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Extraction and Spectrophotometric Determination of Iron(III) with N^1-Hydroxy-N^1,N^2-diphenylbenzamidine in Presence of Azide

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N^1-Hydroxy-N^1,N^2-diphenylbenzamidine (HDPBA) reacts with iron(III) in the presence of azide to give a violet-coloured complex insoluble in water. The mixed ligand complex having a composition of 1:2:2 (Fe: HDPBA:N_3^-) is quantitatively extracted into chloroform at pH 2—5. The violet-coloured complex has an absorption maximum at 530 nm with a molar absorptivity of 4900 l mol^{-1} cm^{-1}. On the basis of this sensitive colour reaction, a highly selective method has been developed for the extraction and spectrophotometric determination of microgram quantities of iron(III). The effect of foreign ions and several experimental variables have been studied. The method is simple, rapid, precise, and free from the regid control of experimental parameters.

N^1-Hydroxy-N^1,N^2-diphenylbenzamidine (HDPBA) and its analogues are typical monobasic and bidentate chelating agents for metal ions.[1—18] These reagents have been used for the spectrophotometric determination of iron(III) in ethanol.[19,20] However, the method is neither sensitive nor selective and suffers from the serious interferences due to many common metal ions. Recently N^1-Hydroxy-N^1,N^2-diarylbenzamidines have been reported[21] as reagents for the extraction and spectrophotometric determination of iron(III) in the presence of azide. This method, though quite selective is relatively less sensitive. Beside these, the method requires a large excess of the reagent for the complete extraction of iron(III) and benzene is used as a solvent which is lighter than water, and in which the reagent is relatively less soluble. Hence, in the present investigation, detailed studies have been made for the extraction of iron(III) with HDPBA and azide in different experimental conditions to overcome these problems. These studies have resulted in the development of simple, rapid, sensitive, and highly selective method for the extraction and photometric determination of iron(III).

The present investigation deals with the extraction and spectrophotometric determination of microgram quantities of iron(III) as a mixed ligand complex with HDPBA and azide. The present method is more sensitive and highly selective than the parent HDPBA method[19] and other methods[21] using HDPBA analogues as reagents. The present paper also describes a new extraction-photometric method for the determination of iron(III) as simple chelate complex with HDPBA in chloroform. However this method is not selective and is relatively less sensitive.

Experimental

Apparatus. A Beckman[R] model 24 UV-VIS spectrophotometer equipped with 1-cm quartz cells was used for absorbance measurements. A Beckman CHEM MATE pH meter was used for the measurements of pH. A Pye Unicam model SP 191 atomic absorption spectrophotometer equipped with a hallow cathode lamp and air-acetylene flame was used for the determination of iron in the aqueous phase.

Standard Iron(III) Solution. A stock solution of iron(III) was prepared by dissolving 4.0402 g of hydrated iron(III) nitrate (BDH, Analar) in 100 ml of 1:5 (v/v) nitric acid and diluted to 1 litre with distilled water. This solution was standardized gravimetrically.[22] A working solution of iron(III) was prepared by diluting a suitable aliquot of stock solution with distilled water to give 0.1 mg of iron(III) per millilitre.

A 1 M (M=mol dm^{-3}) solution of azide was prepared by dissolving sodium azide (BDH, AnalaR) in distilled water. All the other chemicals used were of analytical reagent grade.

Reagent Solutions. The reagent, HDPBA, was prepared by the condensation of *N*-phenylbenzimidoyl chloride with *N*-phenylhydroxylamine in diethyl ether medium at low temperature, mp 163 °C; reported[1,19] 163 °C.

A 0.25% (w/v) solution of the reagent in acetone was used for the formation of simple iron(III)–HDPBA complex and its subsequent extraction into chloroform. A 0.1% (w/v) solution of the reagent in chloroform was used for the extraction of mixed ligand complex.

Procedure for Extraction of Iron(III) as Mixed Ligand Complex. Transfer an aliquot of iron(III) solution containing 30—300 μg of the metal in a 50-ml beaker. To this, add 10 ml of 1 M sodium azide solution and adjust the pH to 2—5 with 2 M hydrochloric acid. Transfer the solution into a 100-ml separatory funnel, wash the beaker with few ml of water, and add the washings to the funnel. Adjust the volume of the aqueous phase to 25 ml and add 10 ml of 0.1% (w/v) solution of reagent in chloroform. Shake the mixture for two min and allow the two phases to separate. Collect the organic phase into a 50-ml beaker containing about 2 g of anhydrous sodium sulfate. Wash the aqueous phase twice with 5 ml of chloroform and add the washing to the main extract. Transfer the coloured extract into a 25-ml volumetric flask and dilute to volume with chloroform. Measure the absorbance at 530 nm against chloroform as a reference.

Procedure for Extraction of Iron(III) as Simple Complex. Transfer an aliquot of iron(III) solution containing 0.05—0.40 mg of the metal in a 50-ml beaker. To this, add 5 ml of 0.25% (w/v) solution of the reagent in acetone and dilute the solution to about 20 ml with water. Adjust the pH of the solution to 8—10 using 1 M ammonia or 1 M hydrochloric acid. Transfer the solution into a 100-ml separatory funnel and wash the beaker with few ml of water and then with chloroform and add the washings to the funnel. Adjust the volumes of aqueous and organic phases to 25 and 10 ml respectively and then proceed as for extraction of mixed ligand complex. Measure the absorbance at 520 nm against chloroform as a reference.

Results and Discussion

Absorption Spectra. The absorption spectra of the reagent (HDPBA), iron(III)–HDPBA complex, and

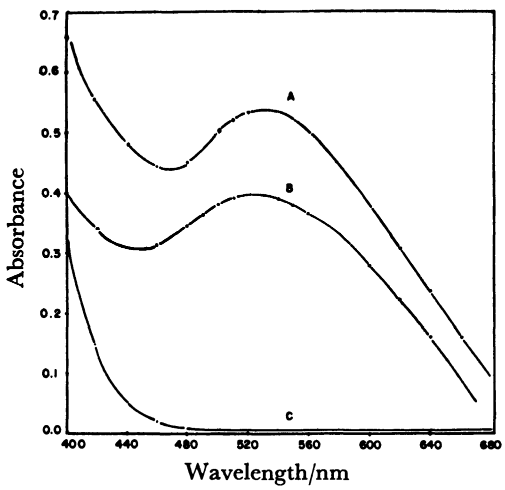

Fig. 1. Absorption spectra of iron(III) complex and reagent.
A: 1.09×10^{-4} M Fe(III) + 1.8×10^{-3} M HDPBA + 0.4 M azide, B: 1.09×10^{-4} M Fe(III) + 1.8×10^{-3} M HDPBA, C: 1.8×10^{-3} M HDPBA in chloroform.

iron(III)–HDPBA–azide complex in chloroform are shown in Fig. 1. The iron(III)–HDPBA–azide complex shows maximum absorption around 530 nm while iron(III)–HDPBA complex shows maximum absorption at 520 nm. Thus, there is a shift in the absorption maximum due to the formation of mixed ligand complex. As the reagent shows negligible absorption in the region of 450—700 nm, the reagent blank can be replaced by chloroform.

Choice of Solvent. Several organic solvents such as benzene, toluene, *o*-xylene, chlorobenzene, *o*-dichlorobenzene, diethyl ether, chloroform, and carbon tetrachloride were found to extract both the simple and the mixed ligand complexes quantitaively. The spectra of both the complexes were found to be similar in all nonpolar organic solvents. However, slight variations in the absorbance values were noticed. Chloroform was found to be the best solvent because the extraction of iron(III)–HDPBA and iron(III)–azide–HDPBA complexes are readily accomplished in it. It was also preferred because of its higher density than water allowing easy separation from the separatory funnel, its low cost, easy to recover and higher solubility of HDPBA in it than in other solvents.

It has also been found that iron(III) as a mixed ligand complex is quantitatively extracted by the chloroform solution of reagent. However, iron(III) as a simple complex can not be quantitatively extracted by the chloroform solution of reagent. Hence, the reagent was introduced in acetone solution to precipitate iron(III) as iron(III)–HDPBA complex and then the complex was quantitatively extracted by chloroform. However, care must be exercised about the amount of acetone in the aqueous phase that it should not exceed more than 50% (v/v). Increasing amount of acetone in the aqueous phase decreases the percent extraction of iron(III) as well as separation of the two phases becomes difficult.

Effect of pH. The optimum pH range for the complete extraction of iron(III)–HDPBA complex was found to be 8—11 while in the presence of azide, the optimum pH range for the complete extraction of iron(III)–HDPBA–azide complex was found to be 2—5. Thus, the pH range for complete extraction of iron(III) has been shifted from basic to the acidic medium due to formation of the mixed ligand complex. It has also been found that there is no formation of mixed ligand complex in the strongly acidic medium as reported by earlier workers.21)

Effect of Amount of Reagents. A 1:8 molar ratio of iron to HDPBA was found to be adequate for the complete extraction of iron(III)–HDPBA complex while a 1:5 molar ratio of iron to HDPBA was necessary for the complete extraction of azide–iron(III)–HDPBA complex. A large excess of the reagent upto 50-fold had no adverse effect. Thus, the present method has a distinct advantage over the reported method.21) in which a large excess of reagent (30-fold) is required for the complete extraction.

The optimum concentration range of azide in the aqueous phase for the complete extraction of iron(III) as a mixed ligand complex was found to be 0.25 to 0.50 M. Higher concentration of azide upto 1.0 M did not have any effect on the extraction. It was also found that the extraction of iron(III)–HDPBA–azide complex is dependent on the concentration of azide in the aqueous phase and not simply on the molar ratio of iron(III) to azide as reported in literature.21)

Effect of Other Variables. Both the simple and mixed ligand complexes were completely extracted into chloroform within 2 min. The chloroform extracts of both the complexes were stable for at least 48 h at 27±2 °C. The volume of the aqueous and organic phases can vary from 1:1 to 5:1 without any adverse effect on the absorbance values or the extraction efficiency of both systems. Variation in temperature of the aqueous phase between 20 and 35 °C did not affect absorbance value of both the systems.

Beer's Law, Optimum Concentration Range, Molar Absorptivity, Sensitivity, and Precision. Beer's law obeys in the concentration ranges 1.8—16 ppm for simple system and 1.2—11.2 ppm of iron(III) for mixed ligand complex system. The optimum concentration ranges for the determination of iron as evaluated from the Ringbom's plot23) are 3.0—14 ppm and 2.4—10 ppm for simple and mixed ligand complex systems respectively. The molar absorptivities of the Fe(III)–HDPBA and Fe(III)–HDPBA–azide complexes are 3.6×10^{3} and 4.9×10^{3} l mol^{-1} cm^{-1} respectively. The photometric sensitivities24) of the colour reactions are 0.0155 and 0.0114 μg cm^{-2} of iron(III) for simple and mixed ligand complexes respectively. Thus, the present method is found to be more sensitive than the literature method21) with similar reagents.

The relative standard deviations for the determination of iron(III) as simple and mixed ligand complexes were found to be ±0.50 and ±0.70% respectively.

Effect of Foreign Ions. The influence of foreign ions was studied by adding known quantities of an ion in question to an aliquot of standard iron(III) solution and determining the iron content according to the procedures described earlier. The tolerence limits of foreign ions (ppm) which causes an error less than

±2% are shown in parentheses.

Mixed Ligand Complex System (*pH=3.0, 6 ppm Iron*). Chloride, nitrate, sulfate (2000); arsenate, phosphate, borate (400); citrate or tartrate (100); cyanide or thiocyanate (40); ammonium (2000); alkali and alkaline earth metals (1000); Zn^{2+} or Cd^{2+} (800); Cr^{3+} or Mn^{2+} (600); Ti^{4+} or Zr^{4+} (800); Al^{3+} or La^{3+} (400); Ni^{2+} or Co^{2+} (400); Cu^{2+} (200); Hg^{2+} (200); Mo^{6+} (50); U^{6+} (50).

Vanadium(V) interferes with the determination. However, its interference was eliminated by its prior extraction at pH 0.5 and then iron(III) was extracted after raising the pH to 3.0

Simple Complex System (*pH=9, 8 ppm Iron*). Chloride, nitrate, sulfate (2000); phosphate, arsenate, borate (400); citrate, tartrate (200); alkali and alkaline earth metals (1000); ammonium (1000); Zn^{2+}, Cd^{2+}, Hg^{2+} (200); Al^{3+}, La^{3+} (200); Cr^{3+} (200); Th^{4+} (200); Ti^{4+}, Zr^{4+} (100); W^{6+} (50). Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, V^{5+}, Mo^{6+}, and U^{6+} interfere with the determination of iron(III) with HDPBA and the method is not selective.

Thus, there is a great improvement in the selectivity of the method for the determination of iron(III) with HDPBA due to formation of mixed ligand complex in the presence of azide. Furthermore, the sensitivity of the method is also increased considerably.

Composition of Complexes. The composition of both complexes were determined by different methods.[25] The ratio of iron(III) to HDPBA in Fe(III) HDPBA complex was determined by continuous variations[26] and mole ratio[27] methods. The result obtained by both methods indicates the formation of 1:3 (Fe:HDPBA) complex. The ratio of iron(III) to HDPBA in the mixed ligand complex was also determined by continuous variations and mole ratio methods. The concentration of azide was kept constant excess for these experiments. To determine the ratio of iron(III) to azide, the concentration of iron(III) was kept constant and HDPBA was taken in constant excess, and then the concentration of azide was varied. Iron(III) was extracted as a mixed ligand complex into chloroform and determined according to the procedure described earlier. The remaining iron(III) in the aqueous phase was determined by atomic absorption spectroscopy and the distribution ratio, D, of iron(III) was calculated at different concentrations of azide in the aqueous phase. Log D was plotted aqainst log $[N_3^-]$. The slope of the curve gave the number of azide ions in the ternary complex. These results indicated the formation of 1:2:2 (Fe:HDPBA: N_3^-) mixed ligand complex. It may be suggested from the composition and extractability as a neutral complex into chloroform that only one HDPBA molecule is deprotonated in the complex formation. However, the structure of the mixed Ligand complex has not been confirmed.

It can be noted that the earlier workers[21] have reported the composition of the mixed ligand complex as 1:1:2 (Fe:HDPBA:N_3^-). In contrast to that, it has been found to be 1:2:2 (Fe:HDPBA: N_3^-) in the present investigation.

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