Coordination Chemistry Reviews, 100 (1990) 323–361
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

POTENTIOMETRY REVISITED: THE DETERMINATION OF THERMODYNAMIC EQUILIBRIA IN COMPLEX MULTICOMPONENT SYSTEMS

ARTHUR E. MARTELL * and RAMUNAS J. MOTEKAITIS

Department of Chemistry, Texas A&M University, College Station, TX 77843-3255 (U.S.A.)

(Received 10 April 1989)

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A. INTRODUCTION

Equilibrium constants for the combination of a metal ion with a ligand in solution, termed formation constants or stability constants, have long been used as a measure of the success or failure of ligand design for the purposes of achieving high thermodynamic stabilities of complexes in solution or for selective complexation of metal ions for the separation of, or discrimination between, metal ions. The advent of computers has revolutionized the determination and calculation of stability constants from equilibrium data so that systems containing many overlapping equilibria in the presence of a number of metal ions or ligands containing many functional groups may now be easily handled. The potentiometric determination of hydrogen ion

0010-8545/90/$13.65

concentration, which accounts for approximately 90% or more of the stability constant data, has therefore emerged as a powerful experimental tool, capable of handling complex multicomponent systems almost as readily as solutions of simple complexes. This new expertise, however, brings with it the possibility of the postulation of unjustified complex species and the generation of meaningless parameters whose purpose is merely to assist in fitting the experimental data. Therefore considerable care and insight into the chemical nature of the complex species under consideration are required to avoid the calculation of meaningless equilibrium constants. The use of computers has also made possible the development of graphical methods for displaying experimental results, such as diagrams showing the relative concentrations of individual complex species as a function of solution conditions such as pH, metal ion concentration or ligand concentration. It is the purpose of this paper to describe the capabilities of the modern computer-assisted potentiometric method for the determination of metal ion ligand stability constants and related equilibrium constants. Several examples will be given to illustrate the power which the potentiometric technique has now achieved through the use of new computational methods.

Because the equipment required for the potentiometric determination of stability constants is relatively inexpensive, the early development of this field was characterized by the proliferation of publications describing work in which stability constants were measured for their own sake, without any apparent basic objective involving principles and concepts of coordination chemistry or without providing information needed in other research fields. The large number of publications on relatively unimportant ligands, repeated studies on simple ligands, together with the appearance of large numbers of papers on mixed-ligand complexes, in which two or more ligands were combined in almost a random fashion, led to a general decline in the prestige of this research area, and it came to be regarded by some as routine. This situation was further aggravated by the appearance of a relatively large number of poor papers involving poor control of experimental conditions or the use of ligands which had not been properly characterized or purified.

The large number of stability constant data, and the poor quality of some of these data, have led to the publication of two types of data compilations. Under the sponsorship of the Subcommission V.6 on Equilibrium Data of the Analytical Division of IUPAC, a series of collections of all published stability constant data has appeared. These volumes were written by some of the more active workers in the field such as Schwarzenbach, Sillen, Martell, Hogfeldt and Perrin [1–5]. The desire to have more reliable stability data available to workers in other fields as well as to coordination chemists has led to a series of books containing "selected" or "critical" stability constants

TABLE 1

Critical evaluations of stability constants

Subject	Author	Publication	
		Date	Ref.
EDTA	G. Anderegg	1977	7
1,10-Phenanthroline, 2,2-bipyridyl and related complexes	W.A.E. McBryde	1978	8
8-Hydroxyquinoline	J. Stary, Yu.S. Zolotov and O.M. Petrukin	1979	9
Fluoride	A.M. Bond and G.T. Hefter	1980	10
Acetylacetonate	J. Stary and J.O. Liljenzin	1982	11
NTA	G. Anderegg	1982	12
Indium	D.G. Tuck	1983	13
Histidine, phenylalanine, tyrosine, L-DOPA, tryptophan	L.D. Pettit	1984	14
Ethylenediamine	P. Paoletti	1984	15
Cyano complexes	M.T. Beck	1987	16
Nucleotide complexes	R.M. Smith, Y. Chen and A.E. Martell	1989	17

[6]. With the recent addition of Volume 6 the critical stability constant series covers all the literature to the end of 1985. While the general guidelines for the selection of critical constants in these volumes have been described [6], the details of the decision making process, for each of the nearly one hundred thousand selections that have been made, are not described. The Commission on Equilibrium Data has also sponsored a series of critical reviews of stability constants for certain types of metal complex systems. The types of complexes covered in these reviews and the publication dates are given in Table 1. In these reviews the details of the selection process are presented for each complex or type of complex. The period covered in each of these critical surveys involves all the stability constants found in the literature up to approximately a year preceding the publication date shown in Table 1. Although these volumes constitute the most thorough assessments of the dependability of the stability constants under consideration, it is apparent that at the present rate of production it will take decades to cover an appreciable fraction of the stability constant literature.

Three important developments have occurred in solution coordination chemistry which have stimulated new activity and increased the significance of the determination and use of stability constants. The first involves major advances in the chemistry of macrocyclic and macrobicyclic (cryptand) complexes, which bring new challenges and requirements for ligand design and synthesis for the development of increased selectivity and thermodynamic stability of metal complexes. This has resulted in the development of many types of complexes with novel properties and important applications in many related fields. Here the success or failure of ligand design for the achievement of metal complex stability and selectivity depends on the stability constants of the complexes formed. A second major development involves new advances in the bio-inorganic chemistry of metal complexes in solution and the increasing significance of metal speciation in the environment. Both of these areas require knowledge of the stabilities of complexes formed in multicomponent systems containing many ligands and metal ions. The third important advance is the development of computational methods for processing equilibrium data for the more rapid and accurate determination of stability constants and the extension of the method to systems containing many metal ions and ligands, which are too complex to have been investigated by the classical methods of determining and handling stability constants. Prior to the development of computer methods the elucidation of the concentrations of metal complex species present in complex biological and environmental systems was not possible.

B. HISTORICAL DEVELOPMENT OF POTENTIOMETRIC DETERMINATIONS OF STABILITY CONSTANTS

The determination of stepwise stability constants for metal complexes of monodentate ligands effectively began with the classic work of Bjerrum [18] on transition metal ammine complexes in aqueous solution. Because of the simultaneous formation of a series of metal complexes, some highly dissociated, a large excess of ammonia was employed to prevent hydrolysis and precipitation of the metal ion, and the calculations were carried out algebraically by the use of mathematical approximations. The first paper which employed an exact algebraic treatment of equilibrium constants and mass balance equations, thus eliminating the approximations of the Bjerrum method, was published a few years later by Calvin and Wilson [19]. Because of the higher stabilities of these complexes a large excess of ligand was not required. The rapid developments in the field which then occurred have been summarized in several books [20–22] which describe in detail the various methods of determining stability constants as well as interpretations of the results then available. During that period the monograph by Rossotti and Rossotti [23] became the outstanding authority on pre-computer methods of data reduction involving many types of metal complex equilibria. It describes in detail the graphical methods and the approximations that were necessary for the determination of equilibrium constants in systems characterized by overlapping equilibria involving several complex species. At that time, because of the complexity of the equilibria occurring in systems containing even relatively few complexes, and the limitations of the algebraic methods then available, calculations involving several approximations were the rule rather than the exception.

With computers the situation has now changed completely. Regardless of the complexity of the system, the number of donor groups on the ligand, the number of ligands present, and the presence of one or more competing ions and the hydrogen ion, the computations can be handled easily with suitable programs. Although solution coordination chemists were at first slow to take advantage of the new computational techniques and at first really used computers to assist them with the classical methods of calculation described in refs. 20–23, many sophisticated programs have now been developed and are available [24–30]. Recently a book devoted entirely to programs for the calculation of stability constants has been published [31]. The computer programs thus far described in the literature employ various strategies and involve a number of methods for data processing. Comparisons between these computation methodologies are reported in the literature [28–31].

The computer programs [32] and subroutines employed for the calculations described in this review were developed by Motekaitis and used extensively by the authors and their coworkers. They are especially well adapted to computations involving pH data, and have the advantage of producing the calculated pH profiles for comparison with the experimental titration curves. The differences between the experimental and calculated values (σ_{fit}) provide a direct measure of the accuracy of the calculations over the whole range of the experiment, as well as a measure of the suitability of the calculated stability constants and other calculated equilibrium constants for the representation of the metal complex system under investigation.

C. EXPERIMENTAL METHODS

(i) Equilibrium constants

Stability constants and related equilibrium constants of metal complexes in solution are nearly always expressed as "concentration" constants or "stoichiometric" constants K_{eq}, in accordance with eqn. (1), rather than as the so-called "thermodynamic" constants K' favored by many physical chemists and indicated in eqn. (2):

$$aA + bB \rightleftharpoons cC + dD \qquad K_{\text{eq}} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{1}$$

$$K' = \frac{a_C^c a_D^d}{a_A^a a_B^b} = \frac{([C]\gamma_C)^c([D]\gamma_D)^d}{([A]\gamma_A)^a([B]\gamma_B)^b} = K_{\text{eq}}\frac{\gamma_C^c\gamma_D^d}{\gamma_A^a\gamma_B^b} \tag{2}$$

The main reason for this practice is the avoidance of the considerable difficulty, bordering on impossibility, of determining activity coefficients of complex charged species in solution. When the quotient of the activity coefficients is kept relatively constant by means of a large excess of an "inert" supporting electrolyte, the concentrations then parallel the activities over a wide range of concentration, when other interferences are avoided.

The main problem in controlling ionic strength is finding a supporting electrolyte that is truly inert. While KCl, KNO_3 and $NaClO_4$ have been used frequently in the past, some of these ions are not inert in many systems. For example, there are metal ions such as Hg^{2+} which have considerable affinity for Cl^-. Macrocyclic and cryptand ligands and many natural ionophores form quite stable complexes of Na^+ and K^+. Thus it seems that a truly inert supporting electrolyte would be a quaternary ammonium salt, such as tetraethylammonium perchlorate. Another problem involves the lack of standardization of both the nature and concentration of the supporting electrolyte. It is important that the same media are employed if meaningful comparisons of stability constants of various types of complexes are to be made.

It has been pointed out by Sillen [33] and Rossotti and Rossotti [23] that the values of the concentration constants K_{eq} are very close to the values of true thermodynamic constants for the ionic medium employed, and the extrapolation of the constants to infinite dilution in that medium involves a nearly horizontal straight line, and can be done very accurately, in contrast with the curved functions obtained when the extrapolation to infinite dilution in pure water is carried out. Thus values of K_{eq} may be employed to calculate the thermodynamic quantities $\Delta G°$, $\Delta H°$ and $\Delta S°$, which are entirely valid in the supporting electrolyte medium employed.

(ii) Stability constants

When possible, stability constants are expressed as the equilibrium constants for the reaction in which the aquo metal ion combines with the most basic form of the ligand:

$$\mathrm{M}^{m+} + \mathrm{L}^{n-} \rightleftharpoons \mathrm{ML}^{m-n} \qquad \beta_{\mathrm{ML}} = \frac{[\mathrm{ML}^{m-n}]}{[\mathrm{M}^{m+}][\mathrm{L}^{n-}]} \tag{3}$$

$$\mathrm{M}^{m+} + 2\mathrm{L}^{n-} \rightleftharpoons \mathrm{ML}^{m-2n} \qquad \beta_{\mathrm{ML}_2} = \frac{[\mathrm{ML}_2^{m-2n}]}{[\mathrm{M}^{n+}][\mathrm{L}^{n-}]^2} \tag{4}$$

In some situations the most basic form of the ligand cannot be formed in aqueous solution in the absence of the metal ion because of its very high basicity (e.g. ligands with certain phenolate, catecholate and amide donor groups) so that the above equilibria cannot be measured. Under such circumstances the metal complex formation constants involve displacement of one or more protons from the ligand, as indicated in eqn. (5):

$$M^{m+} + HL^{(n-1)-} \rightleftharpoons ML^{m-n} + H^{+} \qquad K_{eq} = \frac{[ML^{m-n}][H^{+}]}{[M^{m+}][HL^{(n-1)-}]} \qquad (5)$$

(iii) pH

The potentiometric measurement of stability constants is based primarily on the competition between hydrogen ions and metal ions for coordination sites on the ligand and involves displacement reactions analogous to eqn. (5). Needless to state, it is necessary to measure accurately at least one of the species present at equilibrium and to determine the concentrations of the others from the known composition of the solution. Also, it is obvious that the equilibrium constant cannot be calculated with any accuracy unless the concentrations of each species in an equilibrium such as that in eqn. (5) are high enough to be accurately measurable. This requirement, when disregarded, may lead to serious errors in the calculated equilibrium constants, as discussed below.

The apparatus, consisting of a potentiometer usually equipped with glass and calomel electrodes, is responsive to the hydrogen ion activity but may be calibrated to measure hydrogen ion concentration directly. Detailed considerations of the instrumental techniques for measuring pH and metal complex equilibria, and the precautions that must be observed, are beyond the scope of this review and have been treated in detail elsewhere [20,21,23,32]. At this stage it is merely sufficient to point out that calibration of the equipment to read hydrogen concentration directly is to be preferred, so that the protonation constants of the ligands and other measured acid–base reaction constants will be concentration constants and the calculation of "mixed" or "Brönsted" constants will be avoided. Further, the measured hydrogen ion concentrations may be used directly in the mass balance relationships described below, and measured hydrogen ion activities need not be converted to concentrations by the use of activity coefficients.

It should also be pointed out that the glass electrode potential is linearly responsive to the hydrogen ion concentrations if the supporting electrolyte remains constant and the liquid junction potentials though unknown are also constant. At the extremes of high and low p[H] (above 12 and below 2) this is not the case, thus restricting the working range of the potentiometric apparatus from 2 to 12.

There are many situations, especially at the extremes of high and low p[H] under which potentiometric measurements are not sensitive to the equilibria being measured. Under such conditions, other techniques such as spectrophotometry are useful in the determination of the position of the equilibrium being measured. Also there are indirect methods, in which one metal ion is displaced by another, or a secondary ligand may be employed. Examples of such systems are described in detail elsewhere [32,34,35].

D. COMPUTATIONS

In order to illustrate modern computational methods, a simple system, Ca(II)–EDTA, (EDTA = ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid), is selected. The equilibrium constants for the protonation of EDTA (H_4L, or in the most basic form L^{4-}) are expressed by eqns. (6)–(13):

$H^+ + L^{4-} \rightleftharpoons HL^{3-}$

$$K_1^H = \frac{[HL^{3-}]}{[H^+][L^{4-}]} \tag{6}$$

$$\beta_{HL} = \frac{[HL^{3-}]}{[H^+][L^{4-}]} \tag{7}$$

$H^+ + HL^{3-} \rightleftharpoons H_2L^{2-}$

$$K_2^H = \frac{[H_2L^{2-}]}{[H^+][HL^{3-}]} \tag{8}$$

$$\beta_{H_2L} = \frac{[H_2L^{2-}]}{[H^+]^2[L^{4-}]} \tag{9}$$

$H^+ + H_2L^{2-} \rightleftharpoons H_3L^-$

$$K_3^H = \frac{[H_3L^-]}{[H^+][H_2L^{2-}]} \tag{10}$$

$$\beta_{H_3L} = \frac{[H_3L^-]}{[H^+]^3[L^{4-}]} \tag{11}$$

$H^+ + H_3L^- \rightleftharpoons H_4L$

$$K_4^H = \frac{[H_4L]}{[H^+][H_3L^-]} \tag{12}$$

$$\beta_{H_4L} = \frac{[H_4L]}{[H^+]^4[L^{4-}]} \tag{13}$$

The equilibria found necessary to describe the metal complex equilibria are represented by eqns. (14)–(18):

$$Ca^{2+} + L^{4-} \rightleftharpoons CaL^{2-}$$

$$K_{CaL}^{Ca} = \frac{[CaL^{2-}]}{[Ca^{2+}][L^{4-}]} \tag{14}$$

$$\beta_{CaL} = \frac{[CaL^{2-}]}{[Ca^{2+}][L^{4-}]} \tag{15}$$

$$H^{+} + CaL^{2-} \rightleftharpoons CaHL^{-}$$

$$K_{CaHL}^{H} = \frac{[CaHL^{-}]}{[H^{+}][CaL^{2-}]} \tag{16}$$

$$K_{CaHL}^{Ca} = \frac{[CaHL^{-}]}{[Ca^{2+}][HL^{3-}]} \tag{17}$$

$$\beta_{CaHL} = \frac{[CaHL^{-}]}{[H^{+}][Ca^{2+}][L^{4-}]} \tag{18}$$

With the p[H] profiles involving the measurement of hydrogen ion concentration as a function of added base for a solution containing a 1 : 1 molar ratio of Ca^{2+} to EDTA, with four equivalents of hydrogen ion added initially, the calculations of the metal ion binding constants are carried out. (It should be noted that the protonation constants of EDTA were previously determined by a similar experiment in the absence of Ca^{2+} ion.)

The variable measured is $-\log[H^{+}]$, and it is therefore considered logical to carry out the calculations with an algorithm which calculates p[H] directly and minimizes the sum of the weighted squares of $-\log[H^{+}]$ residuals. This is the feature which distinguishes programs BEST [36] and PKAS [37] from most of the programs previously available for the calculation of equilibrium constants.

The basic algorithm in BEST is defined by eqn. (19):

$$T_i = \sum_{j=1}^{NS} e_{ij}\beta_j \sum_{k=1}^{i} [C_k]\, e_{ij} \tag{19}$$

This equation indicates the mass balance of the ith component in terms of the jth species summed over all species present. Each species concentration consists of a product of the overall stability constant and individual component concentrations $[C_k]$ raised to the power of the stoichiometric coefficient e_{ij}. The EDTA–Ca system is considered to consist of three components: $EDTA^{4-}$ (L), Ca^{2+} (M) and H^{+}. The species possible are $EDTA^{4-}$, $HEDTA^{3-}$, H_2EDTA^{2-}, H_3EDTA^{-}, H_4EDTA, $CaEDTA^{2-}$, $CaHEDTA^{-}$,

H^+ and OH^-. There are three mass equations for total ligand, T_L, total metal ion, T_M, and total initial concentration, T_H:

$$T_L = [L^{4-}] + [HL^{3-}] + [H_2L^{2-}] + [H_3L^-] + [H_4L] + [CaL^{2-}] + [CaHL^-] \tag{20}$$

$$T_M = [Ca^{2+}] + [CaL^{2-}] + [CaHL^-] \tag{21}$$

$$T_H = [HL^{3-}] + 2[H_2L^{2-}] + 3[H_3L^-] + 4[H_4L] + [CaHL^-] + [\text{base}] + [H^+] - [OH^-] \tag{22}$$

In eqn. (22), T_H represents the hydrogen concentration [H] initially present and [base] is base concentration which has been removed by the added titrant (e.g. KOH). The internal computer representations of eqns. (20)–(22) are set up in terms of β values and the concentrations of the individual species, as expressed in eqns. (23)–(25):

$$T_M = [M^{2+}] + \beta_{ML}[M^{2+}][L^{4-}] + \beta_{MHL}[M^{2+}][H^+][L^{4-}] \tag{23}$$

$$T_L = [L^{4-}] + \beta_{HL}[H^+][L^{4-}] + \beta_{H_2L}[H^+]^2[L^{4-}] + \beta_{H_3L}[H^+]^3[L^{4-}] + \beta_{H_4L}[H^+]^4[L^{4-}] + \beta_{ML}[M^{2+}][L^{4-}] + \beta_{MHL}[M^{2+}][H^+][L^{4-}] \tag{24}$$

$$T_H = \beta_{HL}[H^+][L^{4-}] + 2\beta_{H_2L}[H^+]^2[L^{4-}] + 3\beta_{H_3L}[H^+]^3[L^{4-}] + 4\beta_{H_4L}[H^+]^4[L^{4-}] + [H^+] - \beta_{OH}[H^+]^{-1} + \beta_{MHL}[M^{2+}][H^+][L^{4-}] + [\text{base}] \tag{25}$$

For complex systems of this type there are previously calculated β values as well as the unknown values to be determined. The initial calculation uses estimated values of the unknown constants.

At a given measured equilibrium point, the simultaneous eqns. (23)–(25) are solved for each component $[C_k]$. The value of $[C_k]$, representing the calculated concentration of H^+, is compared with the measured hydrogen ion concentration. This process is repeated for all measured equilibrium points.

The use of the algorithm for computing equilibrium constants in BEST [36] involves starting with a set of known and estimated overall stability constants (β values) and computing $[H^+]$ at all equilibrium points, followed by computation of the weighted sum of the squares of the deviations in p[H] indicated by eqn. (26):

$$U = \Sigma w(p[H]_{obs} - p[H]_{calcd})^2 \tag{26}$$

where $w = (v_{i+1} - v_{i-1})^2/(p[H]_{i+1} - p[H]_{i-1})^2$, a weighting factor which serves to lessen the influence of the less accurate p[H] values in the steeply sloping regions of the p[H] profile. The unknown stability constants are then adjusted and the calculations are repeated until no further minimization of U (i.e. the σ_{fit} has been minimized) is obtained, thus giving the final calculated β values. The standard deviation in pH units is expressed by eqn. (27):

$$\sigma_{\text{fit}} = (U/\Sigma w)^{1/2} \tag{27}$$

The program PKAS is a special case of the more general algorithm found in BEST. Both programs may be used to calculate the protonation constants of a multidentate ligand. In terms of central processing unit (CPU) time, the algorithm in PKAS [37] is quite fast for this special case since far fewer algebraic manipulations are made relative to the generalized treatment in BEST. In the refinement of the protonation constants by the use of PKAS rather than BEST there is the advantage of electing reasonably close approximations of the protonation constants from the region of the p[H] profile with which the protonation constant in question is most closely involved.

(i) Species distribution curves

As an aid in visualizing the implications of the calculated constants, a species distribution diagram for 1.00×10^{-3} M EDTA and 1.00×10^{-3} M calcium(II) was calculated with program SPE [32] and is shown in Fig. 1. As the p[H] is varied from 2 to 12, the solution changes from uncomplexed Ca^{2+}, H_4L°, H_3L^-, and a small concentration of H_2L^{2-} to solutions containing only CaL^{2-}. At a pH of about 4, the major species are 0.50×10^{-3} M Ca^{2+}, CaL^{2-} and H_2L^{2-}, with minor concentrations of $CaHL^-$ and HL^{3-}. Such diagrams are not only very useful for visualizing the nature of the equilibrium situation but also helpful in evaluating the calculated constants. The fact that $CaHL^-$ appears with a maximum concentration of only 2.7% of the calcium(II) species casts some doubt on its existence or indicates that its concentration cannot be accurately known under the conditions employed, and that the β value calculated for this species has a relatively large uncertainty.

E. EXAMPLES OF POTENTIOMETRIC STUDIES OF COMPLEX AND UNUSUAL SYSTEMS

In the literature, many or most of the stability constants which were determined by potentiometric measurements did not involve unusual problems, and are reasonably well represented by the methods and guidelines described above. The capability of the method may be extended far beyond

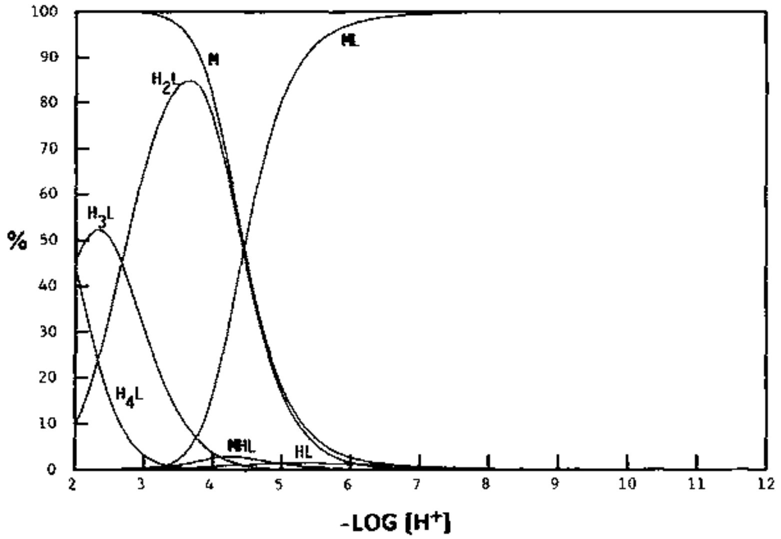


Fig. 1. Species distribution diagram for 0.0010 M calcium(II) and 0.0010 M EDTA at 0.100 M ionic strength and 25.0 ° C.

the straightforward determination of protonation and metal ion formation. The following are several examples of unusual or complex situations which serve to illustrate the power and versatility of the method.

(i) Protonation constants of OBISTREN [38]

OBISTREN **1** (7,19,30-trioxa-1,4,10,13,16,22,27,33-octaazabicyclo-[11,11,11]pentatriacontane), synthesized by Lehn et al. [39], was supplied as the free base in the form of a colorless viscous syrup. Because it is very hygroscopic, it obviously contained a considerable amount of water, and by virtue of having been stored for a month or more, apparently contained a considerable amount of bound carbon dioxide. It was decided to use the sample directly rather than risk loss and possible decomposition in attempted purification. The water content was determined in the calculation of protonation constants (with program PKAS) by allowing the molecular weight to "float" during the calculations (i.e. the molar concentration of the ligand, T_L, considered an unknown) and successive approximations of T_L were made in the reiteration of the pH data. The carbon dioxide impurity was eliminated by keeping the experimental solution at the initial low pH for several hours while inert gas (argon) was bubbled through it. The experimentally measured p[H] profile, illustrated in Fig. 2, is featureless, giving no indication through an inflection point of the concentration of the ligand. From this curve, the six initial trial values of the protonation

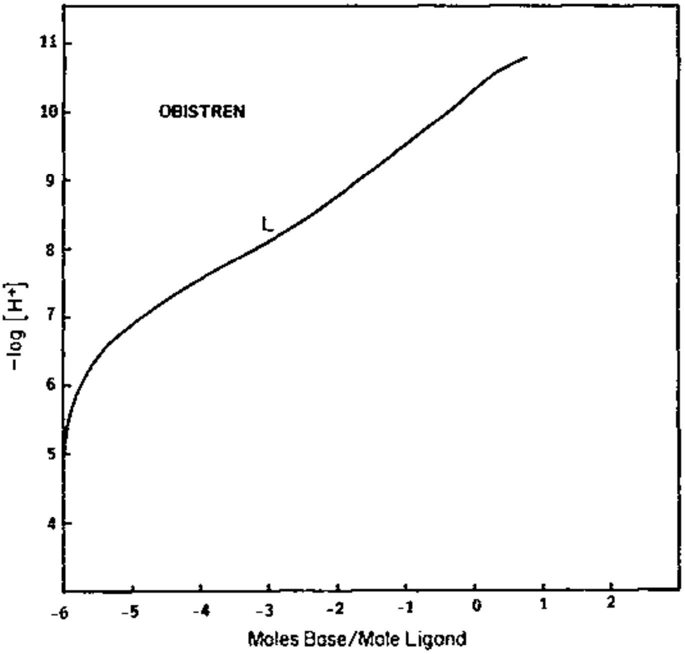
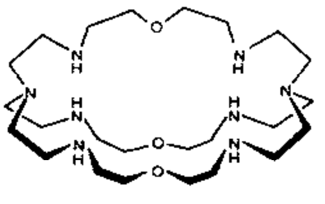
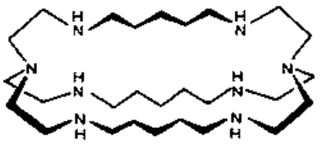


Fig. 2. Potentiometric equilibrium data for OBISTREN at 25.0 °C, $\mu = 0.100$ M (KCl) and $T_L = 1.00 \times 10^{-3}$ M.

constants were estimated, and the value of the "molecular weight" was assumed initially to be 10% higher than that of a pure substance (i.e. the total molar concentration of ligand species was assumed to be 10% lower than the value that would be obtained from the sample of the ligand weighed out, if it were pure). Thus there were seven adjustable unknowns, (six protonation constants and T_L) in the PKAS computer-guided iterations. These values converged rapidly and became constant after about six iterations. The protonation constants thus determined are considered highly accurate, with log K_n values of 9.89, 9.23, 8.29, 7.65, 6.64 and 6.01, with standard deviations (σ_{fit}) of 0.001–0.002 log units.



1 OBISTREN



2 CBISTREN

(ii) Copper(II) complexes of CBISTREN

The experimental sample of the ligand CBISTREN (CBT) **2**, (1,4,10,13,16,22,27,33-octaazabicyclo[11,11,11]pentatriacontane) was provided by M. Hosseini and consisted of a solid octahydrochloride amounting to 41.2 mg, or normally enough for one potentiometric run. The challenge here was to obtain the maximum amount of information from one experimental sample of this very special cryptand. The details of the procedure are described by Motekaitis and Martell [40]. It was decided to investigate the stabilities of the copper(II) complexes by the measurement of the following three potentiometric data sets (the determination of protonation constants is an essential first step in any determination of metal complex stability constants): (1) CBT alone; (2) 1 : 1 molar ratio of copper(II) to CBT; (3) 2 : 1 molar ratio of copper(II) to CBT. The supporting electrolyte selected was 0.100 M $NaClO_4$, because other commonly employed ionic media such as KNO_3 and KCl may involve anion binding to the cryptand, as was found for the closely related cryptand OBISTREN, **1**, [38]. This required the use of NaOH in place of KOH as the standard base, and replacement of the KCl in the calomel reference electrode with saturated NaCl solution. In addition, considerable attention to the determination of the stoichiometric amount of the hydrochloride salt present in the base was necessary, because, as with many salts of polyamines containing one or more very weakly basic groups,

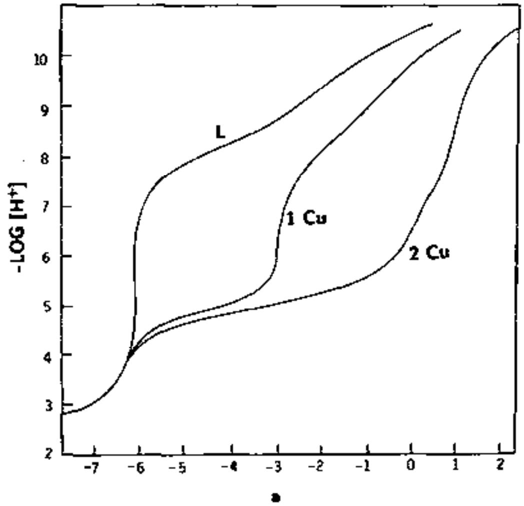


Fig. 3. Potentiometric equilibrium curves for CBT measured in aqueous solution at 25.0 °C and $\mu = 0.100$ ($NaClO_4$) in the absence and in the presence of L : Cu(II) ratios of 1 : 1 and 1 : 2. $T_L = 1.00 \times 10^{-3}$ M. a, moles of base added per mole of ligand present in solution.

the protonation of these groups may not be stoichiometric. In this case the true formula of the hydrochloride salt of CBISTREN was found to be CBT · 7.50HCl · $3H_2O$. Three pH profiles illustrated in Fig. 3 were obtained in the following way. The first run for CBT alone was terminated when the p[H] had been increased to about 12.0. Enough standard $HClO_4$ solution to bring the solution to the acidic starting composition was then added, and the solution was purged with purified N_2 for the removal of any carbon dioxide which may have found its way into the solution in the alkaline region. A molar equivalent of $Cu(ClO_4)_2$ was then added, and another potentiometric run was made by the addition of increments of standard NaOH solution. This procedure was then repeated once more with the addition of a second equivalent of $Cu(ClO_4)_2$. Precautions were taken to maintain the ionic strength at 0.100 throughout the three experimental runs.

Stability constants and related protonation and deprotonation constants were obtained by processing the potentiometric p[H] profiles in the usual way. The details are described by Motekaitis and Martell [32]. The stability constants for the mononuclear complexes were calculated most accurately from the 1 : 1 solutions, with values of the constants in the 2 : 1 solutions held constant, while the most accurate equilibrium constants for the binuclear systems were calculated from the data in the 2 : 1 pH profiles (with constants in the 1 : 1 solutions held constant). The results obtained are given in Table 2.

In order to make significant improvements in the σ-fit of the 2 : 1 p[H] profile it was necessary to include three species which had not been predicted: Cu_2HL^{5+}, $Cu_2(OH)L^{3+}$ and $Cu_2(OH)_2L^{2+}$, where L is the basic form of CBT. All other species are analogous to those formed in the OBISTREN–Cu(II) system [38].

TABLE 2

Log stability constants of copper(II) with CBT at 25.0 °C and $\mu = 0.100$ M ($NaClO_4$)

Quotient	Log *K*	Quotient	Log *K*
$\frac{[ML^{2+}]}{[M^{2+}][L]}$	15.39	$\frac{[M_2L^{4+}]}{[ML^{2+}][M^{2+}]}$	13.36
$\frac{[MHL^{3+}]}{[ML^{2+}][H^+]}$	10.08	$\frac{[M_2HL^{5+}]}{[M_2L^{4+}][H^+]}$	5.40
$\frac{[MH_2L^{4+}]}{[MHL^{3+}][H^+]}$	8.70	$\frac{[M_2LOH^{3+}][H^+]}{[M_2L^{4+}]}$	−7.59
$\frac{[MH_3L^{5+}]}{[MH_2L^{4+}][H^+]}$	7.62	$\frac{[M_2L(OH)_2^{2+}][H^+]}{[M_2LOH^{3+}]}$	−10.81

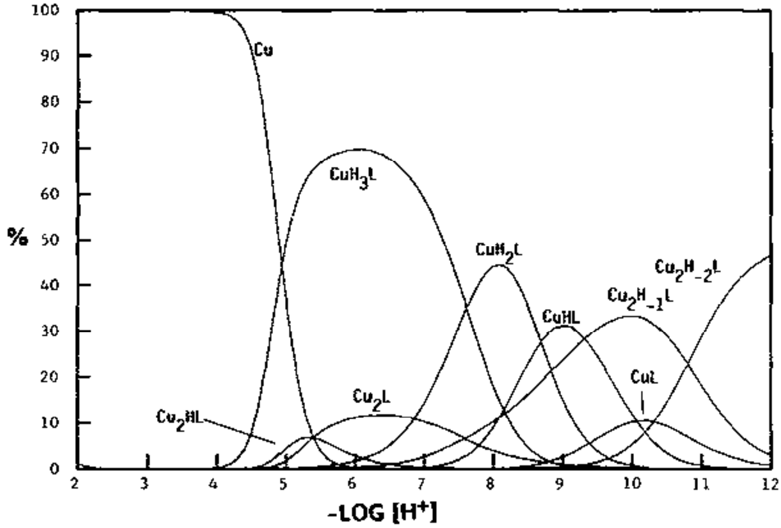


Fig. 4. Species concentration relative to T_{CBT}, in a solution having a CBT : Cu(II) molar ratio of 1 : 1, as a function of $-\log[H^+]$ ($\mu = 0.100$ M; $t = 25\,°C$).

The stability constant data may be employed to calculate the distribution of individual complexes as a function of designated composition parameters as well as pH. The species distribution curves illustrated in Fig. 4 are interesting in that for a solution having a 1 : 1 molar ratio of copper(II) to CBT, considerable concentrations of the binuclear complexes are formed, reflecting the strong binucleating tendencies of cryptand ligands of this type.

(iii) Schiff base formation and oxygenation constants in non-aqueous solutions

The use of the glass electrode for the determination of pH in ethanol–water, methanol–water mixtures, as well as in pure ethanol and methanol has been described by Bates [41]. The determination of $[H^+]$ in dioxane–water mixtures up to 70% dioxane has been described by Van Uitert and Fernelius [42]. The latter solvent system was recently employed to study the equilibrium constants for the formation of cobalt(II) Schiff base complexes and their oxygenation constants [43]. The use of the low dielectric constant mixed solvent was necessary to keep all components in solution. It also provided the advantage of promoting a higher degree of formation of Schiff bases, which are generally highly dissociated in aqueous solution. Low dielectric constant solvents also promote more complete formation of metal complexes.

The example given here to illustrate the method is the potentiometric equilibrium study of the salicylaldehyde, ethylenediamine, 4-methylpyridine, cobalt(II), dioxygen system. The method employed involved the determination of as many dissociation constants and stability constants as possible with simple combinations of the components, before working with more complex mixtures.

Ethylenediamine (EN) was measured separately and was found to have log protonation constants of 9.88 and 7.37. Because EN is a bidentate ligand, the successive 1 : 1, 1 : 2 and 1 : 3 cobalt(II)-to-ligand log stability constants were determined and were found to be 7.36, 6.91 and 3.55. At high p[H] a hydroxobisethylenediaminecobalt(II) species was formed, with a log protonation constant of 9.44. The value of the log protonation constant for 4-methylpyridine was found to be 4.36. The acid dissociation constant of 10.18 in aqueous 70% dioxane for salicylaldehyde was taken from the literature [44]. Since the stabilities of salicylaldehyde complexes are generally low and are significant only at high p[H] and only in the absence of other stronger ligands, determination of the formation constants of Co(II)–salicylaldehyde complexes was considered unnecessary and therefore was not attempted.

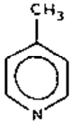
In the absence of cobalt(II), it was found that initially (i.e. at low p[H]) salicylaldehyde and ethylenediamine form a diprotonated mono Schiff base and a diprotonated di Schiff base which possess uniquely different donor groups. The mono Schiff base is terdentate with a basic phenol donor at one end and a basic amino group at the other, with a weakly basic imine donor in between. The bis Schiff base is tetradentate with two adjacent weak imine donors and two strongly basic phenolate donors. It is the cobalt(II) complex of the bis Schiff base which is of interest as an oxygen carrier. The log formation constant for the completely deprotonated mono Schiff base was found to be 3.81 while the log formation constant for the addition of the second deprotonated salicylaldehyde was found to be 4.11.

It was in anaerobic potentiometric experiments utilizing the components of the Schiff base in the presence of cobalt(II) that a series of interactions between the metal ion, the Schiff base chelates and H^+ was found to occur. The mono Schiff base of EN and salicylaldehyde was found to form a deprotonated (normal) chelate and a monoprotonated chelate. From the size of the chelate log protonation constant, 5.58, it is difficult to assign the two coordination sites and the remaining protonation site. A tentative suggestion is that one nitrogen atom and the oxygen atoms are involved in the coordination of cobalt(II) and that the terminal amino group becomes protonated. The log stability constant of the deprotonated mono Schiff base complex was found to be 14.21, indicating coordination of both amino groups and the phenolate oxygen atom. The log formation constant for the cobalt(II) complex of the bis Schiff base is 14.56, reflecting the balance between the loss of nitrogen basicity due to Schiff base formation and the

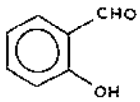
TABLE 3

Stability constants of SALEN–MePY–Co–O_2 system in dioxane–H_2O (70% v/v) ($\mu = 0.100$ M (KCl); $t = 25.0\,^\circ C$)

EN



PY



SH

Quotient	Log value	σ_{fit}
$\frac{[ENH]}{[EN][H]}$	9.88	0.01
$\frac{[ENH_2]}{[ENH][H]}$	7.37	
$\frac{[CoEN]}{[Co][EN]}$	7.36	0.01
$\frac{[CoEN_2]}{[CoEN][EN]}$	6.91	
$\frac{[CoEN_3]}{[CoEN_2][EN]}$	3.55	
$\frac{[CoEN_2OH][H]}{[CoEN_2]}$	−9.44	
$\frac{[PYH]}{[PY][H]}$	4.36	0.03
$\frac{[SH]}{[S][H]}$	10.18	0.02
$\frac{[SEN]}{[S][EN]}$	3.81	
$\frac{[SENH]}{[SEN][H]}$	9.73	
$\frac{[SENH_2]}{[SENH][H]}$	9.25	
$\frac{[S_2EN]}{[SEN][S]}$	4.11	
$\frac{[S_2ENH]}{[S_2EN][H]}$	9.55	
$\frac{[S_2ENH_2]}{[S_2ENH][H]}$	9.24	

TABLE 3 (continued)

Quotient	Log value	σ_{fit}
$\frac{[\mathrm{SENCo}]}{[\mathrm{SEN}][\mathrm{Co}]}$	14.21	0.06
$\frac{[\mathrm{SENHCo}]}{[\mathrm{SENCo}][\mathrm{H}]}$	9.05	
$\frac{[\mathrm{S_2ENCo}]}{[\mathrm{S_2EN}][\mathrm{Co}]}$	4.56	
$\frac{[\mathrm{S_2ENCoOH}][\mathrm{H^+}]}{[\mathrm{S_2ENCo}]}$	−9.93	
$\frac{[\mathrm{S_2ENCo(OH)_2}][\mathrm{H^+}]}{[\mathrm{S_2ENCo(OH)}]}$	−11.12	
$\frac{[(\mathrm{S_2ENPYCo})_2\mathrm{O_2}]}{[\mathrm{S}]^4[\mathrm{EN}]^2[\mathrm{PY}]^2[\mathrm{Co}]^2 P_{\mathrm{O_2}}}$	54.02	0.05
Alternative expression:		
$\frac{[(\mathrm{S_2ENPYCo})_2\mathrm{O_2}]}{[\mathrm{S_2ENCo}]^2[\mathrm{PY}]^2 P_{\mathrm{O_2}}}$	11.06	

gain of one additional donor group. The tetradentate di Schiff base complex with cobalt(II) possesses two axially coordinated water molecules capable of dissociation at high p[H]. It was found that the successive log acid dissociation constants for these are −9.93 and −11.12, giving species of possible importance only at high p[H] values.

In the final experiment, aerobic aqueous dioxane potentiometry on the SALEN–MePY–Co(II)–O_2 system led to the log overall formation constant for the binuclear oxygen complex containing two SALEN, two MePY, two cobalt(II) and one O_2. The log value for this constant is 54.02. This value, together with all the other equilibrium constants determined, are listed in Table 3.

It is seen that the strategy in this investigation was to study all possible protonation and metal complex formation reactions of each ligand separately under the same conditions (temperature, ionic strength and solvent). The constants thus determined were employed as known constants for each successively more complex system in which the original components interacted to form new ligands, thus providing a firm foundation for the calculations for each combination of components. While it is obvious that the reaction of a metal ion with a ligand is sensitive to protonation of the ligand (i.e. there is competition between the metal ion and hydrogen ion for the ligand), there are two reactions which do not involve hydrogen ions. These are neutral Schiff base formation from neutral salicylaldehyde and ethylenediamine (or species having the same degree of protonation as the

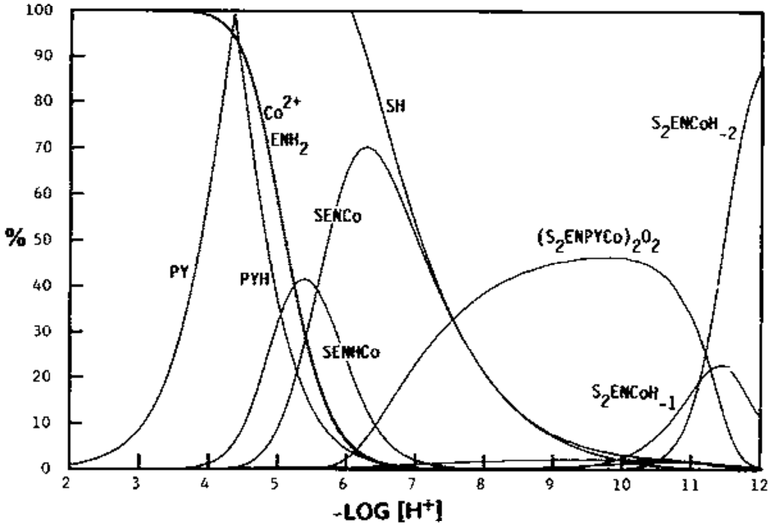


Fig. 5. Species distribution as a function of p[H] ($-\log[H^+]$) in aqueous 70% dioxane, $\mu = 0.100$ M (KCl), $t = 25.0\,^\circ$C and $P_{O_2} = 1.00$ atm. The components consist of ethylenediamine (EN, 2.00×10^{-3} M), salicylaldehyde (SH, 4.00×10^{-3} M), cobalt(II) (2.00×10^{-3} M) and axial base 4-methylpyridine (PY, 4.00×10^{-3} M, 100% excess).

product) and the formation equilibrium of the dioxygen complex itself:

$$O_2 + 2\mathrm{CoSALEN} + 2\mathrm{MePY} \rightleftharpoons (\mathrm{SALEN})_2\mathrm{Co}_2\mathrm{O}_2\mathrm{MePY}_2$$

However, the precursors of both reactions are highly p[H] dependent, and formation of the Schiff base and oxygenation of its cobalt(II) complex shift the equilibrium of the pH-dependent species. The equilibria involved in the formation of all the species in Table 3 strongly overlap, are completely interdependent, and shift with changes in hydrogen ion concentration.

The equilibrium constants in Table 3 may be used to calculate the concentrations of the principal ionic and molecular species in solution as a function of pH, giving the distribution curves illustrated in Fig. 5. It is seen that the dioxygen complex in the solution investigated is stable only in basic solution, and begins to form at a pH of about 6 as the pH is increased. At pH 8–11 it is the dominant complex present, accounting for about 95% of the cobalt(II) present in solution. This type of information is very useful for planning kinetic studies of reactions of such dioxygen complexes with various substrates.

Thus all the constants in Table 3 may be calculated from a series of p[H] profiles determined on solutions of increasing complexity, and those species which do not appear to involve hydrogen ions can be determined from p[H] data if their formation reactions overlap with hydrogen-ion-dependent species.

(iv) Complex systems containing many metal ions and multidentate ligands

It has been stated above that with computer methods now available, the metal chelate stability constants for one or more metal ions and ligand, together with all relevant hydrolysis and protonation constants, provide a complete description of the solution under the conditions for which the constants apply. In principle, the concentrations of all the complexes formed in the solution at equilibrium are known as a function of some solution variable such as p[H]. It is merely necessary to employ an appropriate computer program to transform the equilibrium constant data to the desired species distribution curves of the type illustrated in Figs. 4 and 5. The method is independent of the number of components in the solution and the complexity of the system.

To illustrate the capability of these computational methods the authors recently published an article describing species distribution (sometimes termed "speciation") of a system containing a completely arbitrary and synthetic mixture of five multidentate ligands and six metal ions [45]. The metal ions selected are Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Ca^{2+} and Fe^{3+}, while the ligands employed are, in the form of their anions, citrate (CIT^{3-}), tripolyphosphate (TPP^{5-}), nitrilotriacetate (NTA^{3-}), triaminotriethylamine (TREN), and *N*,*N*′-di(*o*-hydroxybenzyl)ethylenediamine-*N*,*N*′-diacetate ($HBED^{4-}$). In the following discussion, ligand charges are omitted to make it easier to generalize. The concentrations employed are 1.0×10^{-5} M for each ligand and 1.0×10^{-6} M for the metal ions, while the conditions selected are those for which stability constant data are commonly reported, i.e. 25.0 °C and ionic strength 0.100 M. With the ligand concentration an order of magnitude higher than the concentration of metal ions, it is perhaps not surprising that none of the metal ions were found to precipitate over the entire p[H] range from p[H] 2.0 to 11.0. Complex systems involving equilibria with solid phases will be described in the next two sections.

The computations were carried out in FORTRAN 77 with a VAX 11/780 with program SPE [32] for the calculation of species distributions from equilibrium constants. For comparison, parallel calculations were carried out with program MINEQL [46] modified to adapt it to the VAX requirements for linking plotting routines to related functions and for streamlining I/O options. The form of SPE employed was not adapted for treatment of solid phases in equilibrium with species in solution. No precipitates were formed in these systems. SPE has the advantage of giving shorter run times because of its more direct coding. A disadvantage of MINEQL is the fact that the attached data bank contains stability constants taken from non-critical compilations. It was employed for the present calculations only after laborious substitution of critical stability constants for the stability con-

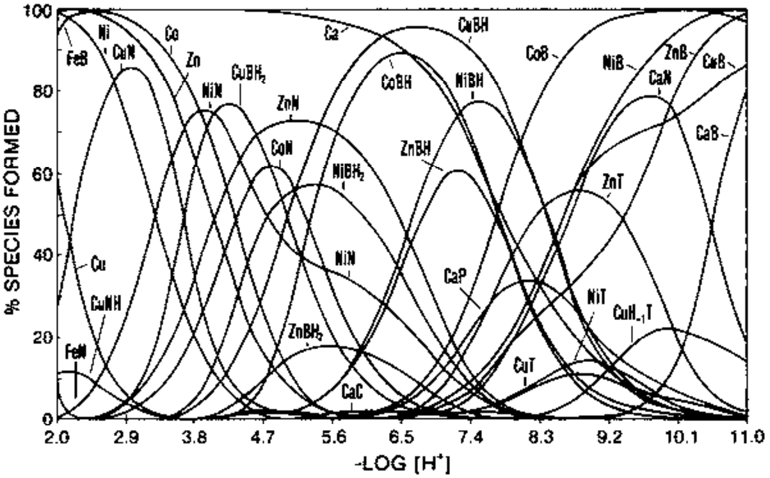


Fig. 6. Species distribution showing only metal-containing species as a function of $-\log[H^+]$: N = nitrilotriacetic acid; T = triaminotriethylamine; C = citrate; B = *N*,*N*′-di(*o*-hydroxybenzyl)ethylenediamine-*N*,*N*′-diacetic acid; P = tripolyphosphate.

stants taken from other sources [2–4]. The 122 species of various types considered capable of forming in the mixture are presented in Table 4(a). The species distributions (p[H] profiles) obtained for this system are given in Fig. 6, while the major species formed at pH 8.0 are summarized in Table 4(b).

TABLE 4(a)

Speciation in complex systems

Component	Type				Total
	Free	MH_iL	$M(OH)_jL$	Solid [a]	
Cu^{2+}	3	12	3	1	19
Ni^{2+}	2	11	1	1	15
Co^{2+}	4	11	2	1	18
Zn^{2+}	5	10	1	1	17
Ca^{2+}	2	10	0	1	13
Fe^{3+}	5	6	5	1	17
NTA	4	–	–	–	4
TREN	4	–	–	–	4
CIT	4	–	–	–	4
TPP	4	–	–	–	4
HBED	7	–	–	–	7
				Total	122

[a] The possibility of a precipitate was included in the calculations but none was found.

TABLE 4(b)

Major species present at pH 8.0

Species	Percentage of metal in the form of the species shown	Species	Percentage of metal in the form of the species shown
CuHBED·H	61	CaTPP	34
CoHBED·H	37	ZnTREN	47
NiHBED·H	62	NiHBED	30
ZnHBED·H	28	CaNTA	28
ZnNTA		CuHBED	27
NiHBED·H_2		ZnHBED	23
NiNTA		CaCIT	
CoHBED	72	CaHBED·H	

The distribution curves at low p[H] in Fig. 6 show Fe^{3+} to be totally complexed, mostly as $FeHBED^-$ but with some $FeNTA^0$. The Cu^{2+} is converted to chelates at pH 4, Ni^{2+} at pH 5 and Zn^{2+} at pH 6. At these levels, Ca^{2+} is partially complexed at pH 5 by citrate as expected. At somewhat higher p[H], CaTPP forms, followed by CaNTA around p[H] 9.2. Finally, above p[H] 10, CaHBED prevails. Thus it is seen that with the exception of Ca^{2+}, all free metal ions are essentially completely complexed above pH 5.8.

The dominant ligand responsible for the complexing of Cu^{2+} is NTA, which forms the $CuNTA^-$ complex, which reaches its maximum concentration at p[H] 3. At slightly higher p[H] values, Zn^{2+} and Co^{2+} form NTA complexes while CuHBED peaks out at 73% at p[H] 4.3. Near p[H] 4 the diprotonated HBED complexes of Ni^{2+} and Zn^{2+} (NiHBED·H_2 and ZnHBED·H_2 respectively) begin to form and this results in the release of NTA. Then, as p[H] is further increased, a series of deprotonations of all HBED complexes occurs giving rise to the progressively deprotonated forms MHBED·H and MHBED. The Zn^{2+}–, Co^{2+}–, Ni^{2+}– and Cu^{2+}–MHBED·H concentrations peak in the pH interval 6–7.5 while the totally deprotonated HBED chelates dominate the higher pH values. In the same pH region, small but significant concentrations of $CuTREN^{2+}$ (pH 8.8), $NiTREN^{2+}$ (pH 9), $ZnTREN^{2+}$ (pH 8.4), $CuTRENH_{-1}$ (pH 9.8) also form. The Ca^{2+} forms three significant species: $CaCIT^-$ at pH 6 (0.3%). $CaTPP^{3-}$ at pH 8.2 (33%) and $CaNTA^-$ at pH 9.6 (70%).

Several conclusions can be drawn from this complex system. First, it is demonstrated that the computer programs employed have the capability of rapidly and efficiently calculating the concentrations of a large number of corresponding equilibrium constants, as well as determining the variation in the species concentrations as a function of pH and of solution composition. It now becomes possible to select the major species that are present under varying conditions from all the possible reacting species. The same principles also apply to much more complex environmental, biological or other systems containing thousands of ligands and potentially hundreds of thousands of species. In view of the capacities of modern computers, such calculations do not pose serious difficulties. The major limitation involved in the application of this technique is the need to obtain accurate equilibrium parameters for all the significant complex species that may be formed. Since it is obvious that direct measurement is impossible, a new approach consisting of the estimation of the necessary equilibrium constants is now being developed. The first steps in this direction are the subject of recent reports [47,48].

(v) Hydroxo and fluoro complexes of aluminum(III)

A recently described example of the use of program SPE [32] is the determination of the hydrolyzed and complex species present in solution in the presence of solid $Al(OH)_3$. Table 5 lists the equilibrium constants for fluoride and hydroxide complexes of aluminum(III). With only the equilibrium data for hydroxo species in solution, the distribution diagram illustrated in Fig. 7 for total metal species concentrations of 10^{-3} M is obtained. In the intermediate p[H] range, hydrolytic complexes, including

TABLE 5

Equilibrium constants for hydroxo and fluoro aluminum(III) complexes

Ligand	Equilibrium quotients	Log *K*	Equilibrium quotients	Log *K*
OH^-	$\frac{[AlOH^{2+}]}{[Al^{3+}][OH^-]}$	8.21 [a]	$\frac{[Al(OH)_2^+]}{[Al^{3+}][OH^-]^2}$	19.0 [a]
	$\frac{[Al(OH)_3]}{[Al^{3+}][OH^-]^3}$	27.0 [b]	$\frac{[Al(OH)_4^-]}{[Al^{3+}][OH^-]^4}$	31.4 [b]
	$\frac{[Al_3(OH)_4^{5+}]}{[Al^{3+}]^3[OH^-]^4}$	41.35 [a]	$\frac{[Al_{13}O_4(OH)_{24}]^{7+}}{[Al^{3+}]^{13}[OH^-]^{32}}$	33.02 [a]
F^-	$\frac{[AlF^{2+}]}{[Al^{3+}][F^-]}$	6.43 [b]	$\frac{[AlF_2^+]}{[AlF^{2+}][F^-]}$	5.20 [b]
	$\frac{[AlF_3]}{[AlF_2^+][F^-]}$	3.9 [b]	$\frac{[AlF_4^-]}{[AlF_3][F^-]}$	2.8 [b]

[a] $t = 25.0$ °C; 0.060 M. [b] $t = 25.0$ °C; 0.010 M.

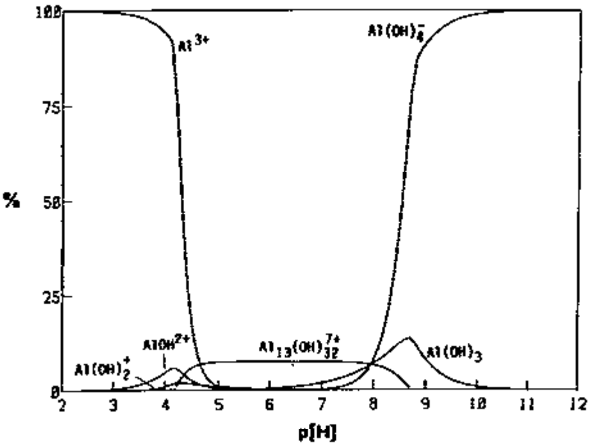


Fig. 7. Relative molar concentrations of hydrolytic species formed from aluminum(III) as a function of $-\log[H^+]$ in the absence of a solid phase ($t = 25.0\,°C$; $\mu = 0.100$ M (KNO_3)). Total concentration of aluminum(III) species is 1.00×10^{-3} M. The 7.6% molar concentration of $Al_{13}(OH)_{32}^{7+}$ constitutes 98.8% of the aluminum(III) present.

$Al_{13}(OH)_{32}^{7+}$, predominate. If solid $Al(OH)_3$ is taken into account by including its k_{sp} ($10^{-33.5}$) in the calculation, an entirely different picture emerges (Fig. 8) whereby the solid predominates over the entire p[H] range except for the extremes below p[H] 4 and above p[H] 11.5. For 10^{-6} M total metal species, the $Al(OH)_3$ complex shows up at a concentration of approximately 5×10^{-8} M (5% of the total) (Fig. 9). In the presence of 5×10^{-5} M fluoride ion, it is seen (Fig. 10) that fluoride competes strongly with hydroxide for aluminum(III) in the acid region, and moves up the p[H] of first precipitation by two units, from about 4 to about 6.

(vi) Metal speciation in sea water

The following example of the evaluation of metal complex speciation in sea water is described as an example of the use of critical stability constants, an expanded database involving estimated constants, and the adjustment of stability constants to satisfy the conditions of the system under consideration, for the determination of metal species present in biological, environmental and other systems containing large numbers of complex compounds. A more detailed account of such calculations on sea water has been described elsewhere [49].

The inorganic composition of sea water was taken from a paper by Ahrland [50] and is presented in Table 6, which shows the concentrations of four major metal ions, nine minor metal ions and five anions. In order to

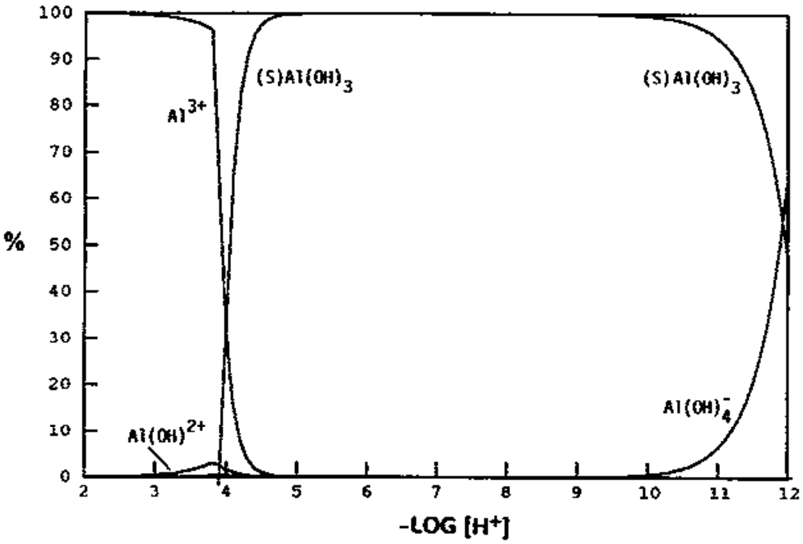


Fig. 8. Relative molar concentrations of hydrolytic species formed from aluminum(III) as a function of $-\log[H^+]$ ($t = 25.0\,°C$; $\mu = 0.100$ M (KNO_3)). Total concentration of aluminum(III) species is 1.00×10^{-3} M. (S)Al(OH)$_3$ represents the relative quantity of precipitated Al(OH)$_3$.

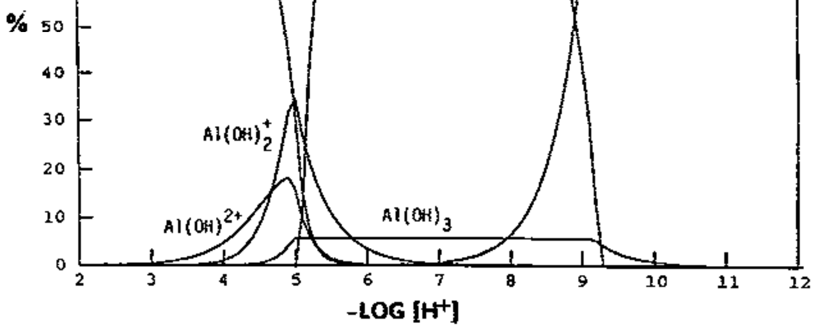


Fig. 9. Relative molar concentrations of hydrolytic species formed from aluminum(III) as a function of $-\log[H^+]$ ($t = 25.0\,°C$; $\mu = 0.100$ M (KNO_3)). Total concentration of aluminum(III) species is 1.00×10^{-6} M. (S)Al(OH)$_3$ represents the relative amount of precipitated Al(OH)$_3$.

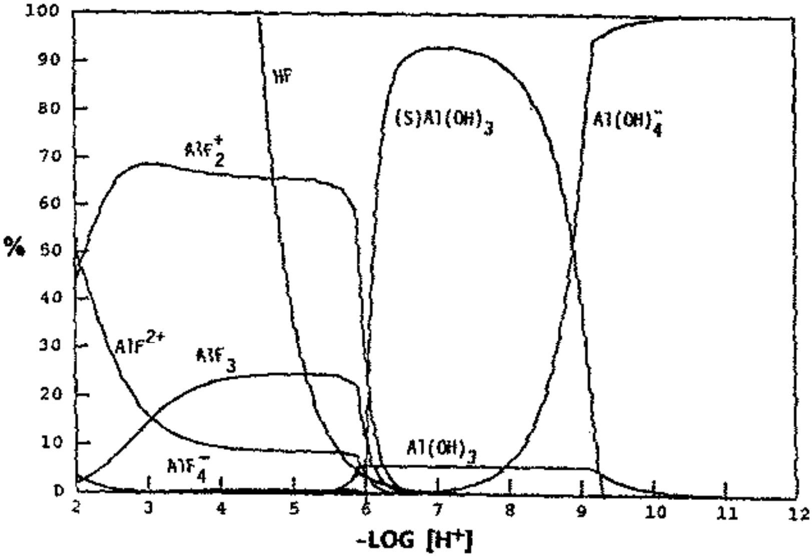


Fig. 10. Relative molar concentration of complex species formed from 1.0×10^{-6} M aluminum(III) ion and 5.0×10^{-5} M fluoride ion ($t = 25.0$ °C; $\mu = 0.100$ M (KNO_3)). (S)Al$(OH)_3$ represents precipitated Al$(OH)_3$.

calculate the complex species formed in this system it was necessary to employ the stability constants for all the soluble complexes that may be formed as indicated in Table 7 as well as the solubility products of solids that may be formed. These values are listed in Table 8. The equilibrium constants listed in Tables 7 and 8 were obtained from *Critical Stability Constants* [6] and include estimated values where necessary to complete the database. All these constants were adjusted to sea water conditions (ionic

TABLE 6

Major and some minor constituents of sea water

Ion	Concentration ($M \times 10^3$)	Trace element	Concentration ($M \times 10^9$)
Na^+	479	Mn	4
Mg^{2+}	54.5	Fe	8
Ca^{2+}	10.5	Ni	5
K^+	10.4	Cu	4
Cl^-	559	Zn	5
SO_4^{2-}	28.9	Cd	0.1
HCO_3^-, CO_3^{2-}	2.35	Hg	0.02
Br^-	0.86	Pb	0.05
F^-	0.075	U	14

TABLE 7

Log stability constants (β values) for soluble components of sea water ($\mu = 0.70$ M; $t = 25.0\,°\mathrm{C}$)

Species	Log β	Species	Log β	Species	Log β
$CaCO_3$	2.21	FeH^{+}_{-2}	−5.88	UO_2SO_4	1.80
$CaHCO_3^{+}$	9.90	FeH^{-}_{-4}	−20.76	$UO_2(SO_4)_2^{2-}$	2.50
$CaSO_4$	1.03	$Fe_2H^{4+}_{-2}$	−3.08	UO_2Cl^{+}	−0.10
CaF^{+}	0.60	$MnHCO_3^{+}$	10.00	UO_2F^{+}	4.4
CaH^{+}_{-1}	−12.20	$MnSO_4$	0.80	UO_2F_2	8.0
$MgCO_3$	2.05	$MnCl^{+}$	−0.20	$UO_2F_3^{-}$	10.55
$MgHCO_3^{+}$	9.80	$MnCl_2$	−0.3	$UO_2F_4^{2-}$	12.00
$MgSO_4$	0.90	$MnCl_3^{-}$	−0.50	UO_2Br^{+}	−0.3
MgF^{+}	1.30	MnH^{+}_{-1}	−10.80	$UO_2H^{+}_{-1}$	−5.8
MgH^{+}_{-1}	−11.70	MnF^{+}	0.70	$UO_2(SO_4)_3^{4-}$	3.7
KSO_4^{-}	0.30	$CuCO_3$	5.60	UO_2CO_3	8.9
$NaCO_3^{-}$	0.63	$Cu(CO_3)_2^{2-}$	7.90	$(UO_2)_3(CO_3)H^{+}_{-3}$	−24.94
$NaSO_4^{-}$	0.33	$CuSO_4$	0.90	$CdCO_3$	2.00
$Fe(SO_4)_2^{-}$	2.00	$CuCl_2$	0.01	$CdCl^{+}$	1.35
$FeCl^{2+}$	0.64	CuF^{+}	0.80	$CdCl_2$	1.70
$FeCl_2^{+}$	0.70	$CuBr^{+}$	−0.20	$CdCl_3^{-}$	1.50
$FeCl_3$	−0.70	CuH^{+}_{-1}	−6.50	CdF^{+}	0.50
FeF^{2+}	5.20	$Cu_2H^{2+}_{-2}$	−14.80	$CdBr^{+}$	1.50
FeF_2^{+}	9.10	$(UO_2)_6H_{-12}$-$(CO_3)_6^{12-}$	−10.46	$CdBr_2$	2.1
FeF_3	12.00	$(UO_2)_2H_{-2}$	−5.90	$CdBr_3^{-}$	2.5
$FeBr^{2+}$	−0.20	$UO_2(CO_3)_2^{2-}$	15.40	$CdBr_4^{2-}$	2.60
FeH^{2+}_{-1}	−2.76	$UO_2(CO_3)_3^{4-}$	20.3	CdH^{+}_{-1}	−9.90
CdH_{-2}	−20.0	$HgSO_4$	1.40	$PbCl^{+}$	0.90
CdH^{-}_{-3}	−31.0	$Hg(SO_4)_2^{2-}$	2.40	$PbCl_2$	1.30
$ZnSO_4$	0.90	$HgCl^{+}$	6.73	$PbCl_3^{-}$	1.4
$ZnCl^{+}$	0.01	$HgCl_2$	13.23	$PbBr^{+}$	1.08
$ZnCl_2$	−1.0	$HgCl_3^{-}$	14.20	$PbBr_2$	1.80
$ZnCl_3^{-}$	0.0	$HgCl_4^{2-}$	15.20	$PbBr_3^{-}$	2.10
ZnF^{+}	0.7	HgF^{+}	1.00	PbH^{+}_{-1}	−7.70
$ZnBr^{+}$	−0.40	$HgCO_3$	10.60	PbH_{-2}	−17.10
ZnH^{+}_{-1}	−10.20	$HgBr^{+}$	9.00	PbH^{-}_{-3}	−27.90
ZnH_{-2}	−19.40	$HgBr_2$	17.10	$Pb_2H^{3+}_{-1}$	−6.30
ZnH^{-}_{-3}	−27.70	$HgBr_3^{-}$	19.40	PbF^{+}	1.40
ZnH^{2-}_{-4}	−37.20	$HgBr_4^{2-}$	21.60	PbF_2	2.50
$ZnHCO_3^{+}$	10.50	HgH^{+}_{-1}	−3.70	HCO_3^{-}	9.54
$NiSO_4$	0.6	HgH_{-2}	−6.30	H_2CO_3	15.54
$NiCl^{+}$	−0.1	$HgHCO_3^{+}$	14.90	HSO_4^{-}	1.2
NiF^{+}	0.5	$PbCO_3$	6.20	HF	2.95
$NiBr^{+}$	−0.6	$Pb(CO_3)_2^{2-}$	8.80	H^{-}_{-1}	−13.76
NiH^{+}_{-1}	−10.10	$PbSO_4$	1.30		

TABLE 8

Log solubility products of solids ($\mu = 0.70$ M; $t = 25.0$ °C)

Phase	Log product	Phase	Log product
MnH_{-2}	14.78	PbF_2	-6.20
$Cu_2CO_3H_{-2}$	-6.00	PbH_{-2}	12.68
CuH_{-2}	9.10	UO_2CO_3	-12.90
$CdCO_3$	-9.60	UO_2H_{-2}	4.10
CdH_{-2}	13.48	$CaCO_3$	-6.60
$ZnCO_3$	-10.80	$CaSO_4$	-3.00
ZnH_{-2}	12.76	CaF_2	-10.60
$NiCO_3$	-7.00	CaH_{-2}	$+22.41$
NiH_{-2}	12.38	$MgCO_3$	-3.70
HgH_{-2}	1.58	MgF_2	-6.70
$PbCO_3$	-11.80	MgH_{-2}	16.43
$Pb_3(CO_3)_2H_{-2}$	-19.40	FeH_{-3}	2.77
$PbSO_4$	-6.0	$MnCO_3$	-8.70

strength 0.7 M) by the use of the correction factors recently published [50]. The computation provides a complete elucidation of the concentrations of free and complexed metal ions and ligands as a function of p[H].

If p[H] 8.0 is selected as an average or representative value for the conditions that apply in the open ocean the percentage of metal ion associated with each anion may be calculated and is presented in Table 9. These data together with the data in Table 6 may be used to calculate directly the concentration of each complex species under the selected conditions. It is seen that the alkali metal ions show little tendency to complex the ligands available, and the alkaline earth ions Ca^{2+} and Mg^{2+} are also primarily uncomplexed, although about 10% of Ca^{2+} is present as the sulfato complex while approximately 8% of Mg^{2+} is in that form. The high level of chloride ion in sea water is predominant in influencing the speciation of Mn^{2+}, Cd^{2+} and Hg^{2+} ions. Lead(II) is primarily present as a carbonato complex with smaller amounts of chloro and hydroxo complexes. Considerable fractions of the Ni^{2+} and Zn^{2+} ions are free (aquo) ions. The ferric ion seems to be nearly completely converted to the colloidal hydroxide while the Cu^{2+} ion is present as a soluble hydroxo complex. There is uncertainty about the speciation of the uranyl ion, UO_2^{2+}, because of the uncertainty in the equilibrium constants for the formation of complexes such as basic chlorides, which may compete with the carbonato complexes. On the basis of the data presently available, all the uranyl ion is converted to soluble uranyl carbonates.

For a sample of sea water with the composition indicated in Table 6 the number of components, including water, is 19. For the reactions that are

TABLE 9

Sea water speciation at pH 8.0

Metal ion	Percentage of metal ion associated with the ligand indicated							
	Cl^-	Br^-	F^-	SO_4^{2-}	$(H)CO_3$ [a]	OH^-	Uncomplexed	Precipitate
Ca^{2+}			0.01	9.8	0.54		79.0	10.6 $CaCO_3$
Mg^{2+}			0.07	8.4	0.45	0.02	91.1	
K^+				2.2			97.8	
Na^+				2.4	0.01		97.6	
Mn^{2+}	34.4		0.01	4.4	0.15	0.12	60.9	
Cd^{2+}	96.8	0.08		0.3		0.05	2.9	
Hg^{2+}	99.9	0.05						
Fe^{3+}						1.71		98.3 $Fe(OH)_3$
Cu^{2+}	1.9			0.2	22.4	73.6	1.85	
Zn^{2+}	41.2	0.02		4.86	0.40	0.47	53.0	
Pb^{2+}	22.32	0.02		0.3	71.9	3.9	1.5	
Ni^{2+}	29.6	0.01		3.1		0.67	66.6	
UO_2^{2+}					100.0			

[a] $(H)CO_3$, carbonate and bicarbonate.

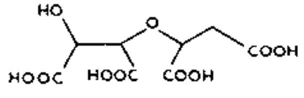
indicated in Tables 7 and 8 the number of soluble species is 141 while 26 insoluble compounds may also be present. This treatment assumes that all possible complexes involving the components in Table 6 are formed at least to a slight extent. Minor components such as complexes of Co^{2+} or non-complexing species such as borate and selenium were not considered.

The species distributions presented in Table 9 should be considered only as a simple model for speciation of metal complexes in the ocean. A complete model would also involve the kinetics of the processes together with the kinetics and equilibria of the various particulate adsorption and desorption phenomena. Such a model should also take into account the various redox processes possible in sea water under anaerobic conditions and in the presence of varying concentrations of oxygen. A complete model would also consider the complexities arising from the presence of the wide variety of organic components which are frequently of an ill-defined nature. Considerable work is required on metal ion affinities and reaction kinetics with particulate and organic systems before a more complete determination of metal speciation under various conditions encountered in sea water can be carried out.

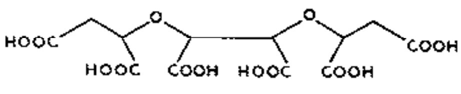
The simple sea-water model described above serves to show how the database and speciation calculations may be used. These methods may be applied to the more complex solutions containing many additional ligands and adsorbing solids, provided that the appropriate equilibrium parameters are available or can be estimated with reasonable accuracy.

(vii) The determination of stability constants from mixtures

Maleic anhydride reacts with tartaric acid in 1 : 1 and 2 : 1 molar ratios to form a mixture of ligands the principal components of which are tartaric–monosuccinic acid (TMS) and tartaric–disuccinic acid (TDS). Because of the asymmetric carbon centers, several forms of each ligand are possible. Protonation constants and mononuclear metal ion formation constants are not expected to differ greatly for such stereoisomers.



TMS



TDS

While the separation of pure TMS and TDS from the mixture is difficult, analytical high performance liquid chromatography has provided complete analyses of the components present. After the removal of extraneous inorganic ions and salts, each preparation of TMS was found to contain tartaric acid in addition to the principal component, and the same was true of the preparation consisting primarily of TDS together with malic acid, maleic acid and fumaric acid. The analyses provided not only the qualitative identification of each component but also quantitative determinations of the percentage compositions of the mixtures. The complete analysis of the components present in the TMS-rich and TDS-rich solutions investigated is presented in Table 10.

The purpose of the research was to determine the protonation constants and stability constants of TMS and TDS under conditions such that the complete separation and purification of each component had not been accomplished, i.e. on mixtures of these components. Since quantitative investigations of such mixtures, as well as of the pure ligands themselves, have not been described in the literature previously, this study represents a

TABLE 10

Compositions of reaction mixtures investigated

Species	Mole fraction (for solutes only)	
	TMS rich	TDS rich
TMS	0.738	0.370
TDS	0.053	0.623
Tartaric acid	0.134	0.007
Malic acid	0.020	–
Maleic acid	0.031	–
Fumaric acid	0.024	–

new procedure for stability constant determinations. The development of such a technique for the study of complex mixtures is made possible by the use of iterative methods and the FORTRAN program BEST [36], which places no constraints on the number and types of components present nor on the number and types of species formed in complex systems studied by potentiometric measurements of p[H].

The basic experimental plan was to make parallel potentiometric p[H] measurements in TMS-rich and TDS-rich solutions followed by data analysis consisting of the following steps: (1) refinement of the TMS constants using TMS-rich data; (2) refinement of the TDS constants using TDS-rich data; (3) a shuttle of the calculation between steps (1) and (2) until the calculated equilibrium constants become constant.

The potentiometric equilibrium measurements of the ligand solutions in the absence and presence of metal ions were carried out by the methods described above. Details of the experimental procedures and a discussion of results have been described [51]. The main concern in this review is to compare the stability constants determined by measurement of mixtures with the values obtained with pure ligands. The data obtained consisted of p[H] profiles with approximately 40–50 p[H] measurements vs. mole of standard base per mole of chelating ligand present in the experimental solution. All proton association constants were calculated with the program BEST [36] with the aid of a Digital PDP/11 computer. Formation constants of the 1 : 1 and 2 : 1 metal–ligand complexes were obtained through least-squares refinement of the 1 : 1 and 2 : 1 p[H] profiles.

The species considered present in the experimental solutions are those which would be expected to be formed according to established principles of coordination chemistry, while taking into account types of donor groups, their numbers and arrangement in the given ligand, the nature of the metal ion, the shapes of the p[H] profiles, and analogous known metal complex systems. Because the two main components, TMS and TDS, had not been reported previously, initial estimates of protonation constants and metal complex formation constants were made by selecting values based on analogous ligands with carboxylate and aliphatic α-hydroxyl groups and adjusting these values to take into account differences in ligand structure. This procedure was employed for both protonation constants and metal ion stability constants. The relevant values of the protonation constants of the minor constituents listed in Table 10 were taken from *Critical Stability Constants* [6]. When data were not available, they were estimated by analogy with similar dicarboxylic acid data. These stability and protonation constants, including the estimated values, are listed in Table 11. It is noted that in most cases the estimated values are assigned one less significant figure than the measured constants.

TABLE 11

Equilibrium constants [a] used to correct for the presence of tartaric, malic, maleic and fumaric acids

Central ion	Equilibrium constant [b]	Log β			
		Tartaric acid	Malic acid	Maleic acid	Fumaric acid
H^+	β_{HL}	3.95	4.71	5.82	4.10
	β_{H_2L}	6.77	7.95	7.57	6.95
Cu^{2+}	β_{ML}	3.42	3.42	3.4	2.0 [c]
	β_{MHL}		6.71		
	$\beta_{MH_{-1}L}$	−1.45	−1.12		
	$\beta_{M_2L_2H_{-3}}$		−5.17		
Cd^{2+}	β_{ML}	1.70	2.36	2.4 [c]	1.9 [c]
	β_{MHL}	4.92	6.05		
Zn^{2+}	β_{ML}	2.68	2.93	2.0	1.5 [c]
	β_{MHL}		6.37		
Ca^{2+}	β_{ML}	1.94	1.96	1.1 [c]	0.48
	β_{MHL}	5.06	5.77		
Mg^{2+}	β_{ML}	1.36	1.70	1.4 [c]	0.5 [c]
	β_{MHL}	4.87	5.61		
Al^{3+}	β_{ML}			3.0 [c]	2.5 [c]
	$\beta_{MH_{-1}L}$	1.18	1.2		
	$\beta_{MH_{-2}L}$	−3.97			

[a] $t = 25.0\,°C$; $\mu = 0.20$ M.

[b] $\beta_{HL} = [HL]/[H^+][L]$; $\beta_{H_2L} = [H_2L]/[H^+]^2[L]$; $\beta_{ML} = [ML]/[M][L]$; $\beta_{MHL} = [MHL]/[M][H^+][L]$; $\beta_{MH_{-1}L} = [MH_{-1}L][H^+]/[M][L]$; $\beta_{MH_{-2}L} = [MH_{-2}L][H^+]^2/[M][L]$; $\beta_{M_2L_2H_{-3}} = [M_2L_2H_{-3}][H^+]^3/[M]^2[L]^2$.

[c] Estimated values.

TABLE 12

Log protonation constants [a] resulting from refinement of data on mixtures of TMS and TDS

n	Log K_n^H [b]	
	TMS	TDS
1	5.73	5.97
2	4.38	5.40
3	3.34	4.40
4	2.41	3.69
5		2.99
6		2.28
σ_{fit}	0.0015	0.0007

[a] Log $K_n^H = [H_nL]/[H^+][H_{n-1}L]$. [b] $t = 25.0\,°C$; $\mu = 0.100$ M (KCl).

The protonation constants for TMS and TDS were determined from TMS-rich and TDS-rich solutions in the absence of metal ions. The presence of tartaric acid in the TDS-rich test solutions and the presence of tartaric, malic, maleic and fumaric acids in the TMS-rich solutions was taken into

TABLE 13

Log stability constants [a] of metal ion TDS and TMS complexes obtained from refinement of data from TDS-rich and TMS-rich solutions

	Cu^{2+}	Cd^{2+}	Zn^{2+}	Ca^{2+}	Mg^{2+}	Al^{3+}
TMS quotients						
$\frac{[ML]}{[M][L]} = K_{ML}$	6.63	4.63	6.31	5.20	3.91	7.63
$\frac{[MHL]}{[ML][H^+]} = K^{H}_{MHL}$	3.70	3.98	3.47	4.43	4.27	2.98
$\frac{[MH_2L]}{[MHL][H^+]} = K^{H}_{MH_2L}$	2.90	3.53	2.85	2.94	–	–
$\frac{[MLH_{-1}][H^+]}{[ML]} = K^{-H}_{MLH_{-1}}$	−7.00	–	–	–	–	−5.05
σ_{fit} for TMS [b]	0.006	0.007	0.002	0.002	0.013	0.003
TDS quotients						
$\frac{[ML]}{[M][L]} = K_{ML}$	9.38	6.80	8.07	6.82	4.53	8.56
$\frac{[MHL]}{[ML][H^+]} = K^{H}_{MHL}$	4.27	4.93	4.53	5.39	5.44	5.73
$\frac{[MH_2L]}{[MHL][H^+]} = K^{H}_{MH_2L}$	–	4.09	3.54	4.37	–	3.23
$\frac{[MH_3L]}{[MH_2L][H^+]} = K^{H}_{MH_3L}$	6.38 [c]	3.18	2.94	2.83	–	–
$\frac{[MH_4L]}{[MH_3L][H^+]} = K^{H}_{MH_4L}$	–	–	–	2.72	–	–
$\frac{[M_2L]}{[ML][M]} = K^{M}_{M_2L}$	4.10	2.69	2.92	3.19	(−0.1) [d]	(1.2) [d]
$\frac{[MLH_{-1}][H^+]}{[ML]} = K^{-H}_{MHL_{-1}}$	–	–	–	–	–	−4.95
$\frac{[M_2LH_{-1}][H^+]}{[M]^2[L]} = \beta_{M_2LH_{-1}}$	–	–	–	–	–	10.96
σ_{fit} for TDS [b]	0.006	0.002	0.004	0.001	0.013	0.006

[a] $t = 25.0\,^{\circ}C$; $\mu = 0.100$ M(KCl). [b] Average values. [c] $[MH_3L]/[MHL][H^+]^2 = K^{2H}_{MH_3L}$.

[d] Values obtained in refinement, but negligible concentrations of species.

account through the use of the data listed in Table 11. The final results of these calculations are presented in Table 12.

The excellent σ_{fit} (0.0015 for TMS-rich and 0.0007 for TDS-rich solutions) provides assurance that the experimental refinement is as complete as can be expected and is comparable with the results achieved in much simpler monocomponent systems. It also shows that the technique employed achieved a good least-squares minimum spread over two solutions with mixtures of species at widely different concentrations.

Potentiometric pH measurements were made in the usual way on equimolar ($\text{moles}_{\text{TDS}} + \text{moles}_{\text{TMS}} =$ mole metal ion) solutions of Cu^{2+}, Cd^{2+}, Zn^{2+}, Ca^{2+}, Mg^{2+}, Al^{3+} by equilibration with TMS-rich and TDS-rich solutions by the process described above for protonation constants. The log stability constants thus determined are presented in Table 13.

After the work on mixtures (TMS rich and TDS rich) had been completed, a small sample of pure TDS in solution was obtained. With this pure ligand, potentiometric determinations of protonation constants and metal ion stability constants were carried out, thus providing a comparison with the determinations that had been made on mixtures. The new values with pure TDS were then employed for determination of the TMS-rich mixture, with corrections based on the minor constituents present (listed in Table 14).

Table 14 lists the protonation constants of pure TDS and those of TMS obtained from the TMS-rich solution. A comparison of the TDS column of Table 14 with that of Table 12 shows that the constants obtained for the major species are either exactly the same or within 0.01 log units. The second protonation constant differs by 0.02 units, while the value which is farthest off differs by 0.08 log units. This remarkable agreement demonstrates the validity of this new method of working with mixtures. From further inspection of the TMS data it is also remarkable that the first

TABLE 14

Protonation constants [a] of TMS and pure TDS [b]

n	TMS	TDS
1	5.73	5.98
2	4.40	5.38
3	3.30	4.40
4	2.44	3.70
5		3.00
6		2.20
σ_{fit}	0.001	0.0005

[a] $t = 25.0\,°C$; $\mu = 0.100$ M. [b] $\text{Log } K_n^H = \dfrac{[H_nL]}{[H^+][H_{n-1}L]}$.

protonation constant is improved, the second differs by 0.02 log units, the third by 0.04, and the last by 0.03. The slightly larger scatter for TMS may be due to the inclusion of literature data (Table 11) for the four additional impurities present in the TMS solution. It is suggested that exact results could be achieved if the protonation constants of tartaric, malic, maleic and

TABLE 15

Final values of log stability constants [a]

	Cu^{2+}	Cd^{2+}	Zn^{2+}	Ca^{2+}	Mg^{2+}	Al^{3+}
TMS constants						
$\frac{[ML]}{[M][L]} = K_{ML}$	6.65	4.62	6.30	5.20	3.94	7.63
$\frac{[MHL]}{[ML][H^+]} = K^{H}_{MHL}$	3.69	3.99	3.46	4.42	4.21	2.99
$\frac{[MH_2L]}{[MHL][H^+]} = K^{H}_{MH_2L}$	2.89	3.48	2.89	2.96	–	–
$\frac{[MLH_{-1}][H^+]}{[ML]} = K^{-H}_{MLH_{-1}}$	−7.0	–	–	–	–	−5.03
σ_{fit} for TMS	0.005	0.007	0.002	0.003	0.011	0.006
Pure TDS constants						
$\frac{[ML]}{[M][L]} = K_{ML}$	9.24	7.02	8.09	6.86	4.40	9.04
$\frac{[MH_2L]}{[ML][H^+]} = K^{H}_{MHL}$	4.04	4.79	4.45	5.33	5.41	5.34
$\frac{[MH_2L]}{[MHL][H^+]} = K^{H}_{MH_2L}$	2.52	4.11	3.60	4.31	–	3.04
$\frac{[MH_3L]}{[MH_2L][H^+]} = K^{H}_{MH_3L}$	3.78	3.17	2.81	2.91	–	–
$\frac{[MH_4L]}{[MH_3L][H^+]} = K^{H}_{MH_4L}$	–	–	–	2.36	–	–
$\frac{[M_2L]}{[ML][M]} = K^{M}_{M_2L}$	3.57	2.52	3.22	2.63	1.59	< 0.2
$\frac{[MLH_{-1}][H^+]}{[ML]} = K^{-H}_{MLH_{-1}}$	–	–	–	–	–	−6.72
$\frac{[M_2LH_{-1}][H^+]}{[M]^2[L]} = \beta_{M_2LH_{-1}}$	–	–	–	–	–	9.36
σ_{fit} for TDS [b]	0.007	0.009	0.008	0.004	0.026	0.012

[a] $t = 25.0\,^\circ C$; $\mu = 0.100$ M (KCl). [b] The σ_{fit} listed is the larger of the two values found for the 1 : 1 and 2 : 1 titrations.

fumaric acids were determined as part of this investigation under conditions identical with those employed for the TMS and TDS determinations.

Because of the large number of donor groups in TDS, the potentiometric studies of this ligand were carried out with both 2 : 1 and 1 : 1 molar ratios of metal ion to ligand. Table 15 presents all the metal ion stability constants obtained with pure TDS. With these more accurate TDS constants, the data obtained from the TMS-rich system were recalculated to obtain the best stability constants for TMS. Because the TDS constants employed as corrections in the calculations of the TMS constants of the TMS-rich mixture were more accurate in this case, the data in Table 15 are considered the best available under the circumstances.

A comparison of the TMS constants in Tables 13 and 15 shows that the agreement is excellent with only minor variations in the second decimal place. The pure TDS values in most cases also agree quite well, within 0.1 or 0.2 log units, with the constants obtained from mixtures only. The M_2L constants disagree somewhat more, but this is expected because, for the TDS-rich mixture, no effort was made to measure solutions with an M : L composition of 2 : 1, so that the stability constants for the binuclear complexes calculated from the 1 : 1 solutions would be expected to be less accurate.

Given so many competing equilibria and the presence of so many buffer reactions, it is remarkable that a precise set of equilibrium constants was obtained from mixtures of the two compounds, containing several impurities. With such good results from such complex systems, it seems that this new analytical technique could also be applied with even more confidence to simpler mixtures to determine individual protonation constants and metal chelate stability constants. The reader is reminded, however, that the successful determinations described above were possible only because the components present in the mixtures investigated were themselves pure and their concentrations were accurately known.

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