not involving diffusion current, using the cell: \( \text{Pt} | \text{Test Solutions; } \text{Cl}^- , \text{AgCl(s)} | \text{Ag} \) even at low concentrations, as low as \( 10^{-5} \) N manganese(II).

All chemicals used, unless otherwise stated, were AnalyR (BDH Ltd., England) products. Potassium dichromate solution, usually 0.4801 g dissolved in 100 ml volumetric flask, was standardised potentiometrically against a standard ferrous ammonium sulphate solution. 0.1 N manganese(II) solution was prepared from manganese sulphate and standardised by the method of Lingane and Karplus. Syrupy phosphoric acid "Pro Analytical" grade (E. Merck) reagent was used throughout this investigation. The more dilute solutions were obtained by the appropriate and accurate dilutions of the stock solutions, and medium of titration 12 M phosphoric acid was adjusted and maintained.

The amperometric titrations were carried out with a modified circuit similar to that described earlier. Platinum microelectrode and silver-silver chloride electrode without an externally applied potential, were submerged in the titration vessel represented by a 50 ml Pyrex beaker with tightly fitting rubber stopper provided with holes for the electrodes, inlet and outlet for nitrogen, and inserting the burette tip. The titration reagents (10\(^{-1}\) to 10\(^{-3}\) N) were administered from a 3 ml semimicroburette graduated in 0.01 ml divisions. During the titration the solution was uniformly and constantly stirred with a magnetic stirrer. The current through the cell was measured by a sensitive galvanometer (0-1 mA) having two variable resistances, one connected in series and the other in parallel, which served for critical damping. The galvanometer readings were noted at regular intervals after each addition of the titration reagents, usually a minute at the beginning of titration and every two minutes when the end point approaches.

The volume of the titration mixture taken initially was always 10 ml, which contained the appropriate amount of manganese(II) and the desired strength of phosphoric acid. The equivalence point was determined graphically from the plot of galvanometer deflections against the volume of titration reagent added, and the curve obtained is of reverse L-type shape. As required by the theory practically no current flows through the circuit before the end point reaches, since the platinum electrode remains polarised. Beyond the equivalence the excess oxidant is reduced at the platinum cathode resulting in a sudden increase in the indicator current because both the electrodes get polarised. The silver-silver chloride is a reversible electrode. Thus, the continuous increase of indicator current in the post-equivalence region provides a sharp end point, which is always reproducible. The reaction is stoichiometric and is completed in reasonable time. The results obtained are good and satisfactory. For quantitative estimations 10 samples between 10\(^{-2}\) and 10\(^{-5}\) N manganese(II) were selected, and for every sample the titrations were performed six times. The average experimental error of this method was estimated, and it is well within \( \pm 1.0\% \) up to 10\(^{-4}\) N. Beyond this range the error exceeds 2.0%.

Department of Chemistry, D. Singh Banaras Hindu University, Sheela Sharma January 3, 1972.


SPECTROPHOTOMETRIC STUDY OF THE COMPLEXATION REACTION BETWEEN YTTRIUM(III) AND ARSENAZO I

Abstract

Arsenazo I has been recommended as a sensitive reagent for the spectrophotometric determination of yttrium(III) in aqueous solution. The violet coloured complex has a \( \lambda_{\max} \) 560 nm at pH 6±0 ± 0.1. The composition of the chelate was found to be 1:1. The stability constant of the chelate has been determined by Job's method, mole ratio method and limiting logarithmic method, at four different fixed values of ionic strength. The value of thermodynamic stability constant of the chelate has been determined to be \( 7.3 \pm 0.2 \). The coloured complex conforms to Beer's law over the yttrium concentration of 0.28 to 5.69 ppm. The Sandell sensitivity is 0.0018 \( \nu/cm^2 \).

3-(O-ARSONOPHENYL)azo-4, 5-dihydroxy-2, 7-naphthalamide disulphonic acid (trivial name Arsenazo I, trihydrate of Arsenazo, abbreviated as ARS 1) reacts with several metal ions to form coloured complexes. Kuznetsov suggested it as a group reagent for colour reactions of rare earths. Its colour reactions with metals like zirconium, aluminium, thorium and uranium have also been reported. Recently Novakovskii and Mushkina have reported the composition and stability of com-
plexes of zinc and cadmium with Arsenazo 1. In the present communication, the composition and stability of yttrium (III)-Arsenazo 1 chelate has been reported for the first time. The violet coloured chelate has a \( \lambda_{\text{max}} \) 560 nm at pH 6.0 ± 0.1 (\( \lambda_{\text{max}} \) of ARS 1 at pH 6.0 ± 0.1 = 510 nm) and a composition 1:1. The chelate is stable between pH 5.0 to 10.0. The value of log K of the chelate was calculated by three different methods: (a) Method of Foley anti Anderson modified by Mukherji and Dey, (b) Mole ratio method and (c) limiting logarithmic method. The experiments were performed at four different fixed values of ionic strength (\( \mu \)) maintained by the addition of suitable quantity of sodium perchlorate solution. The values of log K obtained by different methods are summarised in Table I.

<table>
<thead>
<tr>
<th>Ionic strength (( \mu ))</th>
<th>log K</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>6.1±0.2</td>
<td>(a)</td>
</tr>
<tr>
<td>0.10</td>
<td>5.5±0.2</td>
<td>(a)</td>
</tr>
<tr>
<td>0.15</td>
<td>5.3±0.2</td>
<td>(a)</td>
</tr>
<tr>
<td>0.20</td>
<td>5.1±0.2</td>
<td>(a)</td>
</tr>
</tbody>
</table>

For determining the value of thermodynamic stability constant of the chelate, a graph of average value of log K against \( \sqrt{\mu} \) was plotted and the curve so obtained was extrapolated to zero ionic strength. The value so obtained is equal to 7.3 ± 0.2.

The coloured complex conforms to Beer’s law over the yttrium concentration of 0.18 to 5.99 ppm. The absorbance of the colour reaction remains constant between pH 6.0 to 8.0 at 560 nm and hence the measurements are recommended in this range of pH. The Sandell sensitivity is 0.0018 \( \text{mCcm}^2 \). The average value of molar absorption coefficient calculated at 560 nm and at pH 6.0 ± 0.1 is 43,750.

Electrophoresis experiments and adsorption of colour of the chelate by a resin Amberlite IR-45 (OH), show that the chelate is anionic in nature. This can only be explained if we consider the chelation through two phenolic oxygens, assuming the dissociation of two \(-\text{SO}_3\)H groups under the conditions of study. The following tentative structure may be written for the Y(III)-ARS1 complex.

\[
\text{HO-AS-OH} \quad \text{V}^3+ \quad \text{O}\]

The effect of various anions and cations on the system was also studied and the tolerance limit in each case was determined. ARS 1 can be recommended as a sensitive but not selective reagent for the spectrophotometric determination of yttrium (III) in aqueous solution.

The authors are thankful to Prof. R. H. Saharsrabudhey, Head of the Chemistry Department, Nagpur University, for providing necessary facilities.


MASS SPECTRAL ANALYSIS OF THE PIGMENTS FROM EMBELIA RIBES AND CONNARUS MONOCARPUS LINN.

**Abstract**

Mass spectral examination of pigments from _Embelia ribes_ and _Connarus monocarpus_ revealed the presence of embelin (I), rapanone (II) and a C<sub>9</sub> homologue (III), and embelin, rapanone, C<sub>9</sub> homologue and C<sub>15</sub> homologue (IV) respectively.

It was reported that synthetic rapanone (I) and embelin (II) did not show any noticeable difference in their behaviour on TLC in m.p. and u.v. spectra. However, in I.R. they show appreciable difference in 850-1000 cm<sup>-1</sup> region. It was further observed that M<sup>+</sup> -CO peaks that are normally expected for benzoquinones are markedly absent in these cases. In view of these observations we have re-examined the pigments from _Embelia ribes_ and _Connarus monocarpus_.

_Embelia ribes_ was reported to contain embelin and vilangin. In our present study