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A Polarographic study of Pb (Π) complexes with Bupropion hydrochloride in 40% ethanol-water mixture

Chemistry

KEYWORDS : DC Polarography, Pb(Π), Bupropion hydrochloride, Stability constants

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ABSTRACT

Interactions between lead and Bupropion hydrochloride were investigated at 200 C and 300 C using DC polarography. Measurements were performed in aqueous acetate buffer (pH=5) solutions under physiological ionic strength (0.5 M). Determination of the stiochiometry and stability constants of the Pb(Π) Bupropion hydrochloride complexes was based on the DeFord-Hume methodology. The results were compared with the values calculated by Mihailov's method (mathematical). Complexes formed were in 1:1 and 1:3 ratios at 200 C and 300 C respectively. The values of stability constants, log β1, log β2 and log β3 obtained are 3.11, 4.32, 7.40 at 300 C and only log β1 is found to be 3.22 at 200 C. The formation of the metal complexes was found to be spontaneous and exothermic in nature.

Introduction

Study of complexes of Pb(Π) with antibiotic drugs have been done by Pandey et al[1]. Interactions between pyridine -2, 6- dicarboxylic acid with Cu (Π), Pb (Π) and Cd (Π) ions were characterized in aqueous solutions by means of d.c. polarography[2]. The complexes of Tl^{1+}, Pb^{2+} and Cd^{2+} cations with macrocyclic ligands have been studied in mixed solvents using DC Polarography, differential pulse polarography (DPP), square wave polarography and conductometry[3-4]. The study of Pb(II) –Bupropion system has also been carried out in aqueous and 20% ethanol –water mixture in the previous communications.

The present study was inspired by literature reports, which have shown that several drugs or other ligands can function as chelators and this beneficial role makes them strong candidates for treating lead poisoning[5].

Experimental

The following chemicals were used for all polarographic experiments: Bupropion hydrochloride (3×10^{-2}M), acetate buffer (0.5 M, pH=5), $Pb(CH_3COO)_2$(2.5×10^{-2}M). All solutions were prepared from analytical grade reagents (Merck and Sigma) in triply distilled water and overall study has been done in 40% ethanol-water mixture. Triton X-100(0.005%) was used to suppress the polarographic maxima.

A model CL 357 a polarographic analyzer (from elico) was coupled with the cell for direct current polarographic experiments. The current response and the applied potential were recorded at scan rate 150mV/min. The current voltage measurements were performed with three electrodes assembly, a dropping mercury electrode as working electrode, calomel as reference and platinum as counter electrode. The dropping mercury electrode had the capillary characteristics, m = 2.768 mg/s, t = 3.0 sec, h = 60 cm. pH was adjusted to suitable range by Elico digital pH meter.

Results and Discussion

Pb (Π) gave two electron reversible reduction wave at pH = 5, μ = 0.5 M acetate buffer at 20^0 C and 30^0 C temperature[6].

The polarographic reduction of $2.5x10^{-3}$M Pb (Π) in the presence of different Bupropion hydrochloride concentrations was investigated. The concentration of Pb (Π) and Triton X-100 in the analyte were $2.5x10^{-3}$ M and 0.001%, while the concentration of Bupropion was varied from $1.5x10^{-3}$M to $7.5x10^{-3}$M and current voltage curves were obtained. Increase in $E_{1/2}$ values with increase of the concentration of Bupropion to Pb (Π), coupled with decrease in diffusion current (i_d), indicates the complex formation[7]. Fig 1 shows the resulting polarograms for Pb-Bupropion system in 40% ethanol at 30^0C.

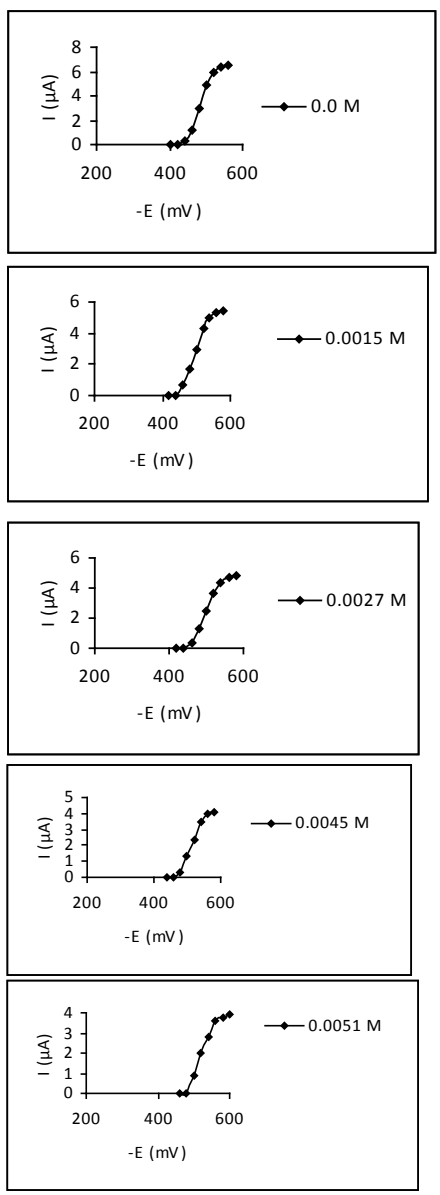

Figure 1. Polarograms of $2.5x10^{-3}$ M Pb (Π) ions in the presence of different ligand concentrations.

All the waves of the complexes were reversible[8], clear from the plots between $E_{d.e.}$ vs. log $i/(i_d-i)$, straight lines with reciprocal slopes of -30±4 mV. The linear dependence of the limiting current on the square root of the height of the mercury column indicates that the reduction of the metal ion is diffusion controlled[9].

The stiochiometry and stability constants of the complexes were determined by monitoring the shifts in half wave potentials of the polarographic waves of metal ions against the ligand concentration. The Deford and Hume[10] method confirmed the formation of 1:1 and 1:3 complexes of Pb (Π) with Bupropion.

Comparison and trend of stability of complexes

The stability constant of a complex is an important basic datum in analytical chemistry, particularly, for predicting interfering elements and for choosing optimum experimental conditions[11-13], such as temperature and concentration.

The stability constant values were determined at different temperatures 20^0 C and 30^0 C which are summarized in Table 2, It is clear from table 2 that stability constant values for 1:1 complex decrease with increase the temperature which suggests that Pb(Π) -Bupropion complexes are more stable at lower temperature[14-15]. Further, the stability constants of the complexes present in the solution were also calculated by mathematical method of Mihailov[16] at 30^0 C at which 1:3 complexes were formed and are compared with the values of stability constants calculated by Deford and Hume's method. The values of stability constants of consecutive metal complexes by Mihailov method were calculated using the following expression[17]

$$\beta_n = A.\frac{a^n}{N!} \qquad (1)$$

where: β_n is the overall stability constant of the ML_n complex; n is the number of ligands in a particular complex, ($1 \leqslant n \leqslant N$); N is the coordination number of the complex forming metal M and A and a are Mihailov's constants, listed in table 1.

Table 1. Mihailov Constant 'a' for various combinations of Bupropion concentrations and 'A' at various Bupropion concentrations at 30^0 C for Pb(II)- Bupropion system

S.No.	Combinations of concentrations of Bupropion (M)	'a'	Concentration of Bupropion (M)	'A'
1.	0.0027 0.0033	264.643	0.0027 0.0033	2.57 2.34*
2.	0.0033 0.0039	1832.460*	0.0039 0.0045	2.74 2.67
3.	0.0039 0.0045	352.787	0.0051 0.0057	2.65 2.62
4.	0.0045 0.0051	371.858	0.0063 0.0069	2.63 2.59
5.	0.0051 0.0057	362.515	Average 'a' =	333.350
6.	0.0057 0.0063	362.606	Average 'A' =	2.64
7.	0.0063 0.0067	286.823		

The value marked asterisk(*) has not been included in average calculations due to its exceptional deviation

The values of stability constants by two different methods are in good agreement; small deviations may be due to two different approaches.

Thermodynamic parameters

The kind of complex species that reduces on a mercury electrode depends on thermodynamic aspects[18-19]. Thermodynamic parameters such as enthalpy change (ΔH), free energy change (ΔG) and entropy change (ΔS) of the complexes have been calculated using the following equations[20].

$$\Delta G = -2.303RT \log \beta \qquad (2)$$

$$\Delta H = - \frac{2.303RT_1T_2\left[\log \frac{\hat{a}_{T_1}}{\hat{a}_{T_2}}\right]}{T_2 - T_1} \qquad (3)$$

$$\Delta G = \Delta H - T\Delta S \qquad (4)$$

Examination of the values of ΔG, ΔH and ΔS in table 2 shows that

a) The negative value of ΔG for the complexation process suggests the spontaneous nature of such process. These values are less negative at higher temperature, confirming that complexes are not stable at higher temperature[21-22]. Further, the successive decrease in free energy at 30^0 C suggests the more stability of 1:3 complexes.
b) The ΔH values are negative, meaning that these processes are exothermic and favorable at lower temperature[23-24].
c) A negative value of ΔS corresponds to a highly ordered activated complex and this implies a small value of the steric factor[25-26].

Table 2. Stability constant and thermodynamic parameters of Pb-Bupropion system in 40% ethanol medium

Composition of complex		Stability constant		ΔG Kcal/ mol	ΔH Kcal/ mol	ΔS cal/ degree/ mol
20^0 C	1:1	3.2186		-4.3003	-4.3052	-0.0168
30^0 C	1:1	DeFord and Hume	Mihailov	-4.3001		
		3.1123	2.9445			
	1:2	4.3228	5.1664	-5.9727		
	1:3	7.4039	7.2129	-10.2297		

Conclusion

The Direct current polarographic studies of the Pb-Bupropion system were performed in 40% ethanol-water mixture at 20^0 C and 30^0 C. The method that is proposed in this work is simple, direct and sensitive. Pb(Π) formed 1:1 complexes at 20^0 C and 1:3 complexes at 30^0 C. which were determined by Deford-Hume method. A complete graphical and numerical calculation of the Deford-Hume method shows its importance in the determination of the coordination number and overall stability constants of these complexes. The stability constants values are also compared with the values calculated by Mihailov's method which are in good agreement. The values of stability constants is quite reasonable therefore, either Bupropion alone or in the form of metal complex could be effective against Pb(Π) toxicity. The negative value of ΔH indicated the exothermic nature of metal-ligand interaction. The complexes were stable at lower temperature which was confirmed by the values of ΔG and stability constants of complexes at lower temperature.

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