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Research Article

Direct Spectrophotometric Determination of Nickel (II) With *p*-Methoxyphenylazo-bis-acetoxime

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ABSTRACT

A new reagent *p*-methoxyphenylazo-bis-acetoxime has been used for spectrophotometric determination of Ni (II). Nickel forms a 1:2 (Ni: R) ethanol soluble light yellow complex with the reagent. The working wavelength was taken at 370 nm (ε-3800) in the *p*H range 7.1-8.1. Beer's law obeyed between 0.117 - 0.939 ppm and Sandell's sensitivity is 15.44 ng/cm^2.The values of log β found from the two different methods were 8.65 and 8.67, respectively. Interference of 24 diverse ions has been examined.

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Keywords: spectrophotometry / *p*-methoxyphenylazo-bis-acetoxime /nickel (II) /hydroxytriazene

1. INTRODUCTION

Arylazo-bis-acetoximes are similar to hydroxytriazenes. Although a number of studies related to nickel (II) determination using hydroxytriazenes as reagents have been done [1-4], no study has yet appeared on arylazo-bis-acetoximes. Thus, in the present communication of our earlier studies a new reagent *p*-methoxyphenylazobis-acetoxime has been used to determine Ni (II) spectrophotometrically.

2. EXPERIMENTAL

2.1. Synthesis of p-methoxyphenylazo-bis-acetoxime

The preparation of *p*-methoxyphenylazo-bis-acetoxime was carried out in three steps. (Scheme:1)

2.1.1. Synthesis of Acetoxime

Hydroxylamine hydrochloride (13.8 gm) was dissolved in minimum quantity of water. Aqueous solution of sodium hydroxide (8 gm) was then added to it. The solution was then cooled in ice water and acetone (14.7 mL) was then added slowly with stirring for a few minutes. Acetoxime separates out as white crystalline solid. It was then filtered and used for coupling.

2.1.2. Diazotisation of p-methoxyaniline

To 0.10 mole of p-methoxyaniline, 24.7 mL hydrochloric acid was added. The p-methoxyphenyldiazonium chloride salt thus formed was dissolved in minimum quantity of water. Maintaining temperture below 5°C, aqueous solution of sodium nitrite (7gm) was then added slowly and dropwise, under mechanical stirring. Diazotised product is then used for coupling.

2.1.3. Coupling of Acetoxime and p-methoxyphenyldiazonium chloride

Freshly prepared acetoxime was dissolved in 150mL of 10% sodium hydroxide solution and then cooled to 0°C by adding crushed ice to it and surrounding the beaker externally with ice-salt mixture. A solution of p-methoxyphenyl diazonium chloride was then slowly added under mechanical stirring to this solution. The pH was always maintained close to 10 and the temperature during the entire course of reaction being kept close to 0°C.A dark brown coloured granular product was formed. This was filtered under suction, washed with petroleum ether (40°C-60°C) to remove the coloured impurities and dried. It was crystallized twice from ethanol. During the crystallization process heating was done very slowly as rapid and prolonged heating decompose the compound. C H N analysis corroborated the purity of compound. The compound was subjected to IR spectral analysis and following bands were observed. IR (KBr) cm-1: 3290 (O-H str.), 3078 (C-H str. Ar), 2981 (C-H str., CH_3), 1632 (N=N str.), 1419 (N-N str.).The spectra showed the compound to be in pure state. IR spectra (KBr) were recorded on FT IR RX1 Perkin Elmer Spectrometer. Physical characteristics of p-methoxyphenylazo-bis-acetoxime are given in Table 1 and the structure of p-MPABA has been given in Figure-1.

Table 1: Elemental analysis of p-methoxyphenylazo-bis-acetoxime (p-MPABA)

Molecular Formula of (p-M**PABA)**	Mol. Wt	M.P. °C	Elemental Analysis			
				C%	N%	H%
$C_{13}H_{20}N_4O_3$	280.32	132	Th.	55.70	19.99	7.19
			Exp.	55.68	19.75	7.02

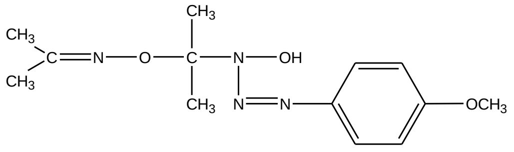
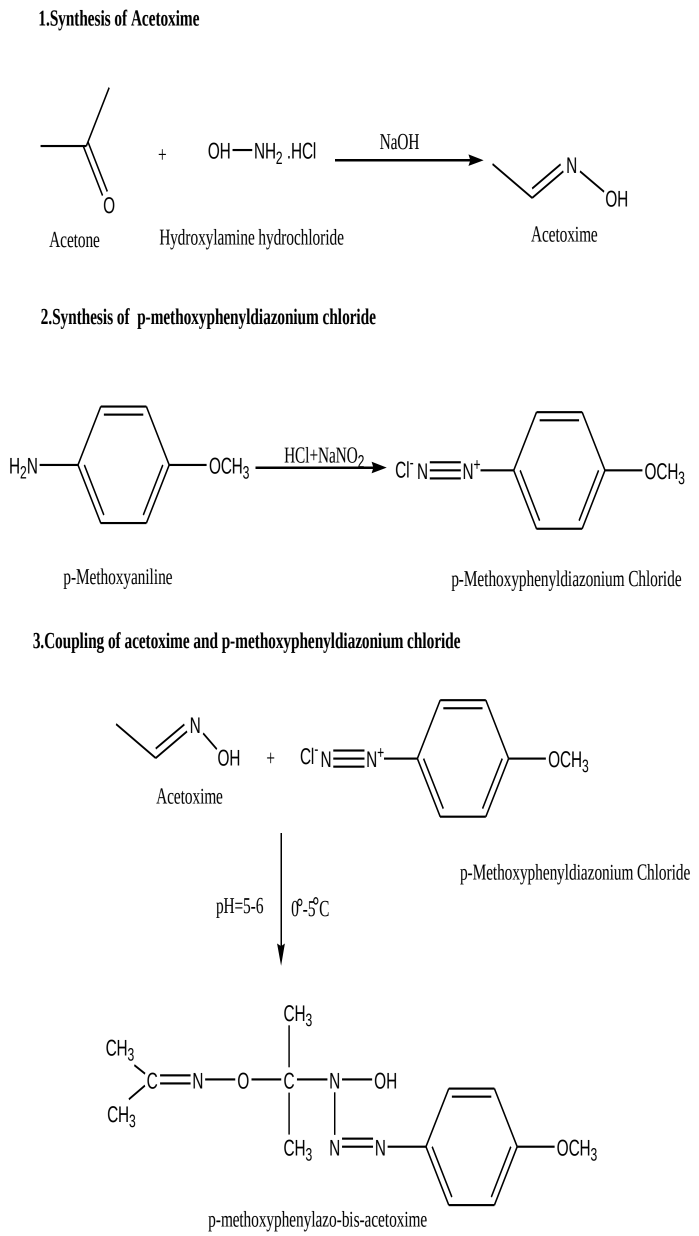


Figure-1:Structure of p-methoxyphenylazo-bis-acetoxime

Scheme:1



2.2. Spectrophotometric determination of Nickel (II) complex with p-MPABA

Reagent solution of desired concentration was prepared by dissolving its requisite amount in ethanol. Nickel (II) solution of desired concentration was prepared by dissolving the requisite amount of nickel chloride hexa hydrate (A.R.) in double distilled water in the usual way and standardised complexometrically with EDTA of corresponding concentration using murexide as an indicator [5]. The desired *p*H of the complex was adjusted with the help of Tris buffer (1%w/v) and perchloric acid (1%v/v). A systronics 106 spectrophotometer was used for absorbance measurements and water proof pH Scan2 tester was used for the pH measurements.

Absorption spectra: Under the optimum condition (pH=7.1-8.1) and fivefold excess of the reagent the absorption spectra of nickel complex was taken. Working wavelength was chosen at 370 nm. Subsequent measurements were made at this wavelength using reagent as a blank. Colour development was instantaneous and all the solutions were made up to desired volume with ethanol.

The composition of the complex was determined by two methods Job's method [6] and Yoe and Jones method [7]. The composition of the nickel complex has been found to be 1:2 (Ni: R) by both of two methods. Beer's law is obeyed in the entire concentration range studied i. e. 0.117 - 0.939 ppm of nickel. The molor absorptivity and Sandell's sensitivity values are 3800 $Lmol^{-1}cm^{-1}$ and 15.44 ng cm^{-2}, respectively, at 370 nm. Standard deviation 'σ' was found to be ± 0.037 for 11.74 ppm of Ni (II), (10 determinations).

Table2: Elemental analysis of 1:2 complex of Ni (II) with p-methoxyphenylazo-bis-acetoxime

Molecular Formula of Complex	MolecularWeight	M.P.°C	Elemental Analysis				
				C%	N%	H%	Ni%
$Ni[C_{13}H_{19}N_4O_3]_2$	617.32	153	Th.	50.59	18.15	6.16	9.51
			Exp.	50.49	18.11	6.09	9.42

Table 3: 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	log β	ΔG at 27°C Kcal mol^{-1}
Harvey and Manning's method	p-methoxy phenyl azo-bis-acetoxime (p-MPABA)	1 : 2	$1x10^{-5}$	0.380	0.253	0.334	$0.2238x10^{-8}$	$4.4686x10^{8}$	8.6501	-11.8760
Purohit's method	p-methoxy phenyl azo-bis-acetoxime (p-MPABA)	1:2	$4x10^{-4}$	1.179	0.648	0.142	$0.2135x10^{-8}$	$4.6822x10^{8}$	8.6704	-11.9028
		1:2	$2x10^{-4}$	1.012	0.506	0.219	$0.21514x10^{-8}$	$4.6473x10^{8}$	8.6672	-11.8984

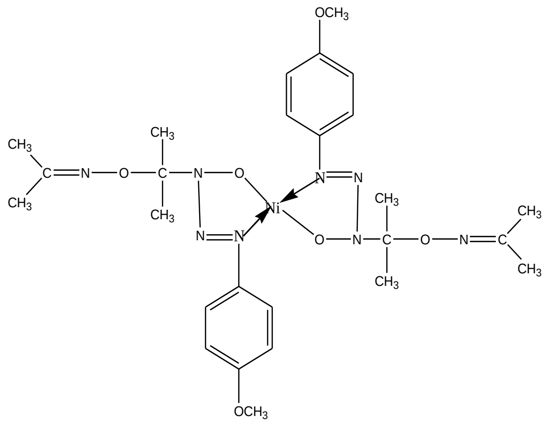


Figure 2: The tentative structure of 1:2 complex of Ni (II) with p-methoxyphenylazo-bis-acetoxime

2.3. Solid complex of Nickel (II) complex with p-MPABA

It has been established that Ni (II) forms instantaneously dark green complex with p-methoxyphenylazo-bis-acetoxime(p-MPABA) in alkaline medium (pH=7.1-8.1).The composition of Nickel complex with p-MPABA has been established by Job's and Mole Ratio methods. The composition of Ni (II) complex has been found to be 1:2 (Ni: p-MPABA). The requisite quantity of p-methoxyphenylazo-bis-acetoxime(p-MPABA) (2.800gm) was dissolved in minimum quantity of ethanol. Similarly requisite quantity of A.R. grade $NiCl_2.6H_2O$ (1.188gm) was dissolved in double distilled water. pH of the Nickel solution as well as p-MPABA solution were adjusted in the range 7.1-8.1 by using tris buffer or perchloric acid. Both the solution was warmed. This was followed by addition of hot solution with continuous mechanical stirring. The ratio in which p-MPABA and Nickel were mixed was 1:2 (Ni: p-MPABA). After complete addition of Nickel solution, the reaction mixture was further stirred for five minutes and kept aside for ten minutes. The green complex formed was filtered under suction and washed with double distilled water to remove un-reacted metal ion. It was then dried and recrystallised with ethanol. Complex formation has been verified by elemental and spectral analysis. Physical and analytical data are given in Table 2. The tentative structure of 1:2 complex of Ni (II) with p-MPABA has been given in Figure 2.

3. RESULTS AND DISCUSSION

Stability constant: The stability constant of nickel complex has been determined by two different methods namely (1) Harvey and Manning's method [8] (using mole ratio curve) and Purohit et al. method [9] (using Job's curve). The log β values obtained from both methods agree well indicating the validity of the methods. Results are given in Table No.3.

Interference studies: Interference studies in presence of 10, 50 and 100 ppm of following 24 cations and anions were performed - 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 11.74 ppm Ni (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 (11.74) could be determined of any interfering species present even at100 ppm level.

4. CONCLUSION

Thus the present investigation has added a new reagent *p*-methoxyphenylazobis-acetoxime for the spectrophotometric determination of Ni (II). This reagent has been shown to be used even in the presence of 14 commonly interfering species as mentioned in the previous paragraphs even up to 100 ppm level. It is easy synthesis; higher yield and economic method for the preparation further enhance its application as spectrophotometric reagent for nickel (II) determination.

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