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## Study of complex formation constants of uranyl and cadmium metal ions with primaquine by using differential pulse voltammetry

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### ABSTRACT

The electrochemical behavior of complexes of primaquine diphosphate with U (IV) and Cd (II) were studied. It was observed that primaquine forms 1:2 complexes with U (IV) and Cd (II) buffer at pH 4.0 by using Differential pulse Voltammetry (DPP). The stability constants of primaquine- metal complexes were evaluated with the DeFord-Hume procedure at different ligand concentrations using DPP. The logarithm values of stability constants of Uranyl and lead complexes are 11.74 and 8.17, respectively.

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### KEYWORDS

Metal complexes;  
Voltammetry;  
Primaquine;  
Cadmium;  
Uranyl.

### INTRODUCTION

Primaquine a well known antimalarial affecting asexual blood forms of human malaria parasites<sup>[1-3]</sup>. belongs to a therapeutically important group of 8-aminoquinolines, being a potential chelating agent, like other derivatives of this group<sup>[4-5]</sup>, primaquine interact with metal ion presents in the biological system and thereby affects their concentration and/or role in the biochemical reaction pathways. The chelating behavior of primaquine may be of interest to pharmacologists, specifically with reference to (a) diseases caused by metal ion deficiency, (b) supply of metal ion to the deficient part and (c) its role in metabolic pathways. Further, information on the structure and nature of the complexes formed is helpful in understanding the therapeutic and toxic effects of the drug. The studied drug Primaquine have high electron density sites, so they may act as powerful electron donors. In the present work complex formation of Pb (II) and U (IV) with pri-

maquine in buffer solution at pH 4.00 have been studied voltammetrically. The overall stability constants of resulting complexes have been evaluated by DeFord-Hume's method<sup>[6]</sup>.

### EXPERIMENTAL

#### Reagents and solutions

All chemicals were purchased from Aldrich and Merck (Mumbai, India) and used without purification. Stock solutions were prepared with double distilled and deionized water.

The stock solution of Primaquine was prepared by dissolving the analytical grade chemical in double distilled and deionized water, which had been previously degassed with nitrogen for 30 minutes. The solution was kept in darkness at 4 °C and was found to be stable over a period of several weeks. Diluted solutions of Primaquine were prepared from the stock just prior to analysis. Pure nitrogen (99.99 %) was used to deaer-

## Full Paper

ate the solutions.

### Instrumentation

The voltametric system used for the studies was Eco chemie, electrochemical work station, model Auto lab 30, the electrode assemblies being a 663 VA stand with GPES computer software for recording and analyses of the voltamogram.

The instrument settings were as follows: The capillary of drop size 04 with the surface area of 0.04mm<sup>2</sup> was used. Before each measurements a stream of pure nitrogen deaerated the solution. The time of purging was 300s and the time of equilibrations was 20s. The potential scans were recorded at scan rate of 10 mVs<sup>-1</sup> and pulse amplitude of 50 mV. All experiments were carried out at the ambient temperature (approximately 25 °C).

### Procedure

The experiments were performed using 9 x 10<sup>-5</sup> M of metal ions concentration while the ligand concentration was from 1.99 x 10<sup>-5</sup> M to 21.99 x 10<sup>-5</sup> M. A stream of pure nitrogen was used for 300 s to remove the dissolved oxygen in the solution before voltage scanning.

### Method of calculation

The modified method of DeFord and Hume was used to determine the stability constants of the irreversible complexes according to the equation

$$(0.434 nF/RT) \Delta E_p + \log [(ip)_M / (ip)_C] = \log \beta_{MLp} + p \log C_L$$

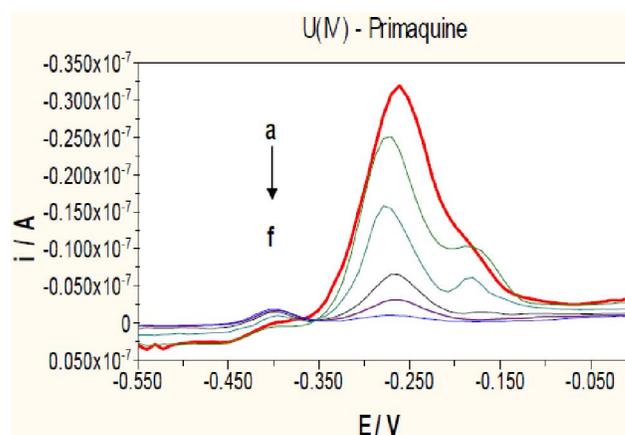
where  $\beta_{MLp}$  is the stability constant of the  $MLp$  complex (where  $M$ , metal;  $L$ , ligand),  $C_L$  is the concentration of ligand,  $\Delta E_p$  is the distance of the peak potentials of the free metal ion and the complex,  $p$  is the ligand/metal value, and  $(ip)_M$  and  $(ip)_C$  are the peak currents of the free metal ion and the complex, respectively. Since no shift was observed in the peak potential in the complexes of primaquine with Cd (II) ions (where  $\Delta E_p$  is constant),  $p$  values were calculated from the slopes of the plots of  $-\log[(ip)_M / (ip)_C]$  versus  $-\log[\text{Primaquine}]$ .

## RESULTS AND DISCUSSION

### Voltammetric characteristics of U(IV) complexes

The voltamogram of complexation of primaquine

with U (IV) in buffer at pH 4.00 are given in Figure 1. U (IV) showed a single reduction peak at -0.261 V. On gradually increasing the concentration primaquine from 3.60 x 10<sup>-5</sup> to 18.00 x 10<sup>-4</sup> mol dm<sup>-3</sup> in the cell containing 9 x 10<sup>-5</sup> mol dm<sup>-3</sup> U (IV) metal solution, result in the shift in peak potential towards more negative side with simultaneous decrease in peak current was observed. With continuous decrease in current, the peak disappeared completely when ligand concentration was almost double to that of metal, indicating that the complex has 1:2 (metal: ligand) stiochiometry. The overall stability constant was determined and found to be  $\log \beta_{1:2} = 11.74$



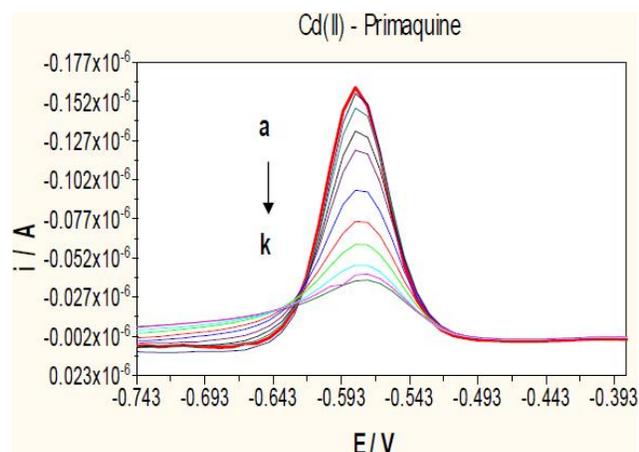
a = 9 x 10<sup>-5</sup> M pure Uranyl in buffer solution

Ligand: b = 3.60 x 10<sup>-5</sup>, c = 7.20 x 10<sup>-5</sup>, d = 10.80 x 10<sup>-5</sup>, e = 14.40 x 10<sup>-5</sup>, f = 18.00 x 10<sup>-5</sup> M

Figure 1 : DPP of 9 x 10<sup>-5</sup> M Uranyl with increasing concentration of primaquine diphosphate (3.60 x 10<sup>-5</sup> M to 18.00 x 10<sup>-5</sup> M) in buffer solution of pH 4.00

### Voltammetric characteristics of Cd (II) complexes

The voltamogram of complexation of primaquine with Cd (II) in buffer at pH 4.00 are given in Figure 2. Cd (II) showed a single reduction peak at -0.582 V. On gradually increasing the concentration primaquine from 1.99 x 10<sup>-5</sup> to 21.99 x 10<sup>-5</sup> mol dm<sup>-3</sup> in the cell containing 9 x 10<sup>-5</sup> mol dm<sup>-3</sup> Cd (II) metal solution, result in the no shift in peak potential, but decrease in peak current were observed. With continuous decrease in peak current were observed up to when ligand concentration was almost double to that of metal, after that no decrease peak current was observed indicating that the complex has 1:2 (metal: ligand) stiochiometry. The overall stability constant was determined to be  $\log \beta_{1:2} = 8.17$ .



a =  $9 \times 10^{-5}$  M pure Lead in buffer solution

Ligand: b =  $1.99 \times 10^{-5}$ , c =  $3.99 \times 10^{-5}$ , d =  $5.99 \times 10^{-5}$ , e =  $7.99 \times 10^{-5}$ , f =  $9.99 \times 10^{-5}$ , g =  $11.99 \times 10^{-5}$ , h =  $13.99 \times 10^{-5}$ , i =  $15.99 \times 10^{-5}$ , j =  $19.99 \times 10^{-5}$ , k =  $17.99 \times 10^{-5}$  M.

Figure 2 : DPP of  $9 \times 10^{-5}$  M Cadmium with increasing concentration of primaquine diphosphate. ( $1.99 \times 10^{-5}$  M to  $21.99 \times 10^{-5}$  M) in buffer solution of pH 4.00

## CONCLUSION

The complexation reaction occurring between metals ions and Primaquine can be followed using differential pulse voltammetry, which allow the identification of the complexes formed as well as the determination of their stability constants. Also it is a fast, cheap and sensitive technique for the study of the formation of complexes.

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