Nickel (II) - Citric Acid Complex Formation in Aqueous Solution

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Abstract

Titrimetric analysis of solutions of nickel(II) chloride and citric acid, H_3L, has led to the characterization of four complexes in the acidic pH range NiL^-, $NiHL$, NiH_2L^+, and NiL_2^{4-}.

Equilibrium constants for the formation of these complexes are reported. Results from a visible spectrophotometric study are analysed in terms of these four complexes.

The stability and possible structures of the complexes are discussed and compared with other nickel-carboxylic acid complexes.

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Introduction

Nickel (atomic number 28) is a member of the first transition series of elements. This series includes the elements vanadium, chromium, manganese, iron, cobalt and copper, all of which are considered as essential elements for plant and animal nutrition (1-5). Nickel and titanium are the only members of this series of elements not yet universally considered as essential, although there is mounting evidence that nickel may be essential (2, 6-10, 100).

1.1 NICKEL IN VEGETATION

Nickel is ubiquitous in the earth and its waters. It constitutes about 0.008% of the earth's crust, the highest levels being found in igneous rocks, which average approximately 0.1% nickel. Of the igneous rocks, the ultrabasic rocks provide the principal sources of nickel. These rocks are high in magnesium and iron, but contain little silica, and the nickel level varies from 0.016% in basalt up to an average of 0.20% in peridotite (11).

Rocks forming the upper part of the earth's crust supply most of the material from which the soils are formed, and therefore the composition of the soils depends on the composition and distribution of various rock types. Farm soils throughout the world contain nickel in the range 0.0003 to 0.1% (11). The higher levels of nickel are found in soils of ultrabasic origin (92), and levels of nickel in soils derived from serpentinite and peridotite substrates have been reported as high as 0.8% (12, 13).

Nickel is widely distributed in plant tissues and has long been considered a normal constituent (14). The nickel concentration in most natural vegetation is in the range 0.05 to 5 ug/g on a dry weight basis (15). Nickel is normally toxic at levels greater than 50 ug/g (15), and the desire to make fertile large areas of barren ultrabasic land has led to wide research on the toxicity of nickel. This field has recently been reviewed by Mishra and Kar (14). All trace elements found in plant and animal tissues, whether essential or not, result in symptoms of toxicity. Nickel is no exception. Symptoms of nickel toxicity include: chlorosis of the leaves, necrosis, stunted growth of roots and shoots, deformation of various plant parts, unusual spottings; and are usually accompanied by a host of growth abnormalities (14).

Several plant species are known to thrive in ultrabasic soils and generally accumulate nickel to abnormally high levels, levels far in excess of those considered toxic. These species form a unique group of plants and there has been interest in their plant chemistry as a result of this accumulation. Brooks (16), has reviewed the accumulation of nickel by plants and has listed thirty-five species which are regarded as hyperaccumulators; that is, the nickel content of the dried leaf material is greater than 0.1%. Several of these species are recorded in Table 1.1, along with several non-accumulating species found over similar substrates. Most of these species are of the genera Alyssum and Homalium. Recent work has resulted in the discovery of further Alyssum accumulators and identified a further genus, Phyllanthus, as a dominant hyperaccumulator (17, 18). These three genera account for about two thirds of the nickel-accumulating species, leaving the other third spread roughly evenly throughout about a dozen other genera.

The geographical distribution of the species is also of interest, in that the Alyssum hyperaccumulators are to be found almost exclusively over the serpentine substrates of the Eastern Mediterranean, and the Homalium and Phyllanthus

Table 1.1 Representative Nickel-Accumulating Plant Species

1. Non-Accumulating

Species	ug/g Ni dry weight	Reference
Hebe odora	11.6	29
Cassinia vauvilliersii	12.0	29
Leptospermum scoparium	8.6	29
Artemisia scoparia	10.0	14
Avena sativa	7.2 - 30 [1]	14
Spinnacia oleraca	4.2	14

2. Hyperaccumulators

Species	ug/g Ni dry weight	Reference
Homalium francii	14500	32
mathienanum	1694	32
kanaliense	9420	32
Hybanthus austrocaledonius	13750	32
Alyssum alpestre	3640	17
bertolonii	13400	17
corsicum	10000	17
Rinorea bengalensis	17500	16
Psychotria dovarrei	47000	16
Sebertia accuminata	11700 [2]	12

1. Plants showed signs of nickel toxicity.
2. Latex was 25.7% Ni on a dry weight basis.

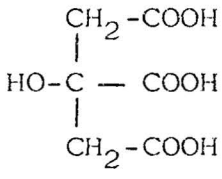
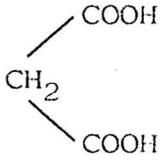
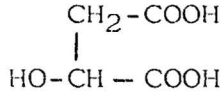
species over similar ultrabasic soils in New Caledonia. Other accumulating species have been found sparingly in South East Asia, Western Australia, and Central Africa.

Plant species which survive in hostile environments are able to do so as a result of tolerance mechanisms. These mechanisms generally take the form of either rejection of the metal so that no nickel is absorbed by the roots; or the storage of the metal at a particular site where it may be sequestered by complexation with naturally occurring ligands (30).

In the case of the nickel accumulators, the former mechanism is obviously not operating. There is evidence that nickel is readily absorbed by the plants as the divalent hexaquo-cation, and is not strongly absorbed when chelated (14). The absorption of nickel by plants is regulated by: (a) the total amount of available nickel in the soil; and (b) the properties of the soil, notably pH and organic matter content. These two conditions appear to be interdependent, in that the soil conditions regulate the amount of exchangeable nickel present.

Once absorbed by the plant, the nickel is probably complexed immediately in order to reduce its toxicity. Nickel is known to form chelate complexes with proteins, amino acids and organic acids (53, 89). Unidentified anionic complexes of nickel occur in xylem exudates of such plants as tomato, cucumber, corn, carrot and peanut (19). Tiffin found that iron (III) in several plant exudates showed the same electrophoretic behaviour as anionic iron (III)-citrate complexes, but suggested that amino acids may act as carriers for nickel, as nickel shows a particular affinity for nitrogen containing ligands (20, 21). However, no association between nickel and amino acids was found in studies of Hybanthus species from New Caledonia (22). Recent work on a number of Alyssum species suggests that the nickel is bound to the dicarboxylic acids, malic and malonic acids (23, 24,25,). The presence of an anionic citrato complex of nickel has been suggested in several species of the genera Sebertia,

Figure 1.1 The Structure of Carboxylic Acids Implicated in Studies of Nickel-Accumulating Plants

Common Name	Structure	Systematic Name [103]
Citric acid		2-hydroxy 1,2,3 propane-dicarboxylic acid
Malonic acid		methane-dicarboxylic acid
Malic acid		hydroxy-1,2 ethane dicarboxylic acid

Hybanthus, Homalium and Geissois, all from New Caledonia (16, 25,26,27). Spectral results suggest that in the hyperaccumulators where the nickel/citric acid ratio is generally greater than one, a 1:1 nickel:citrate species exists.

There is some speculation that the nickel is not immediately chelated by citric acid, although it is probably stored as such (27). If the nickel is translocated as the citrato complex, then unless the plant has other specific mechanisms for the exclusion of both copper and iron, one would expect these two elements to be accumulated also, as they form chelate complexes with citrate of greater stability. This assumes that the stability of the complex is important in translocation. However, this may not necessarily be so. A carrier and exchange mechanism for the uptake and storage of nickel has been suggested (27). A similar mechanism has been postulated for zinc resistant plants (28). However, this suggestion appears to overlook the availability of the metal ions for the uptake by the roots. The pH of serpentinite substrates is near neutral (pH is in the range 6.5 to 7.0) (29), hence the concentrations of the aquo ions of iron (III) and copper (II) will be considerably reduced because of the formation of hydroxides. In vitro, nickel hydroxide does not precipitate until a much higher pH than do iron (III) and copper hydroxides (90).

Due to these suggestions of the possible role of nickel-citrate complexes in some of the nickel-accumulating plant species, it was considered that a more complete study of nickel and citric acid complex formation would be in order.

1.2 FORMATION OF NICKEL-CITRATE COMPLEXES IN AQUEOUS SOLUTION

A complex may be defined as a species formed by the association of two or more simpler species, each capable of independent existence in solution (31). Each complex has a certain stability which describes the degree of association which occurs in a solution containing the species in equilibrium. Quantitatively, the stability of a complex ML is defined by the equilibrium constant for the reaction.

$$M + L \rightleftharpoons ML$$

where M and L are the free metal and ligand respectively. Then

$$K^{\circ} = \frac{a_{ML}}{a_M a_L}$$

where K° is the thermodynamic equilibrium constant and a_i is the activity of the species. Now $a_i = \gamma_i C_i$, where C_i is the concentration of species i, and γ_i is the activity coefficient of the species relating the concentration to the activity. Therefore

$$K^{\circ} = \frac{C_{ML}}{C_M C_L} \cdot \frac{\gamma_{ML}}{\gamma_M \gamma_L}$$

$$= K_C \cdot \frac{\gamma_{ML}}{\gamma_M \gamma_L}$$

where K_C is the concentration quotient for the reaction. As γ_i is a function of the solution's total ionic strength, K° and K_C are related by a function of ionic strength, I. i.e.

$$K^{\circ} = f(I)\ K_C$$

Concentration quotients are generally determined from studies containing relatively large concentrations of some inert electrolyte, in order to maintain as near constant ionic strength as possible. This background electrolyte must not form insoluble species or complexes with the

reactants under study. The thermodynamic equilibrium constant may then be determined by extrapolation to infinite dilution (I=0) of concentration quotients, determined at a number of ionic strengths. In this work however, the equilibrium constants for all species are those concentration quotients determined in a background of potassium chloride to bring the total ionic strength to 0.1 M.

The formation of complexes between nickel and citric acid is complicated in that citric acid has three acidic protons, and hence, there is scope for the formation of protonated complexes. If citric acid is considered to be a triprotic acid, H_3L, where L^{3-} is the citrate ion (see Section 3.1 for discussion on ionization of the fourth proton), and M the metal (in this case nickel), then the following reaction scheme summarizes the equilibria under consideration in the pH range 3 to 8:

$$p\,M + r\,H_qL \rightleftharpoons M_pH_{rq}L_r$$

Here, and in subsequent equilibrium and mathematical expressions, charges have been omitted for clarity.
The equilibrium constants for this scheme are of the form:

$$K_C = \frac{[M_pH_{rq}L_r]}{[M]^p\,[H_qL]^r}$$

Two examples from the general scheme are:

$$M + HL \rightleftharpoons MHL$$

Then $p = q = r = 1$ and

$$K^M_{MHL} = \frac{[MHL]}{[M]\,[HL]}$$

Similarly, for

$$2\,M + 2\,HL \rightleftharpoons M_2H_2L_2$$

$$K^M_{M_2(HL)_2} = \frac{[M_2(HL)_2]}{[M]^2\,[HL]^2}$$

Other equilibria relating various complex species can be characterized with knowledge of the protonation constants of the free ligand.

For example, for the equilibrium

$$ML + H \rightleftharpoons MHL$$

$$K^{ML}_{MHL} = K^{M}_{MHL} \cdot k^{L}_{HL}$$

Nickel-citric acid complexes of the stoichiometry MH_2L^+, MHL, ML^-, $MH_{-1}L^{2-}$, and ML_2^{4-} have been characterized, and stability constants for some reported (34-43, 53). Note that $MH_{-1}L^{2-}$ is a complex species where either the hydoxy proton, or a proton from a co-ordinated water molecule, has been displaced (46). Most of the studies were done at a temperature of 25°C, with experiments being conducted over a wide range of electrolyte backgrounds, including KNO_3, $NaClO_4$ and NaCl. The reported equilibrium constants are shown in Table 1.2.

Field et al, (34), carried out potentiometric experiments using a glass electrode to determine the hydrogen ion concentration. Mixtures of nickel nitrate and citric acid, at ratios of nickel to citric acid greater than one, were studied. The experimental data was analysed in terms of the complex species ML^- and MHL, and it was reported that no evidence for the existence of MH_2L^+ could be found. However, the point was made that if the equilibrium constant was small, then the species may well be present in too low a concentration for it to be detected under their experimental conditions.

An earlier study (35) reported the species MH_2L^+, along with ML^- and MHL, in solutions over a range of nickel-citric acid ratios. The pH was measured using a glass electrode with calomel reference electrode. However, it was then assumed that the measured pH was the negative logarithm of the hydrogen ion concentration and this would impart a systematic error as described in Section 2.4.

Another study has reported equilibrium constants for ML^- and MHL calculated from titration data where nickel was

Table 1.2 Reported Equilibrium Constants of Complexes of Nickel and Citric Acid at 25 °C

Background Electrolyte	$\log K^{M}_{ML}$	$\log K^{M}_{MHL}$	$\log K^{M}_{MH_2L}$	Reference
NO_3^-, 0.1 M	5.50	3.34		34
$NaClO_4$, 0.1 M [1]	5.54	3.30	1.75	35
NaCl, 0.1 M	5.11	3.19		36
$NaClO_4$, 1 M	4.30	2.90	1.45	91
NO_3^-, -	4.25	2.90	1.55	37
NO_3^-, -	4.54			39

1. At 20°C

in ten-fold excess of citric acid (36). In this work, it was also assumed that the measured pH is the negative logarithm of the hydrogen ion concentration. Calculations were included to show that this probably imparted an error in the log of the equilibrium constant of the order of 1%. With to-day's computational aids and knowledge of the behaviour of electrolyte solutions, this is a relatively high error.

A group of workers in the Soviet Union (37) have studied the complex formation by a cation exchange method. Solutions of nickel nitrate and citric acid were allowed to equilibrate after being shaken with a cation exchange resin. The equilibrium constants were then calculated by consideration of the distribution of the species between the resin and solution. The reported value for $\log K^{M}_{ML} = 4.25$ appears low and could well be a function of the method, or due to differences in ionic strength, which was not reported.

Further spectrophotometric and potentiometric studies have reported evidence for the species MHL, ML^{-}, and $MH_{-1}L^{2-}$ (33, 39, 44, 48, 88, 91). In one of these (39), calculations at pH 6, where it was assumed that all MHL would be neutralized and that the hydroxy proton was still intact, resulted in an equilibrium constant for the formation of ML^{-}. This value is quite low compared to more recent work and may well be due to the presence of acetic acid/sodium acetate buffer.

There is mounting recent evidence to suggest the formation of complexes where the ratio of metal:ligand is not 1:1.

The isolation of the species ML^{-} and $M(HL)_2^{2-}$ from solution has been reported (38). No indication of the ratio of nickel to citric acid mixed initially was given, but if citric acid is present in large excess, then the formation of the latter species would be promoted. Early Russian studies (42, 50) report the evidence of both ML^{-} and ML_2^{4-} in the low pH range, and the formation of $MH_{-1}L^{2-}$ in the alkaline region.

Spectral studies (27) suggest the presence of complexes with nickel:citrate ratios of 1:2, and another reports a complex of stoichiometric ratio 3:2 at pH 7.5 to 8.5 (42).

Although their presence has been indicated spectrophotometrically, no equilibrium constants have been reported for complex species of nickel:citric acid stoichiometry 1:2. Additionally, no equilibrium constants for polymeric species have been reported. Campi (35) reported that no evidence could be found for species of the formula M_2H_nL or $M(H_nL)_m$ where $m > 1$, while a recent spectral study indicates that a species of nickel:citric acid ratio 3:2 may be present (42).

Recent studies of the interaction of copper and citric acid have indicated the presence of both species with a 1:2 nickel:citric acid ratio and dimeric species (33, 45). Bottari, in a very extensive study (45), has reported the stepwise formation constants for nine copper-citric acid complexes. The formation of higher ratio complexes may be facilitated by the fact that the study was carried out with excess citric acid. The reported species include: CuL, CuH_2L, CuL_2, $CuHL_2$, $Cu(HL)_2$, CuH_3L_2, $Cu(H_2L)_2$, $Cu_2H_{-2}L$, and $Cu_2(H_{-1}L)_2$. They found no evidence for the species $CuHL$. This conflicts with the results of other workers (33, 35,46, 48). Other reports of polymeric species include: Cu_2L_2 (46), Cu_2L_{-2}, $Cu_2(H_{-1}L)_2$ (47), and Cu_2L (35).

Evidence has been reported for a cobalt-citric acid complex of the form $Co_2(HL)_2$ (38), while several studies have reported equilibrium constants for CoL, $CoHL$, CoH_2L, $CoH_{-1}L$, (35 ,38,44,49), in addition to complexes of 1:2 cobalt-citric acid ratio (50, 51,52).

The iron (III)-citric acid equilibria have been well documented (46, 81,84-87) and equilibrium constants have been reported for the following species: FeH_2L, $FeHL$, FeL, $FeH_{-1}L$, FeL_2, $Fe(H_{-1}L)_2$, $FeH_{-2}L$, $(FeH_{-1}L)_2$.

In the solid state, complexes of more complicated ratios of nickel to citric acid have been characterized. Complexes with nickel:citric acid ratios 3:2, 1:2, 1:1 have been reported (93). In a recent x-ray characterization

(94) at -156° C, the structure of a complex with a nickel-citric acid ratio of 4:3 has been determined. Carbon-13 NMR studies (95) have produced evidence for a discrete complex of nickel and tetraionized citric-acid with ratio 8:6. In the C-13 NMR study, molecular weight determinations indicate that studies of these complexes in solutions of very high ionic strength (concentrations of both components were 0.100 M) should be interpreted in terms of monomeric transition metal complexes of triionized citrate, and tetrameric complexes of tetraionized citrate.

1.3 THIS WORK

Previous equilibrium studies have resulted in the characterization of two nickel:citric acid complexes MHL, ML^-, (where H_3L = citric acid). There have been occasional papers reporting evidence for MH_2L^+, ML_2^{4-}, $MH_{-1}L^{2-}$. However, those studies have not been able to characterize these species, the reported equilibrium constants varying widely. The majority of studies have been carried out in solutions where nickel is in excess, and this could account for the lack of evidence for species other than those with 1:1 nickel-citric acid ratios.

The object of this study was to reinvestigate nickel-citric acid equilibria, and to determine the equilibrium constants from the data for solutions over the range of nickel concentrations from 1×10^{-3} $moll^{-1}$ to 3×10^{-3} $moll^{-1}$, and the range of nickel:citric acid ratios from 1:0.84 up to 1:3. The background electrolyte used, KCl, is one which is more appropriate to physiological conditions in the nickel-accumulating species.

The range of solutions was subject to extensive study by potentiometric titrations and spectrophotometric techniques. Titration data were analysed with the aid of computer programs (listed in Appendix 2), in order to calculate equilibrium constants from $p[H^+]$ measurements. Visible spectra of solutions with a given ratio were recorded over a wide pH range, allowing interpretation of the spectra based on the distribution of species present, given the equilibrium constants which were determined as outlined.