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Original Research Article

Determination of Thermodynamic Stability of a Ni (II) Glycine Complexes in aqueous solution: Potentiometric and Spectroscopic Studies

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ABSTRACT

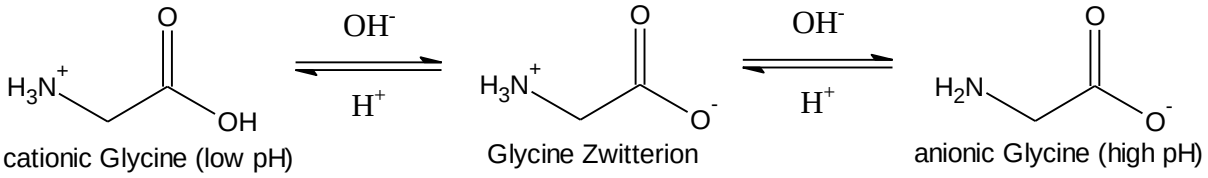
The stability constants of Glycine and Ni(II)Glyx complexes (x = 0-3) in aqueous solution were studied by potentiometric titration at 25°C. The data analysis afforded insight on speciation, which was further confirmed by measuring absorbance in the UV-VIS region, covering a pH range from 2 to 11 to establish the Ni(II)Gly complex extinction coefficients. The potentiometric and spectroscopic data were analyzed using the computer program ESTA. It was shown that the formation of Ni(II)/glycinate complexes are strongly pH dependent. The Ni(II) competes with the protons bound to Glycine at the amine and carboxylate moiety. The successive formation of the NiL, NiL_2 and NiL_3 was observed as the pH was increased. Free Ni(II) complexes with one Glycine ligand above pH 4 followed by further association of another Glycine ligand above pH 6 and again at pH 8 to form the NiL_3 complex. The stability of the complexes is proportional to the number of glycine ligands bound. The analysis of the spectroscopic data supports this trend as an increase in Glycine bound to the Ni(II) center. However, it increases its stability in need of shorter wavelength (higher energy) to excite the electron, suggesting stronger field splitting exerted by the glycine ligand due to higher stability. Thermodynamics study proposed that the increase in stability of the Ni(II) complexes was in this direction: NiL_3 > NiL_2 > NiL Good correspondence between theoretical and experimental data, low standard deviations in the stability constants and low RH lend reasonable confidence in all obtained results.

Keywords: Glycine, Ni(II) complexes, potentiometric, UV-VIS spectroscopy

Introduction

Metal complex formation is much dependent on the proton concentration (pH) of the solution because the metal ion competes with the proton for the same atoms on the ligand [1]. Metallic ions are widely present in the biological systems and play many important roles [2]. Some others are toxic but are tolerated at low levels such as nickel or cobalt because of their interventions in some biological processes [3]. Other cations can cause major health damage if they are present even in trace amounts such lead(II) and cadmium(II) [4]. Indeed, lead is known to cause saturnism when it is present at high concentration in biological medium [5,6]. Cadmium has been reported to block calcium channels in sensory neurons and prevents regular central system functioning [7]. Many researchers have been consequently devoted to the development of methods for the determination of these cations.

Glycine exists as a Zwitterion in aqueous solution. The primary amine is protonated ($-NH_3^+$) and the carboxyl is deprotonated ($-COO^-$) giving the molecule an overall neutral charge. At low pH range (2-3) the latter group is protonated (-COOH) forming a cationic species whereas the latter group is deprotonated ($-NH_2$) at alkaline conditions (pH 9-10) to give the Glycine anion [8,9].



Scheme 1. Glycine ions

For a metal ion, in our case Nickel(II), to form a complex with the Glycine ligand it has to compete with the protonation at the amine nitrogen and the carboxyl oxygen. Thus we expect an increase of complex formation at higher pH (lower concentration of protons) Glycine contains two donor atoms, so we expect it to act as a bidentate ligand and to coordinate with both the nitrogen of the amine and the oxygen of the carboxylate group which results in more excellent thermodynamic stability on behalf of chelating effects. Furthermore, it is to predict that a

maximum of 3 glycine ligands will form a complex with Nickel(II) in a chelated state on the grounds of steric control and availability of coordination sites on the metal.

The aim of the present study to investigate the complexation of Glycine with Ni(II) to form Ni(II)/Glycinate complexes we employ potentiometric titration which is performed on the free acidified ligand and acidified metal: ligand solutions in ratios (metal: ligand) ranging from 1:1 to 1:4 against NaOH. This technique involves the determination of protons displaced from the ligand by chelating to the metal and forming the complex. The ligand undergoes pH titration to obtain its proton stability constants. The titration data is analyzed by ESTA (equilibrium simulation for titration analysis) from which we obtain stability constants for both the ligand and the glycinate complexes [10]. ESTA is a computer program that not only enables sophisticated analyses of potentiometric data to describe speciation but allows modelling of theoretical equilibrium conditions which provides a way to determine if experimental data sufficiently correlates and to undertake error analysis. To minimize deviations in experimentation, the ionic strength was maintained at 0.15 mol dm^{-3} using NaCl as the inert electrolyte under temperature control (25°C). To give a broader scope on the Ni/Gly speciation, a 1:1 metal: ligand mixture was prepared at different proton concentration (2-11). The absorbance was recorded using a spectrophotometer, and ESTA analysis then modelled the extinction coefficients.

Theory

The Z_M-bar and Q_M-bar functions were used to visualise the potentiometric data. Z_M-bar is the average number of ligands bound to the metal ion and is given by [11,12]:

$$Z_{M-bar} = \frac{T_L - [L](1 + \sum_n \beta_{LHn} H^n)}{T_M}$$

where, T_L and T_M are the total ligand, and total metal concentration, respectively. And [L] is the free-ligand concentration;

$$[L] = \frac{T_H - H + OH}{\sum_n (\beta_{LHn} H^n)}$$

It is plotted as a function of the negative log of the free ligand concentration (pL). This function is strictly only defined for simple, mononuclear complexation, as no account is taken of any deprotonation reactions. Even so, it is useful for visualising the experimental data as deviations of the function from ideal behaviour are indicative of what species are formed in solution. Thus, if the Z_M-bar bends backwards, the formation of MLH_{-n} species is indicated. The disadvantage of this function is that the free ligand concentration becomes negative (a physical impossibility but a mathematical possibility given the assumptions in calculating pL) if the hydroxyl species' concentration is too large. For this reason, the Q_M-bar function is also used. While this function is not as easy to interpret as Z_M-bar, it has the advantage that it is plotted against the measured pH and not some derived function. Q_M-bar is the average number of protons released due to complexation. When compared with the number of protons on the ligand (n-bar) at a particular pH, the predominant species' stoichiometry can be estimated.

Q-bar and n-bar are given by [13];

$$Q_{M-bar} = \frac{T_H^* - T_H}{T_M}$$

$$n_{-bar} = \frac{T_H^* - H + OH}{T_L^r}$$

where TH is the total proton concentration and T*H is the calculated total concentration of protons that would be necessary to give rise to the observed pH in the absence of metal ions or instead if no complexation took place.

Experimental

Materials

All chemicals and reagents were of analytical grade and were used without further purification. All chemicals were purchased from Sigma and used without further purification. The metal-ion stock solutions were prepared from analytical grade reagents and their concentration checked titrimetrically [14].

Measurements

All pH-potentiometric measurements were carried out at 25 ºC and at a constant ionic strength of 0.15 mol/ dm^3 (NaCl). The slope of the Metrohm glass electrode was measured using a set of

Metrohm ion analysis pH buffers and the E^o of the electrode calibrated against concentration using strong acid/strong base titrations [15, 16]. Titrations were carried out using a Metrohm 848 Titrino plus in the pH range 2.0 – 11.0 with a ligand and metal: ligand [17]. Particularly useful in the analysis of this system was the Z_M-bar and Q_M-functions [11, 18]. Electronic spectra of the Ni(II) complexes were recorded on a Hewlett Packard 8452A Diode Array Spectrophotometer set in the wavelength range 300 – 820 nm. A set of 10 of approximately 1:2 ratio nickel glycine solutions were prepared to cover the pH range from 2-11 and measured in the absorbance range from 200nm to 800nm. The obtained data were analysed with ESTA to obtain the molar extinction coefficients of the present moieties at pH 7.

Preparation of solutions

The hydrochloric acid solution was diluted, and the exact concentration was determined by titration against standardized NaOH (0.1 mol dm^{-3}). The ligand solution was prepared in standardized HCl by direct weighing of Glycine. The Ni(II) solution was prepared by dissolving $NiCl_2$ in boiled out, glass distilled H_2O to afford ca. 0.02 mol dm^{-3}. Standardization was achieved by titration with EDTA using a murexide indicator.

Results and Discussion

Table 1. Stability constants (log β_{pqr}) for glycine. $\beta_{pqr} = [M_pL_qH_r]/[M]^p[L]^q[H]^r$, I = 0.15 mol.$dm^{-3}$ (NaCl), T = 25 ºC. S.dev denotes standard deviation in log β_{pqr}; R_f^H is the Hamilton R-factor and R_{lim}^H it is limit.

Ligand	p	q	r	$log\beta_{pqr}$	S.dev	R^H	R_{lim}^H	ΔG^o/Jmol^{-1}
LH	**0**	**1**	**1**	**9.66**	**0.01**			**-55.15**
LH_2	**0**	**1**	**2**	**12.35**	**0.02**	**0.01**	**0.001**	**-70.50**

The calculated stability constant of the Proton-Glycine complexes is given in Table 1. The proton complex constants of the Glycine ligand can be expressed two protonation constants where the first stability constant β_{011} (9.66±0.01) represents the equilibrium of one proton (r=1) with the nitrogen binding site (donor ligand), of the amine moiety. (viz. $–NH_2 + H^+ \leftrightarrow -NH_3^+$)

The second stability constant β_{012} (12.35±0.02) therefore describes the carboxylate moiety protonation (viz $-COO^- \leftrightarrow$ -COOH). The precision of the results is confirmed by the good correlation seen between the practical and theoretical values shown in Figure 1. Furthermore, low standard deviations for $\log\beta_{011}/\log\beta_{012}$ and a small R^H value provide a high degree of confidence for these results. Because $R^H > R_{lim}^H$ is to note that the fitting of the data cannot be further statistically optimized.

The complexation free energy (ΔG^o) of the Proton-Glycine complexes can be calculated using the values of first and second stability constants for the protonation process. Protons equilibrium constants are related to the ΔG^o for the complexation reaction as depicted in the below equation:

$\Delta G^o = -2.303\ RT \log \beta$ [19]

Where R represents the gas constant and T is the absolute temperature.

The generated complexation free energies given in Table 1. The negative values for ΔG^o designates a protonation, could be concluded that the protonation of carboxylate moiety occurred more spontaneously that that of amine moiety.

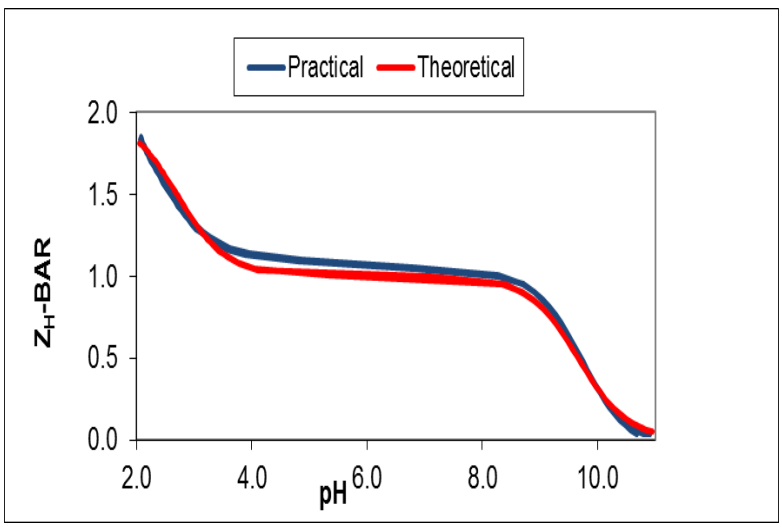


Figure 1. Z_H-bar for the protonation of Glycine, the blue curve is the practical plot; the red curve is theoretical.

The protonation function, $Z_{H[}$-bar, was generated using the refined protonation constants. Good agreement is observed between the calculated function (red) and the experimental data (blue). From the plot, we can see two protonation equilibria in the pH range of 2- 11 in which experimental data were collected. Z_H-bar represents the average number of protons coordinated

per ligand molecule at the specific pH value. At approximate pH 11 Z_H-bar equals 0, indicating that the ligand is in its fully deprotonated form (Gly^-). At Z_H-bar = 0.5 we expect the fully protonated species LH2 and the LH species (zwitterions) to be equimolar. This point is defined as the pKa value and corresponds to about 2.5, which is close to the pKa value of deprotonation of the carboxyl moiety found in the literature as 2.34.

Similarly, at Z_H-bar = 1.5, we expect the zwitterion (LH) and the fully deprotonated species to be equimolar and estimate the pKa to be around 9.6 (literature pK_a (amine) = 9.6). The saddle point between 5 and 7 describes the range where the zwitterion is the major Glycine species present in solution. The speciation of Glycine was generated from the values given in Table 1 and showed the complexation of protons with the glycine ligand. At low pH, we have a high occurrence of fully protonated species deprotonated with increasing pH to form the LH species. As the pH is increased further, the LH is also deprotonated to form the anionic L^- species representing the only species above a pH of 11. Figure 2 describes the relative amount of each Gly/H^+ complex present at a given pH. As observed in the protonation function (Fig 1), we see that at roughly pH 2.4 that both the LH and LH_2 species are present in equal amounts within the solution. At approximately pH 9.6, we find the LH and L1 species to be present in 50: 50 ratio. In the range of pH 5-7, the zwitterion species makes up 100% of the possible Glycine species. The substantial deviations between the experimental pK_a (carboxyl) and the pK_a mentioned in the literature are due to reduced glass electrode sensitivity due to high proton concentrations.

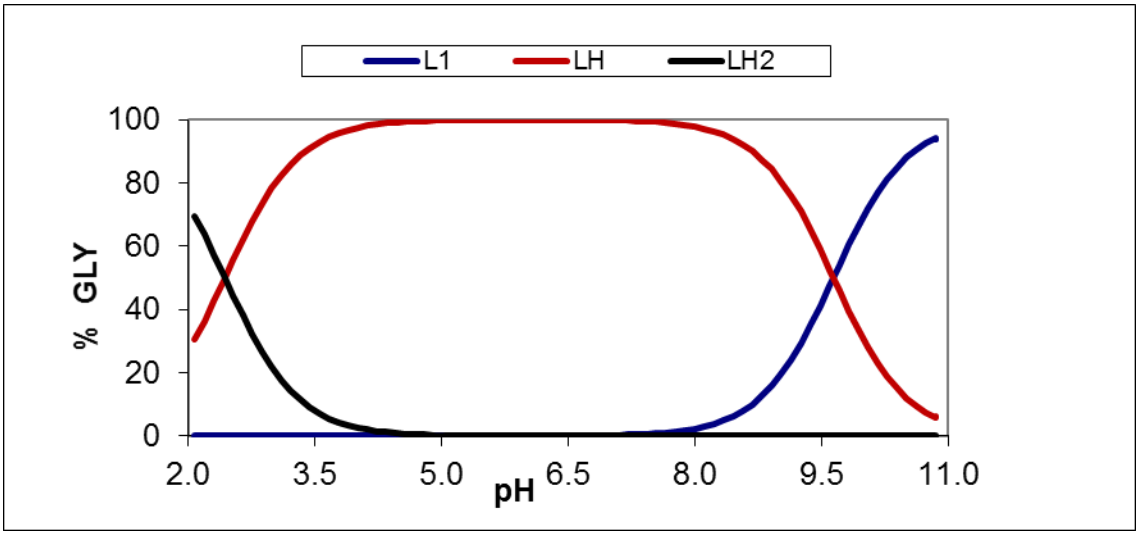


Figure 2. The distribution curve for the glycine/proton complex.

Table 2. Stability constants (log β_{pqr}) for Ni^{2+} of glycine. $\beta_{pqr} = [M_pL_qH_r]/[M]^p[L]^q[H]^r$, I = 0.15 mol.dm^{-3} (NaCl), T = 25 ºC. S.dev denotes standard deviation in log β_{pqr}; R_f^H is the Hamilton R-factor and R_{lim}^H it is limit.

Species	p	q	r	$log\beta_{pqr}$	S.dev	R^H	R_{lim}^H	ΔG^o/Jmol^{-1}
NiL	**1**	**1**	**0**	**5.56**	**0.01**			**-31.74**
NiL_2	**1**	**2**	**0**	**9.55**	**0.02**	**0.03**	**0.004**	**-54.52**
NiL_3	**1**	**3**	**0**	**11.68**	**0.04**			**-66.68**

Table 2 shows the stability constants of the three predominant Ni(II)Gly complexes formed in the pH range of 2-11. ($\log\beta_{110}$ (NiL) = 5.56±0.01, $\log\beta_{120}$ (NiL_2) = 9.55±0.02 and $\log\beta_{130}$ = (NiL_3) = 11.68±0.04). NiL_2 is likely to form a square planar complex as two Glycine moieties bind with both their amine and carboxylate group to form a chelated bidentate ligand on the metal center. The increase of 4 log units in the stability constant from NiL to NiL_2 is likely to be caused by entropic effects as two molecules of water are released while one further glycine associates to the metal centre. Furthermore, the chelation of Glycine with the oxygen and nitrogen to form a cyclic system will provide the complex with higher stability. When the third glycine ligand associates to metal centre another two water molecule will be liberated into a solution which provides a favourable increase in entropic terms, however steric crowding around the relatively small metal are likely to be the reason for a lower increase in *logβ* from NiL_2 to NiL_3 comparatively to NiL to NiL_2 (100 fold to 10000 fold). This trend displays that as the number of Glycine bound, the metal atom increases the stability of the complex is increased. H_2O is a weaker ligand than Glycine. The low standard deviations of the three stability constants and the low value for R^H describe a high degree of confidence. The data can not be statistically improved any further as $R^H > R_{lim}^H$.

In Table 2 Stability constants measure the thermodynamic prediction of Ni(II)Gly complexes formation and could be promptly related to the Gibbs free energy of a reaction. Herein a negative free energy value indicates favorable thermodynamic stability for complex. The displayed data in Table 2 suggest that the enhancement in stability of the prepared complexes is in this order:

$NiL_3 > NiL_2 > NiL$.

Ni(II) is a borderline acid so prefers N, O donor atoms to O, O donor atoms which contribute to increased stability when replacing the H_2O ligands upon complexation. Figure 3 shows Z_M-bar plotted against pL (-log[Glycine]) representing the number of Glycine ligands bound to the Ni(II) ion at different ligand concentrations. At low pL (high pH) the curves show a significant change in slope and seem to be curling back towards the straight line. This phenomenon is called fanning back and indicates the formation of hydroxyl species (MLOH). The theoretical and experimental data show a high degree of overlap, indicating a good correlation of our results.

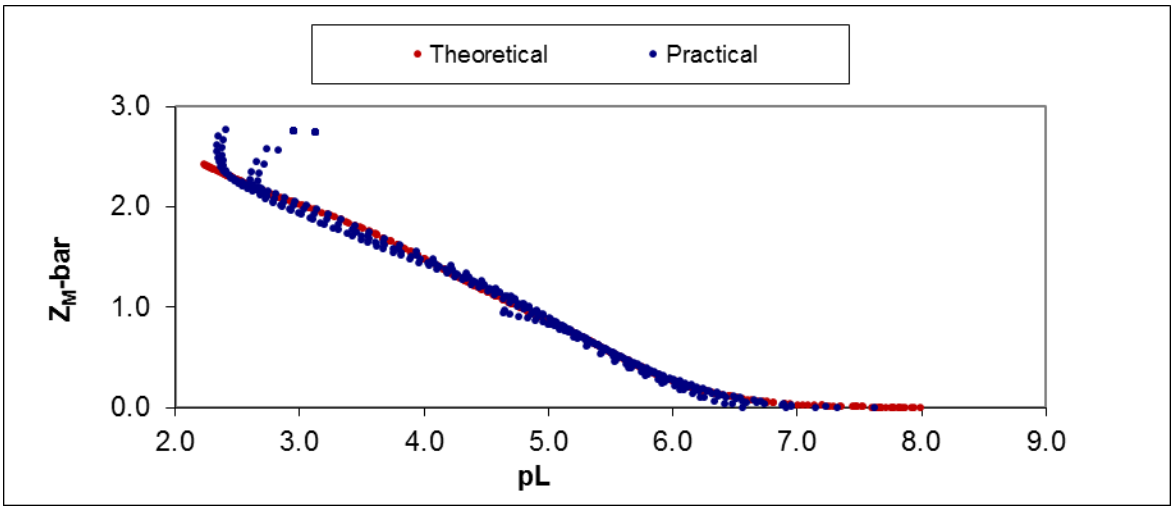


Figure 3. Z_M-bar as a function of pL for Ni(II)/Glycine complex.

Figure 4 shows the plot of n-bar theoretical Q-bar (red) and experimental Q-bar (blue) against pH. The n-bar represents the number of protons bound to the ligand in the absence of Ni(II) at a given pH. Q-bar, as a function of pH, illustrates the number of protons released from the ligand at the corresponding pH value. The zwitterion glycine species is predominant above pH 4 and has one proton bound (see fig. 2). Figure 4 shows a gradual increase in released protons beginning at pH 4 as they are displaced by the competing metal ions that are complexing with the ligand. Above pH 6 another proton is released into solution as the ML species binds an additional glycine ligand to form the NiL_2 complex. The data is inconsistent above pH 9 as the experimental curve strongly deviates from the theoretically simulated values.

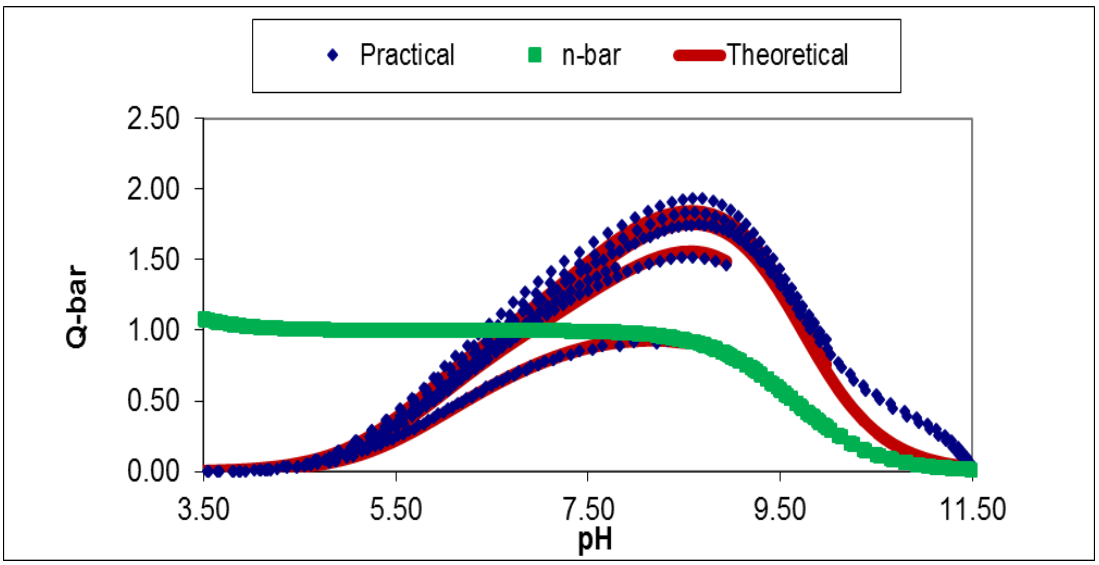


Figure 4. Q_M-bar as a function of pH for Ni(II)/Glycine complex.

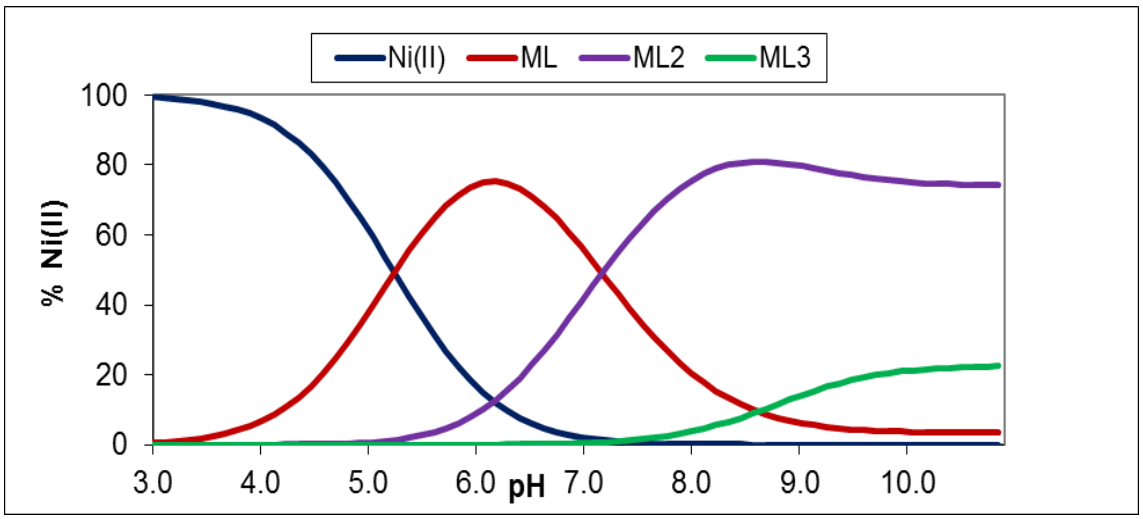


Figure 5. The distribution curve for the Ni(II)/Glycine complex.

The species distribution diagram of Ni(II)/Glycine complexes as a function of pH was calculated using the data in Table 2 is shown in Figure 5. At a pH below 3, only the free Ni(II) ion is present in solution. The pH increases the protons on the glycine ligand are displaced due to their decreasing stability, and the formation of the 1:1 Ni/Gly complex is observed at a pH above 3. We find the highest concentration of the NiL species at pH 6. A further glycine ligand then associates to the Ni(II) metal centre corresponding to the drop in the occurrence of NiL and the

appearance of NiL_2. The NiL_2 species predominates at a pH 8 and experiences a slight decrease in concentration as the third Ni/Gly (NiL_3) species is formed above pH 8.

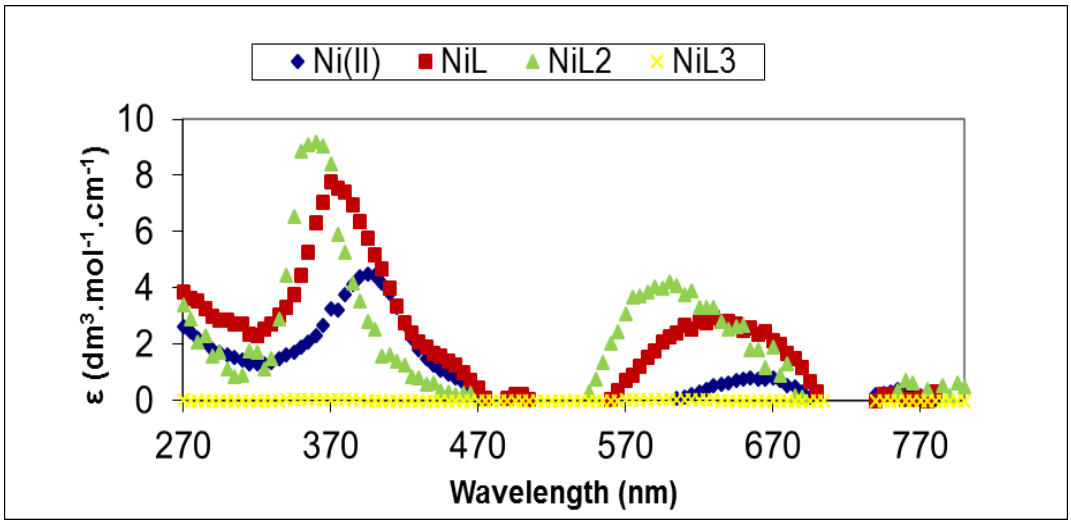
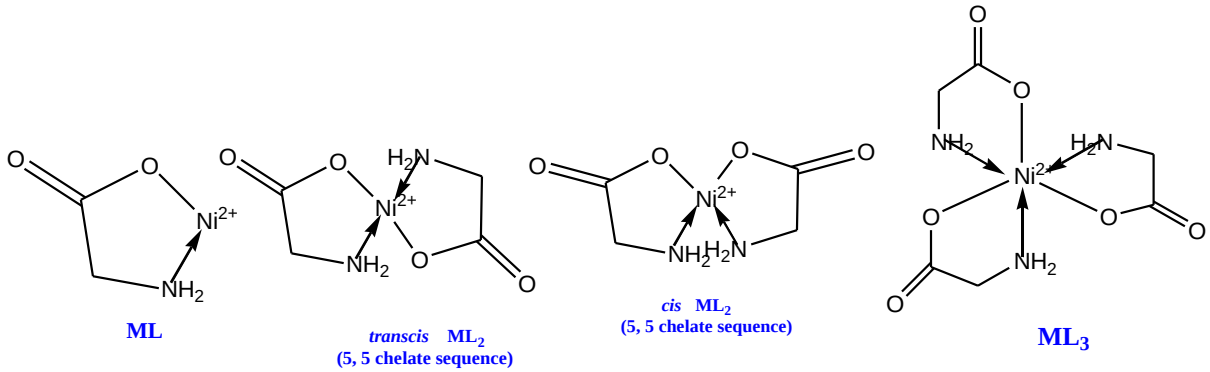


Figure 6. Deconvoluted electronic spectra of individual species.

NiL_2 shows the highest molar absorptivity (molar extinction coefficient) of all complexes formed at pH 7 (9.17 at 360 nm), NiL has the second-highest coefficient with 7.76 at 370 nm which is followed by the free Ni(II) having 4.5 at 395 nm. The NiL_3 species are not formed at pH 7 (significant occurrence only above pH 8), and thus no significant extinction coefficient is determined. We can observe a shift from lower to higher wavelength for maximum absorption going from NiL_2 over NiL to free Ni(II) as the field splitting (Δ_{oct}) increases and light of higher energy is required to achieve the excitation of an electron. (by $E= hc/\lambda$) molar extinction coefficient $\varepsilon = A/\lambda c$ All of the molar extinction coefficients lie in a range of 1-10 $dm^3mol^{-1}cm^{-1}$ which means they are Laport-forbidden, spin-allowed *d-d* transitions occurring in a centrosymmetric octahedral complex. Three transitions are observed in the electronic spectra of the d^8 Ni(II) octahedral complexes. The transitions are from the ground state to the excited states and are all spin allowed [20]. The transitions of each complex around 380 nm are assigned to $^3T_{2g} \leftarrow {}^3A_{2g}$, the transitions around 550 nm correspond to $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ and the lowest energy transitions assigned to $^3T_{1g} \leftarrow {}^3A_{2g}$ are expected to occur at around 900 nm but are not seen in the range of Figure 6.

Conclusion

Glycine was found to forms different Ni(II) complexes in solution and in order to understand the difference in their stability their chemical structures were investigated. The geometries of the various species in solution were successfully determined by potentiometry and spectroscopy. At different pH's the colours of the Ni(II) complexes varied from light yellow to dark. Thermodynamically, The stability of Ni(II) complexes had its maximum at NiL_3 complex. The proposal structures of complexes formed between Ni(II) and Gly in solution by potentiometry and spectroscopy.as the following:



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