

Spectrophotometric Studies on the Composition and Stability of Palladium(II) Chelates with 4-(2-Pyridylazo)-Resorcinol(PAR)

K.K.SAXENA AND R.S.SAXENA

*Department of Chemistry,
Malaviya Regional Engineering College, Jaipur, India.*

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Summary: The formation, composition and stability constants of palladium (II) chelates with 4-(2-pyridylazo)-resorcinol have been studied by spectrophotometric measurements. Two red coloured chelates 1:1 and 3:2 (Pd: PAR) are formed at pH 4.0 and 10.5 with maxs. 490 nm and 520 nm and their log K values are found to be 4.9 and 21.7 respectively.

Introduction

The use of 4(pyridylazo)-resorcinol (referred to as PAR) in the colorimetric determination of elements was developed by Pollard and coworkers[1]. Later on Dey and coworkers[2-6] suggested it to be a suitable photometric reagent for the determination of lanthanides.

It is well known that the donor properties of azo group are weak, but azo compounds, containing a strong donor group in a position ortho to the azo group, form a stable five membered chelate ring[7]. The presence of hydroxyl group in the ortho position to the azo group in PAR makes it a suitable chelating agent. It is, therefore, considered worthwhile to study the chelating properties of PAR with several metals. This communication describes the formation, composition and stability constant of chelates of palladium with PAR at different pH values.

Experimental

A Unicam SP-500 spectrophotometer with matched glass cells (1 cm) was used for absorptiometric measurements. pH was measured on Leeds and Northrup direct reading pH indicator using glass and calomel electrodes. LKB

paper electrophoresis equipment was used to determine the charge on the chelates.

Palladium chloride and PAR were guaranteed Merck reagents and the solutions were prepared in doubly distilled water. For finding out the charge on the chelate, ion-exchange resins were prepared with Amberlite IR-45 (OH) and IR-120(H) both B.D.H. AnalaR grade.

All experiments were performed at $25 \pm 0.1^\circ\text{C}$. The total volume of the mixture prepared for the measurements was kept at 25 ml. The requisite amounts of buffer solutions were added to maintain the desired pH values 4 and 10.5.

Results and discussion

Properties of the reagent and absorption spectra.

In view of the observations of Dey and coworkers [8-10] that the organic chelating agents behave as colloidal electrolytes dilute solutions of the order of 10^{-4} M of PAR were employed to

avoid complications in absorptiometric measurements. With variation in hydrogen ion concentration, PAR changes its colour and region of maximum absorption was found to lie at 390 nm (from pH 1.4 to pH 7.01), 420 nm (7 - 11.5 pH) and 500 nm (11.5 - 13.2 pH) which leads to the conclusion that PAR exists in three different forms depending upon the pH of the solution as suggested by Hiniliuckova and Sommer[11].

Nature of the chelates

The method of Vosburgh and Cooper [12] was employed to determine the nature of the chelates formed in solution. It was found that two red coloured chelates show strong absorbance at 490 nm (pH - 4.0) and 520 nm (pH - 10.5). The composition and stability constants of the chelates at these pH values, however, have been worked out at 570 nm and 550 nm respectively as there was appreciable difference in absorbance at these wave lengths.

Composition of Pd-PAR chelates

For determining the empirical formula of the chelates formed under the experimental conditions, Job's method of continuous variation [13] and mole ratio method [14] were employed. It was found that the combining ratio of Pd : PAR was 1:1 at pH 4.0 (Fig 1) and 3:2 at pH 10.5 (Fig.2) suggesting the formation of Pd(PAR) and Pd₃(PAR)₂ [only two representative figures have been given for the sake of brevity].

Stability constant (K) of Pd-PAR chelates

The apparent stability constants calculated by three different methods are as shown in Table 1.

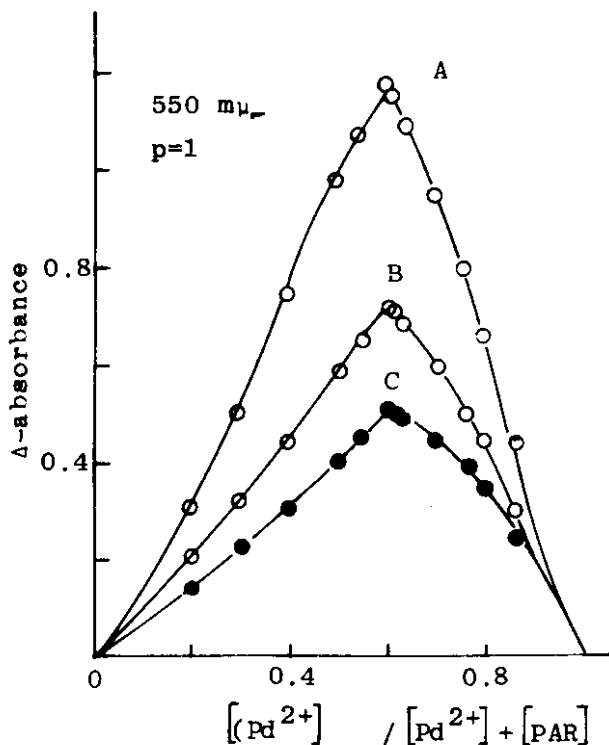


Fig.1: Composition and Stability Constant of Chelate at 550 nm by Job's Methods (p=1, pH=10.5):

Curve A: $C = 2.00 \times 10^{-4}$ M

Curve B: $C = 1.33 \times 10^{-4}$ M

Curve C: $C = 1.00 \times 10^{-4}$ M

Charge on the chelates

In order to find the charge on the chelates, electrophoresis method was employed using the buffer solution of desired pH values as an electrolyte. The period of electrophoresis was two hours which was sufficient for the migration of the charged chelates. Under the experimental conditions, the chelate at pH 4.0 was found to be neutral

Table 1

Method	pH	Log K	pH	Log K
Molecular Extinction Measurements	4.0	5.0	10.5	21.7
Continuous Variation	4.0	4.8	10.5	21.7
Mole Ratio	4.0	4.9	10.5	21.5

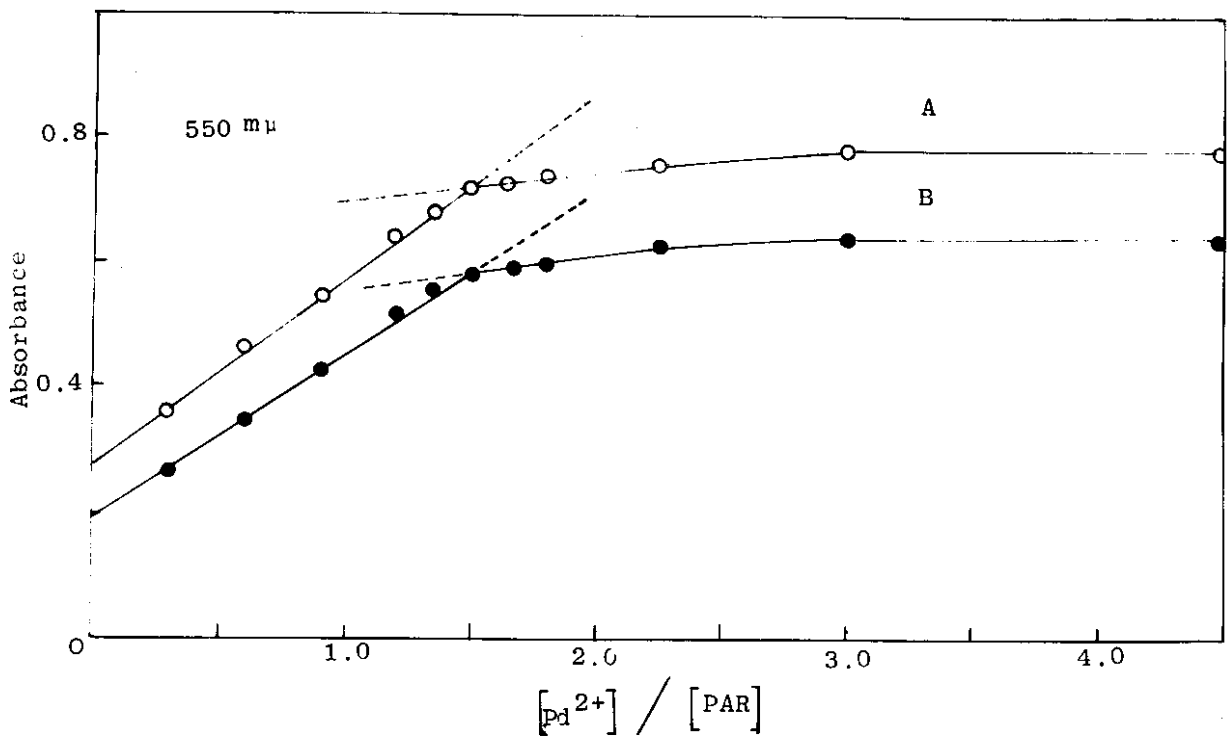


Fig.2: Composition and Stability Constant of Chelate at 550 nm by Mole Ratio Method: (pH=10.5)

Curve A: $[PAR]: 3.33 \times 10^{-5} M$ Curve B: $[PAR]: 2.66 \times 10^{-5} M$

while at pH 10.5 was cationic. The nature of the charge on the chelates was further confirmed by using ion exchange resins where the colour of the chelates at pH 4.0 was not absorbed

by any of the resin and colour of the chelates at pH 10.5 was completely absorbed by resin Amberlite IR-45(H) showing a neutral and cationic charge on the chelate respectively.

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