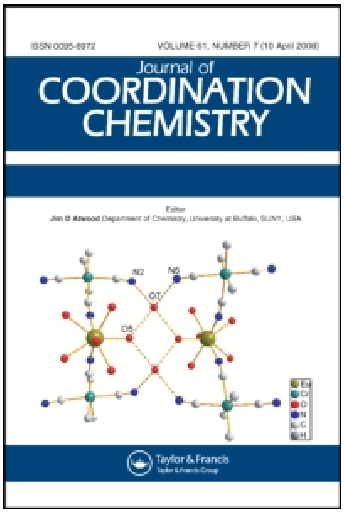

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INFLUENCE OF SYNTHETIC CHELATING AGENTS ON THE SPECIATION OF COPPER, ZINC AND MANGANESE IN PLANT NUTRIENT SOLUTIONS

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INFLUENCE OF SYNTHETIC CHELATING AGENTS ON THE SPECIATION OF COPPER, ZINC AND MANGANESE IN PLANT NUTRIENT SOLUTIONS

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A chemical equilibrium model of a typical plant nutrient solution was constructed and applied, in conjunction with an appropriate data base of equilibrium constants, to the program MINEQL. The output yielded the speciation of the metals in the nutrient solution. Additions of DTPA or EDTA were found to suppress the concentration of copper(II), zinc(II) and manganese(II) aquo ions, the relative decrease in concentration being more marked at pH 7.5 than at pH 4.3 in the case of DTPA but more marked at pH 4.3 than at pH 7.5 in the case of EDTA. These results were found to correspond to the trends observed in experimental observations on hydroponically cultivated bush beans. The results are interpreted in terms of the aquo ions of the three metals considered being the bioavailable species. The possible importance of copper(II)–hydroxy and other dissolved copper(II) species as bioavailable forms was considered but no clear conclusions could be reached.

Keywords: copper, zinc, manganese, speciation, nutrients, bioavailability

INTRODUCTION

The bioavailability of a metal ion to a plant, whether as a nutrient or as a poison, is believed to be determined by the physico-chemical form of the metal ion, that is its speciation.[1] Complexing agents which are present in the surrounding soil or nutrient solution can therefore have effects on the bioavailability of the metal that may be significant. This applies to naturally occurring complexing agents in the soil as well as those that may be added. Synthetic chelating agents such as EDTA‡, DTPA and EDDHA when added as treatments in the nutrition of plants can in some circumstances produce beneficial effects and in others, act detrimentally.[2-7] Lindsay[2,8] proposes that chelating agents act by solubilizing otherwise unavailable metals and carrying the latter by mass flow and diffusion to the plant root. By virtue of the equilibrium between the chelate–metal complex, the free chelate and free metal aquo ion, the last becomes absorbed by the plant, thereby causing a shift in the equilibrium resulting in dissociation of the complex. The free chelate then diffuses back to the source of the metal where further solubilization takes place. In this manner, synthetic chelating agents can act beneficially in that they improve the bioavailability of essential trace metals to plants growing in soil. On the other hand, when added to

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‡EDTA: ethylenediamine tetraacetic acid; DTPA: diethylenetriamine pentaacetic acid; EDDHA: ethylenediamine di (*O*-hydroxyphenylacetic acid).

synthetic nutrient solutions, chelating agents appear to produce distinctly different effects owing to the fact that the majority of the metallic micronutrients are already present as dissolved species in the solution and competitive inhibition[9] or relief from toxicity may result.[14] Iron becomes exceptional in this regard in circumstances under which precipitation of certain hydroxides or oxides of this element may occur.[2,7]

From the research point of view, nutrient solutions constitute tractable types of systems which if applied to suitably designed experiments involving the controlled addition of chelating agents, could potentially lead to improved understanding of the role of speciation in plant nutrition. Unfortunately, at the present time, there is a distinct paucity of publications which report the effects of chelating agents added to nutrient solutions on the uptake of metals by plants. Notable exceptions are contributions by Lindsay,[10] Wallace,[4,5,11] Brown[9,12,13] and their respective coworkers.

Amongst the results reported by Wallace[4,5] are indications of a general tendency for DTPA and EDTA to suppress the uptake of copper, zinc and manganese by bush beans cultivated in nutrient solutions. In an endeavour to shed some light on the mechanism of action of these chelating agents, we have carried out the speciation calculations described in this paper and have sought correlations between our results and the aforementioned trends observed in Wallace's work.

EXPERIMENTAL

In one of Wallace's publications on bush beans,[4] the effects are reported of DTPA and EDTA in the concentration ranges, 10^{-4} to 10^{-3} mol dm^{-3} and 10^{-4} to 5×10^{-4} mol dm^{-3}, respectively, with pH values at two levels, namely, *ca* 4.3 and 7.5. The following trends may be discerned from the results presented. At the lower pH, DTPA had a pronounced effect on copper uptake, a significant although considerably less marked effect on zinc uptake and a weak effect on manganese uptake. Absorption of copper and zinc was adversely affected by DTPA also at pH 7.5. In the case of manganese uptake, DTPA at the higher pH brought about a significantly greater decline than at pH 4.3. The uptake of all three metals generally tended to be reduced by the presence of EDTA at both pH levels. In particular, the copper concentration was significantly affected at the low pH, and concomitant low plant yields were observed. In contrast no adverse effects were observed at high pH and this coincided with much smaller reductions in uptake of all three metal ions. In order to compare these observations with computed speciation results, we developed an equilibrium model of a typical nutrient solution.[14] The composition of the nutrient solution is given in Table I. Apart from all the essential cations and anions, the solution contains a fixed concentration of EDDHA added as the iron(III) chelate and may also contain either DTPA or EDTA, covering concentration ranges as used by Wallace in the relevant experiments.[4]

Amongst the 24 components of the solution, we considered all the complexation and redox reactions that could conceivably take place as well as equilibria between the solution phase and precipitated solid phases that potentially could form. These numbered 251, four and 39, respectively. We also considered interactions with the two atmospheric gases, oxygen and carbon dioxide. We assembled a data base consisting of formation constants, redox potentials, solubility products and Henry's

Law constants corresponding to the aforementioned equilibria. These constants were taken from the literature[15–21] and were adjusted according to the relevant conditions of temperature, *i.e.*, 25°C and an ionic strength of 0.018 mol dm^{-3}. The latter value was computed by successive approximations. Ionic strength corrections of the constants were obtained by using an extended form of the Debye–Hückel equation.[22] No constants for any manganese–EDDHA species were included as there is a paucity in literature data for complexes in this system. This data base can be obtained on request from P.W. Linder.

TABLE I
Composition of the nutrient solution used in the modelling study.

Component	concentration/mol dm^{-3}	Component	concentration/mol dm^{-3}
Ca^{2+}	2.50×10^{-3}[a]	CO_3^{2-}	0.00[a]
Mg^{2+}	1.00×10^{-3}	SO_4^{2-}	3.01×10^{-3}
K^+	5.00×10^{-3}	Cl^-	2.00×10^{-6}
Na^+	2.00×10^{-5} + various[b]	PO_4^{3-}	1.00×10^{-3}
Fe^{3+}	2.00×10^{-5}	$B(OH)_4^-$	5.00×10^{-5}
Fe^{2+}	0.00	MoO_4^{2-}	3.00×10^{-8}
Cu^{2+}	1.00×10^{-6}	NO_3^-	6.00×10^{-3}
Cu^+	0.00	e^-	0.00
Mn^{3+}	0.00	NH_3	1.00×10^{-3}
Mn^{2+}	1.00×10^{-5}	EDDHA^{4-}	2.00×10^{-5}
Zn^{2+}	4.60×10^{-6}	DTPA^{5-}	$0 - 5.00 \times 10^{-4}$[c]
H^+	3.05×10^{-3} + various[b]	EDTA^{4-}	$0 - 5.00 \times 10^{-4}$[c]

[a] For the high pH condition 4.5×10^{-3} mol dm^{-3} was added to the concentrations of Ca^{2+} and CO_3^{2-}. [b] Varied according to the amount of the respective sodium salts of the chelates added. [c] Either DTPA^{5-} or EDTA^{4-} was added to the given solution.

We applied this data base, together with the total concentrations of the 24 components as specified in Table I, to the speciation program, MINEQL.[23] The output from MINEQL provided computed concentrations of all the complexes, concentrations of the free components and the extent of precipitation of solids.

RESULTS AND DISCUSSION

In Table II we have listed the computed concentrations of the copper(II), zinc(II) and manganese(II) aquo ions as well as the sum of the concentrations of all the copper(II)–hydroxy species and the total concentrations of all the dissolved copper(II) species excluding the copper(II) chelate species formed with EDDHA and either DTPA or EDTA.

Effects of DTPA

It may be seen from Table II that at pH 4.3 the copper(II) and zinc(II) aquo ion concentrations fall markedly when DTPA is added to the solution. In contrast, the manganese(II) aquo ion concentration is affected to a much smaller extent by DTPA.

TABLE II

Values computed by MINEQL of log[M]/mol dm^{-3} where M represents the species as indicated, for the nutrient solutions with either DTPA or EDTA present.

		pH 4.3					pH 7.5				
Chelating agent	conc. /mol dm^{-3}	Cu^{2+}	Zn^{2+}	Mn^{2+}	$Cu(OH)_n^{2-n}$[a]	Dissolved Cu[b]	Cu^{2+}	Zn^{2+}	Mn^{2+}	$Cu(OH)_n^{2-n}$[a]	Dissolved Cu[b]
	0.00	−7.79	−5.43	−5.16	−11.30	−7.69	−10.76	−5.63	−5.09	−10.58	−9.26
DTPA	1×10^{-4}	−12.81	−10.28	−5.66	−16.33	−12.69	−15.22	−11.66	−8.13	−15.05	−13.71
	5×10^{-4}	−13.68	−11.12	−6.43	−17.19	−13.59	−15.94	−12.40	−8.87	−15.93	−14.52
EDTA	1×10^{-4}	−12.05	−9.73	−6.28	−15.61	−11.95	−12.42	−10.00	−6.52	−12.24	−10.92
	5×10^{-4}	−12.97	−10.65	−7.17	−16.47	−12.86	−13.17	−10.75	−7.27	−12.99	−11.72

[a] Sum of the concentrations of all copper(II)-hydroxy species. [b] Sum of the concentrations of all dissolved copper(II) species excluding copper(II) chelate complexes.

At pH 7.5 the effect of increasing DTPA concentration on the copper(II) and zinc(II) aquo ions are again similar to those observed at the low pH although zinc is somewhat more greatly affected than the copper. Also, a more significant reduction in the manganese(II) aquo ion concentration occurs at the high pH. Thus for the latter two metal ions the presence of DTPA has the effect of enhancing the reduction in concentration accompanying an increase in pH. If it is assumed that the bioavailable forms of the three metals are the respective aquo ions, then it is clear that these computed trends match Wallace's results qualitatively. Thus viewed facilely, the action of the DTPA is simply to bring about a reduction in the concentrations of the aquo ions of the metals thereby leading to reduced amounts being taken up by the plants growing in the solutions.

It would appear that additional factors may be operative however. This follows from a comparison of the effect of pH, on the one hand as observed by Wallace and on the other hand as indicated in Table II. Whereas Wallace's results indicate a decrease in the reduction of copper and zinc uptake and an increase in the reduction of manganese uptake on adding DTPA at pH 7.5 compared with pH 4.3, this is not indicated in Table II in the case of zinc and only to an insignificant extent for copper. There is accordingly by no means a perfect correlation between Wallace's results and our speciation calculations. In an endeavour to find a better correlation, we have examined the effects of the chelating agents on not only the free aquo ions of the metals, but also the copper(II)–hydroxy complexes as well as all labile dissolved copper(II) species that can potentially form in solution, but excluding those complexes formed with the synthetic chelating agents. The concentrations of the latter two have been included collectively in Table II. The reason for considering the copper(II)–hydroxy species is that these have been suggested as possible bioavailable forms of copper (in addition to the aquo ion) to algae[24] and to *Daphnia magna*.[25] It does not seem too far-fetched, given the present state of knowledge of the subject, to imagine that root membranes may have similarities with respect to metal uptake to the nutrient absorption membranes of the aforementioned or any other living organisms. As it turns out, however, neither the concentrations of the copper(II)–hydroxy species nor those of total dissolved copper, in the presence of DTPA at the higher pH, are sufficiently high to improve substantially the correlation between our computed results and Wallace's observations.

Effects of EDTA

Our computations show that EDTA also suppresses the concentrations of the free aquo ions of copper, zinc and manganese and that the equilibrium concentrations are not greatly influenced by the pH level. The degree of suppression, however, is significantly greater at pH 4.3 than at pH 7.5. These results again correlate quite well with the trends observed in Wallace's study.[4] However, his results suggest further that the actual copper concentration in the plants was in fact greater at high pH than at low pH. As is evident from the computed copper(II) aquo ion concentration in Table II this is not borne out by our study. On considering the total dissolved copper(II) concentration at the low and high pH respectively, however, further improvement of the correlation becomes apparent.

Thus it may be concluded that the comparisons between our computed results and the trends in Wallace's observations are consistent with the view that the aquo ions of copper(II), zinc(II) and manganese(II) are the bioavailable forms of these metals in nutrient solutions and that the action of DTPA and EDTA is to reduce the concentrations of these ions. The possible importance or otherwise of the copper(II)–hydroxy and other dissolved copper(II) species as bioavailable forms is not yet clear however. At the present time this can only be speculated upon but such speculations would require the backing of suitably designed biological experiments to give them validity.

Halvorson and Lindsay[10] conclude from their studies on corn plants grown in nutrient solutions that $10^{-10.6}$ mol dm^{-3} represents a lower limit of the zinc(II) aquo ion concentration required for normal growth. Provided the aquo ion concentration exceeds this lower limit, the corn plants can take up sufficient zinc. On the other hand, when the zinc(II) aquo ion concentration falls below the lower limit, the plants show symptoms of zinc deficiency. This concept of a lower limit is important and presumably applies to all the metallic micronutrients. The actual values are likely to depend on the specific metal and the species of plant.

Since clarification of the role of speciation in the uptake of micronutrients by plants is vital to an understanding of the mechanisms involved in plant nutrition, it is hoped that considerably more effort will be devoted by plant scientists to suitably designed experimentation on the cultivation of plants in nutrient solutions. Particular attention should be given to determining the bioavailability or otherwise of species in solution and to the Halvorson–Lindsay concept of lower limits that are required for plant health. Once a suitable body of biological results is forthcoming, much further work on computation of speciation of metal ions, along the lines described in this paper, could be carried out with a view to advancing knowledge of the absorption of micronutrients by plants.

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