

Degree of complexation of microelement ions by biodegradable IDHA chelator in water and simulated fertilization environment

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The degree of complexation of microelement ions by the biodegradable chelating agent - IDHA was examined in the work. The tests were carried out in water and in a simulated fertilizer environment. In order to compare the obtained results, tests were also carried out for the commonly used EDTA. The performed analyzes allow to determine the influence of the presence of compounds containing macroelements on the degree of binding of microelement ions by the biodegradable IDHA and EDTA chelators. The obtained results make it possible to determine the optimal conditions for the chelation of cations by IDHA, which in the future may be used in the production of micronutrient fertilizers on a large scale.

Keywords: chelates, microelements, fertiliser, degree of complexation.

INTRODUCTION

In industrial-scale production, metal ions can adversely affect the course of many chemical processes and the final properties of the product. The tick-like structure of the chelate prevents undesirable reactions of metal ions^{1,2}. Complexing substances are produced on a large scale and various groups like aminopolycarboxylates, hydroxycarboxylates, and phosphonates can be distinguished between them. Compounds from the group of derivatives of aminopolycarboxylic acids (APCA) are often used in many industries, for example: food, pharmaceutical, cosmetic, paper, textile, metallurgical, fertiliser and many other. They are strong complexing agents, which at low pH form more stable chelates with transition-metal ions than with calcium and magnesium ions³⁻⁸.

Compounds with chelating properties belonging to the APCA group have a negative impact on the environment. The complexing properties of these substances result in the formation of chelates with heavy metal ions. Good solubility in water and a low degree of biodegradation influenced the presence of complexones of anthropogenic origin in surface waters and sewages. There are growing concerns about the direct or indirect environmental impacts of chelators related to:

- a) mobilisation of heavy metal ions absorbed in sediments⁹,
- b) solubilization of radioactive metal ions and increasing their impact on the environment¹⁰⁻¹³,
- c) eutrophication of waters (chelators usually contain a nitrogen atom in their structure)¹⁰,
- d) metal-ligand complexes may increase the bioavailability of heavy metals (the Cd-EDTA complex is more toxic than the free ion of this metal)¹⁰⁻¹⁴.

Popular ligands are increasingly being replaced by their new biodegradable analogues, but they generally have a much lower ability to form stable chelates and are characterised by worse physicochemical properties^{8, 15}.

The use of chelates-containing micronutrient fertilizer in agriculture has increased significantly in recent years. The effectiveness is related to the structure of the molecule. Synthetic chelates are resistant to microorganisms, and stabilise the microelement in a wide range of pH. Their use, even in the absence of micronutrient deficiencies, results in the growth of plants and crops¹. Supplying the soil with microelements in the form of

ions is often associated with the risk of transfer of these metals to forms that are not assimilable by plants, resulting in several times higher micronutrients application during soil fertilization in comparison with foliar fertilization^{16, 17}. The structure of the chelate prevents the reaction of microelement ions with the components of the soil solution, protects against nutrient depletion, and facilitates the uptake of nutrients by the leaves. Chelates are well-soluble in water, but dissociate to a small extent. The gradual release of micronutrients increases their assimilation by plants and prevents their excessive uptake. The use of chelates is more effective than microelement salts, and their structure facilitates the movement of metal ions in the soil solution and later in the tissues of the plant. Micronutrients are taken in the chelated form. Their movement in the plant is as fast as that of ionised molecules. In tissues, microelements are gradually released and used in metabolic processes¹⁸.

Both chelates and microelement complexes can be produced on the basis of synthetic and natural ligands. Natural chelators include lignosulfonic acids, which are byproducts in the production of cellulose, or sulfonic tannins derived from tree bark. Complexes with metal ions also form other substances of natural origin, such as amino acids, humic acids, citrates, and gluconates¹⁹. Natural complexes are less stable than synthetic chelates and often undergo metal or ligand exchange reactions and adsorption into the soil solid phase. The stability of such compounds is affected by many factors and substances in the soil solution, so it is recommended to use them in soilless crops. Synthetic fertiliser chelates belong to the group of aminopolycarboxylic compounds. The use of APCA ligands prevents secondary reactions of the microelement ions²⁰. On alkaline soils, the presence of carbonates and bicarbonates causes these anions to displace the ligand from the chelate, creating insoluble compounds that are not assimilable by plants. On calcareous soils, the cation of the trace element can be displaced by the calcium ion. The released ions may form insoluble hydroxides. Chelators with high values of stability constants do not undergo such reactions²¹.

The EU Fertilisers Regulation includes 11 synthetic chelating agents belonging to the group of aminopolycarboxylic compounds¹⁹. The requirements of the European Directive specify the content of water-soluble, assimilable

ions of microelements. Micronutrient fertilisers should contain at least 80% of the total water-soluble amount of metal ions in the form chelated by a specific chelating agent. 50% of the water-soluble micronutrient must be chelated by a chelating agent approved by the European Parliament and the Council¹⁹.

The aim of this study was to determine the degree of complexation of micronutrient ions by the biodegradable IDHA chelating agent and to compare the obtained results with the commonly used EDTA chelator. The experiments were conducted in various media that simulated fertilizer environments. The 2021 update of European Parliament and Council Regulation 2019/1009, also allows the use of other chelating agents for the production of micronutrient fertilizers¹⁹. The condition that must be met by the chelator is complexation of the total amount of water-soluble microelement ions to a degree of at least 80%. The degree of complexation was determined by differential pulse voltammetry. The results obtained are based on the preliminary assessment of the possibility of using IDHA chelates as a component of compound fertilisers.

MATERIALS AND METHODS

Differential pulse voltammetry (DPV) was used in the experiments. It is an electroanalytic technique based on measuring the dependence of the intensity of the current flowing through a stationary indicator electrode and the potential of this electrode. The voltammetric method is one of the most sensitive analytical methods allowing the concentration of metal ions to be determined in trace amounts. This method enables the simultaneous measurement of several ions and allows the degree of metal oxidation to be distinguished²².

The tests were performed using the AUTOLAB PGSTAT 12 apparatus with GPES software. A mercury electrode (663 VA Stand) operating in SMDE mode (Static Mercury Drop Electrode) was used. The reference electrode was a silver chloride electrode, and the auxiliary electrode was a glass fibre electrode. The total surface area of the mercury drop was approximately 0.25 mm². The step potential was 0.00495 V and the modulation amplitude was 0.00255 V at 0.05 s. The equilibrium time was 5 s. The deposition potential was -1.3 V at 60 s. Each measurement was repeated twice. The degree of complexation of micronutrient ions with IDHA and EDTA was determined on the basis of the peak height of the current intensity, which is directly proportional to the concentration of metal cations present in the solution. Ion concentration was determined on the basis of standard curves determined for each type of micronutrient ion and at each pH value. Analysis were performed, and samples were prepared at room temperature, atmospheric pressure, and a constant concentration of a solution containing the base electrolyte. The degree of complexation was determined on the basis of the difference in the concentration of the metal ion and the metal ion with the addition of a chelating agent according to the formula:

$$\alpha = \frac{c_0 - c_i}{c_0} \cdot 100\%$$

where:

α – degree of ions complexation [%],

c_i – ions concentration after adding the chelator [$\frac{\text{mol}}{\text{dm}^3}$],
 c_0 – concentration of metal ions before adding the chelator [$\frac{\text{mol}}{\text{dm}^3}$].

The degree of complexation of ions, used in the production of micronutrient fertilizers (Zn²⁺, Cu²⁺, Mn²⁺, Fe³⁺), by IDHA and EDTA chelators was determined. Aqueous solutions containing micronutrient ions were prepared from inorganic salts: ZnSO₄ · 7H₂O (p.a., POCH, Gliwice), CuSO₄ · 5H₂O (p.a., POCH, Gliwice), MnSO₄ · H₂O (p.a., POCH, Gliwice), Fe(NO₃)₃ · 9H₂O (p.a., POCH, Gliwice). IDHA tests were performed in the basic electrolyte environment and in the simulated fertilization environments. 33 mass% aqueous solution of IDHA sodium salt was used (tech., ADOB). EDTA (35 mass% aqueous solution of sodium salt, technical, Boruta-Zachem SA), which is a substance commonly used in many industries, was also tested. Both APCA compounds react with metal ions in a 1:1 molar ratio, and this ratio was used in the analysis.

EDTA (acid or salt of ethylenediaminetetraacetic acid) is most often used for the production of microfertilizers (Fig. 1).

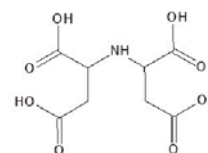


Figure 1. Structural formula of iminodisuccinic acid

This complexon is characterized by very low biodegradation degree in natural conditions. Even after years, high concentrations of this compound are observed in groundwater, lakes, rivers, and drinking waters. It is one of the compounds of anthropogenic origin with the highest concentration in inland European waters. Toxic effects on the environment occur as a result of the ability of EDTA to increase the bioavailability and phytotoxicity of heavy metals and radioactive elements. The increased use of EDTA in agriculture was due to the increased assimilability of chelated micronutrients by plants. The chelator also binds heavy metal ions, which potentially facilitates their absorption by plants and the remobilization of these cations from sludge, bottom, and river sediments. As a consequence, this leads to an increase in the assimilability of toxic elements, not only by plants, but also by living organisms^{9, 15, 23-31}.

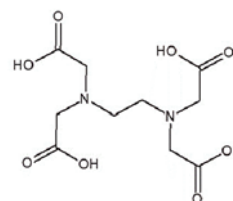


Figure 2. Structural formula of ethylenediaminetetraacetic acid

The sodium salt of iminodisuccinic acid, the tetrasodium salt of *D,L*-aspartate-*N*-(1,2-dicarboxyethyl) acid (IDHA or IDS) (Fig. 2) was first produced by Bayer AG (now Lanxess) in 1998, under the name Baypure CX 100³²⁻³⁴.

IDHA belongs to compounds that are easily biodegradable. IDHA under static test conditions, after a period of microbial adaptation, is completely biodegradable³⁰. The degree of its decomposition after 7 days is 80%³⁵. This ligand has a low impact on the environment. As a result of the degradation of IDHA, *L*-aspartic acid and *D*-aspartic acid are formed, which in the final stage are decomposed into fumaric acid and ammonia^{36, 37}.

Iminodisuccinic acid has five binding sites. This chelator belongs to the pentadent ligands. It is considered a medium strong chelator that can replace the commonly used EDTA, but the durability of this chelate is lower³⁸.

Iminodisuccinic acid is used in the bleaching of cotton, in the production of detergents, as a corrosion inhibitor, in the production of pulp and paper, in ceramics, in the textile industry, in the process of cleaning membranes contaminated with engine oil and in the cosmetics industry^{32, 39}. IDHA is used in the production of micronutrient fertilisers. Since 2005, the Polish company ADOB has been producing fertilizers containing IDHA chelates⁴⁰.

The complexing abilities of ligands depend on the reaction of the environment. In each medium used, tests were carried out at pH equal to 3, 5, 7, 9, 11 and 13, which were regulated using 0.1 M HCl and NaOH solutions. The determinations were made in the basic electrolyte environment and in the simulated fertilization environment. The basic electrolyte in the form of 0.1 M KCl aqueous solution (p., POCH, Gliwice) was used to determine the concentration of Zn²⁺ and Mn²⁺ ions. 0.1 M KClO₄ (p.a., POCH, Gliwice) was used to determine the content of Fe³⁺ and Cu²⁺ ions. In the research, substances commonly used in the fertiliser industry were used as the N, NP, and NPK fertilising medium. The content of the ingredients used corresponded to the content of macroelements in liquid fertilisers. Three types of solutions containing fertilising macroelements were used:

a) nitrogen environment (N)

The system contained urea (p.a., POCH, Gliwice) and ammonium nitrate (p.a., POCH, Gliwice) in a molar ratio of 1:1. The solution of the N environment was prepared by mixing urea together with ammonium nitrate(V) in an equal molar ratio. The 37.5 grams of urea and 50 grams of ammonium nitrate were weighed and then dissolved in 1 dm³ of demineralized water. The solution thus prepared contained 3.5 mass% of total nitrogen, including 1.75 mass% of amide nitrogen and the same amount of ammonium and nitrate nitrogen.

A 25 cm³ sample containing 2.5 cm³ of a solution simulating the fertilization environment was analyzed.

b) nitrogen-phosphorus environment (NP)

The system contained ammonium nitrate(V), urea, and ammonium dihydrogen phosphate(V) (p., POCH, Gliwice). In the vessel, 20.6 grams of urea, 27.4 grams of ammonium nitrate and 129.9 grams of ammonium phosphate were weighed and then dissolved in 1 dm³ of demineralized water. The solution thus prepared contained 3.5 mass% total nitrogen, including 0.96 mass% amide nitrogen, 2.54 mass% ammonium and nitrate nitrogen, and 3.5 mass% phosphorus (8.03 mass% P₂O₅). A 25 cm³ sample containing 2.5 cm³ of a solution simulating the fertilization environment was analyzed.

c) nitrogen-phosphorus-potassium environment (NPK)

The system contained ammonium nitrate(V), urea, ammonium dihydrogen phosphate(V) and potassium chloride (p.a., POCH, Gliwice). Here, 20.5 grams of urea, 27.4 grams of ammonium nitrate, 129.9 grams of ammonium phosphate and 66.9 grams of potassium chloride were weighed and then dissolved in 1 dm³ of demineralized water. The solution thus prepared contained 3.5 mass% total nitrogen, including 0.96 mass% amide nitrogen, 2.54 mass% ammonium and nitrate nitrogen, 3.5 mass% phosphorus (8.03 mass% P₂O₅) and 3.5 mass% potassium (4.2 mass% K₂O). A 25 cm³ sample containing 2.5 cm³ of a solution simulating the fertilization environment was analyzed.

Each analyzed sample contained solutions of microelement cations, chelating compound in a molar ratio of 1:1 with a concentration of 0.001 [$\frac{mol}{dm^3}$], 0.01% gelatine solution (p., POCH, Gliwice), basic electrolyte with a concentration of 0.1 [$\frac{mol}{dm^3}$] or (described above) a solution simulating the fertilizing environment. 25 cm² of the prepared solutions, with the fixed pH value, was placed in an electrolytic vessel. Nitrogen (4.0, Messer) as an inert gas was used for deoxygenation. Then the measurement was made.

RESULTS AND DISCUSSION

From the technological point of view, the structure of the obtained chelates of microelements is not important. In the production of chelated-based fertilizers, the degree of complexation of microelements is the most important, which should be at least 80% of the declared water-soluble content of the microelement. The Fertilizers Regulation does not specify an analytical method that will allow to determine the concentration of unbound ions of microelements, and thus the degree of complexation¹⁹. Differential pulse voltammetry was used in the research, which allows to determine the concentration of metal ions in ppm and even ppb, which allows for the determination of the degree of complexation with high accuracy. Determining the complexing properties of chelators in the water-fertilizer environment is necessary to determine the possibility of their use as a component of compound fertilizers. The degree of the complexation of microelement ions was calculated for different pH values. To determine the appropriate pH values, aqueous solutions of hydrochloric acid and sodium hydroxide were used. The tests for each metal were carried out at pH equal to 3, 5, 7, 9 and 11. Determination of the content of unbound metal ions depends on the chemical properties of the the cations of microelements. Calculation of the degree of complexation is only possible in a specific environment and at selected pH values.

At pH 9 and 11, lower peaks of zinc cations and the precipitation of a white precipitate of zinc hydroxide (Zn(OH)₂) were observed. This made it impossible to complex the ions of this metal, and thus determine the degree of complexation of zinc ions by the tested chelators. Zinc ion chelation was determined at pH 3, 5 and 7. When preparing solutions of copper(II) salts, a blue precipitate of copper(II) hydroxide (Cu(OH)₂) was observed at pH 7, 9 and 11. Voltamperograms of

these solutions the height of the peak from copper(II) cations was lower. Determination of copper(II) ions and determination of the degree of complexation were possible only at pH 3 and 5. Analysis of the concentration of manganese(II) ions and determination of the degree of complexation were possible at pH values close to neutral. Under acidic conditions, the reduction peak overlapped with the H_3O^+ peak. In an alkaline environment, manganese ions precipitate in the form of $Mn(OH)_2$ hydroxide. The concentration of manganese(II) ions and the determination of the degree of complexation were determined at pH 5 and 7. Due to the properties of Fe^{3+} ions, measuring the concentration of this metal ions and calculating the degree of complexation were possible in a narrow pH range.

The degree of complexation of microelement ions in the basic electrolyte environment was determined for IDHA and, for comparison, for the commonly used EDTA (Table 1).

Table 1. The degree of complexation [%] of microelement ions by IDHA and EDTA in water

Microelement ions	pH	EDTA	IDHA
Zn^{2+}	3	93.8	99.9
	5	97.8	96.3
	7	100	98.4
Cu^{2+}	3	30.0	25.7
	5	51.9	52.5
Mn^{2+}	5	92.9	81.9
	7	93.9	86.9
Fe^{3+}	6	75.1	74.2
	6.5	77.3	73.2
	7	74.1	72.5

The degree of complexation of zinc and manganese(II) ions reached the value required in the Regulation above 80% at all pH values. Both ligands chelated the ions to a higher degree at pH 7. The degree of complexation of iron(III) ions was slightly lower. The best results were observed at a pH of 6.5. The lowest degree of chelation was obtained for copper(II) ions. At pH 5, a higher degree of chelation was achieved, which was approximately 50% for both ligands.

Borowiec et al. conducted similar studies that enabled the complexation of zinc ions by other chelators²². Biodegradable EDDS, MGDA, GLDA and other NTA and EDTA amino polycarboxylic compounds were used. The article shows that the authors obtained lower degrees of complexation of zinc ions by biodegradable substances, such as EDDS, MGDA, GLDA, compared to EDTA.

The best results of zinc ion chelation were obtained for EDDS, which is an EDTA analogue.

Comparing the obtained results with the analyzes of Borowiec et al., it can be concluded that IDHA is one of the best chelators among the tested biodegradable ligands. IDHA can be used as a replacement for the commonly used EDTA.

The complexation of microelement ions in the nitrogen environment in the $(NH_2)_2CO-NH_4NO_3$ system, the nitrogen-phosphate environment in the $(NH_2)_2CO-NH_4NO_3-NH_4H_2PO_4$ system and the nitrogen-phosphorus-potassium environment in the $(NH_2)_2CO-NH_4NO_3-NH_4H_2PO_4-KCl$ system was carried out with such pH values as in the case of the basic electrolyte (Table 2).

Evaluation of the degree of complexation of iron ions in the presence of phosphate ions turned out to be impossible. Iron ions reacted with phosphate(V) ions (in the NP environment), forming a sparingly soluble iron(III) phosphate ($FePO_4$) precipitate. The presence of chloride ions (NPK environment) resulted in an additional intensive peak in the voltammograms of copper(II) ions, which made interpretation of the results impossible. The determinations for zinc ions were carried out at pH 3 and 5. Above this value, a precipitate formed.

In a simulated fertilizing nitrogen environment, a higher degree of complexation was obtained for these chelators in comparison to the basic electrolyte environment. EDTA better complexed copper(II) and manganese(II) ions, and worse complexed zinc and iron(III) ions in a nitrogen environment than in water. Zinc, copper(II), and iron(III) ions were worse chelated by IDHA in the fertilising nitrogen environment than in the basic electrolyte environment. IDHA complexed manganese(II) ions to a higher degree under these conditions. Both EDTA and IDHA complexed iron(III) ions to a degree lower than 80%. IDHA bound copper(II) ions to a much lower extent than in the aqueous environment. The pH value of 7 is the most favorable for the chelating efficiency of zinc and manganese ions by both chelators. For iron ions it is 6.5 and for copper ions it is 5.

The chelation reaction of micronutrient ions in a nitrogen-phosphorus environment is less efficient than that in an aqueous or nitrogen environment. It is probably caused by competitive reactions of metal ions with phosphate(V) ions. Only the zinc ions were completely chelated (~100%). Manganese(II) and copper(II) ions were bound by both ligands to a small extent. Under these conditions, a higher degree of complexation of zinc

Table 2. The degree of complexation [%] of microelement ions by IDHA and EDTA in simulated nitrogen, nitrogen-phosphorus and nitrogen-phosphorus-potassium environments

Microelement ions	pH	nitrogen (N) environment		nitrogen-phosphorus (NP) environment		nitrogen-phosphorus-potassium (NPK) environment	
		EDTA	IDHA	EDTA	IDHA	EDTA	IDHA
Zn^{2+}	3	92.2	92.4	100	100	81.8	34.5
	5	93.1	93.6	100	100	83.7	72.2
	7	94.9	97.2	100	100	–	–
Cu^{2+}	3	99.2	15.1	24.9	12.9	–	–
	5	99.4	23.1	33.8	40.8	–	–
Mn^{2+}	5	97.9	88.9	30.7	51.5	34.6	71.8
	7	98.9	91.9	59.7	57.0	63.2	77.5
Fe^{3+}	6	74.8	70.4	–	–	–	–
	6.5	75.6	74.4	–	–	–	–
	7	72.3	71.2	–	–	–	–

and manganese ions by both chelators was also obtained at pH 7, and of copper ions at pH 5.

The degree of complexation in the nitrogen-phosphorus-potassium environment showed a lower degree of complexation of zinc ions and a higher degree of complexation of manganese(II) ions rather than in the nitrogen-phosphorus medium. Only in the case of chelation of zinc ions with EDTA was the degree of complexation required by the Fertiliser Regulation was obtained. An increase in the pH value of the environment had a positive effect on the value of complexation of the analyzed microelement ions by both chelators.

In another article, the degree of complexation of zinc ions in an aqueous environment and in a simulated fertilizer medium by EDDHA and EDDHSA was determined⁴¹. Both ligands chelated zinc cations to a greater extent than IDHA in each analyzed medium. Both EDDHA and EDDHSA stabilize micronutrient ions in a wide pH range and can be used on calcareous and alkaline soils. Both chelators are not biodegradable, and using them in large amounts can have a negative impact on the environment^{30, 31}. It is necessary to search for compounds that will decompose in the environment to simple compounds.

CONCLUSIONS

The degree of complexation of micronutrient ions used in the fertilizer industry by the biodegradable chelator IDHA and EDTA additive in aqueous, and simulated fertilizer environments : nitrogen, nitrogen-phosphorus and nitrogen-phosphorus-potassium was determined. For zinc ions, a high degree of complexation is obtained at pH 7 in aqueous, nitrogen, and nitrogen-phosphorus environments. For copper(II) ions, the highest degree of complexation was obtained at pH 5 in all environments analysed. Manganese(II) ions were most effectively chelated at pH 7, and iron(III) at pH 6.5. The highest degree of the complexation of microelement ions by IDHA was achieved in the environment of basic electrolytes. The addition of substances used in the fertilizer industry to obtain a simulated fertilizer environment negatively affected the value of the degree of complexation of micronutrient ions by EDTA. Tests conducted in water environment achieve a degree of complexation comparable to EDTA.

The IDHA ligand can be used interchangeably with non-biodegradable EDTA, but the chelation reaction should be carried out in an aqueous environment to obtain a higher degree of complexation of metal ions.

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