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Department of P.G. H. M. K. Naidu.

Studies in Chem.stry, D. S. Mahadevappa.*

Research in ChemistrY, University of Mysore, MYSORE 570 006, INDIA, Manasagangotri, Mysore, December 16, 1975.

* To whom communications are to be addressed.


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SPECTROPHOTOMETRIC STUDIES ON Zn**

WITH 7-ω-ANILINO BENZYL-8-QUINOLINOL

(ABQ)

7-ω-Anilino benzyl 8-Quinolinol (ABQ) was first prepared by Pirrone1 and Phillips2 and its chelating tendency was first qualitatively studied by Phillips3. A survey of literature reveals that its stability and spectrophotometric study has not been studied. This study was undertaken by us. The stability, composition and its use as a spectrophotometric reagent for bivalent metal Zn(II) chelate of ABQ has been determined spectrophotometrically in 60% v/v dioxane : water system using Job’s Continuous Variations, molar ratio and slope ratio methods.

Experimental

The ZnSO₄ solution was standardised by EDTA titration and was further diluted to provide 4 × 10⁻³ M Zn** solution. Ligand ABQ (4 × 10⁻³ M) solution was prepared in pure dioxane. Buffer solutions had a pH range of 0.65 to 9.6. The absorbance readings were taken on Bosch-Lomb spectrophotometer at 30 ± 1° in 60% v/v dioxane : water. The spectral study showed λmax at 390 nm at pH 7-6.

The nature of the complex was studied by employing three different methods, namely, Voxburgh and Cooper4, Job’s method of Continuous Variations5 using equimoar solutions Slope ratio6 and Molar ratio6.

Job’s method of continuous variations.—For this measurement 4 × 10⁻⁴ M solutions were employed at 7-6 pH, the absorption being measured at 390 nm. The results showed maximum absorption at 0-33 mole fraction which indicates the formula of the chelate as 1 : 2 (Zn (ABQ))₂. Slope ratio and Molar ratio also gave similar results. The stability constant of the complex as calculated by Dey and Banerjee’s Method8, was 6-2 × 10¹⁸. The free energy of formation was 26-8 K. cal/mole at 30° ± 1° C. The molar ratio method gave stability constant of 4-0 × 10¹⁸. The method is useful for spectrophotometric determination of Zn** by ABQ at 4-8 pH.

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University Department of Y. N. Bhatt.

Chemistry,

University of Bhavnagar, December 26, 1974.

K. K. Patel.

Saurashtra University,

K. J. Shah.

Bhavnagar, December 26, 1974.

R. S. Patel.*

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SPECTROPHOTOMETRIC DETERMINATION OF RUTHENIUM(III) WITH THIORIDAZINE HYDROCHLORIDE

Introduction

Reagents proposed for the spectrophotometric determination of ruthenium have been reviewed1-5. Thioridazine hydrochloride (TH) recommended by the authors for the determination of palladium (II)6 has now been used for the spectrophotometric determination of ruthenium (III).

Experimental

Standard solution of ruthenium (III) was prepared from ruthenium (III) chloride in 1·0 N hydrochloric acid and standardised. A 0·2% aqueous solution of TH was used. All other solutions were prepared from reagent grade chemicals. Beckman Model DB Spectrophotometer was used for absorbance measurements.
Procedure.—Transfer an aliquot of the sample solution which contains from 20 to 200 μg of Ru(III) to a 25 ml volumetric flask. Add sufficient sulphuric acid so that the final solution will be 1-5 N in sulphuric acid. Add 5 ml of 0-2% TH. Dilute to volume with double distilled water. Measure the absorbance vs a reagent blank at 640 nm after 10 minutes. Compare the absorbance with a standard curve to calculate the amount of ruthenium (III).

Results and Discussion

TH forms a blue coloured species with ruthenium (III) instantaneously at room temperature (22°–25° C) in sulphuric or hydrochloric acid. The sensitivity in the four acid media (1·5 N) is in the order—HCl > H₂SO₄ > H₃PO₄ > HAC. The maximum colour development takes place in 10 minutes after mixing the reagents. The stability of the blue colour in 1-5 N H₂SO₄, HCl, H₃PO₄ and HAC is 30, 20, 8 and 5 minutes respectively. Hence sulphuric acid medium has been selected. Nitric acid medium cannot be used as it oxidises TH.

The maximum colour intensity is observed in 0·1-2·5 N H₂SO₄. Above 3·0 N precipitation of the reagent takes place. A fifteen-fold molar excess of the reagent was necessary for the full development of the colour intensity. The blue coloured species assumed to be a radical exhibits absorption maximum at 640 nm at which the reagent does not absorb. The absorbance values remained constant for 30 minutes and were insensitive to temperature in the range 5–50° C. The order of addition of reagents was not critical. Beer's law is obeyed from 0·8 to 8·0 ppm of ruthenium. The optimum concentration range evaluated by Ringbom's method is 1·5 to 7·0 ppm. The Sandell sensitivity of the colour system was found to be 0·022 μg Ru(III) cm⁻². The molar absorptivity was 4·58 × 10³ litre mole⁻¹ cm⁻¹.

With the help of this reagent, as little as 4 ppm of Ru(III) can be determined in presence of 1000 ppm of the ions of Zn(II), Mg(II), Ca(II), Ba(II), Sr(II), fluoride, chloride, bromide, nitrate, sulphate, phosphate, oxalate, acetate; 100 ppm of Ni(II), Co(II), Cu(II), UO₂(II) and EDTA. However the ions of other platinum metals, Au(III), Ag(I), V(III), Ce(IV), thiosulphate and iodide were found to interfere at all concentrations.

Analysis of synthetic samples.—In one phase of the processing system devised for experimental Breeder reactor-II (EBR-II), molybdenum and zirconium alloy were used as solvents in the separation of uranium from ruthenium and other fission products. The results of analysis of ruthenium in the synthetic mixtures corresponding to zirconium-magnesium alloy composition are given in Table I.

### Table I

<table>
<thead>
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<th>Zinc added, mg</th>
<th>Magnesium added, mg</th>
<th>Ruthenium added, μg</th>
<th>Ruthenium found, μg</th>
<th>No. of determinations</th>
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Post-Graduate Department of H. Sanke Gowda, Chemistry, P. G. Ramappa University of Mysore, Manasagangotri, Mysore, India, October 17, 1975.


THE EFFECT OF ULTRASOUND ON THE CATALYTIC ACTIVITY OF COPPER

The reported work-hardening of fcc metals and a 30-100 fold increase in the rate of recrystallisation in oxygen-free, high-conductivity copper, both induced ultrasonically, and the variation of the velocity of ultrasound and attenuation in copper under varying static stress, when viewed in the light of Hutchison's review on ultrasonic absorption in solids, clearly indicate the existence of a definite interaction between ultrasound and dislocations in a solid. If the ultrasound can also bring about an alteration in the catalytic activity of a metal, that will, indeed, provide a new evidence in favour of Cratty and Granato's hypothesis that the surface terminations of dislocations are one type of active centres. A survey of the literature does not reveal any attempt made in this direction, hence, the present investigation.

Square pieces (3·0 cm × 3·0 cm) of copper foils (99-9%, B.D.II.) were used; the gm. equiv. of hydrogen peroxide (0·25 N) decomposed per