

## STUDIES ON THE INTERACTION BETWEEN $Ni^{++}$ WITH DL-ALANINE

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### ABSTRACT

*Potentiometric studies on metal complexes of  $Ni^{++}$  with DL-alanine have been carried out, and the formation constants of its metal complexes have been determined by Bjerrum's method at 25, 30, 40 and 45 °C; and at different ionic strengths (0.07, 0.12, 0.17, 0.22 and 0.32 M) using sodium perchlorate as ionic strength fixer. Also; the thermodynamic equilibrium constants, and the thermodynamic parameters  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  were calculated.*

### INTRODUCTION

The paramagnetic and diamagnetic properties of the nickel (II) complexes have recently come under intensive study Haim, *et al.*, (1963), Ludwig (1963), Sacconi, *et al.*, (1962). The investigations of Krumholz (1953); Figgins and Thompson (1962), (1962); Blight and Curtis (1962) have resulted in some interesting compounds having unusual properties. In the present study the complex formation between the DL-alanine and  $Ni^{++}$  have been carried out using Bjerrum's method Bjerrum (1941), (1957). Three schemes for ligation of DL-alanine with  $Ni^{++}$  were suggested, which are :  $H_2A^+$ , HA, and  $A^-$ ; where  $A^-$  represents the DL-alaninate ion ( $H_2N-CHCOO^-$ ). From the theoretical point of

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*Studies on the interaction between Ni<sup>++</sup> .....*

view, the above three species may exist in solution, however, the first species H<sub>2</sub>A<sup>+</sup> was eliminated based on the obtained values of degree of formation of the ligand number (n).

## EXPERIMENTAL

The pH measurements were made with a Radiometer model pH M -62 digital pH - mV meter equipped with a glass pH electrode model GK C-Cl, which was immersed in a double jacketed cell thermostated at the correct temperature by LKB-BROMMA model 2209 MULTI TEMP. All chemicals used were analytical reagent.

The solvent used in this study is deionized distilled water. Nickel perchlorate water. Nickel perchlorate was prepared by dissolving nickel carbonate in boiling perchloric acid (about 3 M) using a slight excess of the former. The ligand solution was prepared by adding 16 ml. NaOH 0.5 M to 0.7128 gram DL-alanine, then completed to 20 ml. with deionized distilled water.

Different concentrations were prepared by taking the required aliquot of the stock solutions, and dilution were done just before the pH measurements.

The experimental procedure used to determine the stability constant of complexes formed in solution of DL-alanine with Ni<sup>++</sup> metal ions is based on Bjerrum's method, Bjerrum (1941, 1957) which is applicable whenever there are two competing equilibria on the ligand and one of the equilibrium constants is known.

Most equilibrium studies of metal complex formation, the equilibrium constant is evaluated from measurements on solutions containing varying concentrations of metal and ligand. Such concentration changes will produce changes in ionic strength and hence in the values of the formation constant, so that the ionic strength should be kept constant by addition of non-reacting salt (NaClO<sub>4</sub> in the present study).

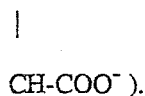
The experiment can be carried out in one of two ways, the change of pH can be

*M. M. Emar, et al.,*

measured as a function of ligand concentration, Bjerrum (1941, 1957). Alternatively the pH can be measured as a function of the concentration of acid or alkali added to constant total metal and total ligand concentration, Irving, *et al.*, (1953). We used the first approach in this study.

## RESULTS AND DISCUSSION

Potentiometric measurements have been made to study the complex formation between the DL-alanine and  $\text{Ni}^{2+}$  ions using Bjerrum's method. Three schemes for ligation of DL-alanine with Ni (II) ions at different ionic strengths and different temperatures are assumed Emar, *et al.*, (1990). The three possible ligands are  $\text{H}_2\text{A}^+$ , HA, and  $\text{A}^-$  where  $\text{A}^-$  represents the DL-alaninate ion ( $\text{H}_2\text{N}-\text{CH}_2$



From the theoretical point of view, the above three species may exist in solution, however, from the calculated values of degree of formation of the ligand number ( $\bar{n}$ ), the first species  $\text{H}_2\text{A}^+$  was eliminated; We assume the possibility of forming  $(\text{NiA}^+ \text{ or } \text{NiA}_2)$  and  $[\text{Ni}(\text{HA})^{2+} \text{ or } \text{Ni}(\text{HA})^{2+}]$  and  $[\text{Ni}(\text{H}_2\text{A})^{3+}]$  depending on which scheme is suggested for the possible interactions.

We now discuss each scheme separately :

### Scheme I :

The HA acts as a bidentate ligand via the carboxylic oxygen and the amino nitrogen, a release of the proton of the Zwitter ion takes place with complexation according to the suggested equilibrium in this scheme. When the data were fitted in the following equation

*Studies on the interaction between Ni<sup>++</sup> .....*

$$\frac{n}{(1-n)} \frac{[HA^+]}{[HA]} = B_1 \frac{[HA]}{[H^+]} + B_2 \frac{[HA]}{[H^+]} \frac{(2-n)[HA]}{(1-n)[H^+]}$$

using a computer program, the results of,  $B_2 \frac{[HA]}{[H^+]}$  were obtained.

The stoichiometric  $K_1 \frac{[HA]}{[H^+]}$  values at the various ionic strengths are extrapolated to the zero ionic strength at the corresponding temperature while thermodynamic value  $K_1^\circ$  is evaluated at 25, 30, 35, 40 and 45°C. Figure (1) shows the plot of  $\log K_1 \frac{[HA]}{[H^+]}$  against  $(1/T)$ . Linear behaviour is observed, and the thermodynamic parameters  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  were obtained.

### Scheme II :

Here HA acts as a monodentate ligand, coordinating, via the carboxylic group, the obtained data were fitted in the following equation :

$$\frac{n}{(1-n)} \frac{[HA^+]}{[HA]} = B_1 \frac{[HA]}{[H^+]} + B_2 \frac{[HA]}{[H^+]} \frac{(2-n)[HA]}{(1-n)}$$

the final results for  $B_1 \frac{[HA]}{[H^+]}$  were obtained.

Owing to that the values of  $B_1 \frac{[HA]}{[H^+]}$  are negative, which simply excludes the possibility of existence of such scheme under the present experimental conditions. It is worthnothing that such scheme reaction is unlikely; due to the fact that the carboxylic group is weakly chelating group.

### Scheme III :

Here the alaninate anion  $A^-$ , where both carboxylic and amino groups are deprotonated, could act as the ligating species. When the dat were fitted in the following equation :

M. M. Emara, et. al.,

$$\frac{\bar{n}}{(1-\bar{n})[A^-]} = B_1[A^-] + B_2[A^-] \frac{(2-\bar{n})[A^-]}{(1-\bar{n})}$$

using a computer program, we recorded the results of  $B_1[A^-]$ . The stoichiometric  $K_1[A^-]$  values at the various ionic strengths are extrapolated to the zero ionic strength at the corresponding temperature, while thermodynamic value  $K_1^\circ$  is evaluated at 25, 30, 35, 40, and 45°C. Figure (2) show the plot of  $\log K_1^{A^-}$  against  $(1/T)$ . Linear behaviour is observed, and the thermodynamic parameters  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  were obtained.

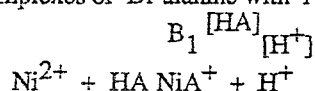
In all the above three schemes, we observe that  $NiA^+$  is the most favored complex than  $NiA_2$ , followed by  $(NiA^+ + H^+)$  or  $(NiA_2 + H^+)$ . This of course is understandable from both statistical as well as energy point view.

The data of  $B_1$  for  $NiA^+$  showed that the tendency of nickel for complexation is good which is reflected to  $B_1[A^-]$  values and the  $\Delta G^\circ$  values.

On the other hand, it is observed that the complexation is less stronger with  $Ni^{2+}$  than the other divalent metal such as copper, Emara, et al., (1990).

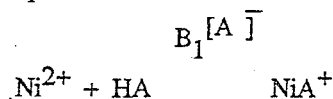
*Studies on the interaction between Ni<sup>2+</sup> .....*

Table (1) Complex formation constants and thermodynamic parameters for complexes of DI-alanine with Ni<sup>2+</sup> assuming that:



Temperature °C	$10^6 K_1 \frac{[HA]}{[H^+]}$	$\Delta G^\circ$ K. J. mole <sup>-1</sup>	$\Delta H^\circ$ K.J. mole <sup>-1</sup>	$\Delta S^\circ$ J. deg <sup>-1</sup> mole <sup>-1</sup>
25	1.96	32.45	15.27	-57.93
30	3.75	31.45	15.27	-53.39
35	4.55	31.47	15.27	-52.60
40	4.25	32.16	15.27	-53.96
45	7.05	31.34	15.27	-50.52

Table (2) Complex formation constants and thermodynamic parameters for complexes of DI-alanine with Ni<sup>2+</sup> assuming that:



Temperature °C	$10^4 K_1 [A^-]$	$\Delta G^\circ$ K. J. mole <sup>-1</sup>	$\Delta H^\circ$ K.J. mole <sup>-1</sup>	$\Delta S^\circ$ J. deg <sup>-1</sup> mole <sup>-1</sup>
25	0.715	-21.97	55.37	259.52
30	1.940	-24.85	55.37	264.75
35	3.850	-27.02	55.37	267.48
40	0.880	-23.62	55.37	252.35
45	0.430	-22.10	55.37	-243.62

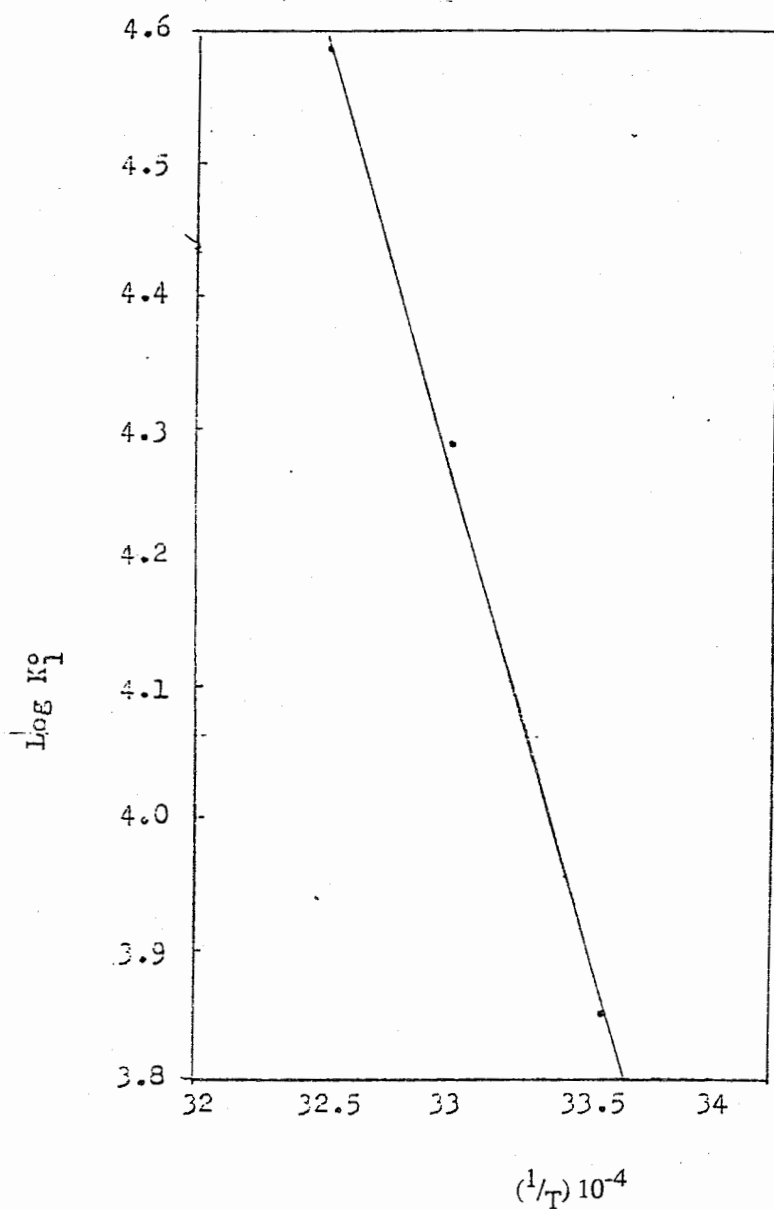
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*M. M. Emara, et. al.,*

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--Fig. (2)  $\log K_1$  against  $(1/T) \cdot 10^{-4}$  for the reaction between Ni (II) and Dl-alaninate ion.



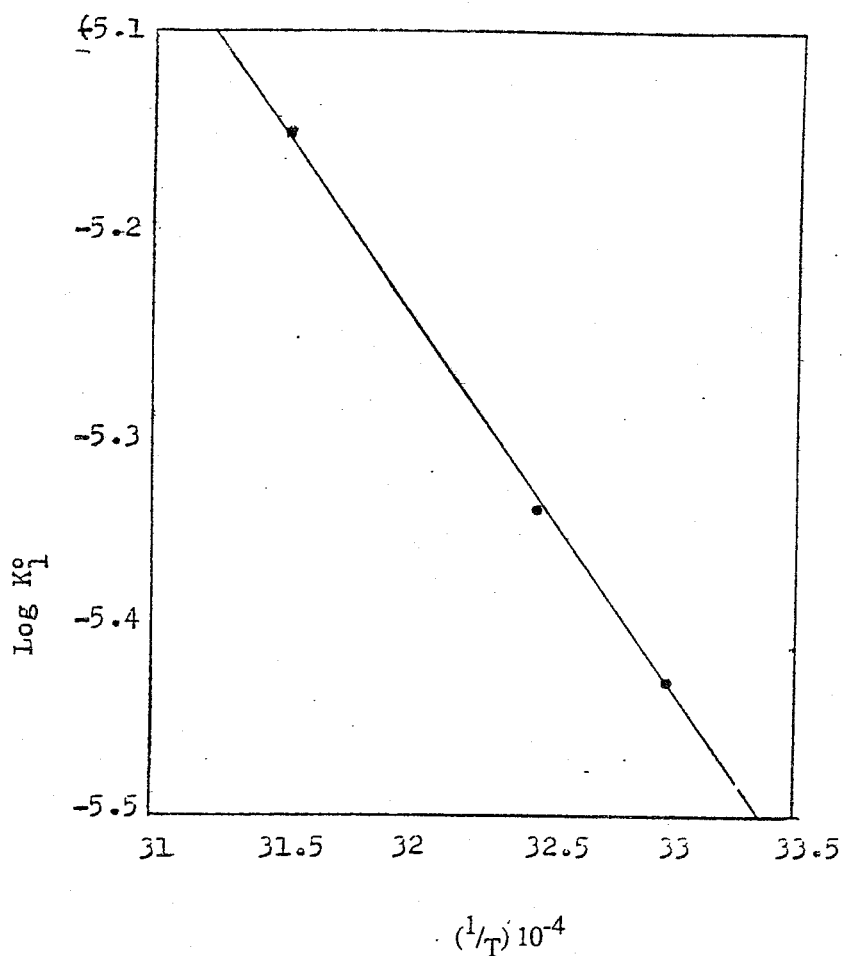


Fig. (1)  $\log K_1$  against  $(1/T) 10^{-4}$  for the reaction between Ni (II) and DI-alaninate ion.