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A SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF IRON (III) BY ADSORPTION OF ITS1-ALLYL-3-(5-CHLORO-2-PYRIDYL) THIOUREA COMPLEX

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ABSTRACT

A simple, economic yet accurate spectrophotometric determination of iron (III) by adsorption of its 1-ally1-3-(5-chloro-2-pyridyl) thiourea complex on microcrystalline naphthalene is described. The complex adsorbed was dissolved in dimethylformamide. The absorbance of the solution was measured at 475 nm against the reagent blank. Beer's law is obeyed in the concentration range 15-140 µg of iron (III) in 10 ml of dimethylformamide. The molar absorptivity was found to be 2.2 x 104 1 ml^{-1} cm^{-1} and sensitivity being 1.67 $x10^{-2}$µg for the absorbance of 0.001. The effect of various parameters namely pH, buffer solution, reagent concentration and naphthalene concentration have been investigated.

KEYWORDS: Thiourea, Naphthalene, Absorbance, Iron (III) Complex

Thioureas and its derivatives have got wide applications as corrosion inhibitors (Yoe and Overholser; 1942), antiviral agent (Mathaur and Bhandari: 1973), potential pesticides (Satake *et al*. 1976) and insecticides (Sarkar *et al*. 1968).

Many substituted thioureas have exhibited analgesic (Holland *et al*. 1968), anti inflammatory (Paria *et al*; 1989), antihypertensive (Mathur *et al*. 1979), hypoglycemic activities (Prakash *et al*. 1979). Derivatives of isothioureas can be used as potential growth inhibitors (Mohabey and Mishra; 1980). Another important therapeutic uses of thiourea derivatives are their antithyroid (Naqui *et al.* 1983), anesthetic (Dhar and Pandit ; 1983) and anticonvulsant activities (Satake and Singh; 1982).

Apart from their biological importance, thioureas are well known for their analytical applications (Holland and Bozic; 1968, Goel ; 1988, Abdul *et al.* 1988).

1-ally1-3-(5-chloro-2-pyridyl) thiourea, a newly synthesized reagent has been found to possess interesting analytical applicants. It forms water insoluble colored complexes with various metal ions viz. Fe (III), Cu (III), Bi (III), Ag (I), U(VI), Ni(II) and Cd(II). The presence of thioketo (>C=S) group in this reagent is responsible for the characteristic color reactions with metal ions. The iron complex is easily adsorbed on microcrystalline naphthalene and trace iron is determined photometrically.

A New method "Analysis of metals by solid liquid separation after liquid-liquid extraction" has been employed for the determination of iron (III). 1-ally1-3-(5-chloro-2-pyridyl)

Thiourea-KI-iron complex was adsorbed on naphthalene in aqueous solution on vigorous shaking naphthalene is aqueous solution on vigorous shaking. The absorbed mixture of the complex and naphthalene was filtered dried and dissolved in dimethylformamide.

The absorbance of the solution was measured at 475 nm and trace amount of iron was determined.

EXPERIMENTAL

Standard Iron (III) Solution

A standard stock solution (1000 ppm) of Iron (III) was prepared by dissolving requisite amount of ferric chloride hexahydrate in distilled water. A 15 ppm solution of iron (III) was prepared by diluting 15 ml of stock solution of ferric chloride to 1000 ml with distilled water. Amount of iron (µg) present in sample solution was determined gravimetrically.

1-ally1-3-(5-chloro-2-pyridyl) Thiourea Solution

A 0.2% solution of 1-ally1-3-(5-chloro-2-pyridyl) thiourea was prepared by dissolving 0.2 g of reagent in 100 ml of methanol.

Naphthalene-Acetone Solution

A 20% naphthalene solution was prepared by dissolving 20g of naphthalene in 100 ml of acetone.

Potassium Iodide Solution

A 0.2% potassium iodide was prepared by dissolving 0.2 g of potassium iodide in 100 ml of distilled water.

Buffer Solutions

A series of buffer solutions were prepared by mixing required volumes of 1M acetic acid and 1M ammonium acetate solution for pH range 3-6 and 1M aqueous ammonia and 1M ammonium acetate solution for pH range 8-11.

All the chemicals used were of analytical reagent grade.

Apparatus

A Toshniwal spectrophotometer (Model CL-10) was used for all absorbance measurements.

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The pH measurements were made with Toshniwal pH meter (Model CL-43) equipped with glass and calomel electrodes.

Procedure

An aliquot of standard sample solutions of iron (III) containing 80-140 g of iron was taken in dry clean tightly stoppered Erlenmeyer flask. To it, 4 ml of acetate buffer solution was added to adjust the pH of the solution to 4.5 and then 3.0 ml of 0.2% 1-ally1-3-(5-chloro-2-pyridyl) thiourea solution was mixed. The contents of the flask were kept standing in hot waterbath (50-60^{0}C) for 15 minutes. Then 3.0 ml of 20% naphthalene solution were added to the solution of iron (III) followed by 3.0 ml of 0.2% potassium iodide solution and shaken vigorously for 2 minutes. The iron (III) complex of 1-ally1-3-(5-chloro-2-pyridyl) thiourea and potassium iodide were adsorbed on microcrystalline naphthalene. It was filtered off, washed with water dried in oven at 50^{0}C. This dry solid was dissolved in dimethylformamide and diluted to 10 ml. The absorbance measurements of iron (III) complex were taken at 475 nm wavelength against the reagent blank which was prepared similarly.

RESULTS AND DISCUSSION

Absorption Spectra

A sample solution 100 µg of iron (III,) 3 ml of 0.2% 1-ally1-3-(5-chloro-2-pyridyl) thiourea solution, 3 ml of 0.2% potassium iodide solution and 4 ml of acetate buffer solution (pH 4.5) was prepared according to the recommended procedure. The iron (III) complex, so formed was adsorbed on microcrystalline naphthalene on vigorous shaking for 2 minutes. The solid mixture of naphthalene and iron (III) complex was dissolved in dimethylformamide and absorbance of the solution was measured at wavelengths between 360–600 nm. The data of absorbance was plotted against the wavelengths and absorption spectra of iron (III) complex solution was obtained against the reagent blank. The iron (III) complex had the maximum absorption at 475 nm wavelength whereas the reagent blank had negligible absorbance at this wavelength. Hence, all absorbance measurements were carried out at 475 nm (γ max) wavelength.

Effect of pH

The relationship between the absorbance and pH of the sample solution containing 100 g of iron was investigated in the pH range 2.0-12.0. The results are shown in table 1. The absorbance was increased with increase of pH upto 4.0 then gave a maximum and almost constant value over the pH range 4.0-8.5 and further decreased sharply beyond pH 8.5. In the present study, the absorbance was therefore measured at pH 4.5.

Effect of Buffer Solution

The effects of varying amounts of buffer solution on the absorbance of iron (III) complex was discussed. The results are shown in table 2. It was found that the absorbance increases lightly with the addition of 1.0-2.5 ml of buffer solution. The absorbance was almost constant only in the range 2.5-5.0 ml of buffer solution. Hence 4.0 ml of buffer solution was chosen for all absorbance measurements.

Effect of 1-ally1-3-(5-chloro-2-pyridyl) thiourea

In order to investigate the effect of reagent concentration on the absorbance of iron (III) complex solution, different amounts of reagent solutions were added to the sample solution containing 120 µg of iron (III) at pH 4.5.

The results are illustrated in Table 3. Absorbance increased slowly upto the addition of 2.0 ml of the reagent solution and practically remained constant in the range 2.0-4.0 ml. Above 4.0 ml of reagent solution, absorbance started decreasing gradually. Therefore 3.0 ml of 0.2% reagent solution were added for the absorbance measurements.

Effect of Potassium Iodide Concentration

To study the effect of potassium iodide concentration on the complexation extraction of iron (III) complex of the reagent, 1-ally1-3-(5-chloro-2-pyridyl) thiourea, different amounts of 0.2% potassium iodide solution were added to the solution containing iron (III) and the reagent and then absorption studies were carried out the 475 m. Results are given in Table 4. Absorbance increased slowly with the increasing amounts of 0.2% potassium iodide solution upto 1.5 ml then became constant in the range 1.5 to 4.5 ml and further decreased about 4.5 ml. Hence 3.0 ml of potassium iodide is used to extract the iron (III) complex from aqueous solution.

Effect of Naphthalene Concentration

To study the effect of naphthalene concentration on iron (III) complex of 1-ally1-3-(5-chloro-2-pyridyl) thiourea and potassium iodide different amount of naphthalene solution were added. The absorption studies were carried out at 475nm. The results are shown in Table 4. It was observed that a constant maximum absorbance in the range 1.0-5.0 ml and then decrease of absorbance beyond 5.0 of naphthalene. Therefore, 3.0 ml of 20% naphthalene solution was added for the complete extraction of iron (III) complex from aqueous solution.

Choice of Solvent

The solubility of iron (III) complex of 1-ally1-3-(5-chloro-2-pyridyl) thiourea and potassium iodide was

examined in various solvents The chelate was easily soluble in dimethylformamide at room temperature. Therefore, dimethylformamide was chosen as the solvent.

Precision

The precision of the method was determined with the ten sample solutions containing 120 µg of iron. The standard deviation calculated to be 0.18%.

Table 1: Effect of pH on Absorbance

pH	Absorbance 475 nm
2.0	0.515
2.5	0.617
3.0	0.638
3.5	0.665
4.0	0.692
4.5	0.713
5.0	0.716
5.5	0.712
6.0	0.714
6.5	0.715
7.0	0.717
7.5	0.718
8.0	0.726
8.5	0.715
9.0	0.713
9.5	0.665
10.0	0.639
10.5	0.639
11.0	0.512
11.5	0.463
12.0	0.396
Iron (III):120 µg; Naphthalene:0.6 gm; 0.2 KI:3.0 ml.	

Table 2: Effect of Buffer Solution

Buffer Solution (ml)	Absorbance 475 nm
1.0	0.615
1.5	0.646
2.0	0.667
2.3	0.695
2.5	0.712
2.7	0.716
3.0	0.714
3.3	0.716
3.5	0.719
3.7	0.717
4.0	0.713
4.5	0.704
5.0	0.726
5.5	0.685
6.0	0.672
6.5	0.676
7.0	0.663
Iron (III) : 120 µg; pH : 4.5; Naphthalene : 0.6 gm	

Table 3: Effect of Reagent Concentration

0.2% reagent (ml)	Absorbance 475 nm
0.0	0.514
0.5	0.532
1.0	0.615
1.5	0.651
2.0	0.715
2.5	0.714
3.0	0.715
3.5	0.716
4.0	0.719
4.5	0.657
5.0	0.633
5.5	0.558
6.0	0.545
6.5	0.476
7.0	0.424
Iron (III) : 120 µg; pH : 4.5; Naphthalene : 0.6 gm	

Table 4: Effect of Naphthalene concentration

20% Naphthalene (ml)	Absorbance 475 nm
0.5	0.712
1.0	0.714
1.5	0.715
2.0	0.716
2.5	0.718
2.7	0.712
3.0	0.717
3.2	0.709
3.5	0.715
3.7	0.713
4.0	0.714
4.3	0.718
4.5	0.716
4.8	0.717
5.0	0.692
5.3	0.691
5.5	0.663
6.0	0.627
Iron (III) : 120 µg; pH : 4.5; Naphthalene : 0.6 gm	

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