# A Study of Thermodynamic Parameters and Thermodynamic Stability of MNII- Antibiotics and Vitamin-BX Systems: A Polarographic Approach

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*Abstract*— Polarographic technique was used to determine the thermodynamic parameters such as enthalpy change (ΔH), free energy change (ΔG) and entropy change (ΔS) of Mn(II) complexes with neomycin, chlortetracyclin, oxytetracyclin, tetracyclin, penicillin-V, and penicillin-G as primary ligands and vitamin-Bx as secondary ligand at pH = 7.30 ± 0.01 and an ionic strength μ = 1.0 M NaClO4 . The study was carried out at two different temperatures i.e. 250C and 350C to determine the thermodynamic parameters.

***Key words:*** Thermodynamic Stability Constant, Thermodynamic parameters of [MnII-antibiotics-vitamin-Bx] Systems

## I. 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. 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 favors 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[2-3]. Therefore, the study of complexes of antibiotics with vitamin-Bx has great importance. In this paper, we report Thermodynamic parameters and Thermodynamic Stability Constant 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.

## II. 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(II) 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 Systronic μ pH meter 361 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, Puna) using Toshniwal polyflex galvanometer (PL-50), Weston cadmium cell was used to standardize 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 stabilize the pH of analyte at 7.30. At this pH, the stability of analyte is not altered. The temperature was maintained at $25^0$C and $35^0$C using thermostat.

## III. Results and Discussion

$Mn^{II}$ gave two electron quasireversible reduction wave at pH = 7.30 ± 0.01 and μ = 1.0 M $NaClO_4$ at $25^0C$[4] and also $35^0$C. The concentration of antibiotics varied from 0.5 mM to 30.0 mM at two fixed concentration of vitamin-$B_x$ 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 $Mn^{II}$ - antibiotics system which showed ternary complex formation of 1:1:1, 1:1:2, and 1:2:1 complexes. Gellings[5] 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. Schaap and McMaster[6-7] method was used to determine the composition and stability constants of complexes. The values of stability constants and thermodynamic parameters of complexes were given in Table 1. Thermodynamic parameters such as enthalpy change (ΔH) free energy change (ΔG) and entropy change (ΔS) of such complexes have been calculated by the following equation[8].

$$\Delta H = \frac{2.303\, RT_1T_2(\log K_2 - \log K_1)}{T_2 - T_1} \quad (1)$$

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

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

It is clear from the values of ΔS, ΔG and ΔH in Table 1. that the values of ΔG are less negative at higher temperature and ΔS is more negative at higher temperature confirmed that the complexes are not stable at higher temperature[9-15].

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| SYSTEM | STABILITY CONSTANTS | | | -ΔH K Cal/mole | | | -ΔG K Cal/mole | | | -ΔS Cal/deg/mole | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 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 $\beta_{21}$ |
| | 25°C/ 35°C | 25°C/ 35°C | 25°C/ 35°C | 25°C/ 35°C | 25°C/ 35°C | 25°C/ 35°C | 25°C/ 35°C | 25°C/ 35°C | 25°C/ 35°C | 25°C/ 35°C | 25°C/ 35°C | 25°C/ 35°C |
| **[Mn – Neomycin – Vitamin-$B_X$]** | 3.46 | 5.16 | 7.72 | 17.64 | 22.68 | 19.32 | 4.71 | 7.03 | 10.52 | 43.36 | 52.49 | 29.50 |
| | 3.04 | 4.62 | 7.26 | | | | 4.28 | 6.51 | 10.23 | 43.34 | 52.47 | 29.48 |
| **[Mn – Chlortetracycline – Vitamin-$B_X$]** | 3.72 | 5.45 | 8.20 | 15.96 | 18.48 | 17.64 | 5.07 | 7.43 | 11.18 | 36.53 | 37.07 | 21.67 |
| | 3.34 | 5.01 | 7.78 | | | | 4.70 | 7.06 | 10.96 | 36.52 | 37.06 | 21.65 |
| **[Mn – Oxytetracycline – Vitamin-$B_X$]** | 4.36 | 6.26 | - | 15.96 | 23.10 | - | 5.94 | 8.53 | - | 33.60 | 48.87 | - |
| | 3.98 | 5.71 | - | | | | 5.60 | 8.04 | - | 33.58 | 48.86 | - |
| **[Mn – Tetracycline – Vitamin-$B_X$]** | 4.50 | 7.46 | 8.93 | 19.32 | 18.48 | 21.84 | 6.13 | 10.17 | 12.17 | 44.24 | 27.87 | 32.42 |
| | 4.04 | 7.02 | 8.41 | | | | 5.69 | 9.89 | 11.58 | 44.23 | 27.85 | 32.41 |
| **[Mn – Penicillin-V – Vitamin-$B_X$]** | 4.63 | 7.95 | 9.00 | 14.70 | 17.22 | 23.94 | 6.31 | 10.84 | 12.27 | 28.14 | 21.40 | 39.15 |
| | 4.28 | 7.54 | 8.43 | | | | 6.03 | 10.62 | 11.88 | 28.12 | 21.38 | 39.14 |
| **[Mn – Penicillin-G – Vitamin-$B_X$]** | - | 8.31 | 9.23 | - | 20.58 | 25.62 | - | 11.33 | 12.58 | - | 31.03 | 43.73 |
| | - | 7.82 | 8.62 | | | | - | 11.02 | 12.14 | - | 31.01 | 43.71 |

Table 1: Thermodynamic parameters of [$Mn^{II}$ – Antibiotics – Vitamin-$B_X$] Systems

The negative values of ΔH show that the reactions are exothermic in nature. The order of stability of the MnII ternary complexes with respect to primary ligand was neomycin < chlortetracycline < oxytetracyclin < tetracycline < penicillin-V < and penicillin-G.

## IV. Conclusion

Stability constants (log β) and thermodynamic parameters such as enthalpy change (ΔH) and entropy change (ΔS) of MnII complexes with neomycin, chlortetracyclin, oxytetracyclin, tetracyclin, penicillin-V, and penicillin-G as primary ligands and vitamin-Bx as secondary ligand were determined by employing polarographic technique at pH = 7.30 ± 0.01 and an ionic strength μ = 1.0 M NaClO4 at 250C and 350C.

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