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3-Hydroxy-3-Phenyl-1-*m*-Chlorophenyltriazene as Spectrophotometric and Complexometric Reagent in the Determination of Iron(III)

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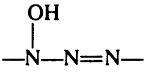
The compounds with common functional group  $-\overset{\mathrm{OH}}{\overset{|}{\mathrm{N}}}-\mathrm{N}=\mathrm{N}-$ are termed as hydroxytriazenes. Proposed hydroxytriazenes was prepared by coupling alkyl or aryl hydroxylamine with an aryl diazonium salt in sodium acetate buffered medium ($pH \cong 5.0$) at 0°C to 5°C. Iron(III) forms a blue colour complex with the reagent 3-hydroxy-3-phenyl-1-*m*-chlorophenyltriazene (R) at room temperature. The complex is stable up to four hours. The composition of the complex [Fe(III) : R] is found 1 : 2 at 650 nm at optimum pH 3.1–3.9. The molar absorptivity and Sandell's sensitivity values are 3244 mol^{-1} dm^{3} cm^{-1} and 17.22 ng/cm^{2} respectively at the working wavelength 650 nm. The Beer's law is obeyed in the concentration range $0.3 - 1.8 \times 10^{-4}$ M of iron. The standard deviation (10 measurements) for 6.7 ppm of iron was found ±0.053 ppm. The interference studies of 30 diverse cations and anions have also been performed. The same reagent was further used as indicator in the complexometric determination of Fe(III) at different variable conditions in presence of 27 diverse ions and this reagent was used in the determination of Fe(III) as spectrophotometrically and complexometrically in sulphide ore sample.

Key Words: Hydroxytriazenes, Iron(III), Spectrophotometric, Complexometric.

INTRODUCTION

Hydroxytriazenes are a well-known group of chelating agents[1]. Their applications as spectrophotometric reagents as well as metallochromic indicators for the complexometric determination of a number of transition metal ions are well established. In the last two decades several hydroxytriazenes[2–12] have been prepared and utilized as reagent for spectrophotometric determination of iron(III). In literature there are three methods[13–15] for the preparation of hydroxytriazenes. In the present work, the proposed hydroxytriazene was prepared by using Elkins

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et al.[13] and Sogani *et al.*[16] method in absolute alcohol by repeating crystallization several times using charcoal as impurity absorber. The purity of the reagent was confirmed by comparing elemental analysis of carbon, hydrogen and nitrogen, colour of the reagent, melting point, shape of the crystal and by four different spot tests[17–20]. The melting point of the proposed reagent was found to be 150°C.

EXPERIMENTAL

Nitrobenzene (99.5%) (Fluka), *m*-chloro aniline AR grade (E. Merck, Germany), zinc dust, sodium nitrite, ammonium chloride, sodium acetate, hydrochloric acid and perchloric acid GR grade (all E. Merck, India) were used. Deionized water (18 mega-ohm resistivity) prepared from Millipore Milli-Q water purification system, USA was used.

Synthesis of hydroxytriazenes

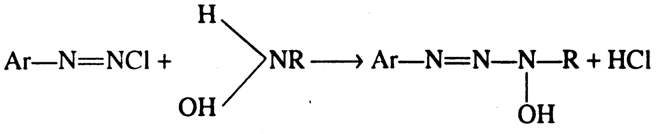
Elkins and Hunter[13] and Sogani and Bhattacharya[14] have reported this method. This method contains four steps as:

(I) Preparation of aryl or alkyl hydroxylamine: Reduction of nitrobenzene was carried out at 60–70°C by zinc dust to form phenyl hydroxylamine.

(II) Preparation of aryl diazonium salt: Diazotization of *m*-chloroaniline was carried out by sodium nitrite at 0°C to form benzene diazonium chloride salt.

(III) Coupling: Coupling of product of I and II was carried out for the preparation of 3-hydroxy-3-phenyl-1-*m*-chlorophenyltriazene reagent at 0 to 5°C using sodium acetate buffer at pH ≅ 5.0.

(IV) Crystallization: Repeated crystallization of crude product was carried out in ethyl alcohol using charcoal.



$$\text{Ar—N{=}NCl} + \begin{matrix}\text{H}\\ \\ \text{OH}\end{matrix}\!\!>\!\text{NR} \longrightarrow \text{Ar—N{=}N—}\underset{\text{OH}}{\underset{|}{\text{N}}}\text{—R} + \text{HCl}$$

R = Alkyl, aryl or substituted aryl group; Ar = aryl group.

3-Hydroxy-3-phenyl-1-*m*-chlorophenyltriazene as spectrophotometric reagent in the determination of iron(III)

All the spectrophotometric measurements were made with a Perkin-Elmer 3B UV-Vis 108 spectrophotometer. Systronics pH-meter 324 was used for the pH measurements. Calibrated pipettes and volumetric flask from Borosil Glass Works Ltd., India were used. The standard stock solution of 1000 ppm of iron was prepared from high metals of 99.99% purity in sub-boiled nitric acid. Subsequent dilutions were done from stock solution in 90% alcohol to get the desired range. Standard stock solution of 3-hydroxy-3-phenyl-1-*m*-chlorophenyltriazene of 1×10^{-2} M was prepared by dissolving requisite quantity in absolute alcohol. The stock solution was further diluted to appropriate dilution as and when required. 1% solutions of perchloric acid and tris buffer were prepared by dissolving requisite quantity in minimum de-ionized water and final volume was made by ethanol. For the interference studies GR grade salts were used.

Procedure: The spectrum of the complex formed with reagent [Fe(III) : R (1 : 6)] was obtained in the wavelength region 380–650 nm against reagent blank. The spectrum of the reagent was also measured in the same wavelength region against ethanol. The working wavelength was chosen such that there was maximum difference between the absorbance due to complex and the reagent. The absorbance of a series of solutions containing iron(III) and the reagent in the molar ratio 1 : 6 was measured against reagent blank at corresponding wavelength at various pH values to determine pH range of constant and maximum absorbance. After optimizing pH and wavelength, required volume from the stock solution of iron and reagent were taken in the ratio of 1 : 6 (Fe(III) : R) in a 10 mL volumetric flask. The optimum pH of this mixture was then adjusted between 3.1–3.9 with the perchloric acid and tris buffer. The volume was made up to 10 mL with 90% ethanol. A blue coloured solution of the complex was formed. To ascertain completion of reaction, the absorbance of the complex was measured against reagent blank at 620 nm. The molar composition of the iron(III) complex with reagent was found using three different methods Jobs method[21], Mole ratio method[22, 23] and slope ratio method[24]. In each case under corresponding optimum conditions of pH, solvent and iron(III) to reagent ratio, the validity of Beer's law was studied. The instability constants (k) and stability constants (β) of iron(III) complexes were determined from mole ratio curve using Harvey and Manning's method[23]. The precision studies were carried out by measuring the absorbance of ten solutions containing the same concentrations of iron(III) and the reagent under optimum conditions and on the basis of their absorbance value standard deviation and percentage error was calculated. The validity of the reagent is confirmed by analyzing sulphide ore samples for iron and further the results were compared by flame atomic absorption spectrometry.

Interference studies: Interference studies in presence of 5 ppm and 50 ppm of 30 different ions, *viz.*, Na^+, K^+, NH_4^+, Cu^{2+}, Pb^{2+}, Cd^{2+}, Ba^{2+}, Mn^{2+}, Zn^{2+}, Mg^{2+}, Sn^{2+}, Hg^{2+}, Ni^{2+}, Ca^{2+}, Co^{2+}, Cr^{3+}, Mo^{6+}, F^-, Cl^-, I^-, Br^-, CH_3COO^-, $C_2O_4^{2-}$, NO_3^-, SO_4^{2-}, CO_3^{2-}, HPO_4^{2-}, PO_4^{3-}, NO_2^-, SO_3^{2-} were carried out. An examination of the interfering studies reveals that 50 ppm of 11 ions, namely, Na^+, K^+, NH_4^+, Ca^{2+}, Cl^-, Br^-, CH_3COO^-, NO_3^-, NO_2^-, SO_3^{2-} and CO_3^{2-} did not interfere in the determination of 6.7 ppm of Fe(III). The tolerance limit of 5 ppm of four ions namely Hg^{2+}, Sn^{2+}, I^- and SO_4^{2-} ions was found to be 5 ppm with respect to 6.7 ppm of Fe(III). However, same ions were found to be interfering at 50 ppm level. Further, remaining15 ions interfered in the determination of Fe(III) even at 5 ppm level.

Sandell's sensitivity

The molar absorptivity of the complex (3244 $mol^{-1}\ dm^3\ cm^{-1}$) was calculated from the Beer's law graph and this value was used for determining Sandell's sensitivity of the complex which is found to be 17.22 ng/cm^2.

Formula for calculation of instability constants and stability constants

$$k_{inst} = 4C^2\alpha^3/(1-\alpha)$$

where C = initial concentration of the iron(III) complex at stoichiometric point (1.5×10^{-4} m)

α = the degree of dissociation = $E_m - E_s/E_m$

E_m = maximum absorbance of undissociated complex obtained from horizontal portions of the mole ratio curve = (0.480)

E_s = absorbance of the complex at stoichiometric mole ratio of the iron(III) to reagent = (0.432)

$\beta = 1/k_{inst}$,

$\Delta G = -2.303\ RT \log_{10} \beta$

G = free energy formation of the complex at 27°C

R = 1.987 cal deg^{-1} mol^{-1} (gas constant),

T = 300 K,

β = stability constant

Complexometric determination of iron(III)

3-Hydroxy-3-phenyl-1-*m*-chlorophenyltriazene also acts as metallochromic indicator in the determination of Fe(III) using EDTA. Optimum pH and temperature range are 2.8–3.2 and 20–35°C. At end point it gives blue to very sharp light yellow colour. 0.55 mg can be determined with good precision. The validity of the reagent has been established by analyzing iron in sulphide ore samples and compared with the results obtained by analyzing same sample solution with potassium dichromate using barium diphenylamine indicator[24].

RESULTS AND DISCUSSION

The composition of the iron(III) complex with 3-hydroxy-3-phenyl-1-*m*–chlorophenyltriazene was determined spectrophotometrically using Job's method[21], mole ratio method[22, 23] and by slope ratio method[24]. The composition of the complex was found 1 : 2 [Fe(III) : R]. The instability constant (k) and stability constants (β) of the complex were found 1.0×10^{-10} and 1.0×10^{10} respectively and ΔG at 25°C is –13.728 cal/mol. The Sandell's sensitivity is found to be good in comparison with other hydroxytriazenes reported. Interference study reveals that iron(III) can be determined in the presence of 11 different ions up to 50 ppm level, namely, Na^+, K^+, NH_4^+, Ca^{2+}, Cl^-, Br^-, CH_3COO^-, NO_2^-, NO_3^- and CO_3^{2-} and up to 5 ppm level in presence of 4 ions, namely, Hg^{2+}, Sn^{2+}, I^- and SO_4^{2-}.

Similarly, 1.109 mg of Fe(III) can be determined complexometrically in presence of 9 ions, namely Na^+, K^+, NH_4^+, Ba^{2+}, Ca^{2+}, Cl^-, Br^-, CH_3COO^- and NO_3^-, up to 50 mg and in presence of 6 ions, namely Cd^{2+}, Zn^{2+}, Hg^{2+}, Co^{2+}, CO_3^{2-} and Mg^{2+} up to 30 mg. Seven ions, namely, Pb^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, I^-, PO_4^{3-} and SO_4^{2-} tolerated up to 10 mg, while the remaining 5 ions seriously interfered even at 10 mg level.

Conclusion

It is established that 3-hydroxy-3-phenyl-1-*m*-chlorophenyltriazene used in the present investigation is quite comparable to most of the spectrophotometric reagents being used in iron(III) determination as spectrophotometric and complexometric reagents. Its easy synthesis, higher yield and economic method of preparation further enhance its applicability as a spectrophotometric and complexometric reagent for iron(III) determination. Thus the present study has introduced a new reagent for iron(III) determination spectrophotometrically and complexometrically.

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