JOTCS A
Journal of the Turkish Chemical Society
Section: A
Chemistry
TURKISH CHEMICAL SOCIETY

EQUILIBRIUM STUDIES ON Ni(II) and Cu(II) COMPLEXES with 4,7-DIMETHYL-1,10-PHENANTHROLINE and ACIDIC AMINO ACIDS in AQUEOUS SOLUTION

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Abstract: The aim of this study is to determine the protonation constants of selected ligands {4,7-dimethyl-1,10-phenanthroline (4,7-dmphen), aspartic acid (asp), and glutamic acid (glu)} and their stability constants of (1:1) and (1:1:1) complexes with Ni(II) and Cu(II) ion have been determined I = 0.1 M KCl and T = 298.15 K. The protonation constants of the 4,7-dmphen, asp, and glu and their stability constants of the (1:1) and (1:1:1) Ni(II) and Cu(II) complexes have been computed performing BEST program. Moreover, SPE program has been used to determine the distribution of the species occurred in aqueous solution medium. The stability constants of the (1:1:1) Ni(II) and Cu(II) complexes are compared with those of the corresponding to the stability of the (1:1) Ni(II) and Cu(II) complexes with regard to Δlog *K* values.

Keywords: Nickel(II), copper(II), 4,7-dimethyl-1,10-phenanthroline, acidic amino acids, potentiometric methods.

Submitted: June 25, 2020. **Accepted:** August 25, 2020.

Cite this: İNCİ D. EQUILIBRIUM STUDIES ON Ni(II) and Cu(II) COMPLEXES with 4,7-DIMETHYL-1,10-PHENANTHROLINE and ACIDIC AMINO ACIDS in AQUEOUS SOLUTION. JOTCSA. 2020;7(3):755–88.

DOI: https://doi.org/10.18596/jotcsa.757923.

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INTRODUCTION

Research on the acidity constants of molecules and their stability constant of metal ions are increasingly becoming more significant and could give an idea about the role of metal ions in biological systems (1). Investigation on the stability of the ternary metal complexes could help against figuring out the driving forces which induced complex formation in biological systems (2-4). As known, the interactions of peptides, proteins, and enzymes with metal ions are of biochemical significance on the other hand they are yet to be entirely understood. For this reason, explanation of this situation in the biological systems could be likely by the determination of acidity constants of the molecules along with their stabilities of metal complexes (5).

4,7-Dimethyl-1,10-phenanthroline (4,7-dmphen) is a chelating agent and has structural features such as being a rigid planar and hydrophobic molecule. Aspartic acid (asp) and glutamic acid (glu), being acidic amino acids, play significant roles in the enzyme active centers, along with in sustaining the solubility and ionic character of proteins. Many studies in the literature have focused on experimentally and computationally determining the protonation constant of ligands and their stability constants of the complexes formed with metal ions (6-8). Recently, we have reported that (1:1) and (1:1:1) palladium(II) and copper(II) complexes of amino acids, 1,10-phenanthroline, and derivatives in aqueous solution (9-14). As a continuation of these studies, the protonation constants of the 4,7-dmphen, asp and glu (Figure 1) and their stability constants of (1:1) and (1:1:1) Ni(II) and Cu(II) complexes have been computed by potentiometric titration methods (T = 298.15 K and I = 0.1 M KCl). The protonation constants of 4,7-dmphen, asp, and glu and their stability constants of the (1:1) and (1:1:1) Ni(II) and Cu(II) complexes have been computed with the BEST program (15) and the

species distribution of (1:1) and (1:1:1) Ni(II) and Cu(II) complexes in these systems was assessed using the SPE program (15). Thus, the tendency of Ni(II) and Cu(II) ions and 4,7-dmphen, asp, and glu to form the (1:1) and (1:1:1) Ni(II) and Cu(II) complexes was identified by calculating their $\log_{10}K$ values.

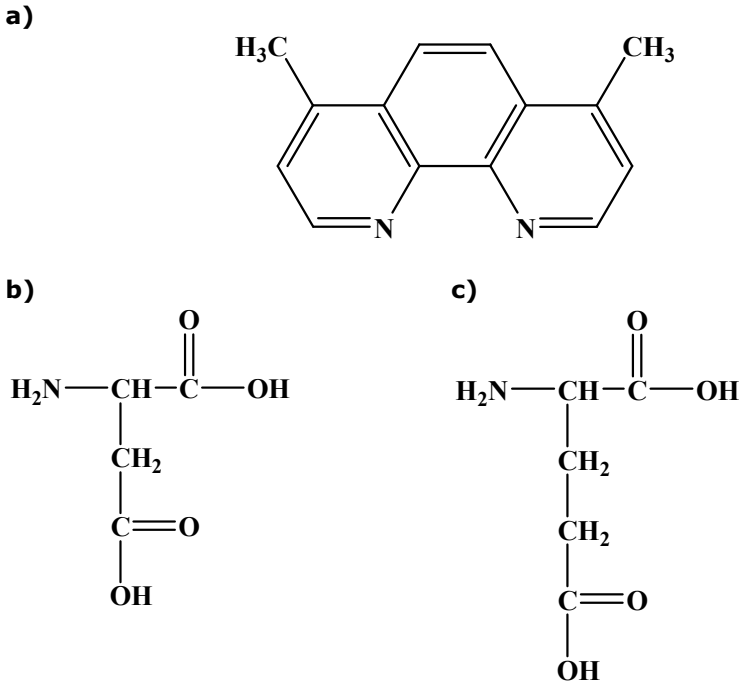


Figure 1. The structures of the ligands used in this study: **a)** 4,7-dimethyl-1,10-phenanthroline (4,7-dmphen) **b)** aspartic acid (asp) **c)** glutamic acid (glu)

EXPERIMENTAL

All ligands and Ni(II) chloride and Cu(II) chloride utilized in this experimental study were purchased from Sigma-Aldrich and the aqueous solution was treated with excess HCl to obtain protonated species. The all experimental details such as instruments, electrode calibration, and data processing were similar to those described in our previous studies (9-14).

The stability constant of the (1:1) and (1:1:1) Ni(II) and Cu(II) complexes, β_{pqrs}, is defined by equations 1 and 2, where *p, q, r,* and *s* are the moles of M(II), 4,7-dmphen, asp/glu and proton (H), respectively, $M_p(4,7\text{-dmphen})_q(\text{asp/glu})_rH_s$ (charges are neglected for clarity).

$$pM + q(4,7\text{-dmphen}) + r(asp/glu) + sH \overset{\beta_{pqrs}}{\rightleftharpoons} M_p(4,7\text{-dmphen})_q(asp/glu)_rH_s \quad (1)$$

$$\beta_{pqrs} = \frac{[M_p(4,7\text{-dmphen})_q(asp/glu)_rH_s]}{[M]^p[4,7\text{-dmphen}]^q[asp/glu]^r[H]^s} \quad (2)$$

RESULTS AND DISCUSSION

Protonation constants of 4,7-dmphen/acidic amino acids

The protonation constant of 4,7-dmphen was previously reported our research group under the same conditions (10). The values of protonation constants for acidic amino acids (asp and glu) were also determined under the same experimental conditions. In these measurements, experimental results are compatible with the literature values (Table 1), according to the differences such as in ionic strength, ionic medium, temperature, etc. (14, 16-17). Potentiometric titration curves of the 4,7-dmphen, asp, and glu are illustrated in Figures 2 and 3, where *m* is base moles added per mole of ligand. The BEST program, which could be one of the most useful computer programs for detection of the acidity constants of molecules and stability constant of the metal complexes from potentiometric data, was used to detect the protonation constants of the 4,7-dmphen, asp, and glu from potentiometric titration data (15).

Table 1. Protonation constants of the selected ligands.

Ligands	$\log_{10}K_1$	$\log_{10}K_2$	Ref
4,7-dmphen	5.89	0.61	(10), 5.95 (16), 5.94 (17)
Asp	9.64 ± 0.02*	3.73 ± 0.04*	9.66; 3.70 (14)
Glu	9.51 ± 0.02*	4.23 ± 0.03*	9.58; 4.16 (14)

*This work. Refs (10) and (14) are our previous studies.

(1:1) complexes of Ni(II) and Cu(II) with 4,7-dmphen/acidic amino acids

The titration curves of Ni(II):(4,7-dmphen) systems are illustrated in Figures 2 and 3. The observed decline in the (1:1) $[Ni(4,7\text{-dmphen})]^{2+}$ curve in comparison to the 4,7-dmphen solution curve alone displays the formation of the (1:1) $[Ni(4,7\text{-dmphen})]^{2+}$. Furthermore, the point of inflection observed at *m* = 2.0 demonstrated that $[Ni(4,7\text{-dmphen})]^{2+}$ was formed. $[Ni(4,7\text{-dmphen})(OH)]^{+}$ starts to occur after *m* = 2.0 and is illustrated by the dashed line in Figures 2 and 3. The equilibrium in the Ni(II):(4,7-dmphen) systems could be defined by the following equations (the overall stability constant of the $[Ni(4,7\text{-dmphen})]^{2+}$ is β, the stepwise stability constant is *K*).

$$Ni^{2+} + H_2(4,7\text{-dmphen})^{2+} \rightleftharpoons [Ni(4,7\text{-dmphen})]^{2+} + 2H^+ \quad (3)$$

$$[Ni(4,7\text{-dmphen})]^{2+} + H_2O \overset{K_{[Ni(4,7\text{-dmphen})(OH)]^+}}{\rightleftharpoons} [Ni(4,7\text{-dmphen})(OH)]^+ + H^+ \quad (4)$$

$$K_{[Ni(4,7\text{-dmphen})(OH)]^+} = \frac{[Ni(4,7\text{-dmphen})(OH)][H^+]}{[Ni(4,7\text{-dmphen})^{2+}]}$$

$$Ni^{2+} + 4,7\text{-dmphen} \overset{\beta^{Ni}_{Ni(4,7\text{-dmphen})}}{\rightleftharpoons} [Ni(4,7\text{-dmphen})]^{2+} \quad (5)$$

$$\beta^{Ni}_{Ni(4,7\text{-dmphen})} = \frac{[Ni(4,7\text{-dmphen})^{2+}]}{[Ni^{2+}][4,7\text{-dmphen}]}$$

The stability constant of the (1:1) [Ni(4,7-dmphen)]$^{2+}$ was computed using the BEST program (12). The experimental results were compared with the literature data and the stability constant of the binary [Ni(4,7-dmphen)]$^{2+}$ is given in Table 2. Potentimetric titrations of the Cu(II):(4,7-dmphen) system was previously reported our research group under the same conditions (10).

The potentimetric titrations of the (1:1) molar ratios M(II):(asp/glu) {M: Ni(II) or Cu(II)} systems were performed (Figures 2 and 3). The observed decline in the (1:1) [M(asp/glu)]$^{+}$ curve in comparison to the alone acidic amino acids (asp and glu) solution curve demonstrates the formation of the (1:1) [M(asp/glu)]$^{+}$. This could be clarified by the release of proton from the coordinated acidic amino acids. The inflection point, at *m* = 2.0, demonstrated that the (1:1) [M(asp/glu)]$^{+}$ was formed. After formation of the [M(asp/glu)]$^{+}$, the titration curve shifting because of the formation of the [M(asp/glu)(OH)] complex. This complex starts to occur after *m* = 2.0 and is illustrated by the dashed line in Figures 2 and 3. The equilibria contained in the M(II):(asp/glu) systems could be defined by the following equations.

$$M^{2+} + H_2(asp/glu)^{+} \rightleftharpoons [M(asp/glu)]^{+} + 2H^{+} \quad (6)$$

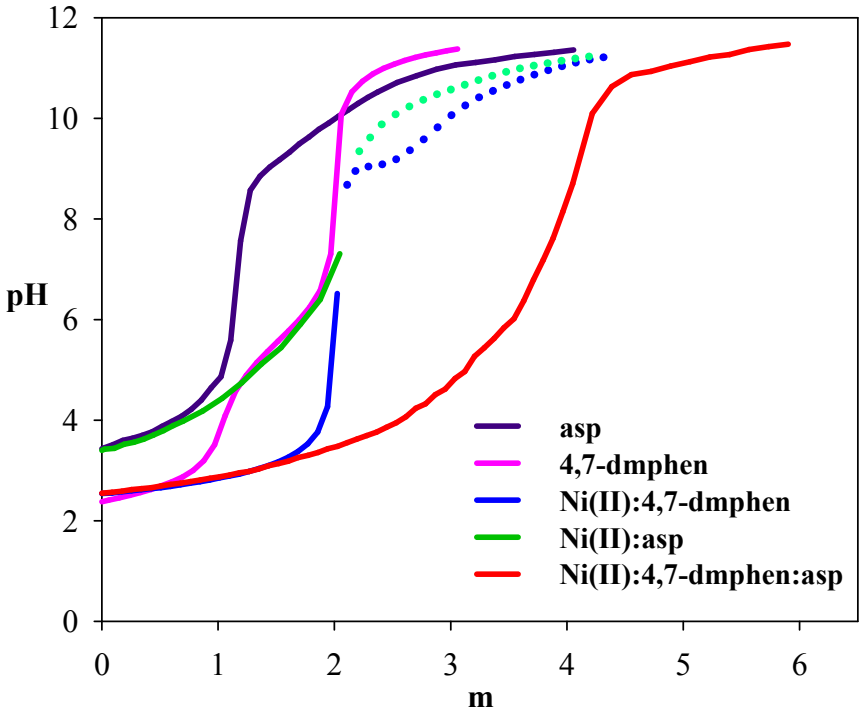
$$[M(asp/glu)]^{+} + H_2O \overset{K^{[M(asp/glu)]^{+}}_{[M(asp/glu)(OH)]}}{\rightleftharpoons} [M(asp/glu)(OH)] + H^{+} \quad (7)$$

$$K^{[M(asp/glu)]^{+}}_{[M(asp/glu)(OH)]} = \frac{[M(asp/glu)(OH)][H^{+}]}{[M(asp/glu)^{+}]}$$

$$M^{2+} + (asp/glu)^{-} \overset{\beta^{M}_{M(asp/glu)}}{\rightleftharpoons} [M(asp/glu)]^{+} \quad (8)$$

$$\beta^{M}_{M(asp/glu)} = \frac{[M(asp/glu)^{+}]}{[M^{2+}][(asp/glu)^{-}]}$$

Taking the likely species into consideration, the stability constants of the (1:1) [M(II):(asp/glu)]$^{+}$ complexes were computed performing the BEST program (15). Table 2 compares the stability constant of the (1:1) [M(II):(asp/glu)]$^{+}$ with literature displaying a good agreements [14,16, 18-20].



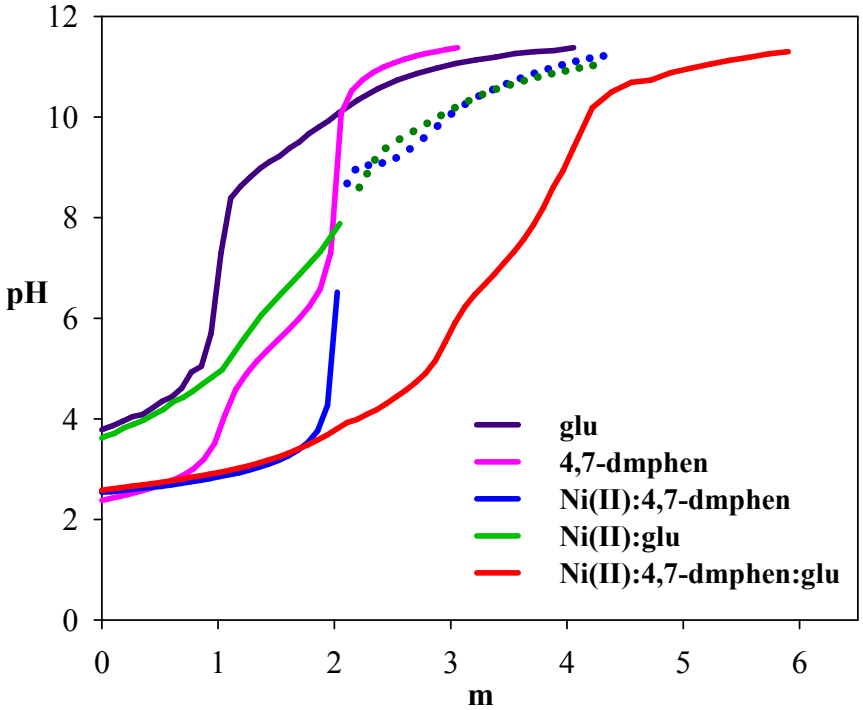
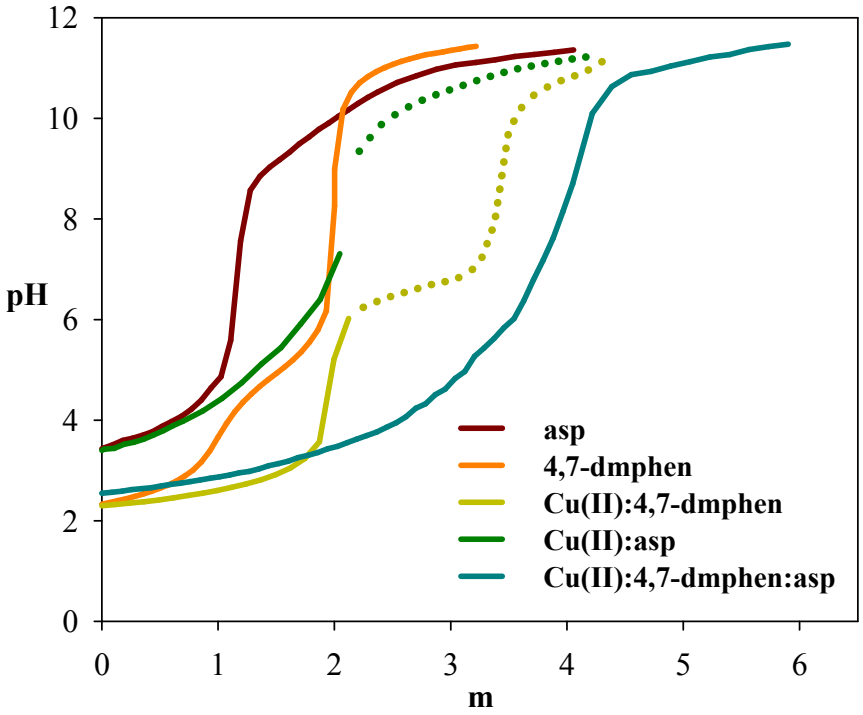


Figure 2. Potentiometric titration curves of the Ni(II):(4,7-dmphen):(asp) and Ni(II):(4,7-dmphen):(glu) systems.



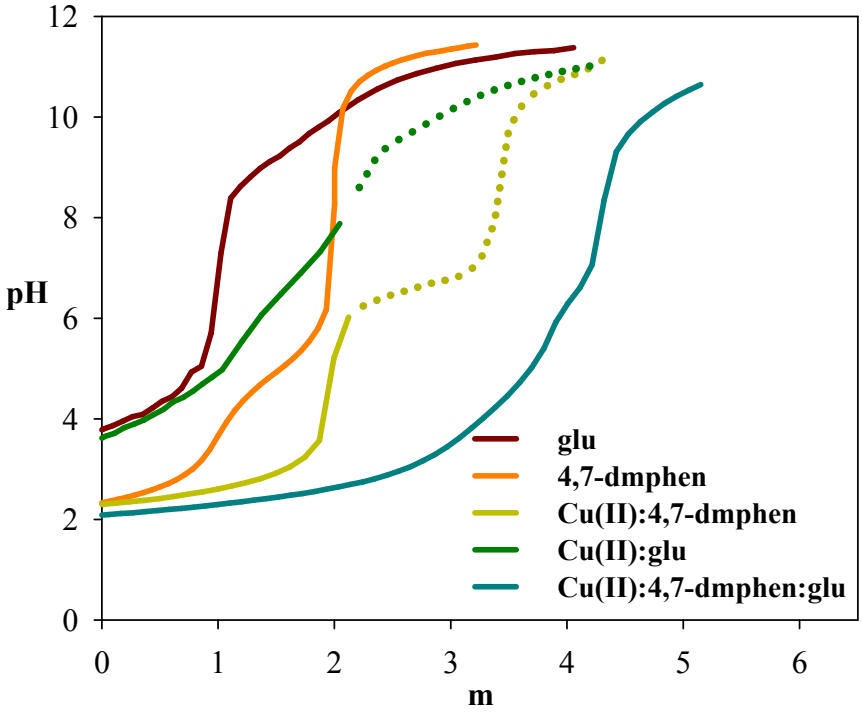


Figure 3. Potentiometric titration curves of the Cu(II):(4,7-dmphen):(asp) and Cu(II):(4,7-dmphen):(asp)systems.

Table 2. Stepwise and overall stability constants of the binary Ni(II) and Cu(II) complexes

Metal	Ligands	$\log_{10}\beta_{ML}$	Refs
Ni(II)	4,7-dmphen	6.64 ± 0.04*	8.44 (16)
	Asp	7.28 ± 0.04*	7.16 (18), 7.20 (19), 7.35 (14)
	Glu	6.02 ± 0.02*	5.90 (20), 5.95 (19), 6.09 (14)
Cu(II)	4,7-dmphen	7.57	(10), 8.76 (16)
	Asp	8.89 ± 0.03*	8.92 (14), 8.83 (19)
	Glu	8.31 ± 0.04*	8.22 (14), 8.50 (19)

*This work. Ref (10) and (14) is in our previous studies.

(1:1:1) complexes of Ni(II) and Cu(II) with 4,7-dmphen/acidic amino acids

The potentiometric titration curves of the M(II):(4,7-dmphen):(asp/glu) systems were given in Figures 2 and 3. In the Ni(II):(4,7-dmphen):(asp/glu) systems, two inflection points were seen at *m* = 3.0 and *m* = 4.0. It was observed that the 4,7-dmphen and acidic amino acids had a buffer region at a lower pH than $[Ni(4,7\text{-dmphen})(asp/glu)]^+$ titration curve and a total of four protons were titrated. This experimental result demonstrates that the 4,7-dmphen and acidic amino acids are bound to the Ni(II) ion in the aqueous solution. Additionally, the potentiometric titration curve of $[Ni(4,7\text{-dmphen})(asp/glu)]^+$ overlaps with binary $[Ni(4,7\text{-dmphen})]^{2+}$ curve in the *m* = 0.0-2.0 buffer region. In this buffer region, firstly, $[Ni(4,7\text{-dmphen})]^{2+}$ is formed. This is followed by the ligation of acidic amino acids occupying the remaining coordination positions. When overlooking at the potentiometric titration curves of Cu(II):(4,7-dmphen):(asp/glu) systems, it was observed that the 4,7-dmphen and acidic amino acids had a buffer region at a lower pH than $[Cu(4,7\text{-dmphen})(asp/glu)]^+$ titration curve and a total of four protons were titrated. This experimental result demonstrates that the 4,7-dmphen, asp, and glu are bound to the Cu(II) ion in aqueous solution. The equilibria contained in the M(II):(4,7-dmphen):(asp/glu) systems could be defined by the following equations.

$$M^{2+} + H_2(4,7\text{-dmphen})^{2+} + H_2(asp/glu)^+ \rightleftharpoons [M(4,7\text{-dmphen})(asp/glu)]^+ + 4H^+ \quad (9)$$

$$M^{2+} + 4,7\text{-dmphen} + (asp/glu)^- \underset{}{\overset{\beta^M_{M(4,7\text{-dmphen})(asp/glu)}}{\rightleftharpoons}} [M(4,7\text{-dmphen})(asp/glu)]^+ \quad (10)$$

$$\beta^M_{M(4,7\text{-dmphen})(asp/glu)} = \frac{[M(4,7\text{-dmphen})(asp/glu)^+]}{[M^{2+}][4,7\text{-dmphen}][(asp/glu)^-]}$$

The obtained protonation constants of the 4,7-dmphen and acidic amino acids, as well as their the stability constants with metal(II) in the (1:1) systems were performed the BEST program (15). These experimental results are given in Table 3.

The relative stability of the (1:1:1) complexes compared to those of the corresponding (1:1) species might be assessed in distinct ways. In most cases $\Delta\log_{10}K$ values are employed (9-11). The $\Delta\log_{10}K$ values have been computed with the Equation 11 and given in Table 3. An example is given for M(II):(4,7-dmphen):(asp/glu) system.

$$\Delta\log_{10}K = \log_{10}K^{M(4,7\text{-dmphen})}_{M(4,7\text{-dmphen})(asp/glu)} - \log_{10}K^{M}_{M(asp/glu)} = \log_{10}K^{M(asp/glu)}_{M(4,7\text{-dmphen})(asp/leu)} - \log_{10}K^{M}_{M(4,7\text{-dmphen})} \quad (11)$$

For experimental systems in this study, the $\Delta\log_{10}K$ values were found negative in $[Ni(4,7\text{-dmphen})(asp/glu)]^+$ complexes (Table 3). The negative $\Delta\log_{10}K$ values of this results demonstrates that the (1:1:1) Ni(II) complexes are less stable than the (1:1) Ni(II) complexes. These values of $\Delta\log_{10}K$ do not mean that the (1:1:1) Ni(II) complexes are not formed. It could be owing to the higher stability of its (1:1) Ni(II) complexes, with a reduced number of geometric structure, coordination sites, steric hindrance (21-22), electrostatic interaction (23-24), different bond type (25). The steric hindrance is one

of the most remarkable parameter due to the fact that the entry of the secondary ligands (asp and glu) faces steric hindrance because of bigger size of the $[Ni(4,7\text{-dmphen})(asp/glu)]^+$ complexes as compared to aqua ion, which restrict the entry of the secondary ligands in the coordination sphere of the Ni(II) ion and thereof declines the stability of the (1:1:1) $[Ni(4,7\text{-dmphen})(asp/glu)]^+$ complexes. The $\Delta\log_{10}K$ values of $[Cu(4,7\text{-dmphen})(asp/glu)]^+$ complexes were found positive (Table 3). The positive $\Delta\log_{10}K$ values of $[Cu(4,7\text{-dmphen})(asp/glu)]^+$ complexes demonstrate that the (1:1:1) Cu(II) complexes are more stable than the (1:1) Cu(II) complexes.

Table 3. Stepwise and overall stability constants of the ternary Ni(II) and Cu(II) complexes.

Metal	Ligand	Amino acids	$\log_{10}\ \check{}_{MAB}$	$\log_{10} K^{MA}_{MAB}$	$\log_{10} K^{MB}_{MAB}$	$\log_{10}K$
Ni(II)	4,7-dmphen	Asp	13.98 ± 0.02*	7.34	6.70	-0.06
		Glu	12.82 ± 0.03*	6.18	6.80	-0.16
Cu(II)		Asp	15.44 ± 0.03*	7.87	6.55	1.02
		Glu	15.01 ± 0.04*	7.44	6.70	0.87

*This work.

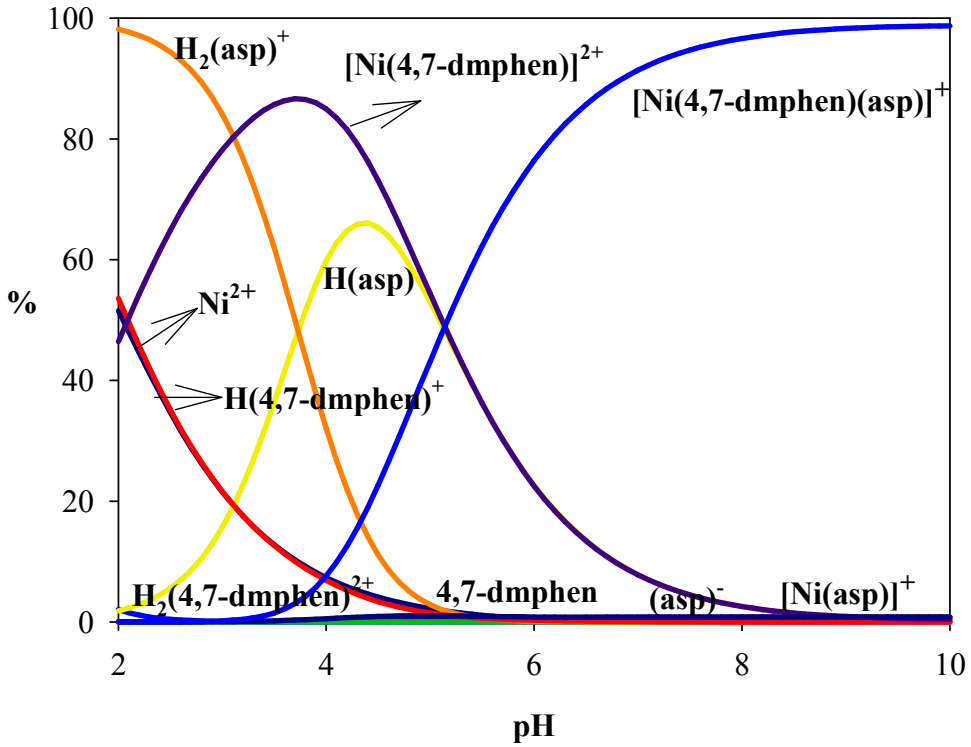
Distribution diagrams of the (1:1:1) complexes of Ni(II) and Cu(II) with 4,7-dmphen/acidic amino acids

Species distribution diagrams have been utilized to define the types of equilibria. Stability of the (1:1:1) Ni(II) and Cu(II) complexes have been computed performing the SPE program (15). The species distribution diagrams of the (1:1:1) Ni(II) and Cu(II) complexes are illustrated in Figures 4-7.

The species distribution curves of Ni(II):(4,7-dmphen):(asp/glu) systems are illustrated in Figures 4 and 5. The $[Ni(4,7\text{-dmphen})(asp/glu)]^+$ begins to occur at pH = 4.0 and, with rising pH, its concentration reaches 97.0% at pH = 8.0. H(asp/glu), $H_2(asp/glu)^+$, $H(4,7\text{-dmphen})^+$, $H_2(4,7\text{-dmphen})^{2+}$, Ni^{2+}, $[Ni(4,7\text{-dmphen})]^{2+}$ at pH = 2.0; $[Ni(4,7\text{-dmphen})]^{2+}$ and H(asp/glu) at pH = 4.0; $[Ni(4,7\text{-dmphen})(asp/glu)]^+$, $[Ni(4,7\text{-dmphen})]^{2+}$, H(asp/glu) at pH = 6.0; and $[Ni(4,7\text{-dmphen})(asp/glu)]^+$ at pH = 8.0 are the predominant species.

The species distribution curves for Cu(II):(4,7-dmphen):(asp/glu) systems are displayed in Figures 6 and 7. In the Cu(II):(4,7-dmphen):(asp) and Cu(II):(4,7-dmphen):(glu) systems at pH 2.0, the concentrations of $[Cu(4,7\text{-dmphen})]^{2+}$ are ca. 76.52 and 71.31 %, respectively. $[Cu(4,7\text{-dmphen})(asp/glu)]^+$ begins to occur at pH = 5.0 and with rising pH, its concentration reaches ~ 98.0 % at pH = ~6.0-10.0. $[Cu(4,7\text{-dmphen})(asp/glu)]^+$ is the predominant species.

a)



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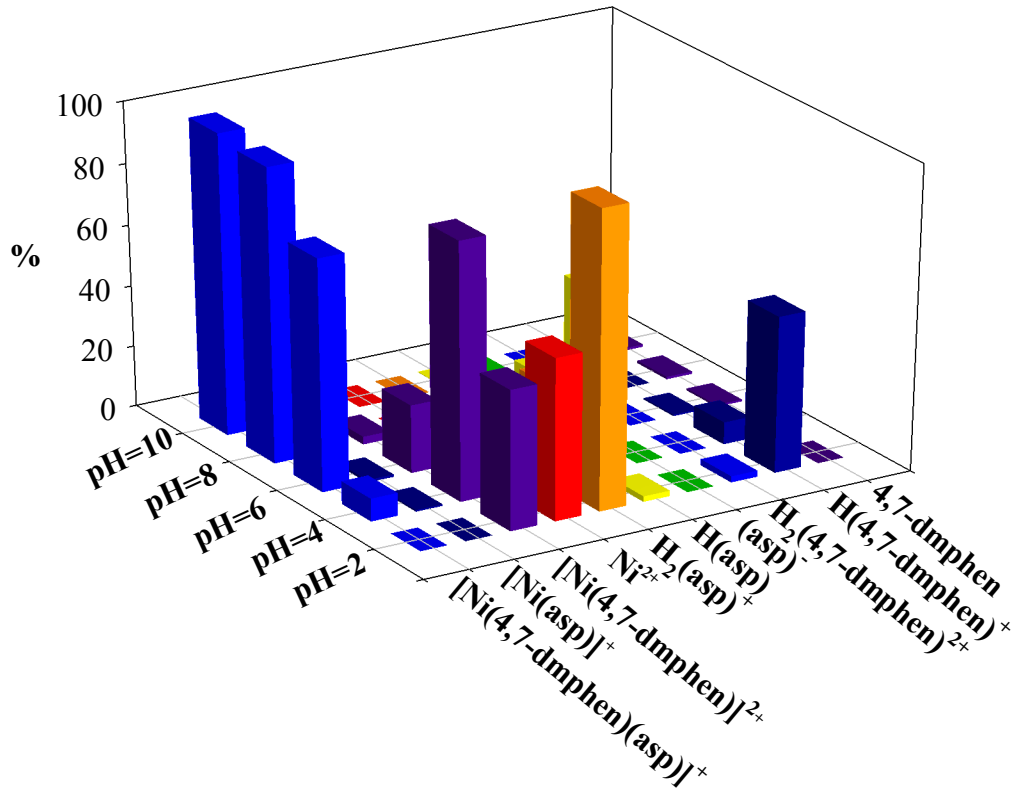
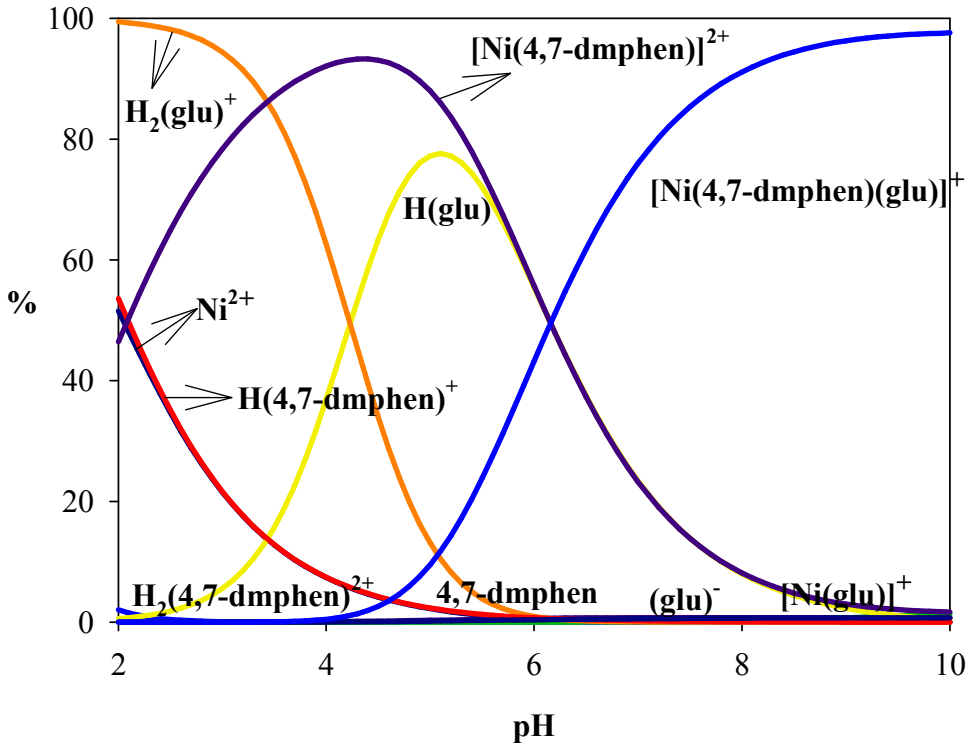


Figure 4. (a) Distribution of species as a function of pH in Ni(II):(4,7-dmphen):(asp) system **(b)** A bar chart of the percentage distribution of the species in aqueous solutions.

a)



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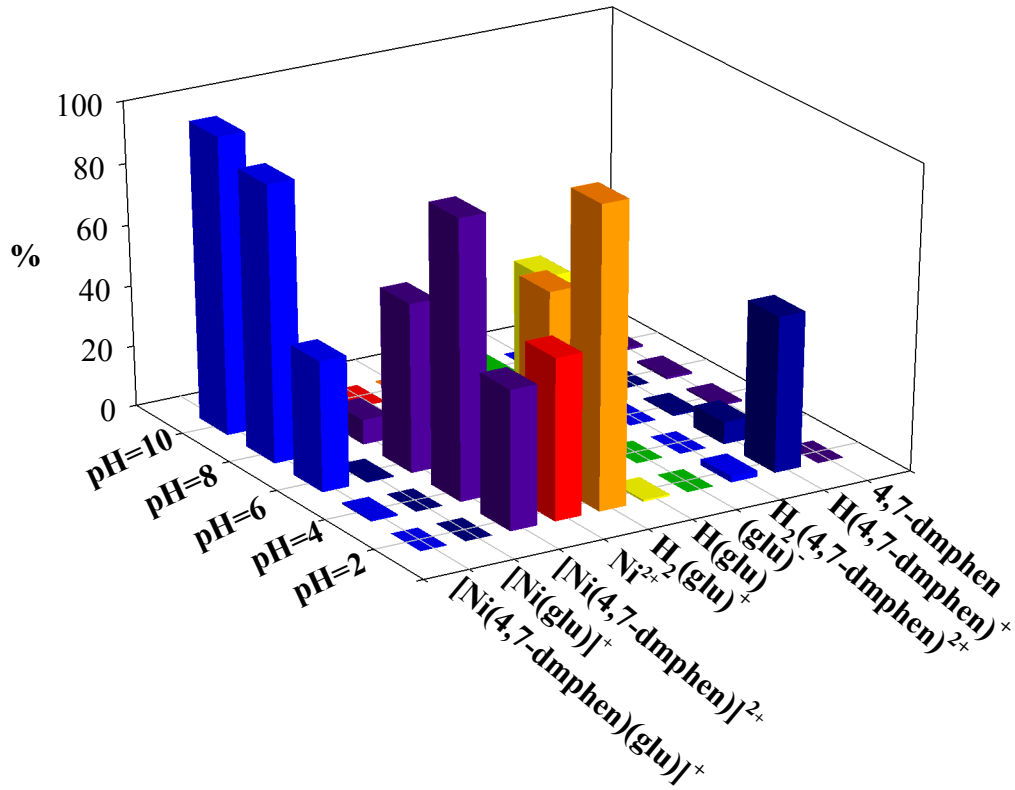
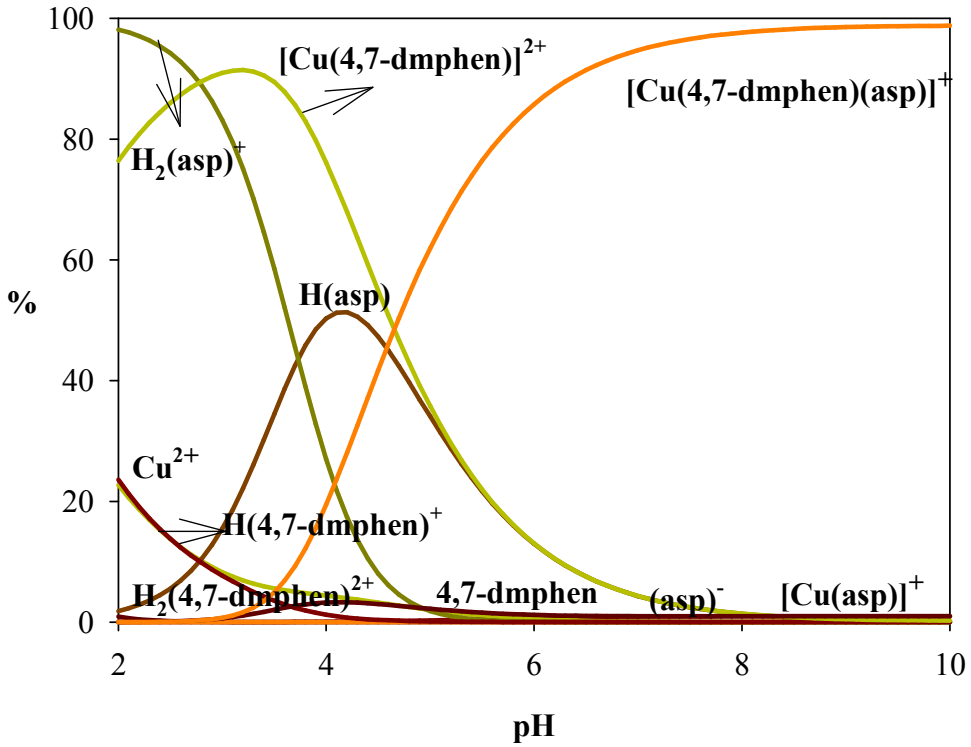


Figure 5. (a) Distribution of species as a function of pH in Ni(II):(4,7-dmphen):(glu) system **(b)** A bar chart of the percentage distribution of the species in aqueous solutions.

a)



b)

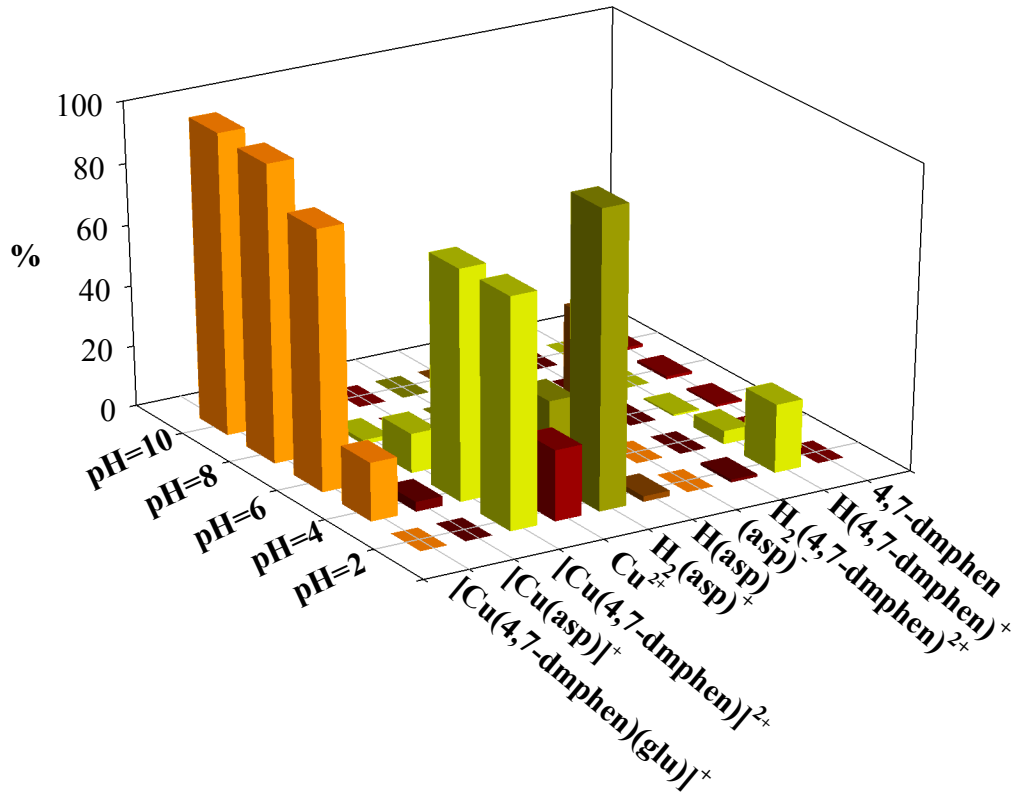
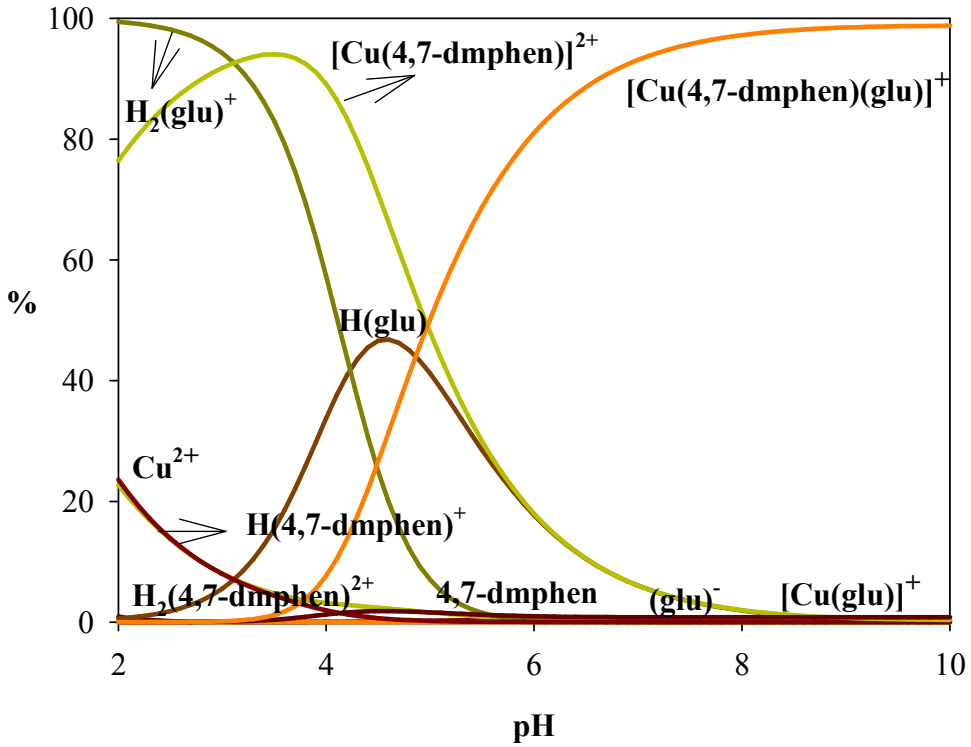


Figure 6. (a) Distribution of species as a function of pH in Cu(II):(4,7-dmphen):(asp) system **(b)** A bar chart of the percentage distribution of the species in aqueous solutions.

a)



b)

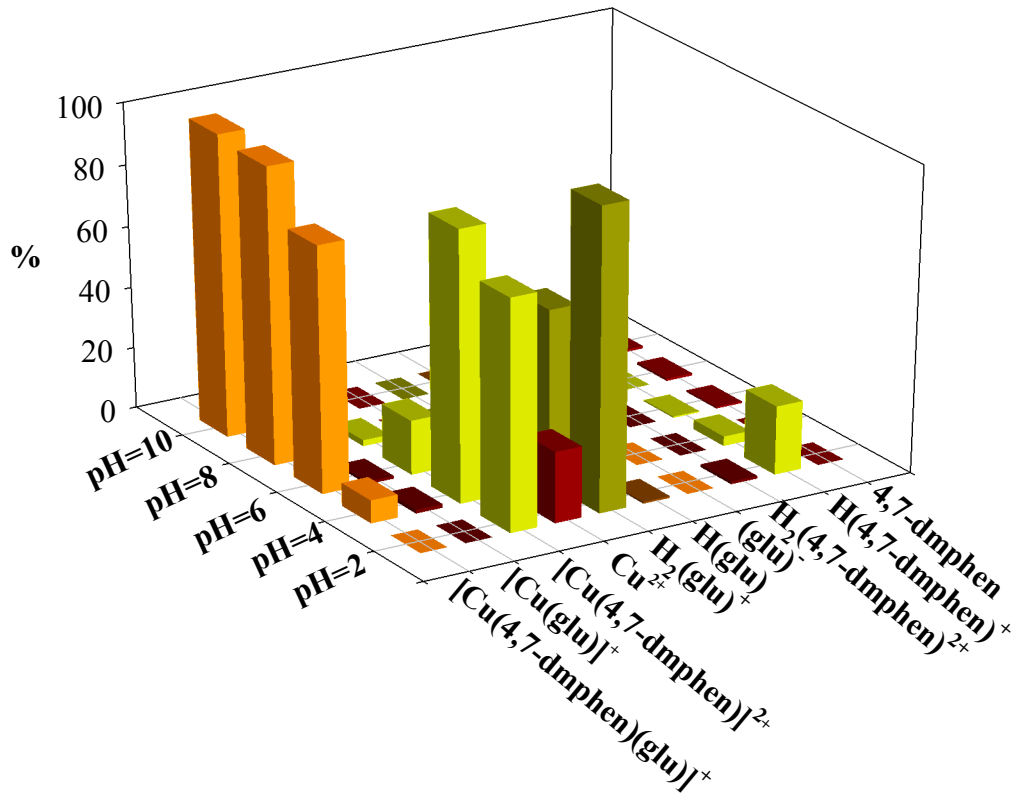


Figure 7. (a) Distribution of species as a function of pH in Cu(II):(4,7-dmphen):(glu) system **(b)** A bar chart of the percentage distribution of the species in aqueous solutions.

CONCLUSIONS

The formation of the (1:1:1) Ni(II) and Cu(II) complexes involving 4,7-dmphen and acidic amino acids using potentiometric titration methods were investigated. Compared to metal(II) ions, the stability constant of the $[Cu(4,7\text{-dmphen})(asp/glu)]^+$ complexes were found higher than $[Ni(4,7\text{-dmphen})(asp/glu)]^+$ complexes which were accordance with Irving-Williams series. Furthermore, glutamic acid complexes were found lower than aspartic acid complexes because of has one additional methylene group in its side chain. The above mentioned parameters and experimental results could be beneficial in understanding the biological behavior of the (1:1:1) Ni(II) and Cu(II) complexes in the biological implementations.

ACKNOWLEDGEMENTS

The author would like to thank Prof. Dr. Rahmiye AYDIN for allowing me to use the facilities at the Inorganic Chemistry Laboratory to conduct in this study.

CONFLICT OF INTEREST

No conflict of interest was declared by the author.

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