541.49:543.4:542.28:546:82

COMPLEX FORMATION AND LIQUID-LIQUID EXTRACTION OF THE COBALT(II) BY 2-HYDROXYTHIOPHENOL AND ITS DERIVATIVES IN THE PRESENCE OF HYDROPHOBIC AMINES SYSTEM

A.Z.Zalov¹, N.A.Verdizade¹, G.V.Babayeva¹, Sh.A.Ibrahimova²

¹Azerbaijan State Pedagogical University

²Baku State University

Zalov1966@mail.ru

Received 25.10.2017

Mixed-ligand complexes of cobalt(II) with hydroxythiophenols (OP) {2-hydroxythiophenol (HTP) and its derivatives (2-hydroxy-5-aminthiophenol (HATP), 4-hydroxy-3-thiolsulfonic acid (HTSA), 4-hydroxy-3-thiolbenzoic acid (HTBA), 4-Nitro-2-hydroxythiophenol (HNTP)} in the presence of hydrophobic amines (Am) have been studied by spectrophotometric methods. Extraction of mixed ligand complexes is maximal at pH 3.6-6.3. The optimum conditions for the formation and extraction of mixed-ligand compounds have been found and the ratios of components the complexes have been determined. The Beer's law was applicable in the range of 0.05–3.2 µg/ml. The effect of foreign ions and reagents on the extraction was studied. The new method is free from common interferences. A procedure has been developed for extraction – spectrophotometric determination of cobalt in different objects.

Keywords: cobalt, solvent, spectrophotometry, ion-associate, hydrophobic amines, hydroxythiophenol.

doi.org/10.32737/0005-2531-2019-4-39-47

Introduction

Cobalt is a transition element of high industrial importance because of its valuable alloying, dyeing, magnetic, catalytic and plating properties. It is also of biological significance due to its ability to be an active center of coenzymes, e.g. vitamin B12 [1]. A great variety of photometric reagents is known for the determination of cobalt. However, the studies aiming to find and investigate new photometric reagents with different functional groups are still going on. For photometric determination of cobalt there are quite selective reagents *o*-nitrozofenole group or a similar structure with the oxime group [2].

Oxyphenolate, oxythiophenolate and di-thiophenolate complexes of cobalt are insoluble in chloroform, while mixed-ligand complexes with hydrophobic amines and aminophenols easily dissolve in various organic solvents [3–9]. In this respect, a very promising reagent is oxythiophenol (OP), which contains one hydroxyl and one sulphohydril groups and is a sulfur-containing analogue of mononuclear polyphenols with one oxygen atoms replaced with sulfur atoms. The present work is devoted to studying the reaction of a complex formation of Co(II) with oxythiophenol (OP) in the presence of hydrophobic amines (Am). Oxythiophenols 2-hydroxythiophenol (HTP) and its derivatives (2-hydr-

oxy-5-aminthiophenol (HATP), 4-hydroxy-3-thiolsulfonic acid (HTSA), 4-hydroxy-3-thiolbenzoic acid (HTBA), 4-Nitro-2-hydroxythiophenol (HNTP) were used in the presence of hydrophobic amines (Am). As hydrophobic amine 2(N, N-dimethylaminomethyl)-phenol (AP₁) and 2(N,N-dimethylaminomethyl)-4-methylphenol (AP₂) were used.

Experimental part

Reagents and apparatus. A stock solution (1µg/ml) of cobalt(II) was prepared by dissolving in water an exact linkage CoSO₄ · 7H₂O in water containing 2 ml concentrated H₂SO₄, and diluted by water to 1 liter [10]. The concentration of the cobalt solution was adjusted gravimetrically [11]. Solutions of OP and Am in chloroform (0.01M) were used. OP were synthesized according to the procedure [12]. Their purity was verified by melting point determination and paper chromatography. The synthesized compound was identified by NMR and IR spectroscopy (Table 1). To create the optimal acidity, 0.1M solutions of KOH and HCl or ammonium acetate buffers were applied. The extractant was purified chloroform.

The absorbance of the extracts was measured using a SF 26 spectrophotometer and KFK-2 photocolormeter. Glass cells with optical path

Table 1. The research results of IR and NMR spectroscopy

Reagent	IR (KBr)	¹ H NMR (300,18 МГц, C ₆ D ₆)
HTP	3470 cm ⁻¹ ν(OH), 3050 cm ⁻¹ ν(CH), 2580 cm ⁻¹ ν(SH), 1580 cm ⁻¹ (C ₆ H ₅).	δ 5.48 (s, 1H – OH), δ 3.57 (s, 1H, – SH), δ 7.8 (s, 2H Ar–H), δ 6.95 (s, 1H, Ar–H), δ 7.05 (s, 1H, Ar–H).
HATP	3460 cm ⁻¹ ν(OH), 3050 cm ⁻¹ ν(CH), 2570 cm ⁻¹ ν(SH), 1418 and 1130 cm ⁻¹ ν(–NH ₂), 1555 cm ⁻¹ ν (C ₆ H ₅).	δ 5.24 (s, 1H– OH), δ 3.32(s, 1H, – SH), δ 7.11 (s, 2H, Ar–H), δ 2.38 (s, 2H, –NH ₂), δ 7.05 (s, 1H, Ar–H).
HTSA	3465 cm ⁻¹ ν(OH), 3050 cm ⁻¹ ν(CH), 2572 cm ⁻¹ ν(SH), 1210 and 1130 cm ⁻¹ ν(SO ₃ H), 1565 cm ⁻¹ ν(C ₆ H ₅).	δ 5.39 (s, 1H,– OH), δ 3.42(s, 1H, 1SH), δ 7.21 (s, 2H, Ar–H), δ 2.59 (s, H, – SO ₃ H), δ 7.15 (s, 1H, Ar–H).
HTBA	3458 cm ⁻¹ ν(OH), 2568cm ⁻¹ ν(SH), 3040 cm ⁻¹ ν(CH), 1420 and 1300 cm ⁻¹ ν(COOH), 1535 cm ⁻¹ ν(C ₆ H ₅).	δ 5.15 (s, 1H,– OH), δ 3.28 (s, 1H, –SH), δ 7.05 (s, 2H, Ar–H), δ 1.42 (s, 1H, COOH), δ 7.26 (s, 1H, – Ar–H).
HNTF	3462 cm ⁻¹ ν(OH), 2564 cm ⁻¹ ν(SH), 3045 cm ⁻¹ ν(CH), 1700 cm ⁻¹ ν(NO ₂), 1535 cm ⁻¹ ν(C ₆ H ₅).	δ 5.16 (s, 1H,– OH), δ 3.25(s, 1H, – SH), δ 7.18 (s, 2H, Ar–H), δ 7.41 (s, 1H, – Ar–H).

of 5 or 10 mm were used. pH of aqueous phase was measured using an I-120.2 potentiometer with a glass electrode. Muffle furnace was used for dissolution of the samples.

General procedure

General procedure for the Determination of Cobalt(II). Portions of stock solutions of cobalt(II) varying from 0.1 to 1.0 ml with a 0.1-ml step, a 2.2 ml portion of a 0.01 M solution of OP, and a 2.5 ml portion of a 0.01M solution of Am were placed into calibrated test tubes with ground-glass stoppers (the volume of the organic phase was 5 ml). The required value of pH was adjusted by adding 1M HCl. The volume of the aqueous phase was increased to 20 ml by using distilled water. In 15 min after the complete separation of the phases, the organic phase was separated from the aqueous phase and the absorbance of the extracts was measured on KFK-2 at room temperature and 540 nm ($\ell=0.5$ cm).

Determination of cobalt(II) in steel [Steel M 441(0.012%Co) and HMu2.5/M 627x (0.055% Co)]. A weighed sample of 0.2 g was dissolved in 20 ml of H₂SO₄ (1:1) was oxidized with a few drops of concentrated nitric acid and evaporated twice to vapor SO₃. The precipitated salt was dissolved in 20 ml of 15% tartaric acid under heating, the solution was cooled, adjusted with water to 100 ml in a volumetric flask, stirred and filtered. An aliquot of 5 ml was put into a separatory funnel then, was added 1 ml of 10% hydroxylamine solution, 1

ml of 3% ascorbic acid were added and there was determined cobalt used in the proposed procedures.

Determination of Co(II) in sewage water and bottom sediments. 1 l taken for analysis of waste water is evaporated to obtain a precipitate, it is not boiled. The precipitate was dissolved in 5 ml of HNO₃, was transferred to a 50 ml flask and diluted to the mark with water.

Determination of Co(II) in plant. A portion of beans (10 g) was crushed and dried in a porcelain dish at 120°C. The dry residue is heated in a muffle furnace at 500°C. The ash was dissolved in diluted (1:1) HNO₃ and evaporate to moist salts, which are then dissolved in water, filtered into a volumetric flask of 100 ml. The cobalt content is determined with OP and AP.

Results and discussion

Charge of the complexes. The charge of the Co(II)–OP binary complexes was determined by electromigration and ion-exchange. Experiments on electromigration in a U-shaped tube and on sorption on EDE-10P anion exchanger demonstrated the anionic nature of the complexes. Under the experimental conditions, these red binary complexes were insoluble in nonpolar organic solvents. However, when AP were introduced the formation of electroneutral chloroform extractable ternary complexes was observed.

Choice of organic solvent. For the extraction of complexes we used CHCl₃, CCl₄, C₆H₆, C₆H₅CH₃, C₆H₄(CH₃)₂, C₆H₅Cl, C₂H₄Cl₂,

isobutanol and isopentanol. The extractivity of the complexes was estimated by the distribution coefficient and recovery. CHCl_3 , $\text{C}_6\text{H}_5\text{Cl}$, $\text{C}_2\text{H}_4\text{Cl}_2$ appeared to be the best extractants. All the further investigations were carried out with chloroform. The concentration of cobalt in the organic phase was determined with 2-nitroso-1-naphthol [11] by photometric measurements after back extraction, while in the aqueous phase it was determined by the difference. The basicity of Am hardly influences the recovery of niobium. After a single extraction with chloroform, 96.9–99.2% of cobalt was extracted as an ion associate.

Effect of pH of the aqueous phase. The effect of pH on the formation of $\text{Co(II)}\text{--OP--AP}$ complex was studied, in order to find a suitable pH that can be adopted in the determination of cobalt(II) (Figure 1). The absorbance was found to be maximum in the pH range 2.3–7.3. Hence further analytical investigations were carried out in media of pH 3.6–6.3 (Table 1). Extraction of Co(II) enhanced with the increase in the acidity of the initial solution; the further increase in acidity led to the gradual decrease of recovery, which was obviously associated with

a decrease in the concentration of the ionized form of OP. Probably, it is present in the solution in the non-dissociated state. At $\text{pH} \geq 7.2$, the complexes were hardly extracted, obviously because of the decrease in the degree of Am protonation.

Influence of reagent concentration and incubation time. For the formation and extraction of mixed-ligand complex (MLC), a 20–25-fold excess of complexing reagents is required; for example, the optimal conditions for formation and extraction of these compounds are provided by $(1.10\text{--}2.25) \times 10^{-3}$ M OP and $(0.92\text{--}1.24) \cdot 10^{-3}$ M AP. A large excess of hydrophobic amine interferes with the determination. However it was found that the presence of excess of the reagent solution does not alter the absorbance of the color reaction. Unlike single-ligand complexes, mixed-ligand complexes of Co(II) with OP and AP were stable in aqueous and organic solvents and did not decompose for two days, or over a month after extraction. The required duration of the phase contact was 10 min (Figure 2).

Fig. 1. Absorbance of Co-HITP-OP extracts function of the pH of the aqueous phase: 1 – Co-HATP-AP_2 , 2 – Co-HTP-AP_2 , 3 – Co-HTST-AP_2 , 4 – Co-HNTP-AP_2 ; $C_{\text{Co(II)}} = 1.7 \cdot 10^{-5} \text{ mol/l}$, $C_{\text{OP}} = 2.0 \cdot 10^{-3} \text{ mol/l}^{-1}$, $C_{\text{AP}} = 2.5 \cdot 10^{-3} \text{ mol/l}^{-1}$; $\lambda = 540 \text{ nm}$, KFK-2, $l = 0.5 \text{ cm}$.

Fig. 2. Effect of shaking time on the absorbance: 1 – Co-HATP-AP_2 , 2 – Co-HTP-AP_2 , 3 – Co-HTST-AP_2 , 4 – Co-HNTP-AP_2 ; $C_{\text{Co(II)}} = 1.7 \cdot 10^{-5} \text{ mol/l}$, $\text{pH } 4.0\text{--}6.0$, $\lambda = 540 \text{ nm}$, KFK-2, $l = 0.5 \text{ cm}$.

Electronic absorption spectra. Neither the metal ion nor the reagent has appreciable absorbance at specified wave lengths. Hence further studies were carried out at 540–565 nm (Figure 3). The reagent has minimum absorbance at the maximum absorbance of the complex. Hence further absorbance measurements were made at 540 nm.

Stoichiometry of the complexes and the mechanism of complexation. Starik–Barbanel relative yield method, equilibrium shift method, crossed lines method and Asmus' method were employed to elucidate the composition of the complex [13]. The results suggest the complex composition of 1:2:2 (Co:OP:AP). The formation of MLC can be presented in the following way. When cobaltion interact with two molecules of OP, they form doubly-charged anionic

complexes, which are extracted with two molecules of protonated AP. Formed ion-association complex between anionic chelates of cobalt(II) with OP and hydrophobic aromatic amines.

Calculation of extent of polymerization of complexes was carried out on the equation [9]. The made calculations showed that MLC in an organic phase won't be polymerized and are in a monomeric form ($\gamma=1.05-1.12$). The values of the molar absorption coefficients ($\epsilon_k=(2.62-3.01)\cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$), biphas stability constants ($\lg\beta=10.02-10.79$), the extraction constants of the complexes ($\lg K_{\text{ex}} = \lg\beta + \lg D = 12.50-13.68$) and the distribution coefficient ($\lg D = [\text{Co}]_{\text{org}}/[\text{Co}]_{\text{aq}} = 2.19-2.90$), as well as the recovery of cobalt ($R = D/100 + V_{\text{aq}}/V_{\text{org}} = 97.5 - 99.5$) are determined [13] (Table 1) [14].

Fig. 3. Absorption of mixed-ligand complexes: 1 – Co–HATP–AP₂, 2 – Co–HTP–AP₂, 3 – Co–HTST–AP₂, 4 – Co–HNTTP–AP₂; $C_{\text{Co(II)}} = 1.7 \cdot 10^{-5} \text{ mol/l}$, $C_{\text{OP}} = (1.10-2.25) \cdot 10^{-3} \text{ mol/l}$, $C_{\text{AP}} = (0.92-1.24) \cdot 10^{-3} \text{ mol/l}$; $\lambda=540 \text{ nm}$, pH 4.0–6.0, KFK-2, $\ell=0.5 \text{ cm}$.

Table 1. Optical characteristics, precision and accuracy of the spectrophotometric determination of Co(II) with OP and AP

Compound	The pH range of education and extraction	The pH range of maximum extraction	R, %	lgD	λ_{max} , nm	$\epsilon \cdot 10^{-4}$	lg β	lg K_{ex}	Working range / μg 5 ml
Co–HATP–AP ₁	3.5–7.2	4.8–6.2	97.5	2.19	540	2.62	10.65	12.84	1.40–95
Co–HATP–AP ₂	3.6–7.3	4.9–6.3	97.7	2.23	542	2.68	10.79	13.02	1.38–95
Co–HTP–AP ₁	3.3–7.0	4.5–5.9	97.9	2.27	545	2.70	10.42	12.69	1.36–96
Co–HTP–AP ₂	3.5–7.2	4.7–6.0	98.0	2.29	548	2.76	10.57	12.86	1.35–98
Co–HTST–AP ₁	2.8–6.6	4.2–5.6	98.4	2.39	550	2.85	10.21	12.50	1.34–100
Co–HTST–AP ₂	3.0–7.0	4.5–5.9	98.5	2.42	555	2.84	10.35	12.79	1.34–97
Co–HTBT–AP ₁	2.5–6.4	3.8–5.3	98.8	2.52	558	2.90	10.07	12.59	1.32–100
Co–HTBT–AP ₂	2.8–6.7	4.0–5.5	98.9	2.55	560	2.93	10.22	12.77	1.30–100
Co–HNTTP–AP ₁	2.3–6.1	3.6–4.9	99.3	2.75	562	2.96	10.93	13.68	1.25–100
Co–HNTTP–AP ₂	2.5–6.2	3.8–5.0	99.5	2.90	565	3.01	10.02	12.92	1.25–100

Fig.4. IR spectra of HATP (a) and the Co(II)–HATP–AP₁ (b).

The existence of clearly defined absorption bands at 2410–2415 cm⁻¹ in the IR spectrum of the complex indicates the coordination of the Am in the protonated form [15]. The disappearance of the band at 2580 cm⁻¹, characteristic for the spectrum of HATP, and appearance of corresponding bands in the spectrum of the complex, which are shifted toward lower frequency, suggests that the sulphur atoms are involved in complex formation. The observed de-

crease in the intensity of the absorption bands at 3200–3600 cm⁻¹ with a maximum at 3460 cm⁻¹ and the appearance of a broad band in the region of 3050–3150 cm⁻¹ shows that the hydroxyl group participates in the formation of a coordination bond (Figure 4).

Proceeding from the obtained data, we propose the following structure for the extracted ternary complex:

Influence of interfering ions. The influence of elements, often accompanying cobalt in various objects, as well as the influence of masking substances, is considered. The influence of the It has been found that the determination of cobalt with OP and AP is not adversely affected by alkali and alkaline-earth metals, W(VI), Mo(VI), Mn(II), Pb(II), V(V), Cr(III) etc. In the optimal conditions, the complex-formation strongly interferes with Fe(III), Cu(II), Zn(II), Ni(II). To eliminate the effect of zinc, cobalt can be determined in phosphate buffer media, with zinc completely masked. To eliminate the influence of iron and nickel, the possibility of acidification after complex formation under optimal conditions has been studied, since cobalt with OP and AP forms kinetically inert complexes. It turned out that acidification up to a pH of 0.8 does not affect the optical density of the solution. In acidic media, iron and nickel complexes are unstable, and as a result the selectivity of the reaction during acidification significantly recourses. Complexes of copper in acid media are stable, therefore, to

eliminate its influence, the possibilities of using masking agents have been studied. It turned out that the definition of cobalt with OP and AP₂ does not contain up to 250 mg of oxalate, tartrate, citrate and fluoride ions, thiourea, ascorbic acid, 0.8 g of pyrophosphate, up to 0.2 g of hydrogen peroxide, up to 0.05 g of EDTA and hydroxylamine unitol interfere. The presence of thiourea greatly increased the selectivity factor in the presence of copper. The results are shown in Table 2.

Effect of Co(II) Concentration. The adherence to Beer's law was studied by measuring the absorbance value of the series of solutions containing different concentrations of the metal ion. A linear calibration graph drawn between absorbance and the metal ion concentration indicates that Co(II) may be determined in the range 0.05–4.0 μg/ml (Table 1). The pertaining calibration graph is shown in the Figure 5. Table 3 shows the data allowing to compare the analytical characteristics of the methods for determining cobalt with some methods already known [16–27].

Analytical applications. The proposed method under the already established optimum conditions was applied for the determination of

Co(II) in various objects. The results presented in Table 4 indicate the successful applicability of the proposed method to real sample analysis.

Table 2. Effect of concomitant ions on the results of the photometric determination of cobalt(II) (40 µg/25 ml of cobalt)

Concomitant ions	Admissible weight excess of concomitant ions by weight				
	HATP +AP ₂	HTP +AP ₂	HTST +AP ₂	HTBT +AP ₂	HNTP +AP ₂
Mg	1900	1950	1930	1800	1900
Cu(II)	40	50	50	45	60
Ti(IV)	75	80	85	70	70
Ni(II)	50	60	50	65	60
Mn(II)	110	100	110	110	90
Zn(II)	85	95	80	75	75
Cd(II)	80	85	80	80	70
Pb(II)	120	125	130	120	110
Al(III)	150	160	160	155	140
Fe(III)	80	75	70	85	60
Bi(III)	160	170	165	160	140
Ga(III)	150	140	130	135	120
In(III)	120	125	125	110	110
Sc(III)	120	100	120	125	90
Cr(III)	130	135	120	90	100
Zr(IV)	150	160	160	150	145
Hf(IV)	140	130	145	140	145
Nb(V)	75	75	75	75	75
Ta(V)	75	75	75	75	75
V(V)	90	80	90	95	100
Mo(VI)	100	120	110	100	90
W(VI)	120	120	120	110	100
F ⁻	200	180	190	200	180
HPO ₄ ²⁻	300	280	290	300	300
C ₂ O ₄ ²⁻	130	140	150	130	120
SCN	250	260	260	240	245
Ascorbic acid	200	210	200	180	190
Tartaric acid	200	180	170	200	190

Fig. 5. Analytical determination of Co(II): 1 – Co–HATP–AP₂, 2 – Co–HTP–AP₂, 3 – Co–HTST–AP₂, 4 – Co–HNTP–AP₂; $C_{OP} = (1.10\text{--}2.25) \cdot 10^{-3} \text{ mol/L}$, $C_{AP} = (0.92\text{--}1.24) \cdot 10^{-3} \text{ mol/L}$, $\lambda = 540 \text{ nm}$, pH 4.0–6.0, SF-26, $l = 1.0 \text{ cm}$.

Table 3. Comparative characteristics of the methods for determining cobalt

Reagent (s)	pH	λ , nm	$\varepsilon \cdot 10^{-4}$	Beer's law range, $\mu\text{g} \cdot \text{ml}^{-1}$	R_{ref}
1-hydroxy-2-naphthoic acid + aniline	6.0–8.0	575	1.08	0.25–110	[16]
diantypyrimethane+naphthalene-2-sulfonic acid	0.5M HCl	615	1.9	20–150	[17]
<i>p</i> -methylisonitroasetophenone	6.8–7.8	380	2.3	0.1–4.0	[18]
4-(2-pyridylazo)resorcinol+xylometazoline hydrochloride	7.0–8.0	535	4.2	0–1.6	[19]
4-(2-pyridylazo)resorcinol+2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride	4.7	515	5.0	2.6	[20]
4-(2-thiazolylazo)resorcinol+2,3,5-triphenyl-2H-tetrazolium chloride	5.2–5.8	525	4.26	0.2–1.5	[21]
Nitrotetrazolium chloride	2.5–4.5	630			[22]
4-(2-thiazolylazo)resorcinol + zephyramine	6.7–10	550	3.42	2.0–5.0	[23]
4-(2-pyridylazo)resorcinol+1,4-diphenyl-1-(3-phenylamino)-1H-1,2,4-triazolol	5.3	520	6.0	1.7	[24]
2,4-dihydroxyasetophenone	9.5	390	2.7	0.12–1.77	[25]
Bromopyrogallol red + Tiven 80	2.0	388	0.06	0.25–40	[26]
1-allyl-3- (5-chloropyridyl)	3.5	495	1.7		[27]
OP + AP	see Table 1				

Table 4. Results of cobalt determination in industrial and natural materials ($n = 6$, $P = 0.95$)

Reagent	Found cobalt $\bar{X} \pm t_p S / \sqrt{n}$, %; (S_r)				
	Analyzed material				
	Steel M 441 (0.012% Co)	Steel HM12,5/M 627x (0.055% Co)	Plant*	Sewage water	Bottom sediments
HATP-AP ₂	0.014±0.0071 (0.057)		(2.1±0.61)·10 ⁻⁴ (0.043)	0.45±0.02 (0.024)	1.34±0.07 (0.012)
HTP-AP ₂		0.055±0.1200 (0.023)		0.485±0.083 (0.032)	
HTST-AP ₂	0.015±0.0011 (0.029)				1.30±0.09 (0.044)
HNTP-AP ₂	0.012±0.0015 (0.036)	0.053±0.0019 (0.034)		0.512±0.01 (0.053)	
ПAP-TX*			(9.43±0.56)·10 ⁻⁴ (0.054)		1.29±0.05 (0.019)
ДAM-HCK*	0.013±0.0011 (0.043)		(8.95±0.47)·10 ⁻⁴ (0.035)	0.490±0.050 (0.041)	
OHK-An*		0.054±0.102 (0.016)	(9.15±0.63)·10 ⁻⁴ (0.047)		1.26±0.05 (0.024)

* Note: The cobalt content in natural objects is in mg/kg; PAR – 4-(2-pyridylazo)resorcinol; TX – 2,3,5-triphenyl-2H-tetrazolium chloride; DAM – Diantypyrimethane; NSA – naphthalene-2-sulfonic acid; HNA – 1-hydroxy-2-naphthalene acid; An – anilin.

Conclusions

1. Mixed-ligand complexes of cobalt(II) with OP and Am have been studied by spectrophotometry. Extraction of mixed ligand complexes is maximum at pH 3.6–6.3. The optimal conditions for the formation and extraction of mixed-ligand compounds have been found.

2. The molar ratio of the reacting Co(II), OP and AP species is 1:2:2. The general formula

of the ternary complexes is $[\text{Co}(\text{OP})_2](\text{APH})_2$. They can be regarded as ion-associates between doubly charged anionic chelates $[\text{Co}(\text{OP})_2]^{2-}$ and protonated AP species.

3. The developed method retains specific interaction of cobalt(II) with OP and AP to form a colored complex and has good sensitivity at room temperature. The proposed method has significant advantage over the other spectrophotometric methods in terms of simplicity

and sensitivity. This proposed method provides good precision and accuracy. A procedure has been developed for extraction-spectrophotometric determination of cobalt in various objects.

References

1. Piatneytskii I.V. Analiticheskaya himiya kobalta. M.: Nauka, 1965. 256 s.
2. Umland F., Iansen A., Tirig D., Viunsh G. Kompleksnye soedineniya v analiticheskoi himii. Teoriya i praktika primeneniya. M.: Mir, 1975. 531 s.
3. Kuliyeu K.A., Verdizadeh N.A. Spectroscopic investigation of the complex formation of niobium using 2,6-dithiolphenol and aminophenols. Amer. J. Analytical Chem. 2015. V. 6. No 5. P. 746–756.
4. Kuliev K.A., Verdizadeh N.A., Gadjieva A.B. Liquid-liquid extraction and spectrophotometric determination of molybdenum with 2,6-dithiolphenol and its derivatives in the presence of hydrophobic amines. Chem. J. 2015. V. 5. No 3. P. 45–53.
5. Kuliyeu K.A., Verdizadeh N.A., Gadjieva A.B., Mamedova S.A. Spectroscopic investigation complex formation of molybdenum with 2,6-dithiolphenol and its derivatives in the presence of hydrophobic amines. Int. J. Chem. Studies. 2016. V. 4. No 3. P. 42–48.
6. Kuliyeu K.A. Spectroscopic investigation complex formation of vanadium using 2,6-dithiol-4-methylphenol and hydrophobic amines. J. Adv. Chem. 2015. V. 11. No 4. P. 3487–3497.
7. Kuliyeu K.A., Verdizadeh N.A. Spectroscopic investigation complex formation of vanadium using 2,6-dithiolphenol and hydrophobic amines. Amer. J. of Chem. 2015. V. 5. No 1. P. 10–18.
8. Zalov A.Z., Verdizadeh N.A., Dzhamalova R.I. Ekstrakcionno-fotometricheskoe opredelenie niobium (V) s 2-gidrokso-5-bromtiofenolom i gidrofobnymi aminami. Azerb. Chem. Journ. 2011. № 1. S. 97–102.
9. Zalov A.Z., Amanullayeva G.I. Spectrophotometric determination of cobalt(II) in a liquid-liquid extraction system containing 2-hydroxy-5-iodothiophenol and diphenylguanidine. J. Appl. Sci. 2016. V. 2 No 7. P. 17–25.
10. Korostelev P.P. Prigotovlenie rastvorov dlia himiko-analiticheskikh rabot. M: Izd-vo AN SSSR, 1961. 218 s.
11. Marchenko Z., Baltcezhak M. Metody spektrofotometrii v UF i vidimoi oblastiakh v neorganicheskom analize. M.: Binom, 2007. 711 s.
12. Kuliev A.M., Aliev Sh.R., Mamedov F.N., Movsumzade M. Sintez aminometilnykh proizvodnykh 2-okso-5-tret-alkiltiofenolov i ikh rasshcheplenie tiolami Zhurn. org. himii. 1976. T. 12. № 2. C. 426–430.
13. Bulatov M.M., Kalinkin I.P. Prakticheskoe rukovodstvo po fotokolorimetricheskoi i spektrofotometricheskoi metodam analiza. M.: Himia. 1986. 432 s.
14. Nazarenko V.A., Poluektova E.N. Izuchenie himizma reakcii ionov mnogovalentnykh elementov s organicheskimi reagentami. Vzaimodeistvie volframa s 8-merkaptihinolinom. Zhurn. analit. himii. 1971. T. 26. № 7. S.1331–1338.
15. Bellami L. Infekrasnye spektry slozhnykh molekul. M.- L.: Mir, 1963. 590 s.
16. Salahova F.I. Spektrofotometricheskoe issledovanie kompleksoobrazovaniia kobalta s 1-okso-2-naftoinoi kislotoi i anilinom. Azerb. Chem. Journ. 2011. № 1. S. 184–190.
17. Denisova S.A., Lesnov A.E., Petrov B.I. Ekstraktsiya tiocyanatnykh kompleksov metallov v raslaivaiushcheisya sisteme voda–diantipirilmetan–naftalin-2-sulfokislota. Izv. Altaiskogo gos. un-ta. Ser. "Himii". 2013. T. 1. №1. S. 151–155.
18. Baytak S., Turker A.R. Determination of lead and nickel in environmental samples by flame atomic absorption spectrometry column solid-phase extraction on Ambersorb-572 with EDTA. J. Hazard. Mater. 2006. V. 129. P. 130–136.
19. Bhadani S.N., Tewari M., Agrawal A., Sekhar C. Extractive-photometric determination of cobalt(II) in steels using 4-(2-pyridylazo)resorcinol and xylometazoline hydrochloride. J. Indian Chem. Soc. 1998. V. 75. No 3. P. 176–177.
20. Divarova V.V., Gavazov K.B., Lekova V.D., Dimitrov A.N. Spectrophotometric investigations on liquid-liquid extraction systems containing cobalt, 4-(2-pyridylazo) resorcinol and tetrazolium salts. Chemija. 2013. V. 24. No 2. P. 81–87.
21. Divarova V., Racheva P., Lekova V. Spectrophotometric determination of cobalt(II) in a liquid-liquid extraction system containing 4-(2-thiazolylazo) resorcinol and 2,3,5-triphenyl-2H-tetrazolium chloride. J. Chem. Technol. and Metallurgy. 2013. V. 48. No 6. P. 623–630.
22. Dospatliev L., Georgieva N.V., Pavlov A.I., Yaneva Z. Extraction-spectrophotometric determination of cobalt in soils by the application of iodine nitrotetrazole chloride. Trakia J. Sci. 2010. V. 8. No 2. P. 235–241.
23. Kazumasa U. The Extraction and spectrophotometric determination of cobalt (II) with 4-(2-thiazolylazo)-resorcinol and zefiramin. Bull. Chem. Soc. Jpn. 1979. V. 52. No 4. P. 1215–1216.
24. Barhate V. D., Patil M. R. Extraktion and spectrophotometric determination of cobalt (II) with p-methylisonitrosoasetophenone. Curr. Sci. 1989. V. 58. No 6. P. 291–293.
25. Raceva P.V., Gavazov K.B., Lekova V.D., Dimitrov A.N. Complex formation in a liquid-liquid extraction system containing cobalt(II), 4-(2-pyridylazo)resorcinol, and nitron. J. Mater. 2013. V. 30. No 1. P. 1–7.

26. Shar G.A., Soomro G.A. Spectrophotometric determination of cobalt(II) as complexes with bromopyrogallol red in micellar media of twen 80. J. Chem. Soc. Pak. 2006. V. 28. No 5. P. 444–447.
27. Agarwal S., Mathur S.P. Photometric determination of cobalt(II) by absorption of its 1-allyl-3-(5-chloropyridyl)thiourea complex on polyurethane foam. Indian J. Chem. 2001. V. 40. P. 544–545.

КОБАЛТИН(II) ГИДРОФОВ АМИН İŞTİRAKINDA 2-ГИДРОКСИТИОФЕНОЛ ВƏ ONUN TÖRƏMƏLƏRİ İLƏ KOMPLEKS ƏMƏLƏGƏLMƏSİ VƏ EKSTRAKSİYASI

Ə.Z.Zalov, N.A.Verdizadə, Ş.Ə.İbrahimova, G.V.Babayeva

Spektrofotometrik metodla kobaltın hidrofob amin iştirakında oksitiofenol (OF) {2-hidroksitiofenol (HTF) və onun törəmələri (2-hidroksi-5-amintiofenol (HATF), 4-hidroksi-3-tiosulfoturşu (HTST), 4-hidroksi-3-tiolbenzoy turşusu (HTBT), 4-nitro-2-hidroksitiofenola (NHTF)} ilə müxtəlifliqandlı kompleks (MLK) əmələ gətirməsi və ekstraksiyası tədqiq edilmişdir. MLK əmələ gəlməsi pH 3.6–6.3 intervalında baş verir. Komplekslərin əmələgəlmə və ekstraksiya şəraiti, tərkibi, fiziki-kimyəvi və analitik xassələri müəyyən edilmişdir. MLK ekstraktı kobaltın 0.05–3.2 mkq/ml qatılıq intervalında Ber qanununa tabe olur. Yeni işlənilmiş metodika müxtəlif obyektlərdə kobaltın ekstraksiyalı-spektrofotometrik təyininə tətbiq edilmişdir.

Açar sözlər: kobalt, ekstraksiya, spektrofotometriya, ion-assosiat, hidrofob aminlər, hidroksitiofenol.

КОМПЛЕКСООБРАЗОВАНИЕ И ЭКСТРАКЦИИ КОБАЛЬТА (II) С 2-ГИДРОКСИТИОФЕНОЛОМ И ЕГО ПРОИЗВОДНЫХ В ПРИСУТСТВИИ ГИДРОФОВНЫХ АМИНОВ

А.З.Залов, Н.А.Вердизаде, Ш.А.Ибрагимова, Г.В.Бабаева

Спектрофотометрическими методами изучены реакции образования разнолигандные комплексы кобальта (II) с окситиофенолом (OP) {2-гидрокситиофенолом (HTP) и его производными (2-гидрокси-5-аминтиофенол (HATP), 4-гидрокси-3-тиолсульфоновая кислота (HTSA), 4-гидрокси-3-тиолбензойной кислоты (HTBA), 4-нитро-2-гидрокситиофенола (HNTP)} в присутствии гидрофобных аминов (Am). Оптимальный интервал кислотности, при котором оптическая плотность максимальна и постоянна, находится при pH 3.6–6.3. Определены условия образования и экстракции, состав, физико-химические и аналитические свойства комплексов. Экстракты ионных ассоциатов кобальта подчиняются основному закону светопоглощения при концентрациях 0.05–3.2 мкг/мл. Разработана методика экстракционно-спектрофотометрического определения кобальта в разных объектах.

Ключевые слова: кобальт, экстракция, спектрофотометрия, ион-ассоциат, гидрофобные амины, гидрокситиофенол.