2-Hydroxy-4-*n*-butoxy-5-bromo propiophenone Thiosemicarbazone as Spectrophotometric Reagent for Iron

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A simple, sensitive and specific spectrophotometric method has been developed for the determination of iron(II) in benzene. The metal ion reacts with 2-hydroxy-4-*n*-butoxy-5-bromo propiophenone thiosemi-carbazone (HBBrPT) forming a dark red coloured complex in the pH range 5.0-9.0. The complex shows maximum absorption at 470 nm. Beer's law is obeyed in the range 13.96 μg/mL. The molar absorptivity and Sandell's sensitivity are found to be 2845 L mol^{-1} cm^{-1} and 0.01962 μg cm^{-2}, respectively. The solid complex have been isolated and charac-terized on the basis of elemental analysis, UV, IR, NMR and mass spectra. 2-Hydroxy-4-n-butoxy-5-bromo propiophenone thiosemicarbazone is found to be a selective and strong chelating agent for iron. The results deduced from Job's method of continuous variation, the mole ratio and the slope ratio method showed that metal: ligand ratio in the complex to be 1:2. The stability constant of the complex found to be 1.22×10^7. The free energy change for the complex formation reaction is found to be -9.989 K cal/mol at 35 ºC. The complex is fairly stable for about 24 h and up to 55 ºC.

Key Words: 2-Hydroxy-4-*n*-butoxy-5-bromo propiophenone thiosemicarbazone, Spectrophotometry.

INTRODUCTION

Thiosemicarbazones have been used for the spectrophotometric determination of iron and other transition metal ions. Thiosemicarbazone are known as analytical reagents[1-5]. Further the metal complexes formed with this reagent are of great medi-cinal value in the treatment of diseases like influenza[6], protozoa[7], small pox[8] and certain kinds of tumour[9]. These reagents are known for their antitubercular activity[10]. Metal chelates of these compounds inhibit tumour growth and increase the activity of some drugs[11]. In the treatment of cancer the active species is the metal chelate of thiosemicarbazone[12]. Metal chelates of these reagents are used as pesticides[13] and fungicides[14] in agriculture.

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EXPERIMENTAL

Shimadzu 160A UV-visible spectrophotometer (Japan) equipped with 1 cm quartz cell was use in these investigations for making absorbance measurements. A pH meter ELICO L 1-120 (ELICO, Hyderabad) is used to make pH measurements. IR spectra of the ligand and complex were recorded on a KBr pellet using Shimadzu-Japan model No. 8400 FTIR.

2-Hydroxy-4-*n*-butoxy-5-bromo propiophenone thiosemicarbazone resaceto-phenone was prepared from resorcinol, propionic acid and anhydrous zinc chloride according to the method of Robinson and Shah[15]. 2-Hydroxy-4-*n*-butoxypropiophenone (HBP) was prepared by using respropiophenone, *n*-butyl bromide and anhydrous potassium carbonate in acetone[16]. Its 2-hydroxy-4-*n*-butoxy-5-bromopropiophenone was prepared by bromination of HBP. Its thiosemicarbazone was prepared by refluxing its alcoholic solution with thiosemicarbazide for *ca.* 4 h[17]. It was crystallized from ethanol. pale yellow crystals were obtained [m.p. 108-109 °C]. The molecular weight determination was carried out by Rast's camphor method. The reagent HBBrPT is easily soluble in ethanol, methanol, chloroform, carbon tetrachloride, benzene *etc.* The structure of the compound is given below (**I**).
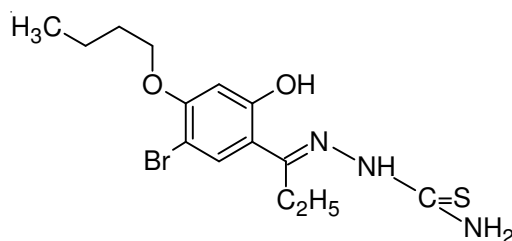
Structure of 2-hydroxy-4-*n*-butoxy-5-bromo propiophenone thiosemicarbazone

The 0.1 M stock solution of Fe(II) has been prepared by dissolving requisite quantity of iron sulphate (A.R.) in distilled water. The amount of Fe(II) in this solution was determined volumetrically using EDTA[18]. A series of buffer solutions with pH values ranging from 5.0-9.0 were prepared using sodium acetate, HCl, ammonia and ammonium chloride. To 1.0 mL of 0.005 M Fe(II) solution, 28 mL buffer solution and 10 mL of HBBrPT in benzene for about 1 min. The appearance of dark red colour complex. The separated organic layer and absorbance was measured at 470 nm against reagent blank.

The effect of various ions on the determination of Fe(II) was studied to find the tolerance levels of this foreign iron the present method the results are presented in Table-1.

The complex formed between Fe and 2-hydroxy-4-*n*-butoxy-5-bromo propio-phenone thiosemicarbazone is stable and can be used for analysis. The method has been applied for the analysis of synthesized mixtures containing Fe(II). The related data is shown in Table-2.

TABLE-1
INTERFERENCE OF DIVERSE IONS

Cations	Tolerance limit (ppm)	Anions	Tolerance limit (ppm)
Zn^{2+}	500	Br^-	50
Pb^{2+}	100	Cl^-	100
Co^{2+}	50	I^-	50
Th^{2+}	500	NO_3^-	500
Sr^{2+}	50	CH_3COO^-	10
Na^+	500	$SO4^{2-}$	500
K^+	500	–	–
Al^{3+}	10	–	–
Ca^{6+}	50	–	–
Pd^{2+}	100	–	–

TABLE-2
ANALYSIS OF SYNTHETIC MIXTURE

Amounts taken (μg)	Found* (μg)
180	180.27
310	309.66
185	184.87

*:Average value of three determinations.

RESULTS AND DISCUSSION

2-Hydroxy-4-*n*-butoxy-5-bromo propiophenone thiosemicarbazone with iron gave dark yellow coloured in basic pH. The absorbance of dark red coloured species at a wavelength corresponding to maximum absorbance *i.e.*, 470 nm remains constant at least 1 h. Studies on the effect of pH on the absorbance revealed that the maximum colour was formed in a solution of pH 7. The studies relating to the effect of Fe(II) showed that a linear relationship exists between metal ion concentration and absorbance in the range 2.79-8.37 μg/mL the molor-absorptivity and Sandell's sensitivity are 2845 mol^{-1} cm^{-1} and 0.01962 μg cm^{-2}, respectively. Spectrophotometric data are presented in Table-3.

TABLE-3
SPECTROPHOTOMETRIC DATA OF Fe(II)-HBBrPT

Characteristics	Results
Molar absorptivity (L mol^{-1} cm^{-1})	2845.00
Sandell's sensitivity (μg cm^{-2})	0.01962
Beer's law validity upto (μg/mL)	13.96000
Opt. conc. range (μg/mL)	2.79-8.37
Stability constant (k)	1.22×10^7
Standard derivation (S)	0.313000
ΔG° (k cal)	-9.98900

As the metal ion Fe(II) forms the coloured complex with the reagent, an attempt is made to determine the composition and the stability constant of the complex. The method of Vosburgh and Cooper's[19] showed that only one complex is formed. To determine the stoichiometry of complex, Job's method[20] related data is shown in Fig. 1 and mole ratio method[21] related data is shown in Fig. 2 are conducted to make these determinations.
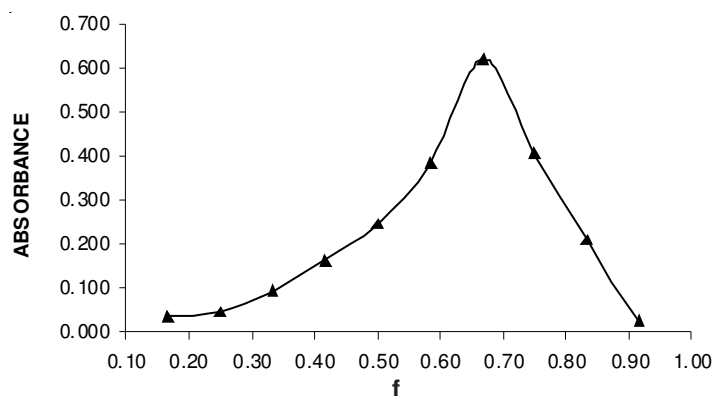
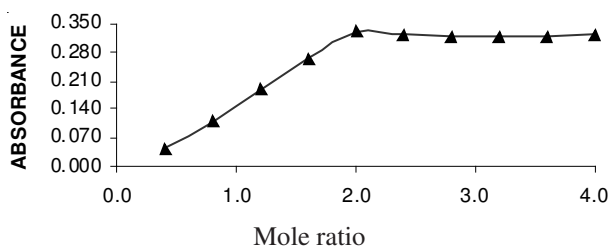Fig. 1. Job's method Fe(II)-HBBrPt complex

Fig. 2. Mole ratio method Fe(II)-HBBrPt complex

It is noticed that Fe(II) forms a stable yellow coloured 1:2 (metal: ligand) complex with 2-hydroxy-4-*n*-butoxy-5-bromo propiophenone thiosemicarbazone. The stability constant of the complex was found to be 1.22×10^7 in Table-4.

TABLE-4
STABILITY OF Fe(II) HBBrPT AT 35 °C

Method Employed	Em	Es	$\alpha = (Em-Es)/Em$	C	K
Job's	0.721	0.621	0.138	0.00250	1.29.E + 07
Mole ratio	0.721	0.330	0.542	0.00025	1.15.E + 07
Average K					1.22.E + 07

Present method, the values of standard deviation, variance and coefficient of variation were calculated using the data of Table-5.

TABLE-5
STATISTICAL EVALUATION OF THE DATA

Standard deviation, S	$\sum (\overline{X} - Xi)/n$	0.313
Variance, S^2	$\sum (\overline{X} - Xi)^2/n - 1$	0.088
Coefficient of variation (%)	$\dfrac{S}{\overline{\overline{X}}}$	0.062

The newly prepared compound was characterized by elemental analysis and infrared. The key bands[22-24] for the ligand and complex are presented in Table-6.

TABLE-6
IR SPECTRA OF HBBrPT AND Fe-HBBrPT

Vibration mode	Frequency in cm^{-1}	
	HBBrPT	Fe-HBBrPT
C-H str (asym)	2941	2954
C-H str (asym)	2869	2869
C-H def (asym)	1498	1481
C-H def (asym)	1381	1384
C-H str	3089	3028
C=C str	1595	1542, 1595
C-O-C (sym)	1232, 1261	1265
C-O-C (asym)	1063	1028, 1064
Ar-OH (intramolecular H-bond)	3242	–
C-Br	557-619	584,619
C=O	1627	1627
C=S	1063-1232	1064, 1090, 1145, 1190, 1226
C=N	1628	1627
N-H	3485	3448
C-N	1352-1261	1265, 1348
C-H	837	831, 842

Conclusion

Fe(II) forms a 1:2 stable yellow colored complex with 2-hydroxy-4-*n*-butoxy-5-bromo propiophenone thiosemicarbazone[25]. This complex is used for the determination of iron in microgram quantities. The stability constant of the complex is 1.22×10^7. The molar absorptivity and Sandell's sensitivity are 2845 mol^{-1} cm^{-1} and 0.01962 µg cm^{-2}, respectively. The method has been applied for the analysis of iron in synthesized mixtures and in alloys.

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