Inorganica Chimica Acta, *91* (1984) 25–31

Solution Studies of Systems with Polynuclear Complex Formation.
3. The Cadmium(II) Citrate System

INGMAR GRENTHE, PETER WIKBERG

Department of Inorganic Chemistry, The Royal Institute of Technology (KTH), S-100 44 Stockholm 70, Sweden

and EBBE R. STILL*

Department of Chemistry, Åbo Akademi, SF-20500 Åbo 50, Finland

Received June 18, 1983

Complex formation between Cd^{2+} and the citrate ion (H_3L = citric acid) in 2 mol l^{-1} $NaClO_4$ at 25 °C was investigated in the pH range 1.3 to 9.5. The experiments were carried out as potentiometric titrations using glass and cadmium amalgam electrodes. The cadmium concentration was varied from 1 to 6 mmol l^{-1} and the citrate concentration from 2 to 50 mmol l^{-1}. The experimental data can be explained by the formation of the complexes CdH_2L^+, $CdHL^0$, CdL^- and CdL_2^{4-} in acidic and neutral solutions and by the formation of the complexes $Cd_2H_{-1}L^0$, $Cd_2H_{-1}L_2^{3-}$, and $Cd_2H_{-2}L_2^{4-}$ in slightly alkaline solutions. The equilibrium constants were refined by the computer program LETAGROP version ETITR and the final values of the constants are given in Table III.

Introduction

The interconnection between toxic trace elements and the quality of the environment is of great concern for mankind. Heavy metals accumulate in biological systems and may reach toxic levels in various food chains when passing through the consumption chains associated with plant and animal life. The levels of the three heavy metals Cd, Hg, and Pb are considered to be of special importance in the environment. All three are known to be inhibitors of various enzyme reactions [1].

Cadmium is easily absorbed through the roots of important food crops [2, 3]. The rapid uptake and translocation of the metal in major grains is of concern as the metal has a tendency to be accumulated by mammals in the liver and kidneys. The retention of the metal ion is related to its binding in the zinc and cadmium protein metallothionein [4].

The general occurrence of citrate in plants and its ability to form chelates with most metal ions suggest that the ligand may play a role in transporting metals in the xylem fluid. The ligand has also been identified as a carrier of iron and other cations [5].

We have an interest in the complex formation between triply as well as quadruply ionized citrate and the metal ions that human beings come in contact with due to our industrial activities [6, 7].

In an extensive investigation of the cadmium citrate (H_3L = citric acid) system, Bottari [8] reported both mononuclear monoligand (CdL^-, $CdHL^0$, CdH_2L^+, CdH_3L^{2+}) and biligand (CdL_2^{4-}, $CdHL_2^{3-}$, $CdH_2L_2^{2-}$, $CdH_3L_2^-$, $CdH_4L_2^0$) complexes. A dimeric species, $Cd_2L_2^{2-}$, was introduced in order to explain the experimental data obtained at pH 7.2, but complexes with quadruply ionized citrate were not reported.

The cadmium complex formed with quadruply ionized citrate has been investigated by Meites [9], and by Patnaik and Pani [10]. It is shown that on formation the basic complex consumes one hydroxide ion *per* cadmium atom, and it is assumed that the complex is mononuclear. The value of the equilibrium constant of the reaction, $CdL^- \rightleftarrows CdH_{-1}L^{2-} + H^+$, varied in Meites' investigation between $10^{-8.8}$ and $10^{-8.4}$ (25 °C, varying ionic strength) in solutions with different total concentrations of metal ion and ligand, whereas a systematic drift around the mean value $10^{-8.3}$ (33 °C, 0.25 mol l^{-1} KNO_3) is observed in the paper by Patnaik and Pani. These trends may be an indication of an incorrect composition of the assumed deprotonated species.

A recent investigation of the lead(II) citrate system [11] reports a whole set of mononuclear and polynuclear complexes. Among the more important polynuclear complexes we find the dimers $Pb_2L_2^{2-}$, $Pb_2H_{-1}L_2^{3-}$ and $Pb_2H_{-2}L_2^{4-}$. Tri- and tetranuclear species were also included in the chemical model which gave the best fit to the experimental data.

The degree of polynuclearity of metal chelates may be governed mainly by the ligand (especially for stereochemical reasons), or by the cation. Of metal complexes with quadruply ionized citrate it is well

---

*Author to whom correspondence should be addressed.

0020-1693/84/$3.00

established that Cu(II) forms a dimeric species of the type $M_2H_{-2}L_2^{4-}$ [6]. Consequently, a dimeric species of the same type is a possibility in the Cd(II)–citrate system.

On the other hand, if we focus our attention on the cation, we can recognize the influence of the hydrolytic behaviour of the cation [12] in the structure of the Ni(II) complex of quadruply ionized citrate ion [13]. The crystal structure can be described as two clusters of $Ni_4OH(H_{-1}L)_3^{5-}$ containing a triply bridging hydroxide ion and the deprotonated hydroxyl oxygen atom of the ligands in a bridging configuration. The principal polynuclear hydrolysis product of nickel(II) is the tetramer, $Ni_4(OH)_4^{4+}$ [12]. It is often assumed that $Ni_4(OH)_4^{4+}$ has a structure similar to $Pb_4(OH)_4^{4+}$, in which the lead atoms are located at tetrahedral positions in the cage structure [12], and the similarity in structure of the two tetranuclear Ni(II) complexes is obvious. The complexes Cd_2OH^{3+} and $Cd_4(OH)_4^{4+}$ are the most prominent polynuclear hydrolysis products of Cd(II), and it follows that complexes with the composition $Cd_2H_{-1}L^0$ and $Cd_4(OH)(H_{-1}L)_3^{5-}$ are interesting alternatives.

Experimental

Symbols

The following symbols are used:

B, b = the concentration of total and free cadmium ions, respectively

H, h = the concentration of total and free hydrogen ions, respectively

A, a = the concentration of total and free citrate ions, respectively.

Citric acid in the text and in the equations is often denoted by H_3L.

The stability constant β_{pqr} for the general species $Cd_pH_qL_r^{2p+q-3r}$ is defined by the equation

$$pCd^{2+} + qH^+ + rL^{3-} \rightleftharpoons Cd_pH_qL_r^{2p+q-3r}$$

Chemicals and Solutions

Stock solutions were prepared from Mercks p.a. $HClO_4$, NaOH, Na_2CO_3, and citric acid ($C_6H_8O_7 \cdot H_2O$).

The $HClO_4$ solution was stantardized against HgO.

The NaOH solution was prepared from a 50% NaOH syrup allowed to stand for more than one week. The concentration of the solution was determined by titration with $HClO_4$ using phenolphtalein as indicator.

The $NaClO_4$ solution was prepared from perchloric acid and waterfree sodium carbonate. The 2.00 mol l^{-1} solution contained 0.04 mmol l^{-1} protolytic impurities and a proton excess of 0.133 mmol l^{-1}.

The $Cd(ClO_4)_2$ solution was prepared according to ref. 14 and analyzed both titrimetrically with EDTA and gravimetrically as $CdNH_4PO_4H_2O$. The results agreed within 0.1%. The proton excess of the stock solution was measured by titration with NaOH using Methyl Red as indicator.

The citric acid solution was prepared from crystals without purification. The acid lost its crystal water in a desiccator containing conc. H_2SO_4 and was analyzed by titration with NaOH. The samples were found to contain 99.5% of citric acid.

Experimental Technique

The measurements were carried out as potentiometric titrations at 25 ± 0.003 °C. In order to keep the ionic strength constant all solutions were made 2.00 mol l^{-1} of Na^+ ions by the addition of $NaClO_4$.

In all titrations both the free hydrogen ion (using an Ingold 201 glass electrode) and the free cadmium ion concentrations were measured. The cadmium amalgam electrode contained 0.01% of cadmium [15]. The amalgam was prepared in a vessel designed by Aladjoff [16]. The electrode showed a Nernstian response to the cadmium ion concentration in the investigated range, one to ten mmol l^{-1}.

The Ag/AgCl electrode used as a reference electrode was prepared according to Brown [17]. For the contact between the reference electrode and the solution a Wilhelm bridge was used [18]. The liquid junction potential of the system was found to be: $E_j = -27\ mV \times h\ mol^{-1}\ l$.

The titrations were performed using a computerized system. Equilibrium was assumed to be attained when the variation of the potential of the glass electrode was less than: 2×10^{-5} V/10 min in acid solution; 2×10^{-4} V/10 min in neutral and alkaline solutions due to limitations in the resolution of the digital voltmeter used.

All additions of titrant were made using two Metrohm dosimat E 412 burettes connected to the computer system.

In addition, potentiometric titrations with a cadmium-ion selective electrode [19] were performed in order to establish the composition of species formed under certain conditions.

Titration Procedure

Two different kinds of titration procedures were used.

In the first procedure both the total cadmium ion and the total citrate ion concentration were maintained constant throughout the titration. The titration started from an H/A ratio of about 4, and the pH of the solution was raised by the addition of strong base. The total ligand concentration was the same in the whole set of titrations. (The protonation constants of the ligand were determined in a titration where the total citrate ion concentration was the same as above). The total cadmium ion concentration was varied from one titration to another.

The second set of titrations was performed in two steps. A cadmium ion solution was titrated with a citrate solution containing a slight excess of hydrogen ions ($H/A \simeq 0.10$). The titration was continued until the excess of the ligand was 20 to 30-fold. Then a base titration was performed by addition of NaOH until a pH value of about 11 was reached.

Results

The Protonation Constants of the Citrate Ion

The protonation constants of the citrate ion were evaluated for the ionic medium used. The mathematical model applied to the experimental data included only mononuclear species. The constants were refined by the least squares program LETAGROP [20]. The final values are given in Table I together with the values reported by Bottari and Vicedomini [21] for the same ionic medium.

TABLE I. Protonation Constants of the Citrate Ion; Values Obtained in the Present Work and Values Reported in Ref. 21.

	Present work	Ref. 21
$\log \beta_{011}$	5.02 ± 0.02	5.18 ± 0.03
$\log \beta_{021}$	9.05 ± 0.02	9.34 ± 0.05
$\log \beta_{031}$	11.80 ± 0.02	12.24 ± 0.07

The protonation constants are determined in a solution of high ionic strength, 2.0 ml l^{-1} $NaClO_4$. Alkali ions have a tendency to form chelates with anions of high charge and a value $\log K(Na^+ + L^{3-} \rightleftarrows NaL^{2-}) = 0.70$ (25 °C, $\mu = 0.1$) has been reported [2]. It is tempting to compare protonation constants obtained in studies using different concentrations of $NaClO_4$ and try to explain the differences as due to sodium ion complexation. We assume that changes in ionic activity factors are negligible, as well as the influence of the reaction $Na^+ + HL^{2-} \rightleftarrows NaHL^-$. The calculation can be based on the concept of side reaction coefficients (α-coeff.) [23]. Table II contains $\log \beta_{011}$ as obtained in studies with three different concentrations of $NaClO_4$ (denoted by μ), the logarithmic value of the side reaction coefficient ($\log \alpha$), and the corresponding first protonation constant corrected for sodium ion complexation ($\log \beta_{011}{}^{corr} = \log \beta_{011} + \log \alpha$).

The remaining differences in the $\log \beta_{011}{}^{corr}$-values in column 4 can be attributed to the influence of ion-solvent interactions. Calculations assuming reasonable values for the ionic interaction coefficients have been performed, and they explain the trend in column 4 (whereas the trend in the $\log \beta_{011}$-values of column 2 will be enlarged).

TABLE II. The Experimentally Obtained and the Corrected First Protonation Constant of the Citrate Ion at Three Different Concentrations of $NaClO_4$.

μ	$\log \beta_{011}$	$\log \alpha$	$\log \beta_{011}{}^{corr}$	
1.0	5.17	0.78	5.95	Ref. 11
2.0	5.02	1.04	6.06	Present work
3.0	4.88	1.21	6.09	Ref. 24

The calculations given in Table II show the influence of sodium citrate complex formation. We want to underline that not only does the protonation constant β_{011} have to be corrected by a factor α but also the stability constants of all metal citrate complexes in order to be comparable. For example, if we want to compare the stability of the lead citrate complexes determined in 1 mol l^{-1} $NaClO_4$ with the corresponding cadmium ones determined in 2 mol l^{-1} $NaClO_4$ we must recognize that the sodium ion complexation of the ligand amounts to about 0.2 or 0.3 logarithmic units (column 3 in Table II). In addition, we have to estimate the influence of ion-solvent interactions.

The Cadmium Citrate Complexes

The mass balance equations will give

$$B = b + \sum_p \sum_q \sum_r p\beta_{pqr} b^p h^q a^r \tag{1}$$

$$H = h + \sum_p \sum_q \sum_r q\beta_{pqr} b^p h^q a^r \tag{2}$$

$$A = a + \sum_q \beta_{0q1} h^q a + \sum_{p \neq 0} \sum_q \sum_r r\beta_{pqr} b^p h^q a^r \tag{3}$$

We prefer to use two summation terms in eq. (3) as

$$a + \sum \beta_{0q1} h^q a = a(1 + \beta_{011} h + \beta_{021} h^2 + \beta_{031} h^3) \tag{4}$$

where the expression in parenthesis can be calculated for a given pH value ($= \alpha_{L(H)}$ in Ringbom's notation [23]).

The principles of predominating species can be applied to specific parts of the titrations in order to get estimates of the equilibrium constants. As an example, in the neutral and slightly acidic pH range the mononuclear complexes CdL^- and $CdL_2{}^{4-}$ will predominate. Equation (1) can then be written

$$(B/b - 1)/a = \beta_{101} + \beta_{102} a \tag{5}$$

A plot of $(B/b - 1)/a$ as a function of a will give β_{101} as the intercept and β_{102} as the slope of a straight line.

A first approximation of the free ligand concentration was calculated from the equation

$$(1 + \sum_q \beta_{0q1} h^q) a = A - 2(B - b) \tag{6}$$

A corrected value of the free ligand concentration was calculated using the estimates of the equilibrium constants and an improved linear relationship (5) was thus obtained.

In more acidic solutions (pH < 3.5) the species $CdHL^0$ and CdH_2L^+ will be the predominating ones. Equation (1) can then be written

$$(B/b-1)/(ha)=\beta_{111}+\beta_{121}h \qquad (7)$$

A plot of (B/b – 1)(ha) *vs.* h will give β_{111} as the intercept and β_{121} as the slope.

Bottari [8] reports a dimeric species, Cd_2L_2, in solutions of pH 7.2. A binuclear monoligand complex, Cd_2L^+, may also be formed as the ligand in the CdL^- complex for steric reasons has at least one free carboxylate group and the hydroxyl group may act as a bridging group.

The existence of the mentioned binuclear complexes was investigated in a titration with a slight excess of cadmium ions. The titration data could fairly well be explained by the complex CdL^- alone and an introduction of the complexes $Cd_2L_2{}^{2-}$ and Cd_2L^+ seemed to be superfluous. The limited solubility of the cadmium citrates in this medium made, however, a further increase of cadmium and citrate concentrations impossible.

In the alkaline range deprotonated and/or ternary complexes with OH^- start to predominate. The titration procedure chosen in our investigation (see above) and the low solubility in the weakly acidic pH-range made it nececessary to use a large excess of the ligand. The experimental data indicated that polynuclear complexes $Cd_pH_{-q}L_r{}^{(2p-q-3r)+}$ are formed. Literature reports [8, 9], and titrations carried out at constant alkaline pH-values show that $q \simeq p$, and the polynuclear complex is written $Cd_pH_{-p}L_r{}^{(p-3r)+}$.

The values of p, r, and β_{p-pr} were determined from three titrations with differing concentrations of both cadmium and citrate ions and with different B/A ratios. The predominating species are $CdL_2{}^{4-}$ and $Cd_pH_{-p}L_r{}^{(p-3r)+}$, and in a first approximation only these species were considered in our equilibrium model. For the calculations the corresponding approximations were introduced in the mass balance equations.

The equilibrium models tested on the experimental data contained in the first instance only one polynuclear complex with quadruply ionized citrate ion. The dominant complex was assumed in turn to be $Cd_2H_{-2}L_2{}^{4-}$, $Cd_3H_{-3}L_3{}^{6-}$, $Cd_3H_{-3}L_2{}^{3-}$, $Cd_4H_{-4}L_4{}^{8-}$ and $Cd_4H_{-4}L_3{}^{5-}$. The complex $Cd_2H_{-2}L_2{}^{4-}$ was rejected due to a systematic drift in the value of β_{2-22}. The best agreement between the titrations was obtained for a model with $Cd_3H_{-3}L_2{}^{3-}$ or $Cd_4H_{-4}L_3{}^{5-}$ as the major polynuclear species.

The following step was to consider an alternative model with two or three polynuclear species present in alkaline solution. A Cd-selective electrode was used in the potentiometric titrations carried out at a constant pH-value. Fig. 1 shows the titration of citrate ion of a concentration of 0.02 mol l^{-1} and 0.005 ml l^{-1}, respectively, with a Cd^{2+} solution at pH ≃ 8.12 (μ = 0.1 (KNO_3)). The two titration curves intersect each other at a titration ratio of about 1.0. A titration of a 0.01 mol l^{-1} citrate solution (not shown in the figure) had an intermediate course intersecting the titrations shown in Fig. 1 at about the same titration ratio.

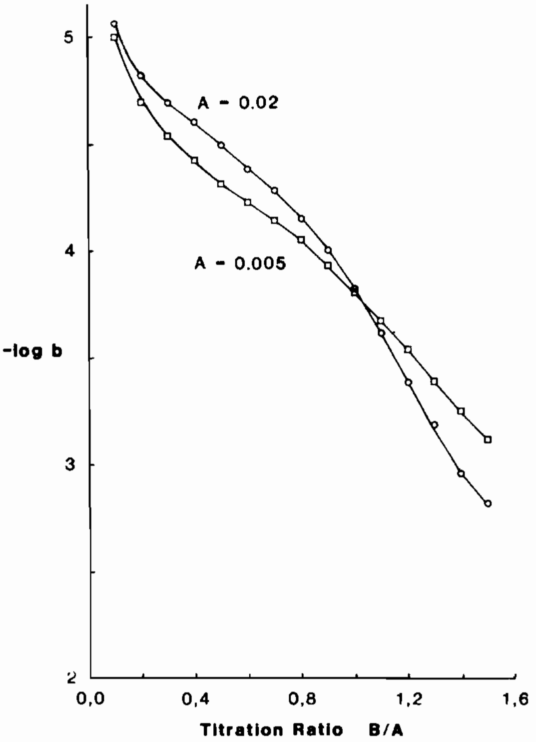

Fig. 1. Titration of 50 ml of 0.02 mol l^{-1} citrate with 0.20 mol l^{-1} $Cd(NO_3)_2$ (–o–), and titration of 50 ml 0.005 mol l^{-1} citrate with 0.05 mol l^{-1} $Cd(NO_3)_2$ solution (–□–) at pH ≃8.12, μ = 0.1 (KNO_3), 25 °C. The figure shows recorded –log b values as a function of titration ratio, B/A.

The lower part of Fig. 2 shows the same titrations as in Fig. 1, but the abscissa is now corrected for the amount of free Cd^{2+} ions in solution. The figure shows the influence of dilution on the course of the titration. With an excess of metal ion in solution the titration curves coincide, which means that the solution behaves as a metal buffer on dilution. If we assume a single complex species dominating in solution it follows (see ref. 6, eq. (10) and the subsequent text) that the metal complex contains only one molecule of citrate as ligand. Consequently, the metal: ligand ratio in the complex can be assumed to be 2:1 and the complex can be written $Cd_2H_{-s}L^{(1-s)+}$.

In solutions containing an excess of ligand (B/A < 1) we observe an increase of free metal ion concentra-

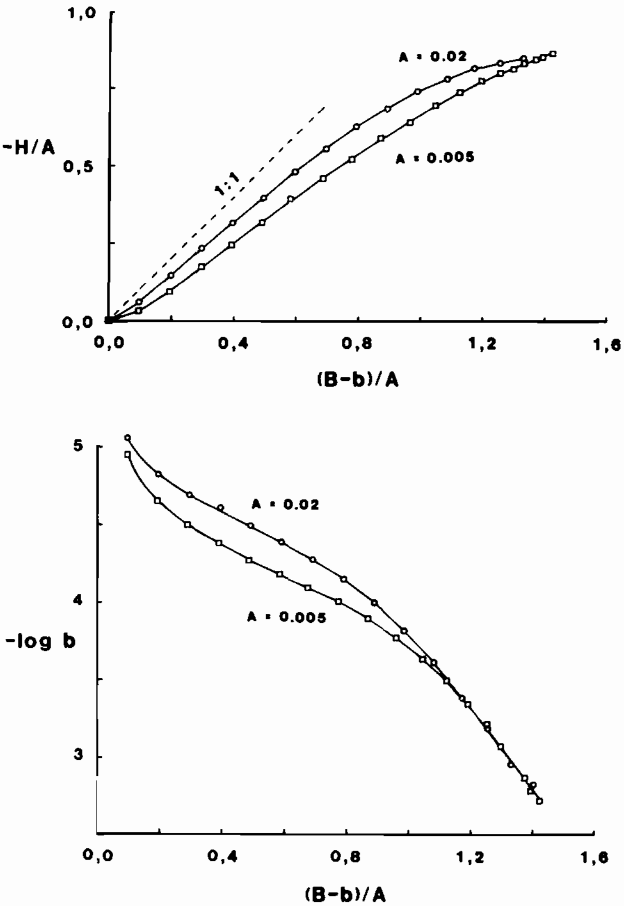

Fig. 2. The figure shows the same titrations as in Fig. 1 but the abscissa is now corrected for the amount of free Cd^{2+} ions in the solution. The upper part of the figure shows the consumption of base required to keep the pH value of the solution constant on addition of cadmium salt solution.

tion on dilution. Such behaviour is an indication of polynuclear complex formation and the spacing between the curves ($\Delta \log b/\Delta \log B$ at constant B/A ratio and constant pH) is a measure of the degree of polymerisation. In the system in question we obtain for the trimer $Cd_3H_{-3}L_3^{6-}$ a theoretical spacing of $-2/3$, for the dimer $Cd_2H_{-2}L_2^{4-}$ the differential quotient will be $-1/2$, whereas for a monomer the value will be 0 and if no complexation occurs the value will be +1. For the other polynuclear species discussed earlier we obtain a spacing of $-1/3$ for $Cd_3H_{-3}L_2^{3-}$ and $-1/2$ for $Cd_4H_{-4}L_3^{5-}$. We observe that the spacing will not give a unique solution for the composition of the complex.

The upper part of Fig. 2 shows the consumption of base that is required to keep the pH constant on addition of the Cd^{2+} salt solution. The total amount of base added at the end of the titration approaches the value 1.0 and the binuclear monoligand complex is written $Cd_2H_{-1}L^0$. The dotted line at the beginning of the titration indicates the theoretical consumption with a predominating complex $Cd_pH_{-p}L_r^{(p-3r)+}$ in solution. The figure shows that at this pH-value we have considerable amounts of cadmium complexed with triply ionized citrate in solution. It follows that the spacing between the titration curves shown in the lower part would have a spacing that is slightly lower than the theoretical one predicted above by assuming complexes formed with the deprotonated ligand.

A rise in pH will cause a higher percentage of hydrolysed complexes and dilution experiments were performed at a pH of 9.0 with a B/A ratio of 2/5. The experiments gave a spacing of *ca.* -0.5 and the two possible complexes are $Cd_2H_{-2}L_2^{4-}$ and $Cd_4H_{-4}L_3^{5-}$. The titrations in Figs. 1 and 2 indicate a 1:1 metal:ligand ratio and the stoichiometry of the complex was settled by a titration at pH 8.90 given in Fig. 3. The figure shows a Cd:OH ratio of 1:1, and the potential jump at $B/A \simeq 1.0$ gives a metal:ligand ratio of 1:1 (the potential jump was accompanied by a precipitation reaction which may obscure the results). The predominating complex under these conditions seems to be the dimer $Cd_2H_{-2}L_2^{4-}$.

Titrations using the cadmium amalgam electrode were also performed in order to establish the composition of the deprotonated species in solution. The total concentration of cadmium and citrate as well as the pH of the solution was varied as widely as possible. The experimental data were best explained by the formation of the complexes $Cd_2H_{-1}L^0$, $Cd_2H_{-1}L_2^{3-}$, and $Cd_2H_{-2}L_2^{4-}$. With three binuclear species in the mathematical model no evidence was found for any higher polymerised species. These titrations were especially designed to establish the composition of the deprotonated species and were not used in the final refinement of the constants due to experimental difficulties in the E_0 titration. (The titrations further showed that the reaction $Cd_2H_{-1}L^0 + L^{3-} \rightarrow Cd_2H_{-1}L_2^{3-}$ is extremely slow).

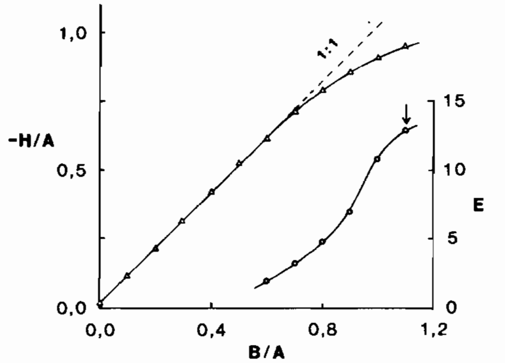

Fig. 3. Titration of 50 ml 0.01 mol l^{-1} citrate with 0.1 mol l^{-1} $Cd(NO_3)_2$ at pH = 8.90. The figure shows the recorded potential (E in mV) of the Cd-electrode and the consumption of base required to keep pH $\simeq$8.90 as a function of titration ratio. The arrow indicates visible precipitation.

The equilibrium model was refined by the least squares program LETAGROP [20]. At first the constants β_{121} and β_{111} were refined from titration data where pH < 4, and all the other constants from the region where pH > 5.5. In the final refinement all constants were fitted simultaneously to all (180) titration points evenly distributed over the investigated pH-range. The results are presented in Table III.

TABLE III. The Final Equilibrium Reactions and Equilibrium Constants Valid in 2 mol l^{-1} $NaClO_4$ at 25 °C.

pqr	Reaction	$\log \beta_{pqr} \pm 3\sigma$
011	$H^+ + L^{3-} \rightleftarrows HL^{2-}$	5.02 ± 0.02
021	$2H^+ + L^{3-} \rightleftarrows H_2L^-$	9.05 ± 0.02
031	$3H^+ + L^{3-} \rightleftarrows H_3L^0$	11.80 ± 0.02
101	$Cd^{2+} + L^{3-} \rightleftarrows CdL^-$	2.67 ± 0.03
111	$Cd^{2+} + H^+ + L^{3-} \rightleftarrows CdHL^0$	6.7 ± 0.1
121	$Cd^{2+} + 2H^+ + L^{3-} \rightleftarrows CdH_2L^+$	10.1 ± 0.2
102	$Cd^{2+} + 2L^{3-} \rightleftarrows CdL_2{}^{4-}$	4.46 ± 0.02
2–11	$2Cd^{2+} + L^{3-} \rightleftarrows Cd_2H_{-1}L^0 + H^+$	max. 1.5
2–12	$2Cd^{2+} + 2L^{3-} \rightleftarrows Cd_2H_{-1}L_2{}^{3-} + H^+$	max. 0.7
2–22	$2Cd^{2+} + 2L^{3-} \rightleftarrows Cd_2H_{-2}L_2{}^{4-} + 2H^+$	– 5.94 ± 0.04

The distribution of the different cadmium citrate complexes in a solution containing 1 mmol l^{-1} cadmium ion and 10 mmol l^{-1} citrate is presented as a function of pH in Fig. 4. A notable concentration of the complex $Cd_2H_{-1}L^0$ can be observed at this rather large excess of the ligand.

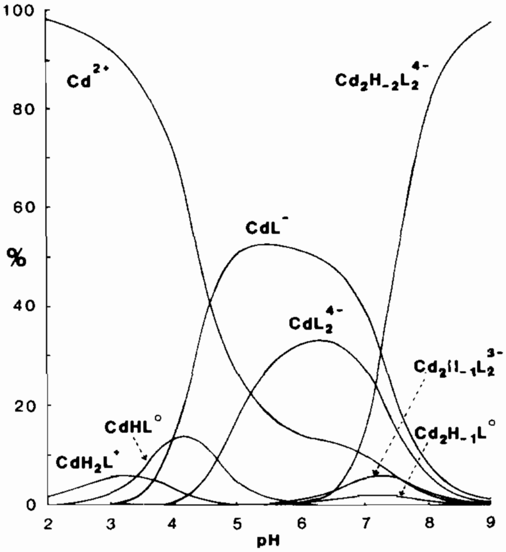

Fig. 4. The distribution of cadmium ion on different species as a function of pH. B = 0.001 mol l^{-1}, A = 0.010 mol l^{-1}. HALTAFALL [14] was used for the calculations taking the equilibrium constants from Table III.

Discussion

The equilibrium constants obtained for the mononuclear complexes in this study are in agreement with those reported by Bottari [8]. The investigation shows weak complex formation between Cd^{2+} and the citrate ion. A result of the weak complex formation is that protonation of the complex starts at rather high pH-values. The protonation of the metal complex and the protonation of the ligand occur in parallel. This behaviour is illustrated in Fig. 5 for the mononuclear monoligand lead(II) and cadmium(II) citrate complexes. It is also not surprising that all combinations of CdH_qL_r for q = 0, 1,..., 2r and r = 1, 2 can be found in solutions of high citrate concentration [8].

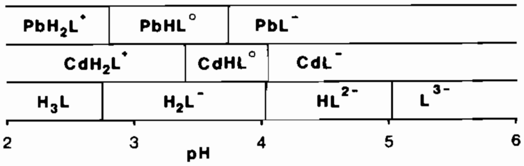

Fig. 5. Predominance diagram for protonated products of PbL^-, CdL^-, and L^{3-} as a function of pH.

In general, the stability of Pb^{2+}-complexes is greater than that of the corresponding Cd^{2+}-complexes (even if the ionic radius of Pb^{2+} is greater than that of Cd^{2+}). A comparison of the stability of the corresponding species in the two metal citrate systems shows an enhanced stability for the lead(II)–citrate complexes amounting to more than one logarithmic unit per metal atom.

Citric acid may serve as a model ligand for humic and fulvic acids in their metal binding ability. An example is the stability of the cadmium(II) and lead(II) complexes of soil-derived fulvic acid (SFA) for which the following values are reported [25, 26] (μ = 0.1 (KNO_3), 25 °C):

$$\text{pH} = 4.0 \quad \log \beta_{Cd-SFA} = 3.2 \quad \log \beta_{Pb-SFA} = 4.0$$

$$\text{pH} = 6.0 \quad \log \beta_{Cd-SFA} = 4.1 \quad \log \beta_{Pb-SFA} = 5.1$$

The ligand can be monodentate, bidentate or tridentate in its metal complexes. In the last two cases the metal coordination involves the central hydroxyl and carboxyl groups [27]. In the solid state these groups of citric acid lie in a plane perpendicular to the plane of the citrate backbone and this coplanarity is preserved in its metal chelates. Hydrogen bonding between the central hydroxyl and carboxyl groups stabilizes the planar conformation of citric acid. In the chelates the cation lies close to the position of this hydrogen atom facilitating the bidentate action of the ligand [27], and the metal atom can be compared to the hydrogen atom in the intramolecular hydrogen bond.

Citrate is considered to be transported through cell membranes in the form HL^{2-}. For conformational reasons outlined above we can speculate that metal citrate complexes can be transported by the same mechanism. The ligand has only oxygen atoms as donor atoms and, consequently, the selectivity of the ligand for metal cations is poor.

People concerned about metal ion pollutants in the environment have found that many animals accumulate doses several thousand times greater than their surroundings and that the metals are concentrated in relatively few tissue types. In the case of the snail *Helix aspersa* certain cells in the hepatopancreas contain intracellular granules that are sites of metal–ion accumulation [28, 29]. A wide variety of trace elements including Cr, Mn, Fe, Co, Zn, Cd, and Pb have been reported to be incorporated into the Ca^{2+} and Mg^{2+} containing phosphate and pyrophosphate granules. The citrate ion is a possible candidate as a transporting ion as citrate meets the following criteria [29]: it is present in the cytoplasm of living cells, can pass through membranes, has little discrimination in its complexing ability towards cations, and is a good coagulating agent (an electrolyte with a high charge).

Competitive interactions between essential elements and toxic metals are important factors in trace element requirements and toxicities. Known antagonists to Cd^{2+} are Ca^{2+} and Zn^{2+}, but also copper and iron [30]. It is known that an elevated Cd intake can adversely affect the Ca metabolism [3], whereas a small deficiency of copper enhances the toxicity of cadmium [30]. The cadmium uptake by plant roots can be diminished by the competitive effect of Ca^{2+} brought about by liming [2] exemplifying the general rule that the ratio of micro- and macronutrients is of importance. In these systems the concentration of the metal ions and the stability of the citrate complexes with Ca^{2+}, Zn^{2+}, and Cd^{2+} are of interest.

Our potentiometric measurements show that deprotonated binuclear Cd(II)–citrate complexes are formed. One of the aims of the present study was to establish the degree of polynuclearity of the Cd^{2+} complexes with quadruply ionized citrate ion. The presence of dimeric species in the cadmium(II) citrate system, as well as in other metal citrate systems, shows that in these systems the extent of polymerisation is governed by the ligand.

Acknowledgements

The authors are greatly indebted to Techn. Lic. Kjell Blomqvist for performing the titrations with the Cd-selective electrode, to Ph.D. Olof Wahlberg for advice in the use of the Cd-amalgam electrode, and to Ph.D. Tom Wallin for introducing P.W. to the computerized titration system available at The Royal Institute of Technology. Financial support to P.W. from the H. F. Arwidson Foundation (Åbo Akademi) and the Research Institute of the Åbo Akademi Foundation is gratefully acknowledged.

References

1 R. J. P. Williams, *Endeavour, 26*, 96 (1967).
2 J. V. Lagerwerff, in 'Micronutrients in Agriculture', Eds. J. J. Mortvedt, P. M. Giordano and W. L. Lindsay, pp. 593–636, Soil Sci. Soc. Am., Madison (1972).
3 E. J. Underwood, 'Trace Elements in Human and Animal Nutrition', 4th Ed., Academic Press, New York (1977).
4 M. Margoshes and B. L. Vallee, *J. Am. Chem. Soc., 79*, 4813 (1957).
5 L. O. Tiffin, in 'Micronutrients in Agriculture', Eds. J. J. Mortvedt, P. M. Giordano and W. L. Lindsay, pp. 199–299, Soil Sci. Soc. Am., Madison (1972).
6 E. R. Still and P. Wikberg, *Inorg. Chim. Acta, 46*, 147 (1980).
7 E. R. Still and P. Wikberg, *Inorg. Chim. Acta, 46*, 153 (1980).
8 E. Bottari, *Ann. Chim. (Rome), 65*, 593 (1975).
9 L. Meites, *J. Am. Chem. Soc., 73*, 3727 (1954).
10 R. K. Patnaik and S. Pani, *J. Ind. Chem. Soc., 34*, 673 (1957).
11 L. G. Ekström and Å. Olin, *Chemica Scripta, 13*, 10 (1978/79).
12 C. F. Baes, Jr. and R. E. Mesmer, 'The Hydrolysis of Cations', Wiley-Interscience, New York (1976).
13 J. Strouse, S. W. Layten and S. E. Strouse, *J. Am. Chem. Soc., 99*, 562 (1977).
14 G. Biedermann and L. Ciavatta, *Acta Chem. Scand., 16*, 2221 (1952).
15 O. Wahlberg, personal communication.
16 I. Aladjoff, *Acta Chem. Scand., 23*, 1825 (1969).
17 A. S. Brown, *J. Am. Chem. Soc., 56*, 646 (1934).
18 W. Forsling, S. Hietanen and L.-G. Sillén, *Acta Chem. Scand., 16*, 901 (1952).
19 E. H. Hansen, C. G. Lamm and J. Ruzicka, *Anal. Chim. Acta, 59*, 403 (1972).
20 P. Brauner, L.-G. Sillén and R. Whiteker, *Arkiv Kemi, 31*, 365 (1969).
21 E. Bottari and M. Vicedomini, *J. Inorg. Nucl. Chem., 35*, 1657 (1973).
22 G. A. Rechnitz and S. B. Zamochnick, *Talanta, 11*, 106 (1964).
23 A. Ringbom, 'Complexation in Analytical Chemistry', Wiley-Interscience, New York (1963).
24 A. F. Donde and A. M. Giuliani, *Ricerca Sci., 33* (II-A), 819 (1963).
25 R. A. Saar and J. H. Weber, *Can. J. Chem., 57*, 1263 (1979).
26 R. A. Saar and J. H. Weber, *Environ. Sci. Technol., 14*, 877 (1980).
27 J. P. Glusker, *Acc. Chem. Res., 13*, 345 (1980).
28 B. Howard, P. C. H. Mitchell, A. Ritchie, K. Simkiss and M. Taylor, *Biochem., J., 194*, 507 (1981).
29 K. Simkiss, *TIBS*, April 1981, p. III.
30 C. F. Mills, *Chem. Brit.*, 512 (1980).