

Scientific paper

Complex Formation in a Liquid-Liquid Extraction System Containing Co(II), 4-(2-Thiazolylazo)resorcinol and Monotetrazolium Salt

Vidka Divarova,¹ Kirila Stojnova,² Petya Racheva¹ and Vanya Lekova^{2,*}

¹ Department of Chemistry and Biochemistry, Faculty of Pharmacology, Medical University Plovdiv, 15A Vasil Aprilov Boulevard, Plovdiv 4002, Bulgaria

² Department of General and Inorganic Chemistry, Faculty of Chemistry, Plovdiv University "Paisii Hilendarski", 24 Tsar Assen Street, Plovdiv 4000, Bulgaria

* Corresponding author: E-mail: vanlek@uni-plovdiv.bg
Tel.: +35932261420

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Abstract

The ion-associated complex formed between the anionic chelate of Co(II)–4-(2-thiazolylazo)resorcinol (TAR) and the monotetrazolium cation of 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2*H*-tetrazolium chloride (INT) in the liquid-liquid extraction system Co(II)–TAR–INT–H₂O–CHCl₃ was studied by the spectrophotometric method. The optimum extraction conditions of Co(II) were established and the extraction equilibria were investigated. The equilibrium constants, the recovery factor and some analytical characteristics were calculated. The validity of Beer's law was checked. The molar ratio of the components in the ternary ion-associated complex Co(II)–TAR–INT was determined and the general formula of the complex was suggested. The effect of various foreign ions and reagents on the process of complex formation in the liquid-liquid extraction system was studied.

Keywords: complex formation; ion-associated chelate; extraction equilibria; UV-Vis spectroscopy

1. Introduction

The cobalt refers to the group of elements essential from biochemical point of view. For example, one of compounds containing cobalt complexes is vitamin B₁₂ which participates in the synthesis of the hemoglobin and affects the protein and lipid metabolism. The cobalt deficiency can lead to hematologic, neuropsychiatric and cardiovascular disorders, while the excessive consumption of cobalt with the food can result in seriously toxicological poisoning.^{1–4} Cobalt is a typical transition metal participating in complex formation. The complexes of cobalt with chelate ligands, containing N and O donor atoms, have industrial, biological, pharmacological and medical applications.^{5–9} The complex formation with azo derivatives of resorcinol *via* phenolic oxygen, azo nitrogen and thiazolyl or pyridylazo nitrogen, gives colored chelates with metal cations.^{10–19} Tetrazolium salts are used as reagents for the extraction-spectrophotometric determination of metals,

e.g. Mo(VI), W(VI), Ge(IV), Tl(III), Nb(V), V(IV), V(V), Ga(III).^{20–22} The preparation and application of ion-associated complexes of anionic chelates of metals with various natural organic and inorganic ligands with N- and O-containing donor atoms and with the participation of mono and ditetrazolium cations is a special scientific research field of the chemistry of the coordination compounds. It is up-to-date topic, not only as a theoretical background for the preparation of novel ion-associated complexes, but mainly due to the possibility for their application in the analytical chemistry for determination of various metals in natural, industrial, pharmaceutical and biological samples, addressing in such a way a number of ecological issues. In our previous research the ion associates of cobalt(II) were described by spectrophotometric investigation of eight different liquid-liquid extraction systems.^{23–26} The extraction equilibria were characterized quantitatively (association constant, distribution constant, extraction constant and recovery factor) and the analytical characteristics (molar absorptivity, Sandell's sensitivity,

adherence to Beer's law, limit of detection, limit of quantification) were calculated. The present work is a part of a thorough and comprehensive study on the ion-associated complexes of cobalt(II) with azo derivatives of resorcinol and mono- or ditetrazolium salts.

Its aim is to study the extraction equilibria of complex formation between of anionic chelate of Co(II)–4-(2-Thiazolylazo)resorcinol (TAR) with the tetrazolium cation of 2-(4-Iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride (INT) in the liquid-liquid system Co(II)–TAR–INT–H₂O–CHCl₃. The overall purpose is an application of the system for determination of cobalt in alloys, biological, medical and pharmaceutical objects.

2. Experimental

2.1. Reagents and Apparatus

- CoSO₄ · 7H₂O (Sigma-Aldrich, Munich, Germany, p. a.), 1000 mg L⁻¹ aqueous solution. Working solution ($C_{\text{Co(II)}} = 1.7 \times 10^{-4}$ mol L⁻¹) was prepared by dilution.
- 4-(2-Thiazolylazo)resorcinol (TAR) (97%, Sigma-Aldrich), dissolved in slightly alkalized distilled water, $C_{\text{TAR}} = 2 \times 10^{-3}$ mol L⁻¹.
- 2-(4-Iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride (INT) (Sigma-Aldrich, p.a.) – 2.0×10^{-3} mol L⁻¹ aqueous solution.
- The acidity of the aqueous medium was set using a buffer solution prepared by mixing 2.0 mol L⁻¹ aqueous solutions of CH₃COOH and NH₄OH.
- The pH was checked by HI 83140 pH meter (Romania).
- A Camspec M508 spectrophotometer (United Kingdom), equipped with 10 mm path length cells, was employed absorbance measurements.
- Organic solvent – CHCl₃ (additionally distilled).

2.2. Procedure for Establishment of the Optimum Extraction-Spectrophotometric Conditions

Aliquots of Co(II), TAR, INT and buffer (pH = 3.0–6.5) solutions were filled into separatory funnels. The resulting solutions were diluted with distilled water to a total volume of 10 mL. Then 10 mL of chloroform was added and the funnels were shaken. A portion of the organic extract was filtered through a filter paper into a cell and the absorbance was read against a blank sample.^{25,26}

2.3. Procedure for Determination of the Distribution Constant

In order to determine the distribution constant K_D , it is necessary to measure the light absorbance A_1 and A_3 , which are respectively the light absorbance after a single

extraction in chloroform under optimum operating conditions and after a triple extraction performed under the same conditions. After that the distribution constant K_D can be calculated according to the ratio $K_D = A_1 / (A_3 - A_1)$. *Single extraction*: the single extraction is conducted with 10 mL of chloroform. After the separation of the two phases, the organic extract is transferred into a 25 mL calibrated flask which is brought to volume with chloroform. The measurement of the light absorbance A_1 is done against a blank sample, prepared under the same conditions. *Triple extraction*: the first stage of the triple extraction is performed with 10 mL of chloroform and the extract is transferred into a 25 mL calibrated flask. During the second stage of the extraction, 8 mL of chloroform are added to the aqueous phase remaining after the first stage. The organic layer is added to that from the first stage. For the third stage of extraction, 7 mL of chloroform are added to the aqueous phase remaining after the second stage and for the third time an extraction is performed. The organic layer is transferred to the previous two. The calibrated flask is brought to volume with chloroform. The measurement of A_3 is performed against a blank sample prepared in the same way.

3. Results and Discussion

3.1. Optimum Extraction-Spectrophotometric Conditions

The absorption spectrum of the extract of the studied ternary ion-associated complex Co–TAR–INT in CHCl₃ was characterized by an absorption maximum in the visible range ($\lambda_{\text{max}} = 520$ nm) (Figure 1). The acidity of the aqueous phase is the most important factor influencing the extraction of the anionic chelate Co(II)–TAR into the organic phase as an ion-associated complex. The maximum and constant extraction of the ion-associated complex was achieved in the pH range from 4.5 to 5.5 (Figure 2). Aceta-

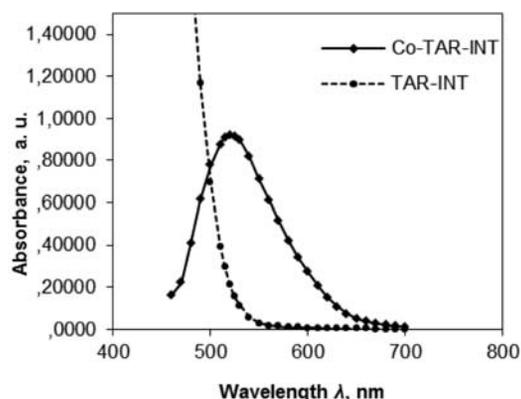
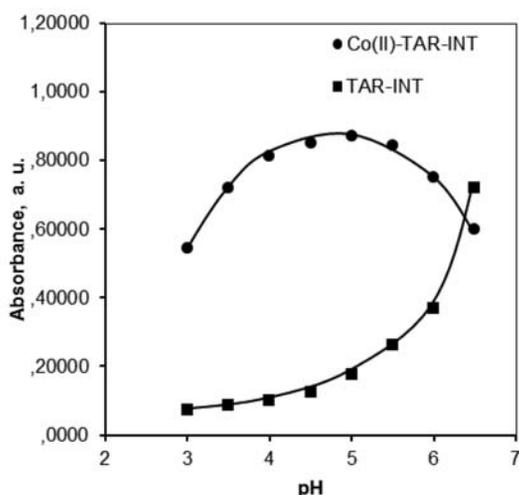


Figure 1. Absorption spectra of the complex Co–TAR–INT and of the blank sample TAR–INT in CHCl₃; $C_{\text{Co(II)}} = 1.7 \times 10^{-5}$ mol L⁻¹; $C_{\text{TAR}} = 1.8 \times 10^{-4}$ mol L⁻¹; $C_{\text{INT}} = 2.0 \times 10^{-4}$ mol L⁻¹; pH = 5.0; $l = 1$ cm

Table 1. Optimum extraction-spectrophotometric conditions and analytical characteristics of the system Co(II)–TAR–INT–H₂O–CHCl₃

Optimum conditions	Analytical characteristic
Absorption maximum (λ_{\max}) 520 nm	Apparent molar absorptivity (ϵ^{-1}) (5.2 ± 0.2) $\times 10^4$ L mol ⁻¹ cm ⁻¹
Volume of the aqueous phase 10 cm ³	True molar absorptivity (ϵ) (5.4 ± 0.2) $\times 10^4$ L mol ⁻¹ cm ⁻¹
Volume of the organic phase 10 cm ³	Sandell's sensitivity (SS) 1.14 ng cm ⁻²
pH of the aqueous phase 5.0	Adherence to Beer's law up to 2.00 $\mu\text{g cm}^{-3}$
Shaking time (τ) 3 min	Relative standard deviation (RSD) 3.6%
Concentration of TAR 1.8×10^{-4} mol L ⁻¹	Limit of detection (LOD) 0.10 $\mu\text{g cm}^{-3}$
Concentration of INT 2.0×10^{-4} mol L ⁻¹	Limit of quantification (LOQ) 0.34 $\mu\text{g cm}^{-3}$

**Figure 2.** Absorbance of Co–TAR–INT extract against TAR–INT extract and of TAR–INT against CHCl₃ vs. pH of the aqueous phase. $C_{\text{Co(II)}} = 1.7 \times 10^{-5}$ mol L⁻¹; $C_{\text{TAR}} = 2.0 \times 10^{-4}$ mol L⁻¹; $C_{\text{INT}} = 2.0 \times 10^{-4}$ mol L⁻¹

te buffer solution with pH = 5.0 was used in all further experiments. The result from these experiments showed that the extraction equilibrium can be achieved within less than 60 s. The prolonged shaking does not have an impact on the absorbance. The next experiments were performed for 3 min. The chelate formation of Co(II)–TAR requires 5.9-fold excess of TAR (1.0×10^{-4} mol L⁻¹) and 9.4-fold excess of INT (1.6×10^{-4} mol L⁻¹) for a maximum association and extraction.

The optimum experimental conditions for the extraction of the ion-associated complex are summarized in Table 1 column 1.

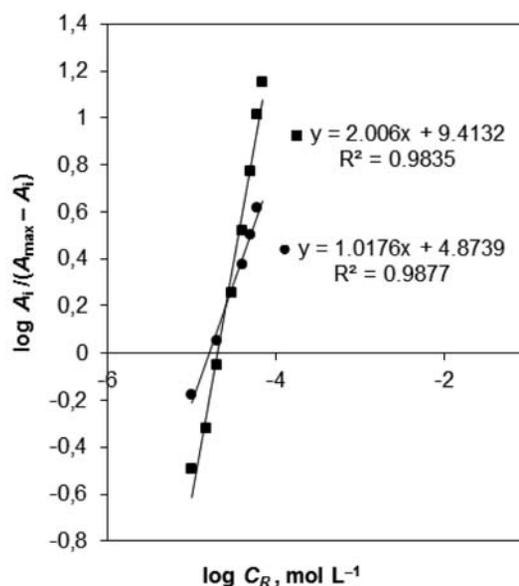
3. 2. Beer's Law and Analytical Characteristics

The range of adherence to Beer's law, i.e. the linear relationship between the cobalt concentration in the aqueous phase and the absorbance of the ion-association complex in the organic phase after extraction was studied us-

ing regression analysis under the optimum conditions for complex formation. The equation of a straight line was found to be $Y = 0.8474 X + 0.0207$ with a correlation coefficient squared 0.9978. Further analytical characteristics, e.g. apparent molar absorptivity ϵ^{-1} , adherence to Beer's law, Sandell's sensitivity, limit of detection and limit of quantification, are shown in Table 1, column 2.

3. 3. Molar Ratios of the Complex

The mobile equilibrium method and the straight-line method of Asmus were applied to prove the molar ratios Co–TAR and Co–INT.²⁷ The results of application of the two independent methods are shown in Figure 3 and Figure 4, respectively. On the basis of the results it can be concluded that Co(II), TAR and INT interact in molar ratio 1:2:1.

**Figure 3.** Straight lines by the mobile equilibrium method for determination of the molar ratios. Co : INT and Co : TAR ($C_{\text{Co(II)}} = 1.7 \times 10^{-5}$ mol L⁻¹); • Co : INT, $C_{\text{TAR}} = 1.8 \times 10^{-4}$ mol L⁻¹; ■ Co(II) : TAR, $C_{\text{INT}} = 2.0 \times 10^{-4}$ mol L⁻¹

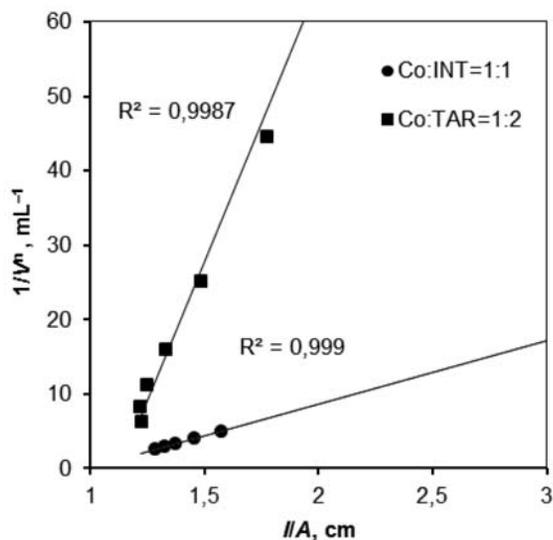
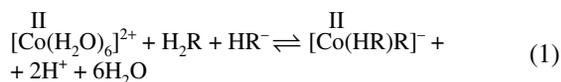


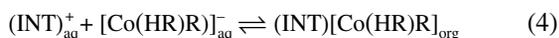
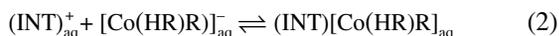
Figure 4. Determination of the molar ratio (n) by the method of Asmus: $C_{\text{Co(II)}} = 1.7 \times 10^{-5} \text{ mol L}^{-1}$; \bullet Co(II) : INT $C_{\text{INT}} = 1.8 \times 10^{-4} \text{ mol L}^{-1}$ $n = 1$; \blacksquare Co(II) : TAR $C_{\text{INT}} = 2.0 \times 10^{-4} \text{ mol L}^{-1}$ $n = 2$

3. 4. Reaction Scheme, Suggested General Formula, Extraction Equilibria and True Molar Absorptivity

In the pH range from 1.5 to 6.5, the reagent TAR is presented in a molecular form (H_2R). The deprotonation of TAR (HR^-) starts at $\text{pH} = 4.0$, while a complete deprotonation (R_2^-) is achieved in the alkaline range ($\text{pH} > 11$).²⁸ The performed experiments showed that the extraction of the ternary ion-associated complex Co(II)–TAR–INT took place in the pH range 4.5–5.5. Under these conditions, an equilibrium between the molecular form of TAR (H_2R) and the monoprotinated form (HR^-) exists in the solution. Hence, the complex formation of anionic chelate Co(II)–TAR is given by the equation (1):



Having in mind the indicated above molar ratio and the reaction of chelate formation of Co(II)–TAR, it can be suggested that the formation of ion-association complex in the aqueous phase, its distribution between the aqueous and the organic phase and its extraction in chloroform can be given by the following equations (2–4):



Therefore, the ion-associated complex chelate of Co(II)–TAR with INT can be represented by the general formula $(\text{INT})[\text{Co}(\text{HR})\text{R}]$. The association process in aqueous phase and the extraction process were investigated and quantitatively characterized. The constants needed for the quantitative assessment of the equilibria were calculated as follows:

(i) the association constant β and the true molar absorptivity ε by the method of Komar – Tolmachev (Figure 5).²⁷ The value of the true molar absorptivity ε is shown in Table 1 column 2;

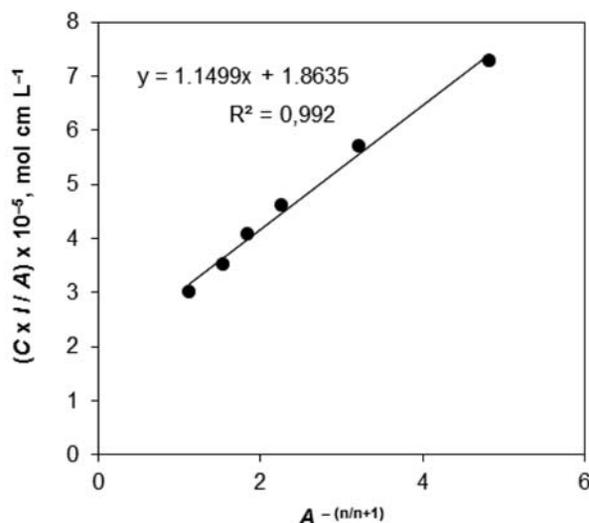


Figure 5. Dependency of (C/lA) on $A^{-n/(n+1)}$ (method of Komar–Tolmachev). $C_{\text{Co(II)}} = C_{\text{INT}} = C \text{ mol L}^{-1}$; A – absorbance; $n = 1$; $l = 1 \text{ cm}$

(ii) the distribution constant K_D and the recovery factor $R\%$:

$$K_D = A_1 / (A_3 - A_1); R\% = 100 K_D / (K_D + 1) \quad (5)$$

where A_1 is the absorption for a single extraction, A_3 – the absorption for a triple extraction;

(iii) the extraction constant K_{ex} :

$$K_{\text{ex}} = K_D \times \beta; \quad \log K_{\text{ex}} = \log K_D + \log \beta \quad (6)$$

The values of the equilibrium constants and the recovery factor are presented in Table 2. They indicate that the ternary ion-associated complex of the chelate Co(II)–TAR with INT is characterized by sufficiently high stability and good extraction. Based on this, it can be proposed that the ion-associated complex of Co–TAR–INT can be successfully used for determination of cobalt in alloys, biological, medical and pharmaceutical objects. For this purpose the effect of various foreign ions and reagents on the process of complex formation was studied.

Table 2. Values of the equilibrium constants and the recovery factor

Equilibrium constant and recovery factor	Value
Equilibrium (2) – Association constant β $\beta = \{(\text{INT})[\text{Co}(\text{HR})\text{R}]_{\text{aq}}\} / \{[\text{INT}]_{\text{aq}}^+ \times [\text{Co}(\text{HR})\text{R}]_{\text{aq}}^-\}$	$\log \beta = (5.10 \pm 0.24)^{\text{a}}$ $\log \beta = (5.16 \pm 0.90)^{\text{b}}$
Equilibrium (3) – Distribution constant K_{D} $K_{\text{D}} = \{(\text{INT})[\text{Co}(\text{HR})\text{R}]_{\text{org}}\} / \{(\text{INT})[\text{Co}(\text{HR})\text{R}]_{\text{aq}}\}$	$\log K_{\text{D}} = (1.25 \pm 0.01)$
Equilibrium (4) – Extraction constant K^{ex} $K^{\text{ex}} = \{(\text{INT})[\text{Co}(\text{HR})\text{R}]_{\text{org}}\} / \{[\text{INT}]_{\text{aq}}^{\text{ex}} \times [\text{Co}(\text{HR})\text{R}]_{\text{aq}}^-\}$	$\log K^{\text{ex}} = (6.35 \pm 0.25)^{\text{c}}$ $\log K^{\text{ex}} = (6.41 \pm 0.91)^{\text{d}}$
Recovery factor $R\%$ $R\% = 100 K_{\text{D}} / (K_{\text{D}} + 1)$	$R = (94.49 \pm 0.05)\%$

^a Calculated by the Holme-Langmyhr method²⁹; ^b Calculated by the Komar-Tolmachev method; ^c Calculated by the formula $K_{\text{ex}} = K_{\text{D}} \times \beta$; β is determined by the Holme-Langmyhr method; ^d Calculated by the formula $K_{\text{ex}} = K_{\text{D}} \times \beta$; β is determined by the Komar-Tolmachev method.

3. 5. Effect of Foreign Ions and Reagents on the Complex Formation

The effect of various foreign ions and reagents on the process of ion-association and complex formation between the anionic chelate Co(II)–TAR and monotetrazolium cation was studied under optimum extraction conditions (Table 1, column 1). The concentration of Co(II) in the presence of the foreign ion was determined from the sequence of Beer's law.²⁷ For an interfering effect a deviation of $\pm 3\%$ from the absorbance of the complex in the absence of foreign ions or reagents was accepted. The results are presented in Table 3.

From them it can be concluded that most of the cations studied do not interfere. The ions of Al(III), Cu(II), Zn(II), Ni(II), Fe(II), Fe(III), Cr(III), V(IV), V(V), SCN⁻ and C₄H₄O₆²⁻ in concentrations, comparable with that of Co(II), also do not hinder the extraction of Co(II) as an ternary associated complex with TAR and INT. However, by the application of the method for different objects, in many cases these concentrations are much higher. For this reason they have to be masked or removed from the extraction system. Fe(II) is readily oxidized and the influence of the Fe(III), Cr(III) and Al(III) is removed after pre-precipitation with NH₃. The separation of Co(II) from Cd(II) and Zn(II) is based upon the different sustainability of their dithizonates to acids.³⁰ Upon extraction with dithizone (pH = 8), dithizonates of Cd(II), Zn(II) and Co(II) pass in the chloroform extract. Upon subsequent pre-extraction with a solution of hydrochloric acid (pH = 2–3), the dithizonates of Cd(II) and Zn(II) are destroyed.³¹ The organic layer is analyzed for Co(II) based on above-mentioned procedure. The interference of Cd(II) is removed by a pre-extraction with dithizone.³⁰ The extraction equilibrium is hindered by Ni(II) and V(V).

4. Conclusion

The complex formation of anionic chelate of cobalt(II)–4-(2-thiazolylazo)resorcinol with the monotetra-

Table 3. Effect of foreign ions and reagents on the complex formation of the ion-associate Co(II)–TAR–INT for extraction in the presence of 5 μg Co(II)

Foreign ion and reagent	Foreign ion and reagent, $\mu\text{g}/10 \text{ cm}^3$ aqueous phase	Co(II) found, μg	R, %
Na ⁺	10 000	4.98	99.56
K ⁺	10 000	4.97	99.52
NH ₄ ⁺	10 000	5.13	102.52
Mg ²⁺	10 000	5.11	102.21
Ca ²⁺	10 000	5.07	101.38
Sr ²⁺	10 000	4.97	99.32
Ba ²⁺	2 500	5.10	101.92
Al ³⁺	50	5.21	104.24
Cu ²⁺	5	4.62	92.31
Zn ²⁺	50	4.27	85.38
Cd ²⁺	100	5.22	104.38
Ni ²⁺	50	3.51	70.22
Fe ²⁺	30	2.78	55.55
Fe ³⁺	10	6.69	133.81
Mn ²⁺	750	5.15	102.92
Cr ³⁺	30	5.18	103.64
Cr(VI)	500	4.74	94.82
V(V)	10	9.17	182.32
V(IV)	60	7.26	145.18
Mo(VI)	10 000	4.88	97.62
W(VI)	10 000	5.06	101.15
F ⁻	10 000	5.05	101.00
Cl ⁻	5 000	4.83	96.62
NO ₃ ⁻	250	4.88	97.54
SCN ⁻	500	4.77	95.42
SO ₄ ²⁻	5 500	5.12	102.41
PO ₄ ³⁻	3 500	5.12	102.34
S ₂ O ₃ ²⁻	6 000	5.12	102.33
C ₂ O ₄ ²⁻	9 000	4.91	98.17
C ₆ H ₅ O ₇ ³⁻	5 000	4.87	97.36
C ₄ H ₄ O ₆ ²⁻	1 000	4.76	95.17
L – ascorbic acid	500	5.21	104.15

zolium cation of 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride (INT) was investigated

by the extraction-spectrophotometry method. In the presence of a monotetrazolium cation, the colored anionic chelate complex Co(II)-TAR forms well soluble in chloroform ion-associated complex. The optimum conditions for the formation and solvent extraction of the ion-associated chelate complex of Co(II) were established. The effect of various foreign ions and reagents on the process of complex formation was studied. The molar ratio of the components, determined by independent methods, shows that the ion-association complex could be represented with the general formula $(\text{INT})^+[\text{Co}(\text{HR})\text{R}]^-$. From the values of the equilibrium constants, the recovery factor and the analytical characteristics of the ion-associated complex Co-TAR-INT it can be concluded that the availability of hydrophilic substitutes in the phenyl radicals of the tetrazolium salt INT stabilizes the ion-associate in the aqueous phase. The bulky organic molecule of INT determined the extractability of the ion-associated complex in organic phase.

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Povzetek

Proučevali smo tvorbo ionskih asociativnih kompleksov med anionskim kelatom Co(II)-4-(2-tiazolilazo)resorcinol (TAR) in monotetrazolijevim kationom 2-(4-jodofenil)-3-(4-nitrofenil)-5-fenil-2*H*-tetrazolijevega klorida (INT) na primeru tekočina-tekočina ekstrakcijskega sistema Co(II)-TAR-INT-H₂O-CHCl₃ z uporabo spektrofotometričnih metod. Proučili smo ekstrakcijsko ravnotežje ter določili optimalne ekstrakcijske pogoje za Co(II). Določili smo ravnotežne konstante, izkoristek ekstrakcije in druge analize karakteristike. Preverjena je bila veljavnost Beerovega zakona. Določili smo molske deleže komponent v ternarnem sistemu Co(II)-TAR-INT in predlagali splošno formulo kompleksa. Določen je bil tudi vpliv različnih ionov in reagentov na proces tvorbe kompleksov in na ekstrakcijski sistem tekočina-tekočina.