International Journal of Scientific Research in Engineering and Management (IJSREM)
Volume: 06 Issue: 03 | March - 2022 ISSN: 2582-3930

Study of Bioinorganic Ternary Complexes of Mn (II) with Antibiotics & Aspirin by Polarographic Technique

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Polarography was used to determine the stability constants (log b) of mixed ligand bioinorganic complexes of Mn (II) with some antibiotics as primary ligands and aspirin as secondary ligand at pH=7.30 ± 0.01 and ionic strength m=1.0 M $NaClO_4$ at 298 K. The waves of Mn and its complexes were quasireversible. Mn (II) formed 1:1:1, 1:2:1 and 1:1:2 complexes. Stability of these complexes is explain on the basis of sizes and basic nature of these Ligands.

INTRODUCTION

Antibiotics are well known naturally occuring compounds produced mostly by plants organisms[1], used in sevreral diseases in plants, animals and human[2,3], have great importance in biological system. On the other hand aspirin is also a biological drug used as antipyratic as well as analgesic. The biochemical, pharmacological and medicinal importance of metal drug complexes in very well established. Some work on Mn (II) complexes with different techniques. A survey of Literature reveals that no refrence is available on Mn (II) ternary Complexes with the presently selected antibiotics and aspirin by polarographic technique, hence, authors have studies the mixed ligand complexation of Mn (II) with neomycin, chlortetracyclin, oxytetracyclin, tetracyclin, penicillin-V and penicillin-G as primary ligand and Aspirin as secondary ligand, using polarographic technique with the view to determine the values of stability constants and kinetic parameters. The position of transition state and effect of size, basicity, steric hinderance due to ligands on stability complexes also discussed.

MATERIAL AND METHODS

Manganese chloride (Aldrich USA), $NaCLO_4$ (Fluka switzerland), antibiotics (Fluka) were used and their solution were prepared in double distilled water. Aspirin is used as its sodium salt. The concentration of metal ions and $NaClO_4$ in the test solution were 0.5 mM and 1.0 mM respectively while 1.0 M $NaClO_4$

was used to maintain the ionic strength as well as used as supporting electolyte. NaCl-agar-agar plug together with sintered disc were used in Latinine-Lingane cell[4] which connect the polarographic cell with SCE[5, 6]. The resistance of cell was lower than 200 ohms as to make no correction for IR.

The pH of the solutions were adjusted to 7.30 ± 0.01 by adding requsite amount of sodium hydroxide and perchloric acid solution. The C-V data for the complex system were recorded after passing the pure hydrogen gas in the test solution.

An Elico (LI-120) pH metere fitted with glass and satureted calomal elecrode were used to record the pH of the test solution. The temperature was maintained constants at 298 K.

A manual polarograph with PL-50 polyflex galvinometer was use to record the current voltage data. The capillary characteristits were $m^{2/3}\ t^{1/6}$ =2.40 $mg^{2/3}\ s^{-1/2}$ at 60.0 cms (calculated) effective height of mercury. The depolariser and ligands (antibiotics and aspirin) were taken in the ratio 1:40:40 and current voltage curves were obtained at different pH values but pH=7.30 ± 0.01 was selected on account of studying the complex formation in human blood pH.

In ternary complexes the concentration of antibiotics was varied from 0.50 mM to 30 mM at two fixed concentration of aspirin i.e. 0.025 and 0.050 M. For the calculation of stability constants b_{11} (1:1:1), b_{12} (1:2:1) and ($\log b_{21}$), (1:2:1) Schaap and Mc Master method[7] was used.

RESULT AND DISCUSSION

Mn (II) gave a well defiend two electron quasirevesible reduction wave in 1.0 M dm-3 NaCLO4 at pH= 7.30 ± 0.01. The values of $E_{1/2}^{(qr)}$ of Mn (II) was found -1.420 V vs SCE which by Gellings method[8,9] gave $E_{1/2}$ = -1.410 V. Similarly $E_{1/2}^{(r)}$ from $E_{1/2}^{(qr)}$ of complexes for corresponding ligand concentration was also calculated. In all these cases it has been observed that irreversivility increased with increase of living concentration. Mn formed 1:1 and 1:2 complexes with aspirin and stability constants are given in table no. 1.

Polarography of [Mn-Chlortetracycline-Aspirin] System

These complexes were studied by varying the concentration of primary ligand chlortetracycline from 0.5 mM to 30 mM at to fixed concentration of secondry ligand aspirin (i.e. 0.025 M and 0.050 M). It is

observed that the half wave potential increased with increase of concentration of secondry ligand i.e. aspirin to the [Mn-chlortetracycline][10] system showed ternary complex formation.

The values of stability constants are given in table no. 1. The polarographic characteristics & F_{ij} [X Y] values for [Mn-chlortetracycline-aspirin] systems are given in table no. 2.

Stability constants of [Mn (II)-antibiotics-aspirin] complexes.

Stability constants for [Mn (II)-antibiotics-aspirin] complexes are given table No. 1. Stability of complexes can be compared by the values of mixing constants log km which is given by the following eq[11] :

$$\text{Log Km} = \log b_{11} - 1/2 [\log b_{20} + \log b^{02}]$$

The values of log Km for [Mn-Neomycin-Aspirin], [Mn-Chlortetracyclin-Aspirin], [Mn-Oxytetracyclin-Aspirin], [Mn-Tetracyclin-Aspirin], [Mn-Penicllin-Aspirin] and [Mn-Penecillin-Aspirin] Complexes were obtained-0.030, -0.370, -0.370, -5.430, +3.852 and -0.150 respectively. Nagative values of log K_m showed that the binary complexes are more stable than their ternary complexes, while the positive values showed that the ternary complexes are more stable than their parent binary complexes[12-14].

The sequence of stability constants of complexes with respect to selscted antibiotic is neomycin < chlortetracycline < oxytetracycline < tetracyclin < penicillin V < penicillin G. It is clear that the neomycin formed the complexes of lowest stability among all the selected antibiotics, which may be due to the fact that number of groups are present in neomycin creating steric. In case of chlortetracyclin, oxytetracyclin and tetracyclin, the oxigen of first carbon atom and oxigen of amide group may take part in complexation with Mn[15-17]. The order of stability constats of these tetracyclins is also in accordence with there pK values[18].

In case of penicillin-V and penicillin-G the >CO of the carboxylic group and ring nitrogen may take part in co-ordination with metal ion. The penicillin-G complexes have higher stability than that of penicillin-V complexes owing to the higher basic strength of penicillin-G than penicillin-V[19,20]

Table No. 01 : Stability constants of [mn-antibiotic-aspirin]complexes (Ref. 10)

Ligands	$Log\beta_{01}$	$Log\beta_{02}$	$Log\beta_{10}$	$Log\beta_{20}$	$Log\beta_{30}$	$Log\beta_{11}$	$Log\beta_{12}$	$Log\beta_{21}$
aspirin	1.85	2.87	-	-	-	-	-	-
Neomycin	-	-	3.40	6.31	8.90	4.20	7.50	9.80
Chlortetracyclin	-	-	4.00	-	9.13	4.63	7.65	10.00
Oxytetracyclin	-	-	4.31	7.50	9.32	4.85	7.70	10.10
Tetracyclin	-	-	4.50	7.80	9.60	4.92	7.90	10.20
Penicillin-V	-	-	4.60	7.96	9.97	5.25	8.20	10.25
Penicillin-G	-	-	4.70	8.00	10.00	5.30	-	10.56

Table No. 02 : The polarographic characteristics & $F_{ij}[X\ Y]$ values for the [Mn(II)-chlortetracyclin-aspirin] system

Mn(II) = 0.5 mM; μ = 1.0 M $NaClO_4$; pH = 7.30 ± 0.01; Temp.=25°C

	Aspirin = 0.025 M (Fixed)							Aspirin = 0.050 M (Fixed)						
Chlortetra. x 10^{-3} M	$(E_{1/2})'$ -V vs SCE	$\Delta E_{1/2}$ V	$\log\frac{I_d}{I_c}$	$F_{00}[X,Y]$ x 10^{2}	$F_{10}[X,Y]$ x 10^{5}	$F_{20}[X,Y]$ x 10^{8}	$F_{30}[X,Y]$ x 10^{9}	$(E_{1/2})'$ -V vs SCE	$\Delta E_{1/2}$ V	$\log\frac{I_d}{I_c}$	$F_{00}[X,Y]$ x 10^{2}	$F_{10}[X,Y]$ x 10^{5}	$F_{20}[X,Y]$ x 10^{8}	$F_{30}[X,Y]$ x 10^{9}
0.00	1.4000	-	-	-	-	-	-	1.4000	-	-	-	-	-	--
0.50	1.4570	0.0570	0.0074	0.8538	1.6431	2.5067	1.3489	1.4675	0.0675	0.0074	1.9345	3.7413	5.0067	1.3489
1.00	1.4729	0.0729	0.0074	2.9356	2.9033	2.5135	1.3560	1.4827	0.0827	0.0074	6.3151	6.2512	5.0132	1.3215
2.00	1.4897	0.0897	0.0149	10.9211	5.4444	2.5273	1.3689	1.4991	0.0991	0.0149	22.6463	11.2912	5.0266	1.3325
3.00	1.4999	0.0999	0.0226	24.0608	8.0095	2.5399	1.3324	1.5090	0.1090	0.0226	49.1469	16.3610	5.0410	1.3669
4.00	1.5072	0.1072	0.0304	42.4491	10.6042	2.5536	1.3400	1.5162	0.1162	0.0304	85.8735	21.4524	5.0536	1.3400
5.00	1.5129	0.1129	0.0384	66.1813	13.2298	2.5680	1.3605	1.5218	0.1218	0.0384	132.9639	26.5800	5.0684	1.3689
6.00	1.5175	0.1175	0.0465	95.2871	15.8758	2.5810	1.3508	1.5264	0.1264	0.0465	190.4907	31.7378	5.0833	1.3890
8.00	1.5250	0.1250	0.0465	170.0563	21.2530	2.6079	1.3495	1.5337	0.1337	0.0465	336.8415	42.0972	5.1074	1.3432
10.00	1.5308	0.1308	0.0548	267.4103	26.7378	2.6348	1.3480	1.5395	0.1395	0.0548	525.6539	52.5590	5.1321	1.3215
20.00	1.5491	0.1491	0.0548	1117.828	55.8898	2.7750	1.3705	1.5574	0.1574	0.0632	2132.023	106.598	5.2680	1.3400
30.00	1.5601	0.1601	0.0632	2624.966	87.4978	2.9036	1.3455	1.5681	0.1681	0.0718	4901.253	163.373	5.4045	1.3486
	log A=0.5096 log B=4.5908			log C=8.3979 log D=9.1300				log A=0.8056 log B=5.0927			log C=8.6989 log D=9.1300			

ACKNOWLEDGEMENT

The authors are thankful to Prof. A.P. Mishra, Head, Department of Chemistry, Dr. H.S. Gour Central University, Sagar (M.P.).

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