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Electrochemical study of complexes of Co (II) with Antibiotic Drug Benzyl Penicillin sodium salt at d.m.e.

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Abstract: Polarographic technique has been used to evaluate the kinetic parameters and formation constants of Co (Π) complexes with benzyl penicillin sodium salt at pH 6.0±0.10 and constant ionic strength (μ = 0.1), HCl in aqueous, aqueous-methanol and aqueous-ethanol mixtures at d.m.e. The effect of concentration and temperature on the half wave potential of the complexes has also been investigated. The reduction of all these complexes is found to be irreversible and diffusion controlled, hence kinetic parameters (K^0_{fh}, αn) of these complexes have been calculated using Meites-Isral method and its modification by Gaur and Bhargava. In all the cases single reduction wave is obtained.
Keywords : DC Polarography, Formal rate constant, Benzyl penicillin sodium salt, Co (II).

Introduction

Consuming large amounts of inorganic cobalt stimulates growth of the thyroid gland. This in trun may lead to the over production of red cells, or a disorder known as polycythemia. Cobalt is present in human body in trace quantities. It has important biochemical role in the form of vitamin B_{12}[1]. It is a central component of vitamin B_{12}. It helps in the formation of red cells and also maintains nerve tissue. Organic cobalt must be obtained from foods such as liver, kidneys, milk oysters, clams, or sea vegetables. It also can be obtained from vitamin B_{12} supplements. Vitamin B_{12}, which is the largest and most complex, family of vitamins-B, is important, for converting fats, carbohydrates and proteins into energy, for assisting in the synthesis of red blood cells and is also critical for the production of RNA and DNA.

Further, Co^{2+} ions serve as important tool for enzymologist, due to its spectroscopic and magnetic properties. It is a useful probe of the enzyme active sites[2]. So it becomes essential to study complexation behavior of cobalt with antibiotic uptake by human beings.

Complexation of antibiotics with metals may influence their nature, properties and pharma-cokinetics. So metal drug complexes are being widely studied by different techniques.[3-12]

Earliar mixed ligand complexes of Co (Π) with pyridine and halide/pseudo halide and complexes of Co (Π) with 2, 4-dihydroxy benzoin in 65% ethanol water media and electrode kinetics of complexes of Co (Π) with atenolol at d.m.e.[13-15] were studied by polarographic technique. The study of the complexes of benzyl penicillin sodium salt, with Pb, Cu in aqueous and non-aqueous (methanol and ethanol) media, was carried out by Pandey et al[16,17].

The electrochemical investigation of Co (Π) ion with benzyl penicillin sodium salt by direct current polarography has been studied so far. Hence in the present investigations attempts have been made to study the complexation of Co (Π) with benzyl penicillin sodium salt in aqueous and aqueous-non aqueous mixture media by direct current polarography.

Experimental

A model CL 357 polarographic analyzer from (elico) was coupled with the cell for direct current polarographic experiments. The current and applied potential were recorded at scan rate 150 mV/min. The current voltage measurements were performed with three electrodes assembly, a dropping mercury

electrode as working electrode, calomel as reference and platinum as auxilary electrode. The dropping mercury electrode had the following characteristics:

m = 2.422 mg/sec.
t = 3.5 sec/drop.
h = 60 cm.

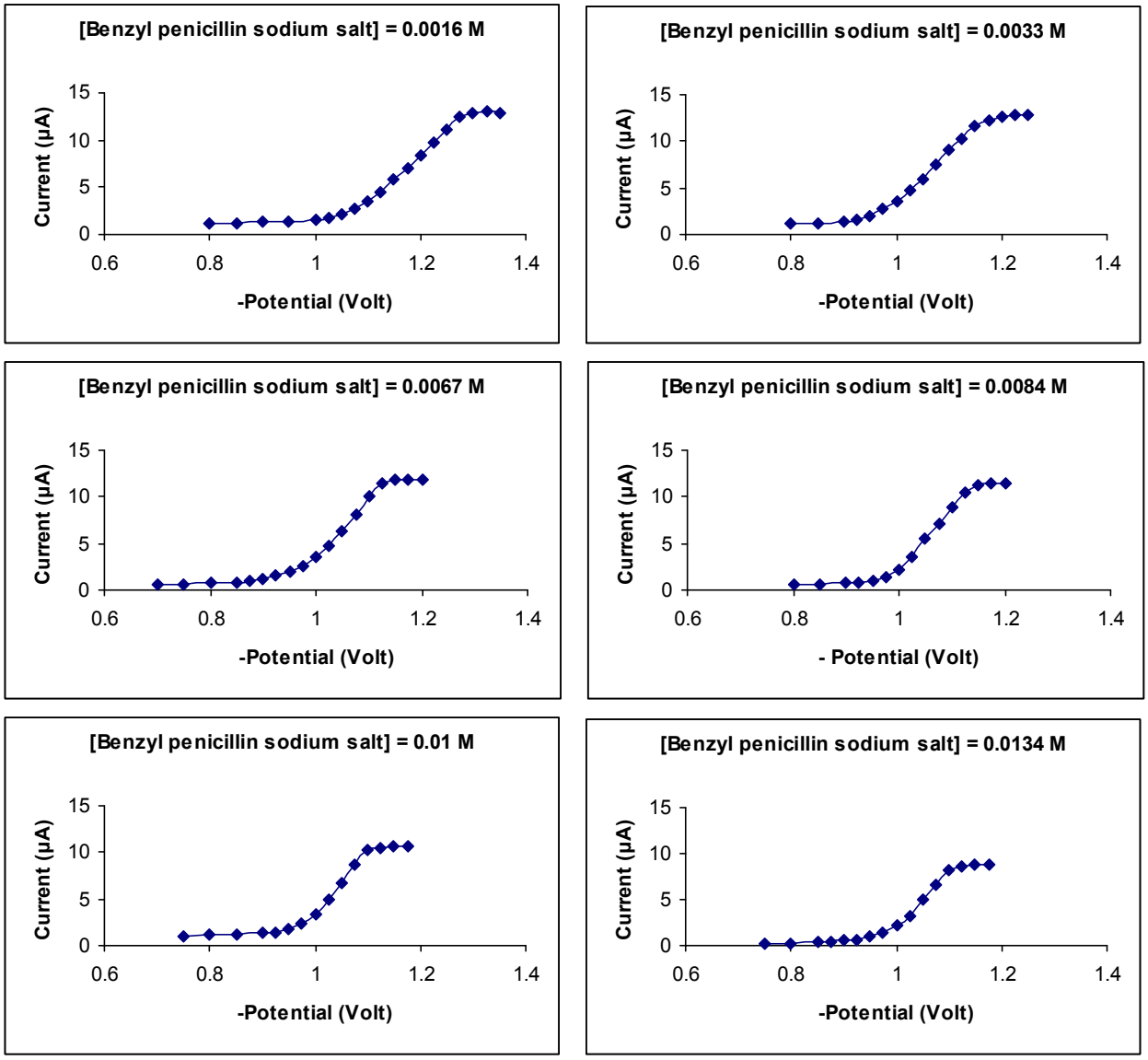
Elico digital pH meter was used to measure pH of the solution.

Analytical grade salt of cobalt nitrate $[Co(NO_3]_2$ was employed for present study. Aqueous buffer (HCI+water) of pH 6 was prepared. All solutions were prepared in double distilled water. Solution of gelatin (0.005%) was used as maxima suppressor. Distilled methanol and ethanol were taken for the study.

Results and Discussion

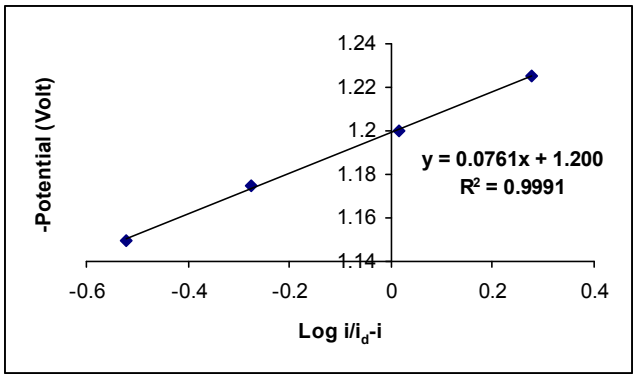
In a polarographic investigation of complexation of metal ions by ligand, the difference between the half-wave potentials ($E_{1/2}$) of the free and complexed metal ion is a measure of the complex stability. The complexation reactions of Benzyl penicillin sodium salt ligand with Co (II) cation studied in aqueous, 20% methanol-aqueous and 20% ethanol-aqueous mixed solvents using DC polarography at 25^0 C and 30^0 C. The polarographic results show that addition of the ligand to Co (II) solutions, shifts the half wave potential for the reduction of the complexed ions towards more positive values. As an example, the polarograms of the Co (II) ion in different concentrations of Benzyl penicillin sodium salt in 20% methanol at 30^0 C are shown in Figure 1. Similar polarograms were obtained for the other systems.

Figure 1. Polarograms of [Co (II) – Benzyl penicillin sodium salt] system in 20% methanol at 30^0 C



Co (Π) gave single well defined wave $E_{1/2}$ = -1.20 volts vs S.C.E.(in aqueous buffer of pH 6). Complexes of Co (Π) with penicillin benzyl sodium salt also gave well define single wave. The irreversibilty of the system was studied by the slope values of the plots of log i/i_d-i vs $E_{d.e.}$ (Figure 2). Similar patterns have been obtained with different concentraions of ligand, having different slope values in different solvents.
The reduction was found to be diffusion controlled which stand confirmed from the plots of i_d vs $\sqrt{h}$.

Figure 2. Plot between log i/i_d-i and voltage of complex of Co (II) with benzyl penicillin sodium salt (3.3 x10^{-3} M) in aqueous medium at 25^0 C



Kinetic Parameters
The kinetic parameters (K^0_{fh}, αn) were calculated from Meites-Israel method and also by the further modified Gaur-Bhargava's method[18].

$$E_{d.e.} = \frac{0.05915}{\alpha n} log \frac{k^0_{fh}\ t^{1/2}}{1.128\ D^{1/2}} - \frac{0.05690}{\alpha n}\ log \frac{i}{i_d - i} \qquad ...(1)$$

Which may be written as with

$$E_{d.e.} = E_{1/2} - \frac{0.05690}{\alpha n}\ log \frac{i}{i_d - i} \qquad ...(2)$$

With

$$E_{1/2} = \frac{0.05915}{\alpha n} log \frac{k^0_{fh}\ t^{1/2}}{1.128\ D^{1/2}} \qquad ...(3)$$

Where α is the transfer coefficient, n is the number of electrons involved in the rate determining step, K^0_{fh} is the forward rate constant of the electron transfer at zero volts, D is the diffusion coefficient and other terms have their usual significance.
Thus, the value of αn was obtained from the slope of the straight line corresponding to $E_{d.e.}$ versus log i/i_d-i. the intercept of the same plot gives the value of $E_{1/2}$ was used to calculate K^0_{fh} after getting the value of D from the Ilkovic equation.

Gaur-Bhargava has extended the Koutecky's treatment for irreversible wave since according to them the diffusion to the electrode surface (mercury drop) is spherical and not a linear one as was assumed by Meites and Israel[19] .
Polarographic characteristics and kinetic parameters of Co(II) with benzyl penicillin sodium salt in aqueous and aqueous-non-aqueous mixtures (20% methanol and 20% ethanol) at two temperatures are shown in table 1 and 2.

Effect of concentration
The shift in $E_{1/2}$ of Co (Π) complexes was found to be positive. It has been generally noted that in cobalt complexes the $E_{1/2}$ is shifted towards positive side[20]. Diffusion current decreases with increase in concentration of benzyl penicillin sodium salt, which confirms complex formation. The plot of $E_{1/2}$ vs. –log C_x results in a straight line. It is therefore reasonable to conclude the complex being reduced is composed of only one species[21]. Further, by increasing the concentration of ligand (drug) it has been observed that the value of $E_{1/2}$ shifted to more positive side suggesting better complexation with increase in concentration of the ligand.

Effect of non-aqueous media
It has been observed that in aqueous medium the $E_{1/2}$ is shifted to more positive side as compared with that of 20% methanol or 20% ethanol medium. This suggests that complexation takes place easily in aqueous medium (table 1 and 2). This can be explained on the basis of Gutmann doner number and viscosity of the solvents. The solvating ability of the solvent, as expressed by Guttman donocity scale, plays a fundamental role in the complexation reaction. The donor number is nearly a molecular property of the solvent, which is easily determined by experiment. It expresses the total amount of interaction with an acceptor molecule, including contribution both by dipole-dipole or dipole-ion interactions and by the binding effect caused by the availability of the free electron pair; to some extant steric properties of the solvent molecules may be contained in it[22]. In a solvent with high solvating ability (high donor number), the solvent can compete strongly with the ligand for the cation, therefore, the interaction between the ligand donor atoms and the metal ions will be decreased.
The value of K^0_{fh} is more in 20% ethanol medium in comparision of 20% methanol and aqueous medium indicating the more irreversibility of Co- benzyl penicillin sodium salt in ethanol than methanol and water.

Table 1. Kinetic parameters for Co (II) - benzyl penicillin sodium salt complex in aqueous, aqueous-methanol and aqueous-ethanol mixtures at 25^0 C

Solvent	Conc. of benzyl penicillin sodium salt (M)x10^{-3}	$E_{1/2}$ – V Vs S.C.E.	Slope (mV)	αn (V)	Dx10^3 (cm^2sec^{-1})	K^0_{fh} ($cm\ sec^{-1}$)	
						M.I.	G.B.
Aqueous	1.6	1.210	78	0.6948	727.542	6.363x10^{-13}	9.685x10^{-13}
	3.3	1.200	76	0.7131	153.802	1.630x10^{-13}	2.480x10^{-13}
	5.0	1.190	73	0.7424	49.970	3.154x10^{-14}	4.799x10^{-14}
	6.7	1.180	70	0.7742	26.669	7.131x10^{-15}	1.085x10^{-14}
	8.4	1.175	67	0.8089	16.245	1.321x10^{-15}	2.011x10^{-15}
	10.0	1.143	65	0.8338	9.766	7.41x10^{-16}	1.120x10^{-15}
	11.7	1.137	62	0.8741	6.707	1.56x10^{-16}	2.38x10^{-16}
20% Methanol	1.6	1.195	83	0.6530	680.461	6.468x10^{-13}	9.842x10^{-13}
	3.3	1.190	82	0.6609	346.163	3.632x10^{-13}	5.526x10^{-13}
	5.0	1.185	80	0.6775	148.359	1.257x10^{-13}	1.912x10^{-13}
	6.7	1.165	77	0.7038	61.229	4.148x10^{-14}	8.361x10^{-14}
	8.4	1.155	74	0.7324	31.796	1.085x10^{-14}	1.652x10^{-14}
	10.0	1.148	72	0.7527	18.393	4.067x10^{-14}	6.189x10^{-15}
	11.7	1.142	70	0.7742	12.270	1.522x10^{-15}	2.315x10^{-15}
	13.4	1.140	69	0.7855	8.812	8.93x10^{-16}	1.262x10^{-15}
20% ethanol	1.6	1.192	86	0.6302	692.432	2.029x10^{-12}	3.088x10^{-12}
	3.3	1.187	85	0.6376	349.013	1.157x10^{-12}	1.761x10^{-12}
	5.0	1.182	83	0.6530	159.349	4.356x10^{-13}	6.629x10^{-13}
	6.7	1.170	78	0.6948	62.389	5.503x10^{-14}	8.370x10^{-14}
	8.4	1.162	73	0.7424	31.796	5.654x10^{-15}	8.590x10^{-15}
	10.0	1.155	70	0.7742	19.158	1.284x10^{-15}	1.955x10^{-15}
	11.7	1.152	68	0.7970	12.792	4.13x10^{-16}	6.28x10^{-16}
	13.4	1.150	67	0.8089	9.191	2.18x10^{-16}	3.32x10^{-16}

Table 2. Kinetic parameters for Co (II) - benzyl penicillin sodium salt complex in aqueous, aqueous-methanol and aqueous-ethanol mixtures at 30^0 C

Solvent	Conc. of benzyl penicillin sodium salt (M)x10^{-3}	$E_{1/2}$ – V Vs S.C.E.	Slope (mV)	αn (V)	Dx10^4 (cm^2sec^{-1})	K^0_{fh} ($cm\ sec^{-1}$)	
						M.I.	G.B.
Aqueous	1.6	1.210	82	0.6609	1059.795	4.912x10^{-12}	7.476x10^{-12}
	3.3	1.190	80	0.6775	198.609	1.274x10^{-12}	1.938x10^{-12}
	5.0	1.160	78	0.6948	85.133	8.426x10^{-13}	1.282x10^{-12}
	6.7	1.120	76	0.7131	41.851	7.850x10^{-13}	1.946x10^{-13}
	8.4	1.000	75	0.7527	26.854	6.214x10^{-13}	9.458x10^{-14}
	10.0	1.080	69	0.7855	13.294	6.399x10^{-14}	9.722x10^{-14}
	11.7	1.065	68	0.7970	12.737	6.142x10^{-14}	4.08x10^{-15}
20% methanol	1.6	1.190	87	0.6229	99.356	3.593x10^{-12}	5.468x10^{-12}
	3.3	1.184	85	0.6302	563.924	2.229x10^{-12}	3.393x10^{-12}
	5.0	1.178	84	0.6452	223.458	8.168x10^{-13}	1.243x10^{-12}
	6.7	1.160	80	0.6775	83.789	1.827x10^{-13}	2.780x10^{-13}
	8.4	1.148	76	0.7131	44.068	3.698x10^{-14}	5.627x10^{-14}
	10.0	1.140	73	0.7424	27.218	9.88x10^{-15}	1.504x10^{-14}
	11.7	1.133	71	0.7633	17.669	3.87x10^{-15}	5.89x10^{-15}
	13.4	1.130	70	0.7742	12.510	2.20x10^{-15}	3.35x10^{-15}
20% ethanol	1.6	1.191	89	0.6089	999.335	6.716x10^{-12}	10.219x10^{-12}
	3.3	1.188	88	0.6159	562.422	3.912x10^{-12}	5.953x10^{-12}
	5.0	1.183	86	0.6302	230.128	1.459x10^{-12}	2.221x10^{-12}
	6.7	1.168	80	0.6775	87.892	1.514x10^{-13}	2.305x10^{-13}
	8.4	1.160	76	0.7131	45.488	2.687x10^{-14}	4.089x10^{-14}
	10.0	1.152	74	0.7324	27.220	1.094x10^{-14}	1.665x10^{-14}
	11.7	1.148	70	0.7742	18.209	1.550x10^{-15}	2.359x10^{-15}
	13.4	1.145	69	0.7855	13.189	8.70x10^{-16}	1.324x10^{-15}

Effect of temperature

It has been observed that when the temperature is increased from 25^0 to 30^0 C the $E_{1/2}$ gets shifted to more positive side (table 1 and table 2). This obviously confirms more complexation at higher temperature. It has been found that at higher temperature value of αn decreases. A decrease in value of αn implies that at higher temperature availability of electrons decreases[23].

Further, K^0_{fh} value also increase with rise in temperature. This shows that system is more irreversible at higher temperature. In 20% methanol and 20% ethanol shifting in $E_{1/2}$ are less positive. It may be due to salvation effect. Calculated values of K^0_{fh} by both the methods Meites-Israel and Gaur-Bhargava are in good agreement with each other.

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