Determination of Stability constants Nickel binary and ternary complexes in aqueous DMSO by Potentiometric method

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Abstract. The stability constants of some of the binary and ternary system involving Nickel(II) have been studied. Bis-(pyridyl) benzilidene acts as a primary ligand. Glycine, L-alanine, L-phenylalanine, L-leucine and L-valine were acts as a secondary ligand. The stability constants of complex are calculated by SCOGS computer program. The reported values are ± 0.02 log unit accuracy. The protonation constants values increase with an increasing percentage of dimethyl sulphoxide. Protonation constants values for the glycine, L-valine ternary complexes higher stability constants indicate that inductive effect is predominant than steric effect. Whereas L-Phenylalanine ternary system has high stability constants than other ternary complexes due to stacking interaction between phenyl ring of phenylalanine and phenyl ring of primary ligand. The order of stability constant of ternary systems is Ni(bpb)(phe)2 > Ni(bpb)(leu)2 > Ni(bpb)(val)2 > Ni(bpb)(gly)2.

Keywords: Bis(pyridyl) benzilidene; Stability constants; Nickel(II); Protonation constants;Complex formation:

1.Introduction
Coordination chemistry is a challenge and the most active research field of inorganic chemistry. Metal ion complexation is an interdisciplinary topic with applications in various fields like Biotechnology, Environmental, Geochemical, Biomineralisation, Agriculture, Plant Biochemistry, Medical, Analytical Chemistry Research, Synthetic Chemistry Research etc. Stability constants are well known tools for solution and it is helpful to determine the properties of metal-ligand reactions for chemists and in chemistry. Metals like aluminium are well known by name, and ligands are what the metals are attached to, such as “acetate” (or) “aluminium acetate”, etc. The total concentration of metal can be computed with specialized computation programs. The concentration of metal depends upon the stability constant of the complex and free concentration of the ligand which is dependent to the corresponding pK and pH values. Very low numeric values of stability constant (between negative values and one) mean that the metal-ligand is not only soluble in water but readily dissociates into the metal ionic form. The ligand, yielding essentially all metal in ionic form at pH as low as stomach acid (about pH 2 to 3) and as high as physiological pH 7.4 (The pH of the main extra cellular body fluids such as serum and lymph). Consequently these metallic ions are available for absorption from the digestive tract and allow life to be sustained in the case of metals that are nutrients, and harm life or terminate life, if the metal is a toxin like Cd (Cadmium) or promote tissue (brain and bone) injury in the case of biologically absorbable complexes of Al (Aluminium). The best experimental procedure for the determination of stability constants is the potentiometric or pH metric titration method in which the experimental procedure involves pH metric titration of solutions containing a known amount of the ligand, containing a known amount of free mineral acid in the absence and in the presence of known amount of metal ion at a fixed temperature. By adding requisite amount of an inert salt, viz., NaClO4, NaNO3 or KNO3 etc. the ionic strength is being maintained at a fixed value.
The auxiliary concentration variables, $\bar{n}_{H^+}$, $\bar{n}$, $P^L$, etc., required for the measurement of preliminary values of proton-ligand and metal-ligand constants by Bjerrum’s method are evaluated. By using the pH titration curves (i.e., plots of pH meter readings against volumes of titrant alkali added at the various stages of titration) following the procedure of Irving and Rossotti. Hydrogen ion concentration $[H^+]$, corresponding to the different readings of the pH meter are calculated according to the procedure of Irving et al. by incorporating the correction for mixed solvents whenever these are added. Measured values of stability constant and the other relevant equilibrium constants are calculated by analysis of the formation functions by computational method described in the literature. The value of $\Delta G^o$ (the logarithm to base 10 of the ionic product of water), and $F$ (activity coefficient of $H^+$ ion) are used from literature. Species distribution curves for each of the systems are obtained by plotting the concentrations of the species against different pH values which are obtained from computer calculation. Formation of the complexation equilibria are made on the basis of these distribution curves. Ethanbutol (ETB), reacts with aqueous Cu$^{2+}$, Co$^{2+}$ and Ni$^{2+}$ at pH11 producing $\left[ M(H_2O)_4\right]^{2+}$ (M = Cu, Co) and $\left[ Ni_2(OH)_2(H_2O)_4(ETB)_2\right]^{2+}$. Nickel (II) at pH 9. However, forms $\left[ NiL_4 ETB\right]^{2+}$, where the ligand L is H$_2$O or NH$_3$ depending on whether NaOH or NH$_4$OH is added to maintain the pH. Spectrophotometric and potentiometric studies suggest that metal-ligand (ETB) formation constant is highest in the case of Cu(II), and $\Delta G^o$ accompanying the Cu-ETB complex formation is also the most negative. The Cu(II), Ni(II) and Co(II) complexes have pseudooctahedral structure as is apparent from their solution magnetic susceptibility and ligand field spectra. Cu(II) is exceedingly large for Cu(II), followed by that for Ni(II) and Co(II). The solution data have been coordinated by isolating the Bph$_4$ salts of the complex cations, viz., $\left[ M(H_2O)_4\right]^{2+}ETB(Bph_4)_{2}$ (M = Cu,Co,Ni), $\left[ Ni(NH_3)_4 ETB\right]^{2+}Bph_4)_{2}$, $\left[ Zn(H_2O)_2 ETB\right]^{2+}Bph_4)_{2}$ and $\left[ Ni_2(OH)_2(H_2O)_4(ETB)_2\right]^{2+}Bph_4)_{2}$. These salts were characterised by elemental analysis, molar conductance, magnetic susceptibilities, EPR (for Cu(II) complex), infrared and UV-visible spectroscopy. The mode of coordination of ETB is also supported by the $^1$H NMR data of Zn(II) complex. In vitro study this is quite consistent with the idea that ETB treatment depletes Cu$^{2+}$ in the physiological system. Dichloro – (DCA) and trichloroacetate (TCA) – cyclic ligand Morpholine(Morph)/thiomorpholine(Tmorph)/Methylmorpholine(Mmorph)/dimethyl-piperazine(DMP) complexes of Nickel(II), Copper(II), Zinc(II) and Cadmium(II) with the compositions [Ni(t morph)$_2$ (DCA)$_2$]$_{2}$, [Ni(t morph)$_2$ (TAC)$_2$]$_{2}$, $2H_2O,[Cu(DMP)_2(TCA)]_{2}$, [ML$_2X_2]_nH_2O$ where M = Zn (II) or Cd (II), L = Morph, DMP or t morph and X = DCA or TCA and n=0 except in case of $[Cd(Morph)_2(TCA)]_{2}$ where n=1 have been synthesized. Some intermediate complexes were isolated by temperature arrest technique (pyrolysis) and characterized. Configurational and conformational changes have been discussed by elemental analysis. IR and electronic spectra, magnetic moment data (in the case of Ni(II) and Cu(II) complexes) and thermal analysis. $E^o_n$, $\Delta H$ and $\Delta S$ for the decomposition reaction of these complexes are evaluated and the stability of the complexes is measured and the stability of the complexes with respect to activation energy is also been compared. A linear correlation are found between $E^o_n$ and $\Delta S$ for the decomposition of the complexes. Bis(pyridyl) benzilide is most important in the biological application and electro chemical properties. From the literature survey no works have been made to study the formation constants of Ni(II) complexes are determined by potentiometric method in DMSO-water medium. The formation constants of the complexes are discussed in terms of medium and the nature of the secondary ligand.

2. Experimental section

2.1 Materials and physical measurements

All reagent or analytical grade chemicals and solvents were purchased from commercial sources and used without further purification. E. Merck sample of sodium hydroxide was dissolved in double distilled water in a pyrex flask. The solution was standardized potentiometrically against a
standard oxalic acid solution. The stock solution of nitric acid was prepared by diluting AR BDH sample to required concentration and titrated potentiometrically against standard alkali solution. Dimethyl sulphoxide (DMSO) was purified by standard method[14]. An AR, BDH sample of potassium nitrate (KNO₃) was dissolved in double distilled water to make the stock solution of strength 1 mol dm⁻³.

2.2 Preparation of Bis(pyridyl) benzilidene (bpb)

An equal molar mixture benzil (0.05 mol dm⁻³) and 2-amino pyridine (0.05 mol dm⁻³) were mixed in 100 mL of ethanol containing 1 mL of acetic acid and refluxed for 9 hr and cooled the solution at room temperature. Then, poured into deionised water, filtered in a buckner funnel. The residue was recrystallised from 50% benzene-pet-ether. The colorless product was filtered in a buckner funnel, dried and recrystallised from benzene pet-ether (40 – 60°C). Yield was 50% (MP 79°C). The purity of the product was checked by TLC method.

2.3 Apparatus

A digital pH/mv meter and accessories having a combined glass-calomel electrode assembly were used in the present investigation. Before starting a titration and after completion of the titration, the pH meter was calibrated with the buffer solution (0.05 mol dm⁻³ potassium hydrogen phthalate).

2.4 Metal ion solution

Approximately 0.04 mol dm⁻³ stock solution of nickel was prepared and standardized.[15]

2.5 Calibration of pH meter in DMSO water medium

A mixture of 57% (v/v) DMSO-water medium was used, since the chelates formed are relatively insoluble in water. Therefore, it was necessary to calibrate the pH meter in DMSO-water medium. To accomplish the following concentration of nitric acid in 57% (v/v) DMSO-water medium were prepared (total volume 30 mL) and pH meter readings (B) values were determined in all cases. To get the correct hydrogen ions concentration in DMSO-water medium, calibration of glass electrode was done. For this, various known concentration of nitric acid in 57% (v/v) DMSO-water was prepared and pH meter readings (B) were determined in all cases. Van Uitert and Hass[16] were shown that the more general relation between hydrogen ion concentration.

\[-\log [H^+] = B + \log f + \log U_H^0\] … (1)

and pH meter reading B is equally valid for water and for DMSO-water medium. Here the activity coefficients (f) of hydrogen ions in the solvent mixture were considered at the same temperature and ionic strength. For water, \(U_H^0 = 1\) and unit activity coefficient in mixed solvent system. Equation (1) showed to calibrate the pH meter in the particular solvent system. From the known concentration of nitric acid, pH was calculated. The following observed values of pH are given in Table 1.

| Concentration of \(H^+\) | Calculated pH | Observed pH |
|--------------------------|---------------|-------------|
| \(1.48 \times 10^{-3}\) | 2.83          | 3.07        |
| \(2.886 \times 10^{-3}\)| 2.55          | 2.89        |
| \(3.97 \times 10^{-3}\) | 2.42          | 2.71        |
| \(5.390 \times 10^{-3}\)| 2.26          | 2.58        |
| \(6.470 \times 10^{-3}\)| 2.18          | 2.55        |
| \(7.592 \times 10^{-3}\)| 2.10          | 2.48        |

-\(\text{Intercept} = -0.81\)
-\(r = 0.998\)

These results indicate that actual pH values are obtained from equation (1).The following mixture a, b, c, d, e and f were prepared from each system and titrated against standard alkali solution using Bjerrum-Calvin pH titration technique.

a) 0.0041652 mol dm⁻³ of nitric acid 3 mL of + 0.1 mol dm⁻³ of potassium nitrate 3 mL + 6 ml of water + 17 mL of DMSO.
b) 0.0041652 mol dm⁻³ of nitric acid 3 mL + 0.1 mol dm⁻³ of potassium nitrate 3 mL + 0.0015 mol dm⁻³ of secondary ligands (α-amino acids) 1.5 mL + 5.5 ml of water + 17 mL of DMSO.
c) 0.0041652 mol dm\(^{-3}\) of nitric acid 3 mL + 0.1 mol dm\(^{-3}\) of potassium nitrate 3 mL + 0.0014779 mol dm\(^{-3}\) of primary ligand 3 mL + 0.00038 mol dm\(^{-3}\) of Ni\(^{2+}\) 3 mL + 4 mL of water + 14 mL DMSO.

e) 0.0041652 mol dm\(^{-3}\) of nitric acid 3 mL + 0.1 mol dm\(^{-3}\) of potassium nitrate 3 mL + 0.0015 mol dm\(^{-3}\) of secondary ligand (\(\alpha\)-amino acids) 1.5 mL + 0.00038 mol dm\(^{-3}\) of Ni\(^{2+}\) 3 mL + 2.5 mL of water + 17 mL of DMSO.

f) 0.0041652 mol dm\(^{-3}\) of nitric acid 3 mL + 0.1 mol dm\(^{-3}\) of potassium nitrate 3 mL + 0.0014779 mol dm\(^{-3}\) of primary ligand 3 mL + 0.0015 mol dm\(^{-3}\) of secondary ligand (\(\alpha\)-amino acids) 1.5 mL + 0.00038 mol dm\(^{-3}\) of Ni\(^{2+}\) 3 mL + 2.5 mL of water + 14 mL of DMSO.

The sodium hydroxide was added from micro burette. The mole ratio of metal to ligand was kept as 1:2:2 in order to fulfill maximum coordination number of the metal ion. The total volume was kept as 30 mL in each case. The temperature of the solution in the titration vessel maintained at 30 \(\pm\) 0.01°C with the help of thermostat.

3. Results and discussion

3.1 Synthesis and characterization

The Bis(pyridyl) benzilidene is most important in the biological application and electrochemical properties. From the literature survey no works have been made to study the formation constants of Ni(II) complexes are determined by potentiometric method in DMSO-water medium. The formation constants of the complexes are discussed in terms of medium and the nature of the secondary ligand.

3.2 UV-spectral studies

Condensation of benzil and 2-aminopyridine was conformed after comparing the ligand spectrum with those of starting materials. The ketogroup of benzil exhibits a band around 285 nm in ethanol medium. This band is disappeared and two new bands are appeared in the ligand at 301 and 245 nm (Fig. 1). This indicates that n \(\rightarrow\) n\(^*\) and \(\pi\) \(\rightarrow\) \(\pi^*\) exist in the ligand [17].

3.3 FT-IR spectral studies

FT-IR spectrum of primary ligand is displayed in Fig. 2. A strong band appeared at 3264 cm\(^{-1}\) assigned to \(\nu\)OH a band at 3062 and 3026 cm\(^{-1}\) ascribed to CH stretching vibration of phenyl and pyridyl ring [18]. A sharp intense band at 1671 cm\(^{-1}\) is assigned to azomethine group present in the compound. A strong intense band at 1598 cm\(^{-1}\) and 1574 cm\(^{-1}\) indicates the C-N stretching vibration. A band at 702 cm\(^{-1}\) is attributed to stretching vibration of CH in phenyl and pyridyl ring.
3.4 Structures of ligands

Scheme and Structure of the primary ligand \( bpb \) is Bis-(pyridyl)benzilidene

The following ligands are used as secondary ligands:

- **Glycine (Gly)**
- **L-Alanine (Ala)**
- **L-Phenylalanine (Phe)**
- **L-Leucine (Leu)**
- **L-Valine (Val)**
3.5 Protonation constants of primary and secondary ligands

The computations of the protonation constants of the \( \alpha \)-amino acids and \( \text{bis}(\text{pyridyl})\text{benzilidene} \) \((\text{bpb})\) and the stability constants of Ni-bpb and its ternary complexes from potentiometric data were carried out with SCOGS computer program. The program SCOGS was used to minimize the standard deviation of the fit (\( \sigma \) fit) between the observed and calculated pH values for the overall titration data\[19,20\]. The protonation constants of glycine (\( \text{gly} \)), L-leucine (\( \text{leu} \)), L-valine (\( \text{val} \)), L-phenylalanine (\( \text{phe} \)) and the stability constants of the Ni(II) complexes are given in Table-2. The values are listed in this Table 2-4 related to the following equilibria. For \( \alpha \)-amino acids,

\[
A^- + H^+ \rightleftharpoons AH (A^- H^+) ; \quad K_{\text{H}}^1 = \frac{[HA]}{[A^-][H^+]} \quad \ldots \quad (1)
\]

\[
HA + H^+ \rightleftharpoons H_2A^+ ; \quad K_{\text{H}}^2 = \frac{[H_2A^+]}{[HA][H^+]} \quad \ldots \quad (2)
\]

Where \( A^- \) stands for the anionic form of the \( \alpha \)-amino acids and \( HA \) the neutral molecule. The constants \( H_1pK \) and \( H_2pK \) are related to the protonations of the amino nitrogen and the carboxyl oxygen, respectively. But, \( H_1pK \) values of secondary ligand not much affected with respect to solvent composition.

When the change of \( \log K_{\text{H}}^2 \) with solvent composition, given in Table-2 is examined for \( \alpha \)-amino acids. It is observed that these values increase with an increasing percentage of dimethyl
sulphoxide. This can be explained by structural changes in the amino acids as the medium become more like dimethyl sulphoxide rich media. In water rich media, however, the reverse will be the case (Table 3). Therefore, one can conclude that the polar form of amino acids, $\text{H}^-\text{A}^-$, dominates to a lesser extent in the dimethylsulphoxide-water medium than in alcohol-water\cite{21}. The primary reason for this is attributed to the stronger salvation of the carboxylated anion in water compared to dimethyl sulphoxide with the solvation of the ammonium ion being similar in the two solvents\cite{22}. Many studies have shown that the equilibrium constant is linearly related to this fraction of the organic solvent\cite{23-27}. The results obtained in this study support this observation.

Table 2: Protonation-ligand and metal-ligand stability constants of binary Ni(II) complexes in aqueous-DMSO medium

| Ligand       | $pK_1$ | $pK_2$ | $\log K_{\text{NiA}}$ | $\log K_{\text{NiA_2/NiB}}$ |
|--------------|--------|--------|------------------------|-----------------------------|
| $\text{bpb}$ | 4.84   | -      | 2.89                   | 4.96                        |
| glycine      | 9.69   | 3.03   | -                      | 14.95                       |
| L-phenylalanine | 9.05   | 3.29   | -                      | 16.33                       |
| L-leucine    | 9.66   | 3.62   | -                      | 15.31                       |
| L-valine     | 9.78   | 4.69   | -                      | 15.42                       |

All the values are $\pm 0.02 \log K$ unit accuracy

Table 3: Protonation-ligand and stability constants of binary Metal(II) complexes in aqueous medium*

| Ligand       | $pK_1$ | $pK_2$ | $\log K_{\text{ML}}$ | $\log K_{\text{ML_2}}$ |
|--------------|--------|--------|-----------------------|-------------------------|
| glycine      | 9.60   | 2.31   | 5.22                  | 4.37                    |
| L-leucine    | 9.67   | 2.83   | 4.74                  | 4.16                    |
| L-phenylalanine | 8.80   | 2.20   | 4.70                  | 3.72                    |
| L-valine     | 9.60   | 2.31   | 4.74                  | 4.24                    |

$^*$ M.R. Patel, Nitin Patel, Mohan Patel and J.D. Joshi, \textit{J. Indian Chem. Soc.}, 70,569-572 (1993).

Table 4: Stability constants of ternary complexes of Ni(II) complexes in DMSO-water medium

| B (Secondary) | $\log K_{\text{NiA}}$ | $\log K_{\text{NiB}}$ | $\log K_{\text{NiA_2}}$ | $\log K_{\text{NiA_2/NiB}}$ | $\Delta \log K$ |
|---------------|-----------------------|-----------------------|-------------------------|-----------------------------|----------------|
| glycine       | 12.71                 | 2.20                  | 15.59                   | -4.54                       |
| L-phenylalanine | 20.12               | 7.50                  | 22.91                   | +0.21                       |
| L-leucine     | 18.38                 | 10.84                 | 21.17                   | -5.74                       |
| L-valine      | 14.29                 | 3.50                  | 17.06                   | -3.26                       |

All the values are $\pm 0.02 \log K$ unit accuracy

3.6 Stability constant of binary and ternary complexes

When a metal ion is in equilibrium with two different ligands, here $\text{bpb}$ (primary) and $\alpha$-amino acids (secondary) which can form ternary complexes with metal ion, equilibria (1-5) forming simple non-protonated \textit{bis} complexes will be represented in the following equations

$$\text{Ni}(\text{bpb}) + \text{bpb} \rightleftharpoons [\text{Ni}(\text{bpb})_2] \quad \ldots \quad (1)$$
$$\text{Ni}(\text{bpb}) + \text{gly} \rightleftharpoons [\text{Ni}(\text{bpb})(\text{gly})] \quad \ldots \quad (2)$$
$$\text{Ni}(\text{gly})(\text{gly}) + \text{gly} \rightleftharpoons [\text{Ni}(\text{gly})(\text{gly})_2] \quad \ldots \quad (3)$$
$$\text{Ni}(\text{gly}) + \text{bpb} \rightleftharpoons [\text{Ni}(\text{bpb})(\text{gly})] \quad \ldots \quad (4)$$
$$\text{Ni}(\text{gly})(\text{gly}) + \text{gly} \rightleftharpoons \text{Ni}(\text{bpb})(\text{gly})_2 \quad \ldots \quad (5)$$

Sigel\cite{54}, two equilibrium constants involved in ternary complexes can be defined as

$$\Delta \log K = \log K_{\text{Ni}(\text{bpb})(\text{gly})_2} - \log K_{\text{Ni}(\text{bpb})(\text{gly})} \quad \ldots \quad (5a)$$
$$= \log K_{\text{Ni}(\text{gly})(\text{gly})_2} - \log K_{\text{Ni}(\text{bpb})(\text{gly})} \quad \ldots \quad (6)$$
The ligand’s affinity that to metal ion or to the complex of [Ni bpb], since is due to more co-ordination sites available for bonding the first ligand to a metal ion than for the second ligand. The $\Delta \log K$ should, in general, negative with Ni$^{2+}$ usually having a co-ordination number of four. The expected value for $\Delta \log K = -0.6$, but the value markedly greater than this is demonstrating a stabilisation of the ternary complex. In fact, positive values mean that it prefers to bond to the complex [Ni bpb] rather to a disproportionation complexes. Statistically, a value of $\log 4$ is to be expected, so that the value for $\log X$ are greater than 0.6 suggest that stabilisation of the ternary complexes. The value of $\log X$ is clearly dependent on the stability of the binary biscomplexes and since these biscomplexes are not intermediate the formation of the ternary complexes$^{[28]}$, the value of $\log X$ may not truly reflect the stability of the mixed ligand complex. However, $\log X$ will tend to be less dependent than $\Delta \log K$ on differences in the charges on ligands Ni $bpb$ (A) and gly(B). Hence, the choice between using $\Delta \log K$ and $\log X$ to give a measure of the stabilisation of ternary complexes, the depend on the particular composition being made.

The stability constants of Ni $bpb$ binary system was determined under similar experimental conditions of $\alpha$-amino acid with Ni(II) systems (Table 2). The $\beta$-values obtained for 1:1 and 1:2 Ni-$bpb$ complex compared with amino acid – Ni binary system. The stability constants of Ni $bpb$ much lesser than Ni($\alpha$-amino acids)$_2$. But, in aqueous DMSO medium formation constants of amino acid binary systems have higher value than in aqueous medium (Table 3). It appears that complex formation between $bpb$ and Ni(II) in the Ni ($bpb$) ($\alpha$-amino acid)$_2$ species involves the formation of chelate ring. The comparison of $\log K^{NiA}_{NiAB}$ (Table 4) and $\log K^{NiB}_{NiAB}$ clearly indicates that all the ligands form five members chelate ring in the NiAB$_2$ complex species. Thus, NiAB$_2$ species would contain five members chelate ring since more co-ordination positions are available for binding the first ligand to metal ion than for second ligand, the high negative values for $\Delta \log K^{NiAB}_2$ indicates that probably stepwise formation of ternary complex. In our present investigation, the $\Delta \log K^{NiAB}_2$ value is negative for glycine, valine and leucine whereas the $\Delta \log K^{NiA}_{NiAB}$ value is positive for phenylalanine ternary systems.

$$\begin{align*}
\text{NiA} + \text{B} & \rightleftharpoons \text{NiAB} \\
\text{NiAB} + \text{B} & \rightleftharpoons \text{NiAB}_2 \\
\Delta \log K^{NiA}_{NiAB}_2 & = \log \beta^{NiA}_{NiAB} - (\log \beta^{NiA} + \log \beta^{NiB})
\end{align*}$$

This indicates that binary Ni-glycine/ L-phenylalanine/L-leucine/L-valine (B) prefers to add to Ni-$bpb$($\alpha$-amino acid) ternary complex rather than to aquted Ni(II). Also, the positive $\Delta \log K^{NiB}_{NiAB}_2$ values suggest that formation of ternary complex, NiAB$_2$ is preferred over the binary complex of NiA or NiB for L-phenylalanine which act as a secondary ligand. Using the stability constants obtained in this work, the effect of substituent in secondary ligand on the complex formation of Ni(II)-$bpb$-$\alpha$-amino acids has been discussed. The $\log \beta$ values for Ni(II) complexes show the nature of $\alpha$-amino acid attached to Ni-$bpb$ system. $\log \beta^{NiA}_{NiAB}_2$ values (Table 4) for the glycine, L-valine ternary complexes higher stability constants indicate that inductive effect is predominant than steric effect. Whereas L-Phenylalanine ternary system has high stability constants than other ternary complexes due to stacking interaction between phenyl ring of phenylalanine and phenyl ring of primary ligand.

### 3.7 Species distribution curves

Estimation of equilibrium concentrations of Ni(II) complexes as a function of pH provides a useful picture of metal ion binding in solutions. The concentrations of the ternary complexes increase with increasing pH (Figs. 7-11). The species distribution pattern for Ni-$bpb$ ($\alpha$-amino acid)$_2$ exists in the non-protonated form. The diagram also shows that only Ni(bpb) ($\alpha$-amino acid)$_2$ species exist in all ternary systems under our experimental conditions.
Fig. 7. Species distribution curves for Ni-val system, pH Vs percentage of species

Fig. 8. Species distribution curves for Ni-bpb-gly system, pH Vs percentage of species

Fig. 9. Species distribution curves for Ni-bpb-phe system, pH Vs percentage of species

Fig. 10. Species distribution curves for Ni-bpb-leu system, pH Vs percentage of species

Fig. 11. Species distribution curves for Ni-bpb-val system, pH Vs percentage of species
4. Conclusion

It is concluded that the presented knowledge is very important. Primary ligand bis(pyridyl) benzilidene was prepared by the condensation of benzil with 2-aminopyridine. The ligand was characterized by microanalysis, UV and FT-IR, melting point, and TLC methods. Glycine, L-phenylalanine, L-leucine and L-valine were used as secondary ligands. The protonation constants, stability constants of binary and ternary systems are calculated by SCOGS computer program. The reported values are ± 0.02 log unit accuracy. The protonation constants of secondary ligand of carbonyl group are higher in aqueous DMSO medium than in aqueous medium. Solvent composition influences the formation constants of binary systems due to the higher stability constant of amino acid Ni system in aqueous DMSO medium than in aqueous medium. Among the ternary systems, phenylalanine ternary system has higher stability constant than other ternary systems employed under this investigation, because of the stacking interaction of phenyl ring of phenylalanine with the phenyl ring of primary ligand. The overall stability constants of ternary systems reveal that ternary complex formation is more favored than binary complex formation. The species distribution diagram shows that ternary complex species are more favoured than binary one. The order of stability constant of ternary systems is Ni(bpb)(phe)₂ > Ni(bpb)(leu)₂ > Ni(bpb)(val)₂ > Ni(bpb)(gly)₂.

Competing interests

The authors declare that they have no challenging interests.

Authors’ contributions

All authors read and sanctioned the final manuscript.

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