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2-Hydroxy-4-n-propoxy-5-bromoacetophenone oxime (HnPBAO) as analytical reagent for the gravimetric determination of Pd(II)

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ABSTRACT

2-Hydroxy-4-n-5-bromoacetophenone oxime (HnPBAO) was developed as a new analytical reagent for the gravimetric determination of divalent palladium ion. In the pH range of 2.0 to 5.0, the reagent gave a light brown precipitate with Pd(II). Job's method and mole ratio method revealed that the stoichiometry of the complex is 1:2 (metal : ligand). Beer's law is obeyed upto 37.25 ppm of Pd(II) at 450 nm. Molar absortivity and Sandell's sensitivity at 450 nm were found to be 7.23×10^{-2} lt $mol^{-1}cm^{-1}$ and 0.147 $\mu g/cm^2$ respectively. The stability constant of Pd(II)- HnPBAO complex is found to be 1.27×10^{10}. Gibb's free energy change for complex formation reaction was found to be -13.86 kcal/mol. The reagent can be used for analysis of Pd(II) in palladised carbon and in a binary mixture containing Pd(II) and Ni(II).

Key words: Oxime, Analytical reagent, 2-Hydroxy-4-n-5-bromoacetophenone oxime (HnPBAO).

INTRODUCTION

Analytical chemistry deals with the use of a wide variety of analytical reagents, which include oximes[1], thiosemicarbazides[2], thiosemicarbazones[3], chalcone oximes, imidazoles[4] etc. These reagents can be used for both gravimetric as well as spectrophotometric determination of transition metal ions. In this work, the use of 2-Hydroxy-4-n-5-bromoacetophenone oxime (HnPBAO) as a gravimetric reagent for the determination of Pd(II) has been reported. To confirm the stoichiometry of the complex and to determine the stability constants of the complex, spectrophotometric methods have been used. The reagent has been used to determine Pd(II) in palladised carbon as well as a binary mixture containing Pd(II) and Ni(II).

MATERIAL AND METHODS

Instruments

Spectrophotometric studies were carried out using "Milton Roy"(Spectronic $20D^+$) spectrophotometer. The buffer solutions of required pH were prepared using (sodium acetate-acetic acid) and (hydrochloric acid-sodium acetate) of suitable concentration and the pH was measured using a pH meter "Equiptronics" [EQ-614].

Synthesis of 2-Hydroxy-4-n-5-bromoacetophenone oxime (HnPBAO)

Resacetophenone was prepared using resorcinol, acetic acid and anhydrous $ZnCl_2$. This was treated with bromine in acetic acid and poured on ice-cold water. The product was crystallized from ethanol. 2,4-Dihydroxy-5-Bromoacetophenone obtained was mixed with anhydrous potassium carbonate, n-propyliodide in acetone and refluxed. Hydroxylamine hydrochloride and sodium acetate were added and solution was again refluxed on a water bath. The mixture was poured on ice and light green solid got precipitated which was crystallized from ethanol (m.p 172 ± 1°C). The reagent was soluble in solvents like ethanol, DMF etc.

The elemental analysis of the reagent showed the percentage of carbon, hydrogen and nitrogen as 45.83%, 4.83% and 4.86% respectively. (The calculated value was found to be 46.12%, 4.72% and 4.68% for carbon, hydrogen and nitrogen respectively).

Stock Solutions

A stock solution of Pd(II) 0.05M was prepared by dissolving the requisite amount (0.8871 gm) of $PdCl_2$ in 2 ml Conc. HCl and diluting it to 1000 ml. The solution was standardized gravimetrically using DMG(5). Experimental solutions of required concentration were prepared by appropriate dilution of the stock solution. Solution of the reagent HnPBAO (0.025M) was prepared by dissolving the oxime in pure ethanol.

Gravimetric procedure

A 0.025M solution of the reagent in pure ethanol was used. Palladium chloride solution (0.025M, 10ml) taken in a clean beaker was diluted to about 100ml with distilled water and pH of the solution was adjusted between 3.0 to 4.0 using sodium acetate-hydrochloric acid buffer. The solution was warmed to 60ºC and a small excess of reagent (0.025, 22ml) was added. The light brown precipitate obtained was digested on water bath for 60 min at 60-70°C. The precipitate was filtered through a previously weighed sintered glass crucible(G4) and washed with warm water followed by ethanol to remove excess of the reagent which might have precipitated on dilution. The chelate was dried to constant weight at 110-115°C in hot air oven, cooled and weighed.

Gravimetric determination of Pd(II)

To establish the applicability of the reagent for gravimetric estimation of Pd(II), the metal ion was determined in the pH range 1.5 to 4.0. The maximum error being ± 1.5%. Estimations were done at pH 3.0 using different aliquots of Pd(II). In all cases the error in Pd(II) content did not exceed ± 0.57% Table 1.

Interference

To study the effect of foreign ions on the gravimetric determination of Pd(II), 8-10 mg of various cations were added to a solution containing 26.60 mg Pd(II) at pH 3.0 and gravimetric estimations were done. It was observed that Ca(II), Mg(II), Ni(II), Sr(II), Cd(II), Ba(II), K(I) and Na(I) do not interfere at this pH but Cu(II), Fe(III) and Co(II) interfere seriously. Many common anions like chlorides, bromides, iodides, nitrates, nitrites, sulphates were not found to interfere.

Table 1: Result of gravimetric estimation of Pd(II) at pH 3.0, Pd(II)- HnPBAO

Weight of Pd(II) taken in mg	Weight of Pd(II) complex in mg	Weight of Pd(II) ion found in	Relative Error	
			mg	%
13.30	84.68	13.24	-0.06	-0.45
26.60	171.02	26.74	+0.14	+0.52
39.91	256.62	40.14	+0.23	+0.57
53.21	341.71	53.44	+0.23	+0.43

Spectrophotometric study of Pd(II)-HnPBAO complex

For taking the absorption spectra, a solution of metal ion (0.005 M, 1ml) and reagent (0.01M, 6ml) was taken in a beaker and the pH was adjusted to 3.0 with buffer and the volume was made upto 25ml with DMF. The absorbance was measured in the range 300-800nm. On plotting the absorbance spectra it was observed that the absorbance of the complex increased continuously towards a shorter wavelength. The spectra showed a shoulder band at 450 nm and hence all the measurements were done at 450 nm.

The Pd(II)-HnPBAO complex was found to be insoluble in chloroform, dioxane, ethyl acetate etc, sparingly soluble in ethyl methyl ketone but was soluble in DMF. For spectrophotometric studies varying amounts of Pd(II) solution were taken and pH was adjusted to 3.0 with [sodium acetate - HCl] buffer and HnPBAO solution was added and the volume was made upto 25 ml with DMF and the absorbance measured against reagent blank.

Validity of Beer's law

The Pd(II)-HnPBAO complex in DMF obeys Beer's law up to 37.25 ppm. Beyond this concentration the absorbance plot showed deviation from linearity (Fig. 1). Standard graph thus obtained may be used for the determination of Palladium in an unknown solution using HnPBAO.

Molar absorptivity calculated from Beer's law plot was found to be 7.23 x 10^2 lt/mol/cm for Pd(II)-HnPBAO at 450 nm and Sandell's sensitivity was calculated and found to be 0.147 µg/cm^2 of Pd(II) at 450 nm.

Stoichiometry of complex

The stoichiometry of Pd(II)-HnPBAO complex was determined by Job's method of continuous variation[6] and Yoe Jone's mole ratio method[7] (Fig. 2-3) Both the methods gave the metal:ligand ratio of the complex as 1:2. This is in agreement with the stoichiometry found from gravimetry.

Stability constant of the complex

The stability constants of the complex were calculated using the formula Ks = $(1-\alpha)/4\ \alpha^3C^2$ where α = (Em – Es)/ Em.

Em = maximum absorbance obtained at the intersect of the two lines

Es = absorbance at the stoichiometric ratio of the metal to the reagent in complex.

The average stability constant found from two methods is 1.27 x 10^{10} from Ks value. Gibb's free energy change for complex formation reaction was calculated and its value was found to be –13.86 Kcal/mol at 27°C.

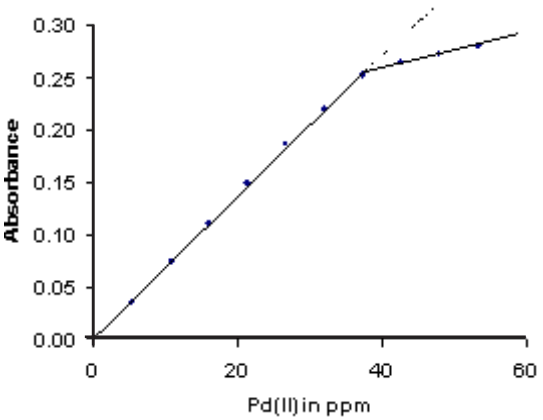

Fig. 1: Beer's Law Plot For Pd(II)-HnPBAO Complex

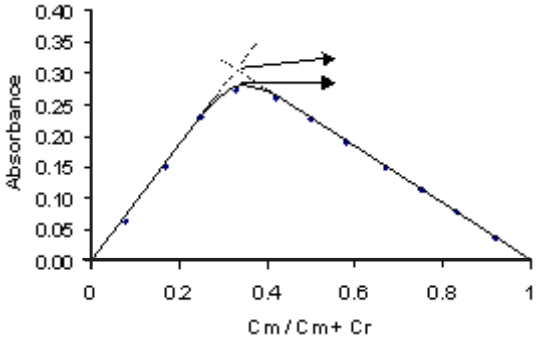

Fig. 2: Job's Method for Pd(II)-HnPBAO Complex Plot of Job's method of variation for determination of M:L ratio 0.001 M Pd(II), 0.001 M HnPBAO, pH = 3.0, λ = 450 nm

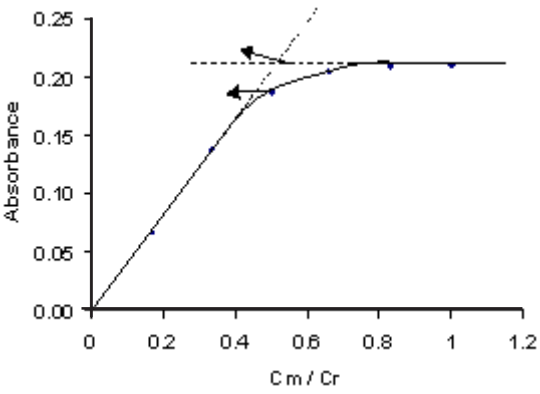

Fig. 3: Mole-Ratio method for Pd(II)-HnPBAO Complex. Plot of Yoe and Jone's method for determination of M:L ratio 0.001 M Pd(II), 0.001 M HnPBAO, pH = 3.0, λ = 450 nm

Table 2: Simultaneous determination of Pd(II) and Ni(II) in a binary mixture using HnPBAO

Metal ion taken in mg.		Weight of Complex in mg.		Weight of metal found in mg.		Error			
Pd(II)	Ni(II)	Pd(II) HnPBAO	Ni(II) HnPBAO	Pd(II)	Ni(II)	Pd(II)		Ni(II)	
						inmg	in%	inmg	in%
53.21	29.35	341.96	317.98	53.48	29.47	+0.27	+0.50	+0.12	+0.40
106.42	29.35	677.75	314.72	106.00	29.17	-0.42	-0.39	-0.18	-0.61
53.21	58.69	338.91	636.94	53.00	59.04	-0.20	-0.39	+0.35	+0.59

Determination of palladium in palladised carbon

A sample of palladised carbon was weighed exactly and dissolved in conc HNO_3 by heating on a sand bath, till a little amount of acid was left. It was treated 2-3 times and then heated to remove excess acid. The solution was diluted to 100 ml.

An aliquot of the above solution was taken in a clean beaker and palladium was determined gravimetrically using HnPBAO. The results were compared with the percentage of Palladium determined using dimethyl glyoxime, a standard method to estimate palladium. Percentage palladium found using HnPBAO is 4.97, using DMG 4.92.

Simultaneous determination of Pd(II) and Ni(II) in binary mixture using HnPBAO

Pd(II) gives a precipitate with HnPBAO at pH 3.0 while Ni(II) does not give precipitate with this reagent at this pH. Ni(II) is precipitated at pH 9.0. Different aliquots of Pd(II) and Ni(II) solutions (0.05 M) were mixed and diluted to 100 ml with double distilled water. pH of this solution was adjusted to 3.0 and the solutions were warmed upto 70°C and treated with slight excess of reagent solution. Light brown precipitate was formed. The precipitate was digested on water bath for 1 hr and filtered through a previously weighed sintered glass crucible (G4) and washed with warm water followed by 90% aqueous ethanol. The chelate was dried at 115^{0}C in a hot air oven, cooled and weighed.

The filtrate along with the washing was concentrated by boiling and the pH of the filtrate was raised upto 9.0 with NH_3-NH_4Cl buffer. A slight excess of reagent solution (0.05 M, 25ml) was added when a light green precipitate was obtained and the precipitate were treated as above and weighed. The results are tabulated in Table 2.

CONCLUSION

2-hydroxy-4-n-propoxy-5-bromo acetophenone oxime (HnPBAO) is a suitable reagent for gravimetric as well as spectrophotometric determination of Pd(II). Many anions and cations were found not to interfere.

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