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POLAROGRAPHIC STUDYAND STABILITY CONSTANT OF BIOINORGANIC TERNARY COMPLEXES OF MN (II) WITH ANTIBIOTICS & PHENACETIN

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Abstract:

Polarography was used to determine the stability constants (log β) of mixed ligand bioinorganic complexes of Mn (II) with some antibiotics as primary ligands and phenacetin as secondary ligand at pH=7.30 ± 0.01 and ionic strength m=1.0 NaClO at 298K. 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 discussed on the basic nature and the of sizes of the ligands under investigation.

Key Words: Stability Constant, [Mn(II)-Antibiotics-Phenacetin] System

Introduction:

Antibiotics are well known naturally occurring compounds produced mostly by plants organisms, used in sevreral diseases in plants, animals and human, have great importance in biological system. On the other handphenacetin is also a biological drug used as antipyretic as well as analgesic. The biochemical, pharmacological and medicinal importance of metal drug complexes are very well established. Some work on Mn (II) complexes with different techniques. A survey of literature reveals that no reference is available on Mn (II) ternary complexes with the presently selected antibiotics and phenacetin by polarographic technique, hence, authors have studied the mixed ligand complexation of Mn (II) with neomycin, chlortetracycline, oxytetracycline, tetracycline, penicillin-V and penicillin-G as primary ligand and phenacetin as secondary ligand, using polarographic technique with the view to determine the values of stability constants. The position of transition state and effect of size, basicity, steric hinderance due to ligands on stability of complexes also discussed.

Material And Methods:

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

An Elico (LI-120) pH meter fitted with glass and saturated calomel electrode were used to record the pH of the test solutions. The temperature was maintained constants at 298 K. The pH of the solutions was adjusted to 7.30 ± 0.01 by adding requisite 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.

A manual polarograph with PL-50 polyflex galvanometer was use to record the current voltage data. The capillary characteristics were mt=2.40 mg s at 60.0cms (calculated) effective height of mercury. The depolariser and ligands (antibiotics and phenacetin) 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 phenacetin i.e. 0.025 and 0.050 M. For the calculation of stability constants b (1:1:1), b(1:2:1) and ($\log\beta_{21}$), (1:2:1) Schaap and Mc Master method was used.

Result and Discussion:

Mn (II) gave a well-defined two electron quasireversible reduction wave in 1.0 M dm-3 $NaClO_4$ at pH= 7.30 ± 0.01. The values of E of Mn (II) was found to be -1.420 V vs SCE which by Gellings method gave E = -1.410 V. Similarly E from E of complexes for corresponding ligand concentration was also calculated. In all these cases it has been observed that irreversibility increased with increase of living concentration. Mn formed 1:1 and 1:2 complexes with phenacetin and stability constants are given in table no. 1.

Polarography of [Mn-Chlortetracycline-Phenacetin] 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 secondary ligand phenacetin (i.e., 0.025 M and 0.050 M). It is observed that the half wave potential increased with increase of concentration of secondary ligand i.e.phenacetin to the [Mn-chlortetracycline] system showed ternary complex formation.

The values of stability constants are given in table no. 1. The polarographic characteristics & F[X Y] values for [Mn-chlortetracycline-phenacetin] systems are given in table no. 2.

Stability Constants of [Mn (II)-Antibiotics-Phenacetin] Complexes:

Stability constants for [Mn (II)-antibiotics-phenacetin] 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:

Log Km=log $\beta_{1/2}$ [log β + log β]

The values of log Km for [Mn-Neomycin-phenacetin], [Mn-Chlortetracycline-phenacetin], [Mn-Oxytetracycline-phenacetin], [Mn-Tetracycline-phenacetin], [Mn-Penicillin-phenacetin] and [Mn-Penicillin-phenacetin] Complexes were obtained-0.030, -0.370, -0.370, -5.430, +3.852 and -0.150 respectively. Negative values of log K 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.

The sequence of stability constants of complexes with respect to selected antibioticis neomycin< chlortetracycline < oxytetracycline <tetracycline<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 chlortetracycline, oxytetracycline and tetracycline, the oxygen of first carbon atom and oxygen of amide group may take part in complexation with Mn. The order of stability constants of these tetracyclines is also in accordance with theirpK values.

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

Table 1: Stability constants of [Mn-antibiotic-phenacetin] complexes (Ref. 10)

Ligands	Logβ_{01}	Logβ_{02}	Logβ_{10}	Logβ_{20}	Logβ_{30}	Logβ_{11}	Logβ_{12}	Logβ_{21}
phenacetin	1.80	2.80	-	-	-	-	-	-
Neomycin	-	-	3.40	6.31	8.90	4.10	7.40	9.70
Chlortetracycline	-	-	4.00	-	9.13	4.50	7.50	9.93
Oxytetracycline	-	-	4.31	7.50	9.32	-	7.65	10.00
Tetracycline	-	-	4.50	7.80	9.60	4.85	7.85	10.12
Penicillin-V	-	-	4.60	7.96	9.97	5.20	8.00	10.20
Penicillin-G	-	-	4.70	8.00	10.00	5.28	-	10.50

Table 2: The polarographic characteristics & F[X Y] values for the [Mn(II)-chlortetracycline-phenacetin] system

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

	Phenacetin = 0.025 M (Fixed)							Phenacetin = 0.050 M (Fixed)						
Chlortetra. x 10^{-3} M	$(E_{1/2})'$ -V vs SCE	$\Delta E_{1/2}$ V	$\log \frac{I_c}{I_i}$	$F_{00}[X,Y]$ x 10^{2}	$F_{10}[X,Y]$ x 10^{4}	$F_{20}[X,Y]$ x 10^{6}	$F_{30}[X,Y]$ x 10^{9}	$(E_{1/2})'$ -V vs SCE	$\Delta E_{1/2}$ V	$\log \frac{I_c}{I_i}$	$F_{00}[X,Y]$ 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	1.4552	0.0552	0.0074	0.7388	14.1830	2.1345	1.3489	1.4659	0.0659	0.0074	1.7048	3.2195	4.2623	1.3489
1.00	1.4709	0.0709	0.0074	2.5220	24.9235	2.1413	1.3569	1.4807	0.0807	0.0074	5.4148	5.3575	4.2691	1.3568
2.00	1.4877	0.0877	0.0149	9.3506	46.6045	2.1547	1.3478	1.4971	0.0971	0.0149	19.3657	9.6542	4.2829	1.3685
3.00	1.4979	0.0979	0.0226	20.5966	68.5565	2.1682	1.3468	1.5070	0.01070	0.0226	41.9856	13.9761	4.2959	1.3462
4.00	1.5052	0.1052	0.0304	36.3539	90.8105	2.1825	1.3689	1.5142	0.1142	0.0304	73.3757	18.3296	4.3103	1.3682
5.00	1.5109	0.1109	0.0384	56.6749	113.290	2.1956	1.3564	1.5198	0.1198	0.0384	113.5743	22.7024	4.3230	1.3492
6.00	1.5156	0.1156	0.0465	81.6420	136.020	2.2085	1.3453	1.5244	0.1244	0.0465	162.7161	27.1098	4.3369	1.3562
8.00	1.5230	0.1230	0.0465	146.0253	182.494	2.2373	1.3689	1.5314	0.1314	0.0465	280.2941	35.0296	4.3651	1.3689
10.00	1.5288	0.1288	0.0548	229.7802	229.750	2.2624	1.3462	1.5374	0.1374	0.0548	449.7113	44.9654	4.3877	1.3214
20.00	1.5472	0.1472	0.0548	964.5707	482.270	2.3983	1.3528	1.5555	0.1555	0.0548	1830.665	91.5304	4.5221	1.3328
30.00	1.5583	0.1583	0.0548	2289.541	763.170	2.5322	1.3480	1.5662	0.1662	0.0632	4234.989	141.164	4.6692	1.3789

Phenacetin = 0.025 M: log A=0.4729, log B=4.5453, log C=8.3279, log D=9.1300

Phenacetin = 0.050 M: log A=0.7583, log B=5.0367, log C=8.6289, log D=9.1300

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