# USE OF SOME NEW CHELATING AGENTS FOR THE COLORIMETRIC DETERMINATION OF IRON

## I. ETHYLENEDIAMINE-BIS-SULPHOSALICYLALDEHYDE

by

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### INTRODUCTION

Numerous organic substances react with ferrous or ferric iron, in solution, to give characteristic colours[1]. The oldest and best known reagent[2], thiocyanate, has been more or less replaced by many of these. The following reagents: 7-iodo-8-hydroxyquinoline-5-sulphonic acid (Loretin or Yatren)[3], *o*-phenanthroline[4], $\beta : \beta' : \beta''$-tetrapyridyl[5] and di-sodium-1 : 2-dihydroxybenzene-3 : 5-disulphonic acid (Tiron or Tifferon)[6] have received considerable attention recently for the spectrophotometric determination of iron.

During the systematic investigation of a series of inner-metallic complex salts of salicylaldehyde and other hydroxyaldehydes with amines, amino-acids and other related compounds, with different metallic ions[7], it was observed that the organic ligand (Schiff's base) formed by the interaction of ethylenediamine and 5-sulphosalicylaldehyde (salicylaldehyde-5-sulphonic acid) gave intense violet-red coloration with ferric iron in solution. This colour intensity is quite high, permitting the detection and estimation of a very small amount of iron. The Schiff's base behaves as a quadridentate ligand, the sulphonic acid group remaining free. The chelate metallic complex formed was isolated in the pure state and its properties were studied.

### EXPERIMENTAL

*Apparatus.* In all the determinations a photoelectric colorimeter (Absorptiometer-Hilger Spekker) was used. Duplicate measurements were also made in a Beckmann Quartz spectrophotometer (D.U. model) using 1 cm correx glass cell. The pH values up to 10 were measured with the glass electrodes using a Cambridge pH meter (Bench type) and the higher pH values were measured with a special alkali electrode.

*Solutions.* Standard ferric iron solutions were prepared by dissolving E. Merck's (G. R. quality) ferric chloride and ferric nitrate in distilled water, free from traces of iron. Standard solutions of different cations and anions were prepared from C. P. reagents, free from traces of iron.

pH *Adjustments.* The hydrogen ion concentrations of the different solutions were adjusted to a known pH value by using standard solutions of sodium hydroxide, potassium hydroxide, hydrochloric acid and nitric acid.

*Reagent*[8]. This was prepared by sulphonating pure dry ethylenediamine-bis-salicylaldehyde (Schiff's base) with five times its weight of concentrated sulphuric acid (d = 1.84) in a water bath for 2-3 hours, with constant stirring of the mixture. A deep orange-red liquid was obtained. Light yellow crystals of ethylenediamine-bis-salicylaldehyde sulphonic acid separated on cooling the solution in an ice and salt bath. The compound is highly soluble in water and gives a light yellow solution. It is insoluble in alcohol, benzene, acetone, chloroform and dioxane. (Found: C, 44.88; H, 3.89; N, 6.51 and S, 14.96%: $C_{16}H_{14}O_8N_2S_2$ requires C, 44.8; H, 3.73; N, 6.54 and S, 14.95%.)

1-2% of the reagent in distilled water, free from traces of iron, was used. The pH of an 1% solution is about 3.58.

## *The colour reaction*

(i) *Effect of hydrogen ion concentration.* The intensity of the colour was found to vary with the hydrogen ion concentration of the solution. It gives a violet-red coloration instantaneously between pH 1.85 and 7.58. At a higher pH (above 7.6) the colour gradually changes (Fig. 1). It has been noted that the optical density increases up to pH 2.8 and then remains unaltered up to pH 5.7. All measurements were therefore made between the pH values 2.8 and 5.5.

(ii) *Maximum absorption (region).* The maximum absorption of the colour in the visible region was determined in a Beckmann Quartz Spectrophotometer using a 1 cm corex glass cell (Fig. 2). The maximum absorption of the coloured complex was found to lie between 510 and 520 mμ. Measurements of absorptions were therefore made with a Green (II) filter in the Hilger Spekker Absorptiometer, having a maximum absorption at 520 mμ. The reagent itself showed little absorption in this range.

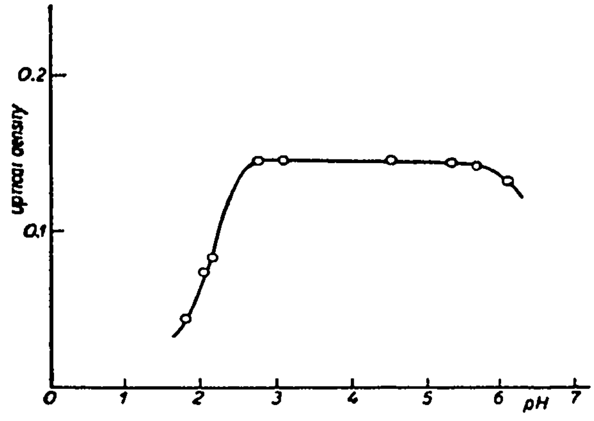

Fig. 1

(iii) *Influence of the reagent.* The reagent itself is slightly coloured (yellow) in aqueous solution but shows negligible absorption at 520 mμ, the wavelength at which the optical density was measured. All measurements were made in the presence of an excess of the reagent. For a solution with a final volume of 50 ml, 10 ml of 1% reagent solution

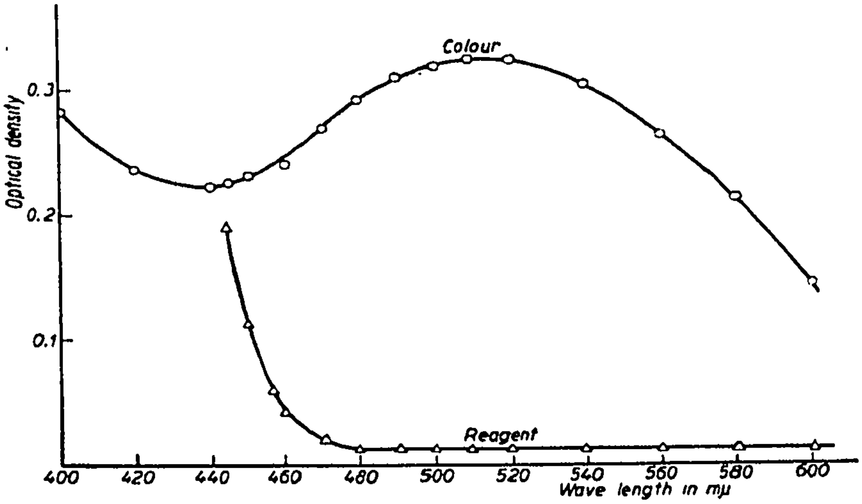

Fig. 2

was sufficient for an iron concentration of up to 5 p.p.m. in the pH range 3.6-4.8. The intensity of the colour formed was not increased by the addition of more reagent.

(iv) *Stability of the colour.* The violet-red colour of the iron complex was quite stable. A solution containing 0.15 mg of iron and 5 ml of reagent at pH 3.6 showed no change in transmittancy even after keeping overnight.

(v) *Influence of temperature.* The optical density of the coloured solution has been found to increase slightly above 40° C and to diminish below 25° C.

TABLE I*

| *Temperature* | *Optical density* |
|---|---|
| 20° C | 0.232 |
| 25° C | 0.240 |
| 30° C | 0.242 |
| 35° C | 0.244 |
| 40° C | 0.248 |

* Fe = 2 p.p.m. and pH = 4.2 approx.

(vi) *Influence of other ions.* Phosphate, $HPO_4^{-2}$, borate, $BO_3^{-3}$, fluoride, $F^-$ and molybdate, $MoO_4^{-2}$ ions have been found to interfere strongly even in very small quantities. The effects of other ions are shown in Table II.

TABLE II

| *Ion* | *Added as* | *Interference* $>$*p.p.m.* |
|---|---|---|
| $Al^{+3}$ | $Al(NO_3)_3$ | 250 |
| $Ca^{+2}$ | $Ca(NO_3)_2$ | 300 |
| $Co^{+2}$ | $Co(NO_3)_2$ | 150 |
| $Cr^{+3}$ | $CrCl_3$ | 100 |
| $Cu^{+2}$ | $CuSO_4$ | 150 |
| $Mg^{+2}$ | $MgCl_2$ | 250 |
| $Mn^{+2}$ | $MnCl_2$ | 180 |
| $Ni^{+2}$ | $NiSO_4$ | 150 |
| $Sn^{+2}$ | $SnCl_2$ | 250 |
| $Zn^{+2}$ | $ZnCl_2$ | 200 |
| $ZrO^{+2}$ | $Zr(NO_3)_4$ | 250 |
| $HAsO_4^{-2}$ | $Na_2HAsO_4$ | 200 |
| $CH_3COO^-$ | $CH_3COONa$ | 200 |
| $C_2O_4^{-2}$ | $Na_2C_2O_4$ | 80 |
| $NO_3^-$ | $KNO_3$ | 200 |
| $SO_4^{-2}$ | $Na_2SO_4$ | 150 |

(vii) *Verification of Beer's law.* The colour was found to obey Beer's law over a wide range of concentration, (Fig. 3). The figure indicates the validity of Beer's law for the coloured system (at 510-520 mμ) over the range from 0.25 to 10 p.p.m.

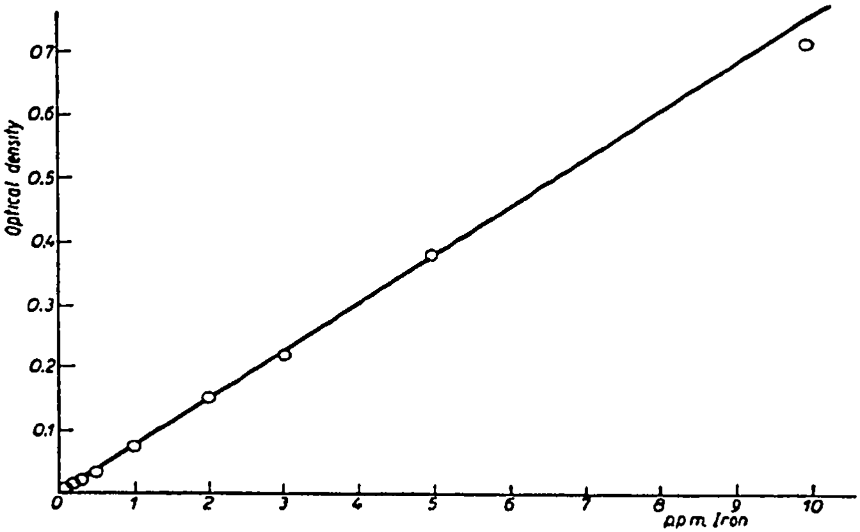

Fig. 3

## *Sensitivity of colour reactions*

Sensitivity measurements were made in photoelectric absorptiometer and the minimum quantity of iron(III) that could be estimated was 0.1 $\gamma$ per cm$^2$ (*i.e.* pD = 7).

## *Metal chelate complex*

Ferric-ethylenediamine-bis-sulphosalicylaldehyde chloride was obtained in the pure state by refluxing ferric chloride (1 mol) with ethylenediamine-bis-sulphosalicylaldehyde (Schiff's base) (1 mol) in aqueous alcohol. The mixture was filtered, while hot, after 2-3 hours. The filtrate, on standing over concentrated sulphuric acid in a desiccator, gave violet-red hygroscopic crystals.

The substance is highly soluble in water and pyridine but only sparingly soluble in alcohol and acetone. It is, however, insoluble in chloroform, benzene, ether and toluene. It is decomposed by mineral acid on warming, but is dissolved in dilute alkalis to give a deep-red coloured solution. [Found: Fe, 10.60; N, 5.28; S, 12.14; Cl, 6.68; C, 36.05 and H, 2.93%; $Fe(C_8H_7O_4NS)_2Cl, H_2O$ requires, Fe, 10.44; N, 5.22; S, 11.95; Cl, 6.62; C, 35.84 and H, 2.98%.]

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## SUMMARY

Ethylenediamine-bis-sulphosalicylaldehyde, which gives strong violet-red coloration with ferric salts owing to the formation of a stable metal chelate complex, $Fe(C_8H_9O_4NS)Cl.H_2O$, has been utilized for the colorimetric determination of ferric iron, using a Hilger-Spekker photoelectric absorptiometer. The maximum intensity of absorption occurs at pH 2.8-5.5 in the green region (510-520 m$\mu$) of the visible spectrum.

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The colour complex has been found to obey Beer's law between 0.25 and 10 p.p.m. The influences of several foreign ions on the reaction have been carefully studied. The metal chelate complex has been isolated and its properties studied.

## RÉSUMÉ

L'éthylènediamine-bis-sulfosalicylaldéhyde, donnant une coloration violet rouge avec les sels ferriques par formation d'un complexe stable $Fe(C_8H_9O_4NS)Cl.H_2O$, a été utilisé pour le dosage colorimétrique du fer(III); on a employé un absorptiomètre photoélectrique Spekker-Hilger. On obtient une intensité d'absorption maximum dans la région du vert (510-520 m$\mu$) aux pH 2.8-5.5. La coloration suit la loi de Beer entre les concentrations 0.25 et 10 p.p.m. L'influence de plusieurs ions étrangers sur la réaction a été examinée. Le chélate formé a été isolé et ses propriétés ont été étudiées.

## ZUSAMMENFASSUNG

Das Äthylendiamin-bis-sulfosalicylaldehyd, welches eine rot-violette Färbung mit den Eisen (III) salzen gibt durch Bildung eines stabilen Komplexes $Fe(C_8H_9O_4NS)Cl.H_2O$, wurde fur die kolorimetrische Bestimmung von Eisen(III) verwendet. Man gebrauchte ein photoelektrisches Absorptionsmessgerät Spekker-Hilger. Man erhält eine maximale Absorption in der grunen Region (510-520 m$\mu$) bei pH 2.8-5.5. Die Farbintensität folgt zwischen den Konzentrationen 0.25-10 p.p.m. dem Beer'schen Gesetz. Der Einfluss von verschiedenen Fremdionen auf die Reaktion wurde untersucht. Das gebildete Chelat wurde isoliert und seine Eigenschaften studiert.

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