Voltammetric determination of stability constants of cadmium and lead complexes with promazine

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ABSTRACT

Interactions of cadmium and lead metals with promazine were investigated by Differential pulse voltammetry. Measurements were performed in sodium acetate buffer at pH 6.00 in aqueous solutions under physiological ionic strength (0.15 mol dm^{-3}). The electrochemical behavior of complexes of Cd (II) and Pb (II) with promazine were studied for determination of the corresponding stability constants ($[M^{2+}] = 9 \times 10^{-5}$ mol dm^{-3}, pH = 6.00; total concentration of promazine from 1×10^{-5} to 1×10^{-4} mol dm^{-3}). It was observed that promazine forms 1:1 and 1:2 complexes with Cd (II) and Pb (II) respectively. The stability constants of the Cd (II)-promazine and Pb (II)-promazine complexes were evaluated with the DeFord-Hume procedure at different ligand concentrations and they were calculated from the dependence of the shift of metal peak potential on the free promazine ion concentration.
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INTRODUCTION

Phenothiazines, which were introduced in the 1950's as antipsychotic drugs are still widely, used as tranquillizers, antihistaminic, antiemetic, sedative, analgesics, and antiparkinson[1]. In view of their importance considerable methods have been reported for their detection and quantification in biological fluids as well as pharmaceuticals and these methods have been reviewed[2-4]. Phenothiazines exhibit certain interesting analytical properties such as liability to oxidation and formation of ion-pair association complex owing to the presence of chemically active sulfur and nitrogen atoms and also protonated nitrogen on side substitutions in their structures. Therefore, there are many spectrophotometric procedures based on the oxida-

tion of these drugs to colored cation radicals using various oxidizing agents such as iodic acid[5], cerium(IV)[6], N-bromosuccinimide[7], dichromate[8], iron(III)[9], 2-iodobenzoate[10], and also extraction of colored ion-association complex of phenothiazines with many acidic dyes into organic solvents such as dichloromethane and chloroform[11-15]. Unfortunately, more of the oxidation methods suffer from several disadvantages like use of long heating step, low sensitivity, very strong acid medium, low range of determination and critical working, and poor selectivity. On the other hand, tedious and time consuming extraction steps, use of organic solvents, strict pH control are the important limitations in the application of procedures based on extraction-ion-association complex formation.
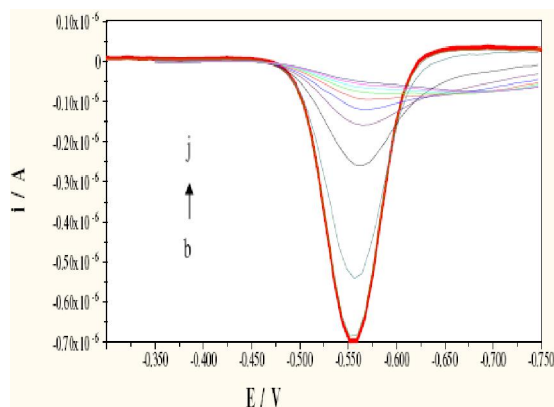
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Figure 1 : DPP of 9×10^{-5} M Cadmium with increasing concentration of Promazine HCl (0.99×10^{-5} M to 8.99×10^{-5} M) in buffer solution of pH 6.00. a = 9×10^{-5} M pure Cadmium[-] in buffer solution. Ligand: b = 0.99×10^{-5}, c = 1.99×10^{-5}, d = $2.99 10^{-5}$, e = 3.99×10^{-5}, f = 4.99×10^{-5}, g = $5.99 10^{-5}$, h = 6.99×10^{-5}, i = 7.99×10^{-5}, j = $8.99 10^{-5}$ M[_]
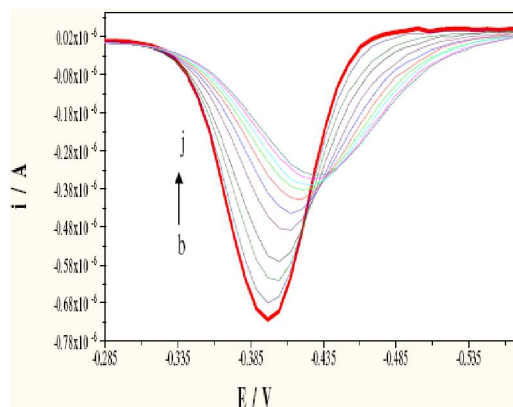

Figure 2 : DPP of 9 x 10^{-5} M Lead with increasing concentration of Promazine HCl (0.99×10^{-5} M to 17.99×10^{-5} M) in buffer solution of pH 6.00. a = 9×10^{-5} M pure Lead[-] in buffer solution. Ligand: b = 1.99×10^{-5}, c = 3.99×10^{-5}, d = 5.99×10^{-5}, e = 7.99×10^{-5}, f = 9.99×10^{-5}, g = 11.99×10^{-5}, h = 13.99×10^{-5}, i = 15.99×10^{-5}, j = 17.99×10^{-5} M[_]

TABLE 1 : Voltammetric measurements of Cadmium[M] – Promazine hydrochloride[L] complexes for the determination of the stability constants Log (K_{ML}^{n+}) by shift in peak potential

Concentration [M]$\times10^{-5}$ M	Concentration [L]$\times10^{-5}$ M	Ep (V)	Ip(A)
9.00	-	-0.551	-7.17×10^{-7}
9.00	0.99	-0.553	-7.02×10^{-7}
9.00	1.99	-0.555	-5.53×10^{-7}
9.00	2.99	-0.558	-2.51×10^{-7}
9.00	3.99	-0.560	-1.38×10^{-7}
9.00	4.99	-0.562	-9.39×10^{-8}
9.00	5.99	-0.565	-6.49×10^{-8}
9.00	6.99	-0.567	-8.98×10^{-9}
9.00	7.99	-0.570	-7.08×10^{-9}
9.00	8.99	-0.572	-6.40×10^{-9}
9.00	9.99	-	-

TABLE 2 : Voltammetric measurements of Lead[M] – Promazine hydrochloride[L] complexes for the determination of the stability constants Log (K_{ML}^{n+}) by shift in peak potential

Concentration [M]$\times10^{-5}$ M	Concentration [L]$\times10^{-5}$ M	Ep (V)	Ip (A)
9.00	-	-0.397	-7.52×10^{-7}
9.00	1.99	-0.397	-7.52×10^{-7}
9.00	3.99	-0.405	-7.04×10^{-7}
9.00	5.99	-0.409	-6.43×10^{-7}
9.00	7.99	-0.413	-5.91×10^{-7}
9.00	9.99	-0.417	-5.09×10^{-7}
9.00	11.99	-0.421	-4.63×10^{-7}
9.00	13.99	-0.423	-4.02×10^{-7}
9.00	15.99	-0.428	-3.88×10^{-7}
9.00	17.99	-0.430	-3.65×10^{-7}
9.00	19.99	-0.430	-3.63×10^{-7}
9.00	21.99	-0.430	-3.64×10^{-7}

In the present work the formation of complexes have been examined by differtial pulse voltammetric study. The overall stability constant of the cadmium (II) and lead (II) complex of promazine in aqueous medium was determined by shift in peak potential.

EXPERIMENTAL

Chemicals and solutions

The following chemical reagents were used for all voltammetric experiments: CH_3COOH (Merk), CH_3COONa (Merk), Promazine.HCl (Aldrich), Cd

$(NO3)_2$ and Pb $(NO3)_2$ (Merk). All the chemicals used in voltammetric measurements were of analytical grade. Double distilled, deionized water was used for preparations of all solutions. The stock solutions of promazine (10^{-2} mol dm^{-3}), Cd $(NO3)_2$ (9×10^{-5} mol dm^{-3}) and $Pb(NO3)_2$ (9×10^{-5} mol dm^{-3}) were prepared in sodium acetate buffer at pH =6.00, The solutions were kept in darkness at 4°C and were found to be stable over a period of several weeks. Diluted solutions of promazine were prepared from the stock just prior to analysis. Pure nitrogen (99.99 %) was used to deaerate the solutions.

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Apparatus and measurements

Electrochemical measurements were carried out using a computerized multipurpose system consisting of AUTOLAB (EcoChemie, Utrecht, The Netherlands), a personal computer (486 DX2-80 MHz 32 Mb RAM) and a Static Mercury Drop Electrode Assembly (SMDE) PAR 303A (Princeton Applied Research, Princeton, USA) with a homemade holder of electrode components The three- electrode system comprising saturated calomel electrode as a reference electrode, carbon electrode as a counter electrode and multimode mercury electrode as a working was used. The electrochemical instrument was controlled by a computer with the following software packages: EAS (Electro Analytical System) and GPES 4.5 (General Purpose Electrochemical System). The capillary of drop size 04 with the surface area of $0.04 mm^2$ was used. Before each measurements a stream of pure nitrogen deareated the solution. The time of purging was 180s and the time of equilibrations was 20s.

A known volume of supporting electrolyte 0.15M Kcl in buffer solution pH 6.00 was taken in sample cell and polarogram was run as a blank. To this solution the metal solutions were prepared to get desired working solution. A known volume of working solution was taken in cell and polarogram was run. Then a step by step increase in concentration of phenothiazine drugs was made using a micropipette the total concentration of the drug was approximately thrice the concentration of metal. The potential scans were recorded using polarographic technique at scan rate of 10 mVs^{-1} and pulse amplitude of 50 mV. The experimental data of voltammetric measurement for the complexation of promazine with Cadmium and Lead ions in aqueous medium are given in TABLE 1 and 2 respectively.

RESULTS AND DISCUSSION

The behavior of cadmium and lead ions in aqueous solution can be affected by a variety of competing reactions, such as hydrolysis, complexation, precipitation/ dissolution, oxidation/ reduction, and sorption/desorption at the surface of particles. Since these reactions change the speciation of these metal ions, they control to a large extent both their toxicity and mobility in a natural system. Speciation is therefore of central importance when studying any metal ion behavior in natural aquatic environments, in which these reactions can all occur simultaneously, but to highly different extents under different conditions[16].

DPV technique has been used for the determination for the determination of the stability constant in the present investigation. The basic observation in classical d.c. polarography is that the half wave potential of a simple ion shifted by complexation. Heyrovsky and Hkovie[17] suggested the first theoretical treatment of the effect of complexation agent upon the reduction potential of a simple ion. This relation between the shift in peak potential and the stability constant is as follows.

$$\Delta Ep = (E_p)_S - (Ep)_C$$

$$= (0.05916/n) \, Log \, Bp + (0.05916 \, p/n) \, Log \, C_L \quad (1)$$

where, $(E_p)_S$ = peak potential of the free cation, $(Ep)_C$ = peak potential of the complexed cation, Bp= stability constant, C_L = total ligand concentration, P= ligand to metal ratio.

Eq. (1) indicates that the plot of ΔEp Vs Log C_L would provide the value of $(0.05916/n)$ Log Bp as intercept and 0.05916 p/n as slope. These plots are used to calculate the stability constants.

Stability constant of cadmium-promazine complexes

The DPP for the complexation of promazine HCl with Cd (II) in pure water are given in figure 1. Cd (II) shows a single reduction peak at -0.551V. On gradually increasing the concentration of promazine from 1×10^{-5} to 1×10^{-4} mol dm^{-3} in the cell containing 9 x 10^{-5} mol dm^{-3} Cd (II) metal solution, result in the shift in peak potential towards more negative side with simultaneous decrease in peak current. With continuous decrease in current, the peak disappears completely when ligand concentration is almost equal to that of metal, indicating that the complex has 1:1(metal: ligand) stiochiometry. The stability constant was calculated from shift in peak potential and was found 2.335.

Stability constant of lead -promazine complexes

On other hand, complexation of promazine HCl with Pb (II) is different. In case of Pb (II) a single reduction peak is observed at -0.397V. On gradually increasing the concentration of promazine from 1×10^{-5} to 1×10^{-4}

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mol dm^{-3} in the cell containing 9×10^{-5} mol dm^{-3} Pb (II) metal solution. From figure 2 it is observed that a single reduction peak of Pb (II) shifted towards more negative side with continuous decrease in current on addition promazine HCl. This decrease in current and shift in peak potential is continued till [M]/2[L] = 0.5 indicating that complex has 1:2 (metal: ligand) stiochiometry. The stability constant was calculated from shift in peak potential and was found 2.226.

CONCLUSION

The complexation reaction occurring between metal ions (i.e Cd (II) and Pb (II)) and promazine can be followed by using DPP, which allow the identification of complexes formed as well as the determination of stability constant. Cd(II) and Pb(II) ions was found to form complexes of 1:1 and 1:2 complexes with promazine respectively.

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