

## КОМПЛЕКСООБРАЗОВАНИЕ В СИСТЕМЕ ЦИНК (II)-ХРОМ (III) -КОБАЛЬТ (II)-ГЛИЦИН-ВОДА

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*Исследование процессов комплексообразования является научной основой при разработке электролитов в гальванотехнике. В работе получены данные по комплексообразованию в системе цинк (II)–хром (III)–кобальт (II)– глицин–вода. Исследование комплексообразования в системе цинк(II)-хром(III)-кобальт(II)-глицин-вода актуально в связи с возможностью разработки процессов электролитического цинкования и получения соответствующих покрытий с высокими показателями коррозионной стойкости. Кроме того, легирование цинковых гальванических покрытий хромом, кобальтом позволяет заменить применение токсичных кадмиевых покрытий и использовать меньшие их толщины. Растворы термостатировали при 25 °С. Для измерения рН применяли прибор HI 2215 рН/ORP Meter. Время спин-решеточной релаксации  $T_1$  измеряли на импульсном ЯМР-спектрометре «Minispectq 20» с частотой 19,75 МГц. Константы образования комплексов и их доли накопления рассчитывались по программе CPESSP. В работе приведены данные проведенных ранее исследований систем хром(III)–вода, цинк(II)–глицин–вода, хром(III)–глицин–вода и цинк(II)–хром(III)–глицин–вода. Получены данные по комплексообразованию в системе хром (III) - кобальт (II)-глицин-вода. Установлено образование гетероядерного комплекса  $\text{CrCoGly}_8^{3-}$ . Установлены составы гетероядерных соединений, доли их накопления и константы образования:  $\text{CrCoZn}(\text{HGly})_5\text{Gly}_3^{4+}$  ( $\lg K = 2,31 \pm 0,01$ );  $\text{CrCoZn}(\text{HGly})_3\text{Gly}_5^{2+}$  ( $\lg K = -1,36 \pm 0,05$ ) и  $\text{CrCoZn}(\text{HGly})_2\text{Gly}_6^+$  ( $\lg K = -4,23 \pm 0,09$ ). Максимальная доля накопления гетероядерных комплексов, как показали исследования, наблюдается в области рН 2...6. В работе высказаны соображения об электрохимической реакционной способности гетероядерных соединений. В частности, отмечено, что электрохимическое восстановление более электроотрицательных металлов, в случае их нахождения в гетероядерном комплексе, должно происходить с меньшим перенапряжением реакции.*

**Ключевые слова:** комплексные гетероядерные соединения, цинк(II), хром(III), кобальт(II), глицин, рН-метрическое титрование, ядерная магнитная релаксация протонов, программа CPESSP

## COMPLEX FORMATION IN THE SYSTEM ZINC (II)-CHROMIUM (III) -COBALT (II)-GLYCINE-WATER

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*The study of complex formation processes is the scientific basis for the development of electrolytes in electroplating. The data on complexation in the zinc (II)–chromium (III)–cobalt (II)–glycine–water system were obtained. The study of complex formation in the zinc (II)–chromium (III)–cobalt (II)–glycine–water system is relevant due to the possibility of developing electrolytic galvanizing processes and obtaining appropriate coatings with high corrosion resistance. In addition, the alloying of zinc electroplating coatings with chromium, cobalt makes it possible to replace the use of toxic cadmium coatings and use their smaller thicknesses. The solutions were thermostated at 25 °C. The HI 2215 pH/ORPMeter was used to measure pH. The spin-lattice relaxation time  $T_1$  was measured on a pulsed NMR spectrometer "Minispecmq20" with a frequency of 19.75 MHz. The constants of the formation of complexes and their accumulation shares were calculated according to the CPESPP program. The paper presents data on previously conducted studies of chromium(III)–water, zinc(II)–glycine–water, chromium(III)–glycine–water and zinc(II)–chromium(III)–glycine–water systems. Data on complexation in the chromium (III)–cobalt (II)–glycine–water system were obtained. The formation of a heteronuclear complex  $\text{CrCoGly}_8^{3-}$  has been established. The compositions of heteronuclear compounds, their accumulation fractions and formation constants were established:  $\text{CrCoZn(HGly)}_5\text{Gly}_3^{4+}$  ( $\lg K = 2.31 \pm 0.01$ );  $\text{CrCoZn(HGly)}_3\text{Gly}_5^{2+}$  ( $\lg K = -1.36 \pm 0.05$ ) and  $\text{CrCoZn(HGly)}_2\text{Gly}_6^+$  ( $\lg K = -4.23 \pm 0.09$ ). The maximum proportion of accumulation of heteronuclear complexes, as studies have shown, is observed in the pH range of 2...6. In this paper, considerations are made about the electrochemical reactivity of heteronuclear compounds. In particular, it is noted that the electrochemical reduction of more electronegative metals, if they are in a heteronuclear complex, should occur with less overvoltage of the reaction.*

**Key words:** complex heteronuclear compounds, zinc(II), chromium(III), cobalt(II), glycine, pH-metric titration, nuclear magnetic relaxation of protons, CPESPP program

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## INTRODUCTION

The study of complexation processes is the scientific basis for the development of electrolytes in modern electroplating. Data on the composition, stability and accumulation of complex compounds depending on the pH of the solution allow us to develop the composition of the electrolyte on a scientific basis, establish the electrolysis mode, investigate the kinetics in more detail and understand the mechanism of electrochemical processes.

The aim of the work is to obtain data on the complexation of Zn(II), Cr(III), Co (II) in glycine-containing aqueous solutions.

The electrolytic production of Zn alloys with metals such as Co, Cr, Ni is being studied most actively due to great practical and theoretical interest.

Thus, it was shown in [1-3] that the co-deposition of zinc with cobalt increases the anticorrosive properties of zinc coatings and can be used to replace toxic cadmium coatings. Electrodeposition of the zinc-cobalt alloy is carried out from glycine-containing solutions [4] and using pulsed current [5].

Zinc-chromium alloys also have increased corrosion resistance compared to zinc, which makes it possible to reduce the thickness of the covers used [6, 7].

Obtaining zinc-chromium-cobalt alloys makes it possible to give coatings, in addition to corrosion resistance, such necessary performance characteristics as microhardness [8]. In [9], it was noted that high-quality zinc-nickel-cobalt alloy coatings were obtained in solutions containing glycine. In addition, the study of multicomponent systems is currently relevant in the case of obtaining high-entropy alloys [10].

## MATERIALS AND METHODS OF RESEARCH

The research methodology and processing of experimental data are described in detail in [11].

In this work, cobalt (II) sulfate, chromium (III) chloride, zinc (II) sulfate, and glycine were used as pure for analysis.

The pH was measured on the HI 2215 pH/ORP Meter with an accuracy of 0.01 units. The solutions were thermostated at 25 °C.

The spin-lattice relaxation time  $T_1$  was measured on a pulsed NMR spectrometer «Minispecmq20» with an operating frequency of 19.75 MHz. The study of complexation by NMR is presented in [12, 13].

The constants of the formation of complexes and their accumulation shares were calculated in the CPESP program [14]. Diagrams of the distribution of complexes were also constructed using the CRESSP program.

## DISCUSSION OF EXPERIMENTAL RESULTS

We have previously investigated the system of zinc (II) – chromium (III) – nickel (II) – glycine – water [11]. The compositions of complex compounds, stability constants and the proportion of their accumulation in solutions with different pH values are established. The electrochemical behavior of aqueous solutions containing heteronuclear compounds is presented in [15, 16].

The study of complex compounds in the Zn(II) – Cr(III) – Co(II) – glycine – water system was preceded by obtaining data in solutions of Cr(III)–water [17], Zn(II) – glycine – water [18], Cr(III) – glycine – water [19] and Zn(II) – Cr(III) – glycine – water [20].

In this paper, the complex formation in the chromium (III) – cobalt (II) – glycine – water system is investigated. Experimental data for the chromium (III) – cobalt(II) – glycine system are presented in Table 1. The formation of a heteronuclear complex  $\text{CrCoGly}_8^{3-}$  is established.

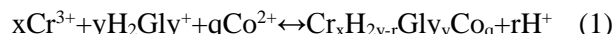
Table 1

## Composition and constants of formalized equilibria of formation of Cr(III)-Co(II)-glycine complexes

Таблица 1. Состав и константы формализованных равновесий образования комплексов Cr(III)-Co(II)-глицин

№	Стехиометрическая матрица				lgK	Комплекс
	Co <sup>2+</sup> (q)	Cr <sup>3+</sup> (x)	H <sub>2</sub> Gl <sup>+</sup> (y)	H <sup>+</sup> (r)		
1	1	1	8	16	-19.08±0.21	CrCoGly <sub>8</sub> <sup>3-</sup>

The formation of the complex occurs according to the scheme (1):



The distribution of connections is shown in Fig. 1. As can be seen from the diagram of the fractional distribution obtained using the CPESP program, the heteronuclear complex  $\text{CrCoGly}_8^{3-}$  prevails at pH values of 2.5...6.

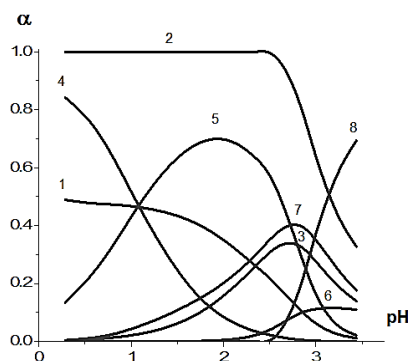


Fig. 1. Diagram of the fractional distribution of mole fractions of compounds in the system chromium (III) - cobalt (II) - glycine depending on pH: 1 - H<sub>2</sub>Gly<sup>+</sup>, 2 - Co<sup>2+</sup>, 3 - HGly, 4 - Cr(HGly)<sub>3</sub>Gly<sup>2+</sup>, 5 - Cr(HGly)<sub>2</sub>Gly<sup>2+</sup>, 6 - CrGly<sub>4</sub><sup>-</sup>, 7 - Cr<sub>2</sub>Gly<sub>6</sub>, 8 - CrCoGly<sub>8</sub><sup>3-</sup>. α - accumulation fraction. C(HGly) = 0.349 mol/L, C(Cr<sup>3+</sup>) = 0.045 mol/L, C(Co<sup>2+</sup>) = 0.046 mol/L

Рис. 1. Диаграмма долевого распределения мольных долей соединений в системе хром(III) - кобальт(II) - глицин в зависимости от pH: 1 - H<sub>2</sub>Gly<sup>+</sup>, 2 - Co<sup>2+</sup>, 3 - HGly, 4 - Cr(HGly)<sub>3</sub>Gly<sup>2+</sup>, 5 - Cr(HGly)<sub>2</sub>Gly<sup>2+</sup>, 6 - CrGly<sub>4</sub><sup>-</sup>, 7 - Cr<sub>2</sub>Gly<sub>6</sub>, 8 - CrCoGly<sub>8</sub><sup>3-</sup>. α - доля накопления. C(HGly) = 0,349 моль/л, C(Cr<sup>3+</sup>) = 0,045 моль/л, C(Co<sup>2+</sup>) = 0,046 моль/л

Experimental data for the Zn(II)- Cr(III)-cobalt (II)-glycine-water system are presented in Table 2.

Table 2

## Composition and constants of formalized equilibria of formation of Cr(III)-Zn(II)-Co(II)-glycine complexes

Таблица 2. Состав и константы формализованных равновесий образования комплексов Cr(III)-Zn(II)-Co(II)-глицин

№	Стехиометрическая матрица					lgK	Комплекс
	Co <sup>2+</sup> (m)	Cr <sup>3+</sup> (p)	Zn <sup>2+</sup> (i)	H <sub>2</sub> Gl <sup>+</sup> (q)	H <sup>+</sup> (r)		
1	1	1	1	8	11	2.31±0.01	CrCoZn(HGly) <sub>5</sub> Gly <sub>3</sub> <sup>4+</sup>
2	1	1	1	8	13	-1.36±0.05	CrCoZn(HGly) <sub>3</sub> Gly <sub>3</sub> <sup>2-</sup>
3	1	1	1	8	14	-4.23±0.09	CrCoZn(HGly) <sub>2</sub> Gly <sub>6</sub> <sup>+</sup>

The formation of the complex occurs according to the scheme (2):

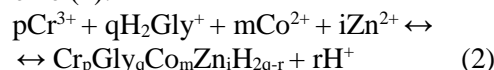


Fig. 2 shows the dependence of the relaxation efficiency- pH of the solution for the systems: Cr(III) – glycine, Cr(III) – Co(II) – glycine, Cr(III) – Co(II) – Zn(II) – glycine.

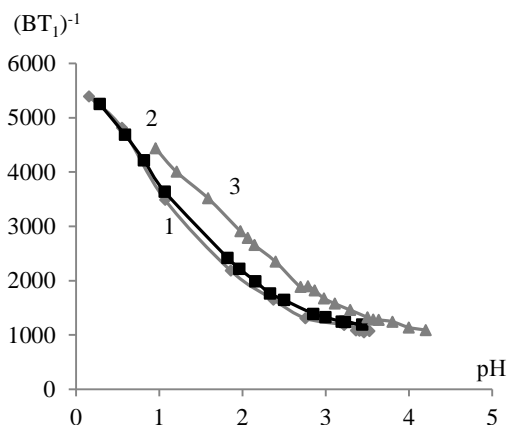


Fig. 2. Dependence of relaxation efficiency for systems:  
1-Cr(III) – глицин, 2-Cr(III) – Co(II) – глицин,  
3-Cr(III) – Co(II) – Zn(II)– глицин

Рис. 2. Зависимость релаксационной эффективности для систем: 1-Cr(III) – глицин, 2-Cr(III) – Co(II) – глицин, 3-Cr(III) – Co(II) – Zn(II)– глицин

The coincidence of curves 1 and 2 (Fig. 2) suggests the possible absence of heteronuclear complexes. During the calculation, only one heteronuclear complex of the composition  $\text{CrCoGly}_8^{3-}$  was identified. Relaxation curve 3 differs significantly from systems 1 and 2 (Fig. 2). The difference in the course of the curves indicates the formation of heteronuclear complexes Cr (III), Co (II), Zn (II) with glycine. The dependence of the distribution of complexes on pH is shown in Fig. 3. These diagrams are also calculated and constructed using the CPESP program.

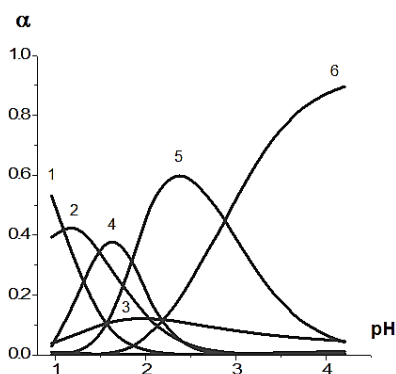


Fig. 3. Diagram of the fractional distribution of mole fractions of complexes in the Cr(III) - Co(II) - Zn(II) - glycine system depending on pH. Accumulation shares of  $\text{H}_2\text{Gly}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{HGly}$  are not shown. 1 –  $\text{Cr}(\text{HGly})_3\text{Gly}_2^{2+}$ , 2 –  $\text{Cr}(\text{HGly})_2\text{Gly}_2^{2+}$ , 3 –  $\text{Cr}_2\text{Gly}_6^0$ , 4 –  $\text{CrCoZn}(\text{HGly})_5\text{Gly}_3^{4+}$ , 5 –  $\text{CrCoZn}(\text{HGly})_3\text{Gly}_5^{2+}$ , 6 –  $\text{CrCoZn}(\text{HGly})_2\text{Gly}_6^+$ .  $C(\text{HGly}) = 0.349 \text{ mol/L}$ ,  $C(\text{Cr}^{3+}) = 0.045 \text{ mol/L}$ ,  $C(\text{Co}^{2+}) = 0.046 \text{ mol/L}$ ,  $C(\text{Zn}^{2+}) = 0.048 \text{ mol/L}$

Рис. 3. Диаграмма долевого распределения мольных долей комплексов в системе Cr(III) – Co(II)–Zn(II)– глицин в зависимости от pH. Доли накопления  $\text{H}_2\text{Gly}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{HGly}$  не показаны. 1 –  $\text{Cr}(\text{HGly})_3\text{Gly}_2^{2+}$ , 2 –  $\text{Cr}(\text{HGly})_2\text{Gly}_2^{2+}$ , 3 –  $\text{Cr}_2\text{Gly}_6^0$ , 4 –  $\text{CrCoZn}(\text{HGly})_5\text{Gly}_3^{4+}$ , 5 –  $\text{CrCoZn}(\text{HGly})_3\text{Gly}_5^{2+}$ , 6 –  $\text{CrCoZn}(\text{HGly})_2\text{Gly}_6^+$ .  $C(\text{HGly}) = 0,349 \text{ моль/л}$ ,  $C(\text{Cr}^{3+}) = 0,045 \text{ моль/л}$ ,  $C(\text{Co}^{2+}) = 0,046 \text{ моль/л}$ ,  $C(\text{Zn}^{2+}) = 0,048 \text{ моль/л}$

The  $\text{CrCoZn}(\text{HGly})_5\text{Gly}_3^{4+}$ ,  $\text{CrCoZn}(\text{HGly})_3\text{Gly}_5^{2+}$ , and  $\text{CrCoZn}(\text{HGly})_2\text{Gly}_6^+$  complexes exist throughout the studied pH region, with accumulation maxima at pH 1.6, 2.5 and 4.4, respectively. The triple complex  $\text{CrCoGly}_8^{3-}$  does not accumulate under these conditions.

As follows from the results of the work carried out, heteronuclear compounds in the system under study mainly dominate in the pH range of 2...6.

The results of the work can be used in the development of electrolytes for electrochemical alloying of zinc with chromium and cobalt.

In the case of electrochemical alloying of zinc coatings with chromium and cobalt, the presence of a positive charge in the complex compounds  $\text{CrCoZn}(\text{HGly})_5\text{Gly}_3^{4+}$ ,  $\text{CrCoZn}(\text{HGly})_3\text{Gly}_5^{2+}$ ,  $\text{CrCoZn}(\text{HGly})_2\text{Gly}_6^+$  creates favorable conditions for their adsorption on the negatively charged cathode surface and should contribute to their recovery.

In conclusion, based on the analysis of literature sources and our research [16], some considerations can be made about the electrochemical reactivity of heteronuclear complexes.

Thus, according to [21] the heteronuclear complex, the orbital of a more electronegative atom makes a greater contribution to the binding orbital of the energy diagram, and the orbital of a less negative atom to the loosening one. Therefore, it can be assumed that the electrochemical reduction of more electronegative metals in the case of their presence in a heteronuclear complex should occur with less overvoltage of the reaction.

The stated consideration agrees with the fact that an increase in the size of complex compounds reduces the activation energy of their cathodic reduction. Thus, it was shown in [22] that an increase in the effective radius of complex compounds reduces the activation energy of their recovery.

In the development of the electrochemistry of heteronuclear compounds, the results of the work [23] may be of interest. Based on quantum mechanical studies, the authors [23] found that in the case when two metals are connected by a bridging particle, a unidirectional flow of electrons from one metal to another occurs in such a system.

It is known that there is a direct connection between ions of different metals in a heteronuclear complex, according to [24, 25], or it is carried out through a bridging particle. If surfactants are used as ligands, as in this work-glycine, which can be adsorbed [26] on the electrode and perform the function of a bridge during charge transfer, it is possible that this will contribute to the joint recovery of ions located in the heteronuclear complex.

## CONCLUSION

The paper presents data on complexation in the systems: Cr(III) – Co(II) – glycine – water; Zn(II) – Cr(III) – Co(II) – glycine – water.

It was found that in the Zn(II) – Cr(III) – Co(II) – glycine-water system, heteronuclear compounds  $\text{CrCoZn(HGly)}_5\text{Gly}_3^{4+}$  ( $\lg K = 2.31 \pm 0.01$ );  $\text{CrCoZn(HGly)}_3\text{Gly}_5^{2+}$  ( $\lg K = -1.36 \pm 0.05$ ) and  $\text{CrCoZn(HGly)}_2\text{Gly}_6^+$  ( $\lg K = -4.23 \pm 0.09$ ) are bound.

The maximum proportions of accumulation of heteronuclear compounds are in the pH range of 2...6.

In the work, based on the analysis of literary sources, considerations are made about the electrochemical reactivity of heteronuclear compounds.

*Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.*

*The authors declare the absence a conflict of interest warranting disclosure in this article.*

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