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A Study of Polarographic Characteristics and Stability Constant of [Zn(II)-antibiotics-vitamin-B_X] Complexes

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Authors' contributions

This research work was carried out in collaboration between all authors. Author SNC performed the statistical analysis, wrote the protocol and the first draft of manuscript. Author FK guided the research and the research paper was prepared under his supervision. Author AP worked on literature search and reviewed the study. Author KC worked on literature search, reviewed the study and approved the final manuscript. All authors read and approved the final manuscript.

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ABSTRACT

Charge transfer reactions between dropping mercury electrode and [Zn(II)-antibiotics- vitamin-Bx] system were studied at pH = 7.30 ± 0.01, μ = 1.0 M NaClO4 at 298 K. The antibiotics were neomycin, chlortetracycline, oxytetracycline, tetracycline, penicillin-V and penicillin-G used as primary ligands and vitamin-Bx as secondary ligand formed 1: 1: 1, 1: 1: 2 and 1: 2: 1 complexes with Zn(II). Electrode kinetics was discussed on the basis of kinetic parameters viz. transfer coefficient (α), degree of irreversibility (λ), diffusion coefficient (D) and rate constant (k). The values of α varied from 0.42 to 0.52 (0.50) confirm that 'transition state' behaves between reactant and product response to applied potential and it lies between dropping mercury electrode (D.M.E) and solution interface. A small variation in potential affects the rate and rate constant greatly.

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Keywords: Stability constant; Kinetic parameter; [Zn(II)- antibiotics - vitamin-B_X] complexes.

1. INTRODUCTION

Para-Amino Benzoic Acid (PABA) is a non-protein amino acid that is widely distributed in nature. Since a small amount of it is present in the vitamin B-complex, it is included as a member of the vitamin family. Since it improves the protein used in the body, and is also related to red blood cell formation, as well as assisting the manufacturing of folic acid in the intestines, it is biologically important [1]. It is essential for the growth of microorganisms, but less essential as a nutrient for the human body. Most often, it is used in sunscreen preparations, since it can help to protect the skin against ultra-violet radiation. However, it is toxic in nature. The human body requires a very small amount, but in excess, it can cause liver damage [2].

The formation of an electrical double layer in the vicinity of a dropping mercury electrode has importance in electrochemical kinetics. It affects the effective difference of potential that favours and hinders the electrochemical reaction and also the concentration of electro active species at D.M.E and bulk of the solution as a result of which rate and rate constant of the reaction are affected greatly. On the other hand, antibiotics such as neomycin, chlortetracycline, oxytetracycline, tetracycline, penicillin-V and penicillin-G are important drugs, which are used against almost all kinds of diseases in animals, plants and human beings [3-4]. Therefore, the study of complexes of antibiotics with vitamin-Bx has great importance. In this paper, we report stability constant(log β) 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-Bx as secondary ligands by polarographic technique for which no reference is available in the literature.

2. EXPERIMENTAL

All the chemicals used were of A.R. grade and their solutions were prepared in double distilled water. For the polarographic study of ternary complexes of Zn(II) with antibiotics, a preliminary experimental set was prepared by keeping overall concentration of metal ion, supporting electrolyte and suppressor (Triton X-100, if required) at 0.5 mM, 1.0M and 0.001% respectively. The concentration of secondary ligand was fixed at 0.025 and 0.050 M. The polarographic data were recorded on a manual polarograph using polyflex galvanometer (Toshiwal PL-50). In Elico-digital pH meter (Model LI-120) with assembly of glass and calomel electrode were used to measure the pH of the test solution. Each test solution was deaerated by passing the pure hydrogen gas through it for 10 min. before recording polarograms. The D.M.E used had the capillary characteristics $m^{2/3} t^{1/6}$ = 2.40 $mg^{2/3}s^{-1/2}$ at 60.0 cm effective height of mercury. The values of stability constant and thermodynamic parameters were determined at two temperatures 25°C and 35°C respectively.

3. RESULTS AND DISCUSSION

Zn(II) gave two electron quasireversible reduction wave at pH = 7.30 ± 0.01 and μ = 1.0 M $NaClO_4$ at 298 K [5-6]. The nature of current-voltage curves for complexes is also quasireversible. The concentration of Zn(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 deareation 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-B_2 i.e. 0.025 M and 0.050 M. The $E_{1/2}$ values became more negative with the addition of vitamin-B_X to the [Zn(II)-antibiotics] system which showed ternary complex formation of 1:1:1, 1:1:2, and 1:2:1 complexes. The natures of current-voltage curves of Mn(II) and Zn(II) their complexes were quasireversible. Mn(II) and Zn(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 metal ligands. Gellings [7] method was used to determine the values of $E_{1/2}^{reversible}$ form $E_{1/2}$ 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 [8] function to evaluate the stability constant β_{ij}, X = neomycin, Y = vitamin-B_X and i and j are their stochiometric numbers respectively) for [Zn(II)-neomycin-vitamin-B_X] 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.

To know the values of β_{11} and β_{12}, the study has been carried out at two constant concentration of secondary ligand [Y] = [Vitamin-B_X] at 0.025 M and 0.050 M respectively. The values of stability constant of complexes were given in Table 3.

To compare the stability of binary and ternary complexes. The values of mixing constant logk was calculated by the following equation [9].

$$\log k_m = \log \beta_{11} - ½ [\log \beta_{02} + \log \beta_{20}] \quad (1)$$

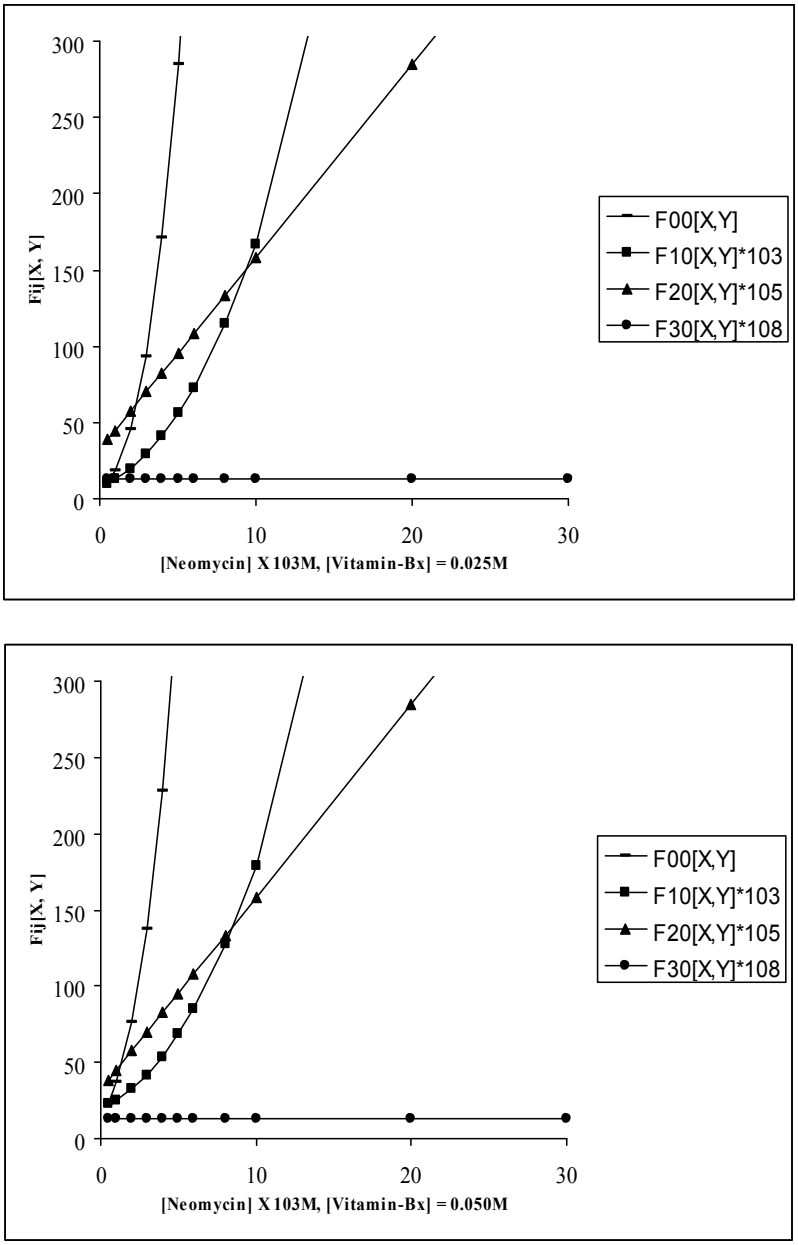

Fig. 1. Polarographic characteristics and F_{ij} [X, Y] values of [Z_n- Neomycin – Vitamin-B_X] system

Table 1. Polarographic characteristics and F_{ij} [X, Y] values of [Zn- Neomycin – Vitamin-B_X] system Zn(II) = 0.5 mM; μ = 1.0 M $NaClO_4$; pH = 7.30 ± 0.01; Temp. = 25°C

[Vitamin – B_X]= 0.025 M (Fixed)								[Vitamin – B_X]= 0.050 M (Fixed)						
[Neo.] $X10^3$ M	$(E_{1/2})^r$ -V vs SCE	$\Delta E_{1/2}$ V	$\log I_m/I_c$	F_{00}[X,Y]	F_{10}[X,Y] X 10^3	F_{20}[X,Y] X 10^5	F_{30}[X,Y] X 10^8	$(E_{1/2})^r$ -V vs SCE	$\Delta E_{1/2}$ V	$\log I_m/I_c$	F_{00}[X,Y]	F_{10}[X,Y] X 10^3	F_{20}[X,Y] X 10^5	F_{30}[X,Y] X 10^8
0.00	0.985	-	-	-	-	-	-	0.985	-	-	-	-	-	-
0.50	1.114	0.0300	0.0074	10.61	10.18	38.64	12.58	1.105	0.0402	0.0074	23.38	22.71	38.64	12.58
1.00	1.118	0.0368	0.0149	18.26	12.74	44.94	12.59	1.111	0.0460	0.0149	37.29	25.27	44.94	12.59
2.00	1.122	0.0481	0.0226	45.03	19.75	57.53	12.59	1.115	0.0552	0.0149	76.59	32.28	57.53	12.59
3.00	1.127	0.0575	0.0226	93.39	29.28	70.12	12.59	1.118	0.0625	0.0226	137.50	41.82	70.15	12.6
4.00	1.135	0.0653	0.026	170.93	41.35	82.75	12.60	1.122	0.0689	0.0226	227.55	53.88	82.75	12.6
5.00	1.138	0.0718	0.0226	285.17	55.93	95.35	12.60	1.128	0.0746	0.0226	354.57	68.50	95.45	12.62
6.00	1.142	0.0773	0.0304	443.89	73.06	108.01	12.61	1.131	0.0797	0.0226	525.78	85.62	108.07	12.62
8.00	1.147	0.0865	0.0384	924.26	114.84	133.23	12.61	1.137	0.0881	0.0304	1032.01	127.49	133.39	12.63
10.00	1.151	0.0941	0.0384	1673.62	166.81	158.55	12.62	1.142	0.0953	0.0304	1806.41	179.43	158.65	12.63
20.00	1.157	0.1186	0.0465	11560.9	577.76	284.75	12.62	1.148	0.1189	0.0465	11833.9	591.09	285.15	12.64
30.00	1.156	0.1337	0.0465	37239.3	1241.12	410.95	12.62	1.153	0.1340	0.0384	37675.7	1255.45	411.55	12.64
log A = 0.75, log B = 3.90, log C = 6.50 , log D = 9.10								log A = 1.10, log B = 4.30, log C = 6.50, log D = 9.10						

Table 2. Kinetic parameters of [Zn- Neomycin – Vitamin-B_X] System Zn(II) = 0.5 mM, μ = 1.0 M $NaClO_4$, pH = 7.30 ± 0.01, Temp. = 25°C

Vitamin – B_X = 0.025 M (Fixed)							Vitamin – B_X = 0.050 M (Fixed)					
[Neo.] $X10^3$ 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} $cm\ sec^{-1}$	$(E_{1/2})^{qr}$ -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	1.000	36.00	0.45	1.18	4.87	5.74	1.000	36.00	0.48	1.18	4.82	5.74
0.50	1.117	42.00	0.42	1.14	3.82	4.48	1.108	42.00	0.42	1.14	3.84	4.48
1.00	1.121	48.00	0.44	1.56	3.48	5.12	1.113	44.00	0.44	1.42	4.48	5.62
2.00	1.125	45.00	0.40	1.52	4.52	3.82	1.118	45.00	0.46	1.84	4.82	4.48
3.00	1.130	42.00	0.42	1.48	4.48	4.48	1.121	35.50	0.40	1.78	4.48	3.84
4.00	1.138	35.00	0.48	1.76	3.42	4.82	1.126	37.00	0.42	1.64	3.47	3.78
5.00	1.142	37.00	0.52	1.84	4.52	4.48	1.132	40.00	0.52	1.42	3.68	3.82
6.00	1.146	44.00	0.52	1.48	3.82	5.56	1.136	35.00	0.52	1.78	3.42	4.42
8.00	1.150	35.50	0.35	1.48	4.48	3.41	1.139	45.50	0.54	1.14	4.41	4.21
10.00	1.154	40.50	0.40	1.56	3.60	3.20	1.143	44.00	0.42	1.46	4.20	4.20
20.00	1.159	42.00	0.42	1.14	3.52	3.82	1.150	40.00	0.40	1.53	4.02	4.45
30.00	1.162	45.00	0.44	1.76	4.82	3.48	1.155	45.50	0.42	1.64	4.20	3.82

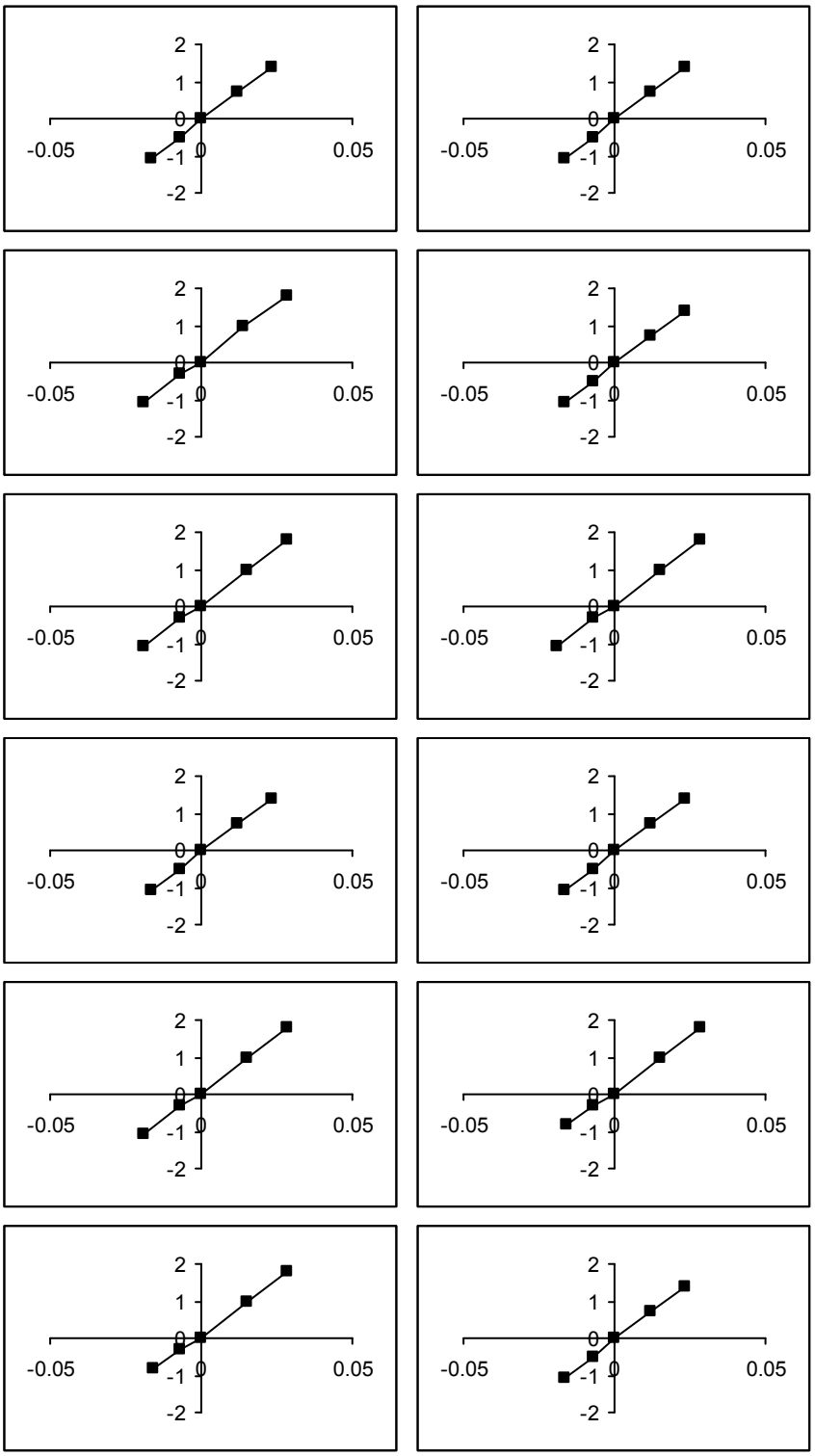

Fig. 2(a). [Zn(II)-Neomycin-Vitamin-B_X] System, [Vitamin-B_X] = 0.025 mM
Plot of ($E^r_{1/2}$-E) Versus log(Z-1), Y-axis = log(Z-1), X-axis = ($E^r_{1/2}$-E)

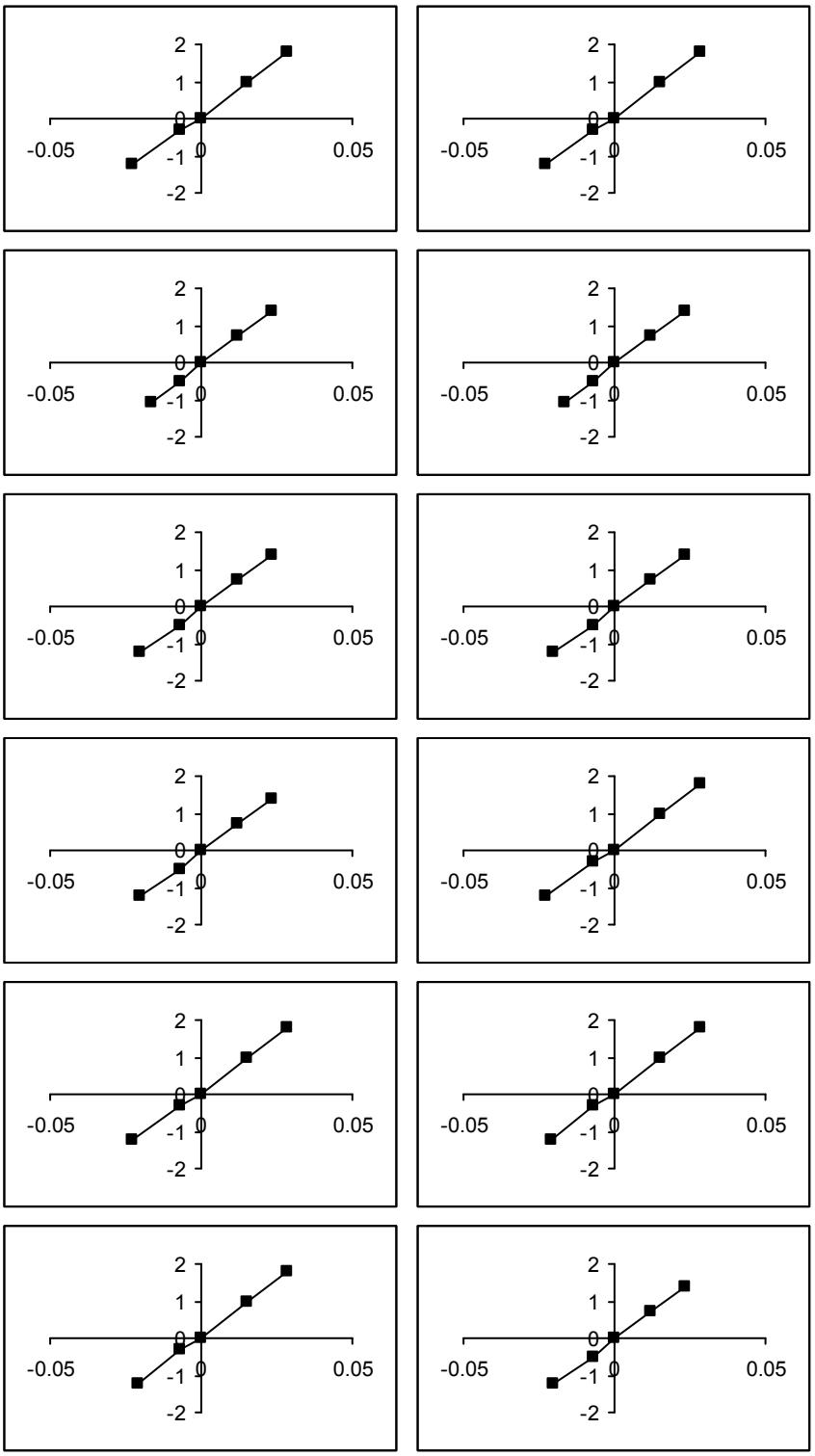

Fig. 2(b). [Zn(II)-Neomycin-Vitamin-B_X] System, [Vitamin-B_X] = 0.050 mM plot of ($E^r_{1/2}$-E) versus log(Z-1), Y-axis = log(Z-1), X-axis = ($E^r_{1/2}$-E)

Table 3. Stability constant of [Zn- Antibiotics- Vitamin- B_X] system Zn (II) = 0.5 mM, μ = 1.0 M $NaClO_4$, pH = 7.30 ± 0.01, Temp. = 25°C

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_X	2.15	3.20	3.60	6.51	9.10	3.75	6.82	-
Chlortetracycline	Vitamin-B_X	-	-	4.40	7.61	9.50	4.72	7.60	9.72
Oxytetracycline	Vitamin-B_X	-	-	4.50	7.81	9.86	4.80	7.93	10.00
Tetracycline	Vitamin-B_X	-	-	4.80	8.01	9.91	5.00	8.20	10.16
Penicillin-V	Vitamin-B_X	-	-	4.91	-	10.00	-	8.31	10.26
Penicillin-G	Vitamin-B_X	-	-	4.96	8.12	10.10	5.23	8.40	10.37

The values of log k_m were -1.10, -0.68, -0.64, -0.60 and -0.43 for [Zn(II)-neomycin-vitamin-B_X], [Zn(II)-chlortetracycline-vitamin-B_X], [Zn(II)-oxytetracycline-vitamin-B_X], and [Zn(II)-tetracycline -vitamin-B_X] and [Zn(II)-penicillin-G -vitamin-B_X] respectively. The positive value of log k_m showed that the ternary complex is more stable than their binary complexes while the negative values of log k_m showed that binary complexes are more stable than their ternary complexes. The complexes of compositions 1 : 2 in case of [Zn(II)-penicillin-V -vitamin-B_X] are not formed therefore; the values of log k_m were not calculated. It is clear from the values of stability constants of complexes that neomycin formed the complexes of lowest stability. In case of tetracycline; all the tetracycline has the same structures except in the difference in R_1 and R_2 position. The lesser stability constant of chlortetracycline complex than that of oxytetracycline complex is due to the presence of more electrons withdrawing Cl at R_1 in the former in place of H in the latter. In case of tetracycline, H is present both at R_1 and R_2 hence; there are least electronic disturbances in tetracycline in comparison to other tetracycline complexes [10-12]. This order of stability supported the order of their pK values of the ligands [13]. In case of both penicillin-V and penicillin-G, it is the ring nitrogen and O of the carboxylic group which take part in complexation with Zn(II). The greater stability of penicillin-G complexes than that of penicillin-V complexes is also supported by the order of the pK values [14-17].

In case of vitamin-B_X, it is the N of the $–NH_2$ group [18-19], which can take part in bond formation with Zn(II). It is clear from the values of stability constant of the complexes that vitamin-B_X and antibiotics used either singly or simultaneously might be effective to reduce the toxicity [20-21] of Zn(II) *in vivo*.

The kinetic parameters viz. transfer coefficient (α), degree of irreversibility (λ) and rate constant (k) were determined by Tamamushi and Tanaka methods [22-23] by plotting ($E^r_{1/2}$-E) against log (Z-1) Fig. 2(a) and 2(b) where the terms have the usual significance} [20-21]. The values of kinetic parameters were given in Table 2. It is obvious from the value of α that the values varied from [Zn(II)-neomycin-vitamin-B_X] 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 [24] were as expected.

4. CONCLUSION

The present study showed that the polarographic reduction of [Zn(II) – antibiotics – vitamin-B_X] was quasireversible. The values of transfer coefficient confirmed that the 'transition state' lies in an exactly between D.M.E and mercury solution interface [25]. The stability constant may be used to reduce metal toxicity, oxidative stress and nephrotoxicity. The thermodynamics parameters showed that the complexes were lesser stable at high temperature and formed with the evolution of heat.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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