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Studies on N^1-Hydroxy-N^1,N^2-diarylbenzamidines as Metal Complexing Agents: Extraction-Photometric Determination of Iron(III) as Thiocyanato and Azido Mixed Ligand Complexes with N^1-Hydroxy-N^1,N^2-diphenyl-*p*-toluamidine(HDPTA)

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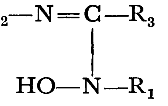
N^1-Hydroxy-N^1,N^2-diarylbenzamidines react with iron(III) in presence of thiocyanate and azide forming coloured complexes which are quantitatively extractable in benzene. The extraction of iron(III) as red Fe(III)–L–$(SCN^-)_2$ complex is quantitative at 0.1—0.6 M hydrochloric acid concentration, whereas the Fe(III)–L–$(N_3^-)_2$ complex gets quantitatively extracted into benzene at pH 1.0—2.5. The ternary iron(III)-thiocyanato complex of N^1-hydroxy-N^1,N^2-diphenyl-*p*-toluamidine(HDPTA) has a fairly large molar absorptivity (1.01×10^4 l mol^{-1} cm^{-1}) and the spectrophotometric method based on this colour reaction is highly selective as almost all common ions including Fe(II) do not interfere. The method employing the formation of ternary iron(III): HDPTA: azide complex is also highly selective.

Thiocyanate is frequently used for the spectrophotometric determination of traces of iron(III).[1)] This method, which is simple, rapid, fairly sensitive and free from interference of Fe(II), and can be applied in strongly acidic medium, suffers from interference due to a large number of experimental factors. These include time of standing, thiocyanate concentration, non-linearity of Beer's law *etc.* Even the modified method[2)] lacks selectivity as various elements such as manganese, zinc, cadmium, copper, nickel, coblat, titanium, uranium, and molybdenum interfere.[3,4)] A recent investigation bases the formation of ternary iron(III)–thiocyanate–*N*-hydroxyethylenediamine-*N*,N^1,N^1-triacetate to develop a fairly selective spectrophotometric method,[5)] but only at the expense of sensitivity.

N^1-Hydroxy-N^1,N^2-diarylbenzamidines,[6—8)] a new type of reagents react with iron(III) forming blue[9)] and red-purple[10)] pH dependent complexes in ethanol. However, in the presence of thiocyanate these reagents produce an intensely red ternary complex which is quantitatively extractable into benzene from hydrochloric acid solutions. The present paper reports the use of N^1-hydroxy-N^1,N^2-diphenyl-*p*-toluamidine (HDPTA) and 18 analogous compounds possessing the general formula-I, for the extractive-spectrophotometric determination of microgram quantitities of iron(III). The present method is sensitive and highly selective as Fe(II) and almost all common ions including those which usually interfere with the parent thiocyanate method and other literature methods[11)] do not interfere. The present paper also describes a new spectrophotometric method based on the benzene extraction of iron(III) as its ternary HDPTA and azide complex. This method, though relatively less sensitive is also very selective.



$$\begin{array}{l} R_2\text{—}N\text{=}C\text{—}R_3 \\ \qquad\quad | \\ HO\text{—}N\text{—}R_1 \end{array}$$

Formula I.

R_3 is *p*-tolyl; R_2 is phenyl, *p*-tolyl, *m*-tolyl, 2,5-dimethylphenyl, 2-methyl-4-chlorophenyl, or 2-methyl-5-chlorophenyl; R_1 is phenyl, *p*-tolyl, *m*-tolyl, or *p*-chlorophenyl.

Experimental

Apparatus. A Carl-Zeiss 'Specord' UV-VIS spectrophotometer and an ECIL UV-VIS spectrophotometer model GS-865 with 1-cm matched quartz and silica cells were employed for recording the spectra and absorbance measurements respectively. A Systronic pH meter type-322 was used for determination of pH values.

Standard Iron(III) Solution. Stock solution of iron(III) was prepared by dissolving about 0.62 g of pure iron wire(E. Merck) in 50 ml of 1:3 nitric acid. It was boiled to expel oxides of nitrogen and diluted to 1 litre. This solution was standardised gravimetrically employing 8-quinolinol.[12)]

One percent aqueous solutions of potassium thiocyanate and sodium azide were also prepared. All the chemicals used were of analytical reagent grade.

Preparation of N-*Hydroxyamidines.* N^1-Hydroxy-N^1,N^2-diarylbenzamidines were prepared by condensation of equimolar quantities of *N*-aryl-*p*-toluimidoyl chloride with *N*-arylhydroxylamine in ether.[13,14)] The resulting hydrochloride was filtered and treated with dilute ammonia to liberate the free base. The free bases were recrystallised from petroleum ether (60—80 °C): benzene (1:2) and the hydrochlorides were crystallised from absolute ethanol. All these compounds showed infrared spectral bands characteristic of N^1-hydroxy-N^1,N^2-diarylbenzamidines.[13,14)]

Solutions of *N*-hydroxyamidines (0.1%) in benzene were used for extraction purposes.

Procedure. Place an aliquot (10 ml) of iron(III) solution containing 50—120 μg of the metal in a separatory funnel. To this, add 5 ml of 1% potassium thiocyanate/sodium azide solution. Adjust the acidity to the required value and dilute to 25 ml. Introduce 25 ml of benzene solution of N^1-hydroxy-N^1,N^2-diphenyl-*p*-toluamidine (0.1%; 0.003 M) and equilibriate for 2 min. Dry the benzene extract over anhydrous sodium sulfate and measure the absorbance at the wavelength of maximum absorption against reagent blank.

Results and Discussion

Absorption Spectra. The absorption spectra of ternary thiocyanate and azide complexes of iron(III) with HDPTA are shown in Fig. 1. HDPTA reacts

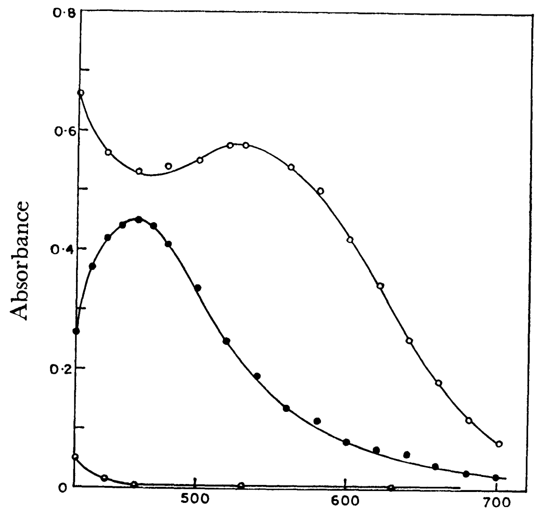


Fig. 1. Absorption spectra of ion(III) ternary complexes and reagent.
-○-: 8.47 ppm Fe(III)+0.1% HDPTA+azide,
-●-: 2.54 ppm Fe(III)+0.1% HDPTA+thiocyanate,
-⊖-: 0.1% HDPTA(w/v) in benzene.

with iron(III) forming blue (λ_{max}, 580 nm) and red-purple (λ_{max}, 540 nm) pH-dependent ethanol-soluble complexes. However, in the presence of thiocyanate an intense red complex (λ_{max}, 460 nm) is developed. The wavelength of maximum absorption of the ternary iron(III)–azide–HDPTA complex is 520 nm. Both these complexes are quantitatively extractable in benzene. As the reagent (HDPTA) shows negligible absorption at 450 nm and onwards, the reagent blank can be replaced by benzene.

Effect of Variables. Various solvents such as chloroform, carbon tetrachloride, toluene, benzene *etc.* were found to extract the ternary complexes quantitatively. However, benzene was found to be the best extracting solvent as in this the sensitivity of the complexes is enhanced and complete extraction is relatively rapidly accomplished.

The acidity of the solutions were maintained with hydrochloric acid and ammonia. If the hydrochloric acid concentration of the aqueous phase in case of thiocyanate system lies in the range 0.01—1.0 M, the position of the absorption band of the benzene extract remains intact. However, the optimum acidity range was found to be 0.10—0.65 M HCl in which iron(III) was quantitatively extracted. The optimum pH range for complete extraction of iron employing HDPTA and azide was 1.0—2.5.

Generally a 30 fold molar excess of HDPTA was adequate for full colour development. In thiocyanate ternary system, a 30 and 130 fold molar excess of the ligand and thiocyanate respectively is necessary for complete extraction of iron(III). The azide ternary system requires a 25 and 100 fold molar excess of hydroxyamidine and azide respectively. The presence of HDPTA, thiocyanate, and azide in large causes no adverse effect. Order of addition of reagents was not critical in these systems.

An equilibriation period of 2 min was sufficient for complete extraction of iron(III) mixed ligand complexes. Prolonged extraction has no harmful effect on the determination. Variation of temperature of the aqueous phase from 20 to 35 °C did not affect the absorbance and λ_{max} of ternary complexes. Both the systems were stable for at least for 30 h at 27±2 °C.

Nature of Complexes. The composition of thiocyanate and azide mixed ligand complexes was determined by curve fitting method.[15] To determine the ratio of Fe(III) to HDPTA, the concentration of iron(III) was kept constant and X^- (SCN^- or N_3^-) was taken in excess and then, the concentration of HDPTA was varried. Log absorbance was plotted against $\log M$ of HDPTA. Similarly the number of X^- attached to Fe(III) were also found out. The results indicated the formation of 1:1:2 (metal: HDPTA: thiocyanate or azide) ternary complexes.

The molar absorptivities of the Fe(III): thiocyanate: HDPTA and Fe(III) : azide : HDPTA complexes are 1.01×10^4 and 4×10^3 l mol^{-1} cm^{-1} respectively. The Sandell sensitivities of the colour reactions are 0.0054 and 0.0140 μg cm^{-2} of Fe(III) for thiocyanate and azide systems respectively. The iron concentration ranges which follow Beer's law are 0.4—4.8 ppm for thiocyanate system and 0.6—12.0 ppm of Fe(III) for azide system. Ringbom plot[16] suggested optimum and effective metal concentration range of 0.8—4.0 and 2.0—11.0 ppm for thiocyanate and azide systems respectively. The relative standard deviation for the determinations based on thiocyanate and azide colour reactions are ±0.82 and ±0.60% respectively.

N^1-*Hydroxy*-N^1,N^2-*diarylbenzamidines as Reagents for Iron(III).* To study the influence of substituents on the complexing properties of the functional grouping, 18 analogues of HDPTA were synthesised and tested for their potentialities towards the extractive separation and spectrophotometric determination of iron. The absorption spectra of the ternary complexes of these reagents were scanned. The average molar absorptivities of the coloured complexes were evaluated at the wavelength of maximun absorption and on the basis of iron content. The experimental details are the same as described for HDPTA. Adherence to Beer's law was tested and confirmed for each system. It is observed that the ternary iron(III) thiocyanate complexes of N^1-hydroxy-N^1,N^2-diarylbenzamidines show maximum absorption at 460—465 nm having molar absorptivities in the range 10100—13400 l mol^{-1} cm^{-1}. Thus, substitution at azomethine or hydroxyl nitrogen atom has no effect on the position of λ_{max}. However, the substitution of the N^1-phenyl group of HDPTA with aryl substituents displayed hyperchromic effect in the order *p*-chlorophenyl>*p*-tolyl>*m*-tolyl. The replacement of the N^2-phenyl group with aryl groups also resulted into hyperchromic shifts, the order being 2-methyl-4-chlorophenyl>2,5-dimethylphenyl>2-methyl-5-chlorophenyl>*p*-tolyl>*m*-tolyl. Thus, N^1-hydroxy-N^1-(*p*-chlorophenyl)-N^2-(2-methyl-4-chlorophenyl)-*p*-toluamidine has the largest value for molar absorptivity. In azide ternary systems only slight variation in the value of λ_{max} and ε_{max} were noticed.

Effect of Diverse Ions. To study the influence of various foreign ions, a fixed amount of iron(III) was mixed with varying amounts of diverse ions and the extraction of iron was carried out according to the recommended procedure. The tolerance limits of diverse ions(ppm) which cause an error less than ±2% are shown in parentheses.

Thiocyanate System. (0.4 M HCl; 2 ppm iron). Alkaline earth and lanthanoide elements (2000); Fluoride (800); phosphate or arsenate(1400); Cu^{2+}(100); Ni^{2+} or Co^{2+} (400); Zn^{2+}(1500); Cd^{2+}(1300); Al^{3+}(600); Cr^{3+}(500); Fe^{2+}(800); Mn^{2+}(600); Se^{4+}(300); Th^{4+} (200); Ti^{4+}(100); Zr^{4+}(700); V^{5+}(50); Mo^{6+}(15); W^{6+}(50); U^{6+}(600).

Manganese(II) inhibits colour development. However, its interference could be overcome by the addition of ammonium peroxomonosulfate.

Azide System. (pH 1.5±0.2; 6 ppm iron). Alkaline earth and lanthanoid elements (1600); Chloride (3000); sulfate(2500); Zn^{2+} or Cd^{2+}(800); phosphate (400); Ni^{2+} or Co^{2+}(400); Cu^{2+}(100); Al^{3+}(500); Cr^{3+} (450); Fe^{2+}(500); Mn^{2+}(200); Th^{4+}(500); Ti^{4+}(100); Zr^{4+}(500); Mo^{6+}(50); W^{6+}(200); U^{6+}(400).

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