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ORIENTAL JOURNAL OF CHEMISTRY
An International Open Free Access, Peer Reviewed Research Journal

www.orientjchem.org

ISSN: 0970-020 X
CODEN: OJCHEG
2012, Vol. 28, No. (2):
Pg. 949-954

Analytical Application of p-chlorophenylazo-bis-acetoxime (p-CPABA) in the Spectrophotometric Determination of Nickel (II)

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(Received: March 12, 2012; Accepted: May 18, 2012)

ABSTRACT

p-Chlorophenylazo-bis-acetoxime has been used for spectrophotometric determination of nickel (II) at 375 nm and a pH of 7.3-8.1. Beer's law is obeyed in the range of (1.0-6.0) × 10^{-5} M. The molar absorptivity and Sandell's sensitivity values are 5,389 L mol^{-1} cm^{-1} and 10.89 ng cm^{-2} respectively. Value of log â is determined by two different method i.e. Harvey and Manning's method and Purohit's method and the values of it are 9.36 and 9.37 respectively. Hydroxytriazenes have been used as analytical reagents for a number of transition metals. Similar compounds arylazobis-acetoximes developed by Bamberger and subsequently used by Sogani and Bhattacharaya as spectrophotometric reagents for determination of various transition metals such as cobalt, iron and copper. In the present paper p-chlorophenylazo-bis-acetoxime (p-CPABA) has besen used for spectrophotometric determination of nickel (II).

Keywords: p-Chlorophenylazo-bis-acetoxime, Spectrophotometric determination of nickel (II),p-CPABA, Acetoximes.

INTRODUCTION

Arylazo-bis-acetoximes are well established analytical reagents for both complexometric and spectrophotometric determination of transition elements. Bamberger[1-5] proved that they possess the same skeleton as hydroxytriazenes and thus their preparative methods as reported by Mai[6-7] involve coupling of diazonium salt with aldoximes or ketoximes. The application of this class of compounds as analytical reagents is shown by various reviews[8-12] as well as papers[12-14] appearing in last many years. In the present communication a new reagent, p-chlorophenylazo-bis-acetoxime (p-CPABA) has been used first time for the spectrophotometric determination of nickel (II). The reagent (p-CPABA) has been synthesized by using standard methods, duly characterized by IR, elemental analysis (CHN) and m.p. determination etc. proving that compound was obtained in pure form. It was used for the spectrophotometric determination of nickel (II). The studies indicate that the method developed is reasonably sensitive with advantage that it can be applied to nickel samples in presence of 24 different anions/cations with a standard deviation of 0.0248 i.e. 0.43% . Thus the compound is a new addition to reagents available for nickel determination.

EXPERIMENTAL

(A)-Synthesis of p-chlorophenylazo-bis-acetoxime (p-CPABA)

p-chlorophenylazo-bis-acetoxime (p-CPABA) was synthesized per standard method. The general method is described below. The synthesis was done in three steps.

Step: 1 Preparation of acetoximes

In the preparation of p-chlorophenylazo-bis-acetoxime (p-CPABA) 0.1 moles of hydroxylamine hydrochloride was dissolved in minimum quantity of water and to it an aqueous solution of 8 gm. of NaOH was added. After cooling the solution in an ice water bath, acetone (14.7ml) was added slowly followed by shaking for few minutes. This resulted in the separation of acetoxime soon as a crystalline solid. The reaction mixture was filtered and directly used for coupling.

Step: 2 Preparation of aryldiazonium salts

p-toludine (0.1 moles) was dissolved in mixture containing 24.7ml of HCl and 25 ml of water. In another beaker 7.0 gm. of sodium nitrite was dissolved in minimum quantity of water. The temperature of the aryl amine hydrochloride solution was maintained between 0-5°C. To this solution, sodium nitrite solution was added drop by drop with stirring. The diazotised product so obtained was directly used for coupling.

Step: 3 Coupling

Freshly prepared acetoxime obtained in step-1 was dissolved in 10% sodium hydroxide solution (150ml) and cooled below 5°C. The temperature of diazotised product obtained from step-2 was maintained between 0-5°C. Then step-2 solution was added dropwise to the solution obtained in step-1 and pH of solution was maintained close to 10 and the temperature during the entire course of the reaction was kept below 5°C. The resultant product was filtered, washed with petroleum ether (40-60°C) and dried. The crude compounds was purified and recrystallized. The purity of the compound was checked by I.R. studies and physical characteristics. The compositions were verified by elemental analysis. All these data have been given in Table 1. p-chlorophenylazo-bis-acetoxime(p-CPABA) was subjected to four spot tests as described by Purohit and this reagent gave positive test with all the four testing methods, proving the purity of the compound.

(a) α-naphthylamine test
(b) Picric acid test
(c) Sulfuric acid test
(d) N, N-Dimethylaniline test

Various peaks given in the Table-2 clearly confirms the presence of all these bands thus proving purity of the compound.

Table 1: Elemental analysis of p-chlorophenylazo-bis-acetoxime (p-CPABA)

Molecular Formula of p-CPABA	Molecular Weight	m.p. °C		Elemental Analysis C%	N%	H%
$C_{12}H_{17}N_4O_2Cl$	272.26	119	Th.	50.61	19.68	5.98
			Exp.	50.13	19.45	5.89

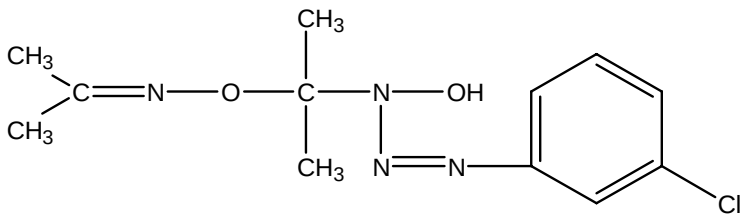

Fig 1. Structure of p-chlorophenylazo-bis-accetoxime

Table 2: Characteristic IR Bands Obtained for p-CPABA

IR Bands Obtained(cm^{-1})			
ν_{OH}	ν_{N-H}	δ_{N-OH}	δ_{N-H}
3558	3315	1082	1510

Table: 3 Result of precision studies

Name of the reagent	Nickel (II) taken in ppm	Nickel (II) found in ppm
p – CPABA	5.869	5.869 ± 0.025

(B)Spectrophotometric determination of Nickel (II) with p-CPABA

Preparation of solutions

Reagent solution

A fresh stock solution of 1.0×10^{-2} M of the reagent(p-CPABA) was prepared by dissolving requisite quantity of the reagent in ethanol .Dilute solution was prepared from this stock solution and when required.

Standard solution of nickel (II)

A 1.0×10^{-2} M stock solution of Ni (II) was prepared by dissolving the requisite quantity of Ni (II) sulphate heptahydrate(A.R. grade) in double distilled water. It was standardized with standard EDTA solution using xylenol orange as an indicator. Weaker solutions were prepared by appropriate dilution of the stock solution with double distilled water.

Solutions for pH adjustment

Tris-buffer solution: An aqueous solution of 2% (w/v) tris buffer was prepared by dissolving it in double distilled water.

Instruments

The spectrophotometric study was carried out on Systronic- 108 UV-Vis spectrophotometer Systronic pH meter-324 was used for pH measurement.

Procedure

Following set of experiments were carried out for the spectrophotometric determination of Ni (II).

Selection of suitable working wavelength

Ni (II) and reagent solution were taken in 10 ml volumetric flask such that in the final solution ratio of metal to reagent was 1:5. Absorbance of solution against its reagent blank was measured in the wavelength region 360- 460nm. The wavelength where there was maximum difference between due to complex and that due to the reagent was selected as working wavelength(375nm).

Effect of pH on absorbance

Absorbance of the solutions at various pH values containing Ni (II) and reagent solutions in the ratio of 1:5 were taken at working wavelength 375 nm against reagent blank. The optimum pH range for constant maximum absorption was selected.

Composition of the nickel (II) complex

The composition of the Ni (II) complex with was determined using Job's method and Yoe and Jone's mole ratio method[13-14].

Job's method

The composition of Ni (II) complex with p-CPABA was determined at two different concentrations with Job's method[13]. For each concentration, set of solutions was prepared by varying the volume of equimolar Ni (II) and reagent solution from 0 to 6 ml. After pH adjustment, the solutions were marked (10 ml.) with ethanol. The absorbance of solution was measured at suitable working wavelength against reagent blank. The second set of this method differed from the first set only in the concentration used. By this method the composition was found to be 1:2 [Ni: R].

Mole ratio method of Yoe and Jone's[14]

In this method Ni (II) concentration was kept constant and reagent concentration was varied. A series of solutions having Ni (II) to reagent ratio 1:0.4 to 1:10 were prepared with maintaining the pH of constant absorbance. Absorbance of each solution of a set was measured at working wavelength against the reagent blank. By this method the composition was found to be 1:2 [Ni: R].

Beer's Law

A set of solution having metal to ligand ratio 1:5 was prepared. The studies were performed under optimum condition of pH, concentration and solvent at corresponding working wave length. The absorbance was measured for the complex against the reagent blank. The straight line shows that the Beer's law is valid in the entire concentration range studied.

Precision Studies

Taking appropriate concentration of Ni (II) and a Ni:R (1:5), a set of ten solutions was prepared under optimum conditions of complex formation. Absorbance of each complex was measured against reagent blank. The results of precision studies reveal that by using this method Ni (II) can be determined at ppm level with good precision.

Interference studies

Interference of various cations and anions in the determination of nickel was studied at 5, 10 and 100 ppm level. Interference was studied using following 24 cations and anions, viz. Na (I), K (I), NH_4 (I), Mn (II), Ba (II), Pb (II), Cd (II), Ca (II), Mg (II), Co (II), Cu (II), Zn (II), Cl^-, Br^-, I^-, F^-, CH_3COO^-, CO_3^{2-}, SO_4^{2-}, NO_2^-, NO_3^-, $S_2O_3^{2-}$,WO_4^{2-} and $C_2O_4^{2-}$. It was observed that in the determination of 5.869 ppm Ni

Table 4a: Spectrophotometric Determination of Ni (II) with p-CPABA

Ni(II)complex with reagent	Composition of the complex [Ni(II):R]	Working Wavelength (nm)	Optimum pH range	Beer's Law range (M)	Molar absorptivity [mol{ 1 cm-1]
p-CPABA	1:2	375	7.3-8.1	1.0 x 10^{-5} to6.0x10^{-5}	5,389

Table 4b: Spectrophotometric Determination of Ni (II) with p-CPABA

Sandell's Sensitivity ng cm^{-2}	Ni(II) taken in ppm	Standard Deviation in ppm	% error	log β from Harvey and Manning'smethod	logβ from Purohit's Method
10.89	5.869	0.0248	0.43	9.36	9.37

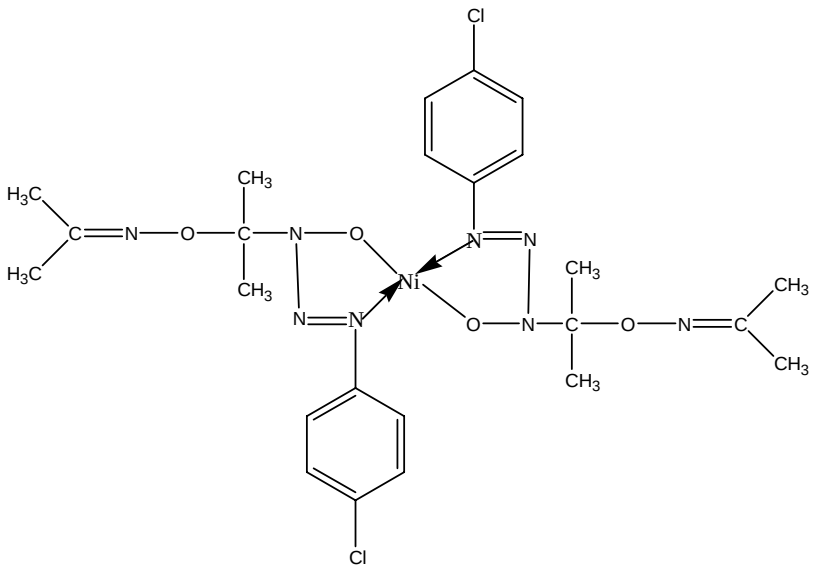

Fig 2. The tentative structure of 1:2 complex of Ni(II) with p-chlorophenylazo-bis-acetoxime

Table 5: Values of log β and ΔG by two different methods

Name of method	Reagent	Composition of complex	Conc. of complex (M)	Em	Es	α	K_{inst}	β × 10^{12}	log β	ΔG at 27°C Kcal mol^{-1}
Harvey and Manning's method	p-chloro phenylazo-bis -acetoxime (p-CPABA)	1 : 2	$5x10^{-5}$	0.268	0.185	0.310	$4.3175x10^{-10}$	$2.3161x10^{9}$	9.3647	-12.8560
Purohit's method	p-chloro phenyl azo-bis-acetoxime (p-CPABA)	1:2	$2x10^{-4}$	0.850	0.740	0.129	$0.0394x10^{-8}$	$2.5359x10^{8}$	9.4040	-12.9099
		1:2	$1x10^{-5}$	0.467	0.370	0.208	$0.0454x10^{-8}$	$2.2002x10^{8}$	9.3424	-12.8254

(II), 10 ppm of Mn (II), Pb (II), Co (II), Cu (II), Zn (II), and $C_2O_4^{2-}$ ions interfered. Ba (II), Mg (II), $S_2O_3^{2-}$ and CH_3COO^- ions interfered at 50 ppm. The remaining 14 ions viz Na (I), K (I), NH_4 (I), Cd (II), Ca (II), Cl^-, Br^-, I^-, F^-,CO_3^{2-}, SO_4^{2-}, NO_2^-, NO_3^- and WO_4^{2-} which did not interfere up to 50 ppm level also did not interfere at 100 ppm in the Ni (II) determination. Thus, it was found that nickel (5.869) could be determined of any interfering species present even at100 ppm level.

Sandell's sensitivity

The molar absorptivity of the Ni (II) complex was calculated from the Beer's law graph and it was found to be ε=5389 L/mol cm. The value thus obtained was used for determining Sandell's sensitivity of the complex that was 10.89ng/cm^2.This value shows that the method is quite sensitive and satisfactory for the determination of Ni (II).

RESULTS AND DISCUSSION

As described in the Table 5, the reagent forms 1:2 complex with p-CPABA. The conditional stability constants have also been given in the table, determined using two different methods. The results agree well as seen from the log â values from both the methods. Precision studies further validate the applicability of method using the reagent. Further, the results of interference studies indicate that the method can be successfully applied in presence of number of cations as well as anions. Hydroxytriazenes as well as acetoximes act as bidentate ligands and in the present case the reagent has been found to form a 1:2 complex with p-CPABA which indicates a tetracoordinated nickel (II) complex with a probable geometry being square-planar.Thus structure of Ni(II):R complex is given in Fig. 2.

REFERENCES

1. DN Purohit; Nizamuddin ;Golwalkar A M; *Rev.Anal. Chem. (Israel)*, **8,** 76 (1985).
2. DN Purohit; Tyagi M P; Bhatnagar R; Bishnoi R; *Rev.Anal. Chem. (Israel)*,**9**, 269 (1992).
3. D Chakravorti; AK Majumdar, *J. Indian Chem.Soc.,* **54,** 258 (1977).
4. RL Dutta; R Sharma, *J.Sc. and Ind. Res.,* **40,** 715 (1981).

5. DK Gorji ; RS Chauhan; AK Goswami; DN Purohit, *Rev.Anal. Chem. (Israel),* **17(4)**, 223 (1998).
6. J Mai *Chem. Ber.,* **25,** 1685 (1892).
7. AE Harvey; DL Manning, *J. Am. Chem. Soc.,* **74,** 4744 (1952).
8. S Ressalan; RS Chauhan, AK Goswami; DN Purohit, *Asian J. Chem.*, **11,** 123 (1999).
9. Bamberger E, et al. *Ber.*,**25,** 1685 (1892).
10. G Ram; RS Chauhan; AK Goswami; DN Purohit, *J. Indian Chem. Soc.*, **80,** 65 (2003).
11. S Khan; R Dashora; A Mehta; AK Goswami, *J. Indian Chem. Soc.,* **80,** 793 (2003).
12. G Ram; RS Chauhan; AK Goswami; DN Purohit, *J. Indian Chem. Soc.,* , 896 (2003).
13. Job P, *Ann. Chim.*, **X-9,** 113 (1928).
14. JH Yoe; AL Jones, *Ind. Eng. Chem. Anal. Ed.,* **16,** 111 (1944).