Spectrophotometric Complex Formation Study of Murexide with Nickel and Cobalt in Aqueous Solution

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Abstract

In the present study, the formation constant and the stoichiometry of murexide complexes with Co (II) and Ni (II) have been determined spectrophotometrically in aqueous solution at 25°C. Two experimental parameters governing the complex formation, pH and time, have been investigated. The formation and stoichiometry constants have been determined by two methods: Job's and mole ratio's methods. The absorption maxima for Co-murexide and Ni-murexide complexes were: 480, 460 nm, respectively. The two Spectrophotometric methods confirm the formation of 2:1 (M:L) complexes with stability arrangement of: Co > Ni. The formation constants (K_f) determined by the Job's method were as follows: 2.06×10^{14} and 1.21×10^{11} for Co-murexide and Ni-murexide, respectively. Also, using mole ratio's method, the formation constants were found to be: 9.18×10^{11} and 6.01×10^{11}. Molar absorptivity values of the studied complexes have also been determined (by Job's and mole ratio's methods) and the average values were: 18235 and 13284 l/mol.cm for Co and Ni, respectively.

Keywords: Cobalt, Nickel, Murexide, Stability Constant, Stoichiometry .

Introduction

The murexide indicator which is a reddish-purple compound has the structure displayed in Fig. 1. This indicator has attracted considerable interest due to its use for metal ion determination in chemical analysis and spectrophotometric fields. It has been utilized as a metal ion indicator; frequently used in conventional EDTA titrations, for a long time [1].
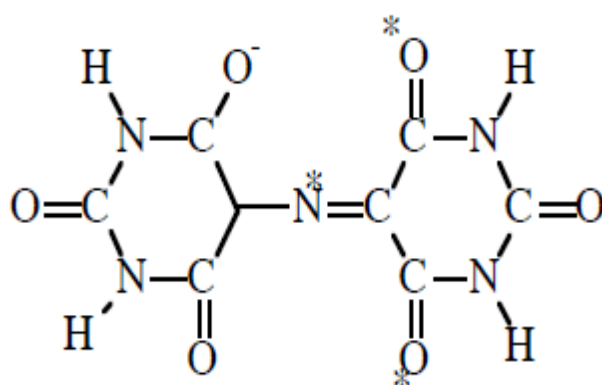
Figure 1. Structure of Murexide

The application of murexide as a metal ion indicator for complexometric determination of calcium, copper, and nickel is well recognized. The murexide also forms coloured complexes with various divalent and multivalent cations and therefore has been employed for the spectrophotometric determination of calcium, strontium, zinc, and the metals of the rare earths such as scandium, yttrium, lanthanum and ytterbium [2]. Though, the murexide complexes with most metal ions are not very stable which could cause some drawbacks in the application of murexide as a metallochromic indicator in aqueous solutions [3]. Therefore, this indicator

has a minimal promise in the literature and limited papers such as surface properties, formation constants of its complexes and complex formation kinetics were tested [4]. Formation constants of metal ion chelates of numerous ligands and especially chelating ligands by means of different techniques such as potentiometric and spectrophotometric methods have been studied. The stability of the metal complexes could be affected by various parameters such as ligand kind, metal ion kind, counter-ions and solvent [5-9]. Evaluation of some thermodynamic parameters of the complexes by potentiometric or spectrophotometric information is a challenging task to acquire and suggest a novel method for selective and sensitized evaluation of trace levels of metal ions. Also, their formation constants can be of importance with the aim of suppose different chemical processes such as isolation, extraction, or preconcentration methods because many elements that appear in trace amounts can be isolated by complexing reagents. The value of formation constant denotes the particular level of tolerance to the interference by other ions. The formation constant relies on several parameters such as the electronegativity, hardness or softness of the donor atoms in ligand structure, topology of ligand and the ionic radial, charge, hard or soft of the metal ion and its atomic number [10-13]. The aim of the present study is to investigate the complexation between murexide and Co (II), and Ni (II) spectrophotometrically and to determine their formation constants by Job's and mole ratio's method.

Material and Methods

Reagents

All reagents were purchased and used without further purification. To keep them dry, they were stored in a desiccator. The milli-Q water was used in this study to prepare the stock solutions and for further dilutions. Murexide (indicated in Fig. 1) (98%) was obtained from SIGMA-ALDRICH. Metal chlorides (cobalt and nickel chlorides) were used for preparing the metal ions solutions. All chemicals (cobalt chloride, nickel chloride, sodium hydroxide, and 37% hydrochloric acid) were ACS reagent grade and obtained from MERCK. The stock of 1.00×10^{-3} M solutions of both murexide and metal ions were prepared in milli-Q water.

UV-VIS Absorption Spectra Analysis

To demonstrate the UV-VIS absorption spectra for murexide and murexide complexes, the Agilent Cary 60 UV-Vis Spectrophotometer was used. The spectra in the range from 300 to 650 nm were recorded at 25°C.

Complex Formation Analysis

The titration procedure was selected to display the absorption maxima of Co-murexide and Ni-murexide complexes in distilled water. A 50 ml of 1.00×10^{-5} M murexide solution was titrated with 1×10^{-3} M metal ion solution stepwise (100 μl additions) and then recorded the spectrum (from 300 – 650 nm). The complexes just developed were examined for their stability against time (till 180 min). The stoichiometry and formation constant were evaluated by method of continuous variation (Job method) [14] and mole ratio method [15].

pH Effect measurements

A 3505 pH meter from Jenway was used to measure the pH of the tested solutions. The pH has been changed using 0.10 M HCl and 0.10 M NaOH solutions.

Results and Discussion

Absorption Spectrum of Murexide in Aqueous Solution

The absorption spectrum of murexide in aqueous solution and before the addition of metal ions have been scanned (300-650 nm) and displayed in Figs. 2 & 3. As shown, murexide exhibits an absorption maximum at 520 nm. From the structure of murexide, this maxima is assigned to π→π* and n→π* conjugated system.

Complexation of murexide with Co(II) and Ni(II)

By complexation of murexide with Co(II) and Ni(II) ions in aqueous solutions, the absorption maximum at 520 nm (shown in Figs. 2 & 3) is shifted to 480 and 460 nm for cobalt and nickel, respectively. Upon complexation, the n electrons (non-bonding electrons of O & N atoms) were coordinated with metal ions and consequently the energy levels n, π, π* are influenced causing the absorption maximum to be shifted. The wavelengths of the absorption maxima of murexide complexes with Co(II) and NI(II) are provided in Table 1.
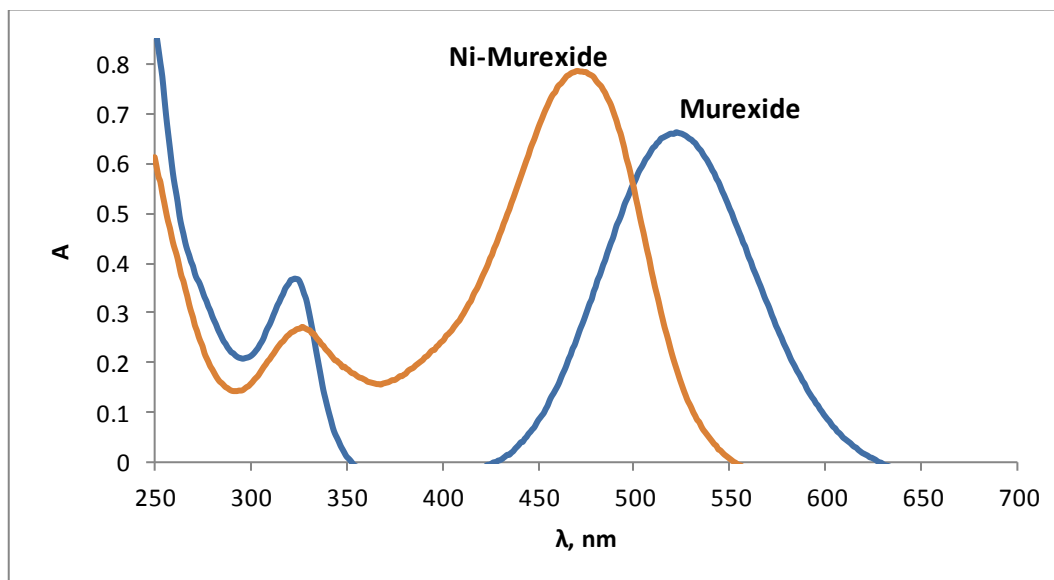

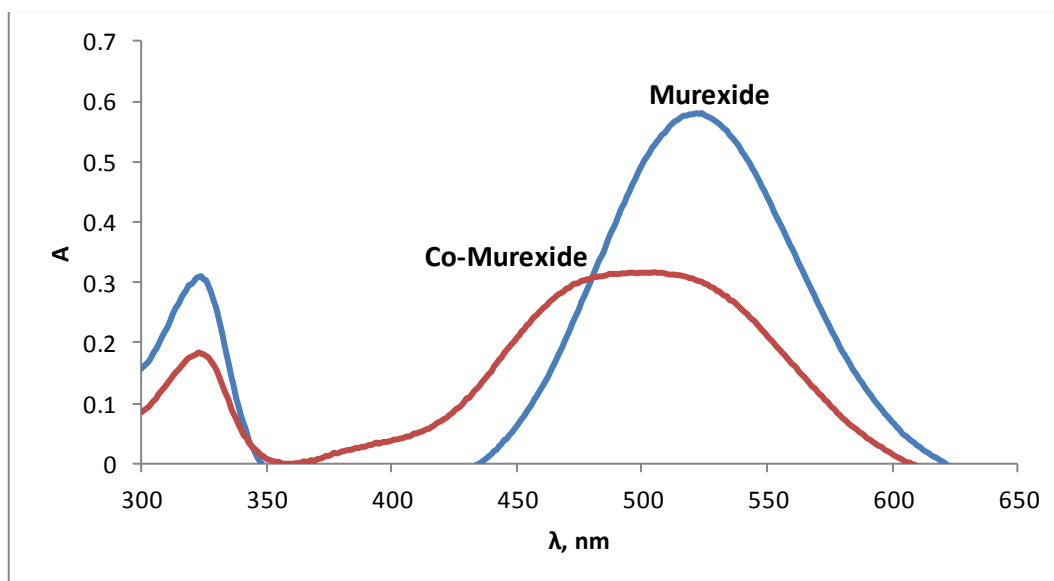**Figure 2. Absorption Spectra of Murexide and Ni-Murexide Complex**

Figure 3. Absorption Spectra of Murexide and Co-Murexide Complex

The Effect of Time on Complexation

The complex just formed couldn't be so stable and thus dissociate after formation and consequently the study of the complex stability against time is a critical parameter. The two components (metal ion and ligand) are mixed at room temperature, and the absorbance is measured immediately. To examine whether the complex being is dissociated or still developed with time, the absorption of the complex is measured each 15 min and till 180 min as shown in Fig. 4. The absorbance of our complexes is slightly decreased with time indicating the dissociation of the two complexes which due to instability of murexide in aqueous solution.
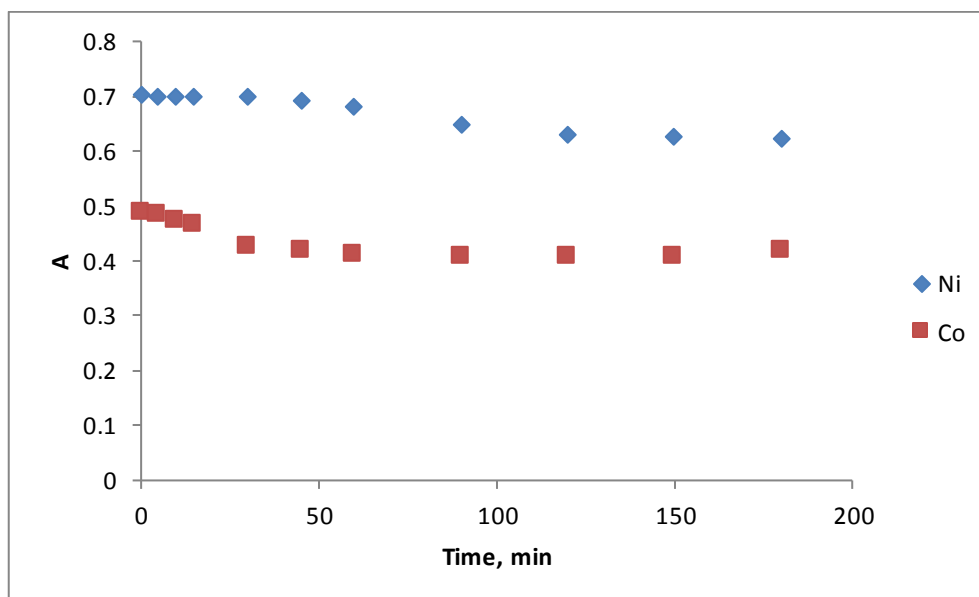
Figure 4. Effect of Time on Ni-Murexide and Co-Murexide Complexes

The Effect of pH on Complexation

The spectra of metal complexes (Co, and Ni) were detected at various pH values. 0.1 M HCl and 0.1 M NaOH solutions were employed to adjust the pH values. The pH is a very important consideration that influences the metal complex formation because all ligands are considered to be weak acids or weak bases which can be protonated or de-protonated according to the pH of the solution. Murexide is a weak base due to the presence of basic nitrogen atoms (Fig. 1). The protonation of the ligand will restrict its capability to complex with metal ion by causing the nonbonding electron-pairs unavailable for complexation and hence reducing the tendency to form complexes with the metal ions. However, the metal ions (Co and Ni) will be precipitated at higher pH values as hydroxides and consequently they will lose the ability for complexation. Therefore, the complex formation equilibria could be affected by the pH value of the solution. The absorption of the two complexes at different pH values is shown in Fig. 5. As can be seen from the figure, the best pH values were: 7.5 – 8.5 for Co (II) and 9.5 -10.5 for Ni and these values are given in Table 1.
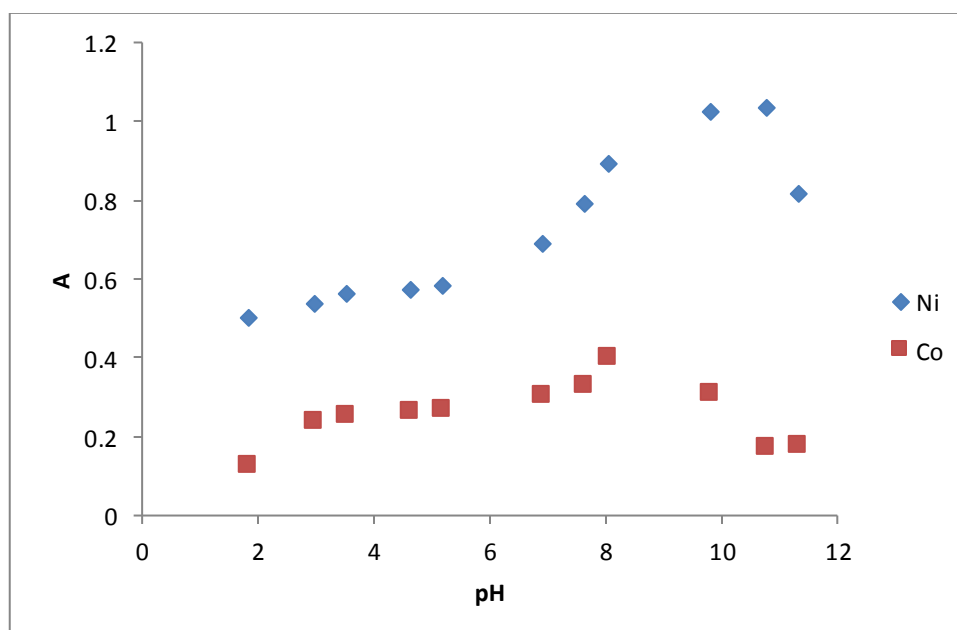
Figure 5. Effect of pH on Ni-Murexide and Co-Murexide Complexes

Determination of Formation Constants (K$_f$) by Job's Method

The method of continuous variation (Job's method) was used to evaluate the stoichiometry and formation constant of the complexes. The absorbance values of the prepared mixtures were drawn versus murexide mole fraction (X$_L$) and shown in Fig. 6 from which the stoichiometry of each complex was then determined. The molar absorptivities, ε, of the prepared complexes were also determined by calculating the concentrations of the complexes at each point and plotting the concentrations versus the absorbance as shown in Fig. 7. Finally, the formation constant of each complex was determined using Job's method. The complex stoichiometry, formation constant, and molar absorptivity values are given in Table 1.
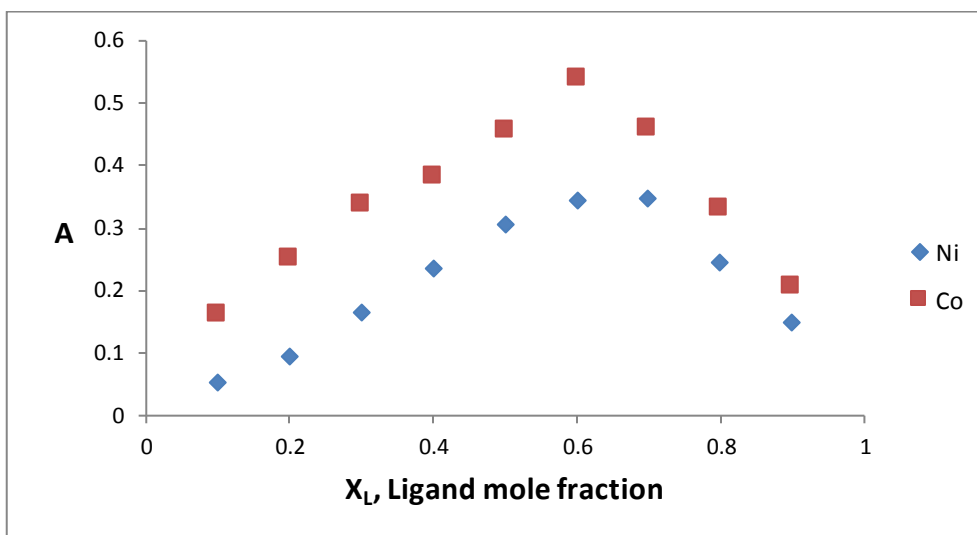

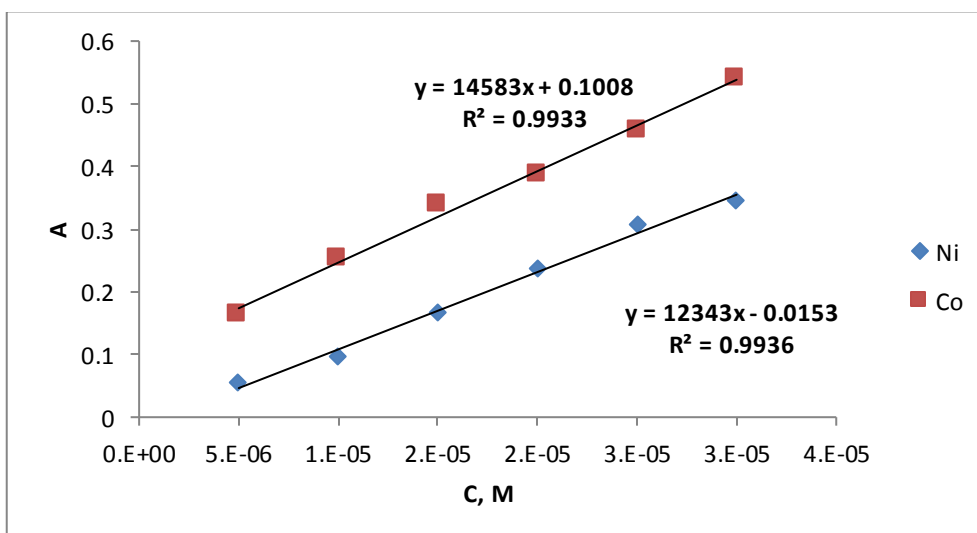**Figure 6. Job$^.$s Plot for Ni-Murexide and Co-Murexide complexes**

Figure 7. Calibration Curves for Ni-Murexide & Co-Murexide complexes (Job$^.$s Method)

Determination of Formation Constants (K$_f$) by Mole Ratio Method

The stoichiometry of murexide complexes with Co(II) and Ni(II) was investigated by the mole ratio method at λ$_{max}$ of each complex. The resulting plots are shown in Fig. 8 and it is obvious that 2:1 (M:L) complexes are formed in the solutions. The formation constants of the resulting complexes were determined at 25ºC by

absorbance measurements of complex solutions in which varying concentrations of metal ions were added to fixed amounts of murexide solution, at λ_{max} of each complex. Formation constants can also be determined from mole-ratio's plots. The complex stoichiometry, formation constant, and molar absorptivity values are given in Table 1. The stoichiometry of all Co-murexide and Ni-murexide complexes were 2:1 (M:L) and the stability order of the complexes had the following order: Co-murexide > Ni-murexide.
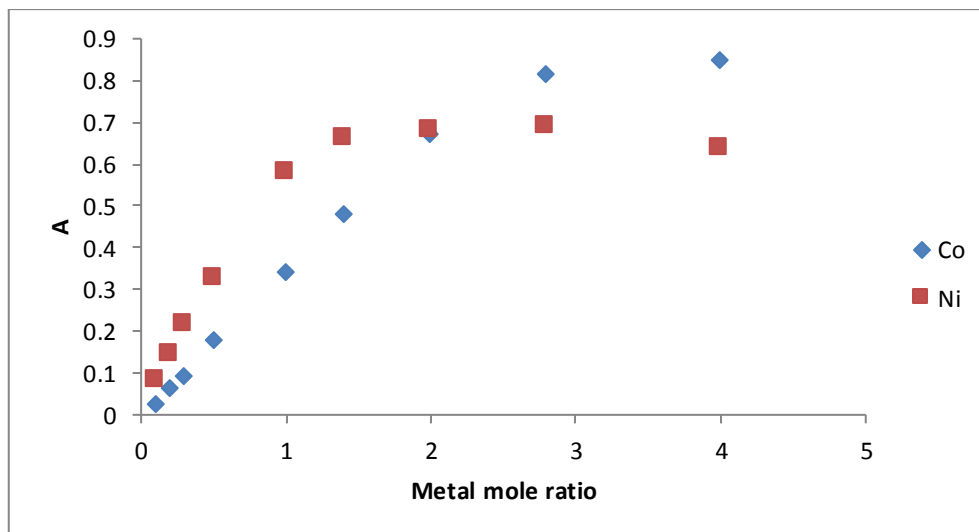

Figure 8. Mole Ratio Method Plot of Ni-Murexide and Co-Murexide complexes
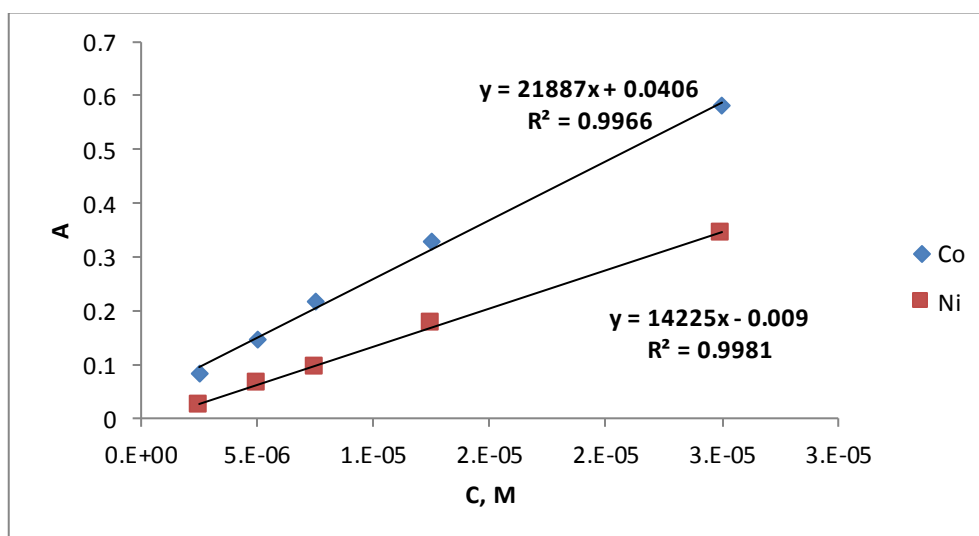

Figure 9. Calibration Curves for Ni-Murexide & Co-Murexide complexes (Mole Ratio's Method)

Table 1. Values of λ_{max}, stoichiometry, formation constant, and molar absorptivity, ε, by Job's Method and Mole Ratio's Method methods

Metal	λ_{max} (nm)	pH	m:n	Job's Method			Mole Ratio's Method		
				$LogK_f$	ε (L.mol^{-1}.cm^{-1})	R^2	$LogK_f$	ε (L.mol^{-1}.cm^{-1})	R^2
Co	460	7.5-8.5	2:1	14.31	14583	0.993	11.96	21887	0.997
Ni	480	9.5-10.5	2:1	11.08	12343	0.994	11.78	14225	0.998

Conclusions

This paper reports the spectrophotometric study of the metal complex of Co (II), and Ni (II) with murexide in aqueous solution. All studied complexes under optimum conditions were stable for at least 3 hours. Stability constants for Co (II), and Ni (II) complexes have been found to be in the order: Co-murexide > Ni-murexide and the values were as follows: 2.06×10^{14}, and 1.21×10^{11} (by Job's method), 9.18×10^{11}, and 6.01×10^{11} (by Mole ratio's method), respectively. The stability is strongly dependent on pH of the solution. The stoichiometric studies by Job method and mole ratio method showed the formation of 2:1 metal to ligand in the two complexes. The molar absorptivity values for Co (II), and Ni (II) were found to be 14583, and 12343 l/mol.cm (by Job's method), and 21887, and 14225 l/mol.cm (by Mole ratio's method), respectively at λ_{max} = 480 and 460 nm, respectively. π-π* and n-π* transitions are responsible for absorption spectra in all complexes indicated by molar absorptivity values.

Conflicts of Interest

Submitting authors are responsible for co-authors declaring their interests.

Funding Statement

Acknowledgments

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