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Liquid–liquid extraction of ion-association complexes of cobalt(II)–4-(2-pyridylazo)resorcinol with ditetrazolium salts

VIDKA V. DIVAROVA[1], KIRILA T. STOJNOVA[1], PETYA V. RACHEVA[2], VANYA D. LEKOVA[1]* and ATANAS N. DIMITROV[1]

[1]Department of General and Inorganic Chemistry, Faculty of Chemistry, University of Plovdiv "Paisii Hilendarski", 24 Tsar Assen Street, 4000 Plovdiv, Bulgaria and [2]Department of Chemistry and Biochemistry, Faculty of Pharmacology, Medical University Plovdiv, 15A Vasil Aprilov Boulevard, 4002 Plovdiv, Bulgaria

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Abstract: The formation and liquid–liquid extraction of ion-association complexes between Co(II)–4-(2-pyridylazo)resorcinol (Co(II)–PAR) anionic chelates and cations of three ditetrazolium chlorides (DTC), *i.e.*, blue tetrazolium chloride (BTC), neotetrazolium chloride (NTC) and nitro blue tetrazolium chloride (NBTC), were studied. The optimum conditions for the formation and solvent extraction of the ion-association complex chelates were determined. It has been found that in the Co(II)–PAR–DTC systems, the reactants are present in the mole ratio 1:2:1 and the general formula of complexes was suggested. The extraction equilibria were investigated and quantitatively characterized by the equilibrium constants and the recovery factors. The analytical characteristics of the complexes were calculated.

Keywords: spectrophotometry; solvent extraction; chelates; extraction equilibria.

INTRODUCTION

Azo compounds are widely used as chromogenic reagents and metallochromic indicators for many metals. 4-(2-Pyridylazo)resorcinol (PAR) was one of the first azo reagents used for the spectrophotometric determination of cobalt due to its high sensitivity as a chromogenic reagent.[1–28] PAR forms intensively colored anionic chelates with cobalt, which can readily react with bulky organic compounds to give ternary complexes with good extraction behavior and analytical potential.[21–32]

Tetrazolium cations (TZ^{n+}) form analytically important ion-association complexes with $Co(SCN)_4^{2-}$,[33,34] and M–PAR anionic chelates, where M is V(V), V(IV), In(III) and Ga(III).[35–39]

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[*] Corresponding author. E-mail: vanlek@uni-plovdiv.bg

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Of particular interest are the negatively charged complex ions of cobalt(II) with PAR, which interact with the monotetrazolium moiety to form ion-association complexes.[40]

This investigation was aimed at studying the formation of ternary ion-associates complexes between the anionic chelates Co(II)–4-(2-pyridylazo)resorcinol (Co(II)–PAR) with ditetrazolium cations in the liquid–liquid extraction system Co(II)–PAR–DTC–H_2O–$CHCl_3$. The purpose is future application of the extraction system for the determination of cobalt(II) in alloys, as well as biological and pharmaceutical samples.

EXPERIMENTAL

Reagents and apparatus

$CoSO_4 \cdot 7H_2O$ (Sigma–Aldrich, *p.a*.). A 1.7×10^{-2} mol dm^{-3} aqueous stock solution was prepared, from which a working solution ($c_{Co} = 1.7\times10^{-4}$ mol dm^{-3}) was obtained by dilution.

4-(2-Pyridyazo)-resorcinol (PAR) (Sigma–Aldrich, 96 %). PAR was dissolved in slightly alkaline distilled water to give a 2.0×10^{-3} mol dm^{-3} solution.

Neotetrazolium Chloride (NTC) (Sigma–Aldrich, p.a.). 3,3′-(4,4′-Biphenylene)bis(2,5--diphenyl-2*H*-tetrazolium chloride). An aqueous 2.0×10^{-3} mol dm^{-3} solution was prepared.

Blue tetrazolium chloride (BTC) (Sigma–Aldrich, *p.a*). 3,3′-(3,3′-Dimethoxy-4,4′-biphenylene)bis(2,5-diphenyl-2*H*-tetrazolium chloride). An aqueous 2.0×10^{-3} mol dm^{-3} solution was prepared.

Nitro blue tetrazolium chloride (NBTC) (Merck, p.a.). 3,3′-(3,3′-Dimethoxy-4,4′-biphenylene)bis[2-(4-nitrophenyl)-5-phenyl-2*H*-tetrazolium chloride). An aqueous 2.0×10^{-3} mol dm^{-3} solution was prepared.

The acidity of the aqueous medium was set using a buffer solution prepared by mixing 2.0 mol dm^{-3} aqueous solutions of CH_3COOH and NH_3.

The organic solvent, $CHCl_3$, was additionally distilled.

The pH was checked using an HI 83140 pH meter (Hanna Instruments, Romania).

A Camspes M 508 spectrophotometer (UK), equipped with 10 mm path length cells, was employed for reading the absorbance values.

Procedure for establishing the optimum operating conditions

The required volumes of the solutions of Co(II), PAR, DTC (NBTC, NTC or BTC) and buffer solution to adjust the pH of the aqueous phase were introduced into a 100 cm^3 separatory funnel. The volume was then brought up to 10 cm^3, 10 cm^3 of chloroform were added and the sample extracted. The phases were left to separate, the organic phase was transferred through a filter paper into a 1 cm cell and its absorbance measured against a blank run in parallel.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of the extracts of the ternary ion-association complexes (TIAC) Co(II)–PAR–DTC in chloroform were characterized by absorption maxima in the visible range (λ_{max}, 515–520 nm), Fig. 1. They are shifted by 5–10 nm as compared to the maximum of the binary Co(II)–PAR complex in aqueous medium (510 nm; pH 3.5–10,[12,30,41]). As the optimum wavelength, $\lambda_{\max}$ = 520 nm was used in all three cases.

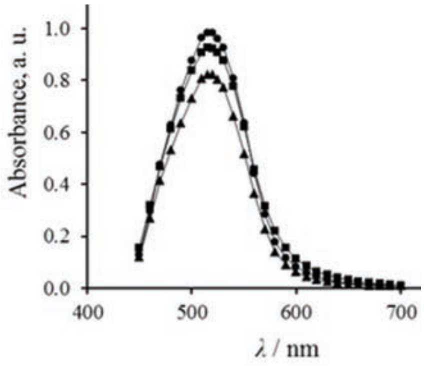

Fig. 1. Absorption spectra of the ternary complexes of Co–PAR–DTC in $CHCl_3$ against blanks: $c_{Co(II)}$ = 1.7×10^{-5} mol dm^{-3} = const; ●: c_{PAR} = 1.4×10^{-4} mol dm^{-3}, c_{BTC} = 2.0×10^{-4} mol dm^{-3}; ■: c_{PAR} = 1.4×10^{-4} mol dm^{-3}, c_{NBTC} = = 2.6×10^{-4} mol dm^{-3} and ▲: c_{PAR} = 0.8×10^{-4} mol dm^{-3}, c_{NTC} = 3.0×10^{-4} mol dm^{-3}.

Effect of pH

The acidity of the aqueous phase has a substantial effect on the extraction of TIAC into the organic phase. The results of pH change on the absorption spectra of the complexes are represented in Fig. 2. The maximum extraction of the TIAC Co(II)–PAR–BTC could be achieved at a pH in the range of 5.0–6.0, the maximum extraction the Co(II)–PAR–NTC at a pH in the range 4.8–7.0, while the maximum extraction of the third complex Co(II)–PAR–NBTC was achieved at a pH in the range 4.2–5.2.

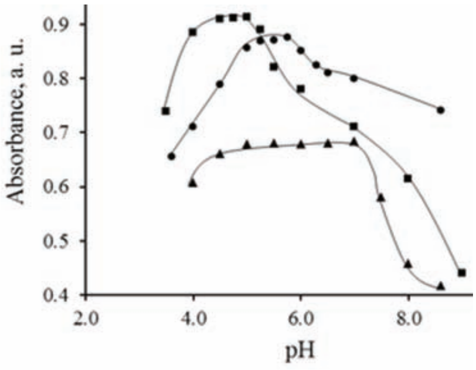

Fig. 2. Absorbance of Co–PAR–DTC extracts against PAR–DTC extracts *vs*. pH of the aqueous phase plots: $c_{Co(II)}$ = 1.7×10^{-5} mol dm^{-3} = const; c_{PAR} = 2.0×10^{-4} mol dm^{-3} = const; c_{DTC} = 2.0×10^{-4} mol dm^{-3} (DTC: ●, BTC; ■, NBTC; ▲, NTC).

Effect of shaking time

The performed experiments showed that maximum extraction of the ion-association complexes in chloroform is achieved at shaking time of not less than 30 s. In all three cases, a longer shaking time did not affect the absorbance. A shaking time of 2 min was used in the further experiments.

Effect of the concentration of the reagents

The complete bonding of Co(II) into a chelate complex requires a 4.2-fold excess of PAR for the TIAC with NTC, a 6.0–fold excess for the TIAC with BTC, and a 9.4–fold excess for the TIAC with NBTC. For maximum association and extraction, the amount of DTC should not be lower than an 8.2-fold excess for NTC, a 9.4-fold excess for BTC, and a 15.5–fold excess for NBTC.

The Beer law and analytical characteristics

To find the region of linear relationship between the cobalt concentration in aqueous phase and the absorbance in the organic phase after extraction, further studies were performed using regression analysis. The analytical characteristics are presented in Table I.

Table I. Characteristics concerning the application of TIAC for extractive–spectrophotometric determination of cobalt in the extraction systems Co(II)–PAR–DTC–H_2O–$CHCl_3$

Analytical characteristic	Ditetrazolium salt (DTC)		
	NTC	BTC	NBTC
$^a\varepsilon'$ / 10^4 dm^3 $mol^{-1}cm^{-1}$	4.81±0.26	5.75±0.20	5.65±0.22
^{b}Beer Law, µg cm^{-3}	up to 1.6	up to 2.2	up to 2.2
^{c}*SS* / 10^{-3} µg cm^{-2}	1.22	1.02	1.04
^{d}*LOD* / µg cm^{-3}	0.05	0.32	0.19
^{e}*LOQ* / µg cm^{-3}	0.16	1.07	0.65

^{a}Apparent molar absorptivity; ^{b}adherence to Beer's Law; ^{c}Sandell's sensitivity; ^{dl}imit of detection; ^{e}limit of quantification

Mole ratios of the complexes and suggested general formula

Using known methods, the mobile equilibrium method[42] and the straight-line method of Asmus,[42,43] it was confirmed the mole ratio of reaction between Co(II):PAR was1:2.[35,37,40,41] The main studies were aimed at establishing the mole ratios of interaction between Co(II) and DTC. In this direction, the mobile equilibrium method (Fig. 3) and the straight-line method of Asmus (Fig. 4) were

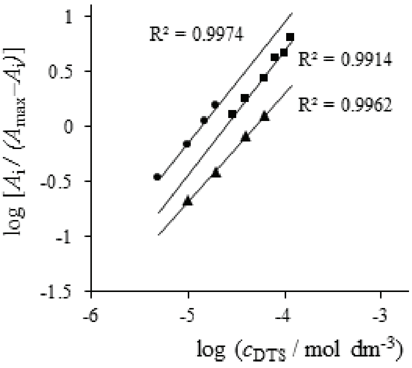

Fig. 3. Straight lines by the mobile equilibrium method during the determination of Co-to-DTC: $c_{Co(II)}$ = 1.7×10^{-5} mol dm^{-3} = const; c_{PAR} = 1.4×10^{-4} mol dm^{-3}, ●, BTC, ■, NBTC; c_{PAR} = = 0.8×10^{-4} mol dm^{-3}, ▲, NTC.

applied. The results of the presented studies show that the mole ratio of Co:DTC (BTC, NTC, NBTC) was 1:1. By means of independent method, the method of the continuous variations,[42] it was confirmed that mole ratio Co(II):NTC was 1:1. Based on the performed studies, it could be concluded that Co, PAR and DTC interact in mole ratio 1:2:1.

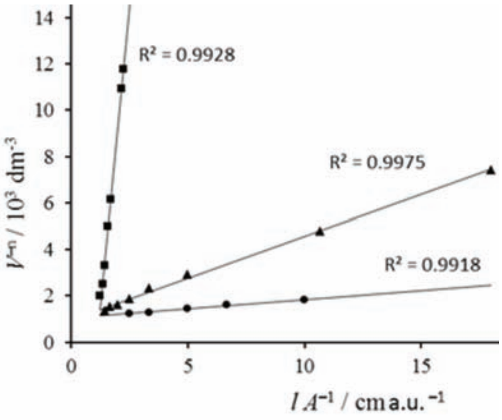

Fig. 4. Determination of the mole ratios of Co-to-DTC by the method of Asmus: $c_{\text{Co(II)}} = 1.7\times10^{-5}$ mol dm^{-3} = const; c_{PAR} = = 1.4×10^{-4} mol dm^{-3}, ●, BTC, ■, NBTC; $c_{\text{PAR}} = 0.8\times10^{-4}$ mol dm^{-3}, ▲, NTC.

The performed extraction–spectrophotometric studies of the systems Co(II)–PAR–DTC–H_2O–$CHCl_3$ gave reason to assume that the contact time between the phases was not sufficient for the oxidation of Co(II) to Co(III). In the aqueous phase, the chelate complex [CoH_2R] was formed between PAR (H_2R) and Co(II), which was deprotonated $[CoR_2]^{2-}$ and reacted with a ditetrazolium salts DT^{2+}.

Having in mind the mole ratio, it could be assumed that the complex formation of anionic chelate Co(II)–PAR in the aqueous phase, the formation of ion-associated complex in the aqueous phase, its distribution between the aqueous and the organic phase and its extraction in chloroform are given by the equations:

$$Co^{2+} + 2\ H_2R \rightarrow [CoR_2]^{2-}{}_{aq} + 4H^+ \tag{1}$$

$$[CoR_2]^{2-}{}_{aq} + DT^{2+}{}_{aq} \leftrightarrows (DT)[CoR_2]_{aq} \tag{2}$$

$$(DT)[CoR_2]_{aq} \leftrightarrows (DT)[CoR_2]_{org} \tag{3}$$

$$[CoR_2]^{2-}{}_{aq} + DT^{2+}{}_{aq} \leftrightarrows (DT)[CoR_2]_{org} \tag{4}$$

Equilibrium constants, recovery factors and molar absorptivities

The equilibrium constants describing quantitatively the equilibria in the aqueous phase and the extraction of the ion associates into the organic layer are calculated as follows:

The distribution constant, K_D, was calculated by comparing the absorbance for a single extraction (A_1) to that of the triple extraction (A_3) in equal volumes:

$$K_D = \frac{\{(DT)[CoR_2]\}_{org}}{\{(DT)[CoR_2]\}_{aq}} = \frac{A_1}{(A_3 - A_1)} \tag{5}$$

The association constant, β, was obtained by the method of Komar–Tolmachev.[42]

The extraction constant, K_{ex}, was calculated using the equation:

$$K_{ex} = K_D\beta;\ \log K_{ex} = \log K_D + \log \beta \tag{6}$$

The method of Komar–Tolmachev enables the true molar absorptivities, ε, and K_D to be calculated, which were then used to obtain the recovery factors, R%:

$$R\% = \frac{100K_D}{K_D + 1} \tag{7}$$

The results are presented in Table II. Analysis of the results showed that sufficiently stable ion associates were formed in the aqueous phase that were quantitatively extracted into the organic phase with high sensitivity.

TABLE II. Values of the equilibrium constants, recovery factors and molar absorptivities of the extraction systems Co(II)–PAR–DTC–H_2O–$CHCl_3$

Parameter	Ditetrazolium salt (DTC)		
	NTC	BTC	NBTC
$\log \beta$	4.31±0.25	4.77±0.32	4.79±0.28
$\log K_D$	1.02±0.01	1.41±0.02	0.96±0.01
$\log K_{\mathbf{ex}}$	5.33±0.51	6.18±0.55	5.75±0.59
R / %	91.25±0.09	95.64±0.11	89.92±0.08
ε^a / 10^4 dm^3 mol^{-1} cm^{-1}	4.62±0.07	6.43±0.28	5.51±0.21

[a]True molar absorptivity

CONCLUSIONS

Liquid–liquid extractions of Co(II)–PAR–DTC–H_2O–$CHCl_3$ systems were studied. The optimum conditions for the formation of the ion-association complex chelates of Co(II)–PAR with DTC in aqueous medium and their quantitative extraction into chloroform were determined. The equilibrium constants and analytical characteristics needed for the quantitative assessment of the extraction equilibrium were calculated, *i.e.*, the association constant, the distribution constant, the extraction constant, the recovery factor, the apparent molar absorptivity, the true molar absorptivity, the limit of detection (*LOD*), the limit of quantification (*LOQ*) and the Sandell sensitivity (*SS*). The validity of the Beer Law was checked. The mole ratio showed that the ion-association complex chelates of Co(II)–PAR with DTC could be represented by the general formula (DT)[Co(PAR)$_2$]. The presence of hydrophobic substituents, methoxy group in the molecule of the ditetrazolium salt BTC, increased the solubility of the ion-association complex in the organic solvent, while the hydrophilic nitro groups in the ditetrazolium salt NBTC reduced the solubility of the associate. For this reason, the ion-association complex of Co–PAR–BTC allowed the determination of Co(II) with a higher sensitivity.

ИЗВОД

ТЕЧНО–ТЕЧНА ЕКСТРАКЦИЈА ЈОН-АСОСОВАНИХ КОБАЛТ(II)-4-(2-ПИРИДИЛАЗО)РЕЗОРЦИНОЛ КОМПЛЕКСА СА ДИТЕТРАЗОЛИЈУМ СОЛИМА

VIDKA V. DIVAROVA[1], KIRILA T. STOJNOVA[1], PETYA V. RACHEVA[2], VANYA D. LEKOVA[1]
и ATANAS N. DIMITROV[1]

[1]Department of General and Inorganic Chemistry, Faculty of Chemistry, University of Plovdiv "Paisii Hilendarski", 24 Tsar Assen Street, 4000 Plovdiv, Bulgaria и [2]Department of Chemistry and Biochemistry, Faculty of Farmacology, Medical University Plovdiv, 15A Vasil Aprilov Boulevard, 4002 Plovdiv, Bulgaria

Испитивано је формирање и течно–течна екстракција јон-асосованих комплекса који настају између анјонског Co(II)–4-(2-пиридилазо)резорцинола и три различита катјонска дитетразолијум-хлорида (плави тетразолијум-хлорид, BTC, неотетразолијум-хлорид, NTC и плави нитротетразолијум-хлорид, NBTC). Одређени су оптимални услови за формирање и екстракцију помоћу растварача јон-асосованих комплексних хелата. Нађено је да у Co(II)–PAR–DTC системима долази до реакције реактаната у 1:2:1 молском односу. Претпостављена је општа формула награђених комплексних врста. Екстракционе равнотеже су испитиване и квантитативно окарактерисане помоћу одговарајућих константи. Поред тога, израчунате су аналитичке константе за одговарајуће комплексне врсте.

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