Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2019, 8 (3): 1179-1186

(International Peer Reviewed Journal)

Study on Adduct Formation Constants of Nickel (II) di(o-chlorophenyl) carbazonate with some Selected N-Bases Spectrophotometrically

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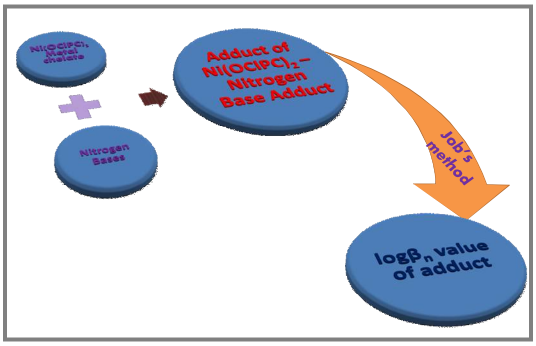
Accepted on 3rd April, 2019

ABSTRACT

Stability constants of adducts formed from nickel(II) di(o-chlorophenyl)carbazonate with various nitrogen bases were determined by Job's method of continuous variation at 27±0.1℃ in chloroform. The impact of the substituent on the variation in the values of stability constants of adduct obtained from the reaction between nickel(II) di(o-chlorophenyl)carbazonate and nitrogen bases in a solution medium has been studied in comparison with adducts of nickel(II) diphenylcarbazonate. The results of our study were discussed by considering basicity of nitrogen bases, steric effects induced by various substituents and ring structure.

Graphical Abstract



Keywords: Steric hindrance, N ligands (nitrogen bases), Spectrophotometer, Stability constant (logβ_n), Nickel(II) di(o-chlorophenyl)carbazonate, Adduct.

INTRODUCTION

Nickel in its Ni^{+2} state forms stable complexes with N, O and S donor ligands [1]. Nickel metal atom plays very important role in industry, environmental and as well biological system [2] where as diphenylcarbazone, di(o-chlorophenyl)carbazone and its analogues are toxic towards bacteria and fungi activities [3]. Diphenyl carbazone and its analogues produce colored metal complexes[3] with metal ions such as Ni^{+2}, Co^{+2}, Cu^{+2} that provides the basis for the spectrophotometric determination of these metal ions. Di(o-chlorophenyl)carbazone is a bidentate neutral molecule, which coordinates through the ketonic oxygen and azo nitrogen to bivalent metal ions viz., Ni^{+2}, Co^{+2}, Cu^{+2} and forms corresponding metal chelates.

From the literature survey, it was found that many researchers were attempted to study the stability constants (logβ_n) of metals with different bases and factors affecting stability of a complex such as ligand basicity, solvent effect & steric effects in adduct formation from metal chelates by different techniques viz., potentiometric titrations [**4, 5**], pH metric titrations [**6, 7**], capillary electrophoresis [**8**], spectrophotometric method [**9, 10**] etc. Atnafu et al. studied the complex equilibria of 1,10-phenanthroline with bivalent metal atoms carried pH metrically [**11**]. Even though it has been noted that there were very few references regarding the logβ_n of adducts of nickel(II) chelates of di(o-chlorophenyl)carbazone with nitrogen bases and also less information is known about the factors which affect the stability of adduct and methods employed were very complicated and requires much time to produce results.

Work reported in this paper is an approach to inspect the stability constant values (logβ_n) of nickel(II)di(o-chlorophenyl)carbazonate [$Ni(OClPC)_2$] with different nitrogen bases in the simplest way by means of spectrophotometrically by considering the steric hindrance and effect of substituents with pyridine and aniline and other nitrogen bases spectrophotometrically by Job's method in chloroform at 27±0.1^{0}C. The method reported in this work to calculate the logβ_n values of adducts is an uncomplicated method of all the available methods, easy to handle and with high precession.

MATERIALS AND METHODS

Apparatus: Bausch and Lomb Spectronic 2000 spectrophotometer was used to record absorbance values of $Ni(OClPC)_2$ chelate and its adduct with nitrogen bases at 27±0.1°C. IR spectra of the ligands is recorded in the range 4000-5000 cm^{-1}. FTIR Perkin Elmer spectrophotometer was employed to get IR spectra of ligand. KBr pellet technique was used to prepare sample for analysis.

Reagents: Analytical grade reagents were used. Di(o-chlorophenyl)carbazone was prepared by the technique depicted elsewhere[**12**], involving persulphate oxidation of di(o-chlorophenyl)carbazide. Di(o-chlorophenyl)carbazone was synthesized by heating o-chlorophenylhydrazine and urea for 3 h at 155°C. The melting point of di(o-chlorophenyl)carbazone was found to be 134°C. Di(o-chlorophenyl)carbazone prepared was confirmed by IR spectra (Figure 1)Aniline, 2-methylaniline, 3-methylaniline (B.D.H), 2,4-dimethylaniline, 2,6-dimethylaniline, 2-chloroaniline, 3-chloroaniline, 4-chloroaniline, 4-bromoaniline (Merck), pyridine (Fisher), 2,4-lutidine, 3,4-lutidine, morpholine, piperidine, 2-chloropyridine (Merck), 2-picoline, 3-picoline, 4-picoline, 2,4,6-collidine(B.D.H) were dried over potassium hydroxide and distilled. The constant boiling fraction was collected and used. 4-Methyl aniline (Aldrich), neocuproine, 2,2'-bipyridyl, 1,10-phenanthroline, ethylenediamine (Merck), 2-aminopyridine, 4-aminopyridine, 2-amino-4-methylpyridine, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline (B.D.H) and nickel chloride hexahydrate (Merck) were used without purification. Chloroform of Fisher AR grade.

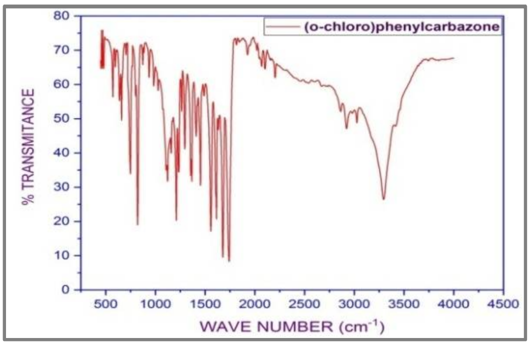


Figure 1. IR spectra of di(o-chlorophenyl)carbazone ligand.

FTIR Spectra of di(o-chlorophenyl)carbazone: In the IR spectra of di(o-chloro) phenylcarbazone, IR band appeared at 1679 cm^{-1} is attributed to the C=O stretching. Band appeared at 3298 cm^{-1} is due to the N-H stretching, peaks obtained at 2943 and 3031 cm^{-1} represents the stretching frequencies of SP^2 hybridized aromatic C-H group in the molecule and IR peaks obtained at 1554 cm^{-1} and 1612 cm^{-1} are attributed to the aromatic C=C in the compound. Single peak at 745 cm^{-1} and 828 cm^{-1} are attributed to the ortho substitution to the benzne ring and C-Cl group in the molecule respectively.

Preparation of nickel(II) di(o chlorophenyl) carbazonate: 1g of nickel chloride hexa hydrate was weighed and which was dissolved in 50 mL of acetate buffer of pH 6, the total content was heated to 60°C and di(o-chlorophenyl)carbazone was dissolved in alcohol which was slowly added to the metal solution with constant stirring. The resultant solution was diluted with water, the precipitate obtained was digested on low heat for about one 1 h. Later it was filtered under suction and washed with water and finally with alcohol. The product obtained was dried at room temperature over phosphorus pentoxide under vacuum for 12 h. The total content of nickel of the resultant complex was found to be 8.70% by phenanthroline-dithizone method [13] (Calculated 8.68%)
Analytical data of metal chelate ($C_{26}H_{18}N_8O_2Cl_4Ni$).

Calculated (%)	Ni 8.70	N 16.59
Found (%)	Ni 8.68	N 16.62

Selection of analytical wavelength: Vosburgh and Cooper method [14] was used to select analytical wavelength, in this technique equimolar solutions of $Ni(OClPC)_2$ and ligand solutions were prepared in chloroform. The absorbance of the metal chelate and adduct formed was scanned in the range of 400-800 nm separately by selecting chloroform as a reference to determine the λ_{max} using a UV-Visible spectrophotometer. The wavelength of maximum absorption was found to be 580nm (Figure 2).

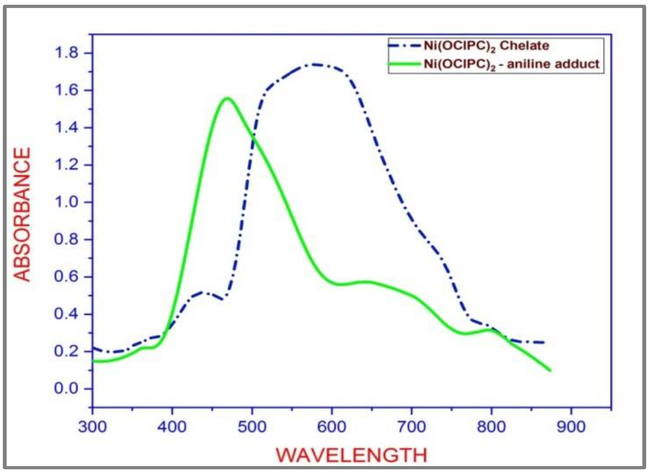


Figure 2. UV-Visible absorption spectra of $Ni(OClPC)_2$ and $Ni(OClPC)_2$-aniline adduct system in chloroform $[Ni(OClPC)_2]=1.5X10^{-5}$ M. $[Aniline]=1.5X10^{-5}$ M.

Determination of adduct formation constants: $\log\beta_n$ values of $Ni(OClPC)_2$ with nitrogen bases have been determined spectrophotometrically by Job's method of continuous variation by selecting maximum absorbance by Vosburgh and Cooper method [14]. To determine adduct formation constants by Job's method, series of solutions were prepared by mixing $Ni(OClPC)_2$ and nitrogen bases in varying proportions [15] keeping both the number of moles of $Ni(OClPC)_2$ and nitrogen base constant but varying mole fractions of $Ni(OClPC)_2$. The absorption of all the adducts prepared by mixing metal chelate and nitrogen base were recorded at a wavelength of 580 nm. Further absorbance values of adduct with varying mole fraction of metal chelate was recorded at 27±0.1°C, and by using these values Job's plots were constructed as shown in figure 3 to 6.

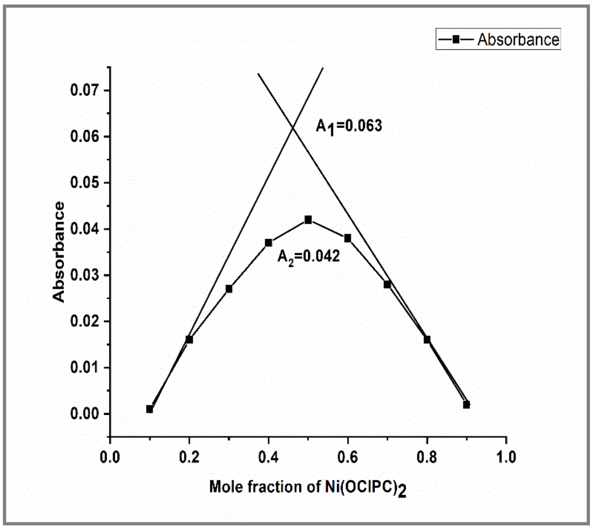


Figure 3. Job's plot of equimolar solutions of $Ni(OClPC)_2$ ($5.9X10^{-5}$M) and 1,10-phenanthroline ($5.9X10^{-5}$M)at 27±0.1°C in chloroform medium.

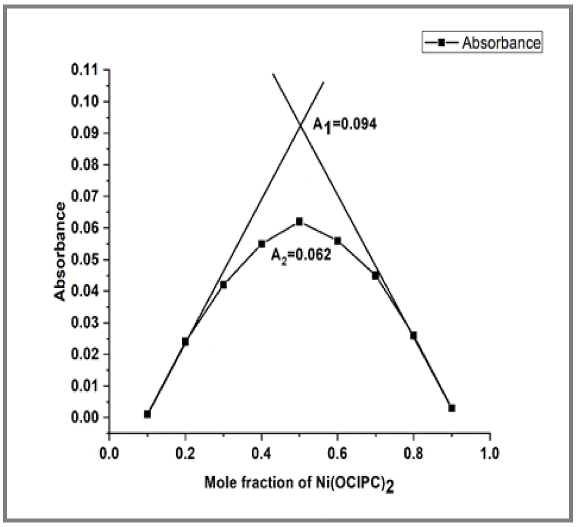


Figure 4. Job's plot of equimolar solutions of $Ni(OClPC)_2$ ($5.9X10^{-5}$M) and 2,2'-bipyridyl ($5.9X10^{-5}$M) at 27±0.1°C in chloroform medium.

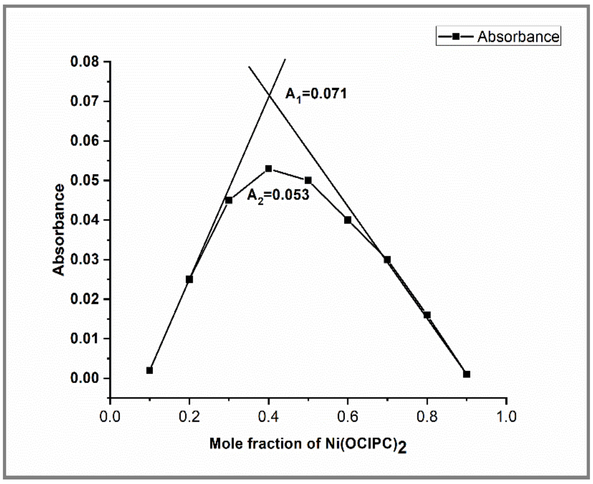


Figure 5. Job's plot of equimolar solutions of $Ni(OClPC)_2$ ($5.9X10^{-1}$M) and pyridine ($5.9X10^{-1}$M) at 27±0.1°C in chloroform medium.

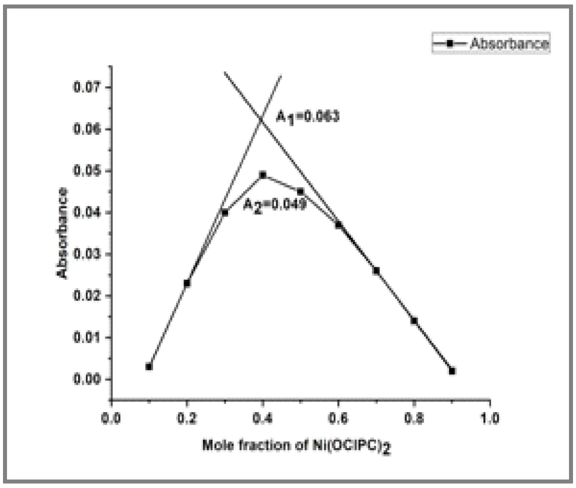


Figure 6. Job's plot of equimolar solutions of $Ni(OClPC)_2$ ($5.9X10^{-1}$M) and 2,4-dimethyl aniline ($5.9X10^{-1}$M) at 27±0.1°C in chloroform medium.

Calculations: Graph was constructed by using the values of absorbance of adduct formed versus mole fraction of a metal chelate [$Ni(OClPC)_2$], logβ_n values of the adducts of $Ni(OClPC)_2$ with nitrogen bases were determined with help of below mentioned equation [15, 16],

$$\log\beta_n = \frac{\left({}^{A_2}/_{A_1}\right)}{\left(1-\frac{A_2}{A_1}\right)\left(C_L - C_M\, X\frac{A_2}{A_1}\right)} \text{……..}(1)$$

Where, βn: adduct formation constant, A_1: absorbance at breakpoint, A_2: actual absorbance, C_M: concentration of $Ni(OClPC)_2$, C_L: concentration of nitrogen base (ligand).

RESULTS AND DISCUSSION

The literature survey concedes that few workers attempted to study the stability constant values of divalent metals with different bases [1, 3, 4, 17]. In continuation with our earlier work on determination of stability constants of nickel(II) chelates with various nitrogen bases[18], the present study of the determination of stability constant of $Ni(OClPC)_2$ with N-bases considered is the most accurate method for evaluation of stability constant of complexes.$Ni(OClPC)_2$metal chelate which was considered for our study is paramagnetic[19], air stable, non-hygroscopic and soluble in polar and non-polar solvents. It forms red colored solution in organic solvents like chloroform and carbon tetrachloride and forms pink color in anilines, substituted anilines, pyridines and substituted pyridines (N-bases), this may be likely due to the interaction between metal chelate and added reagent and hence leads to the evolution of the $Ni(OClPC)_2$–n-base adduct of the following type:

$$\mathrm{Ni(OCIPC)_2 + n\ Base \rightleftharpoons Ni(OCIPC)_2\ .\ nBase}$$

The equilibrium constant of the nickel(II)chelate-base adduct formed from the $Ni(OClPC)_2$ and nitrogen bases can be studied spectrophotometrically. Since $Ni(OClPC)_2$ and nitrogen base adduct of $Ni(OClPC)_2$ absorbs at different wavelengths.A chloroform solution of $Ni(OClPC)_2$ exhibits a λ_{max} at 580 nm and shoulder peak at 430nm, after adding nitrogen base to $Ni(OClPC)_2$ chelate, λ_{max} shifts around 520 nm. The change in the spectra of $Ni(OClPC)_2$ on the addition of nitrogen base could be utilized to determine the formation constant of adducts[20] (Figure 2).

The logβ_n values of the $Ni(OClPC)_2$-nitrogen base adducts calculated from Job's method at 27±0.1°C in chloroform are listed table 1 along with their pKa values.The stabilities of $Ni(OClPC)_2$ adducts with nitrogen bases considered for our study were found to raise in the following order:
2-chloro aniline < 2,6-dimethyl aniline, 2-chloropyridine < 3-chloro aniline < piperidine < 4-bromo aniline < morpholine < 2-methylaniline < 2,4-dimethylaniline < 4-chloroaniline < quinoline < 2-picoline < 2,4-lutidine < 2,4,6-collidine < aniline < 3-methylaniline < 4-methylaniline < 2-aminopyridine < 2-amino-4-methylpyridine < 3-picoline < pyridine < 4-picoline, 3,4-lutidine < 4-aminopyridine < ethylenediamine < 2,9-neocuproin < 2,2'-bipyridyl < 1,10-phenanthroline.

The logβ_n values for adducts of $Ni(OClPC)_2$ with anilines, substituted anilines, pyridines and substituted pyridines increases steadily with the increase in pKa values as expected from general trend. But in case of 2-methylaniline, 2-chloroaniline and2-aminopyridine there is a decrease in the stability of adducts compared to aniline and pyridine respectively, even though their pKa values are higher than aniline and pyridine, which is indicative of steric hindrance caused by the methyl, chloro and amino groups in the ortho position. A similar effect was also seen in 2,4-dimethylaniline, 2,6-dimethylaniline as an impact, these bases form less stable adducts instead of forming stable adducts as hypothecated with a view of pKa values of these bases. The logβ_n value for $Ni(OClPC)_2$-4-chloroaniline adduct was noticed to be greater than that of $Ni(OClPC)_2$-4-bromoaniline. Since it is case of 4-substituted aniline and pyridine logβ_n value strongly based on the electron withdrawing or donating nature of the substituent [21]. Therefore logβ_n of $Ni(OClPC)_2$-4-chloroaniline adduct relative to the $Ni(OClPC)_2$-4-bromoaniline adduct denotes the increased donor capacity of nitrogen atom due to substituent effect. Similarly, stability constant of 2-chloropyridine was observed to be lower than 2-aminopyridine this can also be evaluated to the electron withdrawing or donating behavior of the substituent in nitrogen base.

The logβ_n value of adduct formed from $Ni(OClPC)_2$ with morpholine was found to be very low when compared to its pKa value, this may be because of the decrease in the basicity of the nitrogen atom present in the morpholine ring. On other hands, lower logβ_n value for the piperidine was evaluated to the saturity of the ring. Stability constant value for the $Ni(OClPC)_2$-4-picoline adduct is found to higher than that of $Ni(OClPC)_2$ - pyridine, this is due to the methyl substitution at position 4 is more reactive due to increased basicity and it does not possess any sterically hindering group. The identical outcome was supposed for substitution in the 2-position, as a result much lower logβ_n values were observed for the Ni(OClPC)$_2$ - 2-picoline adduct. Among lutidines, 2,6-lutidine forms weaker adducts, as both the methyl groups being adjacent to the nitrogen atom and hence offers strong steric hindrance. In case of 2,4-lutidine and 3,4-lutidine, there is a contraction in the stability of adducts, which indicates the steric hindrance initiated by the methyl groups present adjacent nitrogen atom. The lower logβ_n values of 2,4-lutidine, 2-picoline and 2,4,6-collidine compared to pyridine are due to the steric hindrance extended by the methyl groups existing at 2- and 6- positions even though their pKa values are higher than pyridine. logβ_n value of 2-aminopyridine and 2-amino-4-methyl pyridine are appeared to be smaller compared to 4-aminopyridine, a contraction in the stability of adducts is raised due to the steric effect offered by the amino group in the ortho position.

Table 1. Adduct formation constants of nickel(II)di-o-chlorophenylcarbazonate and nickel(II) diphenylcarbazonatewith nitrogen bases

Nickel(II) di-(o-chlorophenylcarbazonate) adducts				
Nitrogen Bases	**pKa**	**N**	**λ_{max} (NM)**	**logβ_n**
Aniline	4.63 [15]	2	520	2.31
2-Me aniline	4.44 [15]	2	520	1.31
3-Me aniline	4.73 [15]	2	520	2.39
4-Me aniline	5.08 [15]	2	520	2.64
2,4-di Me aniline	5.00 [15]	2	520	1.33
2,6-di Me aniline	4.10 [15]	2	520	0.92
2-chloroaniline	2.65 [15]	2	520	0.84
3-chloroaniline	3.46 [15]	2	520	1.04
4-chloroaniline	4.15 [15]	2	520	1.50
4-bromoaniline	3.86 [15]	2	520	1.18
Piperidine	11.12 [15]	2	520	1.17
Morpholine	8.35 [15]	2	520	1.30
Quinoline	4.90 [15]	2	520	1.79
Pyridine	5.20 [15]	2	520	3.21
2-picoline	5.90 [15]	2	520	1.83
3-picoline	5.86 [15]	2	520	3.17
4-picoline	6.08 [15]	2	520	3.41
2,4-lutidine	6.79 [15]	2	520	2.11
2,6-lutidine	4.95 [15]	2	520	1.80
3,4-lutidine	6.52 [23]	2	520	3.41
2,4,6-collidine	7.43 [15]	2	520	2.21
2-chloropyridine	-	2	520	0.92
2-aminopyridine	6.82 [23]	2	520	3.03
4-aminopyridine	9.25 [23]	2	520	3.66
2-amino-4-methylpyridine	-	2	520	3.15
2,2'-bipyridyl	4.40 [15]	1	520	5.28
1,10-phenanthroline	4.95 [15]	1	520	5.30
2,9-neocuproin	5.85 [15]	1	520	5.19
Ethylenediamine	6.84 [15]	1	520	5.26

n= number of molecules of base per chelate molecule, logβ_n= stability constant, λmax = maximum absorbance

Ni(OClPC)$_2$-aniline adducts exhibit low values of the formation constant (logβ_n), however, Ni(OClPC)$_{2-}$ pyridine adducts show comparatively higher values of the formation constant, this may be charged due to the weak basic character of aniline and substituted anilines compared to pyridine and substituted pyridines. Thus, it was concluded that bonding in Ni(OClPC)$_2$-L adducts is directly proportional to the basic character the nitrogen bases used for the study. However, bidentate ligands which are considered for our study were appeared to form equally stable adducts. Since adducts formed from bidentate ligands like bipyridyl, 1,10-phenanthroline, ethylenediamine are not adversely influenced by steric hindrance and also because of the re-orientation of the chelate in order to form cis-position for di dentate nitrogen bases [22]. But 2,9-neocuproine, a bidentate ligand which forms a comparatively unstable adduct, formation of the less stable adduct is characterized by the steric hindrance offered by the methyl groups which are adjacent to nitrogen atom blocks the nitrogen atom and hence decreases the stability of adduct.

Further, it was clear that the absorption spectrum of Ni(OClPC)$_2$ chelate remains unchanged on adding 2-nitroaniline, 3-nitroaniline and 4-nitroaniline. This may be diagnosed to the fact that monodentate nitroanilines are extremely weak bases in nature and so for this reason, they are unable to form adducts with the Ni(OClPC)$_2$ under experimental conditions selected for our work.

APPLICATION

Method reported in this work is the simplest, convenient and economic method among all the methods available for the determination of stability constant of adducts. logβ_n values obtained from this work are in good agreement with the other methods reported in literature. Further, results of the work reveals the effect of electron donating or withdrawing nature and steric hindrance caused by the substituents attached to the metal chelate, which suggest that results could be used to predict the stability of hemoglobin-oxygen adduct in human hematology.

CONCLUSION

In the reaction between aniline, substituted anilines, pyridine, substituted pyridines and other bidentate bases with Ni(OClPC)$_2$ chelate, adduct formation constants have been evaluated by Job's method of continuous variation. Further, the influence of electron withdrawing substituents, steric hindrance offered by substituent groups and basicity of nitrogen bases on the stability constant of Ni(OClPC)$_2$ chelate with different mono and bidentate nitrogen bases were studied.

Conflict of Interest: The authors confirm that this article has no conflict of interest.

ACKNOWLEDGEMENT

The authors sincerely thank to the Vijayanagara Sri Krishnadevaraya University, Ballari for providing facilities to carry out this research work.

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