SPECTROPHOTOMETRIC STUDIES ON PLATINUM(IV)-PHENOTHIAZINE COMPLEX

B. KESHAVAN AND H. SANKE GOWDA

Department of Post-Graduate Studies and Research in Chemistry, University of Mysore, Manasagangotri, Mysore, India

ABSTRACT

Phenothiazine forms an yellowish-brown complex with platinum (IV) at a pH value of 0·5–3·5. The colour complex exhibits absorption maximum at 440 nm. A twenty-four-fold molar excess of the reagent is necessary for the full development of colour intensity. Beer's law is valid over the concentration range 0·2–3·4 ppm. The sensitivity of the reaction is 0·02 $\mu g/cm^2$ and the molar absorptivity is $9·72 \times 10^3$ l $mole^{-1}cm^{-1}$. The composition of the complex as determined by the continuous variation and mole ratio methods is 1 : 1 and the apparent stability constant of the complex at pH 2·5 and 27°C has the log K value of 4·2. The effects of buffer, time, reagent concentration and diverse ions are reported.

INTRODUCTION

PHENOTHIAZINE was proposed for the spectrophotometric determination of palladium (II)[1]. The authors have now developed phenothiazine as a sensitive reagent for the rapid spectrophotometric determination of platinum (IV). The proposed method offers the advantages of simplicity, rapidity and good sensitivity without the need for heating or extraction.

EXPERIMENTAL

Standard platinum (IV) solution was prepared by dissolving a known weight of platinum wire (99·99% pure) in hot aqua regia. The resultant solution was evaporated almost to dryness. A small amount of hydrochloric acid was added and the solution was again evaporated to dryness. The treatment was repeated three or four times in order to destroy any nitroso complexes. After the final evaporation, 5 ml of hydrochloric acid was added and the solution was made up to 500 ml with doubly distilled water. The stock solution was further diluted to give a solution of 10 μg/ml. A 0·1% solution of phenothiazine was prepared from recrystallized product in 80% ethyl alcohol. Buffer solutions in the pH range 0·5–5·0 were prepared employing 1 M sodium acetate and 1 M hydrochloric acid solutions. All other solutions were prepared from reagent grade chemicals. Beckman Model DB spectrophotometer was used for all absorbance measurements. ELICO pH meter was used for checking the pH of the solutions.

Procedure.—An aliquot of the stock solution containing 5 to 85 μg of platinum (IV) was transferred to a 25 ml volumetric flask. Sodium acetate-hydrochloric acid buffer (5 ml) and the requisite volume of ethanol to make the final volume of the solution 42% with respect to ethanol and 4 ml of 0·1% phenothiazine solution were added and the solution was diluted to 25 ml with doubly distilled water. The solution was mixed well and the absorbance was measured at 440 nm after standing 20 minutes, against a reagent blank prepared identically without platinum. The amount of platinum was then deduced from the standard calibration curve.

RESULTS AND DISCUSSION

Phenothiazine forms an yellowish-brown complex with platinum (IV) in sodium acetate-hydrochloric acid buffer at room temperature (27 ± 1° C). The optimum pH range for the complex formation is 0·5–3·5. A 24-fold molar excess of the reagent is required to obtain the maximum intensity of colour. The absorbance values remain constant over the range of ethanol concentrations 40–44% (V/V). Below 40% ethanol concentration, the reagent undergoes precipitation and above 44% the maximum intensity of the colour of the complex is not reached. The yellowish-brown complex exhibits absorption maximum at 436–442 nm. The absorption spectra of the reagent and platinum (IV) show that they do not absorb at this wavelength.

The platinum-phenothiazine complex is formed at room temperature and constant absorbance values are obtained only 20 minutes after adding the reagent to the platinum solution in sodium acetate-hydrochloric acid buffer medium containing ethanol. The absorbance values remain constant for one hour after complete complex formation. Beer's law is valid over the platinum concentration range 0·2–3·4 ppm. The optimum concentration range, for the effective spectrophotometric determination evaluated by Ringbom's method[2,3] is 1·0 to 3·0 ppm. According to Sandell's expression, the sensitivity of the reaction is 0·02 $\mu g/cm^2$ and the molar absorptivity is $9·7 \times 10^3$ litre $mole^{-1}$ cm^{-1}. Sample solutions containing 2 μg/ml of platinum (IV) prepared by the standard procedure gave a relative error of ± 0·8% and standard deviation of 0·002.

The following amounts (μg/ml) of diverse ions are found to give less than 2% error in the determination of 2 μg/ml of platinum (IV): rhodium (III) 20; iridium (III) 16; ruthenium (III) 4; osmium (VIII) 0·8; iron (III) 2; cobalt (II) 110; nickel (II) 25; copper (II) 2; sulphate 2500; nitrate 2200; phosphate 1200; chloride 5000; bromide 2000; acetate 2400 and oxalate 260. Palladium (II), gold (III), silver (I) and iodide interfere even in small amounts. Efforts to increase the tolerance limit of cations by the addition of masking reagents were unsuccessful.

Composition and stability constant of the complex.—The composition of the complex formed has been studied by Job's method of continuous variation[4,5] using equimolar solutions and by mole ratio method[6]. The determinations are made in a final volume of 25 ml and at pH 2·5 ± 0·1. The concentration of ethanol is maintained throughout the determinations at 42%. The absorbance of the solutions is measured at 440 nm. The results indicate the composition as 1 : 1. The observations at 410 and 470 nm also confirm the existence of only one complex. The stability constant values of the complex have been determined by two different methods: (*a*) Method of Foley and Anderson[7] modified by Dey and Coworkers[8] and (*b*) Mole ratio method[6]. The values of log K obtained for the platinum-phenothiazine complex at 27° C and at pH 2·5 ± 0·1 are 4·15 ± 0·1 and 4·25 ± 0·1 by the respective methods.

The nature of the complex has been studied by passing an aliquot of the solution of complex through the cation exchange resin, Amberlite IR-120 (H). The complete absorption of the colour of the complex by the ion exchanger has indicated that the complex is cationic.

The sensitivity of the proposed method is found to be more than that of tin (II) chloride[9], anthranilic acid, *o*-amino-phenol-*p*-sulphonic acid[10] and acenaphthenequinone monoxime[11] which have been proposed as sensitive spectrophotometric reagents for platinum (IV).

Determination of platinum in alloys.—Synthetic mixtures corresponding to platinum-rhodium thermocouple wire were prepared and the platinum content was determined following the standard procedure. The results are given in Table I.

TABLE I

Determination of platinum in synthetic mixtures corresponding to platinum-rhodium thermocouple wire

Pt (IV) taken, ppm	Rh (III) added, ppm	Pt (IV) found*, ppm
1·2	0·16	1·210
1·8	0·27	1·808
2·4	0·36	2·400
3·0	0·45	3·020

*The amount of platinum (IV) found is based on ten determinations.

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