

Electrochemical Study of Pencillin Benzyl Salt With Pb(II) in Non-Aqueous Media

MEENA, SUNITA SHARMA and O.D. GUPTA*

Department of Chemistry, University of Rajasthan, Jaipur-302 004, India

E-mail: gupta_od@yahoo.com; meenu_aadi@rediffmail.com

Using DME electrode the comparative investigation on the electro-reduction of Pb(II) with penicillin benzyl salt (PnB) in 1M KCl containing 40 and 60 % DMF have been made by direct current polarographic technique. Values of stability constants were calculated according to DeFord and Hume's method and it was observed that the reduction on DME was reversible and diffusion controlled involving two electrons. DeFord and Hume's treatment suggest that PnG forms 1:1, 1:2 and 1:3 complexes in all the system mentioned above at 30 and 40 °C. The values of overall stability constants ($\log \beta$) obtained are 5.27, 7.82 and 11.39 in 40 % DMF, 5.54, 7.97 and 11.51 in 60 % DMF at 30 °C and 5.23, 7.88 and 11.33 in 40 % DMF and 5.43, 7.91 and 11.48 in 60 % DMF at 40 °C.

Key Words: Pb(II), Penicillin benzyl salt, Stability constants.

INTRODUCTION

With the lower concentration of antibiotics, the *in vitro* activity has been found very effective. The electrochemical behaviour of Ni(II) complexes of norfloxacin (NFX), ciprofloxacin (CFX) and sporfloxacin (SFX) were studied using direct current polarograph differential pulse and AC polarography¹. From polarography values the stability constants ($\log \beta$) were calculated for ternary complexes with different antibiotics²⁻⁴. The complexes and stability constants ($\log \beta$) of tetracycline and oxytetracycline with Cu(II), Pb(II) and UO₂(II) were studied by DC polarography and differential pulse polarography⁵. Polarographic technique has already been used for the determination of stability constants of simple complexes of Cu(II) with different substituted pyrazoles, imidazole, 1-methyl imidazole and neomycin⁶⁻⁸ and simple complexes of Be(II), Pb(II), Cd(II) and Mn(II) complexes of hydroxyl amino acid⁹. Polarographic study of Cu(II), Pb(II), In(II) and Fe(II) with antibiotic and thiamine have also been done^{10,11}.

Present study deals with the simple complexes of Pb(II) with penicillin benzyl potassium salt at 30 and 40 °C in 40 and 60 % DMF. The electrochemical reduction of Pb(II) ion in 1 M KCl shows a single wave involving two electrons.

EXPERIMENTAL

A model CL 357 a polarographic analyses (from Elico) was coupled with the cell for direct current polarographic experiments. The current voltage measurements were performed with 3 electrodes assembly, a DME as working electrode, calomel as reference and platinum as counter electrode. The dropping mercury electrode had the following characteristics $m = 2.422$ (mg/s), $t = 3.5$ s.

Analytical grade lead(II) nitrate was used in this study. The reagent grade potassium chloride was used as supporting electrolyte. All solutions were made in double distilled water and overall study has been done in 40 and 60 % DMF medium at 30 and 40 °C. The reaction solution of Pb(II) was made in double distilled water. High purity, dry nitrogen was used to remove the dissolved oxygen from the reaction solution.

RESULTS AND DISCUSSION

Pb(II)-penicillin benzyl salt in non-aqueous medium: Lead(II) gave a well defined reversible wave in 1 M KCl medium with half-wave potential at -0.37 vs. SCE in presence of 40 and 60 % DMF at 30 and 40 °C. The reduction was found to be reversible. The half wave potential shifted to more negative values with increase in penicillin benzyl salt concentration indicates complexation. The plots of $\log i/i_d - i$ vs. E_{d-e} showed a slope values 27 ± 2 mV indicates reversible two electron reduction. The values of stability constants have been calculated and $\log \beta_1$, $\log \beta_2$ and $\log \beta_3$ are given in Table-5 and data of DeFord and Hume's 12 functions are given in Tables 1-4.

TABLE-1
POLAROGRAPHIC MEASUREMENTS AND $F_i([X])$ FUNCTION VALUES FOR LEAD
PENICILLIN BENZYL SALT SYSTEM IN 40 % DMF
 $Pb^{2+} 25 \times 10^{-3}$ M, $\mu = 1$ M KCl, Temp = 30 °C

C_x (mol)	I_d (divisions)	$E_{1/2}$ (-V vs. SCE)	$F_0([X])$ $\times 10^3$	$F_1([X])$ $\times 10^5$	$F_2([X])$ $\times 10^8$	$F_3([X])$ $\times 10^{11}$
0	77	0.3856	—	—	—	—
0.001	73	0.4662	.5079	5.0688	3.1688	2.4988
0.002	70	0.4872	2.6480	13.2352	5.6676	2.4988
0.003	66	0.5007	7.9031	26.3402	8.1467	2.4922
0.004	64	0.5109	17.8092	44.5205	10.6551	2.4963
0.005	59	0.5182	33.8015	67.6011	13.1402	2.4940
0.006	58	0.5249	57.4586	95.7627	15.6438	2.4956
0.007	54	0.5299	90.5323	129.3304	18.2043	2.5049

The higher values of stability constants show that favourable temperature for the formation of Pb-PnB salt complexes is 30 °C. Value of stability constants show that with increase in concentration of DMF stability increases as 60 > 40 %. Chemical structures of drug and proposed structure of metal complexes are given in Figs. 1-4.

TABLE-2
POLAROGRAPHIC MEASUREMENTS AND $F_i(X)$ FUNCTION VALUES FOR
LEAD PENICILLIN BENZYL SALT SYSTEM IN 60 % DMF
 $Pb^{2+} 25 \times 10^{-3} M$, $\mu = 1 M$ KCl, Temp = 30 °C

C_x (mol)	I_d (divisions)	$E_{1/2}$ (-V vs. SCE)	$F_0([X])$ $\times 10^3$	$F_1([X])$ $\times 10^5$	$F_2([X])$ $\times 10^8$	$F_3([X])$ $\times 10^{11}$
0	76	0.3856	–	–	–	–
0.001	72	0.4717	0.7747	0.7737	4.2369	3.2969
0.002	67	0.4916	3.7148	1.8569	7.2346	3.2973
0.003	66	0.5045	10.7623	3.5871	10.7904	3.2835
0.004	62	0.5146	24.0936	6.0232	14.1829	3.3107
0.005	58	0.5221	45.7600	9.1518	17.6036	3.3327
0.006	57	0.5287	77.2158	12.8691	20.8652	3.3209
0.007	53	0.5336	120.8901	17.2699	24.1712	3.3187

TABLE-3
POLAROGRAPHIC MEASUREMENTS AND $F_i(X)$ FUNCTION VALUES FOR
LEAD PENICILLIN BENZYL POTASSIUM SALT SYSTEM IN 40 % DMF
 $Pb^{2+} 25 \times 10^{-3} M$, $\mu = 1 M$ KCl, Temp = 40 °C

C_x (mol)	I_d (divisions)	$E_{1/2}$ (-V vs. SCE)	$F_0([X])$ $\times 10^3$	$F_1([X])$ $\times 10^5$	$F_2([X])$ $\times 10^8$	$F_3([X])$ $\times 10^{11}$
0	84	0.3750	–	–	–	–
0.001	82	0.4623	0.4524	4.5144	2.8144	2.1744
0.002	80	0.4837	2.3363	11.6766	4.9883	2.1742
0.003	75	0.4975	6.9832	23.2741	7.1914	2.1838
0.004	71	0.5076	15.6101	39.0224	9.3307	2.1727
0.005	63	0.5146	29.7073	59.4127	11.8425	2.1805
0.006	62	0.5215	50.3520	83.9184	13.7031	2.1772
0.007	60	0.5271	79.3741	113.3901	15.9557	2.1882

TABLE-4
POLAROGRAPHIC MEASUREMENTS AND $F_i(X)$ FUNCTION VALUES FOR LEAD
PENICILLIN BENZYL POTASSIUM SALT SYSTEM IN 60 % DMF
 $Pb^{2+} 25 \times 10^{-3} M$, $\mu = 1 M$, KCl, Temp = 40 °C

C_x (mol)	I_d (divisions)	$E_{1/2}$ (-V vs. SCE)	$F_0([X])$ $\times 10^3$	$F_1([X])$ $\times 10^5$	$F_2([X])$ $\times 10^8$	$F_3([X])$ $\times 10^{11}$
0	84	0.375	–	–	–	–
0.001	82	0.4623	0.6656	6.6461	3.8961	3.0711
0.002	80	0.4837	3.6677	16.6833	6.9667	3.0708
0.003	75	0.4975	9.9106	33.0320	10.0970	3.0897
0.004	71	0.5076	22.1472	55.3655	13.1539	3.0822
0.005	63	0.5146	41.9539	83.9059	16.2312	3.0812
0.006	62	0.5215	71.1272	118.5437	19.2982	3.0790
0.007	60	0.5271	111.3538	159.0755	22.3322	3.0725

TABLE-5
STABILITY CONSTANTS FOR LEAD PENICILLIN BENZYL
SALT SYSTEM IN NON-AQUEOUS MEDIUM

System	Composition of complexes	Stability constant 40 % ethanol		Stability constant 60 % ethanol	
		30 °C	40 °C	30 °C	40 °C
[Pb(PnB)] ⁺	1:1	5.27	5.23	5.54	5.43
[Pb(PnB) ₂]	1:2	7.82	7.88	7.97	7.91
[Pb(PnB) ₃] ⁻	1:3	11.39	11.33	11.51	11.48

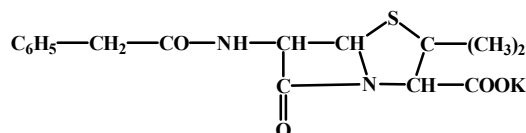
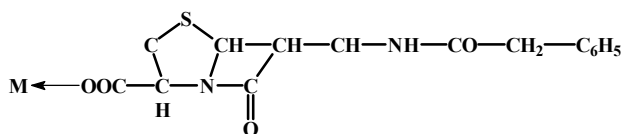
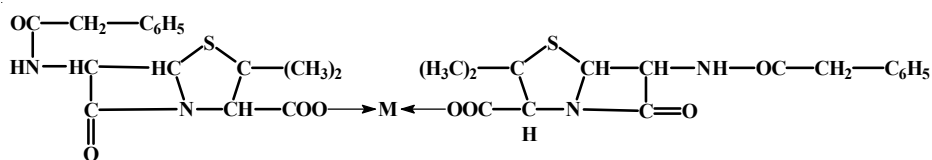
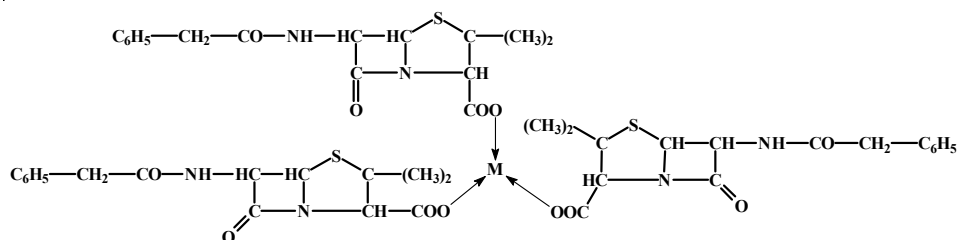


Fig. 1. Penicillin benzyl potassium salt

Fig. 2. Proposed structure of [M(PnB)], M = Pb²⁺Fig. 3. Proposed structure of [(PnB)₂], M = Pb²⁺Fig. 4. Proposed structure of [M(PnB)₃] M = Pb²⁺

The metal ion in absence of ligand is in solvated form. The addition of ligand will be associated with thermal changes. When the ligand molecules replace the solvent molecules from the solvation sphere of the solvated metal ion there may be either absorption or release of heat. The stability constant values increase on addition of ligand shows that the complex formation is an exothermic process. However, it is not always true because the stability constants is governed by other factors like viscosity, electrostatic effects, *etc.*

Thermodynamic functions: The overall changes in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) on complex formation have been determined at 30 °C by Gibbs Helmholtz equation and recorded in Table-6. The negative values of standard (ΔG°) shows that driving tendency of the complexation reaction is from left to right and the reaction tends to proceed spontaneously. The negative value of (ΔH°) suggest that the formation of these complexes is exothermic process. The higher the values of ΔS for 1:3 complex than 1:1 and 1:2 complex shows that 1:3 type complex is more spontaneous.

TABLE-6
THERMODYNAMIC PARAMETERS FOR LEAD PENICILLIN
BENZYL SALT SYSTEM IN 40 AND 60 % DMF AT 30 °C

Systems	303 K	ΔG (Kcal mol ⁻¹)	ΔH (Kcal mol ⁻¹)	ΔS (Cal deg ⁻¹ mol ⁻¹)
Pb(II)-PnB 40 %	1:1	-4187.58	-599.24	11.89
	1:2	-5181.97	-217.30	16.38
	1:3	-6129.36	-417.65	11.85
Pb(II)-PnB 60 %	1:1	-4313.47	-1597.98	8.96
	1:2	-5229.54	-599.24	15.28
	1:3	-6155.47	-199.74	19.65

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