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Thermodynamics in [Mn(II)–antibiotics–bacitracin] mixed system: a polarographic approach

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Abstract

Polarographic technique was used to determine the kinetic parameters, thermodynamic parameters and stability constants (log β) of Mn(II) complexes with neomycin, chlortetracycline, oxytetracycline, tetracycline, penicillin V and penicillin G as primary ligands and bacitracin as the secondary ligand, at pH 7.3 ± 0.01 and an ionic strength $\mu = 1.0$ M ($NaClO_4$) at 25 °C. The study was also carried out at 35 °C to determine the stability constants and thermodynamic parameters viz. enthalpy change (ΔH), entropy change (ΔS) and free energy change (ΔG) of complexes.

Keywords: Stability kinetic parameters; Thermodynamics in [Mn(II)–antibiotics–bacitracin] system

1. Introduction

Manganese is an essential element presents in all living organisms. The primary uses of manganese in medicines are as germicides and antiseptic. Manganese is also a cofactor in a number of enzymatic reaction like phosphorylation, cholesterol and fatty acids synthesis. On the other hand, antibiotics are important drugs which inhibit the growth and even to kill the micro-organisms in dilute solutions. Therefore, antibiotics are used in the treatment of numerous infectious diseases of man, animals and to a lesser degree plants [1,2]. Hence, the complexes of Mn with antibiotics have great importance [3].

A systematic survey of literature reveals that no reference is available regarding the binary and ternary complexes of Mn with selected antibiotics, therefore, authors have undertaken the present study with the view to determine the stability constants (log β), thermodynamics parameter viz. enthalpy change ΔH, free energy change ΔG and entropy change ΔS of complexes. In order to understand the electrode process between d.m.e. and electroactive species, the kinetic parameters like transfer coefficient (α), degree of irreversibility (λ), diffusion coefficient (D) and standard rate constants (k) of [Mn–antibiotics–bacitracin] systems were also determined.

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2. Experimental

All the antibiotics are of Fluka (Switzerland) products and their solutions were prepared in doubly distilled water. Manganese chloride tetrahydrade sigma (USA) and $NaClO_4 \cdot H_2O$ Fluka products were used. The concentrations of Mn and $NaClO_4$ in the test solution were 0.5 mM and 1.0 M, respectively. The test solutions were deaerated by passing pure hydrogen gas before recording the current–voltage data. The pH of the test solution were recorded on a Elico-digital pH meter (Mode, LI-120) and fix at 7.30 by adding requisite amount of sodium hydroxide and perchloric acid [both B.D.H.] as required. Glass and saturated calomal electrodes were used to measure the pH. The current–voltage curves were recorded on a manual polarograph (AJCO electronics, Poona) using Toshniwal polyflex galvanometer (PL-50), Weston cadmium cell was used to standardise the equipment. Latinen and Lingane cell and dropping mercury electrode and saturated calomal electrode were used to obtain current–voltage data. The dropping mercury electrode had a capillary of 5.00 cm long with 0.04 mm diameter. The characteristics of capillary were $m^{2/3}t^{1/6} = 2.40$ mg$^{2/3}$ s$^{-1/2}$ at 60.02 cm (calculated) effective height of mercury. The resistance of the cell was lesser than 200 Ω, therefore, no correction was made for IR. Potassium dihydrogen phosphate–sodium hydroxide buffer was added in the analyte to stabilise the pH of analyte at 7.30. At this pH, the stability of analyte is not altered.

3. Results and discussion

The analytes were prepared by keeping the concentration of metal ion and $NaClO_4$ constant while varying the concentration of primary ligand at a finite concentration of secondary ligand at a constant pH 7.30 at 25 °C. The pH remains constant during the measurements showed that the stability of ligand is not altered during the measurement.

The metal and ligands were taken in the ratio 1:40 in case of binary complexes and 1:40:40 in case of ternary complexes and current–voltage curves were obtained at different pH values, it, has been observed that the maximum shift of $E_{1/2}$ was observed at pH 7.30, therefore, this pH was selected for the present study. A well defined two electron quasireversible reduction wave of Mn(II) was observed in 1.0 M $NaClO_4$ at pH range 7.10–8.50 at 25 °C but pH 7.30 was selected on account of studying the complex formation in human blood pH. 0.001% Triton-X 100 was used as the suppressor. The number of electrons involved in the reduction were determined by Devries and Kroon method [4].

3.1. [Mn(II)–antibiotics–bacitracin] complexes

Ternary complexes were investigated at two constant concentrations of bacitracin (i.e. 0.025 and 0.050 M) and varying the concentration of primary ligand from 0.5 to 30 mM. In each of the mixed system, a shift in the half wave potential to more negative side was observed. The stability constant of ternary complexes were evaluated by employing Schaap and McMaster method [5] which confirmed the formation of 1:1:1, 1:1:2 and 1:2:1 complexes. The data and plots were given in Table 1 and Fig. 1, respectively. The values of stability constant were given in Table 2. The plots of $[(E - 0.0591/n)(\log i_d - i/i)]$ against i for Mn and its complexes were given in Fig. 2.

The waves for Mn(II) and its complexes were quasireversible as confirmed by the kinetic parameters and slopes of current–voltage data given in Tables 3–5, respectively.

The parameter Z, which is a measure of the degree of irreversibility has been calculated by the equation given in the literature [6].

3.2. Thermodynamic parameters of [Mn–antibiotics–bacitracin] complexes

The values of the change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) accompanying the metal ligand complex forming relations have been calculated at 25 and 35 °C using the relations [7].

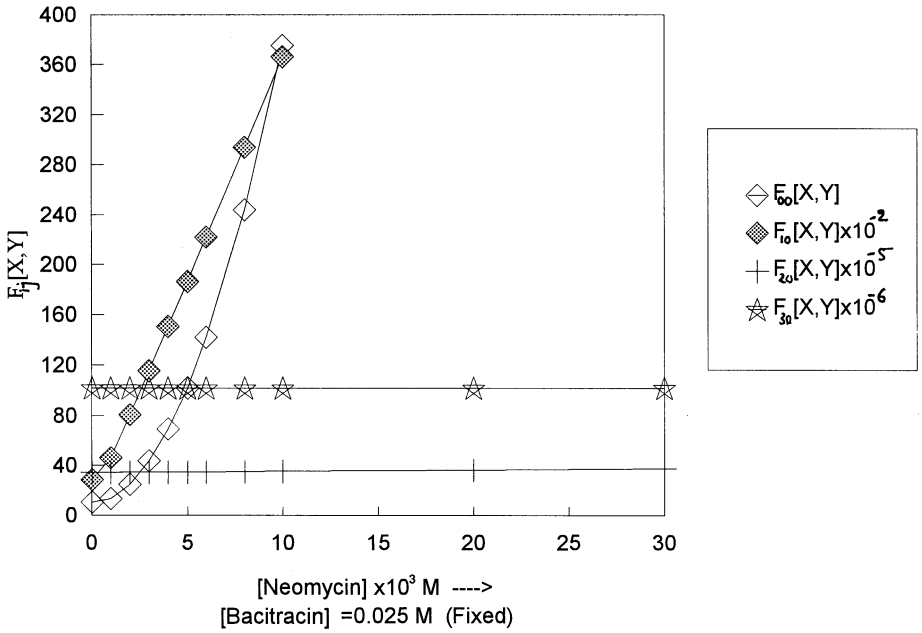
Table 1
Polarographic characteristics and $F_{ij}[X, Y]$ values for the [Mn(II)–neomycin–bacitracin] system

[Neo.] $\times 10^3$ M	[Bacitracin] = 0.025 M (fixed)[a]							[Bacitracin] = 0.050 M (fixed)[b]						
	$(E_{1/2})^{qr} - V$ vs SCE	$(E_{1/2})^{rev}$ – V vs SCE	log I_m/I_c	$F_{00}[X, Y]$	$F_{10}[X, Y]$ $\times 10^{-2}$	$F_{20}[X, Y]$ $\times 10^{-5}$	$F_{30}[X, Y]$ $\times 10^{-6}$	$(E_{1/2})^{qr} - V$ vs SCE	$(E_{1/2})^{rev} - V$ SCE	log I_m/I_c	$F_{00}[X, Y]$ $\times 10^{-1}$	$F_{10}[X, Y]$ $\times 10^{-4}$	$F_{20}[X, Y]$ $\times 10^{-8}$	$F_{30}[X, Y]$ $\times 10^{-6}$
0.00	–	–	–	–	–	–	–	–	–	–	–	–	–	–
0.50	1.452	1.430	0.0074	10.48	28.86	34.48	102.23	1.468	1.441	0.0074	23.88	65.39	6.822	102.31
1.00	1.460	1.434	0.0147	13.66	46.16	34.53	102.31	1.468	1.444	0.0149	30.56	99.54	6.830	102.32
2.00	1.465	1.441	0.0147	25.22	80.90	34.64	102.33	1.475	1.451	0.0149	54.21	168.00	6.84	102.33
3.00	1.472	1.448	0.0226	43.79	115.84	34.74	102.40	1.482	1.458	0.0226	91.67	236.66	6.85	102.23
4.00	1.473	1.454	0.0226	69.44	150.99	34.84	102.40	1.482	1.464	0.0304	142.81	305.52	6.86	102.24
5.00	1.485	1.459	0.0304	102.21	186.34	34.94	102.40	1.492	1.468	0.0304	207.92	374.63	6.87	102.40
6.00	1.488	1.464	0.0304	142.18	221.90	35.05	102.40	1.498	1.473	0.0304	286.95	443.90	6.88	102.41
8.00	1.498	1.470	0.0384	243.95	293.63	35.25	102.41	1.504	1.479	0.0384	487.10	583.12	6.90	102.41
10.00	1.502	1.476	0.0384	375.22	366.18	35.46	102.41	1.505	1.485	0.0384	743.69	723.08	6.92	102.33
20.00	1.520	1.494	0.0384	1491.41	741.18	36.48	102.32	1.528	1.502	0.0465	2891.17	1435.28	7.02	102.33
30.00	1.538	1.504	0.0465	3419.27	1136.74	37.50	102.40	1.545	1.513	0.0548	6524.25	2167.88	7.12	102.33

[Mn(II)] = 0.5 mM; $\mu = 1.0$ M $NaClO_4$; pH 7.30 ± 0.01; temperature = 25 °C.

[a] $\log A = 0.9562$; $\log B = 3.0653$; $\log C = 6.5369$; $\log D = 7.011$.

[b] $\log A = 1.3139$; $\log B = 3.4952$; $\log C = 6.8335$; $\log D = 7.011$.



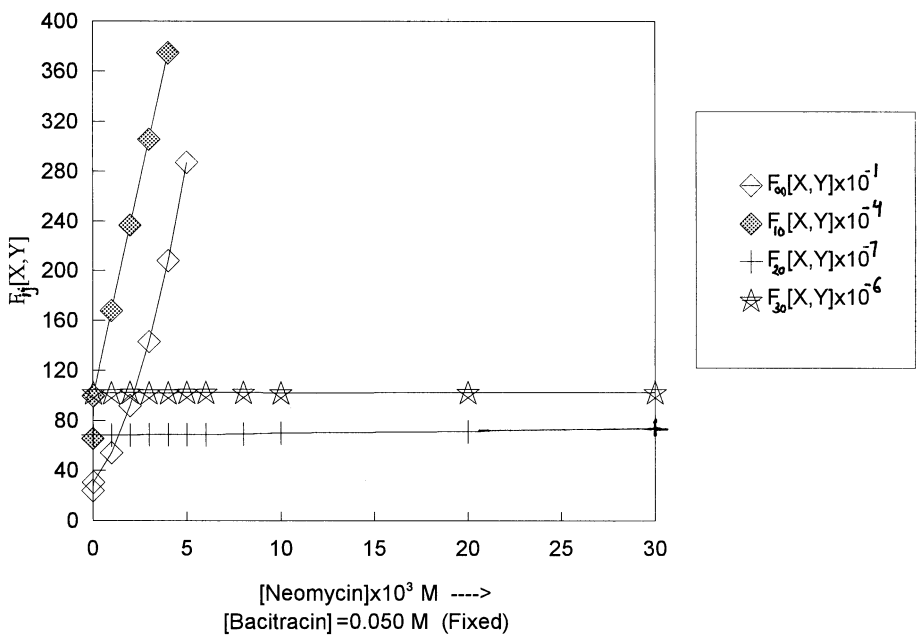


Fig. 1. [Mn-neomycin-bacitracin] system

Table 2
Stability constants of [Mn(II)–antibiotics–bacitracin] system

Ligands	Binary complexes							
	$\log \beta_{01}$	$\log \beta_{02}$	$\log \beta_{10}$	$\log \beta_{20}$	$\log \beta_{30}$	$\log \beta_{11}$	$\log \beta_{12}$	$\log \beta_{21}$
Neomycin	–	–	2.65	4.85	7.011	3.56	6.00	8.13
Chlortetracycline	–	–	3.31	5.02	7.78	4.20	6.38	–
Oxytetracycline	–	–	4.00	–	8.13	4.56	7.56	9.00
Tetracycline	–	–	4.12	7.13	–	–	8.00	9.21
Penicillin V	–	–	4.31	7.76	8.60	5.20	–	10.00
Penicillin G	–	–	4.40	8.00	9.01	5.32	8.20	10.61
Bacitracin	2.40	3.45	–	–	–	–	–	–

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

$$\Delta H = 2.303\ RT_1T_2(\log K_2 - \log K_1)/(T_2 - T_1) \quad (1)$$

$$\Delta G = -2.303\ RT \log K \quad (2)$$

$$\Delta G = \Delta H - T\Delta S. \quad (3)$$

It is clear from the values of ΔS, ΔG and ΔH in Table 6 that the values of ΔS are more negative at higher temperature while the values of ΔG are less negative, confirmed that the complexes are not stable at higher temperature [8]. The negative values of ΔH ensure that the reactions are exothermic in nature.

3.3. Comparision of stability of complexes

The values of mixing constant ($\log K_m$) used to compare the stability of binary and ternary complexes were calculated by the following equation [9].

$$\log K_m = \log \beta_{11} - 1/2[\log \beta_{20} + \log \beta_{02}].$$

The values of $\log K_m$ are -0.590, -0.035, 2.835, -0.405 and -2.130, respectively for [Mn–neomycin–bacitracin], [Mn–chlortetracycline–bacitracin], [Mn–oxytetracycline–bacitracin], [Mn–penicillin V–bacitracin] and [Mn–penicillin G–bacitracin] system. Since $\log \beta_{11}$ is not formed in case of [Mn–tetracycline G–bacitracin] system, therefore, the values of $\log K_m$ were not calculated.

The positive values of $\log K_m$ showed that the ternary complexes are more stable than the corresponding binary complexes, whereas, the negative values showed that the ternary complexes are less stable than binary complexes.

It is clear from the values of stability constants of complexes that the neomycin formed the complexes of lowest stability because of having the steric hindrance between metal and various group present in neomycin.

In case of chlortetracycline, oxytetracycline and tetracycline they make bond with the metal ion through the oxygen of carbon atom and the oxygen of amide group [10]. All the tetracyclines are having the same structure except in the difference in group R_1 and R_2 The lesser stability of chlortetracycline than that of oxytetracycline can be explained on the basis of the presence of electronegative chlorine (at R_1 in chlortetracycline) atom while oxygen in OH of R_2 in oxytetracycline. The chlorine attracts electrons very rapidly from its neighbourhood atoms and groups in chlortetracycline while oxygen does not attract electron as rapidly as chlorine [11], therefore, electronic disturbances is higher in chlortetracycline than in the case of oxytetracycline causes the lesser stability of chlortetracycline than oxytetracycline. The order of stability is also supported by the pK values of these drugs [12–14]. The higher stability of tetracycline is due to the absence of such electronegative atoms as a result of which there is no electronic disturbances in tetracycline.

In case the of penicillin V and penicillin G, the ring nitrogen and oxygen of the carboxylic group may take part in complex formation with Mn [15]. The higher stability of penicillin G complex than that of penicillin V complex is due to the higher basic strength of penicillin G (i.e. $\log K = 4.77$) than that of pencillin G (i.e. $\log K = 3.98$) [15].

The higher stability of penicillin complexes than that of other antibiotics is a result of lesser steric hindrance in penicillin complexes than that of other antibiotics. The trend of stability constants obtained was neomycin < chlortetracycline < oxytetracycline < tetracycline < penicillin V < penicillin G.

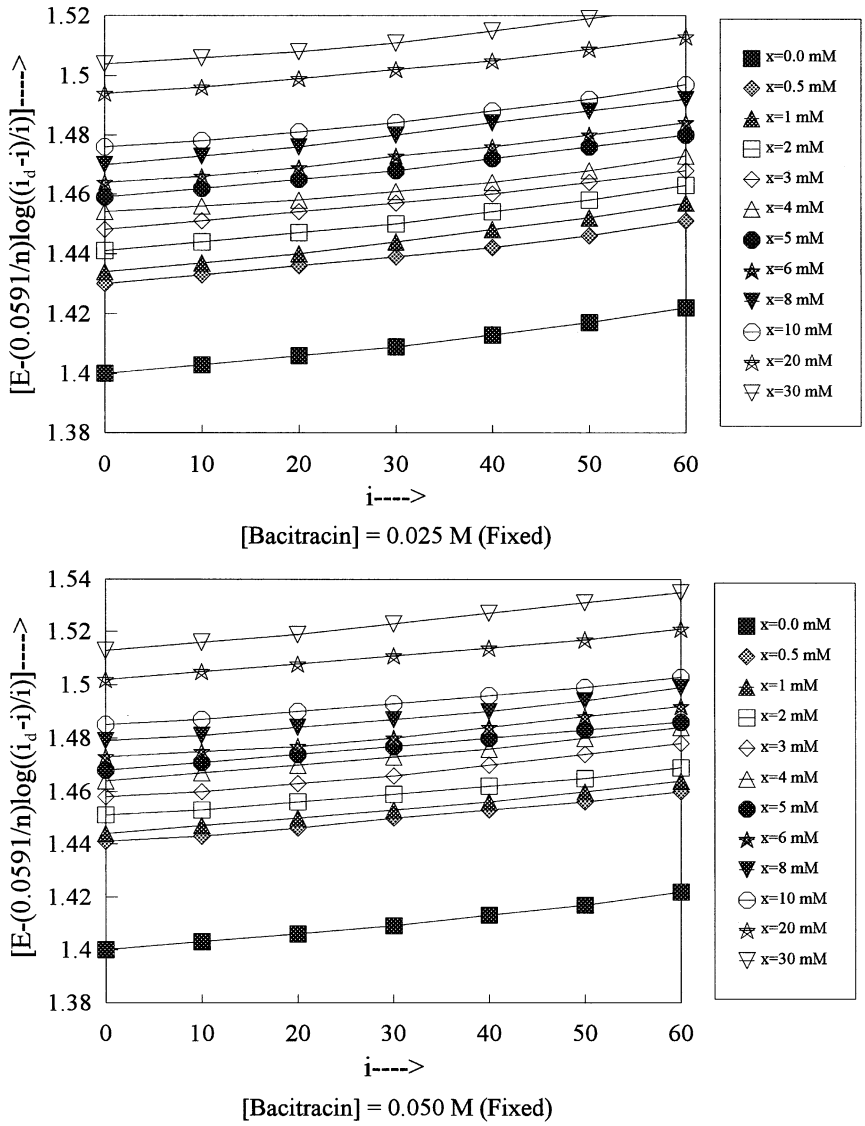


Fig. 2. Plot of [E-RT/nF] $\log[(i_d - i)/i]$ vs i.

Table 3
Kinetic parameters of [Mn(II)–neomycin–bacitracin] system

[Neo.] $\times 10^3$ M	$(E_{1/2})^{qr} - V$ vs SCE	Slope mV	α	λ	$D^{1/2} \times 10^3$ cm^2 s^{-1}	$k_f \times 10^3$ cm s^{-1}	$(E_{1/2})^{qr} - V$ vs SCE	Slope mV	α	λ	$D^{1/2} \times 10^3$ cm^2 s^{-1}	$k_f \times 10^3$ cm s^{-1}
0.00	1.410	40.0	0.53	0.88	4.05	3.58	1.410	40.0	0.53	1.11	4.05	4.51
0.50	1.452	37.5	0.44	1.40	3.98	5.58	1.467	40.0	0.49	1.05	3.98	4.18
1.00	1.460	35.0	0.48	1.11	3.91	4.35	1.467	35.0	0.45	1.25	3.91	4.89
2.00	1.465	35.0	0.48	1.25	3.91	4.89	1.475	35.0	0.51	0.99	3.91	3.88
3.00	1.472	35.0	0.49	1.05	3.84	3.84	1.482	40.0	0.48	1.11	3.84	4.28
4.00	1.473	35.0	0.49	0.99	3.84	3.84	1.482	35.0	0.47	1.25	3.77	4.71
5.00	1.485	40.0	0.47	1.25	3.77	3.77	1.492	37.5	0.46	1.25	3.77	4.71
6.00	1.487	35.0	0.47	1.25	3.77	3.77	1.497	40.0	0.48	1.01	3.77	3.97
8.00	1.497	45.0	0.50	1.18	3.70	3.70	1.504	45.0	0.46	1.46	3.70	5.44
10.00	1.502	40.0	0.47	1.32	3.70	3.70	1.505	40.0	0.47	1.32	3.70	7.20
20.00	1.520	37.5	0.49	1.40	3.70	3.70	1.527	40.0	0.55	0.99	3.63	3.61
30.00	1.537	35.0	0.49	1.32	3.63	3.63	1.545	45.0	0.51	0.83	3.56	2.98

[Mn(II)] = 0.5 mM; $\mu = 1.0$ M $NaClO_4$; pH 7.30 ± 0.01; temperature = 25 °C.

Table 4
Polarographic data for [Mn(II)–antibiotics–bacitracin] system [Bacitracin] = 0.025 M (fixed)

[Neo] × 10^3 M	i_d	i	$\log(i_d - i)/i$	E_{de}	$E^r_{1/2} - E_{de}$	$\log(Z-1)$
0.00	59	10	0.6902	−1.383	−0.017	–
		20	0.2900	−1.397	−0.003	–
		30	−0.0147	−1.409	0.009	0.018
		40	−0.3233	−1.423	0.023	0.638
		50	−0.7447	−1.439	0.039	1.260
		60	–	–	–	–
0.50	58	10	0.6812	−1.413	−0.017	–
		20	0.2788	−1.428	−0.002	–
		30	−0.0300	−1.440	0.010	0.044
		40	−0.3468	−1.452	0.022	0.618
		50	−0.7959	−1.470	0.039	1.277
		60	–	–	–	–
1.00	57	10	0.6721	−1.417	−0.017	–
		20	0.2672	−1.432	−0.002	–
		30	−0.0458	−1.445	0.011	0.131
		40	−0.3716	−1.459	0.025	0.736
		50	−0.8539	−1.477	0.043	1.410
		60	–	–		–
2.00	57	10	0.6721	−1.424	−0.017	–
		20	0.2672	−1.439	−0.002	–
		30	−0.0458	−1.451	0.010	0.070
		40	−0.3716	−1.465	0.024	0.693
		50	−0.8539	−1.483	0.042	1.374
		60		–	–	–
3.00	56	10	0.6628	−1.431	−0.017	–
		20	0.2553	−1.446	−0.002	–
		30	−0.0621	−1.459	0.011	0.089
		40	−0.3979	−1.472	0.024	0.683
		50	−0.9208	−1.491	0.043	1.409
		60	–	–	–	–
4.00	56	10	0.6628	−1.436	−0.018	–
		20	0.2553	−1.450	0.004	–
		30	−0.0621	−1.463	0.009	−0.044
		40	−0.3979	−1.476	0.022	0.594
		50	−0.9208	−1.495	0.041	1.336
		60	–	–		–
5.00	55	10	0.6532	−1.443	−0.016	–
		20	0.2430	−1.458	−0.001	–
		30	−0.0792	−1.470	0.011	0.114
		40	−0.4260	−1.485	0.026	0.756
		50	−1.000	−1.506	0.047	1.528
		60	–			–
6.00	55	10	0.6532	−1.447	−0.017	–
		20	0.2430	−1.462	−0.002	–
		30	−0.0792	−1.475	0.011	0.114
		40	−0.4260	−1.489	0.025	0.714
		50	−1.000	−1.510	0.046	1.493
		60	–	–	–	–

Table 4 (*Continued*)

[Neo] $\times 10^3$ M	i_d	i	$\log(i_d - i)/i$	E_{de}	$E^r_{1/2} - E_{de}$	$\log(Z-1)$
8.00	54	10	0.6434	−1.454	−0.016	–
		20	0.2304	−1.469	−0.001	–
		30	−0.0969	−1.483	0.013	0.203
		40	−0.4559	−1.497	0.027	0.832
		50	−1.0969	−1.520	0.050	1.660
		60	–	–	–	–
10.00	54	10	0.6434	−1.459	−0.017	–
		20	0.2304	−1.474	−0.002	–
		30	−0.0969	−1.487	0.011	0.083
		40	−0.4559	−1.501	0.025	0.750
		50	−1.0969	−1.524	0.048	1.591
		60	–	–	–	–
20.00	54	10	0.6434	−1.477	−0.017	–
		20	0.2304	−1.492	−0.002	–
		30	−0.0969	−1.505	0.011	0.083
		40	−0.4559	−1.518	0.024	0.708
		50	−1.0969	−1.541	0.047	1.555
		60	–	–	–	–
30.00	53	10	0.6335	−1.505	−0.001	–
		20	0.2175	−1.502	−0.002	–
		30	−0.1154	−1.514	0.010	0.044
		40	−0.4881	−1.529	0.025	0.743
		50	−1.2218	−1.555	0.051	1.684
		60	–	–	–	–

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

Table 5
Polarographic data for [Mn(II)–antibiotics–bacitracin] system [Bacitracin] = 0.050 M (Fixed)

[Neo] $\times 10^3$ M	i_d	i	$\log(i_d - i)/i$	E_{de}	$E_{1/2} - E_{de}$	$\log(Z-1)$
0.00	59	10	0.6902	−1.383	−0.017	–
		20	0.2900	−1.397	−0.003	–
		30	−0.0147	−1.409	0.009	0.018
		40	−0.3233	−1.423	0.023	0.638
		50	−0.7447	−1.439	0.039	1.260
		60	–	–	–	–
0.50	58	10	0.6812	−1.423	−0.018	–
		20	0.2788	−1.438	−0.003	–
		30	−0.0300	−1.451	0.010	0.044
		40	−0.3468	−1.463	0.022	0.618
		50	−0.7959	−1.479	0.038	1.241
		60	–	–	–	–
1.00	57	10	0.6721	−1.427	−0.017	–
		20	0.2672	−1.442	−0.002	–
		30	−0.0458	−1.454	0.010	0.070
		40	−0.3716	−1.467	0.023	0.650
		50	−0.8539	−1.485	0.041	1.338
		60	–	–	–	–

Table 5 (*Continued*)

[Neo] $\times 10^3$ M	i_d	i	$\log(i_d - i)/i$	E_{de}	$E_{1/2} - E_{de}$	$\log(Z-1)$
2.00	57	10	0.6721	−1.433	−0.018	–
		20	0.2672	−1.448	−0.003	–
		30	−0.0458	−1.460	0.009	0.005
		40	−0.3716	−1.473	0.022	0.606
		50	−0.8539	−1.490	0.039	1.265
		60		–	–	–
3.00	56	10	0.6628	−1.440	−0.018	–
		20	0.2553	−1.455	−0.003	–
		30	−0.0621	−1.468	0.010	0.025
		40	−0.3979	−1.482	0.024	0.683
		50	−0.9208	−1.501	0.043	1.409
		60		–	–	–
4.00	55	10	0.6532	−1.448	−0.016	–
		20	0.2430	−1.463	−0.001	–
		30	−0.0792	−1.475	0.011	0.114
		40	−0.4260	−1.489	0.025	0.714
		50	−1.000	−1.510	0.046	1.493
		60	–	–	–	–
5.00	55	10	0.6532	−1.452	−0.016	–
		20	0.2430	−1.467	−0.001	–
		30	−0.0792	−1.479	0.011	0.114
		40	−0.4260	−1.493	0.025	0.714
		50	−1.000	−1.513	0.045	1.457
		60	–	–	–	–
6.00	55	10	0.6532	−1.456	−0.017	–
		20	0.2430	−1.470	−0.003	–
		30	−0.0792	−1.482	0.009	0.017
		40	−0.4260	−1.497	0.024	0.671
		50	−1.000	−1.518	0.045	1.457
		60	–	–	–	–
8.00	54	10	0.6434	−1.462	−0.017	–
		20	0.2304	−1.477	−0.002	–
		30	−0.0969	−1.490	0.011	0.083
		40	−0.4559	−1.504	0.024	0.708
		50	−1.0969	−1.526	0.047	1.555
		60	–	–	–	–
10.00	54	10	0.6434	−1.468	−0.017	–
		20	0.2304	−1.483	−0.002	–
		30	−0.0969	−1.496	0.011	0.083
		40	−0.4559	−1.509	0.024	0.708
		50	−1.0969	−1.531	0.046	1.520
		60	–	–	–	–
20.00	53	10	0.6335	−1.486	−0.016	–
		20	0.2174	−1.502	−0.0004	–
		30	−0.1164	−1.514	0.012	0.169
		40	−0.4881	−1.528	0.026	0.785
		50	−1.2218	−1.553	0.051	1.684
		60	–	–	–	–
30.00	52	10	0.6232	−1.498	−0.015	–
		20	0.2041	−1.513	–	–
		30	−0.1347	−1.527	0.014	0.254
		40	−0.5229	−1.542	0.029	0.905
		50	−1.3979	1.572	0.059	1.965
		60	–	–	–	–

Mn(II) = 0.5 mM, $\mu = 1.0$ M $NaClO_4$, pH 7.30 ± 0.01, temperature = 25 °C. Only significant values were given to get the values of $E_{1/2}^{qr}$ and $\log(z-1)$ values. The $(E_{1/2})^{rev}$ values from $(E_{1/2})^{qr}$ were determined by Gelling method.

Table 6
Thermodynamic parameters [Mn(II)–antibiotics–bacitracin] ternary complexes

Systems	Stability constants (25/35 °C)			$-\Delta H$ Kcal/mol (35–25 °C) for difference of 10 °C			$-\Delta G$ Kcal/mol 25/35 °C			$-\Delta S$ cal/deg per mol		
	$\log \beta_{11}$	$\log \beta_{12}$	$\log \beta_{21}$	$\log \beta_{11}$	$\log \beta_{12}$	$\log \beta_{21}$	$\log \beta_{11}$	$\log \beta_{12}$	$\log \beta_{21}$	$\log \beta_{11}$	$\log \beta_{12}$	$\log \beta_{21}$
Mn(II) Neomycin–Bacitracin	3.56	6.00	8.13	10.081	32.764		4.855	8.182	11.087	17.537	82.489	79.184
	3.32	5.22	7.30			34.684	4.679	7.357	10.289	17.539	82.490	79.204
Mn(II) Chlortetracycline–Bacitracin	4.20	6.38	–	20.162	39.904	–	5.728	8.701	–	48.436	104.708	–
	3.72	5.43	–				5.243	7.653	–	48.438	104.711	–
Mn(II) Oxytetracycline–Bacitracin	4.56	7.56	9.00		24.783		6.219	10.310	12.274	20.006	48.567	51.842
	4.27	6.97	8.34	12.181		27.723	6.018	9.824	11.755	20.009	48.568	51.844
Mn(II)Tetracycline–Bacitracin	–	8.00	9.21	–	31.923		–	10.910	12.560	–	60.647	64.976
	–	7.31	8.45			31.923	–	10.303	11.910	–	60.649	64.977
Mn(II)Penicillin V–Bacitracin	5.20	–	10.00	10.081	–		7.092	–	13.638	10.030	–	93.781
	4.96	–	9.01			41.585	6.991	–	12.700	10.032	–	93.782
Mn(II)Penicillin G–Bacitracin	5.32	8.20	10.61	8.821	24.362		7.255	11.183	14.469	5.255	44.224	56.668
	5.11	7.62	9.85			31.923	7.202	10.740	13.884	5.256	44.227	58.568

The stability constants of Mn with antibiotics complexes have great importance in pharmacy. It is clear from the data that, the values of stability constants are not very high, therefore, there drugs can be used to reduce the toxicity of Mn in vivo [16].

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References

[1] D. Perlman, Applied Microbiology, Academic Press, NewYork, 1969, p. 1.
[2] E.W. Nester, C.E. Roberts, N.N. Pearsall, B.J. McCarthy, Microbiology, 2nd ed., Philadelphia, 1978, p. 592.
[3] M. Riaz, N. Pilpel, J. Pharm. Pharmacol. 36 (1984) 153.
[4] T. Devries, J.L. Kroon, J. Am. Chem. Soc. 75 (1953) 2484.
[5] W.B. Schaap, D.L. Mc Master, J. Am. Chem. Soc. 83 (1961) 4999.
[6] R. Tamamushi, M. Tanaka, Z. Phys. Chem. Neue Folge. 39 (1963) 117.
[7] A. Zaddi, F. Khan, Inst. Chem. India 72 (2000) 104.
[8] F. Khan, A.V. Mahajani, J. Ind. Chem. Soc. 61 (1984) 165.
[9] S. Vajhallya, F. Khan, Bull. Chem. Soc. Jpn. 72 (1999) 397.
[10] K. Katakwar, M.S. Kacchawaha, Hindustan Antibiot. Bull. 26 (1984) 9.
[11] (a) R.S. Mulliken, J. Chem. Phys. 2 (1934) 782;
(b) R.S. Mulliken, J. Chem. Phys. 3 (1935) 513.
[12] C.R. Stephens, L.H. Conover, R. Posternack, F.A. Hochslein, W.T. Moreland, P.P. Regma, F.J. Pilgrim, K.J. Brunings, R.B. Woodward, J. Am. Chem. Soc. 76 (1954) 3568.
[13] F.A. Hochstein, C.R. Slephens, J. Am. Chem. Soc. 75 (1953) 5455.
[14] J.M. Desiqueria, S. Carvalho, E.B. Paniago, L. Tosi, H. Beraldo, J. Pharm. Sci. 83 (1994) 291.
[15] B.P. Chakrawarti, A. Tiwari, H.N. Sharma, Ind. J. Chem. 21A (1982) 200.
[16] J.T. Doluiso, A.N. Martin, J. Med. Chem. 6 (1963) 16.