

A Study Of Polarographic Characteristics And Stability Constant Of $[Mn^{II}$ -Antibiotics-Vitamin-B₅] Systems

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Abstract: Polarographic technique was used to study the ternary complex formation of Mn^{II} with neomycin, chlortetracycline, oxytetracycline, penicillin-V and penicillin-G as primary ligands and vitamin-B₅ as a secondary ligand at $pH = 7.30 \pm 0.01$ and $\mu = 1.0 M NaClO_4$ at 298 K. The nature of current voltage curves was quasireversible. Mn^{II} formed 1:1:1, 1:1:2 and 1:2:1 complexes with these drugs as confirmed by Schaap and McMaster method. The sequence of stability constant of complexes was neomycin < chlortetracycline < oxytetracycline < tetracycline < penicillin-V < penicillin-G that can be explained on the basis of nature of ligands and steric hindrance between metals ligands. Kinetic parameters were also determined using Tamamushi and Tanaka method. The value of transfer coefficient (α) confirmed that the 'transition state' behaves between dropping mercury electrode and solution interface. A slight variation of potential affects not only the rate but rate constant greatly.

Keywords: Kinetic parameters, Stability Constant, $[Mn^{II}$ -antibiotics-vitamin-B₅] System

I. INTRODUCTION

Vitamin-B₅ (Pantothenic acid), a water-soluble vitamin, is essential for humans and animals for growth, reproduction, and normal physiological functions. It is a precursor of the coenzymes, CoA and a carrier protein of fatty acid synthesis, which are involved in more than 100 different metabolic pathways including energy metabolism of carbohydrates, proteins and lipids, and the synthesis of lipids, neurotransmitters, steroid hormones, porphyrins and hemoglobin [1, 2]. On the other hand, antibiotics are natural compound produced mostly by plant microorganisms [3]. These antibiotics are used against several fungal and bacterial diseases in plants, animal and human beings [4-6]. The study of antibiotics with vitamin-B₅ has great importance. therefore, In this paper, we report the stability constant ($\log \beta$) and kinetics parameters of complexes viz. transfer coefficient (α), degree of irreversibility (λ), diffusion coefficient (D) and rate constant (k) of complexes using neomycin, chlortetracycline, oxytetracycline, tetracycline, penicillin-V, and penicillin-G as primary ligands

and vitamin-B₅ as secondary ligands by polarographic technique for which no reference is available in the literature.

II. EXPERIMENTAL DETAILS

All the chemicals used were of A.R. grade and their solutions were prepared in conductivity water. Mn^{II} the antibiotics and vitamin-B₅ [(+) pantothenic acid sodium salt] were taken in the ratios of 1:40:40 and current voltage curves were obtained in different pH values. It has been observed that the maximum shift of $E_{1/2}$ was obtained within the pH range 7.10 - 8.50, but pH 7.30 was selected for studying the complexes in human blood pH. A Systronic μ pH meter 361 was used to measure the pH of the analyte at 7.30 ± 0.01 adjusted by using dilute solutions of $HClO_4$ or NaOH as required. Potassium dihydrogen phosphate-sodium hydroxide buffer was added to stabilize the pH of the analyte. The current voltage curves were obtained on a manual polarograph using polyflex galvanometer (PL -50). The polarographic cell was of Latinin and Lingane type in which polarographic

capillary of 5.0 cm in length with 0.04 mm in diameter was used. The $m^{2/3} t^{1/6}$ value was $2.40 \text{ mg}^{2/3} \text{ s}^{-1/2}$ at 60.02 cm effective height of mercury. As the resistance of the cell was less than 300Ω , IR correction was not made.

III. RESULTS AND DISCUSSION

Mn^{II} gave two electron quasireversible reduction wave at $\text{pH} = 7.30 \pm 0.01$ and $\mu = 1.0 \text{ M NaClO}_4$ at 298 K [7-9]. The nature of current-voltage curves for complexes is also quasireversible. The concentration of Mn^{II} NaClO_4 , and triton X-100 (as suppressor) in the test solution were 0.5 mM, 1.0 M and 0.001% respectively. Pure nitrogen gas was passed through the test solution for deaeration before recording the current-voltage curves.

The concentration of antibiotics varied from 0.5 mM to 30.0 mM at two fixed concentration of vitamin-B₅ i.e. 0.025 M and 0.050 M. The $E_{1/2}$ values became more negative with the addition of vitamin-B₅ to the $[\text{Mn}^{II}$ -antibiotics] system which showed ternary complex formation of 1:1:1, 1:1:2, and 1:2:1 complexes. Gellings [10] method was used to determine the values of $E_{1/2}^{\text{reversible}}$ form $E_{1/2}^{\text{quasireversible}}$ by plotting $(E - RT/nF \log i_d - i/i)$ vs i for all the complexes. The data and plots of F_{ij} [X, Y] against [X] (where F_{ij} is a Schaap and McMaster [11] function to evaluate the stability constant β_{ij} , X = neomycin, Y = vitamin-B₅ and i and j are their stoichiometric numbers respectively) for $[\text{Mn}^{II}$ -neomycin-vitamin-B₅] system were given in Table 1. and Fig.1 respectively. The Fig.1 is used to determine the values of functions F_{00} , F_{10} , F_{20} and F_{30} and also to calculate the stability constant. The values of stability constant of complexes were given in Table 3.

The kinetic parameters viz. transfer coefficient (α), degree of irreversibility (λ) and rate constant (k) were determined by Tamamushi and Tanaka methods [12, 13] by plotting $(E'_{1/2} - E)$ against $\log(Z-1)$ {fig. 2 & 3 where the terms have the usual significance} [12, 13]. The values of kinetic parameters were given in table 2. It is obvious from the value of α that the values varied from $[\text{Mn}^{II}$ -neomycin-vitamin-B₅] 0.42 to 0.52 (about 0.50), and value of α for other systems were also about 0.50 confirmed that 'transition state' lies midway between dropping mercury electrode and solution interface. The value of rate constant (k) showed that the electrode process were quasireversible. The values of diffusion coefficient as determined by ilkovic equation [14] were as expected.

[Vitamin - B ₅] = 0.025 M (Fixed)							
[Neo.] X 10 ³ M	(E _{1/2}) ^r -V vs SCE	ΔE _{1/2} V	log I _m /I _c	F ₀₀ [X,Y]	F ₁₀ [X,Y] X 10 ⁵	F ₂₀ [X,Y] X 10 ⁴	F ₃₀ [X,Y] X 10 ⁶
0.00	1.400	-	-	-	-	-	-
0.50	1.451	0.0214	0.0074	5.4	19.52	257.57	10.01
1.00	1.457	0.0257	0.0150	7.67	32.45	258.08	10.01
2.00	1.462	0.0352	0.0150	16.12	58.46	259.08	10.02
3.00	1.468	0.0429	0.0227	29.83	84.67	260.08	10.02
4.00	1.471	0.0492	0.0227	48.86	111.08	261.08	10.02
5.00	1.475	0.0544	0.0227	73.27	137.69	262.09	10.03
6.00	1.480	0.0585	0.0305	103.13	164.50	263.09	10.03
8.00	1.484	0.0657	0.0305	179.41	218.73	265.11	10.04
10.00	1.488	0.0710	0.0385	278.19	273.79	267.11	10.04
20.00	1.491	0.0890	0.0385	1126.44	561.00	277.17	10.05
30.00	1.495	0.0998	0.0385	2609.43	868.33	287.22	10.05
log A = 0.65, log B = 2.80, log C = 6.40, log D = 7.00							
[Vitamin - B ₅] = 0.050 M (Fixed)							

[Neo.] X 10 ³ M	(E _{1/2}) ^r -V vs SCE	ΔE _{1/2} V	log I _m /I _c	F ₀₀ [X,Y]	F ₁₀ [X,Y] X 10 ⁵	F ₂₀ [X,Y] X 10 ⁵	F ₃₀ [X,Y] X 10 ⁶
0.00	1.400	-	-	-	-	-	-
0.50	1.448	0.0308	0.0150	11.43	36.47	50.75	10.01
1.00	1.453	0.0349	0.0150	15.80	61.90	50.80	10.01
2.00	1.458	0.0438	0.0227	32.19	112.91	50.90	10.02
3.00	1.462	0.0516	0.0227	58.85	164.12	51.00	10.02
4.00	1.468	0.0576	0.0305	95.92	215.53	51.10	10.03
5.00	1.471	0.0628	0.0305	143.18	267.14	51.20	10.03
6.00	1.476	0.0671	0.0305	200.99	318.96	51.31	10.04
8.00	1.481	0.0739	0.0385	348.16	423.18	51.51	10.04
10.00	1.488	0.0795	0.0385	537.84	528.22	51.71	10.05
20.00	1.492	0.0970	0.0466	2140.53	1065.45	52.71	10.05
30.00	1.496	0.1076	0.0466	4878.24	1622.87	53.72	10.06
log A = 0.65, log B = 2.80, log C = 6.40, log D = 7.00							

$\text{Mn(II)} = 0.5 \text{ mM}$, $\mu = 1.0 \text{ M NaClO}_4$, $\text{pH} = 7.30 \pm 0.01$, $\text{Temp.} = 25^\circ\text{C}$

Table 1: Polarographic Characteristics and F_{ij} [X, Y] Values of $[\text{Mn}^{II}$ - Neomycin - Vitamin-B₅] System

Vitamin - B ₅ = 0.025 M (Fixed)							
[Neo.] X 10 ³ M	(E _{1/2}) ^{qr} -V vs SCE	Slope mV	α	λ sec ^{-1/2}	D ^{1/2} X10 ⁻³ cm ² sec ⁻¹	k x 10 ⁻³ cm sec ⁻¹	
0.00	1.415	37.00	0.42	2.02	3.98	7.73	
0.50	1.454	42.00	0.48	1.78	3.48	6.25	
1.00	1.458	44.00	0.35	1.45	3.62	4.15	
2.00	1.463	35.50	0.40	1.25	3.45	4.38	
3.00	1.467	37.00	0.52	1.36	3.15	4.78	
4.00	1.474	40.00	0.40	1.36	3.68	6.28	
5.00	1.478	42.00	0.42	1.48	3.17	5.15	
6.00	1.485	35.50	0.44	1.25	3.25	5.18	
8.00	1.489	44.00	0.48	1.14	3.14	6.78	
10.00	1.492	48.00	0.35	1.78	3.64	6.48	
20.00	1.496	35.00	0.54	1.25	3.48	6.48	
30.00	1.502	35.50	0.52	1.14	3.15	4.25	

Vitamin - B ₅ = 0.050 M (Fixed)							
[Neo.] X 10 ³ M	(E _{1/2}) ^{qr} -V vs SCE	Slope mV	α	λ sec ^{-1/2}	D ^{1/2} X10 ⁻³ cm ² sec ⁻¹	k x 10 ⁻³ cm sec ⁻¹	
0.00	1.415	37.00	0.42	2.02	3.98	7.73	
0.50	1.451	40.00	0.40	1.88	3.15	6.14	
1.00	1.457	48.00	0.48	1.45	3.25	6.23	
2.00	1.462	42.00	0.44	1.45	3.64	6.25	
3.00	1.468	35.00	0.42	1.65	3.48	5.23	
4.00	1.472	40.00	0.35	1.38	3.64	5.48	
5.00	1.478	42.00	0.48	1.14	3.15	5.14	
6.00	1.481	45.00	0.42	1.24	3.64	5.15	
8.00	1.485	37.50	0.37	1.79	3.48	4.58	
10.00	1.491	35.00	0.40	1.48	3.64	4.56	
20.00	1.495	42.00	0.40	1.14	3.15	4.23	
30.00	1.498	48.00	0.42	1.88	3.41	5.18	

$\text{Mn(II)} = 0.5 \text{ mM}$, $\mu = 1.0 \text{ M NaClO}_4$, $\text{pH} = 7.30 \pm 0.01$, $\text{Temp.} = 25^\circ\text{C}$

Table 2: Kinetic Parameters of $[\text{Mn}^{II}$ - Neomycin - Vitamin-B₅] System

Ligand		Stability Constants							
Primary	Secondary	log β ₀₁	log β ₀₂	log β ₁₀	log β ₂₀	log β ₃₀	log β ₁₁	log β ₁₂	log β ₂₁
Neomycin	Vitamin-B ₅	2.00	3.16	2.65	4.48	7.00	3.62	5.26	8.00
Chortetracycline	Vitamin-B ₅			3.31	5.02	7.78	-	5.53	8.33
Oxytetracycline	Vitamin-B ₅			4.00	-	8.13	4.43	6.46	9.00
Tetracycline	Vitamin-B ₅			4.12	7.13	-	4.62	7.50	9.13
Penicillin-V	Vitamin-B ₅			4.31	-	-	4.80	8.00	9.20
Penicillin-G	Vitamin-B ₅			4.40	8.00	9.00	4.93	8.53	9.41

$\text{Mn(II)} = 0.5 \text{ mM}$, $\mu = 1.0 \text{ M NaClO}_4$, $\text{pH} = 7.30 \pm 0.01$, $\text{Temp.} = 25^\circ\text{C}$

Table 3: Stability Constant of $[\text{Mn}^{II}$ - Antibiotics- Vitamin- B₅] System

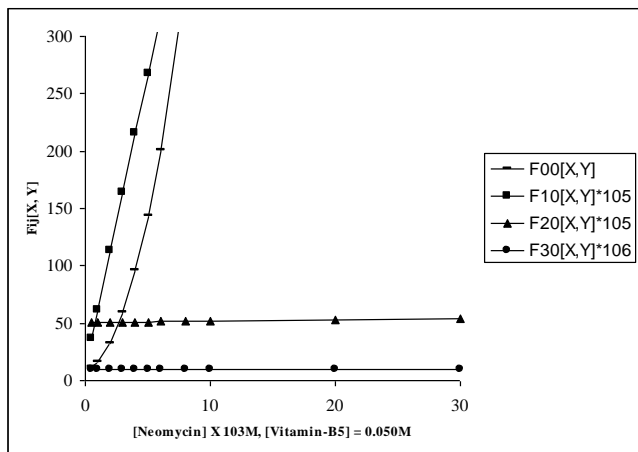
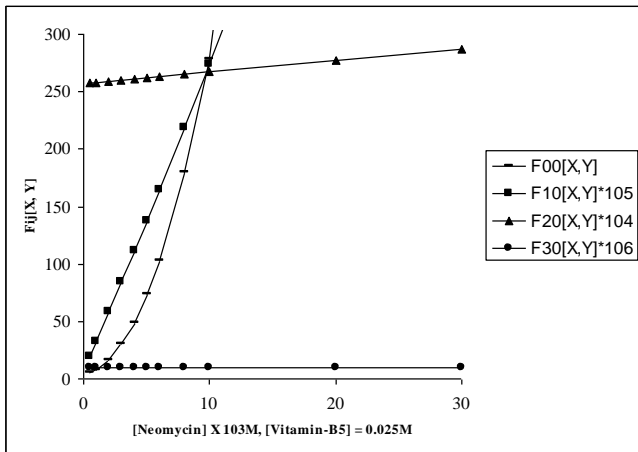


Figure 1: $[Mn^{II}$ -Neomycin-Vitamin- B_5] System

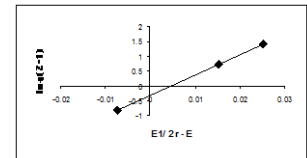
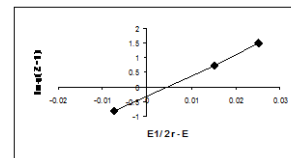


Figure 2: $[Mn^{II}$ -Neomycin-Vitamin- B_5] System, $[Vitamin-B_5] = 0.025mM$ Plot of $(E_{1/2}^r - E)$ vs $\log(Z-1)$, Y-axis = $\log(Z-1)$, X-axis = $(E_{1/2}^r - E)$

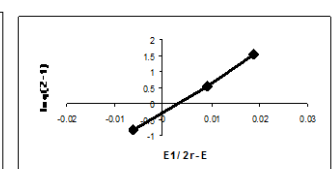
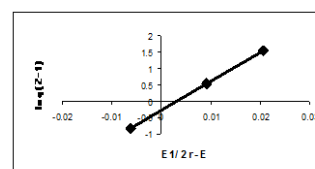
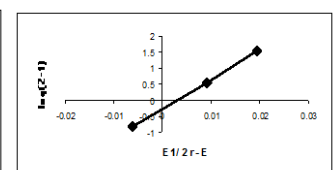
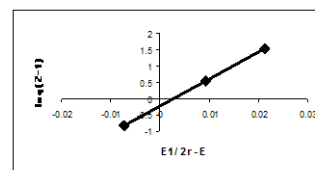
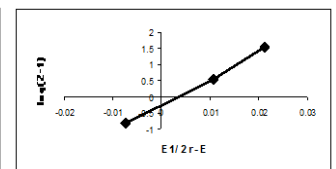
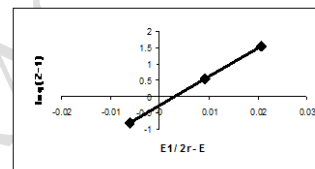
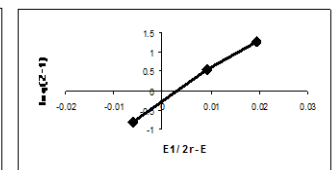
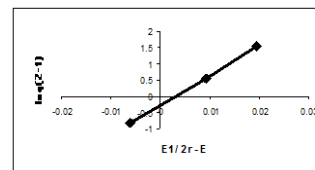
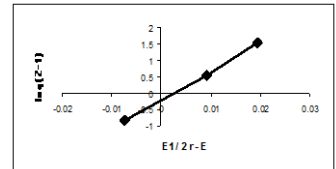
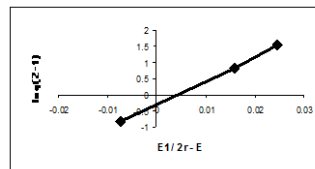
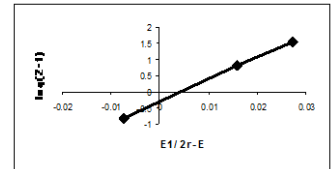
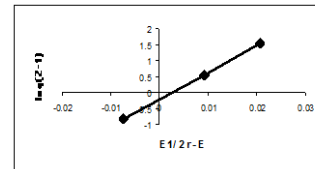


Figure 3: $[Mn^{II}$ -Neomycin-Vitamin- B_5] System, $[Vitamin-B_5] = 0.050mM$ Plot of $(E_{1/2}^r - E)$ vs $\log(Z-1)$, Y-axis = $\log(Z-1)$, X-axis = $(E_{1/2}^r - E)$

IV. CONCLUSION

The present study showed that the polarographic reduction of $[Mn^{II}$ - antibiotics - vitamin- B_5] was quasireversible. The values of transfer coefficient confirmed that the 'transition state' lies in an exact intermediate between D.M.E. and mercury solution interface [15-18].

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