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ELECTROCHEMICAL SYNTHESIS OF ZINC CHELATES IN NON-AQUEOUS MEDIA

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ABSTRACT

Electrochemical synthesis of zinc chelates in non-aqueous media has been studied by polarization, capacitance measurements, infrared spectrometry and electron microscopy. The dependences of the substance content and current yield on current density, ligand concentration, temperature and time were determined. Optimal conditions for the process were determined. The aim of the study is to perform electrochemical synthesis of polycarboxylic acid-based chelates in non-aqueous media and to determine the possibility of electrosynthesis in non-aqueous media. In order to study adsorption and material release, the electrochemical behavior of chelate complexes was studied by measuring the volt-ampere E-gi, i-τ, E-τ and capacitance curves. The measurements were performed using graphite and platinum electrodes in acidic alcohol solutions. Based on preliminary experiments it was found that the influence of the process temperature on the yield of the target product, copper chelate, was very small; increasing the temperature leads to some decrease in the yield of the target product, mainly due to resin formation. end products.

Keywords: Electrochemical Synthesis, Chelates, Bimetals, Potential, Spectrometry, Microfertilizers

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INTRODUCTION

The use of chelate microelements complexes is of interest for replenishment of microelements' shortage in plant rising and feeds. They are participants of metabolism processes in an organism, especially chelates complexes with citric acid (citrates). By now, positive experience in using citrates of biometals in food, pharmaceutical, agrarian industry and medicine has been gained.

By their structure, the chelates are close to natural compounds. They have high biological activity and they are well assimilated. Such natural substances as vitamin B_{12}, chlorophyll, hemoglobin is chelated complexes. The chelate compounds of bimetals in the agro-industrial complex are used as micro fertilizers, feed additives and growth stimulants. They do not saline soil, reduce the level of nitrites and nitrates in plants, and raise the content of vitamins in an organism.[1]

The objective of the research is the electrochemical synthesis of the chelates on the basis of polycarboxylic acids in non-aqueous media and defining opportune zinc of electrosynthesis in non-aqueous media.

EXPERIMENTAL

Electrochemical synthesis of the zinc chelates was carried out in an electrolyze with a dissolving anode. Alternating asymmetric current was used to prevent adhesion to the anode. Different polycarboxylicoxy acids were used as ligands.[2-3] A flow sheet for the synthesis is shown in Fig.-1.

The electric circuit contains a source of current – adjustable reducing transformer for 220V, electrolyze, amperemeter for 200 mA, voltmeter for 200V. The electrolyze consists of two electrodes, one from soluble cuprum (anode), another one from platinum or graphite (cathode). The electrolyte contains organic acid, pyridine; ethyl alcohol was used as the dissolvent. The elemental composition was

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determined on a raster electron microscope JSM-6490LV. IR absorption spectra (disks from of metallo-complexes were measured on Specord-75J spectrometer[4].

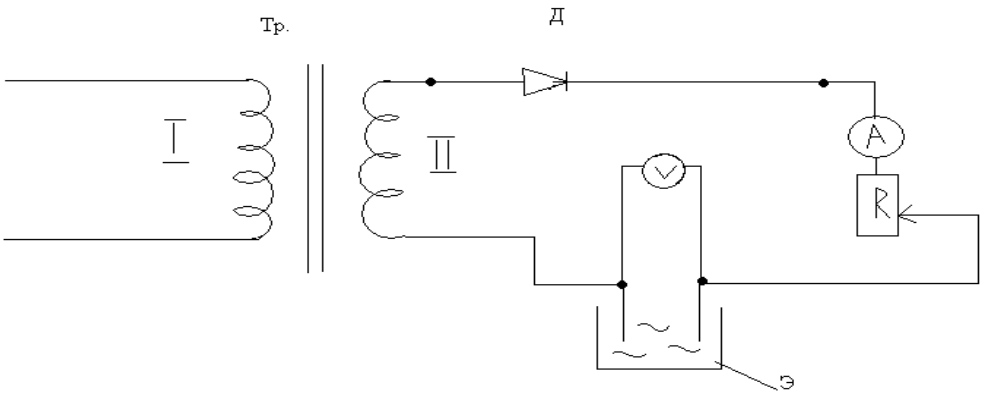

Fig.-1: The Flow Sheet of the Zinc Chelates' Electrochemical Synthesis
Tr. – autotransformer, D – diode of 200K brand, A – amperemeter, R – rheochord, V – voltmeter, E – electrolyze.

Double-electric layer capacity was measured on a unit consisting of alternating current bridge P-568, null indicator φ-550, an electric cell with rotating electrode and vacuum tube RF-13 voltmeter. Alternating sinusoidal voltage with magnitude V =6mV was imposed upon the cell from high-frequency signal generator GZ-3. The voltage value was measured with the help of the vacuum tube RF-13 voltmeter. Coaxial-platinum cylinder by φ = 5.4 cm diameter was used for polarization of the working electrode by the alternating current. The capacity of the platinum cylinder in the general cell impedance was not taken into account.[5] To prevent the effect of the alternating current on the direct one, an impedance coil with inductivity L=I henry was serially included in the chain of the last. The working electrode was polarized by the direct current with the help of potentiostat P-5848. For more careful filtration of the direct current from the alternating, an additional capacity C_{add} =0.5mcf was included into the chain in parallel.

By the results of previously carried out measurements, the most optimal conditions for preparation of the electrode surface such as nitrogen purging time (volume 50ml) in 40 minutes were selected. The electrode rotation velocity is equal to V≈2000rpm. At such velocity, diffusion limitations and the screening effect of gas bubbles, formed on the electrode surface, are practically eliminated. The working electrode before measurement of the set of capacitive curves was treated chemically and subjected to the cathode-anode polarization.[6-7]

After the electrosynthesis, the laid-down settling was filtered and subjected to chromatographic purification. Chromatographically pure samples were used for the measurement of IR-spectra and elemental analysis.

Research of the zinc chelate electrochemical behavior on a graphite electrode in spirit media within the interval of pH=3÷5.

Research of the chelate complexes' electrochemical behavior by measurement of volt-ampere E-ℓgi, i-τ, E-τand capacitive curves was carried out with a view to studying the adsorption and selection of material. The measurements were carried out using graphite and platinum electrodes in acid spirit solutions.

Figure-2 presents volt-ampere zinc curves, characterizing the behavior of the graphite electrode in 0.1 M H_2SO_4 without any additives and in the presence of the citrate. Zinc the volt-ampere record of the background (Curve 1) in the field. $E_к$= -0.8-1.5V represents straightforward dependence with в$E_к$= 0,34 (Where, в = $\frac{\partial \varphi}{\partial \ell \text{ gi}}$). The last is well keeping with these works.[8-9]

When introducing to the solution the zinc chelates 10^{-3}M (Curve 2), the volt-ampere record within the interval of potentials $E_к$=-0.80÷-1.24 Bis shifted to the field of negative potential values. The dependence form φ-ℓgI is held, the slope of Tafel line is not practically changed. At the potential $E_к$= -I.25B, the slope of the line sharply changes with an increase of hydrogen overpotential (η=0.I2B). At that, the current

density reduction to $1 \cdot 10^{-3}$A/cm^2 is observed. This is half-order lower than in the pure background solution. The inhibition effect of the cathode process enhances with an increase of the zinc citrate volume concentration (Curves 3 and 4). Such behavior of the citrate on the zinc e cathode within the interval of potentials $E_к$= - 0.8 = -1.45B, probably, has an adsorptive character. The value $E_к$= -1.25B, at which occurs a sharp change in the slope of the Tafel line, meets the maximal citrate zinc adsorption.

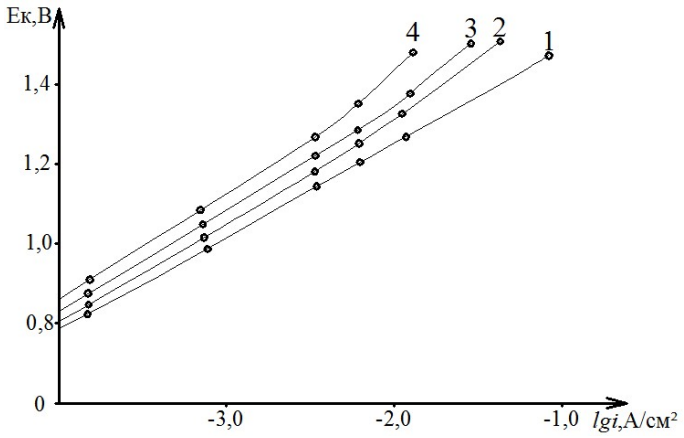

Fig.-2: Volt-ampere Record of 0.1 M H_2SO_4 (curve 1) on the Graphite Electrode with Additives of Zinc Citrate (M): 2-0.003; 3-0.1; 4-0.5.

Inhibition of the cathode process, especially its dependence on the zinc citrate volume concentration, is visually illustrated by the dependence $\ell g \frac{\iota}{\iota_0}$ (Fig.-3).

Between values $\ell g \frac{\iota}{\iota_0}$ (of the inhibition coefficient, Where i – density of the current on the electrode without any additives, i_o– with the addition of the zinc citrate), representing the process' inhibition degree and volume concentration of the additive at Eк= const., there is summate dependence. With the increase of the volume additive zinc concentration, the value $\ell g \frac{\iota}{\iota_0}$ decreases, which also indicates the citrate adsorption within the interval of potentials Eк=-1.1 ÷ -1.4B.

Electrochemical hydrogen reduction inhibition in the presence of the zinc citrate is visually illustrated by "current – time" curves. This really represents the zinc adsorbed molecules setting kinetics at $E_к$= const. (Fig.-4). The curves clearly show the zinc chelate samples' introduction moments (Curves 2 and 3), followed by sharp current decay in the initial period.

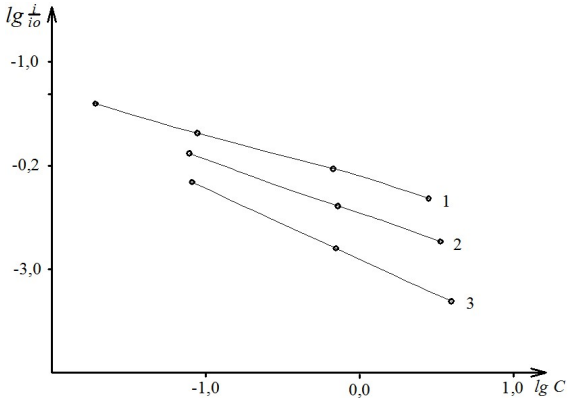

Fig.-3: Dependence of the Inhibition Coefficient on the Zinc Citrate Volume Concentration at Eк– const. (B) Curve1 =-1.1; Curve 2 = -1.25; Curve3 = -1.4.

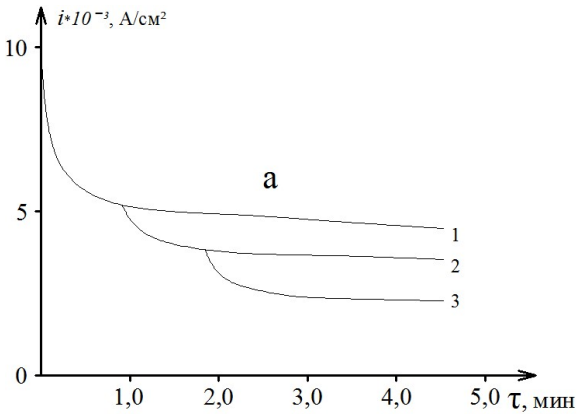

Fig.-4: "Current-time" Curves at Ec = Const; -1.25V (a). in 0.1M. H_2SO_4 (Curve 1) with Zinc Citrate (M): Curve 2-10-3; Curve 3-0,1.

The cuprum citrate adsorption fact is substantiated by data of the capacitive measurements (Fig.-5). When introducing the zinc citrate to $0.1MH_2SO_4$solution (Curves 2 to 4), a noticeable reduction of the double electric layer capacity is observed. With the increase of the additive's vol zinc tume concentration, the double electric layer capacity value decreases i.e. the citrate adsorption increases.

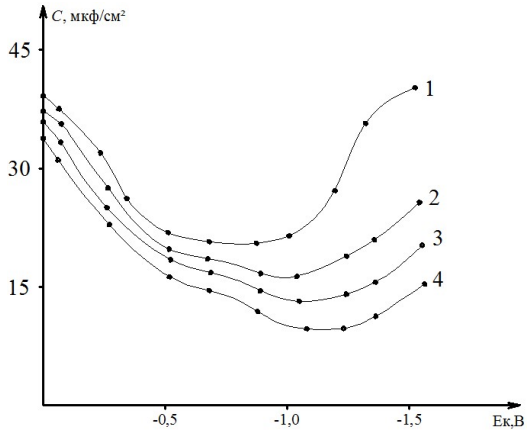

Fig.-5: Curves of the Graphite Elect Zinc Rode Differential Capacity in $0.1MH_2SO_4$ (curve1) with the Citrate Additives (M): $2\text{-}10^{-3}$; 3-0.1; 4-0.5

The electrochemical behavior of other chelates zinc (apple, milk and γ-acetoacetic acids) on the platinum and graphite electrodes is perfectly identical to the electrochemical behavior of the zinc citrate. On the basis of the results of the volt-ampere and capacitive measurements, grazinc phite was selected as the cathode by economic considerations for the electrochemical synthesis.

The electrochemical synthesis of the zinc chelate compounds (II) with a number of polycarboxylic acids (Table-1) was carried out by the following scheme (Fig.-1). The synthesized complex compounds of cuprum are brightly dyed substances of a blue-green palette.

Table-1: The Chelate Zinc Compounds' Electrochemical Synthesis Process Characteristic

No.	Substance	Potential of the beginning of Formation, B	Current Output, %	Current Density, A/cm^2		Area, cm^2	
				Anode	Cathode	Anode	Cathode
I	Bis (2-oxy-propionate) penta cuprum aqua	0,16	59,7	0,084	0,05	5	10

II	2-oxy-2.3-dibutonate penta cuprum aqua	0,65	61,3	0,075	0,05	4	10
III	3-oxy-2,3,4-tri-penta cuprum aqua	0,52	43,8	0,066	0,05	5	10

After the electrosynthesis, the laid-down settling was filtered and subjected to chromatographic purification. Chromatographically pure samples were used for the measurement of IR-spectra and elemental analysis. Table-2 shows data of IR-spectra of the cuprum chelates.

Table-2: IR-spectra of the Zinc Chelates

Cuprum Chelates	Wavenumber (cm-[1])				
	(C-OH)	Ring Fluctuations	(CH)	(Cu-C)	(-OH)
1	1468	989	2921	564	3260
2	1470	988	2935	562	3240

Element	Percent by Weight
Na	0.1
Mg	0.5
Al	0.55
Si	0.6
P	0.31
S	0.14
Cl	0.01
K	0.76
Cu	49.7
Mn	0.28
Fe	0.14
C	30.46

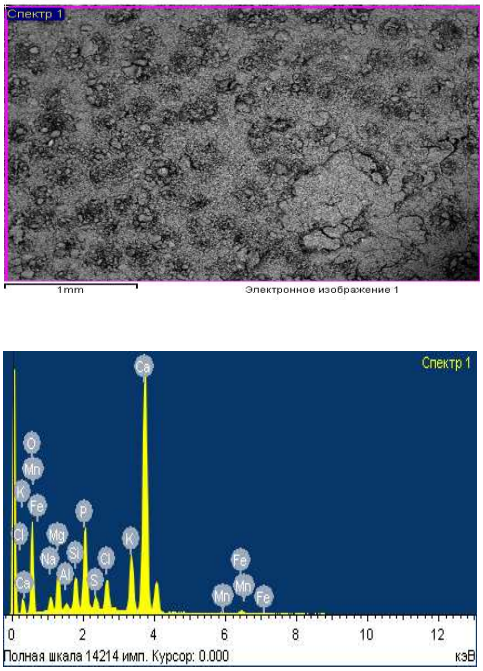

Fig.-6: Elemental Composition of the Zinc Citrate

As is seen from Fig.-6, the content of the zinc is equal to -49.7%. This is much more of the zinc content in chelates, gained chemically, in which content of the cuprum chelates does not exceed 14-15%.

RESULTS AND DISCUSSION

The influence of the electrolyte nature and pH environment on the complex compounds' electrochemical synthesis was considered in a number of works[10]. Authors note the influence of the environment acidity on the output of end products at the recovery of a number of heterocyclic compounds. Figure-7 shows the dependence of the substance output (BB%) and current output (BT%) of the zinc citrate on the electrolyte concentration. As is seen from Fig.-7, the concentration of the free pyridine favorably influences the process. With that, curves of the dependences BB% (Curve 1) and BT% (Curve 2) on the electrolyte concentration pass through a maximum at C= 0.4 M. Apparently, the maximum is conditioned by the formation of salts of initial substances in the electrolyte solution, by an increase in the rate of diffusion of the cuprum ions on the surface of graphite cathode in the field of double electric layer, by increase in the rate of desorption of the end product, the citr zinc **s**ate, from the electrode surface, that is an agreement with data of authors.[11-12]

Figure 8 shows the dependence of the output by BB% and BT% of the zinc citrate on the graphite cathode potential, curve 1 – BB%, curve 2 – BT%.

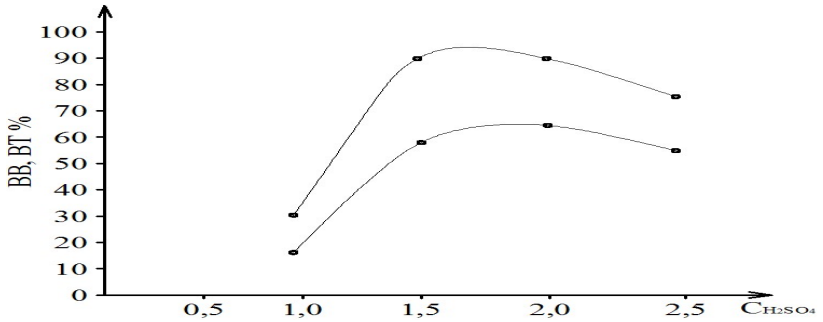

Fig.-7: Dependence of the Output by (the output by BB % Curve 1 and BT% Curve2

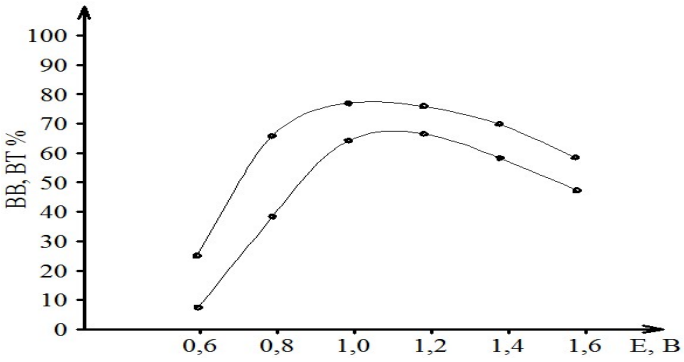

Fig.-8: Dependence of the Output by BB% Curve 1 and BT % Curve 2
of the Cuprum Citrate on the Electrolyte Concentration of the Cuprum Citrateon the Cathode Potential

Influence of the Current Density

Electrochemical synthesis of the chelates occurs in a wildish range of the cathode current densities: from 0.01 to 0.1 A/cm^2. As is obvious, an increase in the current density favorably influences the output of the end product. Figure-8 shows that the cuprum citrate output passes through the maximum at E=-1.1B. With the further increase in the cathode potential, the product output decreases, which is apparently linked with the citric acid desorption. As is known, organic substances may adsorb on the electrode surface at a definite potential. Therefore, E=-1.1B, to outward seeming, meets that potential, when the cuprum chelate maximal adsorption is observed.[11]

Table-3: Temperature Effect on the Electrolysis Process

Outputs, %	Temperature, ºC				
	25	30	40	50	60
Substance Output, %	38	49	68	92	90
Current Output, %	24	32	48	60	58

Temperature dependence BB% and BT% were studied within the limits of 25-60ºC. The electrolysis time effect on the process was studied within intervals of 0,5-3 hours.

Usually, cathode processes are carried out at low-temperature values with a view to simplify the process' technology and draw stable, chemically stable end products. Based on the preliminary experiments, it was established that the process temperature effect on the end product output, the cuprum chelate, is very low, increase in the temperature leads to some reduction of the end product output, generally, at the expense of gumming of the end products.

CONCLUSION

Based on the research, it is possible to make a conclusion that there is the availability of the chelate compounds of biometals by the electrochemical synthesis method in non-aqueous media using the

alternating current. They can be used as chelate fertilizers in plant raising and additives to feed in cattle production.

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