

Preparation and Identification of Metal Ions Complexes for 4-(P-Phenyl azo sulfonic acid)-1-Naphthol Dye

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Abstract

The organic reagent, 4-(p-phenyl azo sulfonic acid)-1-naphthol, was found to be sensitive and selective reagent for the spectrophotometric determination of trace amounts of Cobalt and Nickle. The prepared complexes and azo reagent were characterized using FT-IR and UV-Vis spectroscopic method. The complexes have a maximum absorption at (453) nm and (446) nm for both Cobalt (II) and Nickle (II) (respectively, Beer's law was obeyed in the range (0.5-2.5) ppm of Cobalt and molar absorptivity $\epsilon = 3.24 \times 10^4$ L.mole⁻¹. cm⁻¹, as for Nickle, the range was (0.1-2) ppm and molar absorptivity $\epsilon = 0.96 \times 10^4$ (L.mol⁻¹.cm⁻¹. The accuracy and reproducibility of the determination method for various known amounts of cobalt (II) and Nickle (II) (were tested). The results obtained are both precise (RSD was better than 1.6 %, 3 %) for both Cobalt (II) and Nickle (II) (respectively and accurate (relative error was better than 1 %, 2 %) for both Cobalt (II) and Nickle (II) (respectively).

Keyword: Metal Ions Complexes, 4-(P-Phenyl azo sulfonic acid)-1- naphthol Dye.

Introduction

Essential elements are of important in many biological functions. Metals can be found in enzymes and cofactors required for various processes [1]. Nickel is a constituent of the enzyme urease and considered to be essential to plants and some domestic animals [2]. The deficiency of nickel may lead to health risks such as bone deformities but excess nickel can cause lung cancer and cardiovascular [3]. Cobalt is an essential element for enzymatic functions in all mammals and it is part of vitamin B12, which is important in protein formation and DNA regulation [4]. Exposures to a high level of cobalt lead to serious public health problems and are responsible for several diseases in human such as asthma, pneumonia, and cardiomyopathy [5]. The consumption of large quantities of nickel and cobalt-containing products

in industry inevitably leads to environmental pollution at all stages of production, recycling and disposal. Thus, the determination of trace levels of nickel and cobalt in biological and environmental samples is an important analytical task. The determination of nickel and cobalt in water samples of environmental interest in which it is found at very low concentrations requires the use of pre-concentration method coupled to spectroscopic method [6,7].

In the present study we wish to introduce this reagent as a selective reagent in spectrophotometric determination of micro amounts of cobalt (II) and nickel (II) in simple and sensitive method.

Apparatus: A Shimadzu double-beam UV-visible Spectrophotometer model UV-1650 (Japan) equipped with 1.00 cm quartz cells is used for the scanning study of absorption spectra of the complexes formed. FT-IR Absorption spectra were taken on (Test scan Shimadzu FT-IR 8000 series). Measurements of pH were made using an (Hanna, HI9811-5 pH – meter) equipped with a glass - saturated calomel combined electrode. Melting points of ligand and complexes were obtained with an electro thermal melting point apparatus. Conductivities

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were measured for 10^{-3} M of complexes in DMSO at 25°C using (Alpha digital conductivity model -800).

Standard solutions of copper(II) and Nickel (II): A stock solution of Co^{2+} and Ni^{2+} (100 ppm) were prepared by dissolving (0.0025g) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and (0.0035 g) of $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ in 100 mL distilled water, other working standard solutions were prepared by simple dilution of the appropriate volume of the stock solution with distilled water .

4-(p-phenylazo sulfonic acid)-1-naphthol solutions: 4-(p-phenylazo sulfonic acid)-1-naphthol) was synthesized and recrystallized according to the method mentioned in previous study [8] A stock solution ($1 \times 10^{-3}\text{M}$) was prepared by dissolving 0.082 g of reagent in 250 mL of ethanol. More dilute solution of the reagent was prepared as required.

Preparation of complexes: The complex was prepared by stoichiometric amount from ligand in 100 mL of ethanol then added drop wise with stirring to a stoichiometric amount 2:1 for metal salt in 50 mL distilled water. The mixture was stirred at room temperature for 5 min. The pH of solution was adjusted to optimum pH then left for 24 hr. The solid product thus formed off,

washed with distilled water, and recrystallized from ethanol.

General Procedure: In to a series of 10 mL calibrated flask, transfer increasing volumes of Co (II) and Ni(II) working solutions ($10 \mu\text{g mL}^{-1}$) to the range of the calibration curve, add 1.5 mL and 2.5 mL of 1×10^{-3} M of 4-(p-phenylazo sulfonic acid)-1-naphthol) solution for Co (II) and Ni(II) respectively . The pH (7.6,9.0) for Co (II) and Ni (II) was adjusted with dilute hydrochloric acid and sodium hydroxide solutions. The complexes formed were solubilized in water and diluted up to 10 mL with distilled water. Measure the absorbance at 446 nm for Co (II) and at 453 nm for Ni(II) complexes against a reagent blank .

Results and Discussion

Spectra photometric studies:

I-Absorption spectra: The absorption spectra for Co (II) and Ni (II) complexes with 4-(p-phenylazo sulfonic acid)-1-naphthol) against blank solution are shown in Fig. 2, 3. The maximum wavelengths of two complexes are 453nm and 446 nm, respectively.

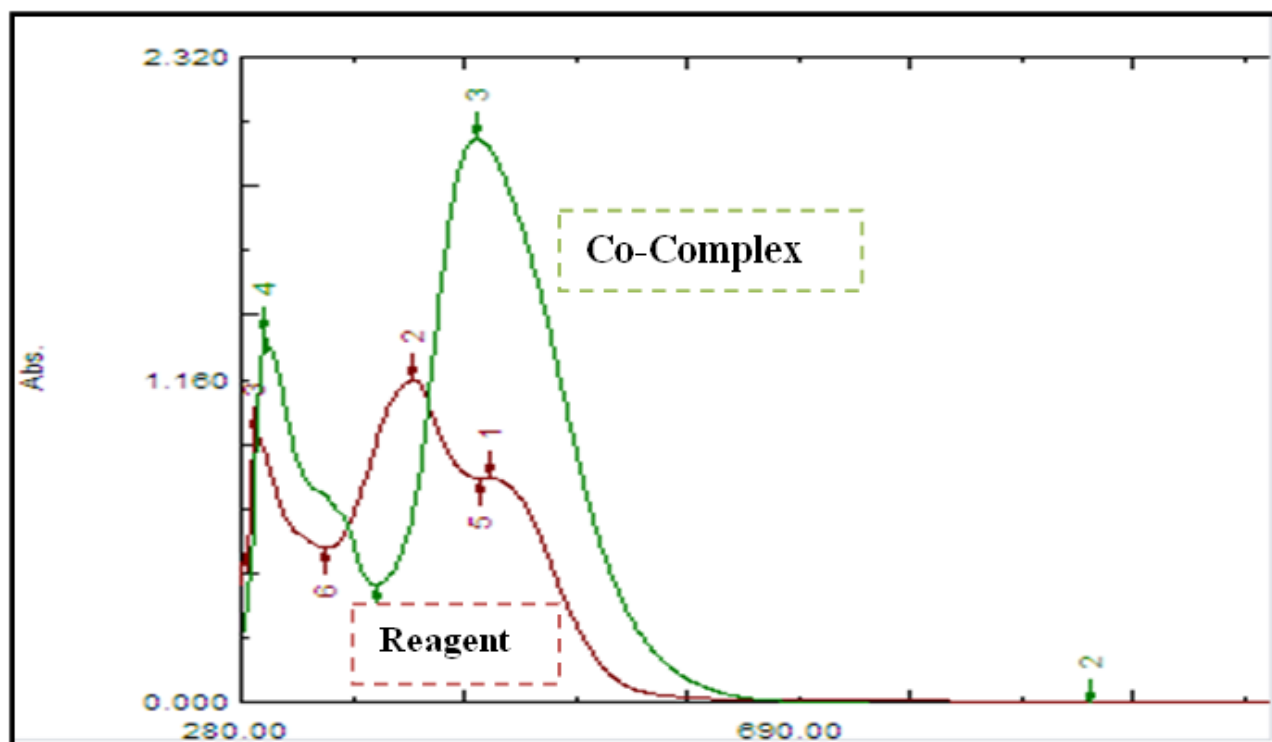


Fig. 2: Absorption spectra of [Co (II) + 4-(p-phenylazo sulfonic acid)-1-naphthol)] treated as described under procedure and against reagent solution as blank.

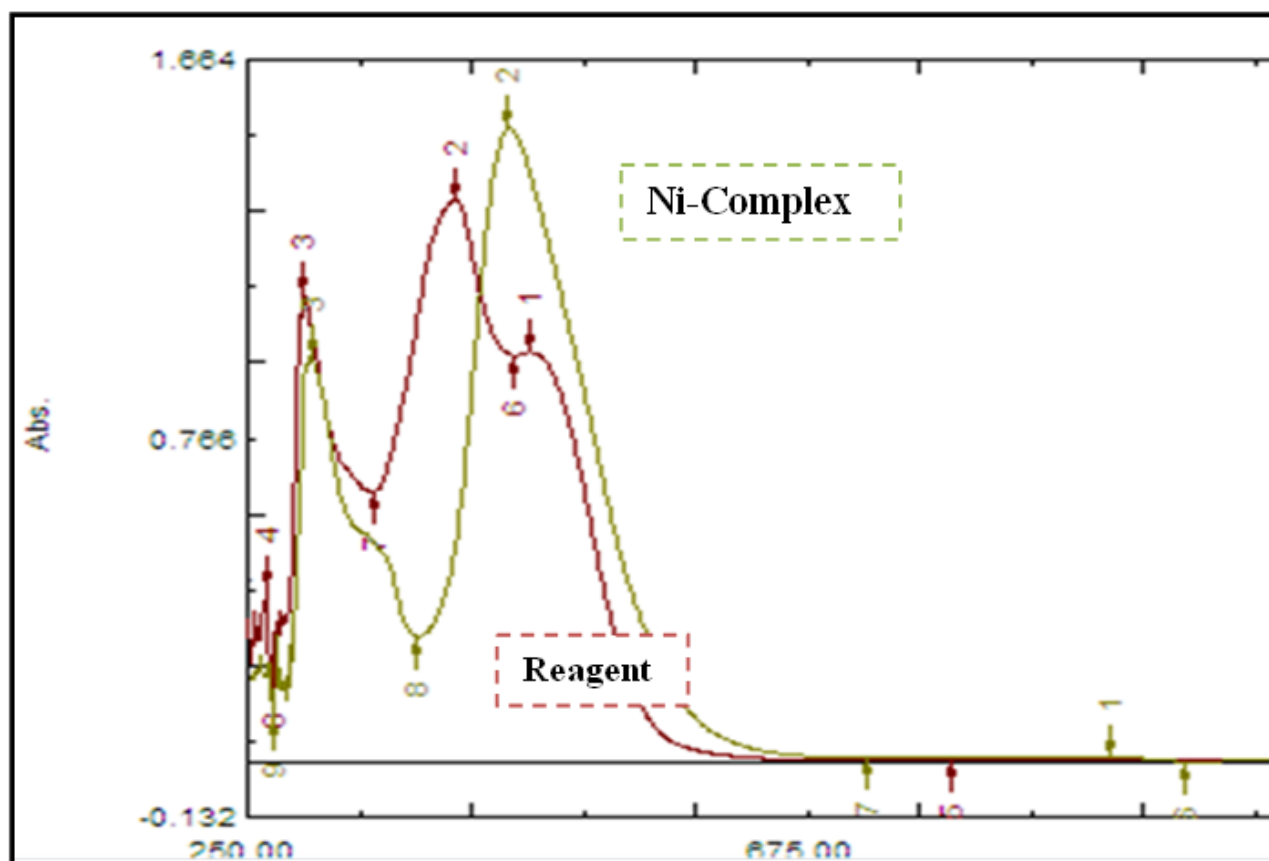


Fig. 3: Absorption spectra of [Ni (II) + 4-(p-phenylazo sulfonic acid)-1-naphthol] treated as described under procedure and against reagent solution as blank.

II-Infrared Spectra: The FT.IR of the free ligand and its complexes with Co (II) and Ni (II) ions are given in Table.1. The IR spectrum of ligand exhibited broad band at 3437.26 cm^{-1} , has been assigned to the naphtholic OH group^[9]. In the spectra of Co(II)- Complex and Ni(II)-Complex the broad weak absorption band around 3392.90 cm^{-1} and 3230.87 cm^{-1} respectively indicates the presence of water in these complexes^[10]. Two absorption bands are observed at 1450.52 cm^{-1} and 1384.94 cm^{-1} in the reagent spectrum, which are due to the azo group ν (N=N). These bands shifted in complexes, which suggest engagement of this group in the coordination with the metal ion^[11,12]. The weak bands observed at 2968 cm^{-1} in the spectrum of reagent which are due to ν (C-H) aromatic. These bands are stable in position in both reagent and metal complexes. The appearance of new bands around (500-400) due to (M-N)^[13,14].

To optimize the conditions for determination of Cobalt (II) and Nickle (II) (such factors as The pH of the solution, the concentration of 4-(p-phenyl azo sulfonic

acid)-1-naphthol) and composition of complexes were evaluated.

Table 1: Selected FT.IR data of reagent and it's complex with Co (II)

Compound	ν (OH)	ν (C-H) arom.	ν (N=N)	ν (M-N)
HL	3437.26 m	2968 w	1450.52 m 1384.94 s	–
[Co (L)]	3392.90 w	2968 w	1490 m 1460 s	550 w
[Ni (L)]	3230.87 w	2968 w	1500 m 1411 s	520 w

S: sharp; m: medium; w: weak

Effect of pH: The effect of pH was also studied at pH range (5 - 10) and the absorbance- pH curves for each complexes measured at certain (λ_{max}) were plotted. Fig.(4) showed a selective pH- absorbance curves. The plateau of the curves represent the completion of the reaction and consequently represent the optimum pH.

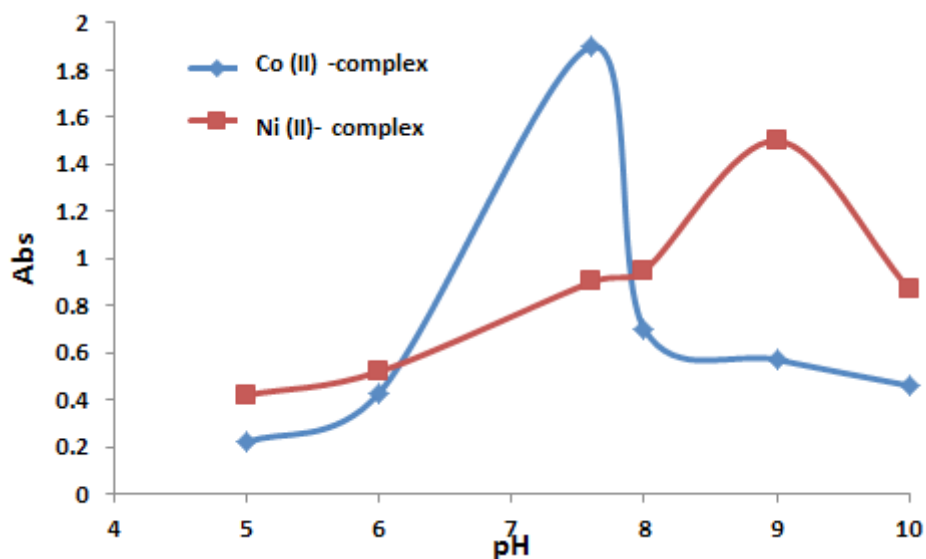


Fig. 4: Effect of PH on complex formation

Table 2: Analytical characteristics of complexes.

Characteristic	Co (II) – complex	Ni (II) – complex
Maximum Absorption peak (nm)	453	446
Beer's law validity range (ppm)	(0.5–2.5)	(0.1–2)
pH range	(6–8)	(8–10)
Sandell's sensitivity $\mu\text{g} \cdot \text{cm}^{-2}$	0.0018	0.0062
Molar absorptivity ($\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)	3.24×10^4	0.96×10^4
Melting point for complex	283C^0	242C^0
Relative Standard Deviation (n= 6)	1.6%	3%

Effect of reagent concentration: Keeping a constant concentration ($10 \mu\text{g} \cdot \text{mL}^{-1}$) of Co(II) and Ni(II) solutions, the effect of reagent concentration (1.0×10^{-3} M) on absorbance of the complexes was studied by varying the amount of the volume of reagent (0.5-4.0) mL. The required volumes of 4-(p-phenyl azo sulfonic acid)-1-naphthol were found to be 1.5 mL and 2.5 mL to complete the reaction of Co (II) and Ni (II) respectively. The result are shown in fig.5.

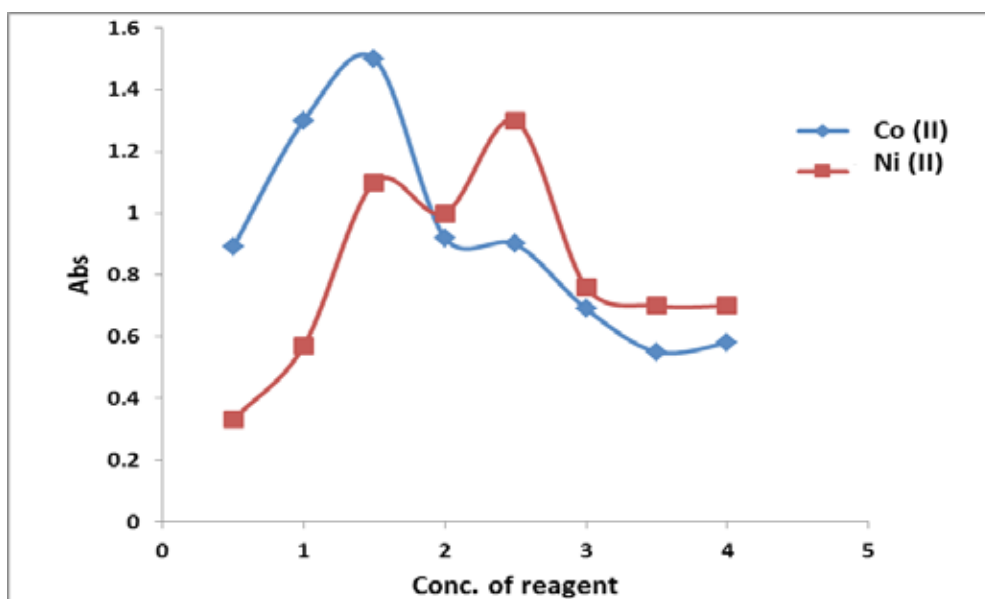


Fig. 5: Effect of reagent concentration

Calibration Graph: The calibration curves obtained show a linear relationship between absorbance and concentration held over range of 0.5-2.5 $\mu\text{g mL}^{-1}$ and 0.1-2 $\mu\text{g mL}^{-1}$ for cobalt and Nickel respectively. The molar absorptivity and Sandell's sensitivity are given in Table.1 .

Composition of the complexes: Job's method of continuous variations^[15] was chosen to study the ratio of metal to reagent, results illustrated in Figures 6. The method indicated that the ratio of metal ion to reagent molecules (M:L) was (1:2) at optimum pH.

Conclusion:

In this study it was shown that 4-(p-phenylazo sulfonic acid)-1-naphthol) could be used as a reagent for the Spectrophotometric determination of Cobalt (II) and Nickel (II). It offers advantages like reliability and reproducibility in addition to its simplicity.

Ethical Clearance: The Research Ethical Committee at scientific research by ethical approval of both environmental and health and higher education and scientific research ministries in Iraq

Conflict of Interest: The authors declare that they have no conflict of interest.

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