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Spectrophotometric Determination of Pt(IV) Using N-(2′-Mercaptophenyl)salicylaldimine & Stepwise Formation Constants of Pt(IV) Complexes

SASWATI P. BAG & SUSIL K. CHAKRABARTI
Department of Chemistry, Jadavpur University, Calcutta 700032

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N-(2′-Mercaptophenyl)salicylaldimine gives highly sensitive colour reaction with Pt(IV) forming a deep green complex with the reagent in the *p*H range 10·5-12. In 60% aqueous ethanol (v/v) it shows λ_{max} at 725 nm and the system obeys Beer's law from 0·1 to 3 ppm of Pt, the optimum concentration range being 0·5-2 ppm of platinum. The % relative error is 2·72. The determination of composition by the methods of continued variation and mole-ratio suggests a metal to ligand ratio of 1 : 3. The molar extinction coefficient is 52677 litre mole^{-1} cm^{-1} while the sensitivity is 0·0037 µg cm^{-2}. The stepwise and overall formation constants were determined by extended Yatsimirskii's, Leden's and Harvey-Manning's methods. Log k_1, log k_2, log k_3 and log K have been found to be 3·95, 3·82, 4·62 and 12·40 respectively by photometric method.

THE Schiff's base N-(2′-mercaptophenyl)salicylaldimine has been found to form insoluble coloured complexes with platinum metals. The reagent has been found to be a very sensitive for photometric determination of Pt(IV) in the *p*H range 10·5-12. Numerous reagents such as *o*-phenylenediamine[1], *p*-nitrosodimethylaniline[2], 2,4,5,7-tetrabromofluorescein ethyl ester[3], 1,4-diphenylthiosemicarbazide[4] are suitable for photometric estimation of the metal, but suffer several disadvantages regarding selection of wavelength and interferences by associated base and platinum metals.

The reagent forms a beautiful green complex with Pt(IV) in 60% aq. ethanol on warming over a water-bath. In the *p*H range 10·5-12 the chelating reagent appears to behave as a tridentate ligand with sulphur, azomethine nitrogen and oxygen as the donor atoms. In 60% aq. ethanol, the complex species shows λ_{max} at 725 nm and is stable for three days.

Materials and Methods

Absorbances were measured with a Unicam SP600 spectrophotometer using 1 cm glass cell.

Reagent — A 1:1 mixture of freshly distilled *o*-aminobenzenethiol and salicylaldehyde in absolute ethanol was refluxed on a water-bath for 3 hr. On keeping for sometime crystals appeared which were filtered, washed with ethanol, chloroform and recrystallized from ethanol; m.p. 137-39°.

A 0·5% solution of the reagent (w/v) in ethanol was prepared for colorimetric study. Standard platinum(IV) solution was prepared by digesting AR platinum wire in aqua regia containing an excess hydrochloric acid[5]. The strength of the solution was verified by reduction with formic acid in the presence of anhydrous sodium acetate.

Solutions of diverse ions were prepared by dissolving AR grade salts in water or dilute hydrochloric acid. Lime distilled ethyl alcohol and doubly distilled water were used for preparing the solutions.

Procedure — An aliquot of the platinum solution ($1·025 \times 10^{-5}M$) was taken and 1 ml of the reagent solution was added to it. Adequate amount of ethanol and water were added to the mixture and *p*H was adjusted to 11·0 by the dropwise addition of dilute NaOH. The solution was warmed for 10 min over a water-bath. The green coloured complex was then cooled and volume made up to 25 ml by adding ethanol. The final solution was 60% in ethanol and 40% in water. A reagent blank was prepared identically, except that the Pt(IV) solution was not added. Absorbance was measured against mixed solvent as blank at 725 nm. The reagent has got no absorption in this wavelength region.

Results and Discussion

Effect of pH, reagent and time — Though the green complex forms at lower *p*H (4 and 5), the maximum colour intensity was obtained only in the *p*H range 10·5-12. 0·75 ml of the solution (0·5%) in absolute ethanol is sufficient for complete development of the colour of a solution containing 2 ppm platinum. Addition of excess reagent up to 7 ml has no effect on the optical density of the system. At higher concentration of the reagent, the colour of the complex changes gradually to yellow.

Calibration curve, optimum range and photometric error — Beer's law is obeyed by the system from 0·1 to 3 ppm of Pt(IV). Ringbom's[6] curve, as obtained by plotting per cent absorbancy (at 725 nm) against log concentration, reveals that the optimum concentration range, where the curve has the steepest slope, is from 0·5 to 2 ppm of Pt(IV). The % relative error per 1% absolute photometric error was obtained according to Ayres[7] and was found to be 2·72%.

Molar absorptivity and sensitivity — Spectrophotometric sensitivities were calculated according to Sandell[8] from Beer's law curve and found to be 0·0037 μg Pt(IV) cm^{-2} where the molar absorptivity is 52677 litre mole^{-1} cm^{-1}.

Effect of diverse ions — Except some alkali and alkaline earth metals, associated base metals and most of the platinum metals were found to interfere in the determination of Pt(IV) at *p*H 11·0 due to precipitation. However, interferences of these can be avoided if the precipitate formed is separated by filtration and subsequent determination of Pt(IV) in the filtrate is carried out. Platinum metals interfere.

Composition of the Complex

The metal-ligand ratio of the complex was ascertained by the modified Job's method[9,10]. Platinum(IV) combines with N-(2'-mercaptophenyl)salicylaldimine in the ratio of 1 : 3 (metal : ligand). This ratio was confirmed by mole-ratio method[13]. The composition of the complex may be formulated as $PtL_2.H_2L$.

Stepwise formation constants of the complex — The calculation of the stepwise formation constants of the complexes was made by graphical extrapolation methods of Yatsimirskii[12] and Leden[13]. The equilibrium concentrations of ligands and the degrees of complex formation were calculated from calibration curves. The construction of required functions and their evaluation were made after proper extension of the methods employed[14].

Following Yatsimirskii's graphical extrapolation method for 1 : 3 complex system, the stepwise formation constants (k_1, k_2 and k_3) were related to different functions, which were constructed from experimental data using the following relations:

$$a_1 = \epsilon_1 k_1 \qquad b_1 = \epsilon_3$$

$$a_2 = \epsilon_2 k_1 k_2 - \epsilon_1 k_1^2 \qquad b_2 = \frac{\epsilon_2 - \epsilon_3}{k_3}$$

$$a_3 = \epsilon_3 k_1 k_2 k_3 - \epsilon_1 k_1^3 \qquad b_3 = \frac{\epsilon_1 - \epsilon_2}{k_2}$$

Conversion of the above equations to a suitable fourth degree polynomial in k_2 was made and the equation was solved by the help of an IBM 1130 computer. The initial guess value of k_2 was obtained following the Newton-Raphson method. Values of log k_1, log k_2 and log k_3 were found to be 4·38, 4·42 and 4·99 respectively. Overall stability constant, K, was calculated considering the absorbance in the presence of a very large excess of the reagent. log K was found to be 13·79.

The first formation constant β_1 (or k_1) following Leden's method can be obtained by constructing a function Ψ_1 employing Eq. 1.

$$\Psi_1 = \frac{\varphi - 1}{L} = \beta_1 + \beta_2 L + \beta_3 L^2 + \ldots . \beta_n L^{n-1} \qquad \ldots(1)$$

Here φ is the degree of complex formation $(C_M)/M$ and $\beta_1 \ldots\ldots \beta_n$ are the respective overall formation constants. Lim $\Psi_1 L \to 0 = \beta_1$. Similarly other values were obtained.

Values of log k_1, log k_2, log k_3 and log K were found to be 3·95, 3·82, 4·62 and 12·40 respectively.

The overall stability constant for the system was also obtained by Harvey and Manning's method[15] from the degree of dissociation α, given by $\alpha = \frac{A_m - A_s}{A_m}$, where A_m is the absorbance with large excess of reagent and A_s is the same with stoichiometric amount of reagent in the complex. This was calculated to be 0·5848. The instability constant of the complex, log K was calculated according to the equation, $K = \frac{(m\alpha c)^m (n\alpha c)^n}{c(1-\alpha)}$ where m and n are, respectively, the numbers of metal ions and ligand molecules in the complex and c is the molar concentration. The calculated dissociation constant was found to be $3{\cdot}115 \times 10^{-14}$ and hence stability constant was $3{\cdot}21 \times 10^{13}$. Value of the overall stability constant (log K) obtained considering the Beer's law data is 13·51.

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