Coloured Chelate of Palladium (II) with Eriochromecyanine RC Suresh C. Shrivastawa, Kailash. N. Munshi* and Arun K. Dey

Many colour reactions and photometric methods are available for the determination of palladium (II). Eriochromecyanine RC (trisodium salt of $5-[\alpha-(3-\operatorname{carboxy}-5-\operatorname{methy})-4-$ 0x0-2: 5-cyclohexadiene-1-ylidene)-2-sulphobenzyl]-3-methyl salicylic acid or sulphohydroxymethyl fuchsone dicarboxylic acid; abbr. ECRC) has been found suitable as a new and quite sensitive chromogenic reagent for the photometric determination of palladium (II). This study also includes observations on the composition, stability and analytical applications of the metal chelate¹⁻⁸.

EXPERIMENTAL

Standard palladium solution : A fresh solution was prepared from Johnson Matthey's Specpure palladium (II) chloride dissolved in hydrochloric acid.

Eriochromecyanine RC solution : ECRC solution was prepared by dissolving the reagent (B.D.H.) in hydrochloric acid and diluting with water. Freshly prepared solutions were always used.

A Unicam SP 500 spectrophotometer with 1 cm glass cells was used for absorbance studies. A Leeds and Northrup direct reading pH indicator with a glass-calomel electrode system was used for pH measurements.

Conditions of Study: All experiments were performed at $25^{\circ}\pm 1^{\circ}$. The chelate formation was instantaneous at pH 4.5, but the mixtures were allowed to equilibrate for 30 mins. In order to determine the nature of the complex formed in solution the modified Job's method by Vosburgh and Cooper was employed^{9'10} and it was concluded that only one chelate is formed under conditions of the study. The composition of the metal chelate was determined using the method of continuous variations⁹ and the mole ratio method¹¹ and was found to be 1 ; 1 (metal : ligand).

- Present Address: Department of Chemistry, Nagpur University, Nagpur. F. Richter, Z. anal. Chem., 1944, 127, 113.
- 1.
- W. E. Thrun, Anal. Chem., 1948, 20, 1117. 2. 3. C. V. Banks and R. V. Smith, Anal. Chim. Acta, 1959, 21, 308.
- 4. E. B. Sandell, Colorimetric Determination of Traces of Metals, Interscience Publishers, New York, 3rd Ed., 1959.
- 5. G. H. Ayres and F. L. Johnson. Anal. Chim. Acta, 1961, 24, 241.
- 6. V. L. Wagner and J. H. Yoe, Talanta, 1959, 2, 223.
- 7. V. K. Gustin and T. R. Sweet, Anal. Chem. 1963, 35, 44.
- 8. W. D. Jabobs, Anal. Chem., 1960, 32, 512.
- 9. P. Job, Ann. Chim. France, 1928, 9, 113.
- 10. W. C. Vosburgh and G. R. Cooper, J. Amer. Chem. Soc., 1941, 63, 437; 1942, 64, 1630.
- 11. J. H. Yoe and A. L. Jones, Ind. Eng. Chem. Anal. Ed., 1944, 16, 111.

1014 SURESH C. SHRIVASTAWA, KAILASH N. MUNSHI AND ARUN K. DEY

Effect of pH on the stability and absorbance of the chelate : The λ_{max} 540 m μ of the chelate holds good from pH 3.5 to 5.0. Absorbance of the chelate is constant at 550 m μ from pH 3.5 to 4.5.

Effect of reagent concentration: It has been found that the maximum intensity of the colour development takes place only when the mixture contains greater than 5-fold concentration of ECRC with respect to palladium.

Beer's Law : The system adheres to Beer's Law over a range of 0.21-5.12 ppm of palladium.

Ringbom Plot: The transmittancy has been plotted against logarithm of the concentration of palladium. The effective photometric range derived from the slope of the curve was found to be $2\cdot13-4\cdot55$ ppm of palladium.

Molecular extinction coefficient: The molar absorption coefficient of the palladium (II)-ECRC chelate was found to be 13,500 at 550 m μ .

Precision of the colour reaction: The average and standard deviations were found to be ± 0.002 and $\pm 0.52\%$ respectively.

Evaluation of conditional stability constant (K): The conditional stability constant has been determined by four different methods, viz., the methods of Dey and coworkers¹², continuous variations, mole ratio and from molecular extinction coefficient measurements¹³.

The average value of log K (K = conditional stability constant; Temperature 25°; pH 4.5) is 5.0.

Proposed structure of the chelate: The chelate has been found to be anionic as noted by electrophoresis as well as by the complete adsorption of the chelate by ion exchange resin Amberlite IR-45 (OH). It has been found that the pH drops from 4.5 to 4.3 due to the complexation showing that the phenolic oxygen participates in the chelation. It is therefore believed that the chelate ring is formed between phenolic oxygen and the adjacent carboxylic oxygen.

The authors are thankful to the Council of Scientific and Industrial Research, New Delhi, for financial aid and for the award of a Research Fellowship to S.C.S.

Chemical Laboratories, University of Allahabad, Allahabad.

Received March 24, 1970

12. A. K. Mukherji and A. K. Dey, J. Inorg. Nuc. Chem., 1958, 6, 314.

13. C. D. Dwivedi, K. N. Munshi and A. K. Dey, Microchem J., 1965, 9, 218.