

CHEMICAL SPECIATION OF NICKEL – GLYCINATE COMPLEXATION

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ABSTRACT

Analytical techniques which facilitate determination of concentrations of metal ions, solvated protons and hydroxo-complexes or equivalent can be used to study the complexation of metal ions and ligands.

Complex speciation measurements using glass electrode potentiometry, which allows a fast, reproducible determination of equilibrium concentrations is an electro-metric titration technique used for the determination of formation constants of ligands. The technique does not disturb the labile equilibrium between metal ions, ligands and protons.

The computer program ESTA (Equilibrium Simulation for Titration Analysis) is a complex and sophisticated speciation program used to analyse potentiometric titration data and to simulate equilibrium distributions of chemical species. This applies weighted least squares objective functions to analytical parameters such as titre volume and emf readings.

The chemical combination of nickel (II)-glycinate-proton system has been chosen and activities of component in the equilibrium system were kept constant by working in a medium of high and constant ionic strength of 150 mmol dm⁻³ sodium chloride inert electrolyte medium, which approximates to that of most biological fluids, in order to express the formation constant in concentration terms.

The experimental protonation curve shows that the ligand has two protonation sites and formation and deprotonation curves show that the metal to ligand complexation ratio is up to 1:3. Estimates for the protonation and formation functions obtained were optimized and the refined constants were calculated. Results were further substantiated by the good superimposability of the experimental and simulated curves. The species distribution diagrams confirm that the complexation between nickel (II) and glycinate is up to 1:3.

Keywords: Speciation, Protonation, Nickel, Glycinate, Formation Constants, ESTA

INTRODUCTION

Quantitative analytical techniques, which are able to monitor concentrations of metal ions, solvated protons and hydroxo-complexes or equivalent can be used to study the equilibrium complex formation between metal ions and ligands. Complex

speciation measurements using glass electrode potentiometry is a well established electro-metric titration technique for the determination of complexation stability constants of a ligand in the presence or absence of metal ions (Linder *et al.*, 1984).

This method allows a generally fast, reproducible, determination of equilibrium concentrations and can also be used with low free concentrations of ions. The labile equilibrium existing between metal ions, ligands and protons is not affected by this technique.

The computer program ESTA (Equilibrium Simulation for Titration Analysis), which was used for this study, is a complex and sophisticated library of programs used to analyse potentiometric titration data and to simulate equilibrium distributions of chemical species (May *et al.*, 1989). This can accommodate systems with as many as ten components forming up to ninety-nine complexes. Titrations involving up to three electrodes and three burettes are permitted. The program applies weighted least squares objective functions to analytical parameters such as titre volume and emf readings. With potentiometric titrations, corrections with respect to liquid junction potentials and ion selectivity of electrodes, variations in ionic strengths, and the associated changes in activity coefficients are taken into account. It supersedes graphical methods and utilizes curve fittings.

The chemical combination of nickel(II)-glycinate-proton system has been selected in this study as it is relatively less complicated from hydrolysis of metal ions and formation of polymeric species. Activities of components in the equilibrium system were kept constant by working in a medium of high and constant ionic strength of 150 mmol dm^{-3} sodium chloride inert electrolyte medium in order to express the formation constant in concentration terms. This concentration approximates to that of most biological fluids.

MATERIALS AND METHODS

Potentiometric titrations were performed in a titration vessel and rapid mixing of the test solution was achieved using a magnetic stirrer. The electrodes used were a glass sensing electrode (Russell SW/B14/757) and a standard calomel reference electrode (Russell CR/B14/5/75). Glass electrode was stored in a solution of 10 mmol dm^{-3} hydrochloric acid and the calomel electrode in saturated potassium chloride when not in use.

The potential readings (emf) were measured to an accuracy of 0.05 mV using a precision digital pH meter (pHM85, Radiometer, Copenhagen).

The titrant, usually sodium hydroxide, was dispensed from a calibrated 20 cm^3 ($\pm 0.01 \text{ cm}^3$) piston burette (Metrohm E485) and it was calibrated by weighing pure water discharged between calibrated marks.

Grade A volumetric glassware was used throughout experiments without recalibration and distilled, degassed, double deionised (DDDD) water (FiSTREEM & Elgastat C 114), which had a resistivity greater than 2 m ohm cm^{-1} was used for the preparation of all solutions.

Both sodium hydroxide and hydrochloric acid were prepared by diluting convols (BDH). The sodium hydroxide solution was replaced regularly to avoid error that caused by absorption of carbon dioxide. Nickel(II) solutions were prepared in

hydrochloric acid to prevent hydrolysis by direct weighing of the chloride salt (BDH, AnalaR). The exact metal concentrations of these solutions were determined by titration with EDTA using murexide indicator (Jeffery *et al.*, 1994). The ligand solution, glycinate (aminoacetate), was prepared by direct weighing (BDH, AnalaR) without further purification and acidified with hydrochloric acid to ensure complete protonation. The elemental analysis of glycine (%C = 31.9, %N = 18.5 & %H = 6.9) is in good agreement with the theoretical values (%C = 32.0, %N = 18.6 & %H = 6.7). Sodium chloride (BDH, AnalaR) was used to maintain the background electrolyte concentration and all solutions were maintained at constant chloride concentration (150 mmol dm^{-3}).

Typical methods of calibrating electrodes against buffers of specific pH are unsuitable in metal-ligand equilibrium studies, owing to the difficulties involved in relating pH values to hydrogen ion activities in the buffer and in the test solutions because of their different ionic compositions. Also the ionic strength of the test solution and of the buffer would differ, so the liquid junction potentials with respect to the two solutions would not be the same.

The method of calibration of electrodes used throughout the experiments was the Gran's graphical method. That is by titrating a strong acid against a strong base, the emf was plotted at each point versus the corresponding value of $-\log [\text{H}^+]$. The calibration of the electrodes employs the relationship of the equation:

$$E_{\text{cell}} = E_{\text{const}} + S \log [\text{H}^+]$$

The relationship between E_{cell} and $\log [\text{H}^+]$ was linear with slope S and the intercept was determined by extrapolation. Deviations from linearity occurred due to low buffering capacity of the system, the effect of hydrogen ion concentration on liquid junction potentials at low pH values and sodium ion interference at high pH values. If the base is contaminated with carbonate, the graph is curved in the region of the equivalence point.

With the use of ESTA computer program, problems that occur due to lack of buffering have effectively been eliminated. ESTA also corrects for deviation in ionic strength from point to point. The calibration was performed by refining the electrode parameters E_{const} , slope S , and the vessel acid concentration while pK_w was held constant. The standard potential of a glass electrode varies from day to day due to asymmetry effects, producing changes in E_{const} . Therefore, the calibration procedure was performed regularly to monitor electrode performances and the E_{const} value was adjusted accordingly.

RESULTS AND DISCUSSION

The pH range covered during the titration was generally 2-11. A constant chloride ion medium of 150 mmol dm^{-3} was maintained in the titration vessel and all measurements were done at the temperature of 25°C . During the ligand protonation studies, the ligand concentration varied from 3 to 20 mmol dm^{-3} with the hydrochloric acid concentration remaining around 20 mmol dm^{-3} . For the metal ligand interactions, various ratios of metal : ligand varying from 1:1 to 1:4 were chosen again maintaining the acid concentration at about 20 mmol dm^{-3} .

The following strategies were followed in the interpretation of results:

- i) Evaluation of the protonation constants first, followed by the evaluation of the formation constants of the complexes.
- ii) Simultaneous evaluation of the protonation and complexation constants.

Results obtained were compared by

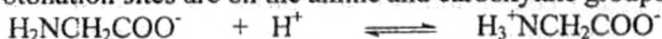
- i) Treating the data from each titration curve separately.
- ii) Treating all the experimental data together.

Glycinate Protonation

Glycine is an amino acid, existing as a zwitter ion under neutral conditions:



The protonation sites are on the amine and carboxylate groups.



Hence there will be a formation of two protonated species of glycinate i.e., $[\text{LH}_2]^+$ and $[\text{LH}]$.

Titration were performed using an acidified glycinate solution as the titrand and sodium hydroxide (100 mmol dm^{-3}) as the titrant. Both vessel and burette solutions contained sodium chloride (150 mmol dm^{-3}) as a background electrolyte.

The experimental formation curve is shown in Figure 1(a). Each symbol represent a different titration having a different glycinate:proton ratio. The curve clearly shows that the ligand has two protonation sites and the protonations occur at $\text{pH} = 2.5$ and 9.5 respectively.

Estimates for the protonation functions were obtained from the curve, using the Bjerrum's method (Bjerrum, 1961). These initial estimates of $\beta_{011} = 9.5$ and $\beta_{012} = 12$ were optimized and the refined constants performed simultaneously are given in the Table 1. Results were further substantiated by the good superimposability of the experimental and simulated [Figure 1(b)] protonation curves.

(In β_{pqr} , p = number of metals, q = number of ligands, r = number of protons)

Table 1: Thermodynamic formation constants for glycinate protonation at 25°C and in 150 mmol dm^{-3} chloride

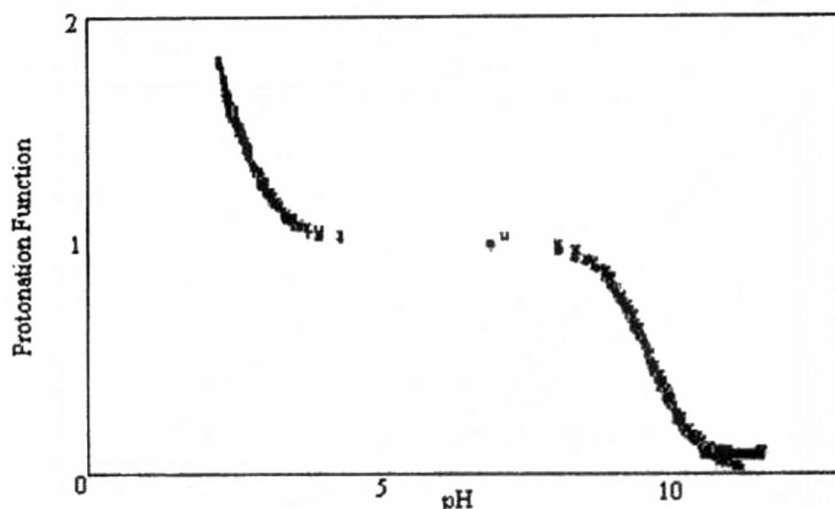
Species q r	Log β	Standard Deviation	Overall Objective Function	R_F	n	N
1 1	9.5	0.2048	1.4839	0.2814	204	2
1 2	12	0.2678				

q = number of ligands

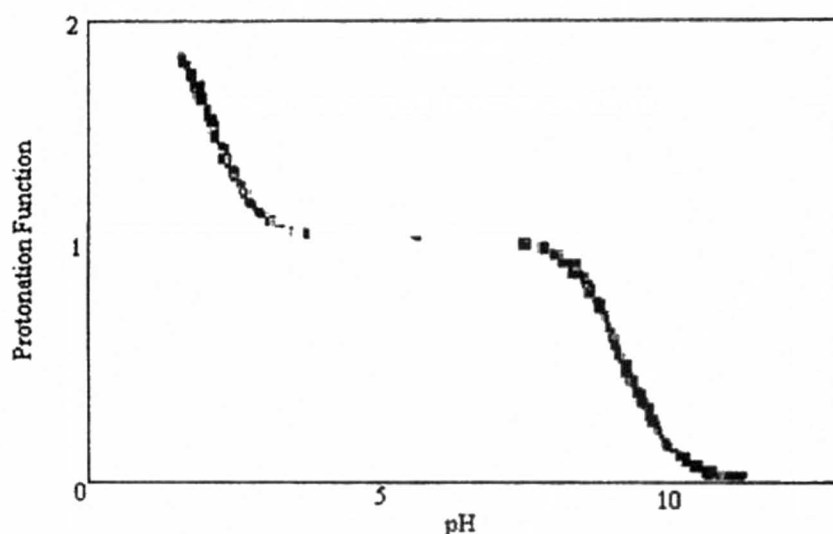
r = number of protons

N = number of titrations

n = number of titration points R_F = Hamilton R-factor



(a) Experimental Formation Curve



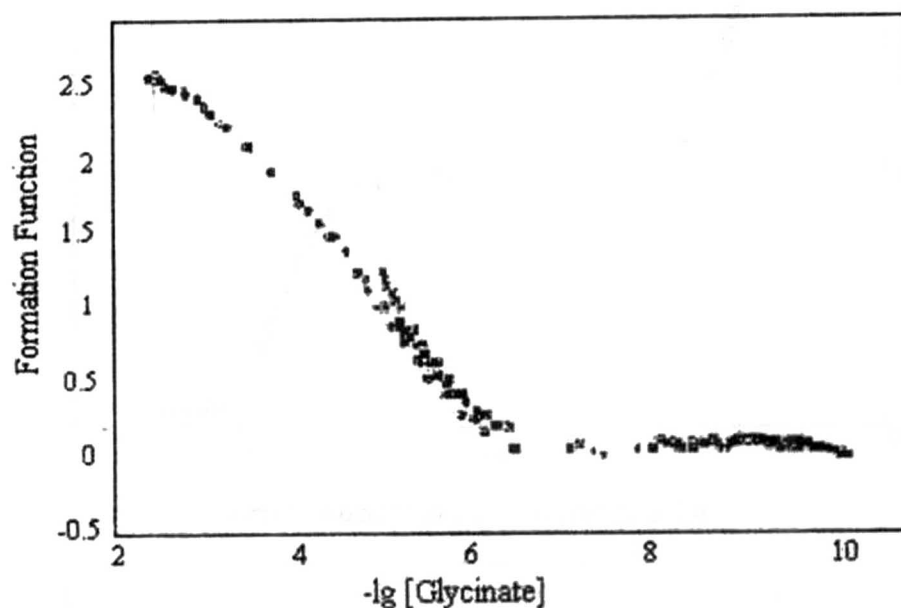
(b) Simulated Formation Curve

Figure 1: Formation Curves for Glycinate Protonation

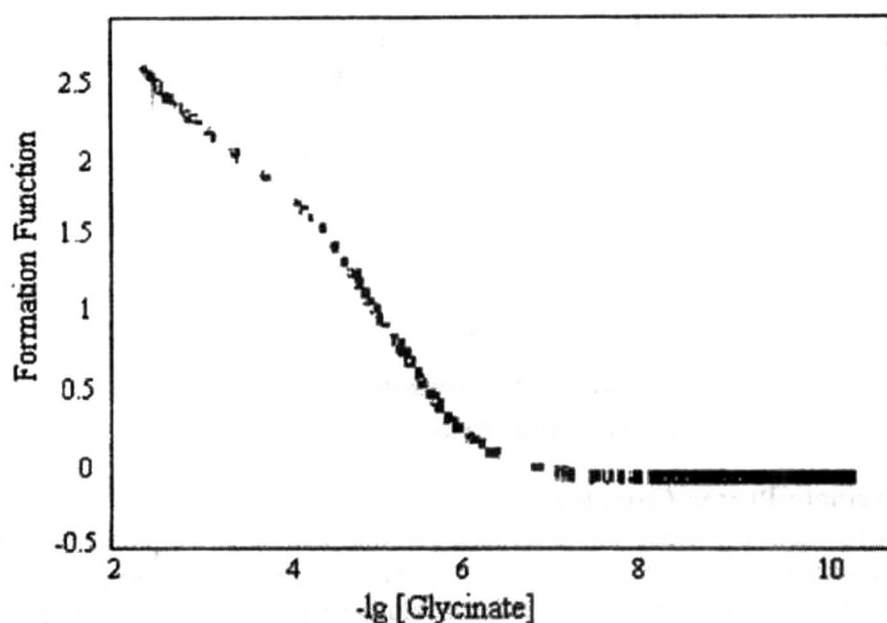
Nickel (II)-Glycinate-Proton Complexation

Nickel(II)-Glycinate interactions in aqueous media provide a simple system with respect to the interactions of the ligand with a metal. Glycine is the simplest amino acid and hydrolysis of nickel ions occurs only at relatively high pH values. There will be formation of mononuclear complexes of the NiL_q type with q ranging from 1 to 3 over the intermediate pH range.

It is assumed that hydroxy species and protonated complexes formed at higher and lower pH values respectively were insignificant within the selected pH range. Interactions between nickel(II) and chloride ions by formation of complexes did not occur within this pH range as no colour change was observed.

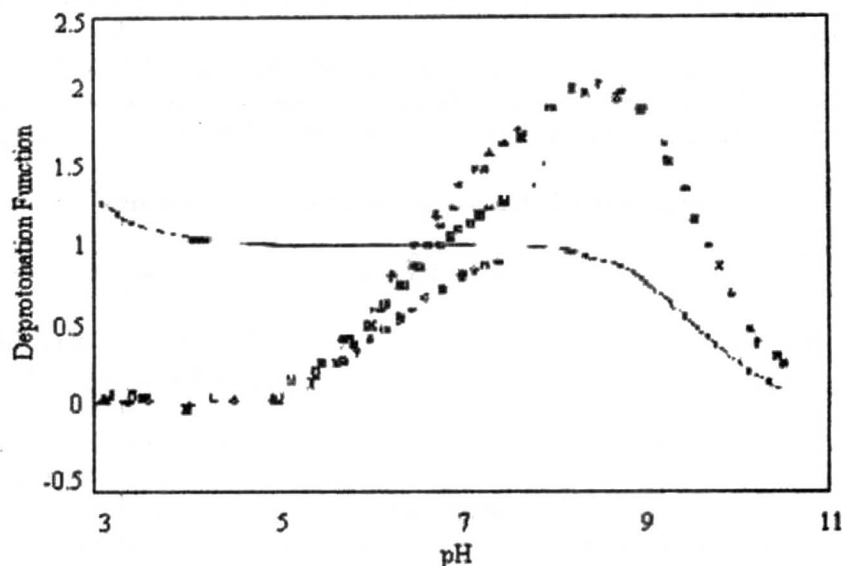


(a) Experimental Formation Curve

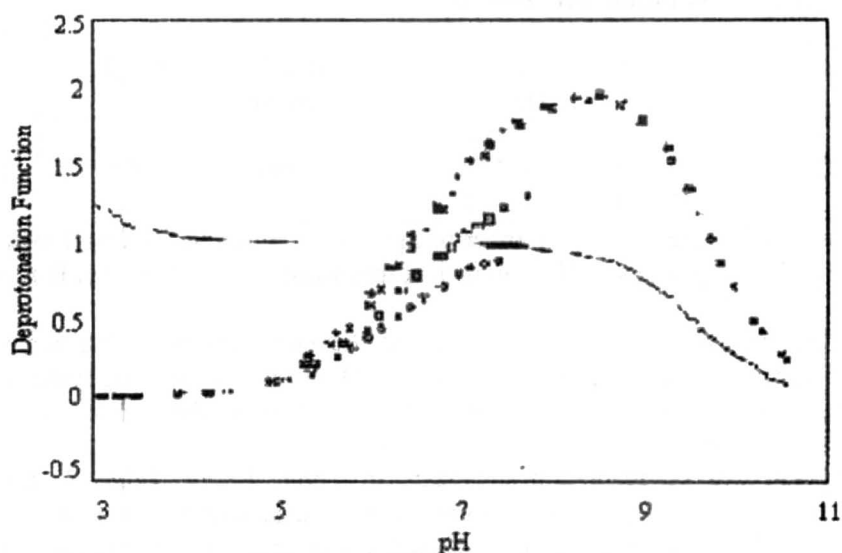


(b) Simulated Formation Curve

Figure 2: Formation Curves for Nickel-Glycinate Proton Complexation



(a) Experimental Deprotonation Curve



(b) Simulated Deprotonated Curve

Figure 3: Deprotonation Curves for Nickel-Glycinate Proton Complexation

Experimental formation and deprotonation curves are in Figures 2(a) and 3(a). Different symbols refer to different titrations having various nickel(II):glycinate ratios and different total nickel (II) and total glycinate concentrations.

The nature of the formation curve indicates that only mononuclear species are formed since no spread of curves occurs (Filella & Williams, 1985). The negligible 'curl back' indicates the absence of hydroxy species. The other information gatherable

from the formation curve is the indication of the species M:L being present with ratios 1:1, 1:2 and 1:3.

However, the deprotonation curve (Figure 3a) facilitates the evaluation of the stoichiometries for other possible species present (Table 2). The evaluation is derived from the integer values of deprotonation function and n (dark line in the graph).

Table 2: Possible species predicted using deprotonation diagrams

pH Region	n	Deprotonation Function	Possible Species
2 – 3	2	0	LH ₂
3 – 8	1	1	LH, ML, ML ₂ , ML ₃
8 – 10	0	1	L, MLOH, ML ₂ OH, ML ₃ OH

Using EAST program it was possible to optimize three possible species. The other species exhibited unacceptable statistics and also indicated that they are formed only up to 5% of the total in all titrations performed. The final model obtained as the best system is shown in Table 3 with the corresponding statistical information.

Table 3: Thermodynamic formation constants for glycinate protonation at 25°C and in 150 mmol dm⁻³ chloride

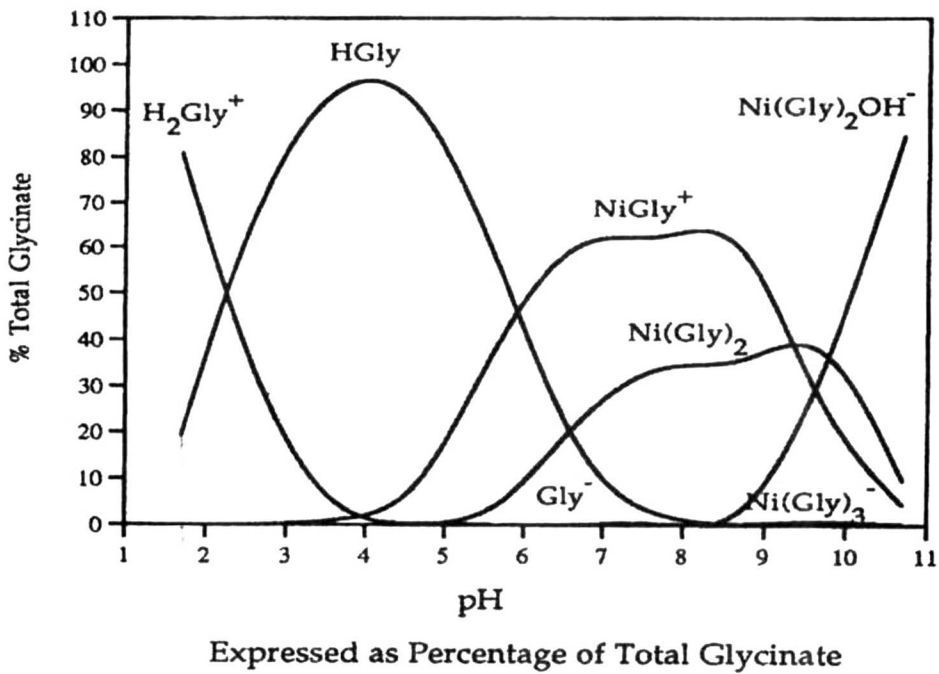
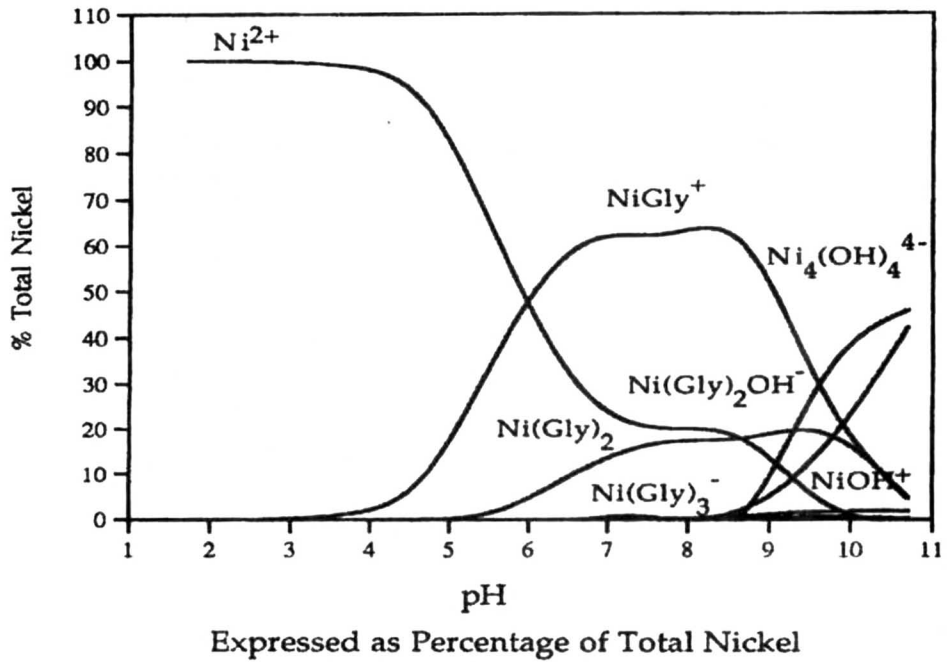
Species			Log β	Standard Deviation	Overall Objective Function	R_F	n	N
p	q	r						
1	1	0	5.6010	0.1948	5.9807	0.0324	160	4
1	2	0	10.2379	0.2236				
1	3	0	12.9747	0.4641				

p = number of metals; q = number of ligands; n = number of titration points;
r = number of protons; N = number of titrations; R_F = Hamilton R-factor

Further support for the 'correctness' of the constants was obtained when the simulated formation and deprotonation curves (Figures 2 b & 3 b) were performed using the optimized constants. These simulated curves showed a well accepted superimposability with the experimental curves.

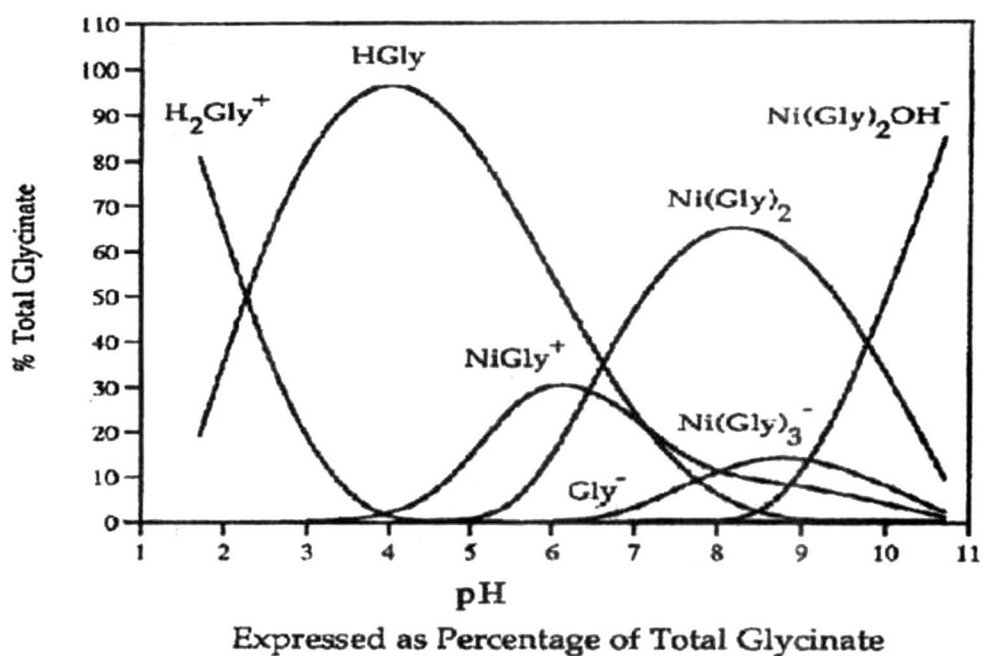
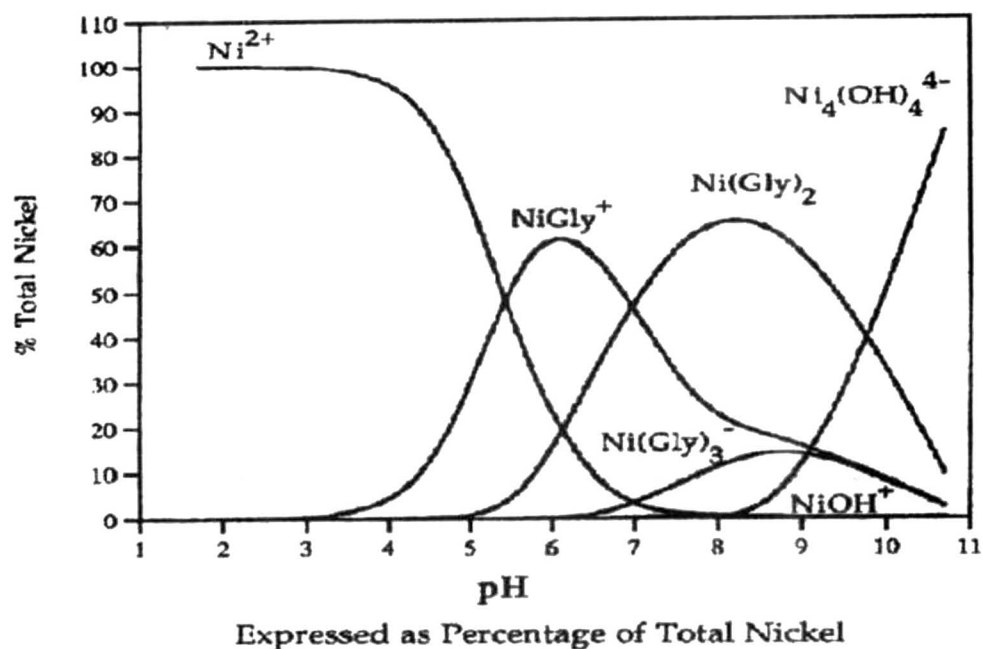
With the use of formation constants in Table 1 and Table 3, the species distribution of the nickel-glycinate system was simulated with pH. This was performed for four metal-ligand ratios, 1:1, 1:2, 1:3 and 1:4 (Figure 4). The results demonstrate the change in the speciation of the system by changing the ratio of metal:ligand. Up to the metal - ligand ratio 1:3, the species distribution changed with the pH and thereafter it was constant. This further confirms that the maximum nickel-glycinate complexation occurs when the metal-ligand ratio is 1:3.

These *in vitro* investigations of metal-ligand-proton interactions to determine the chemical species and to quantify their formations in terms of lg β values are necessary to investigate the steady-state conditions which exist especially in bio-solutions in order to simulate the *in vivo* distribution of metal ions amongst the low molecular mass ligands present in fluids.



Total Concentration of Ni : Gly = 1 : 1

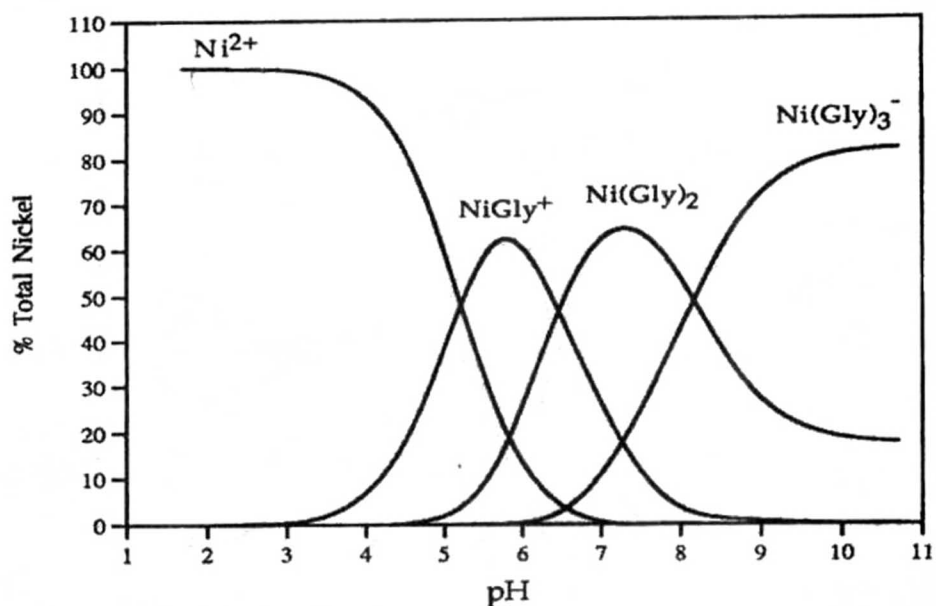
Figure 4 : Nickel – glycinate species distribution



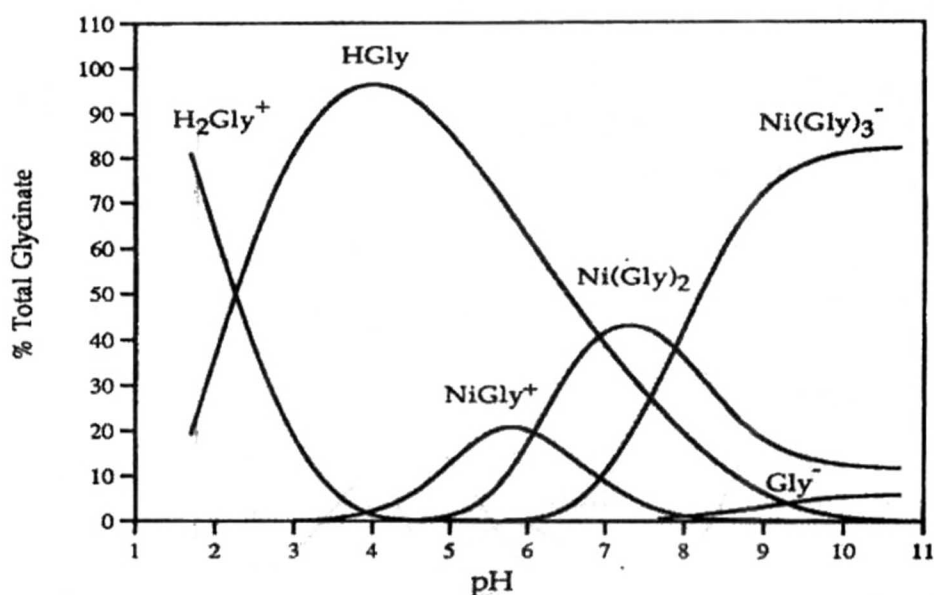
Total Concentration of Ni : Gly = 1 : 2

Figure 4 : Contd..

Chemical speciation of Nickel



Expressed as Percentage of Total Nickel



Expressed as Percentage of Total Glycinate

Total Concentration of Ni : Gly = 1 : 3

Figure 4 : Contd..

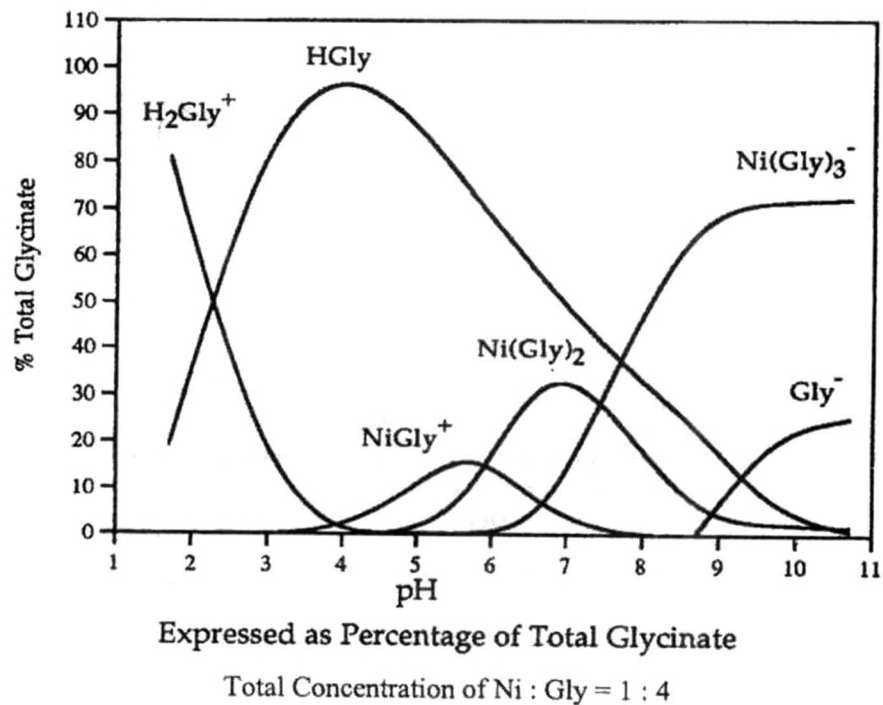
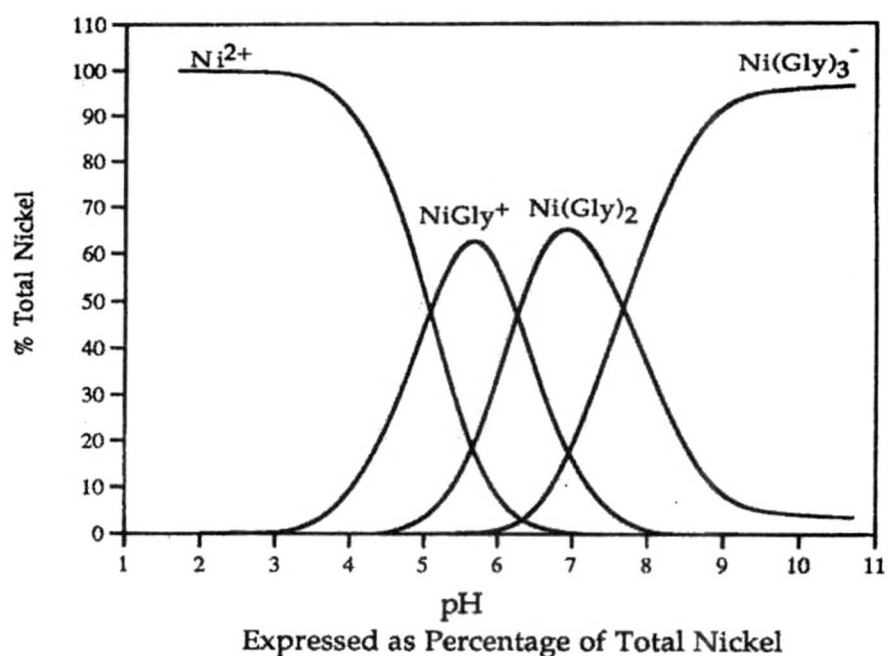


Figure 4: Contd..

ACKNOWLEDGEMENTS

The support given by the Speciation Research Group, Cardiff University of Wales, United Kingdom is greatly acknowledged.

REFERENCES

- Bjerrum, J. (1961), Metal Amine Formation in Aqueous Solution, P. Hasse and Son, Copenhagen.
- Filella, M. and Williams, D. R. (1985). *Inorganic Chimica Acta*, 106(6), 49-57.
- Linder, P. W., Torrington, R. G. and Williams, D. R. (1984). *Analysis Using Glass Electrodes*, Open University Press, England.
- Jeffery, G. H., Bassett, J., Mendham J. & Denny, R. C. (1994). *Vogel's Textbook of Quantitative Chemical Analysis*, Longman, UK.
- May, P. M., Murray, K. and Williams, D. R. (1989). *ESTA User Manual*. University of Wales, Cardiff, UK.