

Modeling and Thermodynamic Values of Complex Equilibrium of Cobalt(II) with Diethylenetriaminepentaacetic Acid in Aqueous Solution

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Abstract: The paper reports the study of the complex formation of cobalt (II) with diethylenetriaminepentaacetic acid (DTPA, H₅L) based on spectrophotometric (SF) and potentiometric data (pH). Complexes of different compositions were found, and equilibrium constants, as well as the stability constants of these complexes, were determined. Accumulation of complexes in proportion is calculated based on the acidity of the medium. The experimental data have been carried out by using mathematical models to assess the solution's possible existence with a wide spectrum of complex particles and to point out those which are quite sufficient to copy the experimental data. In addition, 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: cobalt; stability constants; spectrophotometer; potentiometer

■ INTRODUCTION

It is known that DTPA, being an octadentate pentabasic ligand, forms stable water-soluble complexes with many metal cations including cobalt(II). These complexes are widely used in various fields of science, technology, agriculture, and medicine [1-2]. It is known that all animal and plant organisms need trace elements. The latter should be introduced into living organisms in a biologically active form, easily transported and absorbed. The use of inorganic metal salts for these purposes is ineffective. The most promising substances in this regard are biologically active complexes, especially, DTPA. The introduction of metal complexes into the soil contributes not only to an increase in micronutrient fertilizers but also to their mobility. Some metal complexes with DTPA contribute to the growth and productivity of crops and increase the yield and quality of potato tubers. Iron complexonate with DTPA is a useful tool in the fight against plant chlorosis. Some of the biochemical-complexes are used in animal husbandry and the food industry [3-5]. In medicine, metal complexes can play the role of antidotes, regulators of mineral metabolism, as

anticancer and antiviral, antimicrobial, and diagnostic drugs [6-8]. It should be noted that the cumulative properties of complexions and their complexes are very weakly expressed. Accumulation coefficients indicate a low potential risk of developing chronic poisoning with these drugs.

Cobalt, on the other hand, is a biologically active metal. Excessive "technogenic" intake of this metal in the body has a toxic effect on metabolism and has a carcinogenic effect on the cell [9]. The widespread use of cobalt and DTPA salts necessitates a detailed study of equilibrium in the Co(II)-DTPA system. In the previous studies, cobalt and DTPA complexes have been widely used in agriculture and medicine, the researchers used spectrophotometer measurements and did not use voltage measurements data and programs while the thermodynamic values of the complexes were not calculated [3], thus it is necessary to be studied in more detail. In our current study, the equilibrium constants were measured based on spectrophotometer (SF) and voltage data (pH), and the stability constants of these complexes are determined by using mathematical

modeling 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 Eq. (1):

$$\Delta G^\circ = RT \ln K_{eq} \quad (1)$$

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

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

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

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

■ EXPERIMENTAL SECTION

Materials

The chemical reagents used in this research were diethylenetriaminepentaacetic (DTPA, $C_{14}H_{23}N_3O_{10}$), potassium hydroxide (KOH), sodium hydroxide (NaOH), sodium nitrate ($NaNO_3$), hydrochloric acid (HCl fuming 37%), cobaltous sulfate heptahydrate ($CoSO_4 \cdot 7H_2O$) were purchased from Sigma-Aldrich, Merck (Germany and British). All reagents were used without further purification.

Instrumentation

Instruments used in this research were Spectrophotometer SF-2000 No. 03 11 1120 00 (Russia), pH Meter PW 9421 Philips (England), Electric Balance + 0.0001g L420 B Sartorius (Germany), and Distillate Water Lab Tech (Korea).

Procedure

The complex solution was prepared by dissolving 3.929 g from a reagent grade DTPA in 250 mL distilled water. The solution that concentration 0.04 M of DTPA was clarified by pH-metric titration with a standard solution of 0.1 M KOH. A 0.04 M cobalt(II) solution was prepared by dissolved 2.808 g of $CoSO_4 \cdot 7H_2O$ salt in 250 mL of distilled water. Then Co^{2+} ions were standardized by redox metric titration with a DTPA solution. The necessary acidity of the medium was supported by 0.1 M for both HCl and NaOH solutions. A constant ionic strength ($I = 0.1$ M) was created with $NaNO_3$ solution.

The optical density of the solutions was measured on an SF-2000 spectrophotometer using quartz cuvettes with an absorbing layer length of 1 cm. The concentration of hydrogen ions was measured on an I-160 M ion meter (ES-10601/7 working electrode and ESr-10101 reference electrode). The main absolute error of pH measurement was ± 0.01 . The redox potential value was measured using a platinum electrode EPL-02. All measurements were carried out at a temperature of 20 ± 2 °C. The calculation of equilibrium parameters in the Co(II)-DTPA system was carried out using the computer programs HypSpec (spectrophotometer) and Hyperquad 2008 (potentiometer) [17-18].

■ RESULTS AND DISCUSSION

To study the complexation process in the Co(II)-DTPA system, the absorption spectra of solutions were collected for various values of the acidity of the medium (Fig. 1). A comparison of the obtained spectra with the spectra of Co(II) solution shows that Co(II) complexes with DTPA were already formed in a strongly acidic medium ($pH = 0.5-6.88$). In DTPA's presence, the absorption band of hydrated Co(II) ions at 350 nm disappears while the optical density increases in the region of 450-550 nm with a maximum at 506 nm.

To calculate the composition and stability of the resulting Co(II) complexes with DTPA, the HypSpec program was used. This program allows us to analyze the experimental dependence of the optical density on pH simultaneously for different wavelengths of 300-750 nm in accordance with the selected complexation model. For complexes of the molar composition Co(II):DTPA = 1:1, $Co(H_iL)^{i-3}$ ($i = 0-5$) and $Co(OH)_jL^{(3+j)-}$ ($j = 0-1$), and also hydroxo complexes $Co(OH)_k$ ($k = 1-3$), we performed calculations for various compositional models, including complexness. In the calculations, we used fixed values of the DTPA dissociation constants, previously determined by us by pH metric titration as below. The total hydrolysis constants of Co (II) were taken from the literature as ($K_i = [Co(OH)_i^{3-i}][H^+]/[Co^{2+}]$): $pK_{1w} = 9.7$; $pK_{2w} = 9.1$; $pK_{3w} = 12.7$ ($I = 0.1$, $t = 25$ °C) [19-20]. The HypSpec program allows modeling in automatic mode by comparing the experimental and

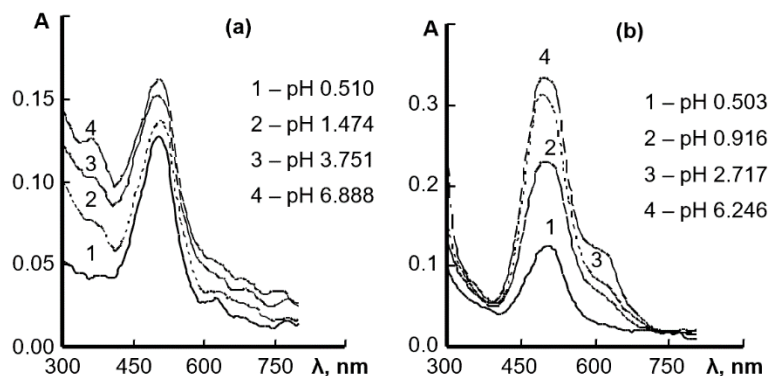


Fig 1. Absorption spectra of (a) Co (II) solution, and (b) Co(II)-DTPA complex. $C_{\text{Co(II)}} = 1.6 \times 10^{-2}$ mol/L, $C_{\text{DTPA}} = 2.4 \times 10^{-2}$ mol/L

calculated spectra represented by the sum of the spectra of all absorbing particles.

For Co(II)-DTPA system in the studied range of medium acidity ($0 < \text{pH} < 7$), the minimum standard deviation corresponds to a model that includes the following particles: Co^{2+} , CoH_2L^- , CoHL^{2-} , CoL^{3-} . The calculated values of the total stability constants are presented in Table 1. Fig. 2 shows a comparison of the experimental and calculated optical density values (at 506 nm) for the established complexation model, which shows their good agreement. At $\text{pH} > 11$, hydrolysis proceeds in the system, and turbidity appears in the solution.

Spectrophotometer method established complex compounds of cobalt with DTPA at different ionic strengths values; $[\text{CoH}_4\text{L}]^+$ ($\lg\beta = 30.18$, $I = 0.1$, 25°C)

$[\text{CoL}^{3-}]$ ($\lg\beta = 19.72$, $[\text{CoHL}^{2-}]$ ($\lg\beta = 22.47$, $I = 0$, 20°C) [22].

The diagram of the molar distribution of complexes in the Co(II)-DTPA system (Fig. 2(b)) allows us to compare the observed spectral changes with the regions of existence of individual complexes characterized by the spectra shown in Fig. 3.

Table 1. Composition and stability constants of complexes in the Co(II)-DTPA system

Complex	$\lg\beta$	Terms, Method
CoH_2L^-	26.55 (± 0.01) SF	I = 0.1 (NaNO ₃), 21 °C SF, pH
	25.38 (± 0.04) pH	
CoHL^{2-}	22.87 (± 0.05) SF	
	22.67 (± 0.02) pH	
CoL^{3-}	18.39 (± 0.10) SF	
	17.79 (± 0.03) pH	

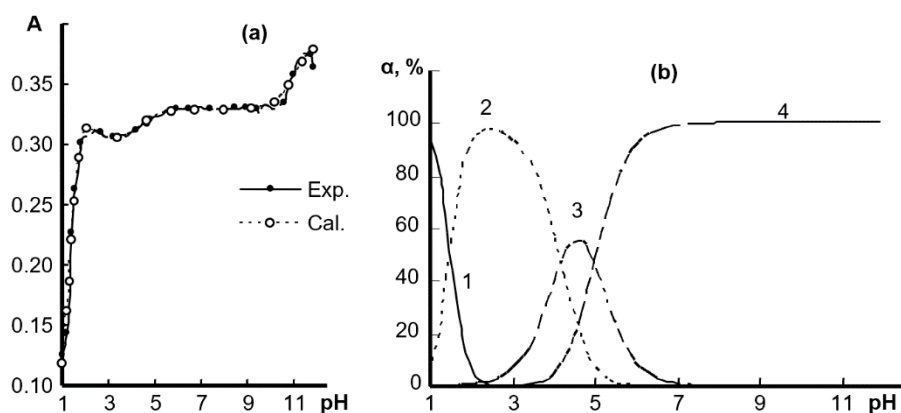


Fig 2. (a) Experimental and calculated dependences of optical density ($\lambda = 506$ nm) and diagram of the molar distribution of complexness. (b) Versus pH for the system Co(II)-DTPA, where Co(II) (1), CoH_2L^- (2), CoHL^{2-} (3), CoL^{3-} (4), $C_{\text{Co(II)}} = 1.6 \times 10^{-2}$ mol/L, $C_{\text{DTPA}} = 2.4 \times 10^{-2}$ mol/L

Three buffer regions are observed on the pH metric DTPA titration curve ($0 < a < 3$; $3 < a < 4$; $a > 4$; a = degree of titration) and one distinct jump at $a = 3$ (Fig. 4). In the presence of Co(II) cations, a decrease in the pH of solutions associated with complexation is observed. To calculate the equilibrium in the Co(II)–DTPA system, the Hyperquad 2008 program was used, designed to process various potentiometer data, including pH-metric ones. Initially, the DTPA dissociation constants were calculated from the DTPA titration curve ($pK_1 = 2.2$; $pK_2 = 2.9$; $pK_3 = 4.4$; $pK_4 = 8.7$; $pK_5 = 10.04$), which were then used as fixed values when calculating the composition and stability of the resulting Co(II) complexes as depicted in Table 1.

In the alkali medium, the oxidation of cobalt in the main layers occurs much more slowly, the final product of which is $CoO(OH)$ or $Co_2O_3 \cdot H_2O$ Fig. 4 [23]. In the absence of oxidation, that is, without access to air, the blue form (α -form) turns into pink (β -form). The unstable α -form is distinguished, which is associated with its organization of two-dimensional particles, which can be considered as the initial structure of a hexagonal layered lattice corresponding to a stable monomorphic β -form. Particles of the α -form are characterized by smaller sizes and a lower degree of perfection of the crystal lattice compared to particles of the β -form.

The experimental and calculated titration curves exhibited a good agreement with the entire pH range and the complexes' corresponding distribution diagram as shown in Fig 5. Compared with spectrophotometer technique, the pH-metric method does not identify the presence of the CoH_3L complex in the system since its existence region lies at lower pH values than those studied. A potentiometer study shows that, at $pH > 7$, the CoL^{3-} complex is formed in solution in the middle region as shown in Fig. 5. The stability constants of complexes established by both methods are reasonably close as given in Table 1.

Thus, the work results show that, at Co (II) concentrations in the range of 2×10^{-4} – 2×10^{-3} mol/L with the excess of DTPA, only soluble complexes are formed in the solution. The formation of insoluble polynuclear complexes under these conditions is not observed. DTPA

is characterized by the formation of protonated complexes with Co(II) already in a strongly acidic medium. In the pH range close to neutral in solution, there is an average CoL^- complexions, whose stability ($\log\beta = 17$ – 18) is only slightly inferior to the stability of the Co(II)–EDTA $^{2-}$ complex ($\log\beta = 16.31$) [24]. The results obtained are consistent with some published data (see Table 1). The high stability and wide pH range of the existence of Co(II) complexes with DTPA are a positive factor when using DTPA for various practical purposes [3,17]. The strong binding of Co(II) cations

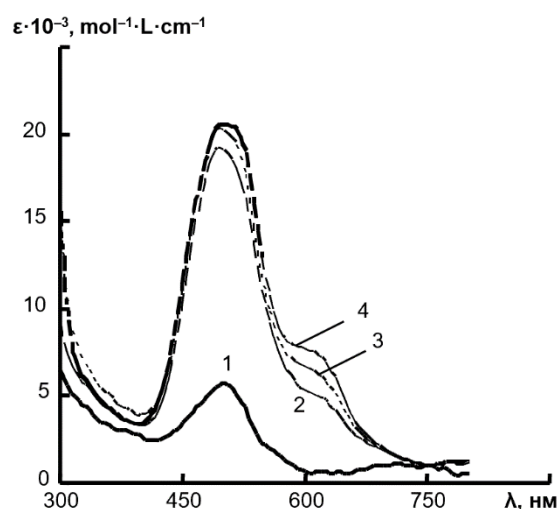


Fig 3. The calculated absorption spectra of the complexes Co(II) with DTPA for Co(II) (1), CoH_2L^- (2), $CoHL^{2-}$ (3) and CoL^{3-} (4), $C_{Co(II)} = C_{DTPA} = 1.62 \times 10^{-3}$ mol/L

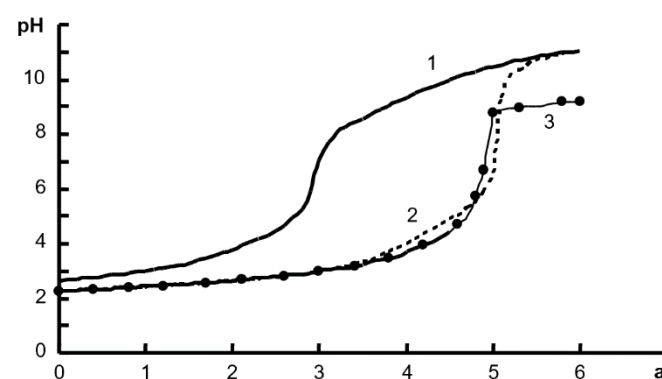


Fig 4. Curves of pH-metric titration of DTPA and its complex with Co(II) for DTPA (1), $C_{DTPA} = 2 \times 10^{-3}$ mol/L and mixtures Co(II)–DTPA with the ratio 1:2 (2) and 1:1 (3)

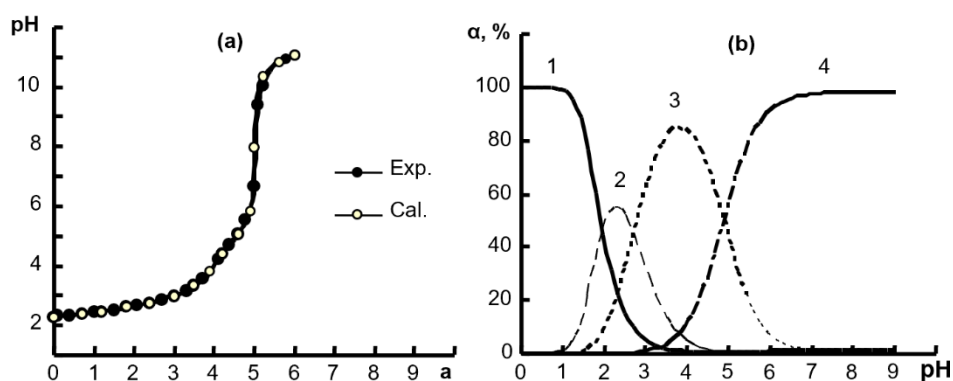


Fig 5. (a) Experimental and calculated pH-metric titrated curves, (b) The molar distribution diagram of complexes in the Co(II) – DTPA system as a function of pH For Co (II) (1), CoH_2L^- (2), CoHL^{2-} (3) and CoL^{3-} (4), $C_{\text{Co(II)}} = C_{\text{DTPA}} = 2 \times 10^{-3} \text{ mol/L}$

under the action of DTPA allows the use of DTPA as a stabilizer of peroxides in household detergents and bleaches. Despite the lack of data on various forms of DTPA in the environment, it can be assumed that a significant proportion of DTPA in natural waters will be in the form of complexes with Co(II) and other metals. This photolysis leads to the degradation of DTPA in nature.

From the dependence of K_{eq} on temperature (T), the thermodynamic function (ΔG° , ΔH° , ΔS°) were calculated. The values were summarized in Table 2 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 [25-27].

The positive value of ΔH° is the indicative of

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.

CONCLUSION

Co(II) complexes have been identified by absorption spectroscopy, pH-meter, and computer-assisted mathematical modeling in the Co(II)-DTPA system. Complexation begins in strongly acidic media and occurs in the range of ΔpH 0.5–6.2 for a 1:1 system. On the other hand, in an alkaline medium in solutions of Co(II) salts, hydrolysis processes are enhanced. In this case, a blue precipitate first forms with increasing pH, while the blue precipitate gradually turns to be purple and finally in pink color.

Table 2. The values of a standard thermodynamic functions (ΔG° , ΔH° , ΔS°) of equilibrium constants for CoH_2L^- , CoHL^{2-} and CoL^{3-} complexes in 25 °C

Complex	$\lg K_{\text{eq}}$	$\Delta G^\circ \text{ kJ mol}^{-1}$	$\Delta H^\circ \text{ kJ mol}^{-1}$	$\Delta S^\circ \text{ J mol}^{-1} \text{ K}^{-1}$
CoH_2L^-	7.37 (± 0.02) SF	-4.948	16.606	39.120
	6.208 (± 0.03) pH	-4.523	15.180	35.761
CoHL^{2-}	12.29 (± 0.04) SF	-6.215	20.858	49.137
	12.09 (± 0.02) pH	-6.175	20.721	48.812
CoL^{3-}	18.39 (± 0.10) SF	-7.214	24.208	57.026
	17.79 (± 0.03) pH	-7.132	23.932	56.375

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