Spectroscopic Studies of a New Mixed Ligand Complex of Fe(III) in Aqueous Medium

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Abstract

A spectrophotometric study of Fe(III) mixed ligand complex has been performed involving 1,4 phenylenediamine (A) and anthranilic acid (B) ligand at 25°C and aconstant ionic strength of μ= 0.05M $NaClO_4$. The optimum pH was found to be pH=4.1. The formation ratio of the new complex is determined to be 2:1:4 of Fe(III):(A):(B). The molar absorptivity was determined to be $\approx 0.5 \times 10^4$. Stepwise spectrum change of the complex formation is recorded by continuous flow system.

Keywords: Mixed ligand complex, Fe(III)

Introduction

Mixed ligand complexes have found an increasing use, particularly in spectrophotometric analysis because of their high sensitivity and selectivity(1). The best reaction of aqueous Fe(III) is with SCN^- ion. The red color is unstable owing to the reduction of Fe(III) by SCN^-.The stability of the complex have been enhanced by adding a second ligand (teraphenylphosphonium chloride) $\epsilon \approx 3.55 \times 10^4 mol^{-1}.dm^3.cm^{-1}$(2). Fe(III) ion with maleic acid as primary and heterocyclic bases as secondary ligands were studied(3). The formation constants of mixed ligand Fe(III)-L-borate complexes (L=bipy, phen, den and trine) in aqueous solutions are in the range of $\log K_{eq} \approx 10\text{-}20$ (4).

Aminobenzoic acid, which is used as a ligand in the present work, have aroused an interest owing to its utility as starting materials for many azodyes, bactericides and anti-inflammatory agent. (5).

The iron-bleomycin complex has been shown to catalyze the oxidation of p-phenylenediamine to a stable, purple colored oxidation product, characterized by an absorption maximum around 520 nm. Molecular oxygen is used for reoxidizing Fe(II)-bleomycin after reduction by p-phenylenediamine(6).

The aim of this work was to synthesize new mixed-ligand complexes of Fe(III) in a solution. As mentioned above, this may increase the sensitivity and selectivity of Fe(III) complexes which is important in quantitative analysis of Fe(III) ion.

Experimental

Apparatus

Jenway 6405 UV-Visible spectrophotometer (with a modified home-made thermostat cell holder) was used for reading absorbance and measuring electronic spectra. A Buchi chromatography pump was used to circulate the sample solution from the reaction vessel to the flow-cell. A Philips pH/mV meter type pw-9419 was used for pH measurements.

(LKB Bromma 2209 multitemp.) circulating thermostat bath was used to control(±0.2°C) the temperature of the system.

Reagents and Materials

All Fe(III) and ligand solutions were prepared freshly before use. (0.005 mol/L) Fe(III) solution was prepared from $Fe(NO_3)_3$ (Fluka) and addition of 2 drops of $HClO_4$ to prevent hydrolysis. (0.005mol/L) of 1,4 phenylenediamine(Fluka) and (0.005mol/L) anthranilic (Merck) were prepared without further purification by distilled water and stored in dark bottles. $HClO_4$ and $NaClO_4$ were Fluka products

General procedure

To determine the absorption spectrum of a given ternary or mixed species $Fe_pA_qB_rH_s$, it is necessary to determine first the absorption spectra of the metal ion Fe(III) and of both ligands (A) (1,4 phenylenediamine) and (B) (anthranilic acid) and of their protonated species, followed by the determination of the absorption spectrum of each binary species formed by Fe(III) with both A and B. Therefore, a series of steps are necessary which can be grouped as follows(7):

1 –The absorption spectrum of each component was determined of all ligand species, under the same conditions of (temperature of 25°C, 0.05 mol/L $NaClO_4$ ionic strength and pH = 4.1± 0.1), followed by the determination of the absorption spectra of each protonated species, which were all negligible at the experimental concentration level (0.0002 mol/L final concentration).

2 –Solutions containing Fe(III) ion and ligand (A), and Fe(III) ion and ligand (B) in several proportions were taken to determine the absorption spectrum of binary species $Fe_pA_qH_s$ and $Fe_pB_rH_s$ if present (no.3 & no.4 in Fig 1).

3 – Solutions of the two ligands A and B were mixed and the absorption spectra was determined also to exclude pre-reaction between them (no. 2 in Fig 1).

4- Solutions containing the ligands and Fe(III) ion in different proportions were taken to determine the absorption spectra of the ternary species $Fe_pA_qB_rH_s$ (Fig 2).

Results and Discussion

Binary systems:

At low concentrations(0.0002 mol/L), the two ligands A , B relatively have no absorption spectra in the visible region, neither when they are mixed at the same (0.0002mol/L) final concentration(no.2 in Fig.1).
Fe(III) solution(0.0002mol/L) visible spectrum is shown (no.1 in Fig.1).

The absorption spectra of each ligand with Fe(III) ion is recorded also. Fe(III) with p-phenylenediamine at the same final concentration levels above, have a low intensity peak at 465nm with molar extension coefficient ≈ 280 $L.mol^{-1}.cm^{-1}$ (no.4 in Fig 1). Fe(III) with anthranilic acid have no detectable peak in the visible region (no.3 in Fig 1). The mixture of the two ligands at the same (0.0002 mol/L) final concentration level have a very weak peak at 460nm with molar extension coefficient ≈ 18 $L.mol^{-1}cm^{1}$.

Mixed ligand complex:

At the same low concentrations of each ligand and Fe(III) ion (0.0002 mol/L each),a fast stepwise color change will happen when the two ligands and Fe(III) ion are mixed. The final spectrum will have a maximum at 662nm with molar absorbitivity ≈4900 $L.mol^{-1}\cdot cm^{-1}$ (fig. 2). At mixing, the solution mixture turns yellow, changes to green within 3-6 seconds, and then turns blue within 2-3 min. The stepwise complex formation spectra are recorded using flow system (Diagram-1). A Büchi chromatography pump (12ml/min flow rate) to draw the reaction mixture through the system. Glass capillary tubes (10cm length and 1mm Ø) were used in the inlet of each of the three solutions (0.0006 M Fe(III), 0.0006M A and 0.0006M B) to control the flow (4ml/min each line). Different reaction tube (PTFE) lengths (20, 30, 38, 50, 61, 72 and 85 cm with 2mm Ø) were used to make the reaction mixture reaches the Quartz flow cell at the required times to record the spectrum change at different times passed over the reaction (Fig.3).

pH-study:

pH study was done to find the optimum pH of the complexation at which maximum sensitivity of the method is reached. 2ml of 0.005mol/L each solution of Fe(III), A and B were mixed with 5ml of 0.5mol/L $NaClO_4$ as ionic strength, the initial pH was adjusted by addition of $HClO_4$ or NaOH and the volume was completed to 50ml in a volumetric flask by distilled water. The optimum pH is (4.1) as shown in Fig(4).

Complex ratio studies:

Fixed amounts of both ligands (0.01 mmole each) were used with different amounts of Fe(III) ions to find the ratio of Fe(III) to the ligands, and the result was 2:1:1 of Fe(III):A:B as shown in fig(5)

The second step was to find the ratio of each ligand to the Fe(III) ion, and this was done by using different mole ratios of B/A with a fixed amount of (0.01mmole) Fe(III) Table (1). The mole fraction of Anthranilic acid in the complex formed is (0.53). The ratio of Anthranilic acid (B) : 1,4phenylenediamine (A) : Fe(III) is(4:1:2) as shown in (Fig. 6) .

The mole fraction of anthranilic acid is about (0.53) (fig. 6), which corresponds to 0.016 mmloe Anthranilic and 0.004 mmole 1,4phenylenediamine to 0.01 mmole Fe(III). (Table1), multiplying these ratios by factor (2.5) results in the final complex ratio of(4:1:2)(B:A:Fe).

Accordingly, the suggested structure of the complex is shown in (Fig. 7). Amine terminal ligation of N,N,N`,N`-teramethyl-p-phenylenediamine have been reported in literature(8), which is consistent with the proposed structure.

Cationic Interferences:

Effect of cationic interferences was studied for different metal ions by applying a calibration curve for Fe(III) without interferences, then adding 2ml of 0.01mol/L cation interference to 10ml of 0.0005mol/L Fe(III) and the final volume is 50ml (pH=4.1 and μ=0.05M $NaClO_4$) and calculating the percentage of error at this concentration level is (0.0001mol./L Fe(III)).

The significant cationic interference is Hg(II) and to a lower extent is Cu(II).

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Table (1) :Determination of mole ratio of the ligands A and B to Fe(III) ion in the complex

mmole	mmole A	$X_B=n_B/n_A+n_B+n_{Fe}$	Abs at
0.001	0.019	0.033333333	0.126
0.002	0.018	0.066666667	0.163
0.003	0.017	0.1	0.224
0.004	0.016	0.133333333	0.32
0.005	0.015	0.166666667	0.331
0.006	0.014	0.2	0.414
0.007	0.013	0.233333333	0.457
0.008	0.012	0.266666667	0.547
0.009	0.011	0.3	0.572
0.01	0.01	0.333333333	0.666
0.011	0.009	0.366666667	0.726
0.012	0.008	0.4	0.776
0.013	0.007	0.433333333	0.867
0.014	0.006	0.466666667	0.908
0.015	0.005	0.5	0.963
0.016	0.004	0.533333333	0.933
0.017	0.003	0.566666667	0.817
0.018	0.002	0.6	0.68
0.019	0.001	0.633333333	0.529

Table (2): Effect of Cationic interference.

[0.0004M] interferences	%Error
0	0
Co(II)	0.68
Ba(II)	1.08
Al(III)	1.36
Pb(II)	0.258
Hg(II)	25.5
Cu(II)	3.52
Zn(II)	2.12

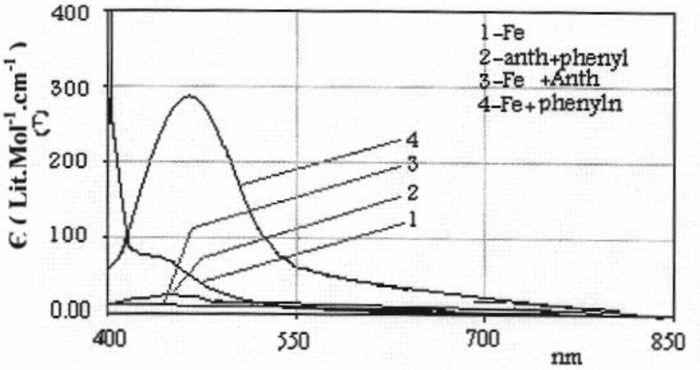


Fig. (1): Spectra and molar absorptivities of 1- Fe(III) ion, 2- Anthranilic acid with p-phenylenediamine, 3- Fe(III) ion with anthranilic acid and 4- Fe(III) with p-phenylenediamine

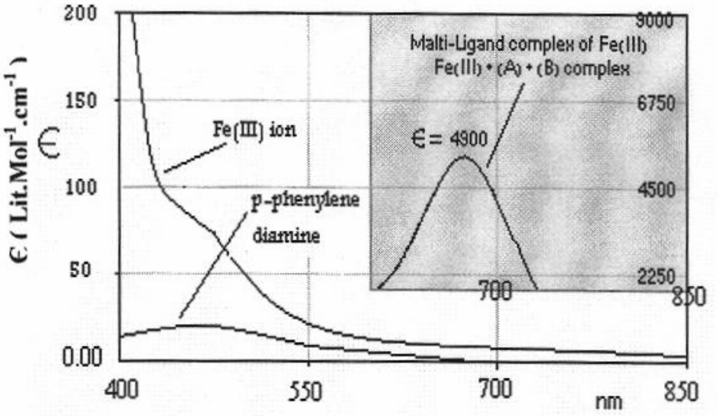


Fig. (2) : Calculated molar absorptivities of Fe(III) ion, p-phenylenediamine and the multi-ligand complex {Fe(III)-anthranilic acid-p-phenylenediamine}

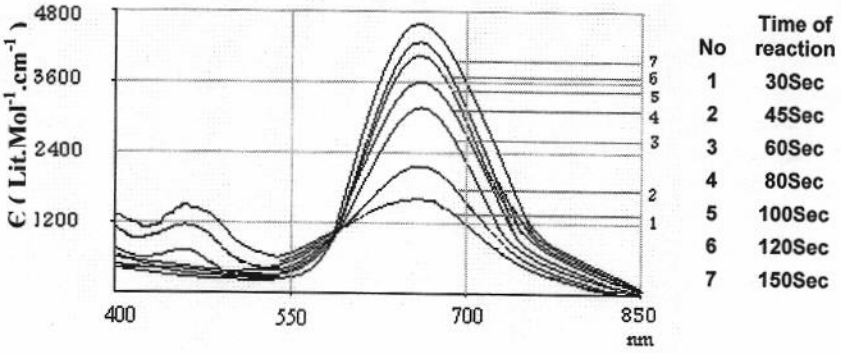


Fig.(3): Stepwise complexation reaction of Fe(III), anthranilic acid and p-phenylenediamine.

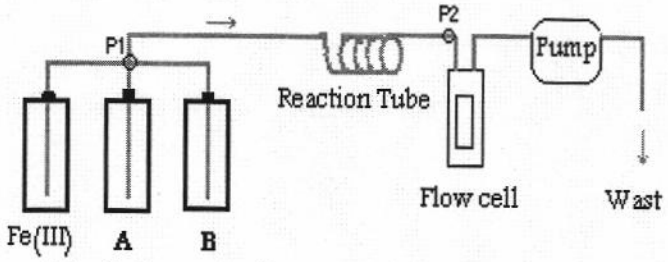


Diagram (1) : Schematic diagram of the flow system designed to record spectrum change at different time of complexation

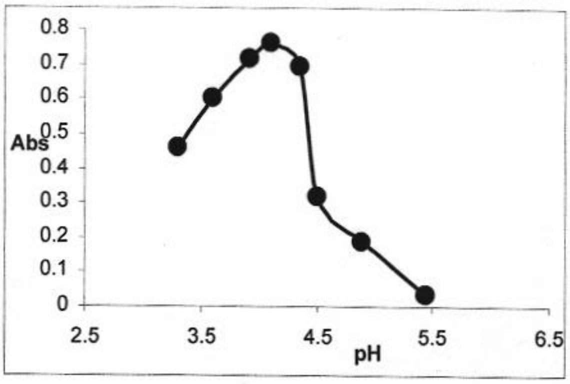


Fig.(4): Optimization of pH

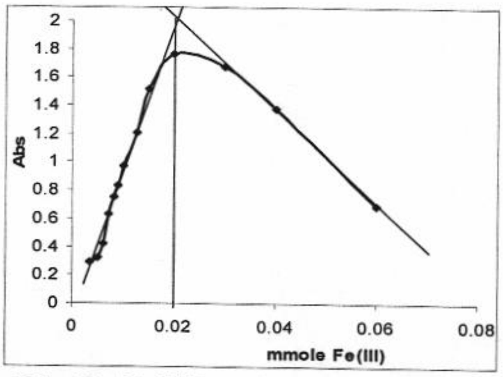
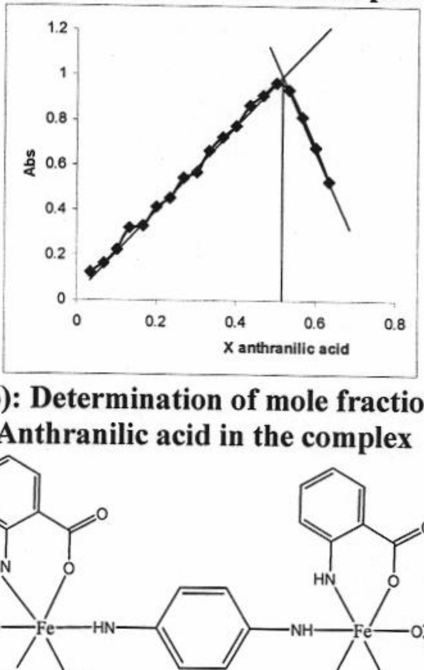


Fig.(5): Fe(III) ratio in the complex



Fig(6): Determination of mole fraction of Anthranilic acid in the complex

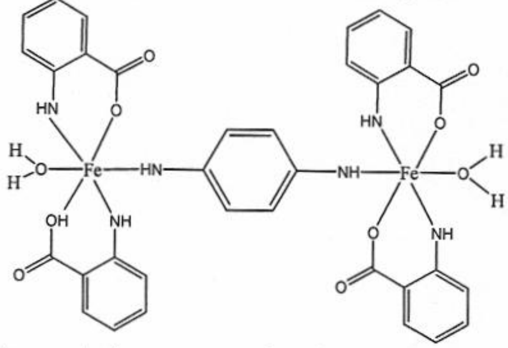


Fig. (7): The Suggested structure for the mixed ligand complex

دراسات طيفية لمعقد جديد من الحديد(III) لخليط من العضائد(Mixed Ligand) الممتزجة في الوسط المائي

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الخلاصة

اجريت دراسات طيفية لمعقد حيوي جديد من الحديد الثلاثي مع (1,4 فنيلين داي امين) عضيدا أوليا (A) و (حامض الانثرانيليك) عضيدا ثانويا (B) . تم تعيين نسبة التكوين للمعقد لتكون (2:1:4) ل Fe(III):(A):(B) .تم ايجاد ثابت الامتصاصية المولاري ($0.5x10^4$). وسجلت ورسمت خطوات التغيير الطيفي لتكوين المعقد بأستخدام نظام الجريان المستمر للخليط.