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*K.D. Pershina, O.K. Trunova, M.S. Artamonov, O.V. Boychuk***ELECTROCHEMICAL PROPERTIES OF Co(II) COMPLEXES WITH RUTIN IN AQUEOUS-ALCOHOLIC SOLUTIONS****V.I. Vernadsky Institute of General and Inorganic Chemistry of the NAS of Ukraine, Kyiv, Ukraine**

Cyclic voltammetry and electrochemical impedance spectroscopy were used to study the effect of pH and the Co:Rut ratio on redox potentials and electrical conductivity of water-alcohol solutions of Co(II) complexes with rutin (Rut). It was found that the reduction potentials for the ratio Co:Rut=1:1 and 1:2 are in the range of  $-0.110$  V to  $-0.197$  V relative to the Ag/AgCl reference electrode, which is significantly higher than the potentials for known flavonoids. In an alkaline medium, the absolute value of the reduction potential increases regardless of the composition of the sample. The measured range of oxidizing potentials for all compounds is in the range of  $+0.02$  V to  $+0.094$  V relative to Ag/AgCl reference electrode, which corresponds to the potentials of compounds with self-oxidizing activity. It is assumed that an increase in oxidative potentials up to  $0.094$  V can characterize the antioxidant activity, which is associated with the manifestation of the autoxidizing properties of the complex in the presence of oxygen and is due to the participation of different binding sites in chelation with the metal. Using the data of electrochemical impedance spectroscopy, the capacity of electrical double layer of a platinum electrode in water-alcohol solutions containing Co(II) complexes with rutin was calculated. An increase in capacitance values by an order of magnitude was observed at a ratio of metal:ligand=2:1 in comparison with the complexes having a ratio of 1:1. The effect of an excess of hydroxyl ions on the charge distribution at the electrode/solution interface was experimentally established, leveling the effect of the Co:Rut ratio on the electrochemical properties.

**Keywords:** cobalt, rutin, metal complex, conductivity, redox potential, capacitance, electrochemical impedance spectroscopy.

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**Introduction**

Recently, the attention of researchers has been attracted by natural polyphenols, which have a wide range of biological activity and which, due to the presence of various reactive centers and functional groups in their structure, have wide synthetic possibilities for further chemical modifications. The most common polyphenolic compounds are flavonoids. In this regard, of particular interest is rutin (3,5,7,3',4'-pentahydroxyflavone-3-rutose, Rut, Fig. 1), which belongs to the group of vitamins P and has antioxidant

properties [1–3].

Flavonoids are effective chelators of metal ions, which are involved in the initiation of free radical processes (via the Fenton reaction), therefore metal phenolate complexes are considered as a means of increasing the antioxidant activity of flavonoids [4–6]. An example is Co(II), the metal cofactor of coenzyme B<sub>12</sub>, and vitamin B<sub>12</sub>. It was shown in ref. [7] that the Co(II) complex with quercetin (2:1) exhibits a higher antioxidant activity than pure flavonoid. In general, important factors for increasing

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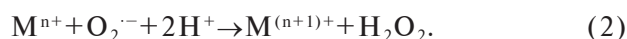
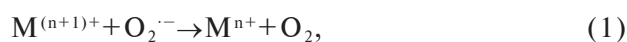
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the antioxidant activity of phenolates are the number and position of OH groups in the structure of flavonoids, coordination centers, the type of metal ion used, the molar ratio of metal:flavonoid, and the pH value of the medium. Depending on the pH value, certain binding sites are involved in chelation, which is primarily associated with the redistribution of electron density in the flavonoid molecule (Fig. 1,b) [8,9].

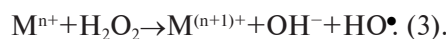
The complexation of flavonoids with metal ions is the result of pronounced electron-donor properties and low reduction potentials (Ec). The range of such potentials is  $-0.25\div-0.75$  V for most flavonoids. The studies of current-voltage dependences have established that flavonoids, which are capable to self-oxidizing and formation of the oxygen radicals, have oxidation potentials in the range from  $-0.03$  V to  $+0.06$  V relative to a saturated calomel electrode (SCE). Flavonoids with auto-oxidizing activity in the presence of oxygen have an oxidize potentials from  $+0.130$  V to  $+0.340$  V relative to the SCE. The range of potential values for self-oxidizing flavonoids is comparable to the domain of formation of the superoxide ion  $O_2^{\cdot-}$  in mitochondrial NADH-CoQ reductase [10]. At the initial stage of complex formation, an electrophilic attack of a metal ion on a flavonoid molecule occurs with the formation of a ligand-metal bond by transferring an electron from the d-orbital of the metal to the  $\pi^*$ -orbital of the flavonol. The structure of the formed complex depends on the nature of the electron density distribution in the ligand, particularly, on the magnitude of the charge on the oxygen atoms with the maximum electron density. For example, the highest negative charge in the rutin molecule is located on the oxygen atom of the carbonyl group ( $-0.393$ ), and the charge on other oxygen atoms range from  $-0.212$  to  $-0.246$ ; therefore, for rutin, coordination

over the oxygen atom of the carbonyl group is preferable [9,10].

Coordination compounds of flavonoids with ions of 3-d metals inhibit free radical processes and affect the ionic balance in the body. In the process of complex formation, flavonoids are able to pass into the oxidized form; however, the structure and biological activity will differ from these parameters of the original flavonoid. For example, Rut complexes with Cu(II), Al(III), Fe(II)/(III), and Zn(II) ions have shown themselves to be compounds with higher antiradical activity than free ligands [5,8,12]. The manifestation of effective antiradical activity of metal complexes of flavonoids can be explained by the fact that the superoxide-dismuting catalytic center in the complex is a metal. In the course of the reaction with the superoxide radical  $O_2^{\cdot-}$ , the metal ion will accept (1) and donate (2) electrons:



At the same time, the resulting superoxide radical quickly dismutates to form hydrogen peroxide  $H_2O_2$ , which, not being a free radical, quickly turns into the most reactive of oxyradicals, the hydroxyl radical  $HO^{\cdot}$  in accordance with the Fenton reaction [13]:



It was shown [8,13,14] that the antioxidant activity of flavonoid complexes is linearly dependent on their redox potential: the lower this potential, the higher the antioxidant activity is. At the same time, the values of the redox potential depend on the number

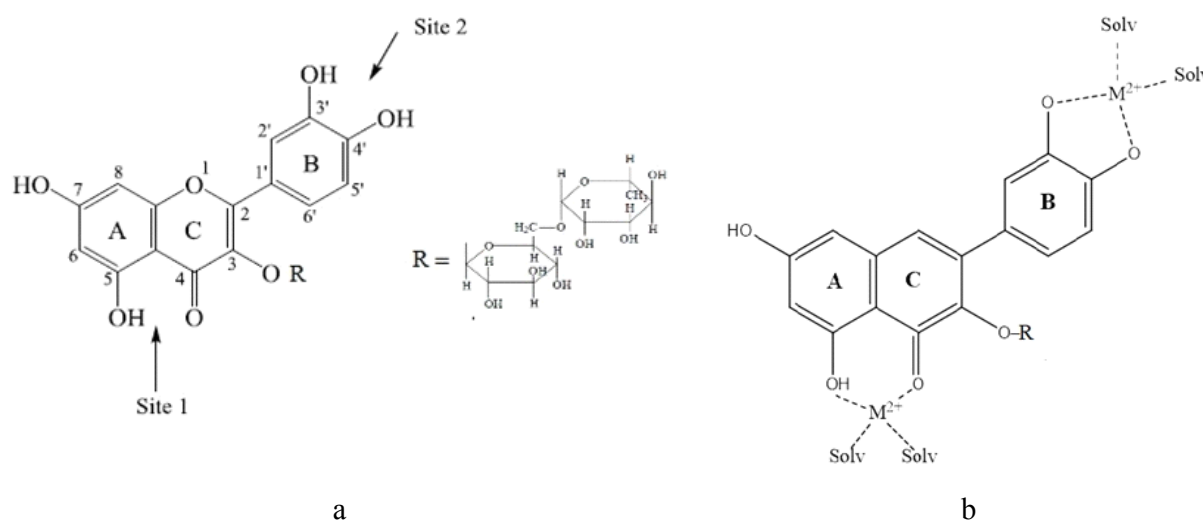


Fig. 1. Schematic representation of the rutin molecule (a) and metal complexes with rutin (b)

of hydroxyl groups and conjugation in flavonoid molecules: the lowest oxidation potentials are observed in ligands with extended conjugation and a large number of hydroxyl groups (quercetin>rutin>galangin>catechin). The antioxidant activity of flavonoids is provided primarily by the 3'- and 4'-ortho-dihydroxyl groups of ring B. These catechin fragments form ortho-semiquinone radicals, which are stabilized by electron delocalization and intramolecular hydrogen bonding. The combination of the C4 carbonyl group and the C2–C3 double bond in the C ring also contributes to the delocalization of  $\pi$  electrons in the B ring. This in turn affects the dissociation of phenolic hydroxyl groups, as well as the stability of the phenoxy radicals formed in the B ring. Ring A is less important than the dihydroxy groups of ring B, which are more easily oxidized [8].

Thus, electrochemical methods provide important information on the redox activity of phenolic compounds, which easily enter into processes associated with electron transfer. Determination of the redox potential makes it possible to screen for the antioxidant activity of both the flavonoids themselves and their metal complexes, which is necessary for the development of new drugs for the treatment and prevention of many diseases occurring against the background of oxidative stress. Therefore, the purpose of this work was to study the electrochemical redox activity of poorly studied aqueous-alcoholic solutions of Co(II) complexes with rutin.

#### Experimental

Complexes of Co(II) with rutin were synthesized in aqueous ethanol solutions (1:2) using cobalt chloride  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$  and rutin. All reagents were of analytical grade and were used without further purification. Rutin was purchased from Sigma-Aldrich, and  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$  was purchased from Energy Chemical Company. Working solutions of cobalt (II) chloride and rutin with a concentration of  $0.001 \text{ mol/dm}^3$  were obtained by dissolving the corresponding weighed portions of the reagents in bidistilled water ( $\text{CoCl}_2$ ) or in aqueous ethanol solutions 1:5 (Rut). Solutions were prepared immediately before the study. The exact concentration of the  $\text{Co}^{2+}$  ion was determined by complexometric titration with the murexide indicator. Studies of a series of Co(II) solutions with a routine concentration of  $1 \cdot 10^{-4} \text{ mol/dm}^3$  were carried out in water-ethanol

solutions (1:2) at various pH (4; 7; and 10) and metal:ligand ratio=1:1 and 2:1 (Table 1).

The pH values were recorded on a Mettler Toledo Seven Easy pH meter (accuracy  $\pm 0.05$ ) at  $20 \pm 3^\circ\text{C}$  and constant ionic strength of  $0.1 \text{ mol/dm}^3$  ( $\text{KNO}_3$ ). The required pH value of the solutions was adjusted with acid (HCl) or alkali (NaOH) solutions.

Cyclic voltammograms (CVA) and electrochemical impedance spectra were measured using the universal electrochemical module Autolab 30 PGSTAT301N MetrohmAutolab. CVA of alcohol-water solutions of complex salts were performed with the Pt electrode with square  $1 \text{ cm}^2$ . All experiments were realized using an Ag/AgCl reference electrode and a platinum grid as a counter electrode. The electrochemical cell was thermostatically controlled at  $25.0 \pm 0.1^\circ\text{C}$  using a water bath. The potential sweep rate was  $0.1 \text{ V/s}$ . Oxidation and reduction potentials were calculated by logarithmic coordinates of the CVA plots. Impedance spectra were measured in a 2-electrode cell with Pt electrodes in the frequency range of  $10^{-2}$ – $10^3 \text{ Hz}$  in air. Calculations of the capacity of the electric double layer were carried out according to the following equation:

$$Z = 1/\omega C,$$

followed by graphical integration of experimental data in coordinates  $Z'$ (Ohm),  $f$ (Hz),  $C$ (F).

#### Results and discussion

CVAs of all samples do not have characteristic peaks associated with the presence of free phenolic groups (Fig. 2) [10]. Therefore, to obtain numerical values of the reduction and oxidation potentials, the method of constructing a semi-logarithmic dependence  $\ln I$  vs.  $V$  was used (Table 2). In samples I–III, the following dependence of the change in the reduction potential ( $E_{pc}$ ) is observed: III<I<II; the values of the oxidizing potential ( $E_{pa}$ ) change in the series II>I>III; the dependence of the potential of zero charge ( $E_0$ ) is as follows: I>II=III (Table 2, Fig. 2).

If we accept the ideas presented in work [12] on an increase in antioxidant activity with a decrease in the oxidizing potential and an increase in the reduction potential, then the maximum antioxidant activity in the equimolar series will be exhibited by the Co–rutin complex obtained at pH 7 (sample II). Differences

Table 1

Studied series of Co(II) solutions with rutin depending on pH and Co:Rut ratio

Sample	pH	Co:Rut ratio	Sample	pH	Co:Rut ratio
CoRut (I)	4	1:1	CoRut (IV)	4	1:2
CoRut (II)	7	1:1	CoRut (V)	7	1:2
CoRut (III)	10	1:1	CoRut (VI)	10	1:2

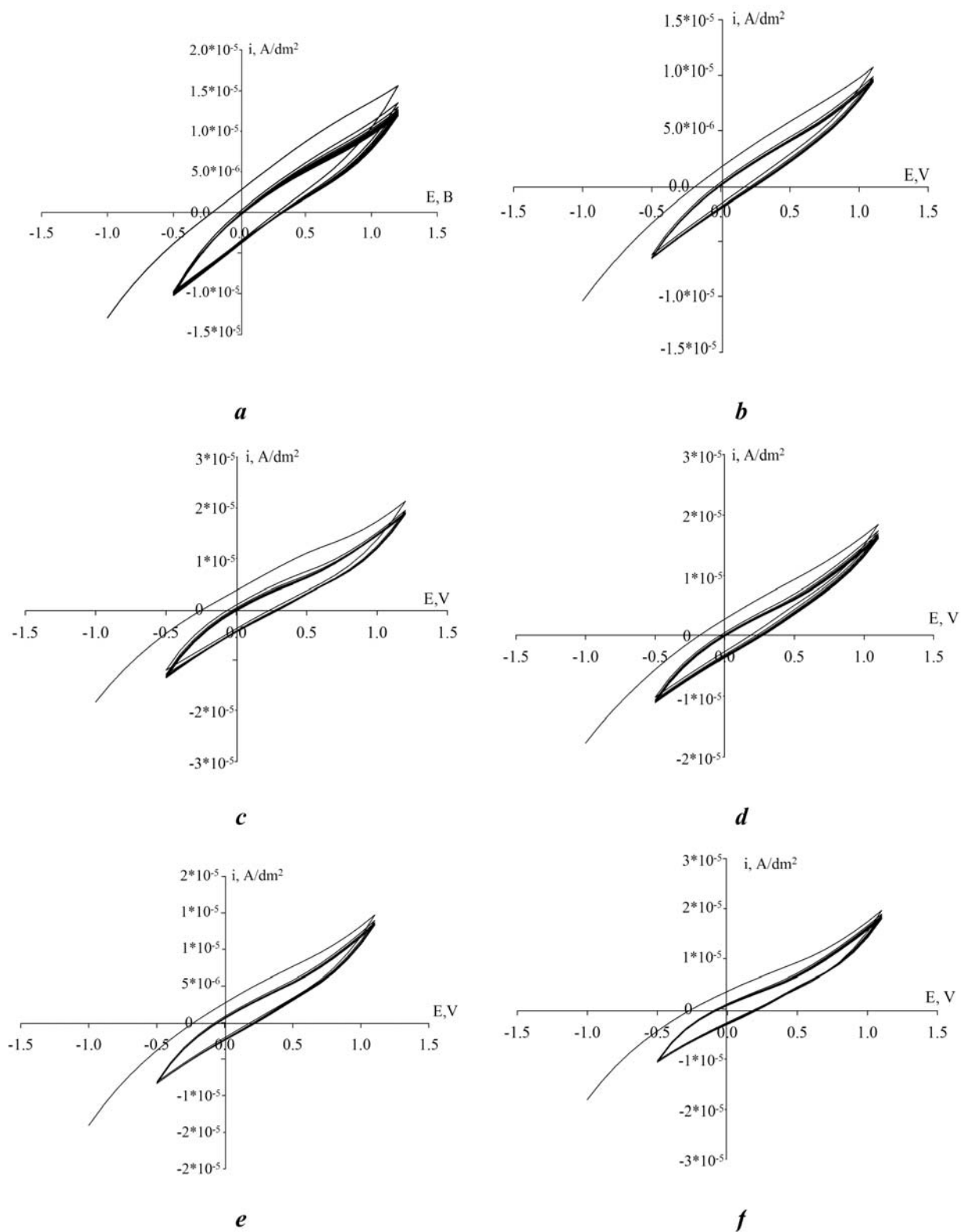


Fig. 2. CVAs for Co(II) complexes with rutin: *a* – sample I, *b* – sample IV; *c* – sample II; *d* – sample V; *e* – sample III; and *f* – sample VI.  $C=10^{-4}$  mol/dm<sup>3</sup>, potential sweep rate 0.1 V/s

in the zero-charge potential of the complex obtained at pH 4 (sample **I**) are apparently due to a more symmetrical adsorption-desorption process of potential-determining ions on the electrode surface (Fig. 2,a, curve in coordinates  $\ln i$  vs.  $E$ ). The values of all oxidation potentials fall within the range of less than +0.130 V, which gives reason to assume that they are prone to self-oxidation with the formation of free radicals [10].

Table 2

Oxidation, reduction and zero-charge potentials of the study samples

Sample	$E_{pc}, V$	$E_{pa}, V$	$E_0, V$
<b>I</b>	-0.110	+0.010	+0.411
<b>II</b>	-0.103	+0.062	+0.315
<b>III</b>	-0.192	+0.002	+0.315
<b>IV</b>	-0.135	+0.094	+0.386
<b>V</b>	-0.091	+0.060	+0.315
<b>VI</b>	-0.197	+0.002	+0.310

For complexes with a metal-ligand ratio of 2:1, the dependence of the decrease in the reduction potential remains  $\text{VI} < \text{IV} < \text{V}$  with a change in the order of increase in the oxidation potentials  $\text{IV} > \text{V} > \text{VI}$ . It is noteworthy that the reduction potentials of the samples of compounds 1:1 and 2:1 do not differ much in their absolute values (Table 2), and the oxidation potentials of samples **III** and **IV** differ by at **III** [12,14].

This fact can be explained by different structures of 1:1 and 2:1 complexes involving different binding sites in chelation. In equimolar complexes in a weakly acid medium, the formation of a Co bond with rutin occurs with the participation of 5-OH and 4-C=O fragments of the A and C rings. The formation of the complex in a ratio of 2:1 occurs both due to the 5-OH and 4C=O groups, and due to the 3',4'-OH groups of ring B [9]. Obviously, in the latter case, due to chelation of the ortho-dihydroxyl fragment of ring B, the antioxidant effect of the complex is suppressed [8,12–14].

The change in the zero charge potential correlates with the change of the oxidation potential in samples  $\text{IV} > \text{V} > \text{VI}$ . The presence of a symbatic dependence of changes in the zero charge potential and the oxidative potential with a high probability indicates the formation of a electric double layer (EDL) precisely by the ions involved in oxidative reactions. In addition, it can indicate the influence of hydrolytic processes, which change the concentration of protons in the reaction medium.

The impedance spectra of the samples with the ratio Co:Rut=1:1 at different pH values (Fig. 3) confirmed the impact of the proton concentration on

the formation of the double electric layer.

In an acidic medium, a significant (more than 1.5 times) increase in the EDL capacity relative to an alkaline medium is observed in the low-frequency range, which is associated with adsorption phenomena at the electrode/solution interface. The change in capacitance values correlates with the change in pH as follows:  $C_{\text{pH4}} > C_{\text{pH7}} > C_{\text{pH10}}$  (Fig. 4).

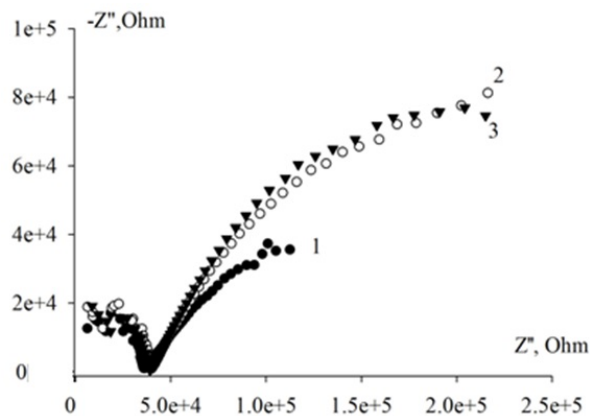


Fig. 3. Nyquist plots for equimolar CoRut complexes at different pH: 1 – pH 4; 2 – pH 7; and 3 – pH 10

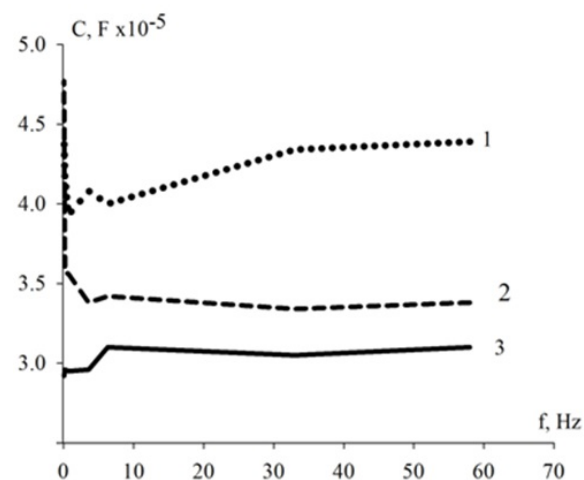


Fig. 4. Capacity value in the low-frequency range for equimolar CoRut complexes: 1 – pH 4; 2 – pH 7; and 3 – pH 10

High values of  $Z'$  (resistance to the movement of electrons or electronic conductivity) suggest the presence of a pseudo-semiconductor structure in the solution, which can change its properties depending on the frequency of the applied electric current and is characteristic of solutions with low ionic strength. The low-frequency range may be approximate to direct current, so the capacitance calculated in this range can apply as the capacitance to the EDL formed



under the specific adsorption of ions on the electrode surface. After the graphical integration of the capacitance and resistance in the low-frequency domain, the charges distributions of samples were obtained. According to this distribution, the negative charge strictly localized in an acidic media (Fig. 5,c).

In a neutral medium, the charge distribution is similar to the distribution in an acidic medium, but with a shift in the frequency range of charge carrier localization to the region of 25–60 Hz (Fig. 5,b). In an alkaline medium, its delocalization is observed (Fig. 5,a). This may be connected to their high mobility in an external electric field due to the presence of at least two anions and at least two cations, which cause instability of the stationary distribution of ions depending on pH. It suggests the competitive nature of the movement of cations and protons, anions, and hydroxyl ions. Such a movement can cause charge delocalization.

When the metal:ligand ratio changes to 1:2, the fraction of electronic conductivity (conductivity in the low-frequency range) increases by an order of magnitude (Fig. 6), which leads to a change in the EDL capacitance (Fig. 7).

The EDL capacitance changes in the following sequence:  $C_{pH7} > C_{pH4} > C_{pH10}$  (Fig. 7). In neutral media, it has a maximum value, and in alkaline media, it has a minimum value. The absolute capacitance values increase by an order of magnitude. The ratio of the potential determining ions also changes depending on the concentration of protons. In a neutral media, the proportion of negatively charged ions increases with a symbate increase in electrical conductivity in the low-frequency range. In an alkaline medium (under conditions of lack of protons), the distribution of negatively charged particles does not differ significantly from samples with a metal: ligand ratio of 1:1.

In compounds of the 1:2 type, charge localization in an acidic and alkaline medium is limited by close frequency ranges of 5–60 Hz in an acidic medium (Fig. 8,c) and 5–50 Hz in a neutral medium (Fig. 8,b). In an alkaline media, the charge distribution is similar to the 1:1 compound type, which may confirm the suppression of the movement of large anions by the competing movement of hydroxyl ions.

### Conclusions

The range of oxidation and reduction potentials of water-alcohol solutions of two types of Co(II) complexes with rutin with a metal/ligand ratio of 1:1 and 1:2 was determined by the electrochemical methods. Their reduction potentials are in the range of  $-0.110$  V to  $-0.197$  V relative to the Ag/AgCl reference electrode, which is much higher than the potentials of most flavonoids. In an alkaline medium, the absolute value of the reduction potential increases regardless of the composition of the sample. The range of oxidizing potentials is from  $+0.02$  V to  $+0.094$  V relative to the Ag/AgCl reference electrode for all samples corresponding to the potentials of compounds with self-oxidizing activity that form free radicals. An increase in oxidative potentials up to  $0.094$  V can characterize antioxidant activity, which is characterized by the manifestation of the auto-oxidizing properties of the complex in the presence of oxygen and is due to the participation of various metal binding sites in chelation. The presence of hydrolytic processes or an increase in the concentration of protons changes the ratio of potential-determining ions at the electrode/solution interface, the structure of the electrical double layer, and its capacitance. In an alkaline medium (under conditions of a lack of protons), the distribution of negatively charged particles does not differ significantly from samples with a metal: ligand ratio of 1:1, but the EDL capacity of complexes increases by an order of magnitude at a metal/ligand ratio of

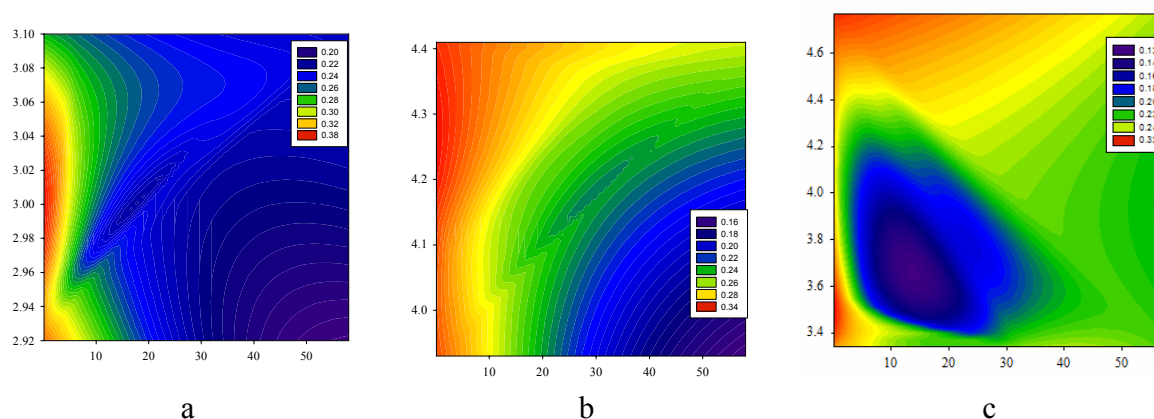


Fig. 5. The ratio of the electrical double layer capacitance and resistance in CoRut cosplexes (1:1) depending on pH: **a** – pH 10; **b** – pH 7; and **c** – pH 4. The predominance of the negative charge is indicated in blue

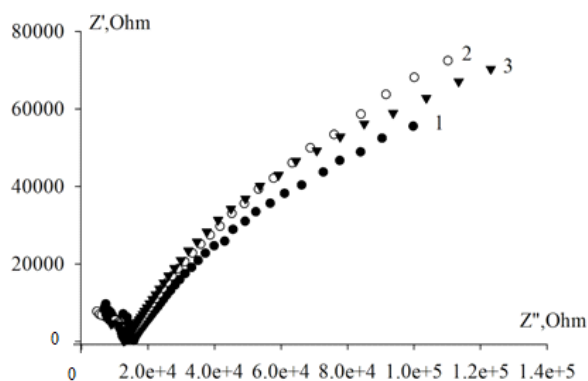


Fig. 6. Nyquist plots for CoRut samples (2:1) at different solution pH: 1 – pH 4; 2 – pH 7; and 3 – pH 10

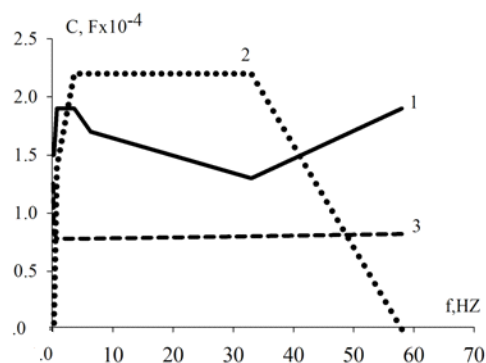


Fig. 7. Capacitance value in the low-frequency range for CoRut samples (2:1): 1 – pH 4; 2 – pH 7; and 3 – pH 10

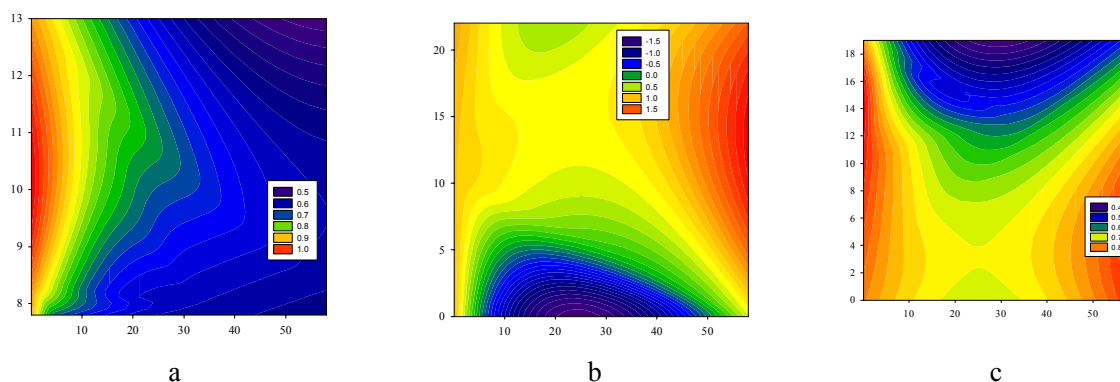


Fig. 8. The ratio of the capacitance of the electrical double layer and the resistance in CoRut samples (2:1) depending on pH: *a* – pH 10; *b* – pH 7; and *c* – pH 4. The predominance of the negative charge is indicated in blue

1:2. An excess of hydroxyl ions have a significant impact on the charge distribution at the electrode/solution interface, and neutralizes the effect of the Co:Rut ratio on the electrochemical properties of water-alcohol solutions of Co(II) complexes with rutin.

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#### ЕЛЕКТРОХІМІЧНІ ВЛАСТИВОСТІ КОМПЛЕКСІВ Co(II) З РУТИНОМ У ВОДНО-СПИРТОВИХ РОЗЧИНАХ

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Методами циклічної вольтамперометрії та спектроскопії електрохімічного імпедансу досліджено вплив рН і співвідношення Co:Rut на окисно-відновні потенціали та електропровідність водно-спиртових розчинів комплексних сполук Co(II) з рутином (Rut). Встановлено, що потенціали відновлення для співвідношення Co:Rut 1:1 та 1:2 знаходяться в інтервалі  $-0,110\text{В}$ – $-0,197\text{В}$  відносно Ag/AgCl електроду, що значно вище потенціалу для відомих флавоноїдів. В лужному середовищі абсолютне значення відновлювального потенціалу збільшується не залежно від складу зразка. Вимірний діапазон окислювальних потенціалів для всіх сполук знаходиться в інтервалі  $+0,02\text{В}$ – $+0,094\text{В}$  відносно Ag/AgCl, що відповідає потенціалам сполук із самоокислювальною активністю. Передбачається, що збільшення окислювальних потенціалів до  $0,094\text{В}$  може характеризувати антиоксидантну активність, яка пов'язана з проявом аутоокислювальних властивостей комплексу в присутності кисню та обумовлена участю в хелатуванні з металом різних сайтів зв'язування. З використанням даних спектроскопії електрохімічного імпедансу розрахована ємність подвійного електричного шару платиного електроду у водно-спиртових розчинах, що містять комплекси Co(II) з рутином. Виявлено збільшення значень ємності на порядок при співвідношенні метал:ліганд=2:1 відносно комплексів із співвідношенням 1:1. Експериментально встановлено вплив надлишку гідроксил-іонів на розподіл зарядів на межі електрод/розчин, який нівелює вплив співвідношення Co:Rut на електрохімічні властивості.

**Ключові слова:** кобальт, рутин, металокомплекси, електропровідність, окислювальний потенціал, ємність, електрохімічна імпедансна спектроскопія.

#### ELECTROCHEMICAL PROPERTIES OF Co(II) COMPLEXES WITH RUTIN IN AQUEOUS-ALCOHOLIC SOLUTIONS

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Cyclic voltammetry and electrochemical impedance spectroscopy were used to study the effect of pH and the Co:Rut ratio on redox potentials and electrical conductivity of water-alcohol solutions of Co(II) complexes with rutin (Rut). It was found that the reduction potentials for the ratio Co:Rut=1:1 and 1:2 are in the range of  $-0.110\text{ V}$  to  $-0.197\text{ V}$  relative to the Ag/AgCl reference electrode, which is significantly higher than the potentials for known flavonoids. In an alkaline medium, the absolute value of the reduction potential increases regardless of the composition of the sample. The measured range of oxidizing potentials for all compounds is in the range of  $+0.02\text{ V}$  to  $+0.094\text{ V}$  relative to Ag/AgCl reference electrode, which corresponds to the potentials of compounds with self-oxidizing activity. It is assumed that an increase in oxidative potentials up to  $0.094\text{ V}$  can characterize the antioxidant activity, which is associated with the manifestation of the autoxidizing properties of the complex in the presence of oxygen and is due to the participation of different binding sites in chelation with the metal. Using the data of electrochemical impedance spectroscopy, the capacity of electrical double layer of a platinum electrode in water-alcohol solutions containing Co(II) complexes with rutin was calculated. An increase in capacitance values by an order of magnitude was observed at a ratio of metal:ligand=2:1 in comparison with the complexes having a ratio of 1:1. The effect of an excess of hydroxyl ions on the charge distribution at the electrode/solution interface was experimentally established, leveling the effect of the Co:Rut ratio on the electrochemical properties.

**Keywords:** cobalt; rutin; metal complex; conductivity; redox potential; capacitance; electrochemical impedance spectroscopy.

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