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Synthesis, spectral and thermodynamic study of mixed metal and mixed ligand complexation of cobalt(II) and nickel(II) in aqueous solution

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ABSTRACT

The method of absorption spectrophotometry was applied to study the complex formation in Co(II)–Ni(II)–amino acid (aspartic H_2Asp and glutamic H_2Glu)–EDTA (H_4Edta) systems for molar ratios of 1:1:1:1:1 components. Mathematical modeling of optical density dependence on the acidity of solution (A=*f*(pH)) for different wavelength in the range 300–950 nm showed that depending on the ratio of the reagents and the solution acidity, formation of the complex $[(CoAsp)Edta(NiGlu)]^{4-}$. Stability constants and electronic absorption spectra of this complex was calculated; thier possible structur was suggested, and also calculated thermodynamic parameters (ΔG, ΔH°, and ΔS°) for the studying complexes were calculated according to the values of stability constant (K_{ST}) at 25 °C obtained from the temperature dependence of stability constant by using van't Hoff equation.

Keywords EDTA, Cobalt, Nickel, Amino acid, Binuclear complexes, Stability constants

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1. Introduction

Complexation in solutions in multi systems metal cation–EDTA–secondary ligand (amines, amino acids, dicarboxylic acids, etc.), depending on the conditions (molar ratio of components, acidity of the medium), can lead to the formation of not only mononuclear homogeneous ligand complexes, but also much more complex in composition and structure of structures - mononuclear mixed-ligand and polynuclear homo ligand complexes, as well as polynuclear mixed-ligand complexes. A series of early works established the formation of similar complexes of doubly charged metal cations with the following composition: $[MEdtaen]^{2-}$, $[M_2en_2Edta]$, $[M_2en_4Edta]$ (M=Ni^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}) [1], $[MGlyEdta]^{3-}$, $[MOxEdta]^{4-}$, $[(MGly_2)_2Edta]^{4-}$, $[(MOx_2)_2Edta]^{8-}$ (M=Ni^{2+}, Co^{2+}; Gly^{-}– glycinate ion, Ox^{2-} –oxalate ion), $[(CuGly)_2Edta]^{2-}$, $[(CuOx)_2Edta]^{4-}$ [2], $[(CdL)_2Edta]$ (L=en, Gly, Ox) [3], $[(NiL_2)_3Edta]$, $[(NiL_2)_4Edta]$, $[(CuL_3)Edta]$ (L=en, Gly); (for complexes containing ligands L, charges are omitted) [4]. Based on the analysis of the electronic absorption spectra of the complexes in solutions and the diffuse reflectance spectra of the complexes isolated in the solid state, it was assumed that in binuclear complexes EDTA performs a bridging function, equally binding two metal cations by independent coordination of two iminodiacetate branches, and the secondary ligand saturates the coordination sphere of metal. In asymmetric three- and four-nuclear complexes, EDTA also acts as a bridging ligand, and its complexity in relation to one cation is reduced to two. The spectrophotometric studies of the Ni(II)–EDTA–secondary ligand systems (various amino acids, ethylenediamine, IDA, NTA, etc.) carried out by us in the development of this topic made it possible to determine the stability constants and the optimal conditions for the formation of two-, three-, and quadrangular mixed-ligand complexes with the composition $[(NiL)_2Edta]$, $[(NiL_2)_2Edta]$, $[(NiL_2)_3Edta]$, $[(NiL_2)_4Edta]$ [5-7], $[(CoL)_2Edta]$, $[(CoL_2)_2Edta]$, $[(CoL_2)_3Edta]$, $[(CoL_2)_4Edta]$, [(NiL)Edta[(CoL)] [8]. Of further interest is the question of the role of the cation (in particular, the compatibility of various cations) in the formation of polynuclear mixed-ligand EDTA complex, as well as the elucidation of the role of the nature of the secondary ligand in the stabilization of such complexes. In this regard, the purpose of this work was to study complexes in the Co(II)–amino acid–EDTA systems (in comparison with the previously studied Ni(II)–amino acid–EDTA systems [6-9], as well as Co(II)–Ni(II)–amino acid–EDTA. Aspartic and glutamic acids, selected as additional ligands, being homologues, form chelate rings of different size and stability with metal cations, which can lead to differences in compatibility during the formation of a mixed-ligand chelating agent with EDTA. The results obtained make it possible to establish some regularities in the formation of binuclear heteroligand ethylenediaminetetraacetates of doubly charged cations 3d-metal and also calculated the thermodynamic parameters (ΔG°, ΔH° and ΔS°) for complexes. The thermodynamic parameters represented by standard free energy change where values of stability constants can be expressed in terms of free energy or standard Gibbs (ΔG°) [10-12], as in Equation (1).

$$\Delta G° = -RT \ln K_{eq} \quad (1)$$

Standard enthalpy change ΔH°of equilibrium constant can be determined from Equation (2) as follows [12-14].

$$\ln K_{eq} = -\Delta H°/RT + \text{constant} \quad (2)$$

The standard entropy change ΔS° for each compound was calculated by using the following Equation (3) [12-16].

$$\Delta G° = \Delta H° - T\Delta S° \quad (3)$$

2. Experimental section

Complexation processes were studied by spectrophotometric titration. The optical density of the solutions was measured on an SF-2000 spectrophotometer (in the range of 300-900 nm with an error of ±0.1 nm) using a specially made attachment with a flow cell with quartz glass (the thickness of the absorbing layer is 1cm). This installation allows you to simultaneously determine the pH value and optical density of the solution. The acidity of the solutions was measured on I-160MI ion meter using an ES-l0601/7 working electrode and an ESR-10101 reference electrode. The required pH value of the solutions was created with analytical grade NaOH and $HClO_4$ solutions. The constancy of the ionic strength (I≈0.2) was maintained with a $NaClO_4$ solution (analytical grade). The studies were carried out at room temperature (20±2) °C. Metal solutions were prepared by dissolving $CoSO_4.7H_2O$ and $NiSO_4.7H_2O$ salts in water; the concentration of metal ions in the solution was determined by complex titration with a standard EDTA solution according to the generally accepted methods. Solutions of a complex and amino acids were prepared by dissolving chemically pure preparations. in distilled water. Mathematical processing of the results was carried out using the computer program HypSpec [17]. The models of the complexes were constructed using the ACD/Labs program [18].

3. Results and discussion

Modeling of equilibrium in the systems under study was carried out by analyzing the ESP and curves A = *f*(pH) obtained for different wavelengths. The HypSpec program used [17] makes it possible to calculate the stability constants of the resulting complexes and their spectral characteristics for the selected complex model. The question of the expediency of taking into account one or another complex form of metal was solved on the basis of minimizing the Fisher criterion, which takes into account the discrepancies between the experimental and calculated values of optical densities for each component of the system. In the calculations, we used the fixed literary values of the hydrolysis constants of nickel(II) and cobalt(II), the dissociation constants of EDTA (H_4Edta) and amino acids (aspartic H_2Asp, glutamic H_2Glu). In the course of the calculations, model was considered [CoAspEdtaNiGlu], in addition to formation of various sets of

complexes in the previous study [8], including metal cations M^{2+} (M=Co^{2+}, Ni^{2+}), EDTA ($Edta^{4-}$), amino acids H_2X (X = Asp^{2-}, Glu^{2-}), namely: 1) homogeneous ligand complexes with the composition $[MH_iEdta]^{i-2}$ (i = 0 - 3), $[MH_iX]$ (i = 0, 1) , MX_2^{2-}; 2) mixed-ligand mononuclear complexes $[MEdtaX]^{4-}$; 3) mixed-ligand heterobinuclear (different-metal) complexes $[(MX')(M'X)Edta]^{4-}$. To study different metal complexes, information is needed on homogeneous metal heteroligand complexes Co(II) and Ni(II). The composition and stability of such complexes for Ni(II) are presented in [6-9], the mixed ligands of the system for the Co(II) and Ni(II) complexes were investigated in this work.

Mathematical processing of the A = *f*(pH) curves for systems Co(II)–H_2Asp–H_2Glu–EDTA showed that in the systems under study, medium mono- and bis-complexes $[(CoAsp)_2Edta]^{4-}$ lgβ = 36.50 ± 0.06, $[(CoGlu)_2Edta]^{4-}$ lgβ = 34.27 ± 0.18, $[CoAspEdta]^{4-}$ lgβ = 21.21 ± 0.30 $[CoGluEdta]^{4-}$ lgβ = 20.23±0.03 [19], $[NiGluEdta]^{4-}$ lgβ = 21.83 ± 0.08, $[NiAspEdta]^{4-}$ lgβ = 21.95 ± 0.12 $[(NiAsp)_2Edta]^{4-}$ lgβ = 37.38 ± 0.09 $[(NiGlu)_2Edta]^{4-}$ lgβ = 35.20 ± 0.13 [6,8,9] Comparison of the values with the data for nickel(II) complexes established under identical conditions shows that, as in the case of many other ligands, Co(II) complexes are less stable than Ni(II). The higher stability of aspartic complexes in comparison with glutamic complexes is also of a general nature and is explained by the more optimal sizes of one of the two chelate rings for aspartic acid (six-membered) compared to glutamic (seven-membered).

The formation of heterometallic mixed-ligand ethylenediaminetetraacetates Co(II) and Ni(II) in the Co(II)–Ni(II)–H_2Asp–H_2Glu–EDTA systems at a molar ratio of components 1:1:1:1:1 is observed in an alkaline medium, whereas while at pH<6, there are mainly uncomplexed Co^{2+} and Ni^{2+} ions, as well as mononuclear complexes Ni(II) of the composition $[NiHEdta]^{-}$, $[CoHEdta]^{-}$, $[CoEdta]^{2-}$, $[NiEdta]^{2-}$ and $[CoAspEdtaNiGlu]^{-4}$ (Figure 1). The formation of binuclear complexes in the presence of amino acids can proceed according to different equations, the equilibrium constant and the constant of dissociation for the complex in Table 1.

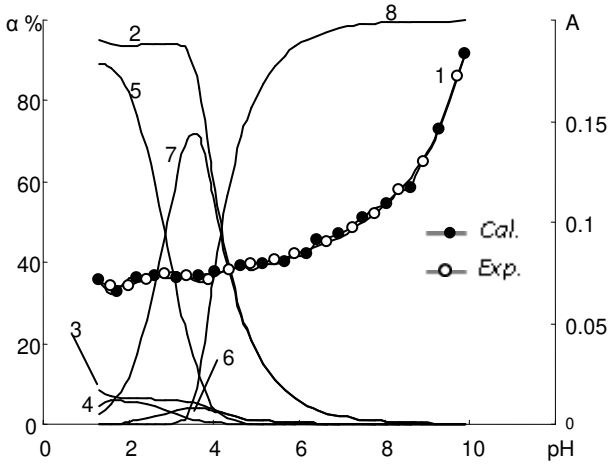

Figure 1 Accumulation fraction (α) and absorbance (A) of the complexes in the Co(II)–Ni(II)–Asp–Glu–Edta system versus pH at a ratio of 1:1:1:1:1 calculated and experimental curves CoNiAspGluEdta(1), Co^{2+}(2) , Ni^{2+} (3), $[CoHEdta]^{-1}$(4), $[NiHEdta]^{-1}$(5), $[CoEdta]^{-2}$(6) , $[NiEdta]^{-2}$(7), $[CoNiAspGluEdta]^{-4}$(8), $C_{Co^{2+}} = C_{Ni^{2+}}$ $0.125 \cdot 10^{-2}$ mol/L at λ=490 nm.

Table 1. The equilibrium constant, stability and thermodynamic values of the complex $[(CoAsp)Edta(NiGlu)]^{4-}$ in 25 °C.

Complex	Reaction equation	logβ	*log*K	ΔG° kJ mol^{-1}	ΔH° kJ mol^{-1}	ΔS° J mol^{-1} K^{-1}
$[(CoAsp)Edta(NiGlu)]^{4-}$	$[NiAsp] + [CoGluEdta]^{4-} \rightleftharpoons [(CoX)Edta(NiX)]^{4-}$	36.93 ± 0.04	9.35 ± 0.02	-5.371	18.584	0.0803

In the series of binuclear complexes, stability changes in the sequence: $[(CoAsp)Edta(NiAsp)]^{4-}$ > $[(CoNiAspGluEdta]^{-4}$ > $[(CoGlu)Edta(NiGlu)]^{4-}$ substitution of glutamate ion for aspartate ion causes a regular increase in the stability of complexes. The stability of all binuclear complexes with aspartate ions as a secondary ligand is slightly higher than for glutamate ions, as well as for mononuclear complexes with the participation of these ligands.

The position of the maxima in the absorption spectrum of the $[(CoAsp)Edta(NiGlu)]^{4-}$ complex is close to those for the $[NiEdta]^{2-}$ and $[CoEdta]^{2-}$ complexes (Figure 2), which indirectly indicates that both cations are associated with EDTA is inside the sphere, and not like the double ionic salt M'[MEdta], when one of the metals forms a normal complexonate with EDTA with hexadentate coordination, and the other is bound outside the sphere, those type $[CoNiAspGluEdta]^{4-}$.

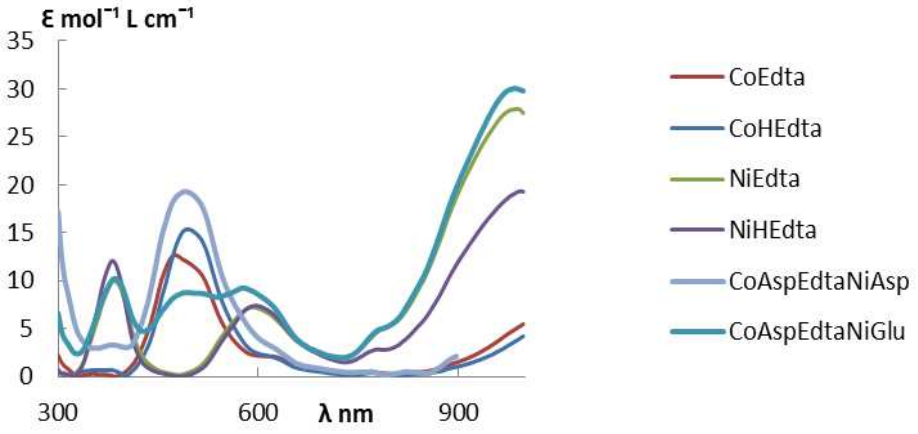

Figure 2 The calculated absorption spectra of the complexes.

The proposed schematic structure and 3D model of the binuclear complex are shown in Figure 3, which is consistent with the literature on the structure of similar complexes [1-4]. The octahedral spheres of metal ions in a homo- or hetero binuclear complex are linked by a di amino ethane EDTA bridge. Moreover, the latter binds equally to each metal ion due to the tridentate iminodiacetate group. Amino acid anions saturate the coordination sphere of metals, forming two chelate cycles, one of which is five-membered, the second is six-membered (H_2Asp) and seven-membered (H_2Glu).

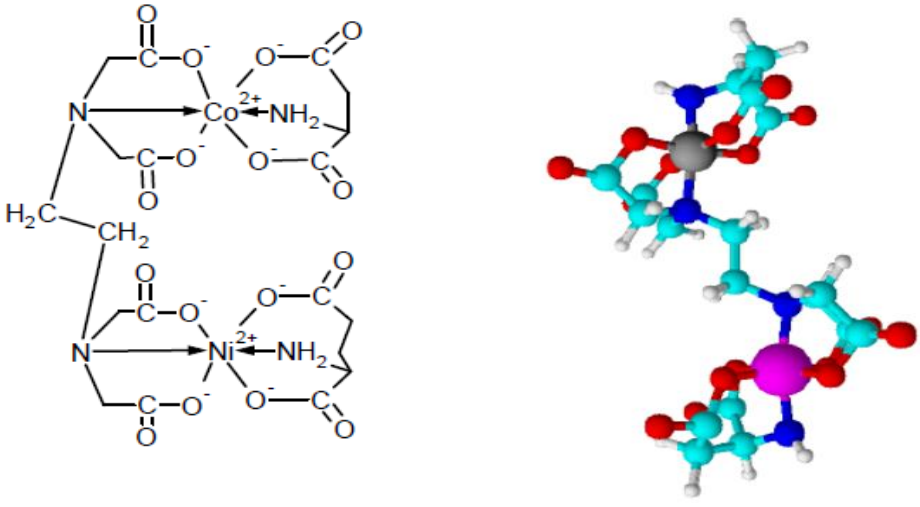

Figure 3 Proposed structure of the complex.

From the dependence of K_{eq} on temperature (T), the thermodynamic function (ΔG°, ΔH°, ΔS°) was calculated. The values were summarized in Table 1 at 25 °C. The ΔG° values were obtained from the reaction of complexes indicating a spontaneous reaction. The positive values of ΔH° (endothermic reaction) were obtained for complexes by using van't Hoff equation. Meanwhile, the ΔS° values indicate that complexes are brought into being [20-21]. The positive value of ΔH° is the indicative endothermic processes, and the formation of these complexes is favored under high temperature. Meanwhile, the negative values of ΔG° indicate the spontaneous process in each case. On the other hand, the positive values of ΔS° indicate some randomness degree during the formation presses.

4. Conclusion

Thus, the results of the work show that in the presence of an excess of Co^{2+} and Ni^{2+} cations with respect to EDTA and only in the presence of additional ligands (amino acids), mixed-ligand heterobinuclear complexes of the composition $[(CoAsp)Edta(NiGlu)]^{4-}$, $[(CoAsp)Edta(NiAsp)]^{4-}$. This is consistent with our data on the formation of homopolynuclear complexes of EDTA with Ni^{2+} cations and a number of other secondary ligands, such as dipyridyl, ethylenediamine, amino acids, IDA, NTA. In all these complexes, EDTA acts as a structure-forming tri- or bidentate (with respect to each metal cation) ligand, and further saturation of the coordination capacity of cations occurs due to secondary low-denominate ligands. The closeness of the electronic structure and ionic radii of Co^{2+} ($3d^7$, r = 72 pm) and Ni^{2+} ($3d^8$, r = 69 pm) determines their good compatibility in heterobinuclear complexes, the stability of which is close to the stability of the corresponding homobynuclear complexes. The role of the nature of the secondary ligand in the stabilization of these EDTA complexes is probably insignificant, as evidenced by the wide range of such ligands that make up these complexes.

Conflict of Interest

The authors report no conflict of interest.

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