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Complexation and Spectrophotometric Determination of Cobalt(II) Ion with 3-(2′-thiazolylazo)-2,6-diaminopyridine

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ABSTRACT

The complexation of 3-(2′-thiazolylazo)-2,6-diaminopyridine (TADAP) with cobalt(II) has been studied spectrophotometrically. The stability constant of TADAP ligand with cobalt(II) ion has been determined at a constant temperature, where the molar ratio of this complex is 1:2 (metal:ligand). TADAP has been prepared and characterized on the basis of FT-IR spectral data. A procedure for the spectrophotometric determination of this complex is proposed where it is rapid, sensitive and highly specific. Beer’s law was obeyed in the range 2.0×10^{-6}-1.2×10^{-5} M at pH 10 to form a green complex. The limit of detection is 5.26×10^{-7} M ($\varepsilon = 1.52 \times 10^{4}$ $l^{-1}mol^{-1}cm^{-1}$ at $\lambda_{max} = 598$ nm).

Key words: cobalt, thiazolylazo dye, spectrophotometry

INTRODUCTION

Cobalt metal powder is a fire hazard. Evidence indicates that minute quantities of cobalt may be detrimental to higher plant life, particularly in water and sand cultures. Cobalt toxicity is characterized by a chlorosis similar to that induced by lack of iron. Growing cattle can consume up to 50 mg cobalt per 100 lb weight for at least eight weeks without harmful effects. Higher dosages are injurious (Greenwood and Earnshaw, 2004).

The spectrophotometric determination of cobalt is usually preceded by a reaction with reagents such as 5-(6-methoxy-2-benzothiazoleazo)-8-aminoquinoline (Zhao *et al.*, 1999), bis(2,4,4-trimethyl penthyl)phosphinic acid (Reddy and Sarma, 1994), 2-amino-cyclopentene-1-dithiocarboxylic acid (Safavi *et al.*, 2004), 5-Br-PADAB (Wada *et al.*, 1982), 2-(2-benzothiazolylazo)-2-*p*-cresol (Carvalho *et al.*, 1996), 2-(5′-bromo-2′-pyridylazo)-5-diethylaminophenol (Oxspring *et al.*, 1996), ammonium 2-amino-1-cyclohexane-1-dithiocarbamate (Khayamian *et al.*, 1999), 2-(2-thiazolylazo)-5-[(N,N-dicarboxymethyl) amino]benzoic acid (Wang and Fulong, 1996), penicillamine and carbocisteine (Walash *et al.*, 2004). However, most of these methods lack sensitivity or selectivity, the procedure are sometimes rather complicated because of the need for extraction to separate interfering ions.

In this work, a type of thiazolyl azo derivative 3-(2′-thiazolylazo)-2,6-diaminopyridine (TADAP) has been synthesized and tested as a possible chromogenic reagent for the spectrophotometric determination of cobalt. It was experimentally observed that 3-(2′-thiazolylazo)-2,6-diaminopyridine forms coloured complexes with cobalt(II). This coloured reaction is utilized in analyzing spectrophotometrically trace amount of this metal.[1]

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MATERIALS AND METHODS

Apparatus

Absorbance measurements were carried out on a Perkin Elmer Lamda 35 UV-vis spectrophotometer. Infrared spectra (4000-200 cm^{-1}) were obtained by a Perkin Elmer system 2000 Fourier transform infrared spectrometer. Nuclear magnetic spectra were recorded at 400 MHz on a Bruker Advance DPX-400.

Reagent and materials

All reagent used were of analytical reagent grade and the water was always distilled. Stock solution of cobalt(II) (AR. grade, Merck) was prepared from nitrate salts. Universal buffer solutions pH 3-11 used in this work were prepared by mixing of mixture of 0.20 M boric acid and 0.05 M citric acid (1:1) with 0.10 M Na_3PO_4 at various ratios. 3-(2′-thiazolylazo)-2,6-diaminopyridine (TADAP) was prepared by the diazotization of 2-aminothiazole.The diazotate formed was coupled with the aromatic substance in cold acidic solution. The ligand 3-(2′-thiazolylazo)-2,6-diaminopyridine was prepared according to published procedure (Garcia *et al.*, 1982). It was crystallized three times from ethanol-water mixture, which gave TADAP as red needle crystal with the melting point of 209-210 °C. The infrared spectrum manifested the following characteristic absorptions $-NH_2$ (aromatic) 1630 (s), -N=N- 1450 (m), C-N (aromatic) 1330 (s), N-H (stretching) 3225 (w), 3442 (w). ^1H NMR spectrum (DMSO-d_6, 400 MHz) was as follow δ 6.113 (1H, d, H_a), 7.401 (1H, d, H_b), 7.572 (1H, d, H_c) and 7.714 (1H, d, H_d).

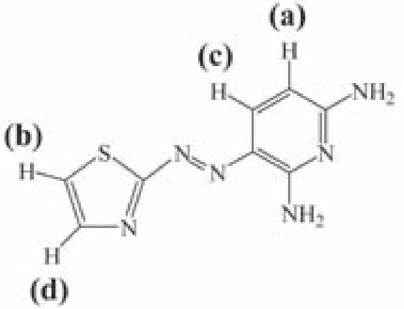

Figure 1 Structure of 3-(2′-thiazolylazo)-2,6-diaminopyridine (TADAP).

General procedure for complex formation between TADAP and cobalt(II)

To a series of solutions in a 25 ml volumetric flask containing 0.5 ml of the ligand (1×10^{-3} M), add 10 ml of buffer pH 10, and then 0.5 ml of cobalt(II) (1×10^{-3} M). Mix the solutions well and dilute with buffer solution pH 10 to 25 ml. After 1 hour, the absorbance at 598 nm was measured against a blank prepared containing all solution except cobalt(II).

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of the ligand TADAP and of its complex with cobalt(II) at pH 10 are shown in Figure 2. It is evident from this figure that the maximum absorption of the cobalt complex is at 598 nm.

Effect of pH

The formation of TADAP complex with cobalt(II) is highly dependent on the pH. The formation of complex between TADAP and cobalt(II) at various pH (Figure 3) shows that TADAP forms complex with cobalt(II) at pH 9-11. However, at pH 10 seems to be most suitable pH for the formation of complex between cobalt(II) and TADAP.

Composition and stability of the complex

TADAP forms a green complex with cobalt(II) at pH 10. The stoichiometry of this complex was verified to be 1:2 (metal:ligand) by applying the continuous variation method (Job’s method) as shown in Figure 4. The time for the absorbance of the complex to reach a stable value was 1 hour at room temperature.

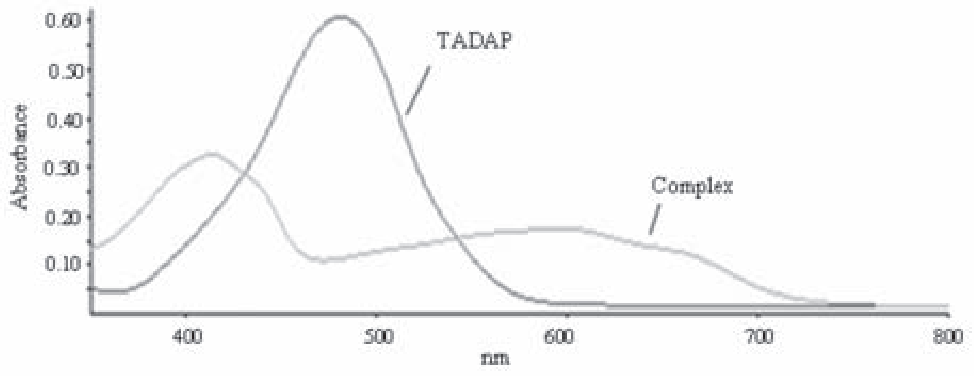

Figure 2 Absorption spectra of TADAP and cobalt(II)-TADAP complex at pH 10.

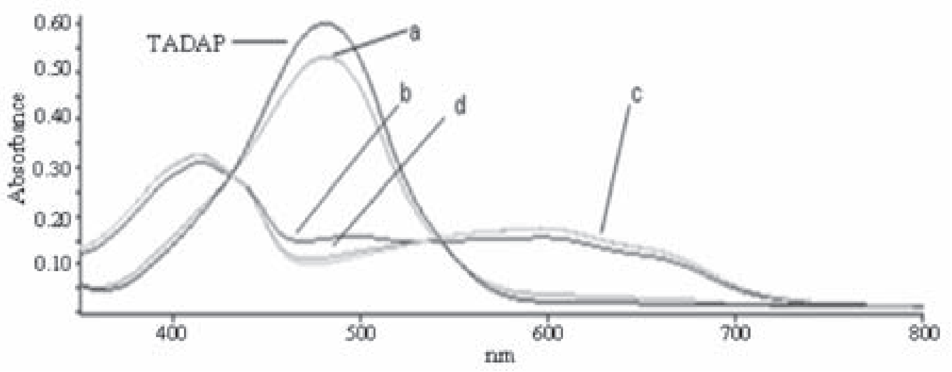

Figure 3 Absorption spectra of cobalt(II)-TADAP complex at pH 8 (a), pH 9 (b), pH 10 (c) and pH 11 (d).

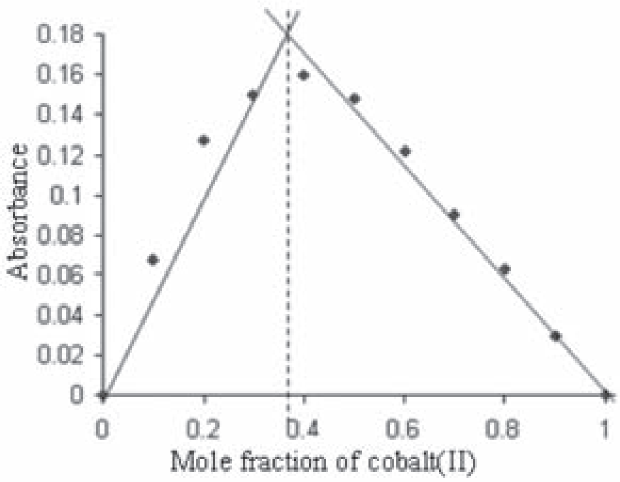

Figure 4 Job's plot of complex between cobalt(II) and TADAP at pH 10.

The stability constant (K_f) of the complex could be determined by using data from the continuous variation method (Job's plot) by assume that only single complex is present. The stability constant (K_f) of this complex is 5.93×10^{10}.

Beer's law and sensitivity of the reagent

Series of standard solutions of cobalt(II) were prepared and complexed with TADAP at their optimum pH. The absorbance of each standard solution is measured. The results obtained show a linear relationship between absorbance and concentration in the range of $2.0 \times 10^{-6} – 1.2 \times 10^{-5}$ M. The molar absorptivity as calculated from the linear part of Beer's law plots was 1.52×10^4 $l^{-1}mol^{-1}cm^{-1}$. The limit of detection was $5.26 \times$ □10^{-7} M.

Effect of other ions

The complex solution between cobalt(II) and TADAP was prepared and measured the absorbance by UV-Vis spectrophotometer at 598 nm. Interferences of various ions in the determination of cobalt(II) at 1.0×10^{-5} M was determined by carrying out the reaction according to the optimised procedure in the presence of various amounts of several cations and anions. The analysis of cobalt(II) was considered to be interfered when the difference between the absorbance of complex and TADAP did not lie in the range of 0.0105-0.0248 (For a normal distribution with mean and standard deviation approximately 95 % of the population values lie within ± 2 standard deviation (SD) of the mean) (Miller, 2000). The results are shown in Table 1.

The results showed that the cations and anions such as Na^+, Fe^{3+}, I^- and Br^- did not interfere in cobalt(II). Nevertheless, Cd^{2+} could be masked by the addition of I^-, Cl^- and SCN^-.

The determination of cobalt(II) in synthetic solutions

TADAP was used to determine quantity of cobalt(II) by spectrophotometric method. Cobalt(II) in synthetic solutions were determined in the presence of interfering metal ions such as nickel(II) and cadmium(II) at 1% by mole of cobalt(II). The results are shown in Table 2. From the results, TADAP could use for the determination of cobalt(II) in aqueous solution when the concentration of cobalt(II) is in the range of 0.4-0.6 ppm, and the results were reliable.

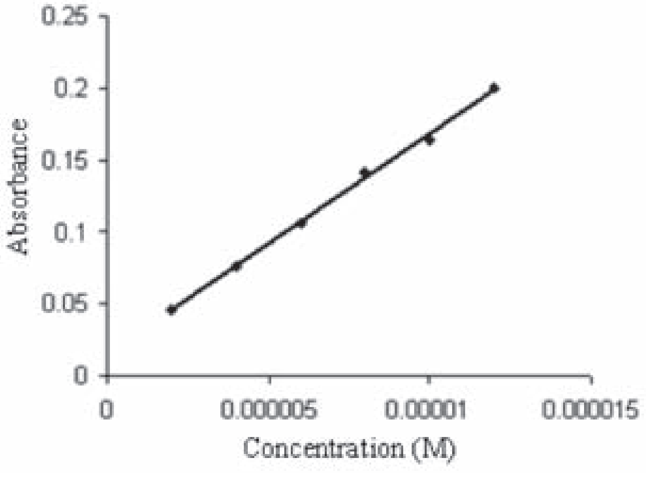

Figure 5 Linear relationship between absorbance and concentration of complex between cobalt(II) and TADAP.

CONCLUSION

The conclusion of this work is that the proposed method for the determination of cobalt(II) is simple and sensitive. TADAP can form complex with cobalt(II) in universal buffer at pH 10. The ratio of cobalt(II) : TADAP is 1 : 2.

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Table 1 Spectrophotometric determination of cobalt(II) using TADAP as analytical reagent in the presence of interfering cations and anions.

Interference ions	Molar ratio of Co^{2+}: Interference ions				
	1:1	1:25	1:50	1:75	1:100
Cd^{2+}	-	+	+	+	+
Na^{+}	-	-	-	-	-
Ni^{2+}	-	-	-	+	+
Ca^{2+}	+	+	+	+	+
Fe^{3+}	-	-	-	-	+
Pb^{2+}	+	+	+	+	+
I^{-}	-	-	-	-	-
EDTA	-	+	+	+	+
$C_2O_4^{2-}$	-	-	+	+	+
SCN^{-}	+	+	+	+	+
Thiourea	+	+	+	+	+
CN^{-}	-	-	+	+	+
$H_2PO_4^{-}$	+	+	+	+	+
Br^{-}	-	-	-	-	-
CH_3COO^{-}	+	+	+	+	+

+ = Interfere
- = Not interfere

Table 2 Determination of cobalt(II) in synthetic solutions.

Synthetic solutions	Concentration of Co^{2+} (M)	Concentration of Co^{2+} found (M)	% Error
Co^{2+}	2.0×10^{-6}	2.48×10^{-6}	24.00
	7.0×10^{-6}	7.84×10^{-6}	12.00
	1.1×10^{-5}	1.07×10^{-5}	2.73
Co^{2+}: Ni^{2+} (100:1)	2.0×10^{-6}	2.51×10^{-6}	25.50
	7.0×10^{-6}	7.75×10^{-6}	10.71
	1.1×10^{-5}	1.16×10^{-5}	5.45
Co^{2+}: Cd^{2+} (100:1)	2.0×10^{-6}	2.55×10^{-6}	27.50
	7.0×10^{-6}	7.90×10^{-6}	12.86
	1.1×10^{-5}	1.05×10^{-5}	4.54

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