The formation of binary and ternary vanadium(V) complexes with arylhydroxylamine, oxine, and several anions has been investigated. A remarkable influence of thiocyanate has been observed on V(V)-arylhydroxylamine complexes. In view of this, the ternary complex formation between V(V)-N-p-methylbenzoyl-N-p-methylphenylhydroxylamine and thiocyanate ion and its extraction have been studied by us and the results are presented in this paper.

The binary golden-yellow V(V) complex with the reagent N-p-methylbenzoyl-N-p-methylphenylhydroxylamine (I) formed in the acidity 0.01-0.5N (HCl) is extractable into chloroform, but it shows no absorption in the visible range and is very unstable. However, forms a stable dark blue-violet complex in the presence of thiocyanate with $\lambda_{\text{max}}$ at 560 nm and the complex is easily extractable into chloroform.

Materials and Methods

The reagent, N-p-methylbenzoyl-N-p-methylphenylhydroxylamine (I) was prepared following the standard method. A 0.5% (w/v) solution of the reagent was prepared in chloroform for spectrophotometric studies. A 2% solution of ammonium thiocyanate was prepared in doubly distilled water and standardised volumetrically. The metal solution prepared from AR ammonium metavanadate was standardised volumetrically. All the other chemicals used were of high purity.

Extraction procedure of vanadium(V) — Dilute HCl was added to an aliquot of the standard metal ion solution (1 ml of 0.1 mg/ml solution) to bring the pH of the solution to one and water was added to make the volume of the aqueous phase 15 ml. Reagent solution (5 ml of 0.5% w/v solution) was added along with chloroform to form chloroform-extractable dark blue-violet ternary complex at pH 1.0 with $\lambda_{\text{max}}$ at 560 nm ($e = 6400$ litre mol⁻¹ cm⁻¹). Beer's law is obeyed in the range 0.4-14 ppm with an optimum concentration range of 1-10 ppm at 560 nm. The photometric error is found to be 2.72. The extracted species is a ternary complex of stoichiometry 1:2:1. On the basis of the bathochromic effect caused by thiocyanate and the high molar absorptivity of the complex formed, a sensitive method for the extraction-photometric determination of vanadium(V) is developed. The method has been applied to steel analysis. The various equilibrium extraction constants $K_{\text{ex}}, K_A$ and $K_{\text{mixed}}$ for the complex system have been also determined.
Determination of Composition and Extraction Constants of V(V) Complexes by Hiskey-Meloche’s Method

In the absence of thiocyanate, the partition of vanadium(V) complex between water and organic solvent is given by Eq. 1,

\[ K_{ex} = \frac{D_0[H^+]}{[HR]_{org}} \]

Hence \( K_{ex} = \frac{D_0[H^+]}{[HR]_{org}} \)

where \( D_0 = \frac{[\text{VO(R)}_2 \text{OH}]_{org}}{[\text{VO}^+]_{aq}} \)

A plot of \( D_0 - pH \) versus \( [HR]_{org} \) is linear and its slope equals 2 which is the number of reagent (R) molecules present per vanadium atom.

The above equation is valid only in the high pH medium but when the acidity is maintained around 1N, the effective \( H^+ \) ion concentration remains constant and so the Eq. (2) reduces to \( K_{ex} = \frac{D_0}{[HR]_{org}} \).

By graphical extrapolation, \( K_{ex} \) is determined from the intercept on the ordinate.

In presence of thiocyanate, the binary complex \( \text{VO(R)}_2 \text{OH} \) is transformed quantitatively into the ternary complex as,

\[ \text{[VO(R)}_2 \text{OH}]_{org} + \text{SCN}^- + \text{H}^+ \rightarrow \text{[VO(R)}_2 \text{SCN}]_{org} + \text{H}_2\text{O} \]

Let, \( E \) be the absorption that is measured on varying the concentration of HR, keeping \( \text{VO}^+ \) constant and \( \text{SCN}^- \) in large excess, then we may write,

\[ E = \epsilon_1 [\text{VO(R)}_2 \text{OH}]_{org} + \epsilon_2 [\text{VO(R)}_2 \text{SCN}]_{org} \]

where \( \epsilon_1 \) and \( \epsilon_2 \) are the molar absorbances of \( [\text{VO(R)}_2 \text{OH}]_{org} \) and \( [\text{VO(R)}_2 \text{SCN}]_{org} \) respectively at \( \lambda_{max} \). Since \( \text{SCN}^- \) is in large excess, \( [\text{VO(R)}_2 \text{OH}]_{org} \) \( \approx \) 0 and so,

\[ E = \epsilon_2 [\text{VO(R)}_2 \text{SCN}]_{org} \]

But in the absence of \( \text{SCN}^- \) ion, however, \( E = \epsilon_1 [\text{VO(R)}_2 \text{OH}]_{org} \). If \( E_{max} \) is the maximum absorption attained by the system and \( E \) is the absorption for a certain amount of HR, then we can write,

\[ D_0 = \frac{[\text{VO(R)}_2 \text{OH}]_{org}}{[\text{VO}^+]_{aq}} = \frac{E}{E_{max} - E} \]

Hence the Eq. (2) may finally be written as,

\[ \log \frac{E}{E_{max} - E} \rightarrow pH = \log K_{ex} + 2 \log [HR]_{org} \]

So, a plot of \( \log \frac{E}{E_{max} - E} \rightarrow pH \) versus \( [HR]_{org} \) will give a straight line with \( K_{ex} \) as the intercept and 2 as the gradient.

Again, from Eq. (3),

\[ K_A = \frac{[\text{VO(R)}_2 \text{SCN}]_{org}}{[\text{VO(R)}_2 \text{OH}]_{org}[\text{SCN}^-][H^+]} \]

On further derivation, we have,

\[ K_A = \frac{E_A - E_{min}}{E_{max} - E_A} \cdot \frac{1}{[H^+] \cdot [\text{SCN}^-]} \]

where, \( E_A \) is observed absorbance at \( \lambda_{max} \) with excess reagent and varying concentration of \( \text{SCN}^- \) under investigation.

\[ E_A = \epsilon_1 [\text{VO(R)}_2 \text{OH}]_{org} + \epsilon_2 [\text{VO(R)}_2 \text{SCN}]_{org} \]

\[ E_{min} = \text{absorbance of the extract when [SCN] = 0} \]

\[ E_{max} = \text{absorbance of the extract when [SCN] is maximum} \]

Hence, the plot of \( \log \frac{E_A - E_{min}}{E_{max} - E_A} \) versus \( [\text{SCN}^-] - pH \) will give a straight line of slope \( n \) (i.e. number of anions bound to the metal ion).

\[ \log K_{ex} \text{ and } \log K_A \text{ may be determined from the intercept of the extrapolated graph. Hence the value of } K_{mixed} \text{ for the ternary complex can be determined from Eq. 8} \]

\[ K_{mixed} = K_{ex} \cdot K_A \]

The extraction constant for the mixed complex system, \( K_{mixed} \) may also be evaluated from Eq. 9,

\[ \text{VO}^+_2 + 2[\text{HR}]_{org} + \text{SCN}^- + \text{H}^+ \rightarrow [\text{VO(R)}_2 \text{SCN}]_{org} + \text{H}_2\text{O} \]

Hence, \( K_{mixed} = \frac{D_{mixed}}{[\text{HR}]_{org} [\text{SCN}^-] [\text{H}^+] / [\text{VO}^+_2]_{aq}} \)

The \( D_{mixed} \) term in Eq. (10) can be replaced by \( E \) as explained during the derivation of Eq. 4. Hence, on further extension, Eq. (10) can be written as,

\[ \log D_{mixed} = \log \frac{E}{E_{max} - E} = \log K_{mixed} + 2 \log [HR]_{org} + \log [\text{SCN}^-] - pH \]

The values of \( K_{mixed} \) for the mixed complex system may be obtained from the intercept of the plot of \( \log \frac{E}{E_{max} - E} \rightarrow 2 \log [HR]_{org} + \log [\text{SCN}^-] - pH \).

Results and Discussion

The mixed complex, V(V)-reagent (I)-SCN, was extracted into chloroform according to the general extraction procedure and the absorption spectra of the extract \( [V(V) = 7.86 \times 10^{-4} M] \) was taken in the range 390-620 nm. The complex exhibits maximum absorption at 430 and 560 nm and all the subsequent measurements were made at 560 nm against solvent as blank where the reagent has no absorption.

The formation of mixed complex took place in both the low (0.01-0.5 N HCl) and high (2-4 N HCl) acidity regions with the same \( \lambda_{max} \) and molar absorptivity (\( \epsilon \)) values. However, for the acidity in the 1N range, requirement of thiocyanate was a little higher and more time was necessary for full colour development. But at low acidity, the binary complex (in the absence of thiocyanate),
golden-yellow in colour, was very unstable, while at high acidity, the complex which changes to violet colour, is stable. Hence the mixed-ligand complex was studied in the pH range ~1 and single ligand complex in the high acidity range.

During the formation of mixed complex of vanadium(V), the concentration of 1 (5 ml of 0.5% w/v solution in chloroform) was kept constant and the concentration of thiocyanate was varied at pH 1.0. Five ml of 1% ammonium thiocyanate solution were found sufficient for full development of colour for 4 ppm of the metal. So, for subsequent measurements, 5 ml of 2% ammonium thiocyanate solution were used. But very large excess of ammonium thiocyanate decreased the colour intensity. Also, the addition of thiocyanate solution simultaneously with the addition of reagent I or before the formation of V(V)-I binary complex, reduced the colour intensity.

The color intensity of the ternary complex system [V(V)-I-SCN] was found to be stable for about 2~4 hr at room temperature. But the same system was found to be stable over 48 hr when it was kept in a refrigerator.

The colour system obeyed Beer's law for 0.4-14.0 ppm of vanadium at 560 nm. The optimum range evaluated from Ringbom's curve was 1-10 ppm. The relative error per 1% absolute photometric error according to Ayres equation was found to be 2.72%. The Sandell sensitivity and the molar absorptivity (calculated from Beer's law values) were 0.008 µg V/cm² and 6400 litre mol⁻¹ cm⁻¹, respectively.

Effect of diverse ions — Interferences due to different ions are less at high acidity in comparison to those at low acidity. Tolerance limit of Ti(IV) can be increased by increasing acid concentration in the solution. Fe(III) may also be removed by extracting the same into solvent ether at 6-8 N HCl solution. In the presence of phosphate, tolerance limits of W(VI) and Zr(IV) can substantially be increased and Cu(II) is tolerated to a higher extent in the presence of EDTA at low acidity. Interference due to Mo(VI) can be avoided by ethyl xanthate extraction. Interferences are also caused by other heavier transition elements e.g. Re(VII), Pd(II), Pt(IV) and Os(VI) but in presence of excess thiocyanate, their tolerance limits can be increased. The results are summarised in Table 1.

<table>
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<th>Interfering ions</th>
<th>Amount tolerated (ppm)</th>
<th>Interfering ions</th>
<th>Amount tolerated (ppm)</th>
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<tr>
<td>Fe(III)</td>
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<tr>
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<td>Os(VIII)</td>
<td>SI</td>
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<tr>
<td>Ce(IV)</td>
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</table>

*SI — Seriously interfered; I — interfered.

The absorption plot of \( \log \frac{E}{E_{\text{max}}} \) vs pH versus \( \log [\text{HR}]_{\text{org}} \) (where HR = I) gave a straight line with gradient 2, indicating the metal : reagent (I) ratio as 1 : 2.

To find the ratio of vanadium(V) to thiocyanate, both the Job's and molar ratio methods could not be applied but it was determined by extended Hiskey-Meloche's method. The solutions were prepared by varying the concentration of thiocyanate at a fixed excess concentration of reagent (I) [5 ml of 0.5% (w/v) solution in chloroform] and the absorbances of the extracts were measured. The plot of \( \frac{E_{\text{A}} - E_{\text{min}}}{E_{\text{max}} - E_{\text{A}}} \) vs pH gave straight line of slope unity. This suggests the metal : thiocyanate ratio to be 1:1.

Evaluation of equilibrium extraction constants of the ternary complex system — The extraction constants, \( K_{\text{ex}} \), for the V(V)-I complex system in the presence of excess thiocyanate ion was determined from the intercept of the plot of \( \frac{E_{\text{A}} - E_{\text{min}}}{E_{\text{max}} - E_{\text{A}}} \) vs pH versus log [HR]_{org} and log \( K_{\text{ex}} \) was found to be 3.86.

The extraction constant, \( K_{\text{A}} \), for the mixed system was similarly obtained from the intercept of the absorptiometric plot of \( \log [\text{SCN}^-] \) vs pH and log \( K_{\text{A}} \) was found to be 3.86.

Hence the equilibrium extraction constant of the mixed ligand system, \( K_{\text{mixed}} \) at room temperature (27°C) was obtained from Eq. (8) and its value was found to be 10.26.

The equilibrium extraction constant, \( K_{\text{mixed}} \) was directly determined from the absorptiometric plot of \( \frac{E}{E_{\text{max}}} - \frac{E_{\text{A}} - E_{\text{min}}}{E_{\text{max}} - E_{\text{A}}} \) vs log [SCN⁻] - pH. The intercept gave the value of log \( K_{\text{mixed}} \) = 10.40. This value is in good agreement with the previous results.

References