ELEMENTAL BIOAVAILABILITY IN NUTRIENT SOLUTIONS IN RELATION TO DISSOCIATION REACTIONS

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ABSTRACT

In general in hydroponic plant nutritional research, as well as in commercial hydroponic plant cropping, the actual nutritional composition is supposed to be exactly the same as the desired one. Furthermore, it is supposed that the nutrients are present in the nutrient solution as free ions. This way of thinking does not take into account the dissociation, complexation and precipitation reactions, occurring in nutrient solutions. These chemical reactions seriously impact elemental speciation and bioavailability. As a result plants will experience a completely different nutritional composition.

An accurate description of the chemical reactions occurring in nutrient solutions gives an accurate insight into mineral composition offered to the plants. This additional information is a valuable tool in interpreting specific effects of the mineral composition of the nutrient solution on dependent variables.

A good knowledge of the chemical reactions occurring in nutrient solutions is the first prerequisite in hydroponic plant nutritional research. In this study the

dissociation reactions occurring in nutrient solutions are investigated. The dissociation reactions of phosphate and carbonate influence both the mineral composition of the nutrient solutions and their bioavailability.

INTRODUCTION

Nutrient solutions can be considered as aqueous solutions of inorganic ions. In these aqueous solutions the elements are not present as free ions. A dynamic equilibrium between dissociation, precipitation and complexation reactions results in a specific elemental speciation. The term speciation indicates the distribution of elements among their various chemical and physical forms like: free ions, soluble complexes, chelates, ionpairs, solid and gaseous phases and different oxidation states, all of which influences their reactivity, mobility and bioavailability. A good knowledge of the chemical reactions occurring in nutrient solutions is the first prerequisite in hydroponic plant nutritional research.

Considering only the six essential macronutrients, nutrient solutions can be considered as an aqueous solutions containing K^+ , Ca^{2+} , Mg^{2+} , NO_3^- , $H_2PO_4^-$ and SO_4^{2-} ions. Lots of standard nutrient solutions contain ammonia in a millimolar range. In practice sometimes tapwater is used, containing bicarbonate in a millimolar range. Therefore also the dissociation reactions of NH_4^+ and HCO_3^- are described.

According to the pH these ions can be present in different dissociation forms. The influence of the pH on the dissociation of these ions is investigated and represented in figures.

MATERIAL AND METHODS

In the calculations the impact of the atmospheric pressure and composition and the impact of the temperature are not taken into account. The used equilibrium constants are only strictly correct at 25 °C, at a constant ionic strength and at an atmospheric pressure of 101325 pascal.

The fraction of the different dissociation forms present in function of the pH, are calculated based on their ionisation constants and represented in figures for a pH range from 1 to 14. These calculations are correct if only the respective ions are present. The magnitude of the acid (base) ionisation constant gives an indication of the extent to which an acid (base) ionises. Strong acids like HNO₃ and H₂SO₄ and strong bases like KOH, Ca(OH)₂ and Mg(OH)₂ are completely dissociated in the considered pH range.

The positive ion “H₃O⁺”, formed by a covalent bonding of the proton to H₂O, involving one of the unshared electron pairs of the oxygen is called the hydrogen ion. Higher hydrates such as H₅O₂⁺ and H₇O₃⁺ are also present, but their stabilities are significantly less than that of H₃O⁺. No unhydrated hydrogen ions appear to exist in aqueous solutions, (Skoog *et al.*, 1976). All protons in water are undergoing rapid migration from one oxygen to another. The average lifetime of an individual H₃O⁺ ion is 10⁻¹³ seconds. The rate of reaction of H₃O⁺ with a base such as OH⁻ in water is very fast but diffusion controlled (Cotton *et al.*, 1980).

RESULTS AND DISCUSSION

1. Nitric acid

Nitric acid is a rather strong monoprotic acid, completely dissociated between pH 1 to 14 (Figure 1). Taking only dissociation reactions into account, the amount of nitrate in a nutrient solution is completely present as NO₃⁻.

2. Phosphoric acid

The polyprotic acid H_3PO_4 contains three ionisable protons, dissociating in three distinct steps. Each successive dissociation has a lower dissociation and is energetically less favourable ($K_{a3} < K_{a2} < K_{a1}$):

Dissolving H_3PO_4 in water results in the formation of a considerable amount of H_2PO_4^- . The second acid ionisation constant (K_{a2}) is much smaller than the first (K_{a1}). The amount of H_2PO_4^- that further dissociates to HPO_4^{2-} is very small. In function of the pH different dissociation forms of phosphoric acid will be formed (Figure 2). The fraction H_3PO_4 (α_0), H_2PO_4^- (α_1), HPO_4^{2-} (α_2), and PO_4^{3-} (α_3), present in function of the pH can be calculated as follows:

1. The fraction H_3PO_4 : $\alpha_0 = 1 / A$
2. The fraction H_2PO_4^- : $\alpha_1 = (K_{a1} [\text{H}_3\text{O}^+]^{-1}) / A$
3. The fraction HPO_4^{2-} : $\alpha_2 = (K_{a1} K_{a2} [\text{H}_3\text{O}^+]^{-2}) / A$
4. The fraction PO_4^{3-} : $\alpha_3 = (K_{a1} K_{a2} K_{a3} [\text{H}_3\text{O}^+]^{-3}) / A$

$$\text{With } A = 1 + (K_{a1} [\text{H}_3\text{O}^+]^{-1}) + (K_{a1} K_{a2} [\text{H}_3\text{O}^+]^{-2}) + (K_{a1} K_{a2} K_{a3} [\text{H}_3\text{O}^+]^{-3})$$

The denominator is the same for each fraction. The fractional amount of each species at any fixed pH is independent of the total concentration of phosphate. The pH of most nutrient solutions varies between 4 and 7. At a pH of 4.6 the phosphate in nutrient solutions is completely present in the dissociation form H_2PO_4^- . Increasing pH to 7.2, equal proportions of H_2PO_4^- and HPO_4^{2-} are present. The bioavailability of H_2PO_4^- is different than that of HPO_4^{2-} (Hai *et al.*,

1966). In this way the pH of the nutrient solution influences both the composition of the nutrient solution and the bioavailability of phosphate.

3. Sulphuric acid

The biprotic acid H_2SO_4 dissociates in two distinct steps. It is a strong acid in its first dissociation and a somewhat weaker acid in its second dissociation step.

In an aqueous solution of sulphuric acid there is no H_2SO_4 present but different proportions of HSO_4^- and SO_4^{2-} , according to the pH (Figure 3). The fraction H_2SO_4 (α_0), HSO_4^- (α_1) and SO_4^{2-} (α_2), present in function of the pH can be calculated as follows:

$$1. \text{ The fraction } \text{H}_2\text{SO}_4 : \alpha_0 = 1 / A$$

$$2. \text{ The fraction } \text{HSO}_4^- : \alpha_1 = (K_{a1} [\text{H}_3\text{O}^+]^{-1}) / A$$

$$3. \text{ The fraction } \text{SO}_4^{2-} : \alpha_2 = (K_{a1} K_{a2} [\text{H}_3\text{O}^+]^{-2}) / A$$

$$\text{With } A = 1 + (K_{a1} [\text{H}_3\text{O}^+]^{-1}) + (K_{a1} K_{a2} [\text{H}_3\text{O}^+]^{-2})$$

Because of the rather strong acid character of HSO_4^- at a pH higher than 4 the only form of sulphate present in the solution is SO_4^{2-} . In nutrient solutions the dissociation of sulphate does not influence the composition nor the bioavailability of sulphate.

4. Potassiumhydroxide, calciumhydroxide and magnesium hydroxide

The hydroxides of potassium, calcium and magnesium are strong bases, completely dissociated in the pH range from 1 to 14 (Figures 4, 5 and 6). The hydrolysis reaction of these three cations does not influence their bioavailability, nor the composition of the nutrient solution.

5. Ammonium

In the past several standard nutrient solutions were developed, containing both nitrate and ammonium as nitrogen source, aiming at a more stable pH of the nutrient solution. Ammonium ions in a nutrient solution are more or less toxic for plants growing under aerobic conditions. As cited by Hewitt (1966), the toxicity of ammonium is determined by the external cell pH, determining the rate of uptake, and the internal cell pH, determining the concentration of undissociated ammonium (Warren, 1962). There is no problem in supplying NH_4^+ to the soil. The ions will be fixed and not freely available for the plant roots. The ammonium ions will gradually be transferred to nitrate by nitrification processes. This nitrogen form is freely available for plant roots. In general never more than 10 % of the total nitrogen content may be supplied in the form of NH_4^+ (Steiner 1984). Ammonium is a weak acid, containing only one ionisable proton:

The fraction of each dissociation form present in an aqueous ammonium solution in function of the pH can be calculated as follows:

1. The fraction NH_4^+ : $\alpha_0 = 1 / A$
2. The fraction NH_3 : $\alpha_1 = (K_{a1} [\text{H}_3\text{O}^+]^{-1}) / A$

$$\text{With } A = 1 + (K_{a1} [\text{H}_3\text{O}^+]^{-1})$$

Up to a pH of 7.5 only NH_4^+ is present (Figure 7). Between a pH of 7.5 to 10.5, NH_4^+ is gradually replaced by NH_3 . Since the pH of most nutrient solutions varies from 4 to 7, dissociation reactions will not influence the bioavailability of ammonium nor the composition of the nutrient solutions.

6. Carbonic acid

Most of Belgian tap-water contains bicarbonate in concentrations that sometimes exceed the 5 millimolar range. If nutrient solutions are made, using tap water, dissociation reactions of carbonic acid are to be taken into account. Carbonic acid is a weak acid that ionises in two distinct steps:

H_2CO_3 does not exist as a stable molecule. It is an equilibrium of H_2O and dissolved CO_2 . $\text{CO}_{2(\text{aq})}$ is often referred to as $\text{H}_2\text{CO}_{3(\text{aq})}$ to emphasise its acidic properties. The value given for K_{a1} is actually for the reaction:

Generally aqueous solutions of CO_2 are treated as if the $\text{CO}_{2(\text{aq})}$ is first converted to H_2CO_3 and then dissociates (Petrucci *et al*, '93). Until a pH of 4.5 only H_2CO_3 is present in an aqueous solution, containing only carbonic acid (Figure 8). If the pH increases from 4.5 to 8, H_2CO_3 is gradually replaced by HCO_3^- . Increasing the pH from 8.5 to 12.5, HCO_3^- is replaced by CO_3^{2-} . In nutrient solutions with a pH lower than 4.5 carbonic acid will not be dissociated. If the pH rises above 4.5, carbonic acid dissociates and the composition of the nutrient solution changes. The fraction H_2CO_3 (α_0), HCO_3^- (α_1) and CO_3^{2-} (α_2), present in an aqueous solution containing only carbonic acid, in function of the pH can be calculated as follows:

1. The fraction H_2CO_3 : $\alpha_0 = 1 / A$
  2. The fraction HCO_3^- : $\alpha_1 = (K_{a1} [\text{H}_3\text{O}^+]^{-1}) / A$
  3. The fraction CO_3^{2-} : $\alpha_2 = (K_{a1} K_{a2} [\text{H}_3\text{O}^+]^{-2}) / A$
- With $A = 1 + (K_{a1} [\text{H}_3\text{O}^+]^{-1}) + (K_{a1} K_{a2} [\text{H}_3\text{O}^+]^{-2})$

In practice all nutrient solutions are in equilibrium with a partial atmospheric $\text{CO}_2(\text{g})$ pressure of at least 35.5 pascal atmosphere. In greenhouses this partial CO_2 pressure is often much higher due to the supply of CO_2 to the plants. Small amounts of $\text{CO}_2(\text{g})$ (1.4×10^{-5} mol/l) will dissolve in the nutrient

solutions and form carbonic acid. This effect is not accounted for since it is only a neglectable small amount of $\text{CO}_2(\text{g})$ that dissolves.

CONCLUSION

A good knowledge of the chemical reactions occurring in nutrient solutions is the first prerequisite in hydroponic plant nutritional research. Due to the strong acid properties of nitric acid and sulphuric acid, their conjugated base pair, respectively nitrate and sulphate are very weak bases. This means that if nitrate and sulphate ions are added to the nutrient solution as a salt they will not hydrolyse. If they are added as an acid they immediately dissociate.

The strong basic properties of potassiumhydroxide, magnesiumhydroxide and calciumhydroxide, see to it that they immediately and completely dissociate. Their conjugated acid pair, respectively K^+ , Mg^{2+} and Ca^{2+} are very weak acids and will therefore not bind with OH^- .

NH_4^+ is a weak acid that only dissociates at pH 7.5, outside the pH range of nutrient solutions (4 - 7). So in nutrient solutions no NH_3 will be present. The dissociation reactions involved with NO_3^- , SO_4^{2-} , K^+ , Ca^{2+} , Mg^{2+} and NH_4^+ do not influence their bioavailability within the pH range of nutrient solutions.

Within the pH range of nutrient solutions dissociation reactions influence the bioavailability of phosphate and carbonate. In comparing plant response to nutrient solution with the same amount of phosphate and/or carbonate at a different pH, not only the pH differs but also the bioavailability of these ions. This confounding between pH and bioavailability should be taken into account in interpreting the results of such experiments.

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FIGURE 5 : Dissociation of Ca(OH)_2

FIGURE 6 : Dissociation of Mg(OH)_2