# Thermodynamics of Stability Constant of Binary Complex of Nicotinamide with Mn++

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**Abstract:** The stability constants of the binary complexes of $Mn^{2+}$ with nicotinamide (NA) were determined from potentiometric pH titrations data at 15.0 , 25.0 and $35.0^{o}C$ and $I = 0.1, 0.2, 0.4$ mol $L^{-1}$ ($NaClO_4$). The formation of binary 1:1 , 1:2 NA-Mn complexes at three different temperatures and the influence of three different ionic strength on their stability were reported. The thermodynamic parameters ($\Delta G_f^o$ , $\Delta S_f^o$ , $\Delta H_f^o$ ) for the complex formation reaction were estimated from stability constant at different temperatures.

**Keywords:** Nicotinamide , stability constant , binary complexes**.**

Nicotinamide (3-pyridine carboxamide)  is a pyridine derivative which is important bioligand for human health.  Nicotinamide (NA) is very prevalent in plants and human tissues.  The NA is not free in body. It may exist in at least two nucleotide structures such as nicotinamide adenine dinucleotide (NAD) and nicotinamide adenine dinucleotide phosphate (NADP).  In the recent decade, the synthesis and structure of new series of bimetallic complexes with NA has been studied by various methods because of biological importance of NA [1-2].

In this paper, the stability constant of the binary complexes of Mn++ with NA have been determined from potentiometric pH titration data at ionic strength (*I* ) 0.1 , 0.2  and 0.4  mol $L^{-1}$ ($NaClO_4$) at 15.0 , 25.0 and $35.0^{o}C$.

## Experimental

*Chemicals*

 All reagents were in analytic grade.  The aqueous stock solution of NA was prepared weekly.

*Measurements*

 Potentiometric measurements were performed by using a digital pH/mV-meter (SCHOTT) with Schott combination glass electrode.   The electrode system was calibrated every day with buffer solutions at pH 4.00 and 7.00 at $25^{o}C$.
   The experimental procedure involved the potentiometric titrations of the solutions of

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a) free $HClO_4$ ($1.0 \times 10^{-2}$ mol $L^{-1}$). b) free $HClO_4$ ($1.0 \times 10^{-2}$ mol $L^{-1}$) + NA ($2.0 \times 10^{-3}$ mol $L^{-1}$). c) free $HClO_4$ ($1.0 \times 10^{-2}$ mol $L^{-1}$) + NA ($4.0 \times 10^{-3}$ mol $L^{-1}$). d ) free $HClO_4$ ($1.0 \times 10^{-2}$ mol $L^{-1}$) + NA ($2.0 \times 10^{-3}$ mol $L^{-1}$) + M ($2.0 \times 10^{-3}$ mol $L^{-1}$). e) free $HClO_4$ ($1.0 \times 10^{-2}$ mol $L^{-1}$) + NA ($4.0 \times 10^{-3}$ mol $L^{-1}$) + M ($2.0 \times 10^{-3}$ mol $L^{-1}$)

The ionic strength of solutions was maintained constant 0.1 , 0.2 and 0.4 mol $L^{-1}$ by addition of the appropriation amount of 1.0 mol $L^{-1}$ $NaClO_4$ stock solution. All of the potentiometric titrations were made over the pH range 2.0-10.0.

*Calculations*

The protonation constants of the ligand were calculated from the potentiometric pH titrations data of solutions (a), (b) and (c) according to Irving and Rossotti's method [3]. For this purpose, the average proton-ligand formation number, $\bar{n}_A$ , at various pH for the ligand was determined according to the literature [4]. The value of $pK_a$ was read directly from $\bar{n}_A = f(pH)$ graph at $\bar{n}_A = 0.5$. For the calculation of stability constants of binary complexes (using the potentiometric titration data of the solutions from (a) to (e) and according to Irving and Rossotti's method [3]), the metal-ligand (M-NA and M-2NA) formation number , $\bar{n}_L$, at various pH for the ligand was determined according to the literature [4]. Then $pL$ values were calculated with using the equation from the literature [4]. Having thus obtained corresponding values of $\bar{n}_L$ and $pL$, the formation curve of the metal-ligand system is drawn and the stability constant is read directly at $\bar{n}_L = 0.5$ , 1.5. The values of $\Delta H_f^o$ were estimated from the temperature coefficient of the stability constants. Assuming that $\Delta H_f^o$ is constant in the range of temperature studied, the $\Delta H_f^o$ values were calculated from relationship $d\ln K/d(1/T) = -\Delta H_f^o$ . The free energy changes, $\Delta G_f^o$ , and the entropy changes, $\Delta S_f^o$ , were calculated from the stability canstants according to the equations $\Delta G_f^o = -RT \ln K$ and $\Delta S_f^o = (\Delta G_f^o - \Delta H_f^o)/T$, respectively. All calculations were done on a personal computer of Pentium III 450 microprocessor using Excel program.

**Results and Discussion**

The protonation contants of NA were determined from corresponding titration curves for each ionic strength ($NaClO_4$) at 15.0, 25.0 and 35.0$^o$C. The potentiometric titration curve for the 1:2 ratio of the ligand at 25.0$^o$C at $I = 0.1$ M ($NaClO_4$) is shown in **Figure 1**. The moles of NaOH ($n$) added after neutralisation of $HClO_4$ are also indicated in the **Figure**. Similar titration curves were obtained at the other temperatures and ionic strengths studied. Each curve exhibits an extremely sharp inflection at a point corresponding to the concentration of protons dissociated as expected and previously reported: NA no proton (in reality protonated NA gives one proton). The buffer regions for 1:1 ratio of NA is between $n = -1$ and $n = 0$ while the buffer regions for 1:2 of NA is between $n = -2$ and $n = 0$. This means that NA is protonated in acidic medium. The determined values of protonation constants and corresponding thermodynamic parameters at the temperatures and ionic strengths are given in **Table 1**. The potentiometric titration curve of Mn-2NA systems at 25.0$^o$C at $I = 0.1$ mol/L ($NaClO_4$) is shown in **Figure 1**. The color of the solutions was brown above pH 3.8 for binary systems. The pH of precipitation was 6.5-7.0 for binary sytems at all temperatures and ionic strenghts studied. In the 1:1 and 1:2 Mn-NA sytems, the titartion curves exhibit an inflection at $n = 0$(where $n$ is the number of moles of bases added per mol of metal ion), indicating the neutralisation of protonated NA's proton. The curves of ligand does not intersect with curve of binary complex as shown in **Figure1**, because the complexation is dependent on

the electrostatic effect of the metal ion and increase NaOH.  The stability constants of 1:1 and 1:2 binary complexes of NA with ion studied and corresponding thermodynamic parameters are presented in **Table 2** and **3**.  The protonation constants of NA increase with increasing temperature while the protonation constants of ligand display a little change with increasing ionic strength. Corresponding enthalpy changes are endothermic. All entropy changes are positive.  Thus, it can be concluded that the higher temperature is favourable for protonation.  The stability constants of both 1:1 and 1:2 binary complex systems of Mn-NA increase with increasing temperature and ionic strength.  The $\Delta \log K$ values($\log K_{M(NA)2}^{MNA} - \log K_{M(NA)}^{M}$ ) are all positive **Table 3**.  The stability constant for 1:2 Mn-NA systems are higher than for the corresponding 1:1 systems, contrary to statistical considerations [4].  The 1:2 complex system is higher stable than the 1:1 Mn-NA complex. The positive enthalpy for 1:1 and 1:2 the manganese complexes are due to the high heat of hydration of $Mn^{++}$.  The heats of hydration of metal ion is in general inversely proportional to the ionic radii.  Therefore, 1:1 and 1:2 the manganese complexes have high values for $\Delta H_f^o$ because of the small ion radius of $Mn^{++}$(0.80 A°) [5].  The enthalpy changes for both complex system formation are approximatly same.  For all the complex systems the entropy changes are positive and thus seem to be the driving force for the complex formation.  The entropy changes for the formation of the 1:2 Mn-NA complex is less positive than for the 1:1 corresponding metal complex but there is no regular change in the values of 1:2 complex.  According to the theory of hard and soft acceptors and donors, NA is nitrogen donor and should thus act as hard/mediumhard ligand [5]. $Mn^{++}$ is a hard acceptor.  Therefore, $Mn^{++}$ prefer to bond over N-atom in order to form the binary complex.  Generally, hard acceptor and hard donors are strongly hydrated in aqueous solutions.  For a hard-hard interaction the large amount of energy is required to break the metal ion-water and ligand-water bond is not compensated by the formation of the new metal-ligand  bond [4].  Therefore, all the systems tend to be endothermic.  Higly positive entropy and enthalpy changes in the formation of Mn-NA complex shows that the solvent interaction are rather important.

**Figure1**  Potentiometric titration curves of  (+) $HClO_4$, (  ) $HClO_4$+2NA, (O) $HClO_4$+2NA+Mn  at $I$=0.1mol/L $(NaClO_4)$ and 25.0$^o$C.
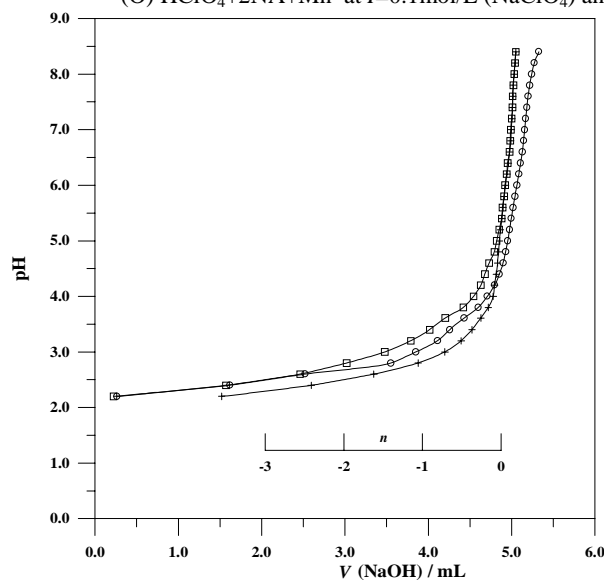
**Table 1** Protonation constans and thermodynamic parameters of NA at different ionic strength

| Ionic strenght (NaClO$_4$)/molL$^{-1}$ | 15.0$^o$C $pK_a$ | 25.0$^o$C | | | | 35.0$^o$C $pK_a$ |
|---|---|---|---|---|---|---|
| | | $pK_a$ | $\Delta H_f^o$ (kJ/mol) | $\Delta G_f^o$ (kJ/mol) | $\Delta S_f^o$ (J/Kmol) | |
| 0.1 | 3.35 | 3.42 | 11 | -20 | 103 | 3.48 |
| 0.2 | 3.35 | 3.39 | 12 | -19 | 105 | 3.49 |
| 0.4 | 3.37 | 3.45 | 12 | -20 | 109 | 3.52 |

**Table 2** For the stability constants of 1:1 Mn-NA and 1:2 Mn-NA systems at different ionic strength and temperature

| Ionic Strenght | 15.0$^o$C | | | 25.0$^o$C | | | 35.0$^o$C | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\log K^{\mathbf{M}}_{\mathbf{M(NA)}}$ | $\log K^{\mathbf{M(NA)}}_{\mathbf{M(NA)_2}}$ | $\Delta\log K$ | $\log K^{\mathbf{M}}_{\mathbf{M(NA)}}$ | $\log K^{\mathbf{M(NA)}}_{\mathbf{M(NA)_2}}$ | $\Delta\log K$ | $\log K^{\mathbf{M}}_{\mathbf{M(NA)}}$ | $\log K^{\mathbf{M(NA)}}_{\mathbf{M(NA)_2}}$ | $\Delta\log K$ |
| 0.1 | 2.88 | 3.13 | 0.25 | 2.98 | 3.22 | 0.24 | 3.10 | 3.32 | 0.22 |
| 0.2 | 2.95 | 3.26 | 0.31 | 3.05 | 3.36 | 0.31 | 3.18 | 3.45 | 0.27 |
| 0.4 | 3.15 | 3.35 | 0.20 | 3.26 | 3.42 | 0.16 | 3.38 | 3.53 | 0.18 |

**Table 3** Thermodynamic parameters for 1:1 Mn-NA and 1:2 Mn-NA systems

| Ionic Strenght | $\log K^{\mathbf{M}}_{\mathbf{M(NA)}}$ | | | $\log K^{\mathbf{M(NA)}}_{\mathbf{M(NA)_2}}$ | | |
|---|---|---|---|---|---|---|
| 0.1 | $\Delta H_f^o$ 19 (15-35$^o$C) | $\Delta G_f^o$ -17 (25$^o$C) | $\Delta S_f^o$ 120 (25$^o$C) | $\Delta H_f^o$ 16 (15-35$^o$C) | $\Delta G_f^o$ -18 (25$^o$C) | $\Delta S_f^o$ 116 (25$^o$C) |
| 0.2 | $\Delta H_f^o$ 20 (15-35$^o$C) | $\Delta G_f^o$ -17 (25$^o$C) | $\Delta S_f^o$ 124 (25$^o$C) | $\Delta H_f^o$ 16 (15-35$^o$C) | $\Delta G_f^o$ -19 (25$^o$C) | $\Delta S_f^o$ 119 (25$^o$C) |
| 0.4 | $\Delta H_f^o$ 20 (15-35$^o$C) | $\Delta G_f^o$ -19 (25$^o$C) | $\Delta S_f^o$ 128 (25$^o$C) | $\Delta H_f^o$ 15 (15-35$^o$C) | $\Delta G_f^o$ -20 (25$^o$C) | $\Delta S_f^o$ 117 (25$^o$C) |

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