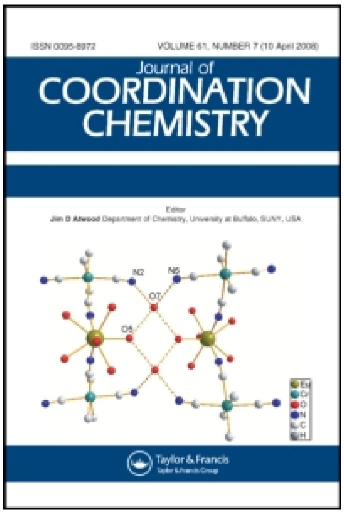

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METAL ION SPECIATION IN COMPLEX MULTICOMPONENT SYSTEMS. SIX METAL IONS AND FIVE MULTIDENTATE LIGANDS

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METAL ION SPECIATION IN COMPLEX MULTICOMPONENT SYSTEMS. SIX METAL IONS AND FIVE MULTIDENTATE LIGANDS

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A multicomponent metal chelate system is set up containing six metal ions of the type commonly found in environmental systems, and five ligands which vary considerably in basicity and metal ion affinity. With the use of critical stability constants, computer calculations are carried out to show the equilibrium distribution of metal ions among the various ligands available as the pH is varied from 2.0 to 11.0. Changes in the total concentrations of Ca(II) are shown to result in considerable changes in the distribution of the remaining metal ions among the available ligands. The methods employed in this investigation are applicable to more extensive and complex multicomponent systems containing thousands of ligands and a large number of metal ions.

INTRODUCTION

Of the thousands of organic compounds in the environment[1] many are complexing agents for metal ions, while others are converted to complexing agents by hydrolysis or oxidation processes that are catalyzed by metal ions, metal complexes and naturally occurring enzymes. The problem of assessing the toxicities of natural and unnatural metal ions in the environment requires a knowledge of the complexes present because toxicities are profoundly influenced by the nature of the ligands with which the metal ions are combined.[1,2] The development of a broad data base of metal ion-ligand affinities in terms of formation constants is now in progress and initial efforts in this area are described elsewhere.[3,4] Once reliable equilibrium parameters are available the problem of determining the speciation of metal complexes and chelates present in complex multicomponent systems containing many diverse metal ions and ligands still remains. The purpose of this paper is to carry out calculations on such a system to determine the metal complex speciation pH profile in the presence of several multidentate ligands varying widely in their affinities for basic (type A) metal ions and transition (less basic) metal ions.

EXPERIMENTAL

Composition of Model System

The system set up for the trial calculations, described in Table I, is designed to investigate a number of trace metal ions, including essential metal ions, frequently found in the environment. Also included is a metal ion, Ca(II), which is frequently found at moderate to relatively high concentrations. the ligands include a chelating agent, citrate (CIT), which is frequently naturally present, and two ligands, tripolyphosphate (TPP) and nitrilotriacetatic acid (NTA), that are frequently released to the environment through commercial or consumer product use. Also included are two ligands triaminotriethylamine (TREN) and *N,N'*-di(o-hydroxybenzyl)ethylenediamine-*N,N'*-diacetic acid (HBED) that have high selectivities and affinities for Cu(II) and Fe(III), respectively.

The concentrations of metal ions selected for the model system indicated in Table I are within the range of trace metal concentrations found in the environment. System II differs from System I in that it has 10^4 times the

TABLE I
Concentrations of metal ions and ligands investigated.

Component	Concentration	
	System I	System II
Cu(II)	1.00×10^{-6}	1.00×10^{-6}
Ni(II)	1.00×10^{-6}	1.00×10^{-6}
Co(II)	1.00×10^{-6}	1.00×10^{-6}
Zn(II)	1.00×10^{-6}	1.00×10^{-6}
Ca(II)	1.00×10^{-6}	1.00×10^{-2}
Fe(III)	1.00×10^{-6}	1.00×10^{-6}
NTA H_3L	1.00×10^{-5}	1.00×10^{-5}
TREN L	1.00×10^{-5}	1.00×10^{-5}
CIT H_3L	1.00×10^{-5}	1.00×10^{-5}
TPP H_5L	1.00×10^{-5}	1.00×10^{-5}
HBED H_4L	1.00×10^{-5}	1.00×10^{-5}

concentration of Ca(II). This high value was selected because it represents a reasonably high limit, and corresponds to the concentration of Ca(II) in sea water.[5]

The concentrations of the ligands present in the model system described in Table I are set at ten times the concentrations of the metal ions in order to insure the preservation of a homogeneous system so that the speciation calculations will reflect only the competition between the ligands present by avoiding side reactions involving precipitation of the metal ions at moderate to high pH.

The equilibrium constants involving metal-ligand iteractions, and the dissociation constants of the ligands, are taken from Critical Stability Constants compilations by Smith and Martell.[6]

Computation

The computations were performed in Fortran 77 on a DIGITAL VAX 11/780 using either Program SPE[7] or Program MINEQL.[8] SPE is an adaptation of the program BEST[9] which in turn was designed to compute multiple equilibrium constants from potentiometric equilibrium data. It was necessary to modify MINEQL extensively for adaptation to the VAX requirements for the linking of plotting routines and related functions and for I/O options which otherwise would produce prohibitive amounts of paper or use up enormous quantities of disk memory space. The only advantage of MINEQL over SPE is the inclusion of a provision for solid phase separation, an option that is presently lacking in SPE. Since in the present problem no precipitates were evidently formed at any pH, SPE gave more favorable run times because of its superior coding. All calculations were carried out at every 0.1 pH unit in the pH range from 2-11.

Data Set

The characterization of a complex environmental model requires the identification of chemical species that can reasonably be expected to be present, and determination of their quantitative interrelationships by use of the appropriate formation constants. These two tasks are interrelated and in practice the number of the species present frequently exceeds considerably the simple sum of the components plus the number of normal (ML type) complexes that may be formed. Frequently, both protonated species MH_iL ($i > 0$), deprotonated species ($i < 0$), hydroxo complexes $M(OH)_jL$ ($j > 0$), various polynuclear species, hydroxo metal ions, and other species are found.

TABLE II
Numbers and types of species that may be formed from the components of the systems modeled in this study.

Component	Type				Total
	Free	MH_iL	$M(OH)_jL$	Solid[a]	
Cu(II)	3	12	3	1	19
Ni(II)	2	11	1	1	15
Co(II)	4	11	2	1	18
Zn(II)	5	10	1	1	17
Ca(II)	2	10	0	1	13
Fe(III)	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.

The numbers of the various types of species which can arise from the interactions between the six metal ions and five ligands selected, in addition to their individual protonation and hydrolysis reactions are summarized in Table II.

For each metal ion in Table II are listed up to 5 forms of the free (*i.e.* aquo and hydroxo complexes) metal ion. In cases where the metal ion concentration is large, the hydrolyzed forms of the metal ion are a negligible fraction of the total concentration except for amphoteric ions. However at 10^{-6} M concentration this approximation becomes less rigorous and therefore all available hydrolysis reactions have been taken into account in this investigation. The divalent ions in Table II possess at least one protonated chelate with each ligand in addition to the normal complex ML. Some metals also undergo hydroxo complex ($M(OH)_jL$) formation. Iron(III) has little tendency to form protonated chelates, because of its tendency to strip all ionizable hydrogens from the ligand. Fe(III) forms at least one hydroxo complex with each ligand except with HBED.

The "free" forms of ligands listed in Table II include all the protonated forms in addition to the totally deprotonated anion.

RESULTS AND DISCUSSION

For System I at low p[H] the distribution curves in Figure 1 show Fe(III) to be totally complexed, mostly as $FeHBED^-$ but with some $FeNTA^\circ$. Copper(II) is converted to chelates at pH 4, nickel at pH 5, zinc at pH 6. At these levels in System I, calcium is partially complexed at pH 5 to citrate as was expected. At somewhat higher p[H], CaTPP forms, followed by CaNTA around p[H] 9.2. Finally above pH 10, CaHBED prevails. Thus it is seen that with the exception of Ca(II), all free metal ions are, to all intents completely complexed above pH 5.8.

The dominant ligand responsible for the complexing of Cu(II) is NTA, which forms the $CuNTA^-$ complex, which reaches its maximum concentration at p[H] 3. At slightly higher p[H] values, zinc and cobalt ions form NTA complexes while CuHBED peaks out at 73% at pH 4.3. Near pH 4 the diprotonated HBED complexes of Ni(II) and Zn(II) ($NiHBED.H_2$ 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

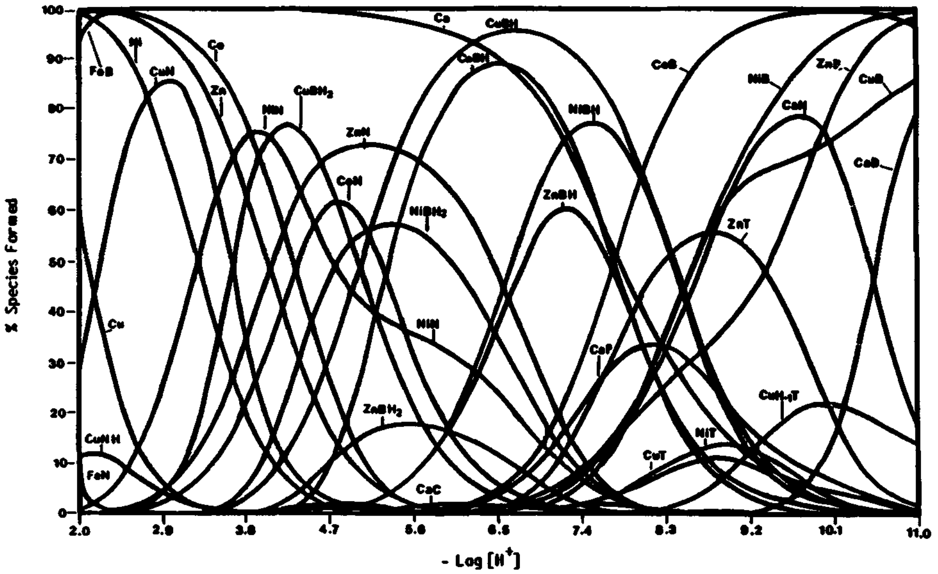

FIGURE 1 Species distribution showing only metal-containing species as a function of $-\log [H^+]$. The components and their analytical concentrations are listed in Table I. System I. N = nitrilotriacetic acid; T = triaminotriethylamine; C = citrate; B = *N,N'*-di(*o*-hydroxybenzyl)ethylenediamine-*N,N'*-diacetic acid; P = tripolyphosphate.

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 to 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) form as well. At 10^{-6} M concentration, 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%).

It is seen in Figure 2 that when System II is compared to System I, the high Ca(II) concentration of 1×10^{-2} M causes virtually negligible changes in the non-calcium speciation below pH 5. However, at higher p[H] values, the large excess of $[Ca^{2+}]$ relative to the ligands present has the effect of depletion of some of the free ligand species, and displacing the remaining trace elements from these ligands. This results in quite a different distribution of metal/ligand species as compared to System I.

Perhaps the most striking result may be found in the high pH region. $CuTRENH_{-1}$ carries about 98% of Cu(II) at pH 11 in contrast to only 14% when Ca(II) is at 10^{-6} M. NiTREN has 99% of the available Ni(II) at this pH while for solutions dilute in Ca(II) this value is only about 1%. Similarly zinc is nearly 100% complexed with TREN in System II but negligibly so in System I. In a parallel fashion, Co(II) is almost 100% complexed with HBED in System I while in System II the Co(II) ion is nearly 100% distributed between CoTREN and $CoTRENH_{-1}$. As expected, FeHBED has near 100% of the iron in both Systems studied.

The main reason for this shift in the complex equilibria can be traced to the substantial formation (> 90%) of $CaCIT^-$, $CaNTA^-$, and $CaTPP^{3-}$ which occurs at pH values of 5.5, 6.0, and 6.5, respectively. In addition $CaHBED^{2-}$ forms to 90% by pH 11. The fact that the latter complex forms too, leaves TREN as the only ligand in substantial concentration uncomplexed to Ca(II). Thus it is evident from these calculations why the distribution favors TREN species when a large excess of Ca(II) is added to the metal ions and ligands in System I.

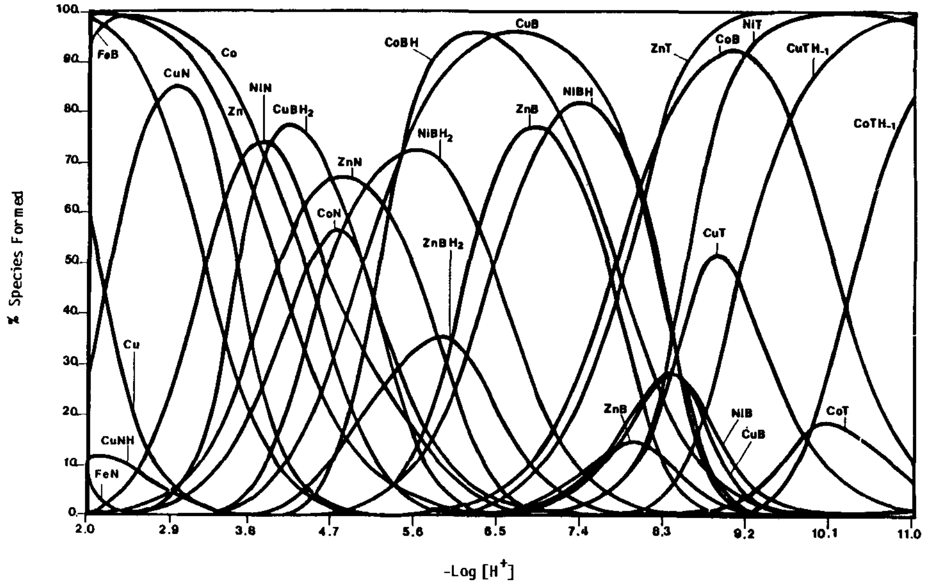

FIGURE 2 Species distribution showing only metal-containing species as a function of $-\log [H^+]$. The components and their analytical concentrations are listed in Table I, System II. Abbreviations as in Figure 1.

The implications of these computations are of significance for an appreciation of the role played by the presence of Ca(II) in significant concentrations in the relative speciation of metal complexes in multicomponent systems. Normally, it is assumed that at a given pH in the presence of excess ligands, each metal ion would generally distribute itself among the available ligands in accordance with the magnitudes of the corresponding stability constants. While this is true at p[H] values higher than the protonation constants of the complexes formed, the existence of stable protonated complexes gives rise to unexpected reversals of this anticipated order. However, in the presence of Ca(II) concentrations at the level of that in ocean water, the trace ligands are swamped with Ca(II) and as a consequence, certainly by pH 7, all of the ligands, except those with a large number of basic amino groups, nearly quantitatively become associated with this ion. Equation (*1*) shows the competition between a metal ion and Ca^{2+} for the ligand L:

$$M^{m+} + CaL^{c} \rightleftharpoons ML^{m+c-2} + Ca^{2+} \quad K_{disp} = \frac{[ML^{m+c-2}]\,[Ca^{2+}]}{[M^{m+}]\,[CaL^{c}]} \qquad (1)$$

It is clear that equation (*1*) represents a displacement reaction wherein the metal ion of charge m+ displaces the divalent Ca(II) ion from a chelate of net charge c. The relative degree to which this displacement occurs with a series of metal ions depends not only on the stability of the chelate formed, ML, but also on the stability of the CaL complex which is initially present when substantial excess of Ca is available. This equilibrium constant is given by the ratio K_{ML}/K_{CaL}, or $\log (K_{disp}) = \log (K_{ML}) - \log (K_{CaL})$.

With the introduction of an additional pseudo-stability constant, K_{eff}, defined by (*2*)

$$\log K_{eff} = \log K_{disp} - \log[Ca^{2+}] \qquad (2)$$

TABLE III
Normal and effective stability constants (log values) of metal ions with ligands.

	Log K_{ML}					Log K_{eff}				
Ligand	Cu(II)	Ni(II)	Co(II)	Zn(II)	Fe(III)	Cu(II)	Ni(II)	Co(II)	Zn(II)	Fe(III)
NTA	13.10	11.50	10.38	10.66	15.90	8.71	7.11	5.99	6.27	11.51
TREN	18.80	14.50	12.60	14.40	a	b	b	b	b	b
CIT	5.90	5.35	5.00	4.86	11.20	4.39	3.84	3.49	3.35	9.69
TPP	8.30	6.75	6.94	7.50	10.00	5.10	3.55	3.74	4.30	6.80
HBED	23.69	19.31	19.89	18.37	39.68	16.40	12.02	12.60	11.08	32.39

[a] Stability constant unknown or interaction non-existent. [b] K_{eff} values can be taken as K_{ML}, since Ca(II) does not bind TREN.

it is easier to appreciate the effects of the added calcium. The greater the calcium ion concentration the smaller the equilibrium constant K_{eff}. This relationship may be applied to the pH region where the calcium chelate is nearly quantitatively formed. Where chelate protonation and deprotonation and metal hydrolysis reactions are not negligible, suitable further modifications must be made, resulting in a more complex relationship.[10]

$$\begin{aligned}\text{Log } K_{eff} = {} & \log K_{ML} - \log(K_{CaL}[Ca^{++}] + 1 + [H]\beta_1{}^{H} \ldots [H]^{n}\beta_n{}^{jH}) \\ & - \log(1 + [OH]\beta_1{}^{OH} \ldots [OH]^{m}\beta_m{}^{OH})\end{aligned} \qquad (3)$$

Where $\beta_i{}^{H} = [H_iL]/[H]^i[L]$; $K_{ML} = [ML]/[M]\,[L]$, and $\beta_i{}^{OH} = [M(OH)_i]/[M]\,[OH]^i$

Values of K_{eff} for the system under study, defined by equation (*2*) (*i.e.*, without protonation or deprotonation reactions) are given in Table III.

It is apparent from Table III is that the Log(K_{eff}) is smaller by at least several orders of magnitude than the normal stability constant for each divalent metal/ligand combination. The HBED chelates become 7 orders of magnitude lower. Finally, there seems to be a general levelling effect resulting from the excess Ca(II) ion. For example, the difference in Log K_{ML} for Cu(II) TPP relative to Cu(II) CIT is 2.40, but the differece in Log K_{eff} for the same ligands is reduced to only 0.71. Similarly for Ni(II) with these ligands the corresponding differences are 1.40 and 0.29. Other metals follow a similar pattern.

Thus it is now clear why the presence of calcium ion in large concentrations yields a marked change in the speciation of the remainder of the trace metal ions under consideration. Thus it would not be surprising to find differences in metal ion behavior in bodies of water possessing different amounts of calcium(II) or magnesium(II). More specifically, in Table IV are listed the major species (> 10%) at pH 7 (as a model for fresh water) and pH 8.1 (at high Ca(II) concentration) for conditions that might approximate the situation in sea water.

The MHBED.H complexes at pH 7 remain about the same as in System I except for the Zn(II) complex, which increases by 22%. The ZnNTA complex becomes negligible, while CoHBED remains about the same. At the higher pH most of the MHBED complexes drop in concentration while the TREN complexes grow in importance. It is seen that the various Ca(II) complexes are forming nearly quantitatively at each pH when an excess of this metal ion is present, with the exception of the polyamine which has little Ca(II) affinity.

We wish to draw several conclusions from these results. This research first demonstrates that the computer programs employed have the capability of rapidly and efficiently calculating the concentrations of over one hundred individual species in complex systems of several metal ions and ligands from the

TABLE IV
Major species present[a] at pH 7 and pH 8.1.

	System I		System II	
Species	pH 7.0	pH 8.1	pH 7.0	pH 8.1
CuHBED.H	95	61	94	54
CoHBED.H	83	37	88	28
NiHBED.H	63	62	73	54
ZnHBED.H	55	28	77	16
ZnNTA	29			
NiHBED.H_2	20		26	
NiNTA	15			
CoHBED	13	72	13	70
CaTPP		34	93	99
ZnTREN		47	10	71
NiHBED		30		25
CaNTA		28	98	100
CuHBED		278		27
ZnHBED		23		14
CaCIT			97	97
CaHBED.H				25

[a] Numbers given are the percentage of the metal present in the form of the species indicated, except for Ca(II) in System II, where the percentage of the ligand in the Ca(II) complex is identified.

corresponding equilibrium parameters, as well as determining the variation of the species' concentrations as a function of pH and of component composition. In this way it now becomes possible to pick out the major species that are present under varying conditions of all the reacting species involved. The same principles also apply to much more complex environmental or other systems containing thousands of ligands and potentially hundreds of thousands of species. In view of the reliabilities and capacities of modern computers, the calculations do not pose any serious difficulities. The major limitation involved in the application of this technique is the need to obtain appropriate and accurate equilibrium parameters for all the significant complex species that may be formed in the environment. 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 separate reports.[3,4]

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