Pakistan J. Sci. Ind. Res., Vol. 23, Nos. 3–4, June–August 1980

SPECTROPHOTOMETRIC DETERMINATION OF IRON AFTER EXTRACTION OF THE Fe (III) – SCN SYSTEM BY HIGH MOLECULAR WEIGHT AMINES

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(Received September 25, 1978; revised January 12, 1980)

An investigation of the complex formed between iron (III) and thiocyanate in hydrochloric acid solutions has been carried out, and its extractability by a high molecular weight (HMWA) tertiary amine in organic solvents examined. The blood red complex of hexathiocyanatoferrate (III) is qantitatively extractable from an aqueous phase into an organic phase containing Allamine 336. On the basis of this extractability a method has been developed for the spectrophotometric determination of traces of iron (0.1–1 ppm) in presence of other elements. The homologous nature of the absorption spectra of the coloured species in the aqueous and amine phases indicate the presence of the same absorption species in each medium. The extractability of the complex by HMWA suggests that the coloured species is anionic.

INTRODUCTION

The use of alkali thiocyanates as complexing reagents for the colorimetric estimation of a number of metals has been known for sometime. More recently advantage has been taken of the use of thiocyanate complexing as a method of chemical separation [1]. An intensive study of the distribution of many metal thiocyanates to ethyl ether at various NH_4SCN concentrations has been made by Bock [2], and it has been shown that a sizeable number of metal thiocyanates are extractable to the organic solvent. The present authors after a study of the extraction of thiocyanate complexes of Pd(II) [3], Mo(VI) [4] and Ti(II) [5] into HMWA, undertook the present work of extraction of Fe(III) - SCN for a spectrophotometric determination of iron. In the later work it was reported that Fe(III) also forms various kinds of complexes with thiocyanate, which have been studied toward this end.

Thiocyanate is extensively used for the determination of iron, even though other reagents may give better results. In spite of its limitations, which are often too serious, the thiocyanate method is a valuable one in applied analysis [6]. The intensity of the coloured species, is dependent on many factors and fades rapidly in aqueous phase. Acetone [7], 2-methoxy ethanol [8] has been recommended for the purpose. The ferric thiocyanate complex can be extracted by amyl alcohol, a mixture of amyl alcohol and ether [9], a mixture of monobutyl ether of ethylene glycol and ethyl ether [10], ehtyl acetate [11] and n-butyl phosphate [12]. With some of these solvents, the stability of the colour is greater than it is in water. Sulfate apparently has less effect when an immiscible solvent is used [13]. Isobuty alcohol has been recommended by Thompson [14] for the extraction but the colour intensity has been reported to be increasing and decreasing with passage of time.

An unusual method of obtaining a stable solution of the thiocyanate complex involves extraction with ethyl ether saturated with sulfur dioxide [15]. Baily [16] used methyl ethyl ketone for the stabilization of the colour. Zeigler [17] extracted the coloured species into organic phase after precipitating it as tributylammonium hexathiocyanatoferrate (III). Luca [18] measured the distribution of macro concentrations of iron (III) over a rather broad range of iron (III) and trilauryl ammonium chloride concentrations using the diluent *o*-xylene. Burken [19] studied the equilibrium constants of the extracted anionic complex after its extraction into trinonylamine.

No attempt, however, appears to have been made in extracting the coloured complex species into organic phase containing an amine for the spectrophotometric determination of iron. As the coloured species form series of complexes, efforts were made to establish the parameters that are favourable towards formation of an extractable stable species. Investigation towards this lead to the quantitative extraction of the coloured species under optimal conditions for spectrophotometric determination of iron.

EXPERIMENTAL

Apparatus. Spectronic 20.

Reagents. Iron Standard Solution: Ferric chloride (10 g) were dissolved in a few ml of HCl. The solution was diluted to 1 l and standardised volumetrically.

Potassium Thiocyanate: 20% (aq) solution (w/v) 1.5*M*.

Allamine 336: The solution (5%, v/v) was prepared either in chloroform or in thiophene-free benzene. All other chemicals used were of Analar grade.

Formation of the Fe (III) – SCN Complex and Extraction by Amines. The blood red complex was formed by adding thiocyanate into a solution containing iron in presence of HCl. Amine solution (5 ml) in organic phase was added to the coloured solution of iron in a separating funnel and was shaken for 1 min. The phases were allowed to separate and the coloured complex was quantitatively extracted into the organic phase as no trace was ever found in the aqueous phase. The colour of the complex after extraction was the same as in the aqueous phase. The organic phase was collected in a dried flask after passing it through a small filter paper (5 cm) to remove suspended water droplets. The absorption spectrum was determined with respect to a blank containing all the reagents, but no iron and extracted in the same way. The spectrum shows the maximum absorption at 480 nm.

Calibration, Sensitivity and Stability. Known concentrations of iron were extracted by the foregoing procedure and absorbance measured at 480 nm. For solutions containing between 0.5–5 μg/5 ml, i.e. 0.1–1.0 ppm Beer's law was closely obeyed. The molar absorption coefficient is 3.3×10^5. An optical density of 0.1 corresponded to 0.33 μg whereas the same corresponds to 0.8 μg of iron by the standard aqueous method; thus the present method is 2.5 times more sensitive and the colour is fairly stable for 3 hr. At the end of this period there is a gradual fading and lowering of the intensity of colour, and reaches half of its value after 24 hr. The stability of amine/organic solvent extract was found to be dependent on four factors; (a) KSCN concentration, (b) the type of solvent, (c) the type of amine, and (d) pretreatment of amines.

Various concentrations of thiocyanate were examined and concentration in the range of 0.24–0.42*M* was found to be the most suitable for maximum colour intensity and efficient extraction. Thiocyanate solutions should be freshly prepared. Similarly the effect of HCl concentration on overall extraction was noted and a concentration in the range of 0.25–0.35*M* was found to be the most suitable for maximum colour intensity and efficient extraction. The effect of HCl and KSCN on the intensity of colour are shown graphically in Figs. 2–3 respectively.

Solvent Effect. When chloroform is used as the solvent, the extract is stable only for a short period of 10–15 min after extraction and slight turbidity then appears alongwith fading of colour and results are sometimes not reproducible. A benzene solution of the Allamine 336 when used as extractant, a very clear solution was obtained. This was in conformation with our earlier work in extraction of metal

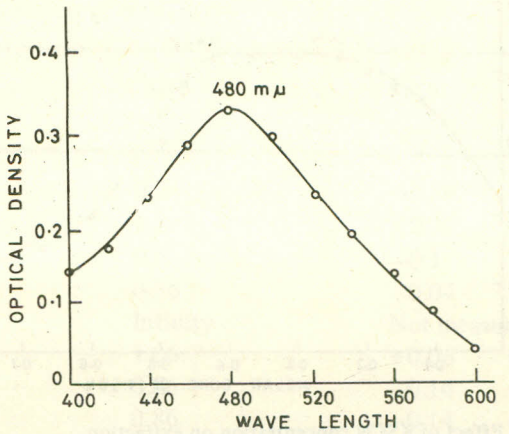

Fig. 1. Absorption spectrum of Fe(III) – SCN system after extraction into organic amine-phase.

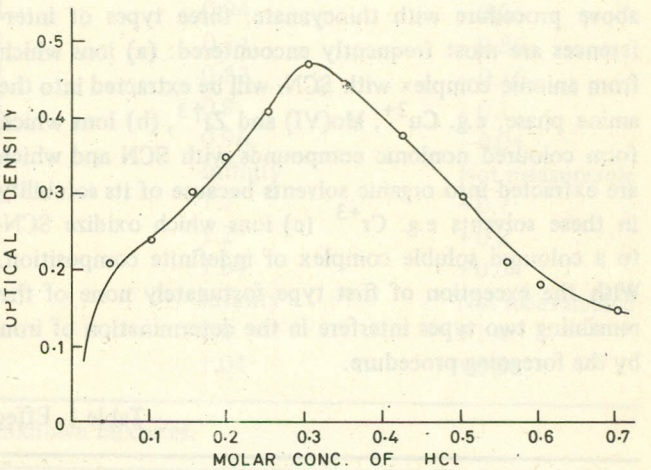

Fig. 2. Effect of HCl concentration on extraction.

anionic complex species [3].

Pretreatment of Amine. Pretreatment of amine with an aqueous phase containing all the reagents except iron was essential for the overall stability of the extracted species. It is indicative of rather the unstable nature of the anionic complex which is greatly affected by a slight variation. In all subsequent extraction pretreatment amine was used.

Procedure

Take 1–3 ml iron solution containing (1–10 μg)iron in a separating funnel and add 5 ml KSCN followed by 1 ml of 2.5*M* HCl. Shake the contents and add 5 ml of pretreated amine (Allamine 336) solution in benzene. Shake the two phases for 0.5–1 min either manually or by a mechanical shaker and allow the phases to separate. Filter the amine layer through a small filter paper into a 5–10 ml flask to remove the suspended water droplets and make up the volume to 10 ml with organic diluent. Measure the absorbance at 480 nm after 15 min of extraction against a blank

$$K_3[Fe(SCN)_6].H_2O + 2R_3\overset{+}{N}H\overset{-}{A} \rightarrow R_3(NH_3)Fe(SCN)_6$$
(aq) (org) (org)

$$2R_3N + 2HA + Fe(SCN) + 2KSCN \rightarrow$$
(org) (aq) (aq)

$$2R_3(NH)_2\,Fe(SCN)_6 + 2\,KA$$
(org) (aq)

The fact that the absorption spectra of the complex species is the same with all the amines in organic phase would indicate that the absorbing species is the same in each case. The fading of colour of the complex in aqueous phase indicates the instability of the complex which when bonded with a high molecular weight amine under favourable concentration of thiocyanate and HCl is sufficiently stable to make use of it as a very sensitive spectrophotometric method. The sensitivity of the absorbing species and the high molar absorption coefficient also indicate that the peak being used at 480 nm is the only peak in the spectrum. This is also indicated by the size of the molar extinction coefficient.

Acknowledgement. Supply of HMWA by Professor Kai Grjotheim and Dosent Gunnar Thorseen, Technical University, Trondheim (Norway) is gratefully acknowledged.

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