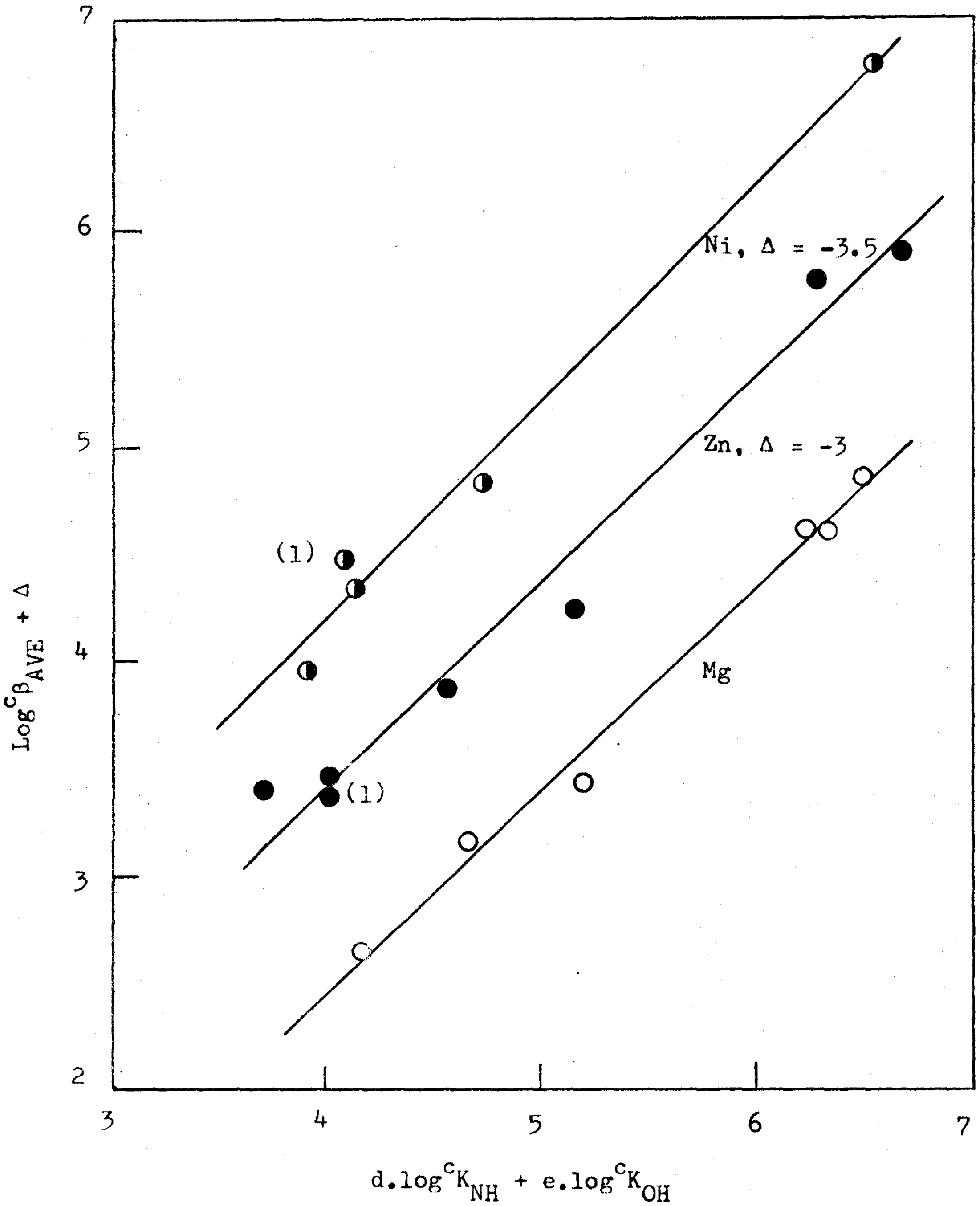


Figure 26. $\mathrm{Log}^c\beta_{AVE} + \Delta$ versus $(d\cdot\log^c K_{NH} + e\cdot\log^c K_{OH})$ for the complexes of several 8-hydroxyquinoline derivatives in 50% v/v dioxane-water at 20.0°C and I = 0.3. Data is from references (17) and (41). Δ = 0 unless specified.

$\log{}^c\beta_{AVE}$ and $\log{}^cK_{OH}$ for the metal complexes of 5-halo-8-hydroxyquinolines. The use of their data also yields a non-linear relationship between $\log{}^c\beta_{AVE}$ and $(d\cdot\log{}^cK_{NH} + e\cdot\log{}^cK_{OH})$. The halogens are σ-acceptors and π-donors and, in general, the π-donor property is the more important(41,59). Hammett reaction constants suggest that the σ-acceptor property is essentially constant for the halogens but that the π-donor property is greatest for fluorine and least for iodine(59).

The value of $\log{}^cK_{OH}$ for the 5-fluoro, 5-chloro-, 5-bromo and 5-iodo derivative is 11.04, 10.46, 10.41 and 10.10, respectively. The O-H bond in 8-hydroxyquinoline has appreciable covalent character(63,64) and, therefore, the charge on the oxygen is reduced. The donation of π-electrons by the halo substituent destabilizes the charge on the phenolate oxygen formed on dissociation. Thus, the stability of the O-H complex is expected to vary regularly with the halo substituent.

On dissociation of a predominantly electrostatic complex, there is relatively little change in the charge of the phenolate oxygen. Therefore, π-donation by the halo substituent is expected to exert little influence on the stability of the metal complex. Since π-donation by the halo substituent influences O-H complex stability considerably more than metal complex stability, a linear relationship between $\log{}^c\beta_{AVE}$ and $(d\cdot\log{}^cK_{NH} + e\cdot\log{}^cK_{OH})$ should not be expected.

Several workers(41,44,60,61) have concluded that the disagreement between the data of Irving and Rossotti(17) and of Williams et al.(41) is due to metal-ligand π-bonding. The present work shows that the data of Irving and Rossotti, of Williams and of this thesis are indeed in agreement. The apparent discrepancies in the behavior of a given metal-ion vanish if both the N-M and O-M interactions are considered, i.e., the metal complex stability must be correlated with both the nitrogen and oxygen donor-atom basicity. There is no need to postulate metal to ligand π-bonding.

Correlations with Redox Potentials

Metal-complex stability data available in the literature have been successfully correlated with the function $(d\cdot\log {}^{c}K_{NH} + e\cdot\log {}^{c}K_{OH})$. The purpose of this section is to show that the redox potentials of the Fe(III) complexes of several 5-substituted-8-hydroxyquinolines determined by Tomkinson and Williams(94) can also be correlated with $(d\cdot\log {}^{c}K_{NH} + e\cdot\log {}^{c}K_{OH})$. These workers found a non-linear relationship between the redox potential and $\log {}^{c}K_{OH}$. (The data for the Fe(III) complexes of 5-formyl and 5-cyano-8-hydroxyquinoline did not obey this relationship.)

Figure 27 shows the plot of the redox potential versus $\Delta(d\cdot\log {}^{c}K_{NH} + e\cdot\log {}^{c}K_{OH})$ where

$$\begin{aligned}\Delta(d\cdot\log {}^{c}K_{NH} + e\cdot\log {}^{c}K_{OH}) &= (d\cdot\log {}^{c}K_{NH} + e\cdot\log {}^{c}K_{OH})^{Fe(III)} \\ &\quad - (d\cdot\log {}^{c}K_{NH} + e\cdot\log {}^{c}K_{OH})^{Fe(II)}. \qquad (70)\end{aligned}$$

Two correlations of the redox potentials are possible. If the data for 5-formyl and 5-cyano-8-hydroxyquinoline are excluded, the correlation is non-linear. The correlation, however, is linear if the data for 7-iodo-8-hydroxyquinoline-5-sulfonic acid is excluded. This is the only halo-substituted ligand. The results of Beimer and Fernando(59) have shown that $\log {}^{c}\beta_{AVE}$ for metal complexes of 5-halo-8-hydroxyquinolines gives a non-linear correlation with $\log {}^{c}K_{OH}$. The exclusion of the data for 7-iodo-8-hydroxyquinoline-5-sulfonic acid is more justifiable than the exclusion of the data of 5-formyl and 5-cyano-8-hydroxyquinoline. A

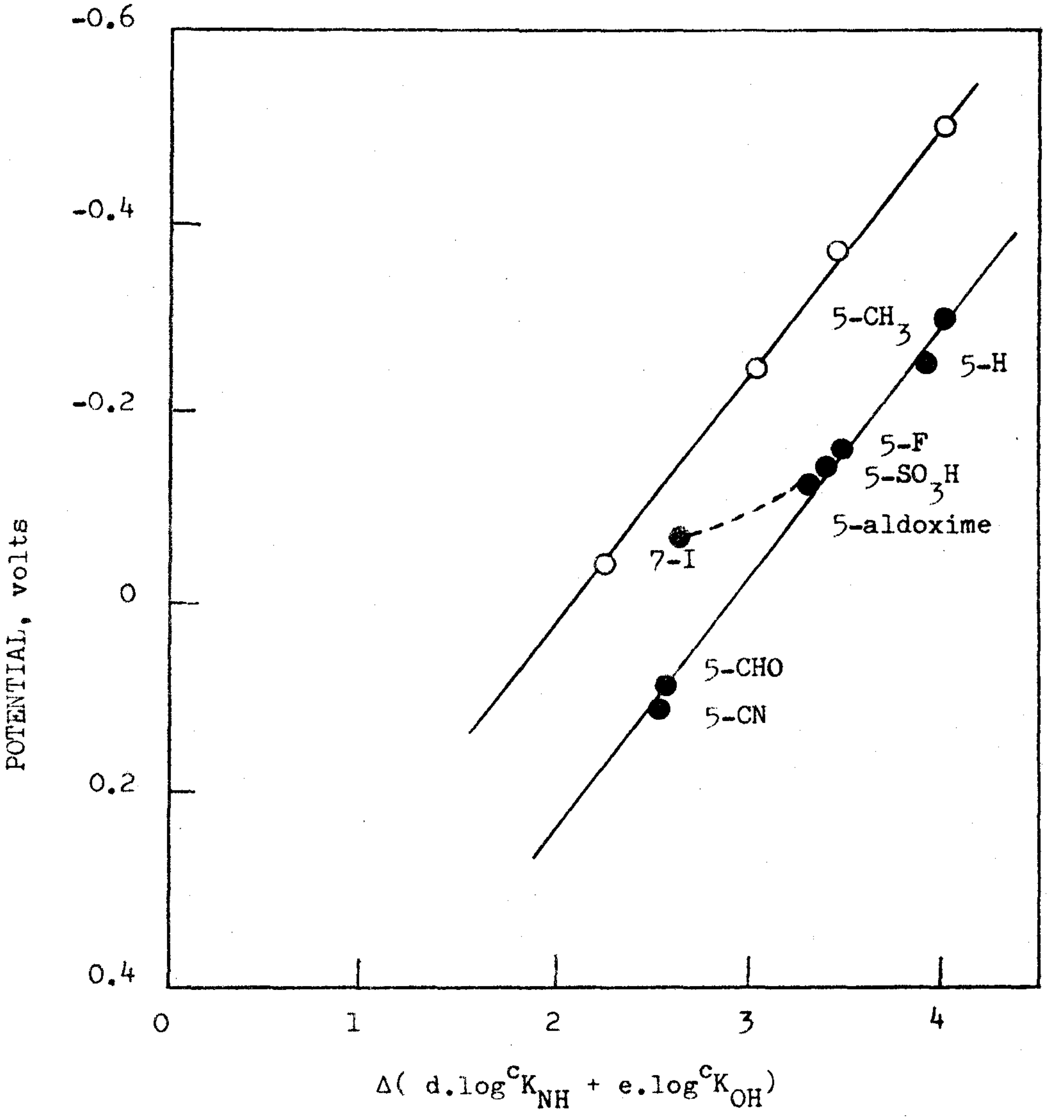


Figure 27. Potential of Fe(III) complexes of 8-hydroxyquinoline derivatives as a function of $\Delta(d\cdot\log^{c}K_{NH} + e\cdot\log^{c}K_{OH})$. Open circles denote half-wave potential in 60% v/v dioxane-water (25.0°C, I = 0.1). Filled circles denote redox potential$^{(41)}$ in 50% v/v dioxane-water (20.0°C, I = 0.3).

further reason for selecting the linear relationship between the redox potential and $\Delta(d\cdot\log^c K_{NH} + e\cdot\log^c K_{OH})$ is given below.

The half-wave potentials, $E_{1/2}$, of the Fe(III) complexes of several 8-hydroxyquinolines were determined in 60% dioxane-water and I = 0.1 (sodium perchlorate). The values of the half-wave potential and $\Delta(d\cdot\log^c K_{NH} + e\cdot\log^c K_{OH})$ are summarized in Table XXVI.

The plot of $E_{1/2}$ versus $\Delta(d\cdot\log^c K_{NH} + e\cdot\log^c K_{OH})$ is illustrated in Figure 27. This correlation is linear and parallels that of the redox potential.

Relative Importance of N-M and O-M Bond

Irving and Rossotti (18) had suggested that the relative importance of the N-M and O-M bonds could be determined by studying the effect of solvent composition on the stability of the metal-ligand and of the corresponding proton-ligand complexes. The results presented earlier in this thesis showed that this method fails because the solvent effect is essentially independent of the metal-ion (and proton). The relative importance of the N-M and O-M bond, however, can be calculated from the sensitivity parameters determined from the correlation between metal-complex stability and basicity of the ligand donor atom(s).

The following discussion is limited to those metal-ions which were shown to form predominantly electrostatic complexes. Equation (67) can be rewritten as

$$\log^c \beta_{AVE} - b = \frac{z_M}{r_M}(\alpha\cdot\log^c K_{NH} + \beta\cdot\log^c K_{OH}). \tag{67}$$

The term $\frac{z_M}{r_M}(\alpha\cdot\log^c K_{NH} + \beta\cdot\log^c K_{OH})$ represents the total contri-

TABLE XXVI

Half-Wave Potentials of Fe(III) Complexes in 60% v/v Dioxane-Water at I = 0.1

Ligand	$E_{1/2}$ (volts)	$\Delta(d\cdot\log {}^{c}K_{NH}+e\cdot\log {}^{c}K_{OH})$
8-Hydroxyquinoline	-0.50	4.04
5-Chloro-8-hydroxyquinoline	-0.37	3.43
5-Acetyl-8-hydroxyquinoline	-0.24	3.12
5-Nitro-8-hydroxyquinoline	-0.02	2.28

bution of the metal-ligand bonds to complex stability. The percentage contribution of the N-M bond is given by

$$\frac{\alpha \cdot \log {}^{c}K_{NH} \times 100\%}{\alpha \cdot \log {}^{c}K_{NH} + \beta \cdot \log {}^{c}K_{OH}}$$

and of the O-M bond by

$$\frac{\beta \cdot \log {}^{c}K_{OH} \times 100\%}{\alpha \cdot \log {}^{c}K_{NH} + \beta \cdot \log {}^{c}K_{OH}} .$$

For a given ligand, the percentage contributions of the N-M and O-M bonds are independent of the metal-ion, but are dependent solely on the basicity of the ligand donor atoms. Of course, the total contribution of both bonds varies directly with the stability of the complex. The total contribution is greater the larger is z_M/r_M for the metal-ion. Only the O-M bond was found to be significant in the complexes of Mg(II), Ca(II) and Mn(II).

Table XXVII illustrates that the variation in the percentage contributions of the N-M and O-M bonds for the complexes of a given metal-ion with the ligands used in this study is small (9%).

The percentage and total contributions of the metal-ligand bonds vary with the solvent composition. For example, the percentage contribution of the N-M bond for 8-hydroxyquinoline varies from 40 to 31% in passing from 20 to 75% v/v dioxane-water. The calculated difference in the <u>total</u> contribution by the N-M and O-M bonds is 0.5 and 0.2 for the complexes of Aℓ(III) and Ca(II)*, respectively. The average stability, however, changes

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*Aℓ(III) and Ca(II) have the greatest and least value of z_M/r_M for the metal-ions used in Figures 13 to 17.

TABLE XXVII

Percentage Contributions of N-M and O-M Bond
in 60% v/v Dioxane-Water
(25.0°C, I = 0.1)

Ligand	N-M (%)	O-M (%)
8-Hydroxyquinoline	34	66
5-Chloro-8-hydroxyquinoline	26	74
8-Hydroxyquinoline-5-sulfonic acid	34	66
5-Acetyl-8-hydroxyquinoline	32	78
5-Nitro-8-hydroxyquinoline	25	75

by 1.5 units (as shown in Figures 13 to 17). Thus, the effect due to the difference in the strengths of the Aℓ-ligand and Ca-ligand bonds is approximately 20% of the observed effect of changing the solvent composition. Therefore, it is not surprising that the solvent effect was found to be essentially independent of the metal-ion. Rather, as concluded earlier, the neutralization of ionic charge is the important factor in the solvent effect.

The calculation of the percentage contributions of the metal-ligand bonds is a quantitative method of evaluating the relative affinity of donor atoms towards a given metal-ion. For example, in predominantly electrostatic complexes, the charged oxygen has a greater affinity for the metal-ion than does the neutral nitrogen but this relative affinity varies with the ligand even in a family of closely related ligands. This method can be extended; i.e., the study of the complexes of substituted 8-mercaptoquinolines would yield the relative affinity of a charged sulfur and a neutral nitrogen. Then, the relative affinity of oxygen and sulfur can be calculated. To date, the measurement of these affinities has been only qualitative(84,131).

The relative contributions of the N-M and O-M bonds in the covalent complexes of Ag(I) and Pb(II) have not been evaluated because the data are insufficient to allow the choosing and testing of a metal-ion property in correlations between $\log {}^{c}\beta_{AVE}$ and $\log {}^{c}K_{OH}$.

Selectivity of 8-Hydroxyquinoline Ligands towards Metal-Ions

8-Hydroxyquinoline is an unselective reagent. It forms chelates with forty-three metal-ions(132). One of the purposes of this thesis is to determine whether the selectivity of this ligand and its derivatives can be improved either by changing the solvent composition or by changing the basicity of the donor atoms. The results of this study illustrate that the effect of solvent composition is essentially independent of the metal-ion, i.e., no selectivity advantage is obtained by varying the solvent composition.

The selectivity of a ligand in a non-precipitation* chelation reaction depends on the pH, the solution stability of the proton complex(es) and the solution stability of the metal complex. It is shown below that the important factor in comparing the selectivity of several related ligands towards a group of metal-ions is the solution stability of the proton complex(es).

Table XXVIII summarizes the concentrations of the stepwise complexes of Fe(III), Aℓ(III), Ni(II), Zn(II), Fe(II), Mn(II) and Mg(II) with some 8-hydroxyquinoline derivatives in 60% v/v dioxane-water at pH 2.50. The concentration of each metal complex is reported as a percentage of the stoichiometric concentration of that metal-ion. The results clearly show that the selectivity of the ligands at pH 2.50 decreases with increasing ligand acidity (i.e., decreasing metal-complex stability). For example, for 8-hydroxyquinoline, there is very little uncomplexed Fe(III) whereas Zn(II), Fe(II), Mn(II) and Mg(II) are essentially uncomplexed. By comparison, for 5-nitro-8-hydroxyquinoline, only Mg(II) remains essentially uncomplexed.

The solution pH and the stability of the proton complexes determine the concentration of the chelating form of the ligand. These factors are

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*For a precipitation reaction, the intrinsic solubility must also be considered.

TABLE XXVIII

Concentration of Metal-Complexes as a Percentage of the Analytical Concentration of the Metal-Ion in 60% v/v Dioxane-Water

(25.0°C, I = 0.1)

Concentration of ligand = 3.5×10^{-2}M

Concentration of each metal = 5.0×10^{-4}M

pH = 2.50

Species	Percentage Concentration			
	Oxine	5-Chloro-oxine	5-Acetyl-oxine	5-Nitro-oxine
$\log {}^{c}K_{NH}$	3.97	2.55	2.93	1.61
$\log {}^{c}K_{OH}$	11.53	10.64	9.05	7.19
Fe^{3+}	0.6	0.2	-	-
FeL^{2+}	9.4	1.8	-	0.1
$FeL_2{}^{+}$	55.6	8.4	1.9	2.7
FeL_3	34.4	89.8	98.1	97.2
$A\ell^{3+}$	63.6	0.3	4.4	0.2
$A\ell L^{2+}$	18.4	14.1	59.0	1.7
$A\ell L_2{}^{+}$	17.6	57.1	26.0	23.9
$A\ell L_3$	0.4	28.5	10.7	74.2
Ni^{2+}	88.5	23.2	1.0	-
NiL^{+}	10.9	55.4	19.3	1.0
NiL_2	0.5	21.4	79.7	99.0

TABLE XXVIII (Cont'd.)

Species	Percentage Concentration			
	Oxine	5-Chloro-oxine	5-Acetyl-oxine	5-Nitro-oxine
Zn^{2+}	99.1	89.5	46.1	1.0
ZnL^{+}	0.9	9.8	40.8	27.6
ZnL_2	-	0.7	13.1	71.4
Fe^{2+}	99.6	95.7	49.8	5.1
FeL^{+}	0.4	4.2	43.1	39.2
FeL_2	-	0.1	7.1	55.7
Mn^{2+}	100.0	99.9	99.7	23.4
MnL^{+}	-	0.1	0.3	74.5
MnL_2	-	-	-	2.1
Mg^{2+}	100.0	100.0	100.0	100.0
MgL^{+}	-	-	-	-
MgL_2	-	-	-	-

important in comparing the selectivities of several ligands towards the same metal-ions, as shown in Table XXVIII. The solution stability of the metal complex and the concentration of the chelating form of the ligand determine the concentration of the metal complex. For the basic ligand, 8-hydroxyquinoline, the concentration of the ligand anion is small at pH 2.50, and the concentration of the metal complex is determined mainly by its solution stability. As the basicity of the ligand decreases, the concentration of the chelating form of the ligand (at pH 2.50) increases, and becomes more important in determining the concentration of the metal complex. Since the concentration of ligand anion is independent of the metal-ions, the selectivity of the ligand must decrease, as observed.

It may be concluded that the observed lack of selectivity of the less basic ligands is ultimately due to the high concentration of the chelating form of the ligand. A true comparison of the selectivity of several ligands must be made at the same concentration of ligand anion. This, however, is not an experimentally useful quantity.

Discussion of Errors

The determination of equilibrium constants is subject to errors in precision and accuracy. The largest source of error arises from the measurement of pH. This error is present in both the spectrophotometric and potentiometric methods. Recent improvements in the design of pH meters and electrodes permit the measurement of pH with a precision of a few one-thousandths of a pH unit, so that the largest precision error in pH measurement results from the uncertainty in the values of the standard buffer solutions used to calibrate the pH meter. This uncertainty is about ±0.01 pH unit.

Errors due to changes in activity coefficients are eliminated by the use of a background electrolyte and the Van Uitert and Haas correction factor. The correction factor allows conversion of hydrogen-ion activities to stoichiometric hydrogen-ion concentrations. The equilibrium constants determined in this study are thus concentration constants. These constants are valid only for the exact solution conditions under which they were determined.

Errors in accuracy affect the absolute value of equilibrium constants. In general, however, all errors in accuracy are essentially constant for titrations involving the same ligand and a series of metal-ions. Therefore, formation constants resulting from such titrations can be compared with some certainty.

The formation constants reported in the present study were calculated by least-squares fit of the best line to a linear form of the formation function. This method uses a large amount of the experimental data and also eliminates the subjective factor. Other methods which have been proposed(107) often use only a small portion of the data or require graphical procedures which may introduce subjective errors.

A detailed analysis of error in both ligand protonation and chelate formation constants was performed. Taken into consideration were the errors in the concentrations of metal-ion, perchloric acid and sodium hydroxide solutions, in the delivered volumes of reagents and solvent components, in the pH (~0.01 units), and in ligand protonation constants. Both the positive and negative accumulative errors were used to calculate new equilibria constants. The error in the ligand protonation constants were calculated to be ±0.02 units for the data of five titrations. For chelate formation constants, the error was found to be ±0.09 units.

Suggestions for Further Work

The findings of the present work suggest further research in three areas. First, the stability of the complexes formed between 8-hydroxyquinoline derivatives and other class (b) metal-ions (e.g., Sn(II), Tℓ(III), etc.) should be determined. A property of the metal such as the ionization potential can be chosen to calculate the sensitivity parameters, d and e, for covalently bonding metal-ions.

Second, an attempt should be made to apply the findings of this thesis to the metal complexes of nitrogen and oxygen donor atom ligands other than substituted 8-hydroxyquinolines (e.g., imidoacetic acid).

Third, the methods used in this study should also be applied to the metal complexes of ligands having other than nitrogen and oxygen donor atoms (e.g., 8-mercaptoquinoline, acetylacetone, etc.). In this manner, the relative affinities of donor atoms towards a series of metal-ions can be determined. Many of the data required to carry out the latter two suggestions are available in the literature. A major disadvantage, however, is that, in general, only the basicity of the most basic donor atom has been determined. The basicity of all donor atoms is required to apply the methods used in this thesis.

SUMMARY

1. Glass electrode correction factors have been calculated for 20, 40, 50, 60 and 75% v/v dioxane-water. The pH range in which these correction factors remain constant has been extended by the use of a 8-hydroxyquinoline buffer. The concentration dissociation constant of water has been determined in 20, 40, 50, 60 and 75% v/v dioxane-water. The value of p_cK_w in 50% v/v dioxane-water agrees with those values in the literature(102,105).

2. The protonation constants of 8-hydroxyquinoline, 5-chloro-8-hydroxyquinoline, 8-hydroxyquinoline-5-sulfonic acid, 5-acetyl-8-hydroxyquinoline, 5-nitro-8-hydroxyquinoline have been determined in several solvent media ranging from 0 to 75% v/v dioxane-water (at 25.0°C and $I = 0.1$).

3. The chelate formation constants for the reaction of these 8-hydroxyquinolines with Mg(II), Ca(II), Mn(II), Ni(II) and Zn(II) have been determined in several dioxane-water media. For Ag(I), Fe(II), Pb(II), Aℓ(III), Sc(III), Fe(III) and Ce(III), the formation constants were determined only in 60% v/v dioxane-water.

4. The behavior of the average stabilities of metal-ligand and proton-ligand complexes with variation in solvent composition indicates that the effect of the solvent on complex stability is essentially independent of the metal-ion. Thus, a change in the solvent composition exerts no influence on the selectivity of the 8-hydroxyquinolines towards a series of metal-ions.

5. The scant data on the effect of the solvent composition on the stability of S-H and S-M complexes indicate similar behavior to the corresponding O-H and O-M complexes. It was concluded that the solvent effect of primary importance in complexation is charge neutralization.

6. The ionic potential of the metal-ion has been shown to be the important parameter that determines the slope of the correlation between metal-complex stability and ligand basicity for electrostatically bonded complexes. The sensitivity parameters that measure the degree of dependence of metal-complex stability on ligand basicity were calculated and used to correlate the data obtained by previous workers.

7. The relative importance of the N-M and O-M bond to complex stability has been calculated and shown to be independent of the metal-ion in electrostatically bonded complexes.

8. It has been shown that the important factor in the comparison of the selectivity of several ligands towards the same metal-ions (at a given pH value) is the basicity of the ligands and not the solution stabilities of the metal complexes. Selectivity increases with the basicity of the ligand.

9. The data for the Ag(I) and Pb(II) complexes indicate covalent bonding in these complexes. No further calculations were made in this study. Instead, suggestions for further study of the 8-hydroxyquinoline complexes of class (b) metal-ions have been made.

APPENDIX I

POTENTIOMETRIC DETERMINATION OF PROTONATION CONSTANTS

TABLE I

PROTONATION CONSTANTS OF 8-HYDROXYQUINOLINE-5-SULFONIC ACID IN WATER

VOL. NAOH	PH(CORR.)	P	PK(CALC.)
0.000	2.400	2.098	
.400	2.449	2.093	
.600	2.474	2.086	
1.000	2.527	2.067	
1.200	2.558	2.063	
1.600	2.624	2.048	
2.000	2.697	2.024	
2.400	2.786	2.005	
2.800	2.892	1.978	
3.000	2.953	1.962	
3.200	3.021	1.943	
3.400	3.098	1.922	
3.600	3.183	1.895	4.115
3.800	3.277	1.863	4.077
4.000	3.378	1.824	4.048
4.160	3.466	1.788	4.036
4.320	3.556	1.747	4.025
4.480	3.647	1.701	4.016
4.640	3.747	1.625	4.020
4.960	3.942	1.544	4.018
5.120	4.042	1.486	4.017
5.280	4.148	1.426	4.019
5.440	4.260	1.365	4.020
5.600	4.389	1.304	4.028
5.700	4.478	1.264	4.034
5.800	4.582	1.225	4.045
5.900	4.699	1.185	4.056
6.000	4.844	1.145	4.075
6.700	7.759	0.856	8.532
6.800	4.883	0.807	5.505
6.900	7.987	0.771	8.514

TABLE I CONTINUED

7.000	8.079	0.729	8.508
7.100	8.165	0.687	8.506
7.200	8.243	0.644	8.501
7.300	8.318	0.602	8.498
7.400	8.398	0.560	8.503
7.500	8.468	0.518	8.499
7.600	8.541	0.476	8.499
7.700	8.614	0.434	8.498
7.800	8.690	0.392	8.499
7.900	8.769	0.350	8.500
8.000	8.857	0.308	8.506
8.100	8.947	0.267	8.508
8.200	9.047	0.225	8.511
8.300	9.152	0.184	8.506
8.400	9.289	0.144	8.516
8.500	9.442	0.106	8.514
8.600	9.628	0.070	

PK1 = 4.3175 PK2 = 8.8272

EVALUATION OF DATA PRECISION, SIGMA = 5.8980E-02*

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*E-xx denotes 10^{-xx}.

TABLE II

PROTONATION CONSTANTS OF 8-HYDROXYQUINOLINE IN 20 VOLUME PERCENT DIOXANE-WATER

VOL. NAOH	PH(CORR.)	P	PK(CALC.)
0.000	3.204	2.011	
.400	3.528	1.985	
.600	3.706	1.958	
.800	3.871	1.925	
1.000	4.015	1.886	4.907
1.200	4.143	1.845	4.880
1.400	4.254	1.802	4.863
1.600	4.355	1.759	4.852
1.800	4.446	1.714	4.844
2.000	4.535	1.670	4.842
2.200	4.621	1.624	4.842
2.400	4.705	1.579	4.844
2.600	4.788	1.534	4.847
2.800	4.875	1.488	4.855
3.000	4.964	1.443	4.864
3.200	5.055	1.397	4.874
3.400	5.156	1.351	4.890
3.600	5.267	1.306	4.911
3.800	5.396	1.260	4.942
4.000	5.554	1.214	4.989
4.200	5.769	1.168	5.075
4.400	6.130	1.122	5.274
4.500	6.495	1.099	
4.600	7.674	1.076	
4.700	8.585	1.054	
4.800	8.924	1.031	
4.900	9.119	1.008	
5.000	9.262	.986	
5.200	9.468	.941	
5.400	9.624	.896	10.558
5.600	9.746	.851	10.503
5.800	9.854	.806	10.474
6.000	9.947	.762	10.452
6.200	10.035	.717	10.439
6.400	10.117	.673	10.431

TABLE II CONTINUED

6.600	10.195	.629	10.425
6.800	10.268	.586	10.419
7.000	10.339	.543	10.414
7.200	10.413	.500	10.414
7.400	10.486	.459	10.413
7.600	10.559	.418	10.414
7.800	10.631	.377	10.414
8.000	10.708	.339	10.418
8.200	10.785	.302	10.421
8.405	10.868	.266	10.428
8.600	10.943	.234	10.428
8.800	11.028	.205	10.441
9.000	11.107	.179	10.445

PK1 = 4.8857 PK2 = 10.4078

EVALUATION OF DATA PRECISION, SIGMA = 3.3557E-02

TABLE III

PROTONATION CONSTANTS OF 5-CHLORO-8-HYDROXYQUINOLINE IN 40 VOLUME PERCENT DIOXANE-WATER

VOL. NAOH	PH(CORR.)	P	PK(CALC.)
0.000	2.464	1.716	2.866
.180	2.491	1.712	2.885
.360	2.519	1.707	2.902
.540	2.547	1.698	2.911
.720	2.573	1.682	2.903
.900	2.605	1.674	2.920
1.080	2.638	1.663	2.932
1.260	2.671	1.649	2.937
1.440	2.707	1.635	2.947
1.620	2.741	1.614	2.943
1.800	2.781	1.598	2.953
1.980	2.822	1.578	2.958
2.160	2.868	1.559	2.971
2.240	2.913	1.574	3.042
2.520	2.961	1.508	2.975
2.700	3.017	1.484	2.989
2.940	3.091	1.442	2.990
3.120	3.154	1.410	2.997
3.360	3.246	1.364	3.004
3.540	3.321	1.326	3.005
3.780	3.438	1.272	3.011
3.960	3.539	1.229	3.013
4.200	3.711	1.170	3.022
4.380	3.878	1.123	3.023
4.620	4.249	1.057	
4.800	5.166	1.005	
4.920	7.942	.961	
5.100	8.809	.892	9.726
5.280	9.199	.823	9.866
5.460	9.441	.754	9.927
5.640	9.627	.685	9.964
5.820	9.781	.616	9.986
6.000	9.917	.547	9.999
6.240	10.090	.455	10.012

TABLE III CONTINUED

```
          6.480         10.260         .364       10.018
          6.720         10.434         .274       10.011
          6.960         10.637         .186        9.996
          7.200         10.881         .103        9.939
          7.680         11.472        -.020
          8.160         11.863        -.082
          8.640         12.085        -.126

PK1 =  2.9600  PK2 =  9.9748

EVALUATION  OF  DATA  PRECISION,  SIGMA  = 2.1219E-02
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TABLE IV

PROTONATION CONSTANTS OF 5-ACETYL-8-HYDROXYQUINOLINE IN 60 VOLUME PERCENT DIOXANE-WATER

VOL. NAOH	PH(CORR.)	P	PK(CALC.)
0.000	2.567	1.670	2.875
.200	2.597	1.659	2.884
.400	2.628	1.647	2.892
.600	2.659	1.633	2.895
.800	2.693	1.619	2.904
1.000	2.727	1.603	2.908
1.200	2.763	1.586	2.914
1.400	2.798	1.566	2.913
1.600	2.837	1.546	2.918
1.800	2.877	1.525	2.921
2.000	2.920	1.504	2.926
2.200	2.966	1.481	2.933
2.400	3.013	1.456	2.937
2.600	3.062	1.430	2.939
2.800	3.117	1.403	2.947
3.000	3.174	1.375	2.952
3.200	3.234	1.345	2.955
3.400	3.298	1.313	2.956
3.600	3.371	1.280	2.962
3.800	3.453	1.247	2.969
4.000	3.545	1.212	2.976
4.200	3.656	1.177	2.988
4.400	3.788	1.140	2.999
4.600	3.976	1.103	3.035
4.800	4.275	1.065	
5.000	5.292	1.025	
5.200	7.607	.974	
5.400	8.003	.921	
5.600	8.230	.868	9.049
5.800	8.397	.816	9.043
6.000	8.529	.763	9.036
6.200	8.647	.710	9.036
6.400	8.755	.657	9.038
6.600	8.855	.604	9.039

TABLE IV CONTINUED

```
        6.800          8.951          .552          9.041
        7.000          9.046          .499          9.044
        7.200          9.143          .446          9.049
        7.400          9.243          .393          9.055
        7.600          9.347          .340          9.060
        7.800          9.462          .288          9.068
        8.000          9.588          .235          9.075
        8.200          9.748          .182          9.096
        8.400          9.958          .129          9.130
        8.600         10.287          .077

PK1 =  2.9358  PK2 =  9.0433

EVALUATION  OF  DATA  PRECISION,  SIGMA  = 1.2231E-02
```

TABLE V

PROTONATION CONSTANTS OF 5-NITRO-8-HYDROXYQUINOLINE IN 75 VOLUME PERCENT DIOXANE-WATER

VOL. NAOH	PH(CORR.)	P	PK(CALC.)
0.000	2.303	1.106	1.376
.200	2.327	1.110	1.421
.400	2.351	1.112	1.454
.600	2.374	1.110	1.464
.800	2.397	1.104	1.463
1.000	2.422	1.102	1.476
1.200	2.452	1.107	1.533
1.400	2.479	1.104	1.542
1.600	2.505	1.095	
1.800	2.534	1.090	
2.000	2.566	1.088	
2.200	2.602	1.088	
2.400	2.636	1.082	
2.600	2.674	1.078	
2.800	2.716	1.075	
3.000	2.760	1.070	
3.200	2.812	1.069	
3.400	2.869	1.067	
3.600	2.933	1.064	
3.800	3.006	1.061	
4.000	3.098	1.060	
4.200	3.212	1.060	
4.400	3.362	1.058	
4.600	3.579	1.055	
4.800	4.023	1.052	
5.000	6.015	1.027	
5.200	6.624	.973	
5.400	6.894	.920	
5.600	7.083	.866	7.895
5.800	7.235	.813	7.873
6.000	7.362	.759	7.861
6.200	7.481	.706	7.861
6.400	7.582	.652	7.855
6.600	7.686	.599	7.860

TABLE V CONTINUED

6.800	7.787	.545	7.866
7.000	7.887	.492	7.873
7.200	7.988	.438	7.880
7.400	8.103	.385	7.899
7.600	8.228	.331	7.923
7.800	8.368	.278	7.953
8.000	8.543	.224	8.004
8.200	8.781	.171	8.095
8.400	9.202	.117	8.325

PK1 = 1.4846 PK2 = 7.8953

EVALUATION OF DATA PRECISION, SIGMA = 2.3599E-02

TABLE VI

PROTONATION CONSTANTS OF SEBACIC ACID IN 20 VOLUME PERCENT DIOXANE-WATER

VOL. NAOH	PH(CORR.)	P	PK(CALC.)
0.000	3.704	1.963	
.200	3.925	1.940	
.400	4.122	1.911	
.600	4.276	1.877	5.130
.800	4.395	1.842	5.122
1.000	4.495	1.806	5.114
1.200	4.593	1.770	5.117
1.400	4.663	1.733	5.102
1.600	4.735	1.696	5.095
1.800	4.790	1.659	5.076
2.000	4.853	1.622	5.069
2.200	4.906	1.585	5.054
2.400	4.962	1.547	5.044
2.600	5.005	1.510	5.022
2.800	5.051	1.473	5.003
3.000	5.094	1.435	4.981
3.200	5.141	1.398	4.961
3.400	5.179	1.360	4.930
3.600	5.225	1.323	4.903
3.800	5.263	1.285	4.864
4.000	5.303	1.248	4.821
4.200	5.339	1.210	4.765
4.400	5.374	1.173	4.695
4.600	5.414	1.136	4.609
4.800	5.451	1.098	
5.000	5.487	1.061	
5.200	5.524	1.023	
5.400	5.556	.986	
5.600	5.599	.948	
5.800	5.634	.910	
6.000	5.675	.873	6.512
6.200	5.714	.835	6.420
6.400	5.750	.798	6.346
6.600	5.786	.760	6.288

TABLE VI CONTINUED

```
          6.800          5.926          .723          6.343
          7.000          5.867          .685          6.205
          7.200          5.906          .648          6.171
          7.400          5.946          .610          6.141
          7.600          5.993          .573          6.120
          7.800          6.044          .535          6.105
          8.000          6.086          .498          6.082
          8.200          6.134          .460          6.065
          8.400          6.185          .423          6.050
          8.600          6.244          .385          6.041
          8.800          6.298          .348          6.024
          9.000          6.365          .310          6.018

PK1 =  5.1408  PK2 =  5.9660

EVALUATION  OF  DATA  PRECISION,  SIGMA  = 1.4423E-02
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TABLE VII

PROTONATION CONSTANTS OF DITHIOETHYLSULFIDE IN 40 VOLUME PERCENT DIOXANE-WATER

VOL. NAOH	PH(CORR.)	P	PK(CALC.)
0.000	6.625	2.000	
.200	8.619	1.951	
.400	8.995	1.903	
.600	9.174	1.854	9.942
.800	9.334	1.806	9.952
1.000	9.431	1.757	9.925
1.200	9.496	1.709	9.882
1.400	9.553	1.660	9.841
1.600	9.624	1.612	9.821
1.800	9.698	1.563	9.808
2.000	9.800	1.515	9.826
2.200	9.849	1.466	9.791
2.400	9.975	1.418	9.831
2.600	10.012	1.370	9.780
2.800	10.107	1.321	9.782
3.000	10.161	1.273	9.736
3.200	10.205	1.225	9.667
3.400	10.260	1.177	9.591
3.600	10.306	1.128	9.474
3.800	10.362	1.080	
4.000	10.421	1.032	
4.200	10.452	.984	
4.400	10.516	.936	
4.600	10.574	.889	11.476
4.800	10.625	.841	11.348
5.000	10.682	.793	11.267
5.200	10.730	.746	11.198
5.400	10.795	.699	11.161
5.600	10.856	.652	11.129
5.800	10.913	.606	11.100
6.000	10.985	.560	11.090
6.200	11.065	.516	11.092
6.400	11.138	.471	11.088
6.600	11.228	.429	11.104

TABLE VII CONTINUED

6.800	11.302	.387	11.102
7.000	11.372	.346	11.095
7.200	11.474	.310	11.127
7.400	11.542	.272	11.114
7.600	11.637	.241	11.140
7.800	11.711	.209	11.134
8.000	11.781	.180	11.121
8.200	11.849	.153	11.106
8.400	11.913	.128	11.080
8.600	11.964	.101	11.015
8.800	12.016	.078	
9.000	12.057	.051	

PK1 = 9.9085 PK2 = 11.0166

EVALUATION OF DATA PRECISION, SIGMA = 2.3093E-02

TABLE VIII

PROTONATION CONSTANTS OF 8-MERCAPTOQUINOLINE IN 60 VOLUME PERCENT DIOXANE-WATER

VOL. NAOH	PH(CORR.)	P	PK(CALC.)
0.000	2.666	1.291	2.280
.200	2.696	1.269	2.263
.400	2.728	1.247	2.245
.600	2.766	1.231	2.243
.800	2.805	1.211	2.233
1.000	2.834	1.176	2.164
1.200	2.888	1.166	2.176
1.400	2.937	1.145	2.166
1.600	2.990	1.122	2.134
1.800	3.045	1.095	
2.000	3.127	1.082	
2.200	3.218	1.064	
2.400	3.334	1.046	
2.600	3.481	1.026	
2.800	3.731	1.011	
3.000	4.309	.993	
3.200	7.626	.943	
3.400	8.314	.876	9.162
3.600	8.634	.809	9.260
3.800	8.850	.741	9.307
4.000	9.021	.674	9.336
4.200	9.173	.607	9.361
4.400	9.310	.539	9.379
4.600	9.441	.472	9.392
4.800	9.576	.405	9.409
5.000	9.707	.338	9.414
5.200	9.850	.270	9.419
5.400	10.017	.203	9.424
5.600	10.212	.136	9.408
5.800	10.499	.069	
6.000	10.941	.003	

PK1 = 2.1974 PK2 = 9.3800

EVALUATION OF DATA PRECISION, SIGMA = 2.2323E-02

APPENDIX II

POTENTIOMETRIC DETERMINATION OF CHELATE FORMATION CONSTANTS

TABLE I

METAL CHELATES OF 8-HYDROXYQUINOLINE-5-SULFONIC ACID

PROTONATION CONSTANTS(4.037, 8.495)

MAGNESIUM STABILITY CONSTANT, PERCENT DIOXANE = 0

NO.	N-BAR	PL
1	0.095	5.857
2	0.126	5.386
3	0.262	4.889
4	0.447	4.575
5	0.642	4.369
6	0.839	4.190
7	1.038	4.049
8	1.238	3.921
9	1.439	3.819
10	1.638	3.723
11	1.838	3.630

LOG K1 = 4.28, LOG K2 =3.59

STANDARD DEVIATION = 0.09

CALCIUM STABILITY CONSTANT, PERCENT DIOXANE = 0

NO.	N-BAR	PL
1	0.280	4.254
2	0.510	3.947
3	0.743	3.756
4	0.977	3.616
5	1.211	3.527
6	1.445	3.443
7	1.679	3.367
8	1.913	3.303

LOG K1 = 3.66, LOG K2 =2.26

STANDARD DEVIATION = 0.09

TABLE I CONTINUED

MANGANESE STABILITY CONSTANT, PERCENT DIOXANE = 0

NO.	N-BAR	PL
1	0.272	7.074
2	0.328	6.796
3	0.442	6.325
4	0.705	5.888
5	1.002	5.558
6	1.369	5.187
7	1.775	4.797
8	1.986	4.595

LOG K1 = 5.98, LOG K2 =4.94

STANDARD DEVIATION = 0.09

NICKEL STABILITY CONSTANT, PERCENT DIOXANE = 0

NO.	N-BAR	PL
1	0.103	9.929
2	0.181	9.727
3	0.327	9.508
4	0.506	9.249
6	0.661	9.062
7	0.850	8.869
8	1.049	8.653
9	1.266	8.427
10	1.490	8.182
11	1.706	7.908
12	1.911	7.600

LOG K1 = 9.11, LOG K2 = 8.31

STANDARD DEVIATION = 0.02

TABLE I CONTINUED

ZINC STABILITY CONSTANT, PERCENT DIOXANE = 0

NO.	N-BAR	PL
1	0.113	9.377
2	0.187	9.001
3	0.287	8.726
4	0.426	8.446
5	0.603	8.180
6	0.800	7.922
7	1.011	7.669
8	1.231	7.411
9	1.461	7.129
10	1.683	6.750
11	1.884	6.311

LOG K1 = 8.31, LOG K2 =7.08

STANDARD DEVIATION = 0.02

TABLE II

METAL CHELATES OF 8-HYDROXYQUINOLINE

PROTONATION CONSTANTS(3.970, 11.530)

SILVER STABILITY CONSTANT, PERCENT DIOXANE = 60

PROTONATION CONSTANTS(3.970, 11.530)

NO.	N-BAR	PL
1	0.148	6.814
2	0.346	6.396
3	0.545	6.099
4	0.744	5.806
5	0.942	5.509
6	1.141	5.173

LOG K1 = 7.35

CALCIUM STABILITY CONSTANT, PERCENT DIOXANE = 60

4	0.539	4.440
5	0.671	4.273
6	0.797	4.108
7	0.915	3.953
8	1.026	3.816

LOG K1 = 4.42

STANDARD DEVIATION = 0.01

```
                    TABLE  II  CONTINUED

ALUMINUM  STABILITY  CONSTANT, PERCENT  DIOXANE = 60

       NO.          N-BAR          PL
       ----        -------        ----

         1          0.505        11.949
         2          0.643        11.790
         3          0.848        11.663
         4          1.076        11.543
         5          1.502        11.271
         6          1.772        10.890
         7          1.885        10.448
         8          1.930        10.230
         9          2.263        10.035
        10          2.345         9.823
        11          2.453         9.584
        12          2.608         9.303
        13          2.818         8.865
        14          2.850         7.773

LOG K1 = 11.50,  LOG K2 = 12.02,  LOG K3 = 10.30

(LOG K1.K2.K3)/3 = 11.25

STANDARD  DEVIATION = 0.05

IRON(III) STABILITY  CONSTANT, PERCENT  DIOXANE = 60

       NO.          N-BAR          PL
       ----        -------        ----

         1          1.512        13.303
         2          1.625        13.170
         3          1.726        13.009
         4          1.854        12.827
         5          1.959        12.587
         6          2.111        12.307
         7          2.293        11.963
         8          2.536        11.585
         9          2.775        11.369

(LOG K1.K2.K3)/3 = 12.59

STANDARD  DEVIATION = 0.06
```

TABLE II CONTINUED

LEAD STABILITY CONSTANT, PERCENT DIOXANE = 60

NO.	N-BAR	PL
1	0.219	11.492
2	0.325	11.135
3	0.467	10.819
4	0.569	10.625
5	0.670	10.439
6	0.762	10.252
7	0.855	10.007
8	0.929	9.739
9	1.002	9.139
10	1.092	8.525
11	1.272	8.023
12	1.407	7.742

LOG K1 = 10.87, LOG K2 = 7.50

STANDARD DEVIATION = 0.08

TABLE III

METAL CHELATES OF 5-CHLORO-8-HYDROXYQUINOLINE

PROTONATION CONSTANTS(2.552, 10.641)

SCANDIUM STABILITY CONSTANT, PERCENT DIOXANE = 60

NO.	N-BAR	PL
1	0.991	10.418
2	1.072	10.221
3	1.179	10.078
4	1.319	9.803
5	1.449	9.547
6	1.500	9.297
7	1.607	9.092
8	1.693	8.903
9	1.829	8.652
10	2.034	8.293
11	2.323	7.437
12	2.674	6.762

(LOG K1.K2.K3)/3 = 9.46

STANDARD DEVIATION = 0.03

IRON(II) STABILITY CONSTANT, PERCENT DIOXANE = 60

NO.	N-BAR	PL
1	0.148	9.044
2	0.253	8.972
3	0.365	8.897
4	0.482	8.815
5	0.607	8.730
6	0.739	8.633
7	0.837	8.535
8	1.013	8.426
9	1.158	8.305
10	1.306	8.160
11	1.456	7.972
12	1.609	7.691
13	1.764	6.966

LOG K1 = 8.60, LOG K2 = 8.05

STANDARD DEVIATION = 0.07

TABLE III CONTINUED

NICKEL STABILITY CONSTANT, PERCENT DIOXANE = 60

NO.	N-BAR	PL
1	0.388	10.637
2	0.471	10.532
3	0.610	10.378
4	0.743	10.251
5	0.807	10.208
6	0.980	10.056
7	1.036	9.999
8	1.178	9.872

LOG K1 = 10.29, LOG K2 = 9.72

STANDARD DEVIATION = 0.02

CERIUM STABILITY CONSTANT, PERCENT DIOXANE = 60

NO.	N-BAR	PL
1	0.105	8.507
2	0.147	8.257
3	0.242	8.048
4	0.327	7.928
5	0.453	7.771
6	0.571	7.654
7	0.635	7.604
8	0.767	7.504
9	0.835	7.457

(LOG K1.K2.K3)/3 = 7.23

STANDARD DEVIATION = 0.08

TABLE IV

METAL CHELATES OF 5-ACETYL-8-HYDROXYQUINOLINE

PROTONATION CONSTANTS(2.928, 9.047)

SILVER STABILITY CONSTANT, PERCENT DIOXANE = 60

NO.	N-BAR	PL
1	0.155	6.249
2	0.402	5.387
3	0.513	4.741

LOG K1 = 6.79

MANGANESE STABILITY CONSTANT, PERCENT DIOXANE = 60

NO.	N-BAR	PL
1	0.105	7.852
2	0.192	7.525
3	0.294	7.302
4	0.482	7.038
5	0.767	6.748
6	1.124	6.456
7	1.516	6.121
8	1.719	5.913

LOG K1 = 6.76, LOG K2 = 6.35

STANDARD DEVIATION = 0.03

TABLE IV CONTINUED

IRON(II) STABILITY CONSTANT, PERCENT DIOXANE = 60

NO.	N-BAR	PL
1	0.153	9.320
2	0.264	9.074
3	0.360	8.838
4	0.439	8.746
5	0.552	8.593
6	0.678	8.498
7	0.834	8.402
8	1.003	8.300
9	1.184	8.182
10	1.399	8.059
11	1.511	7.982
12	1.735	7.788

LOG K1 = 8.56, LOG K2 = 7.60

STANDARD DEVIATION = 0.07

ZINC STABILITY CONSTANT, PERCENT DIOXANE = 60

NO.	N-BAR	PL
1	0.110	9.175
2	0.285	9.054
3	0.383	8.960
4	0.493	8.866
5	0.621	8.769
6	0.748	8.716
7	0.808	8.605
8	0.961	8.491
9	1.118	8.361
10	1.312	8.223
11	1.495	8.044
12	1.697	7.801

LOG K1 = 8.50, LOG K2 = 8.23

STANDARD DEVIATION = 0.04

TABLE IV CONTINUED

LEAD STABILITY CONSTANT, PERCENT DIOXANE = 60

NO.	N-BAR	PL
1	0.221	9.376
2	0.312	9.257
3	0.424	9.135
4	0.519	8.994
5	0.605	8.901
6	0.708	8.807
7	0.824	8.633
8	0.905	8.503
9	1.040	8.275
10	1.194	7.969

LOG K1 = 9.03, LOG K2 = 6.52

STANDARD DEVIATION = 0.05

TABLE V

METAL CHELATES OF 5-NITRO-8-HYDROXYQUINOLINE

PROTONATION CONSTANTS(1.608, 7.188)

ALUMINUM STABILITY CONSTANT, PERCENT DIOXANE = 60

NO.	N-BAR	PL
1	0.601	7.500
2	0.953	7.473
3	1.064	7.411
4	1.366	7.366
5	1.608	7.304
6	1.874	7.233
7	2.095	7.172
8	2.233	7.122
9	2.369	7.063
10	2.460	6.981
11	2.572	6.950

LOG K1 = 7.20, LOG K2 = 7.41, LOG K3 = 6.78

(LOG K1.K2.K3)/3 = 7.13

STANDARD DEVIATION = 0.09

MAGNESIUM STABILITY CONSTANT, PERCENT DIOXANE = 60

NO.	N-BAR	PL
1	0.131	5.783
2	0.166	5.453
3	0.274	4.980
4	0.457	4.643
5	0.658	4.421
6	0.864	4.256
7	1.073	4.120
8	1.283	4.005
9	1.491	3.903
10	1.701	3.806

LOG K1 = 4.29, LOG K2 = 3.95

STANDARD DEVIATION = 0.04

TABLE V CONTINUED

SCANDIUM STABILITY CONSTANT, PERCENT DIOXANE = 60

NO.	N-BAR	PL
1	0.629	7.755
2	0.838	7.754
3	1.020	7.681
4	1.252	7.558
5	1.390	7.425
6	1.518	7.316
7	1.693	7.121
8	1.800	6.934
9	1.952	6.776
10	2.064	6.686
11	2.270	6.501
12	2.453	6.350
13	2.679	6.162

(LOG K1.K2.K3)/3 = 7.19

STANDARD DEVIATION = 0.06

IRON(III) STABILITY CONSTANT, PERCENT DIOXANE = 60

NO.	N-BAR	PL
1	1.837	7.856
2	1.936	7.846
3	2.032	7.836
4	2.150	7.796
5	2.254	7.785
6	2.313	7.763
7	2.368	7.738
8	2.470	7.723
9	2.529	7.695
10	2.690	7.693
11	2.778	7.669

(LOG K1.K2.K3)/3 = 8.63

STANDARD DEVIATION = 0.04

TABLE V CONTINUED

CERIUM STABILITY CONSTANT, PERCENT DIOXANE = 60

NO.	N-BAR	PL
1	0.527	6.421
2	0.655	6.131
3	0.766	5.996
4	0.877	5.893
5	1.033	5.784
6	1.218	5.660
7	1.444	5.527
8	1.568	5.453
9	1.700	5.376
10	1.841	5.295
11	1.985	5.203
12	2.138	5.108
13	2.459	4.889
14	2.627	4.759

(LOG K1.K2.K3)/3 = 5.69

STANDARD DEVIATION = 0.04

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