

Ewelina KLEM-MARCINIAK¹, Marta HUCULAK-MĄCZKA¹,
Krystyna HOFFMANN^{1*} and Józef HOFFMANN¹

INFLUENCE REACTION TIME TO DEGREE OF COMPLEXATION ZINC IONS BY FERTILIZERS CHELATING SUBSTANCES

WPLYW CZASU REAKCJI JONÓW CYNKU Z NAWOZOWYMI SUBSTANCJAMI CHELATUJĄCYMI NA STOPIEŃ SKOMPLEKSOWANIA

Abstract: In recent years, a big problem for agriculture is the shortage of available micronutrients in the soil, thus reducing yields. This deficiency is due to the intensification of agriculture, cultivation of new species of plants require fertilization and a significant share of soils with low content of available micronutrients, which is why in recent years looking for the appropriate forms in which they can be applied to not have a negative impact on the environment. Of particular importance in the field of micronutrient fertilizers gained chelates. These compounds are characterized by stability. Chelating agents stabilize the cations of microelements in a wide pH range. Their application optimizes supplement micronutrient deficiency. Adaptation of nutrients to the needs of the plants can reduce the negative impact on the environment, without causing soil salinity, as in the case of salt micronutrients. Can be applied to both soil and foliar application. They are produced in the form of liquid or fine-crystalline. In the European Union are set chelating agents used as additives for liquid fertilizers. These are synthetic compounds belonging to the aminopolycarboxylic compounds (APCAs) which form stable complexes which are soluble in water. APCAs form chelates of trace elements in a molar ratio 1:1. The most commonly used component is the disodium salt of ethylenediaminetetraacetic acid (EDTA). The Regulation of the European Parliament and of the Council EC No 2003/2003 of 13 October 2003 includes the requirements for chelates used in agriculture. In accordance with these requirements complex the trace element level should be at least 80 % of the declared water-soluble, the total metal content. Download time micronutrient by the plant in the soil environment should correspond to the period degradability. Too low biodegradability may adversely affect the environment, causing mobilization heavy metals from bottom sediments and lead to phytotoxic complexes. Formal requirements resulted in the continued search for new chelating agents, and improving the technology used. The aim of the study was to determine the degree of complexation of the selected ions of micronutrients with chelating substance at different reaction times. The molar ratio of metal-ligand equal to 1:1. The degree of complexation was determined by differential pulse voltammetry. Was selected micronutrient zinc. Comparison was made to a compound belonging to the group of derivatives of aminopolycarboxylic compounds and for substances of natural origin – amino acid. These

¹ Institute of Inorganic Technology and Mineral Fertilizers, Wrocław University of Technology, ul. Smoluchowskiego 25, 50–372 Wrocław, Poland, phone: +48 71 320 20 65, fax +48 71 328 04 25.

* Corresponding author: krystyna.hoffmann@pwr.edu.pl

studies will help determine the optimal response time complexation of micronutrients by chelating agents commonly used in the fertilizer industry.

Keywords: chelate, micronutrients, liquid fertilizers

Introduction

Plants need for proper development of both macro and micronutrients. These components cannot be replaced by another element, as they play an important role in the metabolism of plants and plant without them cannot go full cycle of vegetation. Macronutrients are acting as building blocks and are taken from the soil in large quantities. For micronutrients include about thirty elements. For micronutrients used as fertilizer formulations include eight of them, iron, manganese, zinc, copper, boron, molybdenum, nickel and chlorine. They participate in biochemical processes, mainly as an essential element for the proper functioning of the enzymes. Also have a stimulating effect on the efficiency of macronutrients. The need for these elements is much smaller than in the case of macronutrients (several to several hundred grams per 1 ha of cultivated area) [1].

The demand for plant micronutrients depends on many factors such as soil pH, content of clay and humus in the soil, microbial activity of the substrate, on the type, variety and age of the plant. Micronutrient fertilization should ensure maximum uptake of fertilizer with high efficiency, the diverse elements depending on the demand and enable the use of plant fertilizer for intervention. This has led to the development of micronutrient fertilizer industry. Such fertilizers are produced in order to ensure optimum and effective nutrition while minimizing adverse impacts on the environment. Excess micronutrients in the soil solution can lead to eutrophication, heavy metals mobilization from the bottom sediments and rivers and, consequently, to introduce them into the food chain. Microelement fertilizers are produced in the form of liquid or fine-crystalline. Liquid fertilizers are characterized by an effective and fast response and high efficiency.

Microelements are applied in various forms: the macronutrient fertilizers containing trace elements, in the form of inorganic salts, in the form of glazes fertilizer, in the form of liquid fertilizers containing micronutrients and in the form of chelates. In recent years the most commonly used are trace elements chelates. These compounds are resistant to external factors, are characterized by high durability, ensure a high degree of bioavailability of micronutrients in plants. There is a low probability of phytotoxicity. Fertilizer chelates are readily soluble in water. Thanks to the structure of the chelate can be acquired in whole or may be subject to a slow dissociation so that the ions are released gradually, allowing for optimal supplement the shortage without any negative impact on the environment. Micronutrient fertilizer chelates are 2 to 5 times more effective than the sulphate salts [2–5].

Selected for use as fertilizers are substances that allow a sustainable manner micronutrient cations stabilize a wide range of pH and in the presence of other nutrient. Particular stability characterized by compounds belonging to the aminopolycarboxylic compounds (APCAs). These substances form a chelate with the trace element in a molar

ratio metal to ligand equal to 1:1. Such compounds are widely used in the manufacture of detergents, fertilizers, textiles and paper. The fertilizer industry uses ligands like in Table 1. It can be acid or sodium, potassium or ammonium salts.

Table 1

Fertilizers chelating agents [4]

No.	Designation	Alternative designation	Chemical formula
1	ethylenediaminetetraacetic acid	EDTA	$C_{10}H_{16}O_8N_2$
2	2-hydroxyethylethylenediaminetriacetic acid	HEEDTA	$C_{10}H_{18}O_7N_2$
3	ethylenetriaminepentaacetic acid	DTPA	$C_{14}H_{25}O_{10}N_5$
4	ethylenediamine- <i>N,N'</i> -di[(<i>ortho</i> -hydroxyphenyl)acetic acid]	[<i>o,o</i>] EDDHA	$C_{18}H_{20}O_6N_2$
5	ethylenediamine- <i>N</i> -[(<i>ortho</i> -hydroxyphenyl)acetic acid]- <i>N'</i> -[(<i>para</i> -hydroxyphenyl)acetic acid]	[<i>o,p</i>] EDDHA	$C_{18}H_{20}O_6N_2$
6	ethylenediamine- <i>N,N'</i> -di[(<i>ortho</i> -hydroxy-methylphenyl)acetic acid]	[<i>o,o</i>] EDDHMA	$C_{20}H_{24}O_6N_2$
7	ethylenediamine- <i>N</i> -[(<i>ortho</i> -hydroxy-methylphenyl)acetic acid]- <i>N'</i> -[(<i>para</i> -hydroxy-methylphenyl)acetic acid]	[<i>o,p</i>] EDDHMA	$C_{20}H_{24}O_6N_2$
8	ethylenediamine- <i>N,N'</i> -di[(5-carboxy-2-hydroxyphenyl)acetic acid]	EDDCHA	$C_{20}H_{20}O_{10}N_2$
9	ethylenediamine- <i>N,N'</i> -di[(2-hydroxy-5-sulfo-phenyl)acetic acid] and its condensation products	EDDHSA	$C_{18}H_{20}O_{12}N_2S_2 + n \cdot (C_{12}H_{14}O_8N_2S)$
10	iminodisuccinic acid	IDHA	$C_8H_{11}O_8N$
11	<i>N,N'</i> -di(2-hydroxybenzyl)ethylenediamine- <i>N,N'</i> -diacetic acid	HBED	$C_{20}H_{24}N_2O_6$

Currently, the most widely used chelating agents is the disodium salt of ethylenediaminetetraacetic acid (EDTA). However, there is a high probability that this substance does not have sufficient biodegradability. The compound may be present in the soil for up to 15 years [6–8].

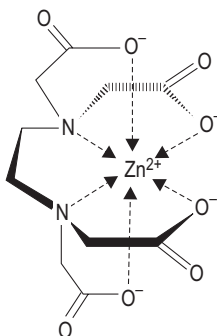


Fig. 1. EDTA complex with zinc ions

Due to the existing problem of environmental pollution by biodegradable chelates constantly looking for new substances, which may in future become a replacement for existing substances [9–10]. In recent years, the market has been introduced foliar amino acid complexes. Amino acids are the second type of natural compounds that plants produce to solubilise and translocation minerals. Digestibility of amino acid chelates in foliar is close to 100 %, they are less phototoxic to plants. Their application allows having a positive impact on the biochemical processes (precursors for the synthesis of plant hormones) and metabolic products. Plants manufacture these compounds to make minerals biologically available in the cell. As with organic acids, amino acid compounds also play a role in mineral uptake into plant tissue, because of the increase permeability effect of the amino acid on the cuticle. As in the case of feed additives used bioactive amino acids derived from the hydrolysis of proteins (*L*-form). Hydrolysis of protein is expensive to produce. This problem caused that amino acid compounds are application only in rare type of plants. Amino acid ligands are most often used: tryptophan, methionine, glycine, glutamic acid, proline and lysine.

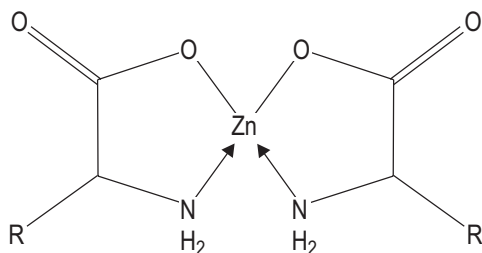


Fig. 2. Amino acid complex with zinc ions

These compounds are called stimulants or anti-stress agents. In Poland such formulations are applied after the winter, drought or floods in order to reduce the effects of stress plants. In Western European countries are used in the normal cycle of crops [11–13].

Materials and methods

For the determination of the reaction time to degree of complexation, were done a series of experiments in different molar ratios of metal-ligand. In experiments was used zinc. The micronutrient was introduced into the system in the salt form – heptahydrate zinc sulphate(VI) prod. POCh. Used ligands were synthetic derivative which belonging to aminopolycarboxylates group and natural ligand. Synthetic ligand introduced into the system in the form of disodium salt of ethylenediaminetetraacetic acid (EDTA) prod. POCh Gliwice and natural ligand, *L*-lysine, prod. Sigma-Aldrich

The effect of time on the reaction metal-ligand of complexation degree checked using differential pulse voltammetry.

The degree of zinc complexation was determined by differential pulse voltammetry. This method consists in measuring the current flowing from the sample during electrolysis depending on the linearly changing potential. Measurements were made of

Eco Chemie camera: AUTOLAB PGSTST 12 GPES software. Mercury electrode was used 663 VA Stand Methrom company working in SMDE mode (Static Mercury Drop Electrode). The reference electrode was silver chloride electrode, auxiliary electrode and a glassy carbon electrode. The experiments were repeated three times, and the results of arithmetic mean.

Table 2

The value of the voltammetric analysis used when the content of zinc ions

Parameters	The value of a given parameters
Size of mercury drop	0.25 mm ²
The value of the step potential	0.00495 V
Modulation amplitude	0.00255 V
Modulation time	0.05 s
Equilibration period	5 s
The value of the deposition potential	1.3 V
Time of deposition	60 s
The scope of the potential for Zn ²⁺	-1.2 V to -0.7 V

The study was conducted in an aqueous medium in the presence of basic electrolytes. Measurements of the degree of complexation of zinc ions are carried out in the presence of 0.1 mol/dm³ KCl at pH 7. The used ligands were: synthetic ligand EDTA and the natural ligand *L*-lysine. Using differentia reaction time 300, 600, 900 and 1200 s.

The test sample with a capacity of 25 cm³ containing zinc ions and a chelating ligand provided in the supporting electrolyte and the measurement cell was subjected to stirring for 300, 600, 900 and 1200 s and deoxygenating for 300 s. From the obtained voltammogram read potential reduction of metal ions [V] and the signal height. Micronutrient concentration was determined on the basis of the signal current. The resulting signals are proportional to the concentration of ions in solution. Ion complexed trace element is electrically neutral. The degree of complexation was calculated from the difference in concentration before and after the chelation reaction.

The degree of complexation was calculated from the following formula:

$$X = \left(\frac{C_0 - C}{C_0} \right) \cdot 100\%$$

where: X – degree of zinc complexation [%],

C_0 – zinc ion concentration in the nil sample [mol/dm³],

C – concentration of unbound zinc ions [mol/dm³].

Results and discussion

Figure 3 shows a voltamperogram of zinc ions complexed by *L*-lysine at various reaction times. Used 4 different times: 300, 600, 900 and 1200 s. On the basis of the

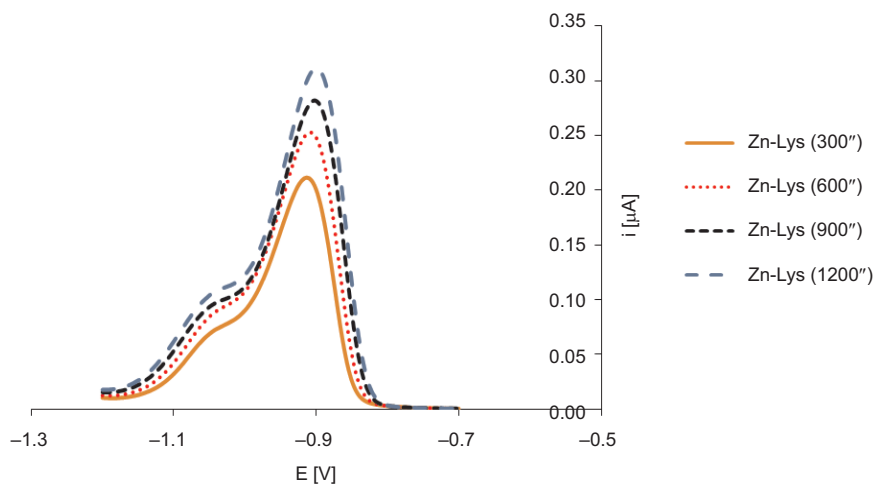


Fig. 3. Voltamperogram of zinc and *L*-lysine complex in different reaction time

signal, concentration of zinc ions in each of the systems, and the calculated degree of complexation.

Experiments were performed under the same conditions for the complexation of substances belonging to the aminopolycarboxylic compounds: disodium salt of ethylenediaminetetraacetic acid. Figure 4 shows a voltamperogram of zinc ions complexed by EDTA at various reaction times.

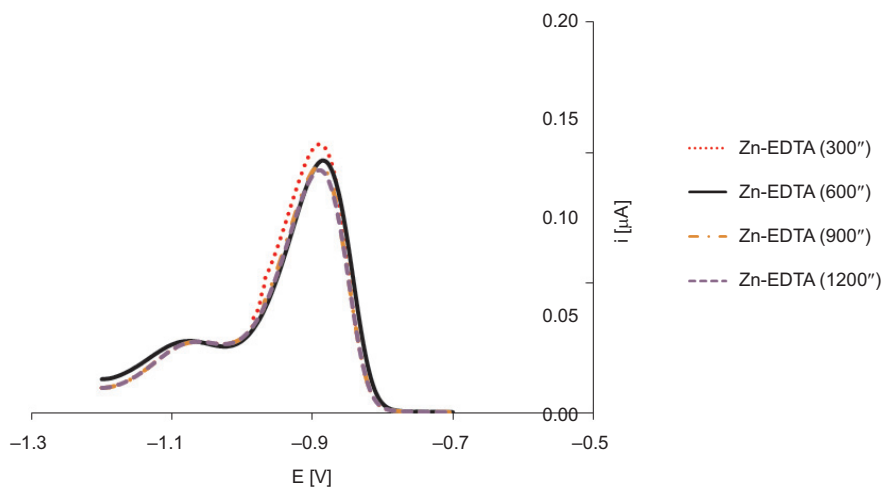


Fig. 4. Voltamperogram of zinc and EDTA complex in different reaction time

The degree of complexation was calculated on the basis of the above voltamperograms. Comparison of the results for both of complexing agents is given in Table 3.

Table 3

Effect of reaction time the degree of complexation of zinc ions by *L*-lysine and EDTA

Time [s]	Degree of zinc ions complexation [%]	
	Zn-Lys	Zn-EDTA
300	33.33	98.51
600	30.92	99.23
900	29.05	~100.00
1200	21.71	~100.00

Conclusions

On the basis of the interpretation of the obtained voltamperograms can determine the degree of complexation of zinc ions. In the case of synthetic substances the conditions laid down in Regulation (EC) No 2003/2003 of the European Parliament and of the Council of 13 October 2003. These requirements have been met with a molar ratio of metal to ligand equal to 1:1. In the case of a natural substance, these requirements were not met. Probably other reaction conditions will influence the formation of stable complex which is characterized by a greater degree of complexation.

The obtained results indicate that increasing the zinc reaction time of the disodium salt of ethylenediaminetetraacetic acid will increase the degree of complexation slightly. In the case of a system comprising zinc ions and amino acids to increase the reaction time causes a slight decrease in the degree of complexation.

Research has shown that the reaction time of fertilizer zinc ion chelating substance to a minor extent, affects the degree of complexation.

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WPLYW CZASU REAKCJI JONÓW CYNKU Z NAWOZOWYMI SUBSTANCJAMI CHELATUJĄCYMI NA STOPIEŃ SKOMPLEKSOWANIA

Instytut Technologii Nieorganicznej i Nawozów Mineralnych, Wydział Chemiczny
Politechnika Wrocławska

Abstrakt: W ostatnich latach dużym problemem dla rolnictwa jest niedobór przyswajalnych mikroelementów w glebie, co powoduje zmniejszenie plonów. Niedobór ten spowodowany jest intensyfikacją rolnictwa, uprawą nowych gatunków roślin wymagających nawożenia oraz znacznym udziałem gleb o niskiej zawartości przyswajalnych mikrośladników, dlatego w ostatnich latach poszukuje się odpowiednich form, w jakich, można je aplikować, by nie miały negatywnego wpływu na środowisko.

Szczególne znaczenie w branży nawozów mikroelementowych zyskały chelaty. Związki te dzięki swojej kleszczowej strukturze cechują się trwałością oraz swoistą inertinością w roztworze glebowym. Chelatory stabilizują kation mikroelementu w szeroki zakresie pH. Ich stosowanie pozwala w sposób optymalny uzupełnić niedobór mikroelementów. Dostosowanie zawartości składników pokarmowych do potrzeb roślin pozwala ograniczyć negatywny wpływ na środowisko, nie powodując zasolenia gleb, jak w przypadku stosowania soli mikroelementów. Mogą być aplikowane zarówno doglebowo, jak i dolistnie. Produkowane są w formie płynnej lub drobnokryształicznej. W krajach Unii Europejskiej określone są substancje chelatujące stosowane jako dodatki do nawozów płynnych. Są to związki syntetyczne należące do grupy aminopolikarboksyłowych (APCAs), które tworzą trwałe kompleksy rozpuszczalne w wodzie. APCAs tworzą chelaty z mikroelementami w stosunku molowym 1:1. Najczęściej stosowanym komponentem jest sól disodowa kwasu etylenodiaminotetraoctowego (EDTA). W Rozporządzeniu Parlamentu Europejskiego i Rady WE nr 2003/2003 z dnia 13 października 2003 r. znajdują się wymogi dotyczące chelatów stosowanych w rolnictwie. Zgodnie z tymi wymogami stopień skompleksowania mikroelementu powinien wynosić przynajmniej 80 % deklarowanej, rozpuszczalnej w wodzie, całkowitej zawartości metalu. Czas pobierania mikroelementu przez roślinę w środowisku glebowym powinien odpowiadać okresowi degradowalności. Zbyt niski stopień biodegradacji może negatywnie wpłynąć na środowisko, powodując remobilizację metali ciężkich z osadów dennych i prowadzić do powstania fitotoksycznych kompleksów. Wymogi formalne spowodowały, że nadal poszukuje się nowych substancji chelatujących oraz ulepsza się stosowane technologie.

Celem badań było określenie stopnia skompleksowania wybranego jonu mikroelementu przy różnym czasie reakcji z substancją chelatującą. Zastosowano stosunek molowy metal-ligand równy 1:1. Stopień skompleksowania wyznaczono z wykorzystaniem voltamperometrii plusowej różnicowej. Wybrany mikroelementem był cynk. Porównanie wykonano dla związku należącego do grupy pochodnych aminopolikarboksyłowych oraz dla substancji pochodzenia naturalnego – aminokwasu. Badania te pozwolą określić optymalny czas reakcji kompleksowania mikroelementów przez substancje chelatujące powszechnie stosowane w branży nawozowej.

Słowa kluczowe: chelaty, mikroelementy, nawozy płynne