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DETERMINATION OF THE COMPOSITION AND STABILITY CONSTANT OF COBALT (II) POLYLIGAND CITRATE-MOLYBDATE COMPLEXES.

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The complex formation of cobalt (II) with citrate (cit^{3-}) and molybdate (MoO_4^{2-}) ions in 0.3 mol·l^{-1} Na_2SO_4 solution at 20°C was studied by spectrophotometric method. It has been established that in a citrate-molybdate electrolyte at pH 9.0, cobalt (II) ions form, depending on the ratio of the equilibrium concentrations of ligands: molybdate $[Co(MoO_4)_2]^{2-}$, citrate $[Co(cit)_2]^{4-}$ and polyligand complexes $[Co(cit)_m(MoO_4)_n]^{+2-(3m+2n)}$. The composition of $[Co(cit)(MoO_4)]^{3-}$ polyligand complexes was determined, the equilibrium constant K_e of the reaction of their formation and their stability constant ($lg\beta_{MLX}$ = 5.86) The dependence of the degree of formation of molybdate, citrate and polyligand complexes of cobalt (II) in citrate-molybdate electrolyte on the logarithm of the ratio of equilibrium concentrations of ligands was calculated.

Keywords: cobalt (II), molybdate, citrate and polyligand complexes, composition, equilibrium constant, stability constant, spectrophotometry.

INTRODUCTION. In modern electroplating, polyligand electrolytes are widely used for applying functional coatings with metals and alloys. This is due to the fact that polyligand electrolytes are non-toxic, stable, and easily disposed of. In addition, acid-type polydentate ligands form a wide range of stable complex compounds with almost all metal ions and have a pronounced ability to be compatible with weak-field ligands in one coordination sphere to form polyligand electrochemically inactive complexes (EIAC). The advantage of polyligand electrolytes is also a high buffer capacity and, as a consequence, a slight alkalinization of the near-cathode layer during their long-term operation.

When choosing ligands for polyligand electrolytes, one should be guided by the basic ideas of modern ligand field theory, the nature of chemical bonds, the requirements of their non-toxicity and indifference to electrode processes occurring during the reduction of metal complexes. Properly selected ligands for complex electrolytes lead to the formation of EIAC in

the polyligand electrolyte, which makes it possible to purposefully influence the inhibition of the electrode process, the composition of electrochemically active complexes (EAC), the mechanism of the process, and consequently, the morphology, structure and functional properties of the resulting metal coatings and alloys [1, 2].

The effect on the inhibition of electrode reactions occurring in a polyligand electrolyte and, consequently, on the morphology, structure, and functional properties of coatings obtained by binary and ternary alloys of cobalt, nickel or iron with refractory metals (Mo, W, and Re) is impossible without reliable data on the composition of electrolytes, the stability constants of monoligand and polyligand complexes of these metal ions with citrate and molybdate ions, the composition of electrochemically active complexes (EAC), the mechanism of electrode processes and the kinetic regularities of limiting stages.

Information about the composition of complex compounds, including polyligand ones, in the bull of a citrate-molybdate electrolyte, the areas of their existence and predominance make it possible to consciously influence the choice of the optimal composition of the electrolyte, the kinetics and mechanism of deposition of binary and ternary alloys of molybdenum with metals of the iron subgroup and, consequently, the structure and functional properties of the resulting coatings.

The object of study is the processes of complex formation that occur in a citrate electrolyte for the deposition of binary and ternary alloys of cobalt with refractory metals (Mo, Wo, and Re), which are of not only scientific but also practical interest [3–5], since these alloys have valuable physicochemical and operational properties, which makes them indispensable for practical use.

Previously [6], we found that in a pyrophosphate–citrate electrolyte at pH9.0, not only monoligand citrate $[Co(cit)_2]^{4-}$ and pyrophosphate $[Co(ppi)_2]^{6-}$ complexes, but also polyligand complexes of cobalt (II) with citrate-(cit^{3-}) and pyrophosphate– (ppi^{4-}) ions $[Co(ppi)_m(cit)_n]^{+2-(4m+3n)}$, their composition $[Co(ppi)cit]^{5-}$, the equilibrium constant K_e of the reaction of their formation and the constant of their stability were determined ($lg\beta_{MLX}$ = 8.47).

The purpose of this work is to determine the composition and stability constant of polyligand complexes of cobalt (II) with citrate (cit^{3-}) and molybdate – (MoO_4^{2-}) ions by the spectrophotometric method; to study the effect of the ratio of ligands equilibrium concentrations on the ionic composition of the electrolyte.

EXPERIMENT AND DISCUSSION OF THE RESULTS. Cobalt(II) forms with citrate (cit^{3-}) ions, depending on the pH of the solution and the equilibrium concentration of the ligand, protonated and non-protonated complex $[CoH_2cit]^+$, [CoHcit], $[Cocit]^-$, $[Co(cit)_2]^{4-}$ citrate compounds [7, 8]. Polymeric, polynuclear complex compounds of cobalt (II) with citrate of various compositions [9, 10], which have magnetic properties [10] and biological compatibility [11, 12], have been synthesized and isolated in the solid state. The authors of [13] also studied the thermodynamic parameters (ΔG^o, ΔH, ΔS) of the formation of protonated citrate complexes $[CoHcit]^-$ at pH 6, a temperature of 25°C in a 100 mM·l^{-1} $NaClO_4$ solution. With molybdate (MoO_4^{2-}) ions, cobalt (II) also forms protonated and non-protonated complex compounds $[Co(HMoO_4)_6]^{4-}$, $[CoMoO_4]$, $[Co(MoO_4)_2]^{2-}$ [7, 8].

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In the absence of cobalt(II) ions in the test solution, Mo(VI) can form mononuclear and polynuclear protonated hydroxide complexes with citrate [14]. The composition of the mononuclear and polynuclear complex compounds isolated from the solution corresponds to the formulas: $K_4[MoO_3(cit)]\cdot 2H_2O$ and $K_4[(MoO_2)_2O(Hcit)_2]\cdot 4H_2O$, respectively.

The data on the possibility of formation of polyligand complexes of cobalt(II) with citrate (cit^{3-}) and molybdate (MoO_4^{2-}) ions in a molybdate-citrate electrolyte, their composition and stability constant are practically absent in the literature.

Under the conditions of spectrophotometric studies at component concentrations, $mol\cdot l^{-1}$: C_{Co}^{2+} 0.01; C_{cit}^{3-} 0.01; C_{MoO4}^{2-} 0–0.10; Na_2SO_4 0.30; pH 9.0, as is seen from absorption spectra of cobalt(II) complexes in a citrate-molybdate electrolyte (Fig. 1), only polyligand complexes of cobalt(II) $[Cocit(MoO_4)]^{3-}$ are formed in the system under study according to the reaction:

$$[Co(cit)_2]^{4-} + [MoO_4]^{2-} \leftrightarrow [Cocit(MoO_4)]^{3-} + cit^{3-}. \quad (1)$$

This is confirmed by the results of further studies presented in this paper.

Thus, the study of polyligand complexes of cobalt (II) with citrate (cit^{3-}) and molybdate (MoO_4^{2-}) ions is certainly of scientific interest, since polyligand electrolytes based on them are promising for use in electroplating for obtaining electrocatalytic coatings of binary and ternary alloys of cobalt, nickel or iron with refractory metals (Mo, W and Re).

The processes of formation of polyligand complexes of cobalt (II) from citrate- (cit^{3-}) and molybdate- (MoO_4^{2-}) ions in a molybdate-citrate electrolyte, determination of their composition and stability constants were studied by spectrophotometric method. Spectrophotometry is one of the most precise methods for determining the composition and stability constants of colored complex compounds. Methods for determining the composition, stability constants of colored metal complexes from spectrophotometric measurements, their scope, advantages, limitations and disadvantages are discussed in detail in the monograph by A.K. Babko [6].

The spectrophotometric study of the formation of polyligand complexes of cobalt (II) with citrate– (cit^{3-}) and molybdate– (MoO_4^{2-}) ions causes significant difficulties, since along with them, depending on the pH of the solution, monoligand protonated and nonprotonated citrate and molybdate cobalt (II) complexes. The distribution of cobalt (II) complexes in the bulk of the 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.

The equilibrium concentrations of citrate– (cit^{3-}) and molybdate– (MoO_4^{2-}) ions in the test solution strongly depend on the pH of the solution, since they are anions of weak acids, citrate H_3cit and molybdate H_2MoO_4. Therefore, when conducting spectrophotometric studies, it is necessary to maintain an optimal and constant concentration of hydrogen ions (pH=const) in order to form complex ions of constant composition at a certain ratio of concentrations of the main components of the test solution (C_{Co}^{2+}/C_{cit}^{3-} = const) and a variable concentration molybdate ions ($C_{MoO4}^{2-} \neq$ const).

The values of the equilibrium concentrations of free ligands $[cit]^{3-}$ and $[MoO_4]^{2-}$ were determined from spectrophotometric studies, taking into account their total concentrations

and the pH of the solution according to the equation (2) [15]:

$$[L]^{m-} = C_{H_mL} / 1 + \sum_{i=1}^{i=m} K_i [H^+]^m , \qquad (2)$$

where C_{HmL}, $[L]^{m-}$ are the total and equilibrium concentrations of ligands (citrate and molybdate) in the test solution, mol·l^{-1} respectively; K_i are the general stability constants of citrate and molybdate ($pK_1 = 5.68$; $pK_2 = 10.03$; $pK_3 = 12.90$ and $pK_1 = 6.00$; $pK_2 = 7.02$ respectively) [8].

Composition of the studied solutions, mol·l^{-1}: C_{Co}^{2+} – 0.01; C_{cit}^{3-} – 0.01; C_{MoO4}^{2-} – 0 (*1*); 0.002 (*2*); 0.01 (*3*); 0.02 (*4*); 0.05 (*5*); 0.10 (*6*); Na_2SO_4 – 0.30; pH 9.0. Analytical grade reagents were used to prepare electrolytes. The studied solutions pH was corrected on an electronic pH meter (pH-150 MI) with NaOH and H_2SO_4 solutions.

The absorption spectra of solutions of the cobalt (II) complexes under study were recorded on a UV-VIS Spectrophotometer UV mini 1240 (Shimadzu) in a 1 cm cuvette at a temperature of 20 °C.

The composition and stability constant of polyligand complexes of cobalt (II) with citrate- (cit^{3-}) and molybdate- (MoO_4^{2-}) ions formed in the system under study at pH 9.0 were determined from the data of spectrophotometric measurements by the method of isomolar series. In this case, the ratio of the total concentrations of cobalt (II) ions and citrate ions remained constant ($C_{Co}^{2+} / C_{cit}^{3-} = 1:1$), while the concentration of molybdate ions C_{MoO4}^{2-} varied from 0 to 0.10 mol l^{-1}.

The relationship between absorbance and concentration of the studied solution is ideally described by the Lambert-Beer law [16, 17]:

$$D = l \cdot \sum \varepsilon_i C_i , \qquad (3)$$

where D is the absorption of the solution; l is the thickness of the absorbing layer (cell 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.

It should be emphasized that, according to the Lambert – Beer law [16, 17], the property of the measured system must be a strictly linear function of the molar concentration C_i of absorbing complexes.

The ratio of the coordination numbers m and n of the polydentate ligands cit^{3-} and MoO_4^{2-} during the formation of polyligand complexes $[Co(cit)_m(MoO_4)_n]^{+2-(3m+2n)}$ of constant composition (m/n = const) was determined by the Harvey and Manning slope ratio method [6, 16] from the dependence of the absorption of solution D on the total concentration of molybdate ions C_{MoO4}^{2-} at a constant ratio of the total concentrations of cobalt(II) and citrate ions $C_{Co}^{2+} / C_{cit}^{3-} = 1:1$, solution pH, and wavelength λ.

Analysis of the data of spectrophotometric studies (Fig. 1) at constant total concentrations of cobalt(II) ions, citrate C_{cit}^{3-}, solution pH and wavelength λ in the coordinates $D = f(C_{MoO4}^{2-})$ [6, 16] (Fig. 2) , where D – absorption of the test solution; C_{MoO4}^{2-} the total concentration of molybdate ions made it possible to determine the composition (ratio of the coordination numbers of polydentate ligands m/n) in the polyligand complex $[Co(cit)_m(MoO_4)_n]^{+2-(3m+2n)}$ formed in the system under study at pH 9.0. Curves $D = f(C_{MoO4}^{2-})$ obtained at wavelengths λ = 529 (3), maximum absorption in the system under study, 550 (2) and 560 (1) nm, indicate the formation of stable polyligand complexes of cobalt (II).

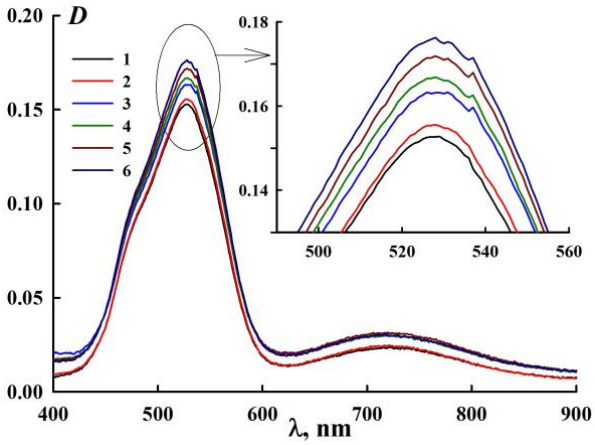

Fig. 1. Absorption spectra of cobalt (II) in citrate-molybdate electrolyte at pH 9.0, component concentrations, mol·l^{-1}: C_{Co}^{2+} – 0,01; C_{cit}^{3-} – 0,01; C_{MoO4}^{2-} – 0 (*1*); 0,002 (*2*); 0,01 (*3*); 0,02 (*4*); 0,05 (*5*); 0,10 (*6*).

The horizontal section observed on the absorption curve $D = f(C_{MoO4}^{2-})$ at a 10-fold excess of molybdate ions (Fig. 2) indicates the almost complete binding of cobalt (II) ions into the colored polyligand complex $[Co(cit)_m(MoO_4)_n]^{+2-(3m+2n)}$ or $[Cocit(MoO_4)]^{3-}$ [6, 16], since citrate– (cit^{3-}) and molybdate–(MoO_4^{2-}) ions are polydentate ligands, and allows us to calculate it molar absorption coefficient. The abscissa of the intersection points of two straight lines constructed from the slopes of the curvilinear sections of the experimental curves $D = f(C_{MoO4}^{2-})$ (Fig. 2) is equal to (1). This indicates that the molar ratio of the coordination numbers of polydentate ligands m/n in the polyligand complex $[Co(cit)_m(MoO_4)_n]^{+2-(3m+2n)}$, formed in the system under study at pH 9.0, is equal to 1. Therefore, in an alkaline medium (pH 9.0) with a 10-fold excess of molybdate ions, polyligand complexes of the composition $[Co(cit)(MoO_4)]^{3-}$, since the maximum coordination number is m=n=1.

The composition of polyligand complexes $[Co(cit)_m(MoO_4)_n]^{+2-(3m+2n)}$ formed in the system under study, and not only the ratio of coordination numbers m/n, was determined by the Bent and French method [6, 16], and their constant stability by the equilibrium shift method proposed by Bodlander and Abegg [6].

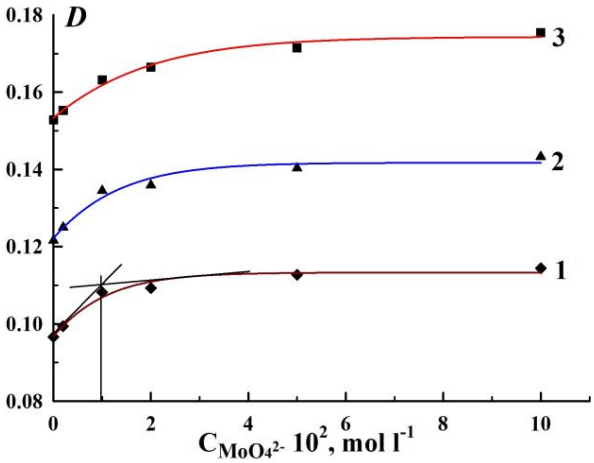

Fig. 2. Curves of formation of polyligand complexes of cobalt (II) in 0.30 mol·l^{-1} Na_2SO_4 solution at pH 9.0 and at wavelengths λ = 529(3), 550(2), and 560(1) nm. Component concentration, mol·l^{-1}: C_{Co}^{2+} – 0,01; C_{cit}^{3-} – 0,01.

The results of the analysis of spectrophotometric data (Fig. 1) at wavelengths λ = 500, 529, 550 and 560 nm in coordinates: $D = f[C_{cit}^{3-} / (C_{cit}^{3-} + C_{MoO4}^{2-})]$ (cr. 2, 4, 6, 8) and $D = f[C_{MoO4}^{2-} / (C_{MoO4}^{2-} + C_{cit}^{3-})]$ (cr. 1, 3, 5, 7) [6, 16], where *D* – absorption of the test solution; C_{MoO4}^{2-} and C_{Cit}^{3-} are the total concentrations of ligands, mol·l^{-1}, are shown in fig. 3. The obtained linear dependences indicate the formation of stable polyligand complexes of cobalt (II) with citrate-(cit^{3-}) and molybdate–(MoO_4^{2-}) ions of composition $[Co(cit)_m(MoO_4)_n]^{+2-(3m+2n)}$. The abscissa of the point of maximum absorption x_{max} in the system under study, as can be

seen from Fig. 3 does not depend on the wavelength λ and is equal to:

$$x_{max} = C_{cit}^{3-} / (C_{cit}^{3-} + C_{MoO4}^{2-}) = n / (n + m) = 0.5. \quad (4)$$

Hence, the molar ratio of the maximum coordination numbers of polydentate ligands m/n in the $[Co(cit)(MoO_4)]^{3-}$ polyligand complex formed in the system under study at pH 9.0 is 1.

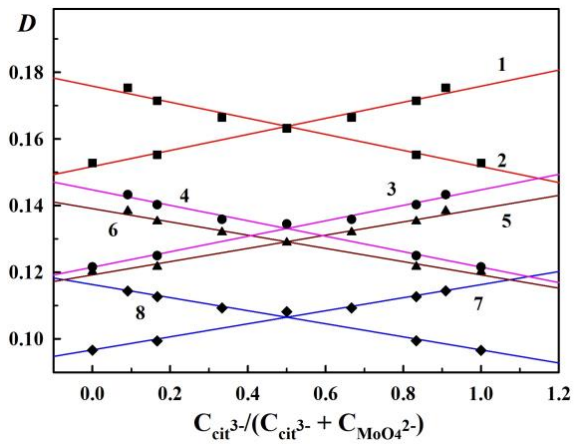

Fig. 3. Dependence of cobalt (II) complexes absorption in a citrate-molybdate electrolyte at pH 9.0 and wavelengths λ = 500 (5, 6), 529 (1, 2), 550 (3, 4), and 560 (7, 8) nm. The composition of the studied solutions, mol·l^{-1}: C_{Co}^{2+} – 0.01; C_{cit}^{3-} – 0.01; C_{MoO4}^{2-} – 0 (1); 0.002 (2); 0.01 (3); 0.02 (4); 0.05 (5); 0.10 (6); 0.010 (7).

The composition of the $[Co(cit)_m(MoO_4)_n]^{+2-(3m+2n)}$ polyligand complexes formed in the system under study at pH 9.0, their stability constant β_{MLX} was determined from spectrophotometric data by the method proposed by A.K. Babko [6]. The maximum optical density of the test solution corresponding to the horizontal section on the absorption curve $D = f(C_{MoO4}^{2-})$ shown in Fig. 2, denoted by D_o, and the optical density of the solution at a certain equilibrium concentration of molybdate ions $[MoO_4]^{2-}$ until the complete binding of the ligand into the colored polyligand complex $[Co(cit)_m(MoO_4)_n]^{+2-(3m+2n)}$ via D_x. Since the optical density of the solution D_x is proportional to the concentration of the colored cobalt (II) polyligand complex, then the ratio $[Co(cit)_m(MoO_4)_n]^{+2-(3m+2n)} / [Cocit]^- = [D_x / (D_o - D_x)]$. So, from the dependence $lg[D_x / (D_o - D_x) = f[lg([cit]^{3-} / [MoO_4]^{2-})]$, shown in fig. 4a, it is possible to determine the composition of the polyligand complexes formed in the system under study at pH 9.0, the equilibrium constant K_e of their formation according to the reaction:

$$[Co(cit)_2]^{4-} + [MoO_4]^{2-} \leftrightarrow [Co(cit)(MoO_4)]^{3-} + cit^{3-}. \quad (5)$$

According to equation (4), the equilibrium constant K_e of the reaction of formation of polyligand complexes $[Co(cit)(MoO_4)]^{3-}$ is equal to:

$$K_e = \beta_{MLX} / \beta_2, \quad (6)$$

where β_{MLX} and β_2 are the stability constants of polyligand $[Co(cit)(MoO_4)]^{3-}$ and citrate complexes $[Co(cit)_2]^{4-}$ according.

Dependences $lg[D_x / (D_o - D_x)] = f[lg([cit]^{3-} / [MoO_4]^{2-})]$ (cur. 1, 2) and $lg[D_x / (D_o - D_x)] = f[lg([MoO_4]^{2-} / [cit]^{3-})]$ (cur. 3, 4), as can be seen from Fig. 4 are rectilinear, the abscissa of the intersection point of which is equal to 0. This indicates that the molar ratio of the equilibrium concentrations of lidentate ligands $[cit]^{3-} / [MoO_4]^{2-}$ in the polyligand complex $[Co(cit)_m(MoO_4)_n]^{+2-(3m+2n)}$ is equal to 1, that is, m=n=1. Thus, polyligand complexes $[Co(cit)(MoO_4)]^{3-}$ are formed in the system under study at pH 9.0. Tangent of the slope of the straight line $lg [D_x / (D_o - D_x)] = f [lg([MoO_4]^{2-} / [cit]^{3-})]$ (Fig. 4,

cur. 3, 4) is 0.5618 and is equal to the logarithm of the equilibrium constant K_e of the formation of polyligand complexes $[Co(cit)(MoO_4)]^{3-}$. The value of the equilibrium constant K_e calculated by equation (4) is 3.6459. Hence, the stability constant of $[Co(cit)(MoO_4)]^{3-}$ polyligand complexes according to equation (5) is $7.29 \cdot 10^5$ ($lg\beta_{MLX} = 5.86$).

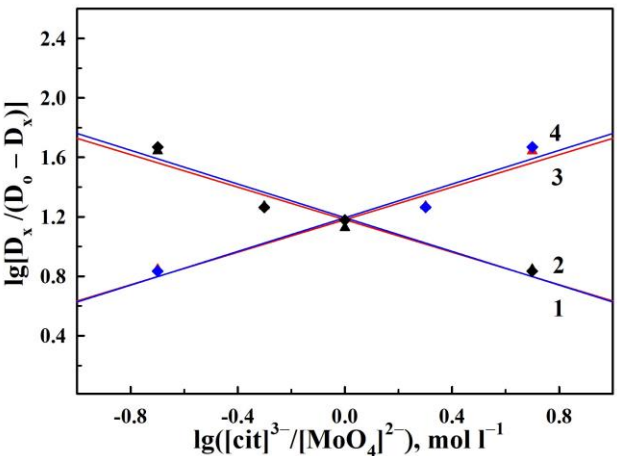

Fig. 4. Dependence of the function $lg[D_x / (D_o - D_x)]$ on the logarithm of the ratio of equilibrium concentrations of ligands $lg([cit]^{3-}/[MoO_4]^{2-})$ (cur. 1, 2) and $lg([MoO_4]^{2-}/[cit]^{3-})$ (cur. 3, 4), obtained by the method of equilibrium shift in the studyed system at pH 9.0, C_{Co}^{2+} ion concentration 0.01 mol·l^{-1}, wavelength λ = 529(1. 3) and 550 (2. 4) nm.

The composition of polyligand cobalt (II) complexes, and not only the ratio of the coordination numbers of polydentate ligands m/n, was determined from spectrophotometric data (Fig. 1) also by the equilibrium shift method [6]. The dependence $lg[D_x /(D_o - D_x)] = f(lg[MoO_4]^{2-})$ was obtained in the system under study at pH 9.0, total concentration of C_{Co}^{2+} ions – 0.01 mol·l^{-1}, and wavelengths λ =500, 529 and 550 nm, is shown in fig. 5.

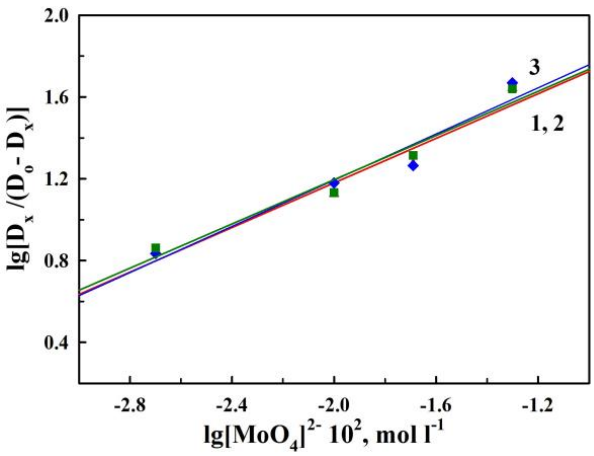

Fig. 5. Dependence of function lg $[D_x / (D_o - D_x)]$ on the logarithm of the equilibrium concentration of molybdate ions in citrate-molybdate electrolyte at pH 9.0, concentration of components, mol·l^{-1}: C_{Co}^{2+} – 0.01; C_{cit}^{3-} – 0.01 and wavelengths 500 (1), 529 (2) and 560 (3) nm.

The tangent of the slope of the straight line $lg[D_x / (D_o - D_x)] = f(lg[MoO_4]^{2-})$ (Fig. 5, cur. 3) is 0.5556 and is equal to the logarithm of the equilibrium constant K_e of the formation of polyligand complexes $[Co(cit)(MoO_4)]^{3-}$. The value of the equilibrium constant K_e of the reaction of their formation calculated by equation (4) is 3.5942. Hence, the stability constant of $[Co(cit)(MoO_4)]^{3-}$ polyligand complexes, according to equation (5), is equal to $7.19 \cdot 10^5$ ($lg\beta_{MLX} = 5.86$).

The value of the stability constant of polyligand complexes $[Co(cit)(MoO_4)]^{3-}$ calculated from spectrophotometric data ($lg\beta_{MLX}$ = 5.86) is consistent with the value of this constant calculated from pH-potentiometric data ($lg\beta_{MLX}$ = 6.25) [7] which testifies to their authenticity. The reasons for the discrepancies in the values of the stability constants of the

polyligand complexes $[Co(cit)(MoO_4)]^{3-}$ are due not only to the methods of their determination, but also to different values of the ionic strength and temperature of the studied solutions. Thus, taking into account the above, it should be noted that the question of the composition and stability constant of polyligand citrate-molybdate complexes of cobalt (II) should be considered resolved.

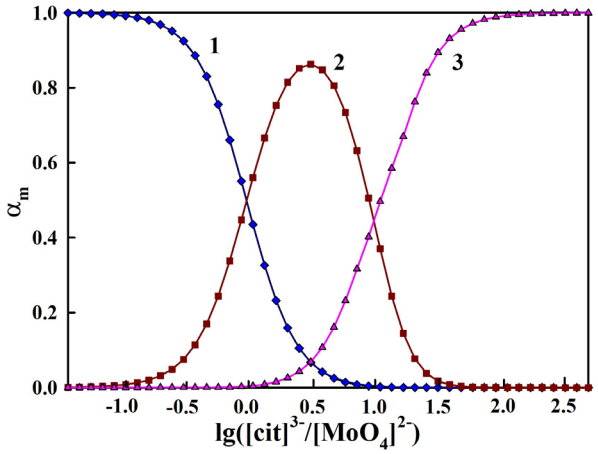

Fig. 6. Dependence of the degree of formation of molybdate (1), citrate (2), polyligand (3), cobalt (II) complexes in molybdate-citrate electrolyte on the logarithm of the ratio of equilibrium concentrations of ligands: 1– $[Co(MoO_4)_2]^{2-}$; 2 – $[Co(cit)_2]^{4-}$; 3 – $[Co(cit)(MoO_4)]^{3-}$.

Taking into account the stability constants of molybdate $[Co(MoO_4)_2]^{2-}$ ($lg\beta_2$ = 3.09), citrate $[Co(cit)_2]^{4-}$ ($lg\beta_2$ = 5.30) and polyligand $[Co(cit)(MoO_4)]^{3-}$, ($lg\beta_{MLX}$ = 5.86) of cobalt (II) complexes, the dependence of the degree of their formation in a molybdate-citrate electrolyte on the logarithm of the ratio of the equilibrium concentrations of ligands lg ($[cit]^{3-}$/ $[MoO_4]^{2-}$). In a molybdate-citrate electrolyte, as can be seen from Fig. 6, molybdate complexes $[Co(MoO_4)_2]^{2-}$ exist depending on the ratio of equilibrium concentrations of ligands lg($[cit]^{3-}$/ $[MoO_4]^{2-}$) in the range from 0 to +1, citrate complexes $[Co(cit)_2]^{4-}$ – in the range from 0 to +2, and polyligand complexes $[Co(cit)(MoO_4)]^{3-}$ – in the region >0).

CONCLUSIONS. It has been established that, in a citrate-molybdate electrolyte at pH 9.0, cobalt (II) ions form with citrate- (cit^{3-}) and molybdate- (MoO_4^{2-}) ions, depending on the ratio of the equilibrium concentrations of the ligands, non-protonated molybdate $[Co(MoO_4)_2]^{2-}$, citrate $[Co(cit)_2]^{4-}$ and polyligand complexes $[Co(cit)_m(MoO_4)_n]^{+2-(3m+2n)}$). The composition of $[Co(cit)(MoO_4)]^{3-}$ polyligand complexes was determined, the equilibrium constant K_e of the reaction of their formation and their stability constant ($lg\beta_{MLX}$ = 5.86) were calculated. Polygand complexes $[Co(cit)(MoO_4)]^{3-}$ ($lg\beta_{MLX}$ = 5.86) are more stable than molybdate $[Co(MoO_4)_2]^{2-}$ ($lg\beta_2$ = 3.09) and citrate $[Co(cit)_2]^{4-}$ ($lg\beta_2$ = 5.30) cobalt (II) complexes.

The dependence of the degree of formation of molybdate $[Co(MoO_4)_2]^{2-}$, citrate $[Co(cit)_2]^{4-}$ and polyligand $[Co(cit)(MoO_4)]^{3-}$ complexes of cobalt (II) in a citrate-molybdate electrolyte on the logarithm relative to equilibrium concentrations ligands.

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ВИЗНАЧЕННЯ СКЛАДУ ТА КОНСТАНТИ СТІЙКОСТІ ПОЛІЛІГАНДНИХ ЦИТРАТНО-МОЛІБДАТНИХ КОМПЛЕКСІВ КОБАЛЬТУ (II)

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Спектрофотометричним методом вивчено комплексоутворення кобальту (II) з цитрат- (cit^{3-}) і молібдат- (MoO_4^{2-}) іонами в 0,3 моль·л$^{-1}$ розчині Na_2SO_4 за 20 °С. Установлено, що в цитратно-молібдатному електроліті при pH 9.0 іони кобальту (II) утворюють залежно від співвідношення рівноважних концентрацій лігандів молібдатні $[Co(MoO_4)_2]^{2-}$, цитратні $[Co(cit)_2]^{4-}$ та полілігандні комплекси $[Co(cit)_m(MoO_4)_n]^{+2-(3m+2n)}$. Визначено склад полілігандних комплексів $[Co(cit)(MoO_4)]^{3-}$, обчислено константу рівноваги K_r реакції їхнього утворення та константу їхньої стійкості ($lg\beta_{MLX} = 5.86$). Розраховано залежність ступеня утворення молібдатних, цитратних та полілігандних комплексів кобальту (II) в цитратно-молібдатному електроліті від логарифму відношення рівноважних концентрацій лігандів.

Ключові слова: кобальт (II), молібдатні, цитратні та полілігандні комплекси, склад, константа рівноваги, константа стійкості, спектрофотометрія.

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