A stoichiometric study on the reaction between ferric ion and p-chloro-n-phenyl-p-chlorobenzo hydroxamic acid

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ABSTRACT

A stoichiometric study on the reaction between ferric ion (Fe (III)) as metal and p-Chloro-N-phenyl-p-Chlorobenzohydroxamic acid as ligand ((abbreviated in this paper as PCNPPCBHA)) was attempted . The ligand PCNPPCBHA was synthesized[1,2] and identified[3,4]. The pH at maximum extraction of the ligand PCNPPCBHA to the metal iron (III) was determined spectrophotometrically and the ratio of the ligand: metal i.e. PCNPPCBHA: Fe^{+3} was determined by the use of the continuous variation method and confirmed by the slope ratio method.

Key words: Stoichiometric, Ferric ion, ligand (PCNPPCBHA).

INTRODUCTION

The chemistry of hydroxamic acids has received considerable attention [5,6], and this interest is also connected with a variety of their pharmaceutical and industrial applications [7,8]. Particularly important in their role as siderophores, as well as a model system for natural siderophores. [9, 10] Siderophores are low- molecular weight multidentate ligands.

EXPERIMENTAL

All chemicals used were AnalaR grade. All solutions were prepared according to the usual analytical procedures using double distilled water.

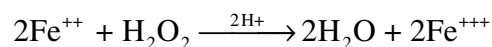### pH-determining solutions
1.0M , 2.0 M , 3.0M and 3.5 M HCl.

Acetate buffer solutions
A series of buffer solutions ranging from pH 1.0 to pH 7.0 were prepared. Buffer solutions of pH 1.0 and pH 2.0 were prepared from a mixture of 0.2 M hydrochloric acid and 0.2 M potassium chloride in different proportions ; solutions ranging from pH 3.0 to pH 7.0 were prepared using 0.2M acetic acid and 0.2M sodium acetate in different proportions. They were all adjusted to the exact value by some drops of sodium hydroxide or hydrochloric acid using a pH –meter.

Oxidation of Fe (II) to Fe (III) with hydrogen peroxide
25 cm^3 of 10^{-3} g /cm^3 Fe (II) were transferred to a 400 cm^3 beaker. 10 cm^3 of 20 % V / V hydrogen peroxide and 2 cm^3 of concentrated hydrochloric acid were added . The mixture was heated to boil to expel the excess of hydrogen peroxide .

$$2Fe^{++} + H_2O_2 \xrightarrow{2H+} 2H_2O + 2Fe^{+++}$$

The oxidized solution was transferred to a 250 cm^3 volumetric flask and was diluted to volume

by double distilled water . The concentration was 10^{-4} g / cm^3 Fe (III).

A\ Extraction and spectrophotometric determination of Iron(III)
(determination of the pH at maximum extraction)

5 cm^3 portions of 10^{-4} g / cm^3 Fe (III) were pipetted into a series of 25 cm^3 volumetric flasks and completed to the mark with adjusted pH – determining solutions ((acetate buffer solutions ranging from pH 1.0 to pH 7.0 and pH – determining solutions 1.0M , 2.0 M , 3.0M and 3.5 M HCl)) . The solutions were transferred to a series of 100 cm^3 seperatory funnels and were extracted with an equal volume (25 cm^3) of 0.5 % w/v

PCNPPCBHA in chloroform , with vigorous shaking for two minutes. Blood red colour was observed. The two layers were separated : (1) The organic layer (lower phase) and (2) the aqueous layer (upper phase). The aqueous layers were taken for further analysis to determine the pH at maximum extraction.

Analysis of the aqueous layer of by spectrophotometric procedure[11]

The standard ((calibration curve)) for iron $^{+3}$ and the sample ((aqueous layer)) were carried out at the same time for spectrophotometric procedure .

B \ The standard ((calibration)) curve

0.0 , 5.0 , 7.5 , 10.0 , 12.5 , and 15.0 cm^3 of 10^{-5} g / cm^3 (w/v) Fe (III) solution , 20.0 cm^3 double distilled water , 5.0 cm^3 of concentrated hydrochloric acid , 1.0 cm^3 of 2 % w/v potassium persulphate and 10.0 cm^3 of 20 % w/v potassium thiocynate solution were transferred to seperatory funnels successively. The solutions were extracted with five 10.0 cm^3 portions of (1:1) isobutyl alcohol and carbon tetrachloride (50 % v /v) , with vigorous shaking for two minutes each. The organic layers were combined in 50 cm^3 volumetric flasks. The absorbance was measured at 485 nm using 1 cm cell. Results are shown in table (1) and represented graphically in figure (1) .

C\ The sample

From the aqueous layer in A , 5cm^3 were transferred to a seperatory funnel. The analysis was carried out as in B. Results are shown in table (2)

RESULTS AND DISCUSSTON

Spectrophotometric studies on Iron^{+3} – p-Chloro– N- Phenyl -p-Chlorobenzohydroxamic acid complex
The continuous variation method

The ratio of the ligand: metal i.e. PCNPPCBHA:Fe $^{+3}$ was   determined by the application of the continuous variation method [12], [13]. Results are shown in table (3) and represented graphically in figure (2) . The blank used was chloroform.

Table 1: Absorbance of the standard solutions for the calibration curve of Iron^{+3} at λ 485 nm

Absorbance	Medium HCl	Concentration of Fe (III) in ppm
0.150		1.0
0.275	"	1.5
0.389	"	2.0
0.521	"	2.5
0.625	"	3.0

Table 2: Absorbance of the aqueous layer from the extraction of Iron^{+3} with PCNPPCBHA

pH	Absorbance at λ 485 nm
1M HCl	0.120
2M HCl	0.125
3M HCl	0.271
3.5M HCl	0.215
Acetate pH 1.0	0.109
2.0	0.122
3.0	0.044
4.0	0.019
5.0	0.017
6.0	0.018
7.0	0.045

* pH at maximum extraction implies the lowest value of the of the absorbance i.e. at pH = 5.0

The slope ratio method

The ratio of the metal Iron^{+3} to the ligand PCNPPCBHA was confirmed by the application of the slope ratio method[14] which was found 1:2.

Results are shown in table 4 and represented graphically in figure 3.

The Calibration curve of Iron^{+3} – PCNPPCBHA system

A standard calibration curve of Iron^{+3} – PCNPPCBHA system was carried out against chloroform as blank. Results are shown in table 5 and represented graphically in figure 4 .

Jop[12] has pointed out , that the method of continuous variation is simple and rapid for determining the formula of a compound , provided that only a single compound is formed. If more than one compound is formed, the method can still help in giving information about the formulae of compounds if the compounds are sufficiently stable. Caution is necessary in such cases. The shape of the curves in the continuous variation method sometimes may give indication to the existence of more than one compound[13].

Many of the relation in this paper presuppose the validity of Beer –Lambert law [15]. True variations of the law can arises when moderately concentrated solutions are used, but can usually be neglected when working with dilute
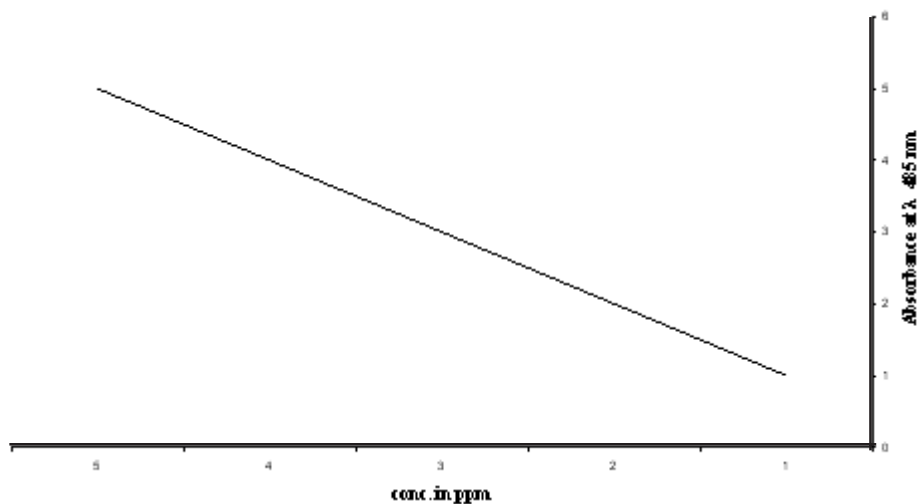

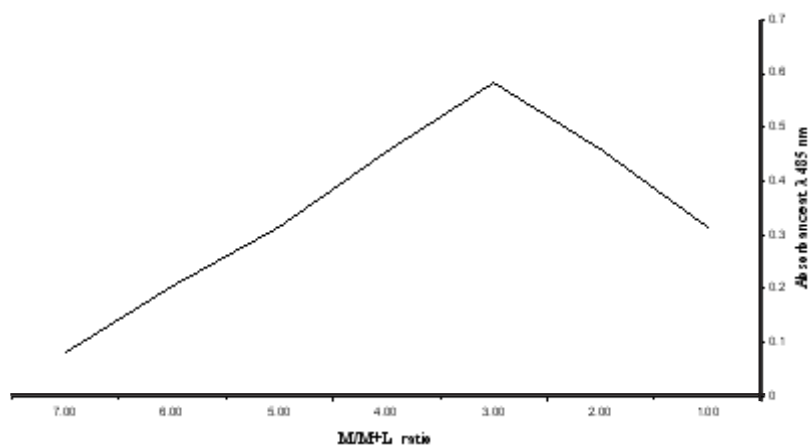**Fig. 1: The calibration curve of Fe(III) for the extraction with PCNPPCBHA**

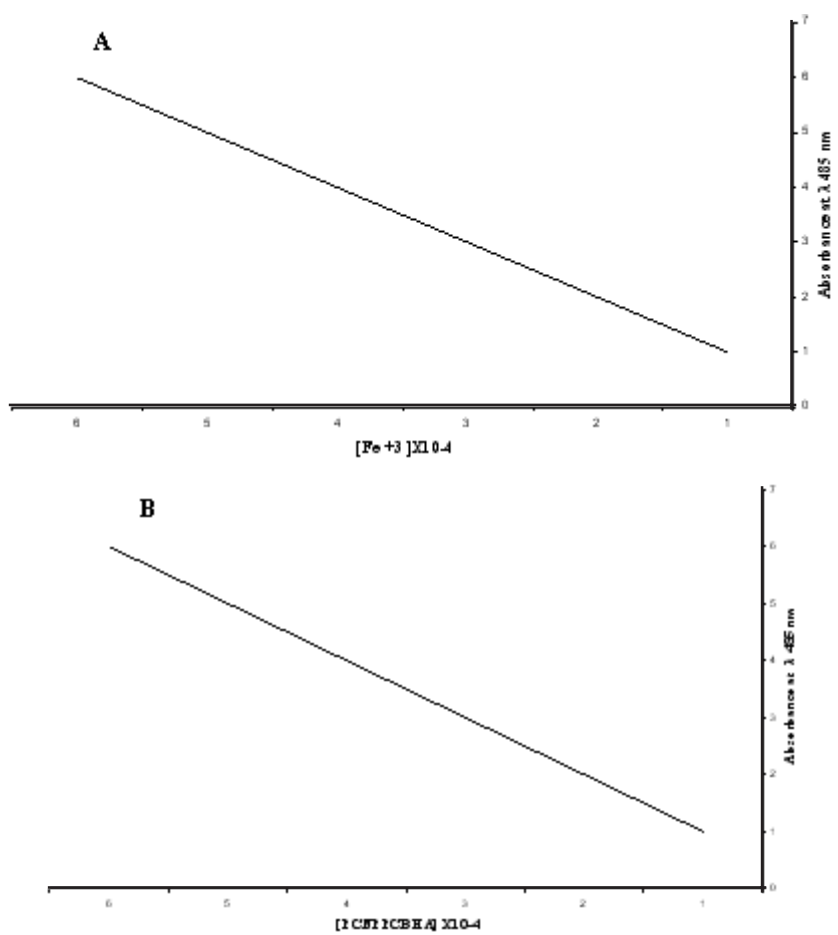**Fig. 2: The continous variation plot of Fe(III) - PCNPPCBHA**

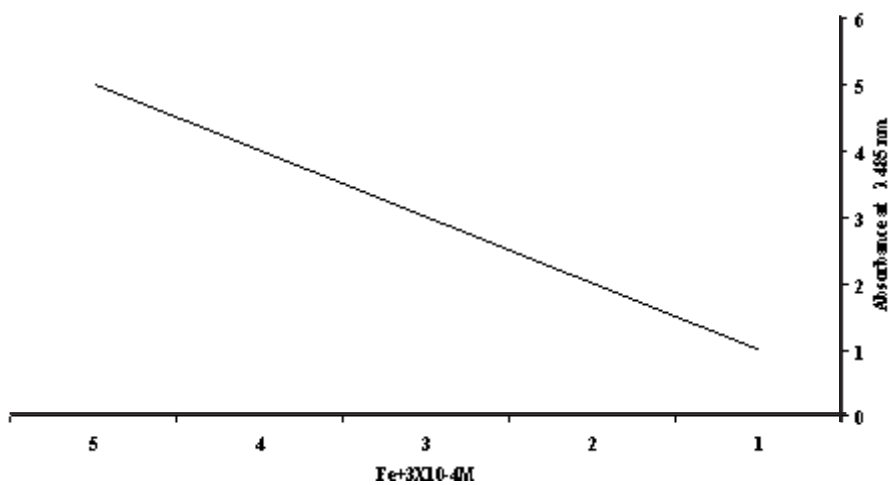**Fig. 3: The slope ration plot of Fe(III)-PCNPPCBHA system**

Fig. 4: The calibration curve for Fe(III)-PCNPPCBHA system

Table 3: Continuous variation method for Iron^{+3} – PCNPPCBHA system

Solution	1	2	3	4	5	6	7
Vol. of Fe^{+3} 1x10^{-3} in cm^3	2	3	4	5	6	7	8
Vol. of Acetate pH^5 in cm^3	2	2	2	2	2	2	2
Vol. of Dist.H$_2$O in cm^3	6	5	4	3	2	1	0
Vol. of ligand 1x10^{-3} in cm^3	8	7	6	5	4	3	2
Vol. of chloroform added to the ligand before added to the metal in cm^3	2	3	4	5	6	7	8
$\frac{M}{M+L}$	0.20	0.30	0.40	0.50	0.60	0.70	0.80
Absorbance at λ 520 nm	0.314	0.459	0.583	0.455	0.315	0.205	0.081

Table 4: Slope-ratio method for Iron^{+3} - PVNPPCBHA system

Solution	1	2	3	4	5	6
Vol. of Fe^{+3} 1x 10^{-3} in cm^3	1	2	3	4	5	6
Vol. of Acetate pH 5 in cm^3	3	3	3	3	3	3
Vol. of Dist.H$_2$O in cm^3	6	5	4	3	2	1
Vol. of ligand 1x10^{-3} in cm^3	5	5	5	5	5	5
Vol. of chloroform added to the ligand before added to the metal in cm^3	5	5	5	5	5	5
[Fe+3] x10^{-4} M	1	2	3	4	5	6
Absorbance at λ 485 nm	0.131	0.187	0.252	0.315	0.395	0.449
Set B						
Vol. of Fe^{+3} 1x10^{-3} in cm^3	5	5	5	5	5	5
Vol. of Acetate pH 5 in cm^3	3	3	3	3	3	3
Vol. of Dist.H2O in cm^3	2	2	2	2	2	2
Vol. of ligand 1x10^{-3} in cm^3	1	2	3	4	5	6
Vol. of chloroform added to the ligand before added to the metal in cm^3	9	8	7	6	5	4
[PCNPPCBHA] x10^{-4}M	1	2	3	4	5	6
Absorbance at λ 485 nm	0.104	0.218	0.342	0.458	0.571	0.962

Table 5: Calibration curve for Iron^{+3} - PCNPPCBHA system

Solution	1	2	3	4	5
Vol. of Fe^{+3} 1x10^{-3} in cm^3	1	2	3	4	5
Vol. of Acetate pH 5 in cm^3	5	5	5	5	5
Vol. of Dist.H$_2$O in cm^3	4	3	2	1	0
Vol. of ligand 1x10^{-3} in cm^3	10	10	10	10	10
[Fe^{+3}] x10^{-4} M	1	2	3	4	5
Absorbance at λ 485 nm	0.378	0.446	0.515	0.578	0.641

solutions. The ligand PCNPPCBHA forms 1:2 complex with Fe (III) at pH 5.0 ((the minimum value of the absorbance table (2))) that corresponds the maximum absorption in a value of 0.35 M / M +L in the continuous variation method curve figure 2 , and this confirmed by the slope ratio curve figure 3 . This system is closely resemble the systems CO^{+2} : PCNPPCBHA and Cu^{+2} : PCNPPCBHA i.e. forms 1:2 complex[16].

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