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Determination of stability constant of mixed ligand complexes of Ni(II) and Cu(II) metal ions with Diethylenetriamine (DET) and Ethylenediamine(en), Glycine (gly), alpha-Alanine (alpha-ala), Phenylalanine (ph-ala). Oxalic acid (ox), Tyrosin (tyr)

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Abstract

Transition metal form complex with ligand and this metal complexes play very important roles in biological system. Metal complexes is a branch of biological inorganic chemistry. This field has important implications in many other sciences, ranging form medicine to the environment. It is an interdisciplinary science. Scientists working in different areas of Chemistry, Biochemistry, Biology, Physiology, Agriculture, Physics and even Mathematics. Furthermore, studies of the roles of metal ions is biological system often involve development of relevant chemistry. The analysis of the representative species distribution curves shows that in the pH range 1-4 metal ion M(II) is the major species. In the pH range 4-7 for Cu(II) complex or above in case of Ni(II) complexes the species MA, ML, MAL exist, where M = Ni(II), Cu(II) and A = Diethylenetriamine (DET) and L = Oxalic acid, Tyrosin, Ethylenediamine, Glycine, alpha- Alaline, Phenylalanine, The percentage of the species MA_2, ML_2 are very less. In the present study, the ligand A, are characterized by three pK^H values. pK_1^H and pK_2^H corresponds to two -NH_2 protons and pK_3^H corrosponds to -NH proton. It is observed that for the metal ligand formation constant $\log K_1$ and $\log K_2$, the difference ($\log K_1$ - $\log K_2$) is more in case of Cu(II) as compare to Ni(II). The ΔlogK value was calculated by using SCOGS computer program. The value of ΔlogK are more negative of Cu(II) complex compair to Ni(II) complex. So, the complex of Ni(II) is more stable than Cu(II) complexes.

Key words: Stability, Ternary Complex, Diethylenetriamine (DET), SCOG etc.

I. Introduction

Mixed ligand complexes pley in an importent role in biological process as exemplified by many intances in which enzymes are known to be activated by metal ions[1-2]. Such complexes have been implicated in the strong and transport of active substances through membrance. Many mixed ligand complexes are finding application in the microelectronic industry, chemical vapour deposition of metals and drugs[3]. Mixed ligand complexe have been used in the analysis of seme-condactor materials. Vapour mixed ligand complexes of Co(II) with salicylaldehyde and substituted salisaldehydes have been synthesized by Patel *et al.* Sulfur-containing amino acids easily react with Pd(II) because of the great tendency of sulfur (a soft Lewis base) to form bonds with these metals (soft Lewis acids)[4].

Most of the transition metal form complex with ligand and this metal complexes play very important roles in biological system[5]. Metal complexes is a branch of biological inorganic chemistry. This field has important implications in many other sciences, ranging form medicine to the environment. It is an interdisciplinary science. Scientists working in different areas of Chemistry, Biochemistry, Biology, Physiology, Agriculture, Physics and even Mathematics. Furthermore, studies of the roles of metal ions is biological system often involve development of relevant chemistry.

In a complex where two or more ligands of the same type are bonded with a metal ion is called a binary ligand complexes and if the different types of ligand are present, then the complexes is said to be ternary complexes or mixed ligands complex[6]. It is now generally agreed that in a solution containing metal ions and two different suitable ligands are usually combined. Metal ion is living bodies are mostly coordinated to other chemical species present in the bodies. Not only many ligands compete for a metal ion but metal ions also compete for a species ligand. Metal ion displaced one another in accordance with the formation constants of their coordinated compounds. It has been observed that the stability constant of the mixed ligang complex depends on the nature of the metal ions[7] and the nature of the ligands. The stability constant may be used to reduce metal toxicity, oxidative stress and nephrotoxicity. The thermodynamics parameters showed that the complexes were lesser stable at high temperature and formed with the evolution of heat[8].

The study of metal complexes has played a vital role in the medicinal, analytical, environmental and biological sciences[9]. The stability constants of metal complexes with drugs are important to know the proper dose of drugs and their adverse effect with all other components of blood streams[10]. The stability of complexes plays a major role in elucidation of mechanism of drug action. The acute action of drug and their complex formation in complex media is depend on metal ligands selectivity and stability constants[11]. The study of metal complexes with drugs shows that they are more potent than drugs[12]. The drug forms harmless stable complexes during the detoxification of metal poisoning[13]. Most of transition metal complexes are involved in storage, transport, and catalytic processes[14-15]. The effectiveness of any molecule as a drug depends on its coordination behaviors, body temperature and extra cellular fluid pH condition. The formation of mixed ligand complexes of Nickel and Coper with Diethylenetriamine (DET) and Oxalic acid, Tyrosin, Ethylenediamine, Glycine, α - Alaline, Phenylalanine as lignds have great socio economic importance and unique significance in the field of biochemistry[16-17]. The relative stability of the ternary complexes compared with corresponding binary complexes can be qualitatively expressed in many different ways[18]. Stability of mixed ligand complexes is mainly affected by the characteristics of approaching secondary ligand[19]. Stability constant directly interfere of dielectric constant, solvent-solvent interaction, solute-solvent interaction and solute-solute-solvent interaction[20]. The values of standard enthalpy and standard entropy for complexation processes change with the nature of binary solvent mixtures[21] and on temperature[22]. The analytical applications of ternary complexes of different ligands influence in the formation of complexes[23].

Therefore it is necessary to investigate the mixed ligand complexes of Ni(II) and Cu(II) involving various types of bi- and tri- dented biologically important ligands.

II. Objectives :

The aim of the present works is to prepare the mixed ligand complexes [MAL], where M refers to Ni(II), Cu(II) and A refers to Diethylenetriamine (DET), L refers to Oxalic acid (ox), Tyrosin (tyro), Tryptophans (tryp), Phenyl Alanine (ph-ala), α- Alanine (α-ala), Glycine (gly), Ethyldiamine (en) etc. bi-dented biologically important ligands.

The line of approach of the present works may be summarized below:

(i) Preparation of ternary complexes. (ii) Determination of the stability constant of the complexes. Stability constant of complex compound is very essential for MRI, Catalysis for RNA cleavage, kinetics of reaction, Radiopharmaceuticals, Molecular recognition, Macrocyclic complexes, Host-guest interactions, Enthalpy determination, Cation and Anion selective complexation, Supramolecular complexes, Action of Drug, Environmental effects, Metallomics (including peptides) etc. For imbalance of stability constant above phenomena would be disorder. So, Studies are required to determine the stability constant. Result obtain from the present work would be helpful in the development of biological, pharmaceutical and physiological implication in the future.

III. Methodology/Experimental Design

(a) Preparation of metal perchlorate :

Metal perchlorate will be prepared from analytically pure metal carbonate by treatment with 70% perchloric acid (A.R). The resulting solids will be vacuum filtered, washed with ethanol till free from excess acid and recrystallized several times from ethanol(metal perchlorates are partially soluble in alcohol).

(b) Stability Constant determination:

Potentiometric titration will be carried out in aqueous media using pH meter with accuracy 0.01 pH unit using 0.2 M NaOH solution. The solutions of reagents will be prepared in double distilled and deionized water. The freshly prepared NaOH solution will be used as a titrant for pH metric titrations. It will be standardized with oxalic acid according to the literature method[24]. The 1.0 M $NaClO_4$ solutions were prepared to maintain the 0.2 M ionic strength of the titration solutions by taking required amount of sodium perchlorate. The metal solutions also will be standardized according to literature method[25]. The pH electrode will be calibrated in aqueous solution using buffer solution of pH 4.01 and 6.86. As usual pH metric titration method[26] will be used for solution works. The stability constant of metal complexes will be determined potentiometrically by using SCOGS[27] computer program.

IV. Experimental

Potentiometric Determination Stability Constant :

The stability of ternary complexes have been determined in terms of $\Delta \log K = \log K^{MA}_{MAL} - \log K^{M}_{ML}$ value, i.e. the difference in the tendencies of L to bind with the free metal ion and the metal ion already bound to another ligand. Irving Rossotti titration technique has been used to determine the formation constants of the ternary complexes using SCOGS (Stability Constant of Generalized Species) computer program[22].The activity coefficient of H^+ under experimental condition has been considered to be equal to unity and the value of the ionic product of water 14.167 has been used. For the determination of formation constants all solutions were titrated potentiometrically against standard 0.02M sodium hydroxide solution. In all the cases acid concentration was kept 2.00×10^{-2} M and the total ionic strength (I) of the solution was maintained at 0.2M.

For the determination of the formation constants of the ternary complexes [MAL], the following solution (50cm^3) having M:A:L in the ratio 1:1:1 were prepared. 0.02M $HClO_4$, 0.002M metal perchlorate, 0.002M ligand (A), 0.002M ligand (L) and 0.174M $NaClO_4$ set was titrated against standard alkali. All the titrations were carried out in aqueous medium and the temperature was maintained at 25°C±1°C during the progress of titration. Titrations were carried out by using TOA pH-METER HM- 2OS, having an accuracy of ±0.01 pH unit. The glass electrode was calibrated using buffer solutions of pH 6.86 and 4.01. Hence the stability constants calculated are stochiometric constants. The calculations were carried out by computer, Dell, Optiplex, GX 280.

Table 1. Proton ligand formation constant of ligands and formation constant of their Cu(II) binary complexes in aqueous medium with I = 0.2 M ($NaClO_4$) at 25°C ± 1°C.

Ligands	log K_1^H	$logK_2^H$	log K_{CuL}^{Cu}	log $K_{CuL_2}^{Cu}$
Oxalic acid	3.88	2.33	4.90	8.42
Ethylenediamine	10.43	7.12	10.05	18.88
Glycine	9.58	2.42	7.00	14.37
α-alanine	9.65	2.18	7.63	14.68
Phenylalanine	9.22	1.96	7.49	14.11
Tyrosine	9.33	1.72	7.39	14.02
Tryptophan	9.43	2.03	7.97	15.33
Diethylenetriamine (DET)	9.65	9.14	15.58	21.31

Table 2. Proton ligand formation constant of ligands and formation constant of their Ni(II) binary complexes in aqueous medium with I = 0.2 M ($NaClO_4$) at 25°C ± 1°C.

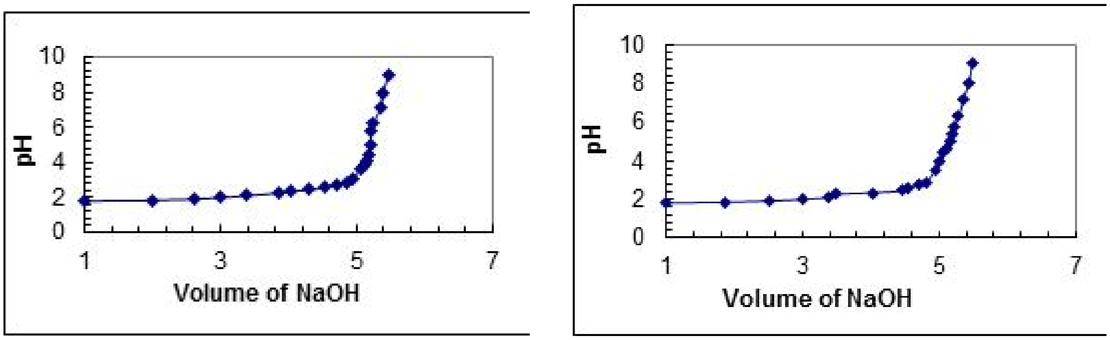
Ligands	log K_1^H	$logK_2^H$	log K_{NiL}^{Ni}	log $K_{NiL_2}^{Ni}$
Oxalic acid	3.88	2.33	4.27	5.58
Ethylenediamine	10.43	7.12	7.78	14.58
Glycine	9.58	2.42	6.00	10.46
α-alanine	9.65	2.18	5.53	9.56
Phenylalanine	9.22	1.96	4.81	8.56
Tyrosine	9.33	1.72	4.77	8.89
Tryptophan	9.43	2.03	5.31	9,73
Diethylenetriamine (DET)	9.65	9.14	8.92	16.28

Table 3. Stability constant of mixed ligand complexes [Cu(DET)(L)] in aqueous medium with I = 0.2 M ($NaClO_4$) at 25°C ± 1°C.

System	log K_{CuAL}^{Cu}	log K_{CuA}^{Cu}	log K_{CuAL}^{CuA}	log K_{CuL}^{Cu}	ΔlogK
[Cu(DET)(Ox)]	18.03	15.58	2.45	4.90	-2.45
[Cu(DET)(en)]	21.53	15.58	5.95	10.05	-4.10
[Cu(DET)(gly)]	19.49	15.58	3.91	7.00	-3.09
[Cu(DET)(α-ala)]	20.22	15.58	4.64	7.63	-2.99
[Cu(DET)(Ph-ala)]	21.48	15.58	5.9	7.49	-1.59
[Cu(DET)(Tyr)]	20.02	15.58	4.44	7.39	-2.95
[Cu(DET)(Tryp)]	20.89	15.58	5.31	7.97	-2.66

Table 4. Stability constant of mixed ligand complexes [Ni(DET)(L)] in aqueous medium with I = 0.2 M ($NaClO_4$) at 25°C ± 1°C.

System	$\log K^{Ni}_{NiAL}$	$\log K^{Ni}_{NiA}$	$\log K^{NiA}_{NiAL}$	$\log K^{Ni}_{NiL}$	ΔlogK
[Ni(DET)(Ox)]	12.59	8.92	3.67	4.27	-0.60
[Ni(DET)(en)]	15.87	8.92	6.95	7.78	-0.83
[Ni(DET)(gly)]	13.96	8.92	5.04	6.00	-0.96
[Ni(DET)(α-ala)]	13.77	8.92	4.85	5.53	-0.68
[Ni(DET)(Ph-ala)]	13.09	8.92	4.17	4.81	-0.64
[Ni(DET)(Tyr)]	13.14	8.92	4.22	4.77	-0.55
[Ni(DET)(Tryp)]	13.7	8.92	4.78	5.31	-0.53



Curve-1 Curve-1

Fig. 1. Potentiometric titration curves of aqueous solutions containing metal ions, Diethylenetriamine (DET) and L. (each 0.001M). Curve (1) : Cu^{2+} + Diethylenetriamine (DET) + Oxalic Acid ; Curve (2) :Ni^{2+} + Diethylenetriamine (DET) + Oxalic Acid

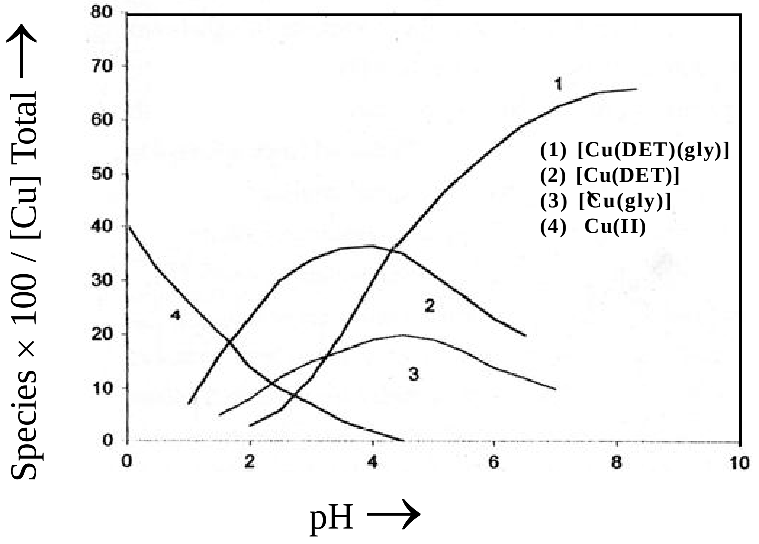


Fig –2: Species distribution diagram for the [Cu (DET) (gly)] ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

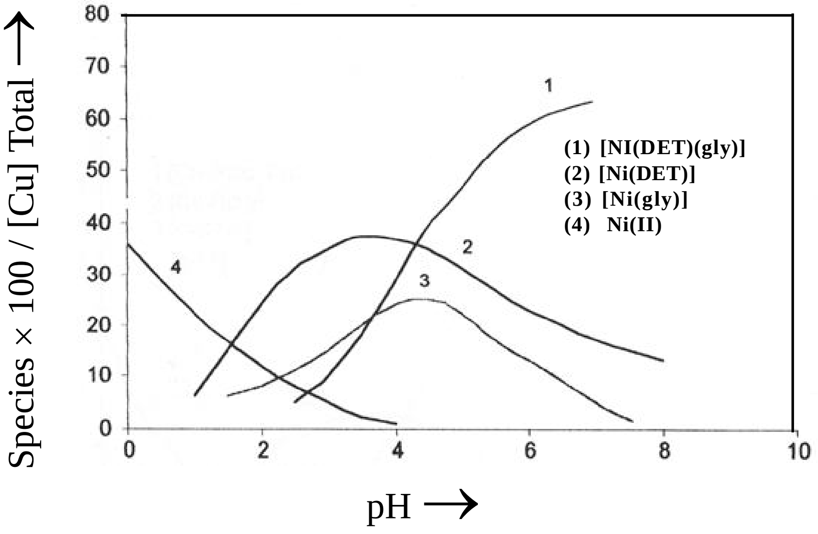


Fig. 3. Species distribution diagram for the [Ni (DET)(gly)] ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

V. Result and Discussion

The analysis of the representative species distribution curves shows that in the pH range 1-4 metal ion M(II) is the major species. In the pH range 4-7 for Cu(II) complex or above in case of Ni(II) complexes the species MA, ML, MAL exist(where M = Ni(II), Cu(II) and A = Diethylenetriamine (DET) and L = Oxalic acid, Tyrosin, Ethylenediamine, Glycine, alpha-Alaline, Phenylalanine). The percentage of the species MA_2, ML_2 are very less. In the present study, the ligand A, are characterized by three pK^H values. pK_1^H and pK_2^H corresponds to two $-NH_2$ protons and pK_3^H corresponds to -NH proton. It is observed that for the metal ligand formation constant logK_1 and logK_2, the difference (logK_1 - logK_2) is more in case of Cu(II) as compare to Ni(II). This is due to the tri-dentate nature of the ligand. When the first ligand coordinates with the metal (formation constant K_1) the ligand occupies three equatorial positions. When the second ligand coordinates with the metal ion (formation constant K_2) the ligand is forced to occupy one equatorial and two axial positions. The ligand is put to more strain in Cu(II) as compair to Ni(II) due to axial distortion in Cu(II) complexes. Hence logK_2 in [[CuA_2] complexes is considerably lowered as compared to [NiA_2] complexes. Similar observation has been made in case of tridentate ligands earlier also.

As DET are neutral ligand, in the formation of ternary complexes [MAL] there is no electrostatic repulsion and hence $logK_{MAL}^{MA}$ should not be much lower than $logK_{ML}^{M}$. This is observed in the ΔlogK value of NI(II) complexes which show less negative ΔlogK values. However, in case of Cu(II) complexes ΔlogK values are more negative. This can be explained as follows. The tridentate ligand DET occupy the three equatorial positions around the metal ion. Hence in the formation of the ternary complex the bidentate ligand L has to occupy one equatorial and one axial position. In case of Cu(II) ternary complexes, the ligand is strained in occupying the axial position and hence its tendency to coordinate with the metal ion in the ternary complexes is less than the binary complexes, where the bidentate ligands occupies two equatorial positions. Hence

K_{MAL}^{MA} is less than K_{ML}^{M}, and ΔlogK is more negative. In the absence of Jhan-Teller distortion in Ni(II) complexes the bidanted ligand does not feel any strain in occuping one equatorial and one axial positions and hence the ΔlogK is less negative.

The effect is more in case of bidentate aromatic ligands with rigid positions of the coordinating atom. Hence Δ(ΔlogK) (=$\Delta\log K_{Ni}$ - $\Delta\log K_{Cu}$) is more in case where L= phenylalanine (ph-ala) and tyrosine (tyro) and its derivatives than in the aliphatic dicarboxylic acid, amino acids or diamines.

It can be possible that during the formation of ternary complexes the bidented ligand occupies two coordination sites in the equatorial position and the tridented amine changes position to two equatorial and one axial. In order to investigate this, studies were carried out with [M(DET)L] complexes. For large chain length of DET, it will realizes less strain in occupying the axial position and hence ΔlogK should be less negative in Cu(II) complexes and Δ(ΔlogK) should have lower value. It is observed to be so. Moreover changing the size of the bidentate ligand has less effect on Δ(ΔlogK) value as observed in[M(A)(oxalate)] and [M(A)(α-alanine)] complexes. This suggests that the tridentate ligand may be occupying two equatorial and one axial positions or that there is a dynamic exchange of coordination sites of the two ligands. So, The value of "logK are more negative of Cu(II) complex compair to Ni(II) complex. So, the complex of Ni(II) is more stable than Cu(II) complexes.

VI. Conclusion

It is interesting to study that the various factors which affect the stability of the ternary complex. The proton-ligand formation constant and formation constant of binary complexes were first refined. These values were used as fixed parameters for the refinement of the formation constant of the ternary complexes. For large chain length of DET, it will realies less strain in occupying the axial position and hence ΔlogK should be less negative in Cu(II) and Ni(II) complexes. In the absence of Jhan-Teller distortion in Ni(II) complexes the bidanted ligand does not feel any strain in occuping one equatorial and one axial positions and hence the ΔlogK is less negative. The more positive value of Δlog K, the complex is more stable. It is observed that Δlog K value is less negative in complexes of [Ni(DET)(L)] compair to complex [Cu(DET)(L)] (where, L = Oxalic acid, Tyrosin, Ethylenediamine, Glycine, alpha-Alaline, Phenylalanine,). So the complex [Ni(DET)(L)] is more stable compare to complex [Cu(DET)(L)].

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VII. Reference

1. G. H. Bell, J. N. Davidson, *Text Book of Physiology and Biochemistry*, E. S. Livingstone, Edinburgh, *39*, (1994).
2. R.B.Martin and R.Parados, J. Inor. Nucl, Chem 9, 1238, 1970.
3. Warad D U, Satish C D & Chandrasekhar S.Bajgus, Proc Indian Acad Sci, 112, 400 (2000).
4. Amani S. Alturiqi "Determination of Stability Constants of Mixed Ligand Complexes of Palladium(II) with Venlafaxine Drug and Sulfur Ligands" Asian Journal of Pharmaceutics,V-11(3); P:551-555, (2017).
5. Dugas H,Bio-Organic Chemistry (Springer, New York) 1995, 407.
6. Shin H K Chi K.M, Farkas J, Smith M J H, Kodas T T & Duesler E N, Inorg Chem, *31,* 424 (1992).
7. Sigel H, " Metal ion in biological System" Mareel dekker,(2) 1973, (13) 1981, J Indian Chem. Soc. Vol-72, No.-1, November-(1995).

8. Santosh Narayan Chadar, Farid Khan, Abhay Pandey and Keerti Chadar "A Study of Polarographic Characteristics and Stability Constant of [Zn(II)-antibiotics-vitamin-BX] Complexes" Asian Journal of Chemical Sciences *2(1),* P-1-8, (2017).
9. Nair MS, Neelakantan MA. *Indian J Chem ; 38A*, 575-578 (1999).
10. Sigel H, Marcel. Metal Ions in Biological Systms, Dekker, Inc New York 1973; 2.
11. Thomas G. Medicinal Chemistry, John Wiley and Son Co. Ltd. London. (2002).
12. Richards FM, Wyckoff HM, Allewel NM. Neurosciences, Rockfeller University Press New York1969; 901.
13. Gopalan R, Ramalingam V. Concise Coordination Chemistry, Vikas Publishing House Private Ltd New Delhi 2007; 338.
14. Underwood EJ. Trace Elements in Human and Animal Nutrition, Academic Press 1977; 4.
15. Caumul P, Boodhoo K, Burkutally SB, Seeruttun S, Namooya N, Ramsahye N, Joondan N. Res *J Pharm Biol Chem Sci.; 5(1)*, 494-501 (2014).
16. A. Y. Majid, M. B. Sarhan, A. N. Al. Najjar, "Stability constant of some metal ion complexes (4 Amino Hippuric acid) in aqueous Solutions," *Journal of Al. Nahrain University*. Vol.11, pp.1-8 (2008).
17. Y. Arafat, S. Ali, S. Shahzadi, M. Shahid, "Preparation, Characterization and Anitimicrobial activities of Bimetalic Complexes of Sarcosine with Zn(II) and Sn(IV)," *Chemistry and application,*vol.7, pp.164-167 (2013).
18. A. K. Mapri, "Stability Constants of Mixed Ligand Complexes of Transition Metal(II) ions with 4-bromo-2-{(E)-[(4- methoxy-2-methylphenyl)imino]methyl}phenol and 1-{(E)-[(2-methyl-5- nitrophenyl) imino]methyl} naphthalen-2- ol, "*Journal on Advanced Chemical Science*, vol.2(3), pp.353-355 (2016).
19. Ammar Qasem, Mazahar Farooqui, Sayyed Hussain "Determination of the stability constants of mixed ligand complexes of phenytoin sodium drug and glutamine by potentiometric methos," *Int. J. Chem. Sci.*, vol. *13(4),* pp.1575-1583 (2015).
20. A. B. Wadekar, D. T. Tayade, "Studies in Conditional Stability Constants and Confirmation of Complex of Cu (II), Cd (II) and Cr (III) with SubstitutedThiocarbamidonaphthols Spectrophotometrically," *Jnternational Journal of Pharmacy and Pharmaceutical research,*Vol. *6,* pp.684-688 (2016).
21. Malihe Samdi Kazemi, Bita Shamshirgaran, "Determination of the Stoichiometry, Stability Constant of Complexes Formation and Thermodynamic Parameters between 15-Crown-5, 1, 4, 8,11-Tetrathiacyclotetradecane and 1, 7-Diaza-12-crown-4 Macrocyclic Ligands in Acetonitrile –Methanol Binary Solvent Mixtures," *Int. J. Electrochem. Sci.*, vol. *11*, pp. 3415 – 3424 (2016).
22. N.Tanaji Bansode, "Determination of formation constants and themodynamic parameters of trifluoperazine-metal complexes by potentiometric method," *Der Pharma Chemica*, vol.*7(6)*, pp.59-63 (2015).
23. Aysen Kurt Cucu, Emine Arslan, Serap Karaderi, "The Determination of the Stability Constant of Finasteride Complexes with Various Metals by Potentiometric and Spectrophotometric Methods," *Marmara Pharmaceutical Journal*, vol. *20*, pp. 408-414 (2016).
24. A. I . Vogel, "A Textbook of Quantitative Inorganic Analysis," Pergamon Green and Co. Ltd. London, pp. 539, (1975).
25. G. Schwarzenbach, "Complexometric Titrations," Menthuen and Co. Ltd. London, pp.79-82 (1975).
26. M. R. Ullah, M. A. Kabir, N. Sultana, S. Z. Haider and N. A. Pasha "Reaction of Monosodiu Glutamatewith transition metal cation," *J. Bangladesh Acad, Sci.*, Vol. *27(1)*, pp.51-56 (2003).
27. I.G. Sayce, and V.S. Sharma, Talnta, "Computer calculation of equilibrium constant of some ternary complexes," *Talanta*, vol. *19*, pp. 831 (1972).