DETERMINATION OF POLYLIGAND COMPLEXES OF COBALT (II) WITH CITRATE AND PYROPHOSPHATE IONS

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In the work it is shown by the spectrophotometry method that depending on the concentration ratio of ligands $[PPi^{4-}]/[Cit^{3-}]$ in the pyrophosphate-citrate electrolyte, cobalt (II) ions form not only citrate $[Co(Cit)_2]^{4-}$ and pyrophosphate $[Co(PPi)_2]^{6-}$, but also polyligand complexes $[Co(PPi)_m(Cit)_n]^{+2-(4m+3n)}$. The composition of polyligand complexes $[Co(PPi)Cit]^{5-}$ was determined, and the equilibrium constant of the reaction of their formation and the constant of their stability were calculated ($p\beta = 8.47$). The dependence of the degree of formation of citrate, polyligand, and pyrophosphate complexes of cobalt (II) in the pyrophosphate-citrate electrolyte on the logarithm of the ratio of equilibrium concentrations of ligands is calculated.

Keywords: cobalt (II), polyligand complex, composition, stability constant, spectrophotometry.

INTRODUCTION. The structure of metal and alloy coatings deposited from complex electrolytes, the uniformity of their distribution on the sample surface are determined by the magnitude of the overvoltage of the cathodic process – a preliminary chemical reaction and the magnitude of activation energy of electrochemically active complexes (EAC). Overvoltage is the most important characteristic of the electrode process, as it affects the morphology, structure and functional properties of metal and alloy coatings. In the development of technological processes for coating from complex electrolytes not only the composition and stability of coordination compounds, but also the

geometric structure and electronic configuration of the EAC are important. These factors ultimately determine the rate and mechanism of electrode processes.

Monoligand and polyligand (pyrophosphate, citrate and pyrophosphate-citrate) electrolytes have been widely used for the deposition of coatings of binary and ternary alloys of refractory metals (Mo, W and Re) with iron subgroup metals (Fe, Co, Ni), in particular cobalt. [1].

A pyrophosphate-citrate electrolyte was chosen as the study object because it allows the deposition of high-quality coatings of molybdenum, tungsten, and rhenium alloys with

cobalt with a higher current efficiency than monoligand electrolytes [1–9]. These alloys have valuable physicochemical and operational properties [2], which make them indispensable in practical use.

Determining the ionic composition in the bulk electrolyte for polyligand systems such as electrolyte containing cobalt (II) ions and two ligands simultaneously – citrate (Cit^{3-}) and pyrophosphate (PPi^{4-}) is an important and challenging task. Information on the composition of complex compounds in the bulk of pyrophosphate-citrate electrolyte, kinetics and mechanism of deposition of alloys will allow to control the relevant processes of their production, and hence the structure and functional properties of the resulting coatings.

The aim of the work aim is to establish the composition and determine the stability constant of polyligand complexes of cobalt (II) with Cit^{3-} and PPi^{4-} ions by spectrophotometric method and to study the effect of the ionic composition in the electrolyte on the ratio of ligand equilibrium concentrations.

Cobalt (II) ions form with Cit^{3-} and PPi^{4-} ions, depending on the solution pH and the equilibrium concentration of ligands, protonated and unprotonated pyrophosphate $[CoHPPi]^{-}$, $[Co(HPPi)_2]^{4-}$, $[Co(HPPi)(PPi)]^{5-}$, $[CoPPi]^{2-}$, $[Co(PPi)_2]^{6-}$ and citrate $[CoH_2Cit]^{+}$, $[CoHCit]$, $[CoCit]^{-}$, $[Co(Cit)_2]^{4-}$ complexes [10, 11]. Polymeric, polynuclear complexes of cobalt (II) with citrate of the compositions $[Co_4(Cit)_4 [Co(H_2O)_5]_2]^{4-}$, $K_3[Co_2(Cit)_2(H_2O)_4]\cdot 6H_2O$ were synthesized and isolated in solid the state [12, 13] and others, which have magnetic properties [13] and biocompatibility [14, 15]. The thermodynamics of protonated cobalt (II) citrate complexes formation have also been studied [16]. There are no data on the possibility of formation of polyligand complexes of cobalt (II) with Cit^{3-} and PPi^{4-} ions in the pyrophosphate-citrate electrolyte, their composition and stability constant are not available in the literature.

Spectrophotometry is one of the most pretentious methods for determining the composition and stability constants of colored complex compounds. General characteristics of methods for determining the composition and stability constants of metal complexes from spectrophotometric measurements, their advantages, scope, limitations and disadvantages are detailed in the monograph of A.K. Babko [17].

The spectrophotometric study of the formation of polyligand complexes of cobalt (II) with Cit^{3-} and PPi^{4-} ions involves significant difficulties, because along with them in the system under study, depending on the pH of the solution, there may also exist monoligand protonated and unprotonated citrate and pyrophosphate complexes of Co (II). The distribution of complexes in the bulk electrolyte in this case strongly depends on the equilibrium concentration of metal ions, the ratio of the equilibrium concentrations of free ligands and the pH of the solution.

Since Cit^{3-} and PPi^{4-} ions are anions of weak acids, their equilibrium concentrations in the test solution depend on the pH of the solution and can be determined by the pH-potentiometric method. Therefore, when conducting spectrophotometric studies it is necessary to maintain the optimal and constant concentration of hydrogen ions (pH = const) to form complex ions of constant composition at a certain ratio of the concentrations of the main components of the investigated solution $C_{Co}^{2+}:C_{PPi}^{4-}$ and $C_{Co}^{2+}:C_{Cit}^{3-}$ = const.

The values of the equilibrium concentrations of free ligands [PPi]$^{4-}$ and [Cit]$^{3-}$ were determined from the spectrophotometric studies, considering their total concentrations and the pH according to the equation (1) [18, 19]:

$$[L]^{m-} = \frac{C_{H_mL} - n^*(C_{Co^{2+}} - [Co]^{2+})}{1 + \sum_{i=1}^{i=4} K_i[H^+]^i}, \quad (1)$$

where $C_{H_mL,}$ [L]$^{m-}$ are the total and equilibrium concentrations of ligands (citrate and pyrophosphate) in the test solution (mol·l^{-1}) respectively; $C_{Co}{}^{2+}$ and [Co]$^{2+}$ are the total and equilibrium concentrations of cobalt (II) ions in the test solution (mol·l^{-1}) respectively; n* is the average coordination number of pyrophosphate and citrate complexes formed in the test solution; K_i is the general stability constants of citrate and pyrophosphate ions (pK_1 = 5.68; pK_2 = 10.03; pK_3 = 12.90 i pK_1 = 8.30; pK_2 = 14.30; pK_3 = 17.00; pK_4 = 19.50) [20].

The equilibrium concentrations of free ligands [Cit]$^{3-}$ and [PPi]$^{4-}$, determined by spectrophotometric studies conditions based on their total concentrations, mol·l^{-1}: $C_{Co}{}^{2+}$ = 0.01; $C_{PPi}{}^{4-}$ = 0.05; $C_{Cit}{}^{3-}$ = 0.05 at the solution pH 9.0 according to equation (1) [18, 19] are 3.0·10^{-2} and 2.5·10^{-2} (n* = 2); 4.0·10^{-2} and 3.3·10^{-2} (n* = 1),respectively. The ratio of free ligand equilibrium concentrations [PPi]^4 : [Cit]$^{3-}$ in a pyrophosphate-citrate electrolyte at a pH of 9.0 practically does not change, that is [Cit]$^{3-}$ / [PPi]$^{4-}$ = 1.2 at 1 ≤ n* ≤ 2.

The relation between the absorption and composition of the studied solution in the ideal case described by the Lambert – Bouguer – Beer law [21, 22] is:

$$D = l \cdot \sum \varepsilon_i C_i, \quad (2)$$

where D is the absorption of the solution; l is the thickness of the absorbing layer (cuvette length, cm); ε_i is the molar absorption coefficient of the i-th particle at a given wavelength λ and temperature; C_i is the molar concentration of the absorbing particle.

The main requirement for the spectrophotometric method is that the absorption of the solution D, property of the measured system must be, according to the Lambert – Beer law, a strictly linear function of the molar concentration of absorbing complexes C_i. In addition, the colored complex should have high stability (stability constant), constant composition (in a wide range of ratios of the concentrations of the main components and pH of the solution), as well as high color intensity per 1 g mole of the substance (molar absorption coefficient ε_i) [23, 24].

EXPERIMENT AND DISCUSSION OF THE RESULTS. Composition of the studied solutions, mol·l^{-1}: Co^{2+} = 0.01; PPi^{4-} = 0.05; Cit^{3-} = 0.05; Na$_2$SO$_4$ = 0.30; pH 9.0. Analytical grade reagents were used to prepare electrolytes. The pH of the studied solutions was corrected on an electronic pH meter (pH-150MI) using NaOH and Na$_2$SO$_4$.

The absorption spectra of the studied solutions of cobalt (II) complexes were recorded on a UV-VIS Spectrophotometer UV mini 1240 (Shimadzu) in a 1 cm cuvette.

The possibility of the formation of polyligand complexes of cobalt (II) from Cit^{3-} and PPi^{4-} ions was studied by the method of isomolar series [17, 21, 25] at a constant ionic strength of the solution (0.3 mol·l^{-1} Na$_2$SO$_4$) using initial solutions with a constant ratio of the concentrations of ions $C_{Co}{}^{2+}$: $C_{Cit}{}^{3-}$ = 1 : 5 and $C_{Co}{}^{2+}$: $C_{PPi}{}^{4-}$ = 1 : 5. The use of this solution is due to the fact that at pH 9.0, in contrast to the citrate solution with $C_{Co}{}^{2+}$: $C_{Cit}{}^{3-}$ = 1 : 2 it is

impossible to experimentally prepare an initial pyrophosphate solution with a constant concentration ratio of $C_{Co}^{2+} : C_{PPi}^{4-} = 1 : 2$ because under these conditions, partial hydrolysis of the cobalt(II) salt and, as a result, clouding of the solution take place, since the solubility product of cobalt(II) hydroxide $SP(Co(OH)_2) = 1,8\cdot10^{-18}$ [26]; the instability constant K of $[Co(PPi)_2]^{6-}$ pyrophosphate complexes is $1.8\cdot10^{-9}$ [10]; the total concentration of cobalt (II) ions in the test solution is 0.01 mol·1^{-1}.

To establish the composition and determine the stability constant of the polyligand complexes of cobalt (II) formed in the system under study, the absorption of the solution $D,$ as a function of its composition was determined by the method of isomolar series (Ostromyslensky Zhoba method) [17, 21, 25]. A series of solutions was prepared by mixing initial solutions with a constant concentration ratio of $C_{Co}^{2+} : C_{Cit}^{3-} = 1 : 5$ (x ml) and $C_{Co}^{2+} : C_{PPi}^{4-} = 1 : 5$ ($10 - x$) ml at a constant total concentration of cobalt (II) ions ($C_{Co}^{2+} = 0.01$ mol·1^{-1}) and wavelength λ. In this case, the total concentration of metal ions in the studied solutions remains constant, and the ratio of the total concentrations of ligands $C_{PPI}^{4-} : (C_{PPi}^{4-} + C_{Cit}^{3-})$ decreases from 1 to 0. The ratio of the total concentrations of ligands $C_{Cit}^{3-} : (C_{PPi}^{4-} + C_{Cit}^{3-})$ increases from 0 to 1. The ratios of the equilibrium concentrations of free ligands $[PPi]^{4-}:([PPi]^{4-} + [Cit]^{3-})$ and $[Cit]^{3-}:([Cit]^{3-} + [PPi]^{4-})$ change in a similar way.

The absorption spectra of the studied solutions are shown in Fig. 1. The presence of two isosbestic points on the absorption curves at the wavelengths $\lambda = 592$ and 632 nm allows us to assume that there are three complex compounds in the solution under study, namely: citrate $[Co(Cit)_2]^{4-}$, pyrophosphate $[Co(PPi)_2]^{6-}$

and polyligand complexes of cobalt (II). At the isosbestic point ($\lambda = 592$ nm), as can be seen from Fig. 1, two complex compounds are in equilibrium: pyrophosphate $[Co(PPi)_2]^{6-}$ (curve 1) and polyligand $[Co(PPi)_m(Cit)_n]^{+2-(4m+3n)}$ (curves 2–6) cobalt(II) complexes. Citrate complexes $[Co(Cit)_2]^{4-}$ do not take part in the equilibrium, since curve 7 does not pass through this isosbestic point ($\lambda = 592$ nm).
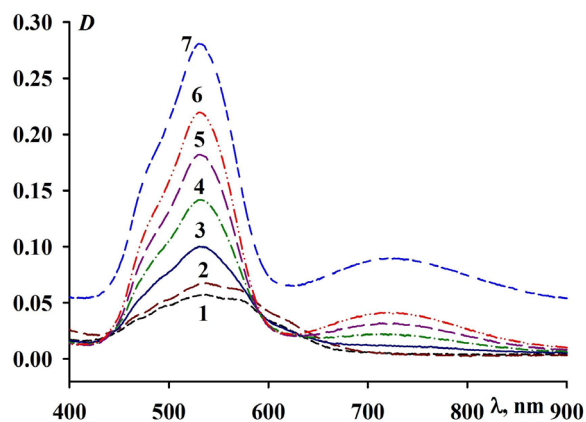

Fig. 1. Absorption spectra in pyrophosphate-citrate electrolyte obtained by the isomolar series method at pH 9.0, a concentration of cobalt (II) ions of 0.01 mol·l^{-1} with the ratio of concentrations $C_{PPi}^{4-} : C_{Cit}^{3-} = 10 : 0$ (1); 9 : 1 (2); 7 : 3 (3); 5 : 5 (4); 3 : 7 (5); 1 : 9 (6); 0 : 10 (7).

Since $[Co(Cit)_2]^{4-}$ citrate complexes do not take part in the formation of polyligand complexes $[Co(PPi)_m(Cit)_n]^{+2-(4m+3n)}$, the equilibrium between the latter and pyrophosphate complexes $[Co(PPi)_2]^{6-}$ is described by the equation:

$$[Co(PPi)_2]^{6-} + [Cit]^{3-} \leftrightarrow [Co(PPi)Cit]^{5-} + + [PPi]^{4-} . \quad (3)$$
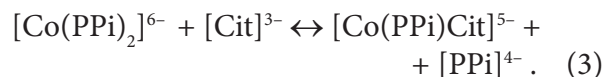
Therefore, the equilibrium constant K_r of the reaction for the formation of polyligand complexes of cobalt (II) is:

$$K_r = \beta / \beta'_2 , \quad (4)$$

where β and β'_2 are the stability constants of polyligand and pyrophosphate complexes $[Co(PPi)_2]^{6-}$, respectively.

It should be noted that the interpretation of spectrophotometric data for the systems under study, in which three or more complex compounds are formed, can be ambiguous [26], since the error in determining the stability constants of the corresponding complexes increases. In this case, the determination of the stability constants of the complexes formed in the system under study from spectrophotometric data must be carried out at a wavelength corresponding to the isosbestic point in absorption spectra, at which the extinction coefficients of all absorbing species are equal ($\varepsilon_1 = \varepsilon_2 = \dots = \varepsilon_n = \varepsilon^\star$) [26].

The results of the analysis of spectrophotometric data are shown in Fig. 2 at the wavelengths λ = 500 and 540 nm in the coordinates: $D = f\,[\,C_{PPi}^{4-}]\,/\,[C_{PPi}^{4-} + C_{Cit}^{3-})$ (curves 1, 2) and $D = f\,(C_{Cit}^{3-}\,/\,(C_{Cit}^{3-} + C_{PPi}^{4-})$ (curves 3, 4) [21, 25], where D is the absorption of the test solution, C_{PPi}^{4-} and C_{Cit}^{3-} are the total concentrations of ligands. The linear plots indicate the formation of stable polyligand complexes of cobalt (II) with Cit^{3-} and PPi^{4-} ions in the system under study. The abscissa of the point of maximum absorption x_{max} does not depend on the wavelength $\lfloor$ = 500 (curves 1, 3) and 540 nm (curves 2, 4) and is given by:

$$X_{max} = C_{PPi}^{4-}\,/(C_{PPi}^{4-} + C_{Cit}^{3-}) =$$
$$= n\,/(n + m) = 0.5. \qquad (5)$$

This is consistent with the data [21] that when a polyligand (mixed) complex with the composition MLX is formed by the reaction:

$$ML_2 + MX_2 \leftrightarrow 2\,MLX, \qquad (6)$$

the partial mole fraction of each of the complexes ML_2 and MX_2 is 0.50 since $\alpha_1 + \alpha_2 = 1$.
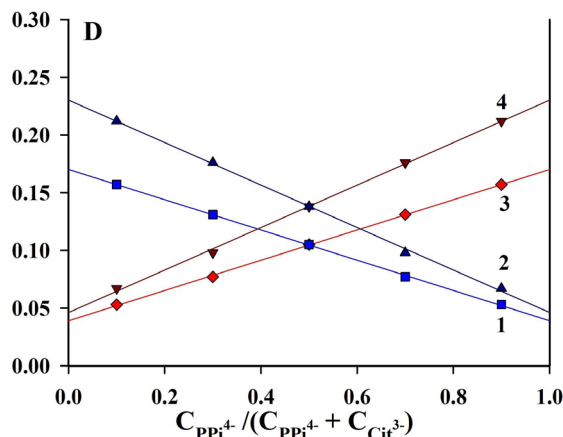

Fig. 2. Absorption of isomolar series in a pyrophosphate-citrate electrolyte at pH 9.0 and wavelengths λ = 500 nm (curves 1, 3) and 540 nm (curves 2, 4) and the concentration of cobalt ions in the investigated solutions C_{Co}^{2+} = 0.01 mol·l^{-1}.

The obtained data (Fig. 2) make it possible to determine the composition of the cobalt (II) polyligand complexes formed under the experimental conditions. The maximum coordination numbers m and n for the polydentate ligands PPi^{4-} and Cit^{3-} of cobalt (II) polyligand complex formed in the system under study, as follows from Fig. 2 and equation (5), are equal to m = n = 1. Thus, polyligand complexes $[Co(PPi)Cit]^{5-}$ are formed in the pyrophosphate–citrate electrolyte at pH 9.0.

The composition of the cobalt (II) polyligand complexes formed in the system under study under given conditions and their stability constant were also determined by the equilibrium shift method [17]. We denote the maximum absorption of the solution under study at the corresponding wavelength λ = 500 nm by D_o, and the optical density of the solution at certain ratios of equilibrium concentrations of ligands $[PPI]^{4-}\,/\,[Cit]^{3-}$ until almost complete binding of the central ion into a colored polyligand complex D_x. Since the

optical density of the solution by D_x is proportional to the concentration of the colored complex $[Co(PPi)_m(Cit)_n]^{+2-(4m+3n)}$, the ratio is $[Co(PPi)_m(Cit)_n]^{+2-(4m+3n)} / [Co(PPi)_2]^{6-} = D_x / (D_o - D_x)$. So, from the plots of $\lg D_x / (D_o - D_x) = f (\lg [PPi]^{4-}/ [Cit]^{3-})$ (Fig. 3a, curve 1) and $\lg D_x / (D_o - D_x) = f (\lg [Cit]^{3-}/ [PPi]^{4-})$ (Fig. 3a, curve 2) it is possible to establish the composition of the cobalt (II) polyligand complexes that are formed in the studying system at pH 9.0 and their stability constant.

The plots of $\lg D_x/(D_o - D_x) = f (\lg [PPi]^{4-}/ [Cit]^{3-})$ (Fig. 3a, curve 1) and $\lg D_x/(D_o - D_x) = f (\lg [Cit]^{3-}/[PPi]^{4-})$ (Fig. 3a, curve 2) are rectilinear; the abscissa of the intersection point

of them $\lg ([PPi]^{4-}/ [Cit]^{3-}) = 0$. This indicates that the molar ratio of the equilibrium concentrations of polydentate ligands $[PPi]^{4-}/[Cit]^{3-}$ in the polyligand complex $[Co(PPi)_m(Cit)_n]^{+2-(4m+3n)}$ is 1, i.e. m=n=1 . The ratio $[Cit]^{3-}/[PPi]^{4-}$, as can be seen from Fig. 3a, curve 2 is 1. Thus, polyligand complexes $[Co(PPi)Cit]^{5-}$ are formed in the system under study at pH 9.0. The slope of the straight line $\lg D_x/(D_o-D_x) = f(\lg [PPi]^{4-}/[Cit]^{3-})$ (Fig. 3a, curve 1) is –0.4886 and is equal to the logarithm of the equilibrium constant Kr of the reaction of formation of polyligand complexes $[Co(PPi)Cit]^{5-}$. The value of the equilibrium constant Kr calculated from equation (3) is 0.3246.
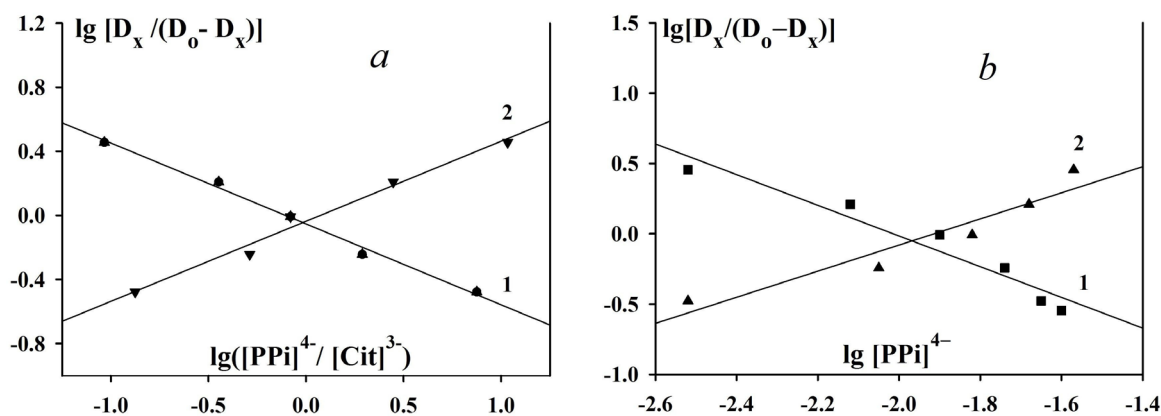

Fig. 3. Dependences $\lg D_x / (D_o - D_x)$ obtained by the method of equilibrium shift in the studied system at pH 9.0, the concentration of ions C_{Co}^{2+} – 0.01 mol·l⁻¹, the wavelength λ = 500 nm on $\lg([PPi]^{4-}: [Cit]^{3-})$ (Fig. 3a, (1)); on $\lg([Cit]^{3-}: [PPi]^{4-})$ (Fig. 3a, (2)); on $\lg[PPi]^{4-}$ (Fig. 3b, (1)) and on $\lg[Cit]^{3-}$ (Fig. 3b, (2)).

The value of the stability constant β of $[Co(PPi)Cit]^{5-}$ polyligand complexes calculated by the equilibrium shift method [17] using experimental data (Fig. 3a) according to equation (4) is 1.80·10⁸ (pβ = 8.26).

The composition of cobalt (II) polyligand complexes, and not only the ratio of coordination numbers m/n, was determined from spectrophotometric data (Fig. 1) by the equilibrium

shift method [17]; plots of $\lg D_x / (D_o - D_x) = f (\lg [PPi]^{4-})$ (Fig. 3b, curve 1) and $\lg D_x / (D_o - D_x) = f (\lg [Cit]^{3-})$ (Fig. 3b, curve 2) obtained from the spectrophotometric data (Fig. 1) by the equilibrium shift method in the system under study at pH 9.0, the total concentration of C_{Co}^{2+} ions – 0.01 mol·l⁻¹, and the wavelength λ = 500 nm (Fig. 3b) are shown in Fig. 3b.

The slope of the straight line $\lg D_x/(D_o-D_x)$

$= f (\lg [PPi]^{4-})$ (Fig. 3b, curve 1) at $[Cit]^{3-} \rightarrow 0$ is equal to the coordination number m of the polyligand complex for $[PPi]^{4-}$ ions and is 1.07:

$$\lim \frac{\partial \lg[D_x /(D_0 - D_x)]}{\partial \lg[P_2O_7]^{4-}} = m. \qquad (7)$$

The value of the coordination number n, calculated from the slope of the straight line $\lg D_x / (D_o - D_x) = f (\lg [Cit]^{3-})$ at $[PPi]^{4-} \rightarrow 0$, is 0.96. The obtained values of the coordination numbers m and n (m=n=1) indicate the formation of $[Co(PPi)Cit]^{5-}$ polyligand complexes in the pyrophosphate–citrate electrolyte at pH 9.0.

The composition of $[Co(PPi)Cit]^{5-}$ polyligand complexes in a pyrophosphate–citrate electrolyte was confirmed by the Newman and Hume method [27]. This method is one of the most reliable methods for determining the composition of polyligand complexes and their formation constants [25]. The equilibrium constant Kr of reaction (3) for the formation of $[Co(PPi)Cit]^{5-}$ polyligand complexes in the system under study at pH 9.0 calculated by the Newman and Hume method (Fig. 4a) according to the equation:

$$D = C_{Co} \cdot \varepsilon_{Cit-PPi} - 1/K_r[(D - C_{Co}\cdot\varepsilon_{PPi})\cdot \\ ([PPi]^{4-}/ [Cit]^{3-}), \qquad (8)$$

where $\varepsilon_{Cit-PPi}$ and ε_{PPi} are the molar absorption coefficients of the polyligand and pyrophosphate complexes of cobalt (II), respectively, is 0.5755.

As can be seen from Fig. 4a, the experimental points lie on a straight line, which confirms the correctness of the determination from equation (8) of the numbers of coordination groups of ligands (m=n=1) in the polyligand complex $[Co(PPi)_m(Cit)_n]^{+2-(4m+3n)}$. Thus, polyligand cobalt (II) complexes $[Co(PPi)Cit]^{5-}$ are formed in the system under study at pH 9.0.
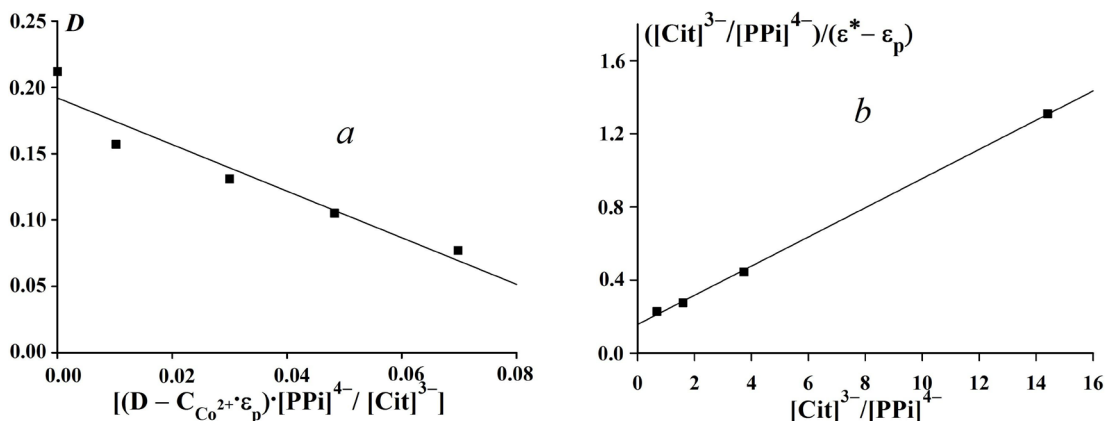

Fig. 4. Graphical determination of the equilibrium constant K_r of the polyligand cobalt (II) complexes formation reaction in pyrophosphate-citrate electrolyte at pH 9.0, wavelength $\lambda = 500$ nm by the method: (a) – Newman and Hume; (b) – Watters.

The equilibrium constant Kr of formation of $[Co(PPi)Cit]^{5-}$ polyligand complexes at pH 9 by reaction (3) was also determined by the Watters method [28] (Fig. 4b) according to the equation:

$$([Cit]^{3-}/[PPi]^{4-})/(\varepsilon^* - \varepsilon_p) = 1/[(\varepsilon_{зм} - \varepsilon_{пiр})\cdot K_r] + \\ + 1/(\varepsilon_{зм} - \varepsilon_{пiр})\cdot(([Cit]^{3-}/[PPi]^{4-}), \qquad (9)$$

where $\varepsilon_{Cit\text{-}PPi}$ and ε_{PPi} are the molar absorption coefficients of a polyligand and a pyrophosphate complex of cobalt (II), respectively; $\varepsilon^{\star}$ is the average coefficient of molar absorption of all forms of cobalt (II) ions.

The value of the equilibrium constant Kr of the reaction of formation of polyligand complexes $[Co(PPi)Cit]^{5-}$ formation reaction, calculated from the slope of the linear plot of $([Cit]^{3-}/[PPi]^{4-})/(\varepsilon^{\star}-\varepsilon_p) = f\,([Cit]^{3-}/[PPi]^{4-})$, which is $1/(\varepsilon_{Cit\text{-}PPi} - \varepsilon_{PPi}) = 0.0794$ (Fig. 4b), and the y-intercept $(1/(\varepsilon_{зм} - \varepsilon_{пір})K_r = 0.160)$ is 0.4963. The value of the equilibrium constant Kr of formation of polyligand complexes obtained by the Watters method [28] agrees with the Kr value obtained by the Newman and Hume method [27] (0.5755).

The stability constants of $[Co(PPi)Cit]^{5-}$ polyligand complexes calculated by the Watters [28], Newman and Hume [27] methods using the equilibrium constants Kr of the reaction of their formation of 0.4963 and 0.5755 respectively, in accordance with Eq. (4) are $2.76\cdot10^8$ (pβ = 8.44) and $3.20\cdot10^8$ (pβ = 8.51), respectively. The obtained average value of the stability constant of $[Co(PPi)Cit]^{5-}$ polyligand complexes (β = $2.98\cdot10^8$ (pβ = 8.47)) agrees with the value calculated from experimental data (Fig. 3a) by the equilibrium shift method (pβ = 8.26).

Taking into account the stability constants of citrate $[Co(Cit)_2]^{4-}$ (pβ_2 = 5.30), pyrophosphate $[Co(PPi)_2]^{6-}$ (pβ'_2 = 8.74) and polyligand $[Co(PPi)Cit]^{5-}$ (pβ = 8.47) complexes of cobalt (II), the dependence of the degree of their formation in a pyrophosphate-citrate electrolyte on the ratio of equilibrium concentrations of ligands lg ($[PPi]^{4-}/[Cit]^{3-}$) was calculated (Fig. 5). As can be seen from fig. 5, citrate complexes $[Co(Cit)_2]^{4-}$ exist in the range of the ratios of equilibrium concentrations of ligands lg ($[PPi]^{4-}/[Cit]^{3-}$) from –1 to +1, polyligand complexes $[Co(PPi)Cit]^{5-}$ in the range from –1 to +2, and $[Co(PPi)_2]^{6-}$ pyrophosphate complexes in the range >0.
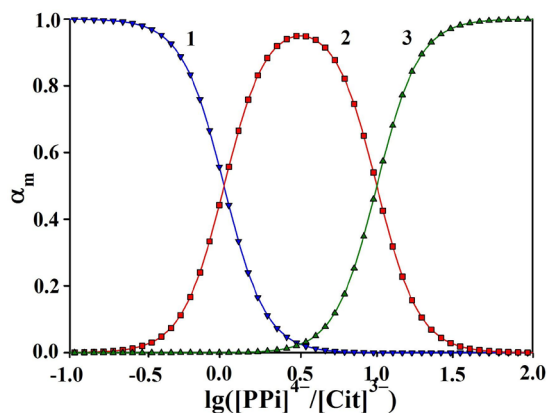

Fig. 5. Dependence of the degree of formation of citrate (1), polyligand (2) and pyrophosphate (3) complexes of cobalt (II) in pyrophosphate-citrate electrolyte on the logarithm of the ratio of equilibrium concentrations of ligands: *1* – $[Co(Cit)_2]^{4-}$; *2* – $[Co(PPi)Cit]^{5-}$; *3* – $[Co(PPi)_2]^{6-}$.

CONCLUSIONS.

It has been established that in a pyrophosphate-citrate electrolyte at pH 9.0, cobalt (II) ions form with Cit^{3-} and PPi^{4-} ions not only citrate $[Co(Cit)_2]^{4-}$ and pyrophosphate $[Co(PPi)_2]^{6-}$, but also polyligand complexes $[Co(PPi)_m(Cit)_n]^{+2-(4m+3n)}$. The composition of $[Co(PPi)Cit]^{5-}$ polyligand complexes was determined, the equilibrium constant Kr of the reaction of their formation and their stability constant (pβ=8.47) were calculated. In terms of stability, $[Co(PPi)Cit]^{5-}$ (pβ = 8.47) polyligand complexes approach pyrophosphate complexes $[Co(PPi)_2]^{6-}$ (pβ'_2 = 8.74). The dependence of the degree of formation of citrate, polyligand, and pyrophosphate complexes of cobalt

(II) in a pyrophosphate-citrate electrolyte on the logarithm of the ratio of equilibrium concentrations of ligands was calculated.

ВИЗНАЧЕННЯ ПОЛІЛІГАНДНИХ КОМПЛЕКСІВ КОБАЛЬТУ (II) З ЦИТРАТНИМИ ТА ПІРОФОС-ФАТНИМИ ІОНАМИ

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Спектрофотометричним методом встановлено, що у пірофосфатно-цитратному електроліті іони кобальту (II) утворюють залежно від співвідношення концентрацій лігандів $[PPi^{4-}]$ / $[Cit^{3-}]$ не тільки цитратні $[Co(Cit)_2]^{4-}$, пірофосфатні $[Co(PPi)_2]^{6-}$, а й полілігандні комплекси $[Co(PPi)_m(Cit)_n]^{+2-(4m+3n)}$. Визначено склад полілігандних комплексів $[Co(PPi)Cit]^{5-}$, обчислено константу рівноваги реакції їхнього утворення та константу їхньої стійкості ($p\beta = 8.47$). Розраховано залежність ступеня утворення цитратних, полілігандних та пірофосфатних комплексів кобальту(II) в пірофосфатно-цитратному електроліті від логарифму співвідношення рівноважних концентрацій лігандів.

Ключові слова: кобальт (II), полілігандні комплекси, склад, константа стійкості, спектрофотометрія.

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