

# Study Metal Ligand Stability Constant by Ph Metric Technique - A Review

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#### Abstract:

This paper deals with review of stability constants of some metal complexes. The review is divided into two parts, a theoretical aspects and literature survey. In this paper, complexes of metal ions particularly transition metals & lanthanides are reviewed.

#### **Keywords:**

Metal-ligand stability constant(logK), proton-ligand stability Constants(pK), pH metric titration and thermodynamic studies.

#### Introduction:

Coordination compounds play very important role in numerous chemical, biological and biochemical activities e.g. Chlorophyll, a magnesium complex essential for photosynthesis in plants; Haemoglobin, an iron complex, which carries oxygen to living organism cells; Coenzyme-Vitamin B12, a cobalt complex which serves as a prosthetic group in metabolic activities of living organisms. The study of enzyme has revealed that the site of reaction in biological systems is frequently a complexed metal ion. Coordination compounds have also played a very important role in biological activities for removal of undesirable and harmful metals from living organisms. The application of coordination chemistry is varied in the field of biological, biochemistry, medicine, agriculture, organometallic chemistry, solid state chemistry, catalysis and molecular receptors and devices. The metal ion complexes as a catalyst are invariably involved in various industrial processes. Stability constant is well known tool for solution chemist, biochemist, and chemist. In general to help for determination the properties of metal-ligand reactions in water and biological system [1]. In the study of coordination compound in solution, first and foremost requirement is the knowledge of stability constant of complex. For correct interpretation of complex, the knowledge of stability constant is essential. Reliable information of stability constant is of great importance in analytical and separation procedure. To remove undesirable and harmful metals from living organism, chelating agents are very much useful in biological systems. This gives importance to the study of determination of stability constant of metal complexes. The complexes have been extensively studied in solution as well as in solid state by many workers, due to it's remarkable properties and high stability. With the help of various experimental techniques, the extensive work in coordination complexes has been made possible and has lead in a number of empirical conclusions which have been detailed by

Martell[2]. The stability of complex in solutions is depending on nature of central metal ion and ligands. The most important characteristics of the central atom which influence the stability of complex compounds are the degree of oxidation, the radius and electronic structure. Stability is dependent on the same characteristic in the ligand as considered for the cation in the case of complexes with monoatomic ligands. The strength of binding of ligand to the central metal ion is depending on structure of ligand molecule or ions [3- 4]. The stability of complexes is dependent upon the size and number of chelating rings also. The structure of chelating agent determines the size of the chelating rings and the number of rings formed on chelation. Ley has concluded that five and six member rings of amino acid chelates are the most stable [5]. Pfeiffer has observed that, in general the five member ring is more stable when the ring is entirely saturated. But when one or more double bonds are present, the six member ring is favoured [6]. Schwarzenbach *et al* have observed that there is a decrease in chelate stability with the increase in ring size [7]. Tihile have observed increase in the value of formation constant with the presence of electron donating



group [8]. S.V. Thakur have studied the stability of complex with changing temperature [9]. Irving and Williams give the stability order of metal complex of transition metal ion as  $Mn2+\langle Fe2+\langle Ni2+Zn2+[10]$ . Though vast amount of work has been done on stability constant of metal complexes. Many workers study the effect of transition metal on a stability of complex by pH metrically [11-13]. Also there is a investigation of stability constant of ligand with lanthanide metals[14-17]. The stability of metal complexes with medicinal drugs perform greater role in the biological and chemical activity [18].

#### **Literature Review:**

study the stability constant, so that, we developed the environmentally benign protocol for the synthesis of Schiff bases and determine the stability constant of these Schiff bases by the pH-metric method.

In 2022 Hashmat Ali *et al.* have studied the stepwise and overall stability constants of the complexes of pfluorobenzoylthioacetophenone with Nickel (II), Manganese (II), Cadmium (II) and Mercury (II) have been determined potentiometrically using Calvin-Bjerrum Potentiometric technique as modified by Irving and Rossotti. The effect of Fluorine substituent on the solution equilibria of ligand as well as on the stabilities of complexes formed has been studied. The order of stabilities of the metal complexes has been discussed.[19]

In 2022 G.B.Akat *et al.* have reported well known method of PH metrically chemical equilibrium studies of transition metal complexes of Ca(II), Cu(II) and Cr(II) transition metal ions with Lamivudine (3CT) drug (D) and a series of eight amino acids (A) have been investigated at 300C temperature and 0.1 Molar ionic strength Sodium perchlorate (NaClO4) in aqueous solution. During reaction formation of various possible complex species had been evaluated and analysed by using the special computer program and discussed in terms of various relative stability parameters. By using Calvin and Bjerrum as Proton ligand stability constants (pKa) and metal ligand stability constants (LogK) of metal complexes were determined the method which was as modified by Irving and Rossetti methods at various temperatures [20] In 2021 A. N. Sonar have studied the stability constant of substituted heterocyclic drug with rare earth metal ion have been investigated by CalvinBjerrum's pH-metric titration technique, as modified by Irving and Rossoti, was used to determine at 0.1 M ionic strength at room temperature in 70 % Ethanol-Water mixture. The data obtained use to estimate the values of proton-ligand stability constant (Pk ) and Metal -ligand stability constant (logK). It is observed that transition metal ion form 1:1, 1: 2 complexes with all the systems [21]

In 2020 Serap Karaderi *et al.* in the present work, binary complexes of Copper(II), Cadmium(II) and Zinc(II) with metformin hydrochloride have been studied potentiometrically. Stability constants of binary complex systems have been estimated by the method proposed by Irving-Rossotti at 25°C and 0.11M ionic strength (NaClO4) in aqueous solution. The conditional formation constants of the complexes formed between ligand and metal were calculated according to pH function. The maximum values of the conditional formation constants were found to be in accordance with the mixed metal-ligand complex formation constants of the mixed metal-ligand complexes. As a result of the experimental study, the values of stability constants of metal-ligand complexes at 25°Care as noted below: logK1=8.45; logK2=8.30 for Zn(II)-Metformin hydrochloride; logK1=8.78; logK2=8.00 for Cu(II)-Metformin hydrochloride: logK1=8.18; logK2=7.36 for Cd(II) – Metformin hydrochloride.[22]

In 2019 Ashvini Sonone *et al.* were prepared Schiff bases by refluxing the mixture of pyrazole aldehyde and triazole in dry methanol 80-90 C and 3-4 drops of acetic acid added. synthesized imine linkage generalizes the scope of o Results: reaction. The yield of Schiff bases is very high in dry methanol. The proton-ligand stability constant has Conclusion: calculated by using Calvin-Bjerrum titration technique. The observation from titration curve is shown that the deviation of (A+L) at pH range 2.5 to 3.0. (A+L+M) curves were deviated at pH range for Ni(II) is 3.6-4.0, Co(II) is 3.0-3.5, Zn(II) is 3.2-3.6 & Mn(II) is 3.6-3.8. The change in color observed that, yellow to white with Ni(II) and Zn(II), and yellow to brown in Co(II) and Mn(II), this indicates the formation of complex between Ligand and Metal. [23]



In 2019 Zamzam Taher Omar (Al-Ahdal) *et al.* have studied the interaction of Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) metal ions with organic ligand N- [(E)-(4-Hydroxy-3-methoxyphenyl) methylene] isonicotinohydrazide have been studied by pH-metric technique at  $27\pm10$ C in 70% (v/v) ethanol – water medium at 1M (NaClO4) ionic strength. Organic ligand was synthesized by condensation of equimolar mixture of Anti-mycobacterial agent with aromatic aldehyde. The reaction progress and purity of organic ligands were confirmed by thin layer chromatography. Formation of organic ligands was confirmed with the help of MP, IR, 1H NMR, 13C NMR and elemental analysis. The stability constants of these binary complexes were evaluated and order of stability constant found as Cu (II) > Co (II) > Mn (II) > Ni (II) > Zn (II).[24]

In 2019 Vijay S. Jagtap have studied stability constant is one of the very important concepts in coordination chemistry. Various methods use to determine stability constant. In the present work pH-metric study of substituted pyrazole carboxylic acid derivatives with metal ions Ni(II) at temperature 298K is done in 70% DMF-Water mixture. The interaction have been studied at 0.1M ionic strength by Bjerrum method as adopted by Calvin and Wilson. The data obtained were used to estimate and compare the values of proton ligand stability constant (pk) and metal-ligand stability constants (logk). From estimated data (pk and logk), the effect of substituents were studied. Ligand L1 1- phenyl-3-(4'- methyl) phenyl-1H- pyrazol-4-carboxylic acid and Ligand L2 1- phenyl-3-(4'- bromo) phenyl-1H- pyrazol-4-carboxylic acid are used for present work.[25]

In 2016 S. V. Thakur *et al.* have studied the stability constant of Zonisamide with trivalent rare earth metal ions Ce3+, Pr3+, Nd3+, Pm3+ and Gd3+ using a pH metric titration technique in aqueous medium at 25°C temperature and at an ionic strength of 0.2M NaClO4 were studied. The method of Calvin and Bjerrum as adopted by Irving and Rossotti has been employed to determine metal-ligand stability constant (logK) values. The trend in the formation constants follows the order: Pr3+ < Ce3+ < Nd3+ < Pm3+ < Gd3+[26]

In 2015 R.R.Tayade *et al.* in the present work, effect of metal ion Fe(III) on the properties of complexes of substituted imidazolinone in 70% (DMF+water) mixture at 298K had studied. The interaction have been studied at 0.1M ionic strength by Bjerrum method as adopted by Calvin and Wilson. It is observed that Fe(III) metal ion form 1:1 complex with ligands (L1& L2). The data obtained were used to estimate and compare the values of protonligand stability constant (pk) and metal-ligand stability constants (logk). From estimated data (pk and logk), the effect of substituents were studied. Ligand used for present work were (L1) 1-[2-hydroxy-5-(3 Chloro phenyl azo) benzylidene amino]-2-phenyl-4- benzylidene-5-oxoimidazoline (L2)1-[2-hydroxy-5-(4-bromo phenyl azo) benzylidene amino]-2-phenyl-4-benzylidene-5-oxoimidazoline.[27]

In 2015 D. S. Hedaoo *et al.* have reported Refractive index measurement for the solutions of four derivatives of 2,3-Dihydroquinazolin-4(1H)-one is done using Abbe's refractometer. From the data of refractive index and density, molar refraction (Rm) and polarizability constant ( $\alpha$ ) are calculated. The values of these parameters and their variations are used to explain interactions taking place in the solution.[28]

In 2015 M. M. Kalaskar *et al*.have studied the viscometric measurements of recently synthesized drugs viz. 2- Amino [ 4-(3-nitro phenyl)-6-phenyl-1,6-dihydro]-1,3-pyrimidine (L1) and 2-Amino [4,6-diphenyl-1,6-dihydro]-1,3- pyrimidine (L2) were carried out at different temperature by preparing the solutions of different concentrations in 60% DMF-water solvent. The results obtained during this investigation through light on the dipole association of the compound, the intermolecular attraction between solute and solvent, polarizability and mutual compensation of dipoles.[29]

In2015 Atmaram K. Mapari have studied Binary and ternary complexes of the type M-Y and M-X-Y [M = Co(II), Ni(II), Cu(II) and Zn(II); X = 2-{(E)-[(4- chlorophenyl)imino]methyl}phenol and Y = 1-[(1E)-N-(2-bromo-6- methylphenyl)ethanimidoyl]naphthalen-2-ol have been examined pHmetrically at 27  $\pm$  0.5oC and at constant ionic strength,  $\mu = 0.1$  M (KCl) in 75 : 25 (v/v) 1,4-dioxne-water medium. The stability constants for Binary (M-Y) and ternary (M-X-Y) systems were calculated.[30]

In 2014 Mohamed M. Shahata have reported the association equilibria of PHQ and PHQcoordinated with some transition metal cations such as: Al(III), Ca(II), Cd(II), Cu(II), Fe(III),



Mg(II), Ni(II), Pb(II) and Zn(II) ions were studied using potentiometric technique. The association constant (Ka) of PHQ was calculated from the average number of protons attached per repeating unit in the PHQ matrix (nA) at different pH values. This value of pKa which formed was found to be 7.75. The titration curves revealed that the metal ion replaces protons and coordinates to the polymer matrix. In addition, the use of such titration curves could be computed of the formation constants (log  $\beta$ ) of the different species exist at equilibrium. The formation constant (log  $\beta$ ) for different molar ratios of species such as 1:2, 1:1 and 2:1 for metal : polymer matrix, in solution were computed and the results were discussed. The value of n and PL for the metal ions under investigation were calculated at different pH values. The Formation Constant (log  $\beta$ ) of the coordinated polymer based on PHQ–Metal ion were computed using n – PL system. Mathematical calculations of differential change of n ( $\Delta$  n) gave a sharp signal for calculations of formation constant (log  $\beta$ 1, log  $\beta$ 2 and log  $\beta$ 3) which indicate to the protonation degree. The analyses of potentiometric data helped us to determine each value of the formation constant and/or partial formation constant for the metal ions such as: Al(III), Ca(II), Cu(II), Cu(II), Co(II), Fe(III), Mg(II), Ni(II), Pb(II) and Zn(II) coordinated with PHQ matrix .[31]

In 2014 Dr. Y. K. Meshram *et al.* have studied the interaction between Co(ll), Ni(ll) and Cu(ll) Metal Ions and 2-Hydroxy-4-Methyl-5-Chloro Acetophenone (L1) and Benzophenone have been studied at 0.1M Ionic Strength in 70% DMF water mixture by Bjerrum method as adopted by Calvin and Wilson. It is observed that Co(ll), Ni(ll) and Cu(ll) Metal ions form 1:1 and 1:2 complexes with ligands (L1 & L2). The data obtained were used to estimate and compare the values of proton-ligand stability constant (pK) and metal-ligand stability constants (log k). From estimated data (pK and log k), the effects of substituents were studied.[32]

In 2014 A.A.Ramteke *et al.* in the present work, study the stability constants of the complexes of chloro pyrazoles with some metal ions and see the effect of various ionic strengths on the stability constants. The interactions of Cu (II), Tb (III) and Nd (III) metal ions with ligand i.e.  $3 - (4 - \text{Chlorophenyl}) - 4 - (2 - \text{furanoyl}) - 5 - (2 - \text{hydroxy phenyl}) - \text{pyrazole at various ionic strengths in 70% dioxane-water medium have been investigated by Calvin-Bjerrum pH metric technique at 270C. The obtained data was used to study the correct mechanism of the complexation reaction and the obtained results were used to study the thermodynamic constant.[33]$ 

In2014 R. R. Tayade *et al.* have studied the interaction between Ni(II), Cu(II) and Zn(II) metal ions and substituted imidazolinone have been studied at 0.1 M Ionic Strength in 70 % DMFwater mixture by Bjerrum method as adopted by Calvin and Wilson. It is observed that Ni(II), Cu(II) and Zn(II) metal ions form 1:1 complex with ligands (L1& L2). The data obtained were used to estimate and compare the values of proton-ligand stability constant (pK) and metal-ligand stability constants (logk). From estimated data (pK and log k), the effects of substituents were studied. Ligand used for present work were (L1) 1-[2-hydroxy-5-(3 Chloro phenyl azo) benzylidene amino]-2-phenyl4-benzylidene-5-oxoimidazoline (L2)1-[2-hydroxy-5-(4bromo phenyl azo) benzylidene amino]-2-phenyl-4-benzylidene- 5-oxoimidazoline.[34]

In 2014 Dr. A. D. Khambre, Dr. M.L.Narwade have studied the Interaction of metal ions with Pr(III),Nd(III) and Gd(III) metal ions with i) 2-Hydroxy,3-Bromo,5-Chloro,4-Methoxy,N-(Orthonitro Phenyl) Chalcone Imine(L1). ii) 2-Hydroxy,5-Chloro,5-Methoxy,N-(Orthonitro Phenyl) Chalcone Imine (L2). iii) 2-Hydroxy,5-Chloro Chalcone Dibromide (L3). iv) 2-Hydroxy,5-Chloro,4-Methoxy Chalcone Dibromide (L4). v) 2-Hydroxy,3-Bromo,5-Chloro,4-Methoxy Chalcone Dibromide (L4). v) 2-Hydroxy,3-Bromo,5-Chloro,4-Methoxy Chalcone Dibromide (L5). have been studied at 0.1M Ionic strength.It is observed that, Pr(III),Nd(III) and Gd(III) metal ions form 1:1 and 1:2 complexes with L1 to L5. The substituted Schiff's Bases & Dibromo Chalcones show formation of simultaneous complexes.The order of proton-ligand stability constant is as pKL3>pKL2>pKL5>pKL1>pKL4. The data obtained for pK and logK are used i)To see the effect of substituents,ii) To check the validity of logk = a.pK + b.Here proton-ligand & metal-ligand stability constants have been studied pH-metrically by Calvin-Bjerrum titration technique.[35]

In 2014 A. G. Gotmare *et al.* have reported the proton-ligand and metal-ligand stability constants of the complexes of Cu(II), Ni(II),Co(II) with 1-Benzothiazol2-yl-3-(2-hydroxy phenyl)-5-(4-methoxy phenyl) pyrazoline (L1), 1-Benzothiazol-2-yl-3-(2-hydroxy phenyl)-5-phenyl pyrazoline (L2), 1-Benzothiazol-2-yl-



3-(2-hydroxy phenyl)-5-(4-chloro phenyl) pyrazoline(L3 ), 1-Benzothiazol-2-yl3-(2-hydroxy-5-methyl phenyl)-5-(4-methoxy phenyl) pyrazoline (L4 ), 1-Benzothiazol-2-yl-3-(2-hydroxy-5-methyl phenyl)-5-(4-chloro phenyl) pyrazoline(L5 ) and 1-Benzothiazol-2-yl-3-(2-hydroxy-5-methyl phenyl)-5-phenyl pyrazoline(L6 ) have been determined by pH-metric method in medium of 80% acetone-water mixture at 0.1M ionic strength and at  $(30 \pm 0.1)$  0C temperature.[36]

In 2013 Anita Gupta this present work is a report on the stability constant values of a worthy antibiotic, Ampicillin Trihydrate; D[-]-α-aminobenzyl penicillin; ABP; a semi-synthetic derivative of penicillin with various biologically vital bivalent metal ions (Co2+, Ni2+, Cu2+, Zn2+, Cd2+, Sn2+, Hg2+ and Pb2+) recorded in water-ethanol medium 50% V/V at three different temperatures (298K, 308K, 318K)maintaining ionic strength at 0.1M KNO3. The effect of temperature was also studied and the corresponding thermodynamic functions  $\Delta G^{\circ}$ ,  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  were calculated and discussed. It is significant to study the stability constants of drugs with these metal ions as they may already be present in human body. The proton-ligand and metal-ligand stability constants were determined by Calvin- Bjerrum pH titration techniques as modified by Irving and Rossitti. This analysis was carried out in order to determine the pk1 H and log k1, values at 298 K, 308 K and 318 K. The metal to ligand mole ratio was maintained at 1:5 in order to fulfil the maximum coordination number of metal ion. The titrations were done in a titration cell with three openings, kept immersed in a thermostated bath. The formation curves were plotted by taking value of n A (the degree of formation of metal-ligand complexes) against pH of the system. These plots indicate that these metal ions form 1:1 complexes with ABP. The results show that the pK1 H values increases with an increase in temperature. The order of metal-ligand stability constants (log k1) has been found to be Cu2+> $Zn2+>Cd2+>Pb2+>Sn2+\approx Hg2+>Co2+>Ni2+[37]$ 

In 2013 A. B. Naik, M. L. Narwade have studied the stability constants of 1-phenyl-3-(2-hydroxy-4methylphenyl)-5-methylpyrazole (PHMPMPz) and their complexes with Pr (III) and Sm (III) metal ions have been determined in 70% v/v dioxane-water media at different ionic strength (0.02, 0.04, 0.06, 0.08, 0.1) mol.dm-3 at 300.15K by pH metry method. The pK and logK values decrease with increase in ionic strength of medium, which indicated the opposite charges on reacting species. The values of stability constants for Sm (III) were greater than Pr (III) metal ion. The thermodynamic stability constants at zero ionic strength have also been determined.[38]

In 2013 M. M. Kalaskar and M. P. Wadekar the present study is being down on synthesis of chelating agent, which might have selectively for single metal ion. In the view of these consideration the chelating nature of azomethine derived from the para-aminobenzoic acid and substituted benzaldehyde towards the metal ions mainly Fe(III) is undertaken. Many fold aspects of complexasation of these azomethine is still lacking. Thus it was decided to undertake such work, the synthesis, characterization of some azomethine and study their magnetic susceptibility after complexarion. The synthesis of azomethine and Fe(III) complexes still not mentioned in any record because of the oxidizing nature of Fe(II) ion in solution. Therefore, the main aim of azomethine complexes and to study their magnetic susceptibility.[39]

In 2013 Olagboye S.A *et al.* have studied L- Metal- ligand complexation in solutions was studied in water-methanol media by pH-metric titration with the standard glass electrode at ionic strength of 0.1M KNO3. The titrations were carried out at various temperatures 35oC, 45oC, and 55oC and the pKa values (stability constants) were determined. Copper (II) with benzimidazole gave pKa's of 2.86, 2.52, and 2.46; Stability constant (logK) 338.80, 331.13 and 288.40 while Nickel (II) benzimidazole gave pKa's 2.51, 2.60 and 2.38 and Stability constant (logK) 323.59, 398.11 and 239.85 respectively. It was revealed that the stability constants of the metal complexes decreased as the temperature increases. Formation constants obtained for these complexes showed that metal- ligand ratio were in the range of 1:1 and 1:2. The thermodynamic parameters were also determined at the working temperatures and the results obtained showed negative  $\Delta$ H and Gibb's free energy ( $\Delta$ G) indicating exothermic and spontaneous reactions.[40]

In 2012 Suresh D. Dhage, Mahesh B. Swami the present work deals with the study of proton ligands and metal- ligands Constant of Binary and ternary complexes. Where M= Innertranition metals, L= Primary ligands( malic acid, ,maleic acid and Malonic acid) and secondary ligands B = Glycine have been studied Potentiometrically in biologically relevant conditions. At ionic strength  $\mu$ = 0.1M NaClO4. All the



ligands forns 1:1:1 ternary complexes, the relative stability of ternary complexes expressed in terms of statistical parameter  $\Delta \log k$  and -  $\Delta \log k$  values suggest that the formation of ternary complexes are favorable and variation of  $\Delta \log k$  has been explained in terms of metal-ligand- $\pi$  interaction, size of chelate ring, and steric factor.[41]

In 2011 Sumer D.Thakur *et al.* have studied the interaction between Th(III), Sm(III), Nd(III) and Pr(III) metal ions and 2-Mercapto-4-(4'-Aminophenyl)-6-(2'-Hydroxy-5'-Bromophenyl)Pyrimidine [M4AHBP](L1)and2-Mercapto-4-(2'-Chlorophenyl)-6-(2'-Hydroxy-5'Bromophenyl)

Pyrimidine[M2CHBP](L2) have been studied at 0.1 M Ionic Strength in 70 % Dioxane-water mixture by Bjerrum method as adopted by Calvin and Wilson. It is observed that Th(III), Sm(III), Nd(III) and Pr(III) Metal ions form 1:1 and 1:2 complexes with ligands (L1 & L2). The data obtained were used to estimate and compare the values of proton-ligand stability constant (pK) and metal-ligand stability constants (log k). From estimated data (pK and log k), the effects of substituents were studied.[42]

In 2011 K. Kiranmai *et al.* have studied the formation constants of binary and ternary complexes of Schiff bases MEMIIMP, MIIMP, BMIIMP, CMIIMP, MMIIMP, MIIBD and some N,O; N,N; O,O donor ligands with Co (II), Ni (II), Cu (II) and Zn (II) have been determined by potentiometrically at 0.1M KNO3.in aqua organic medium. The effects of temperature and ionic strengths on binary systems have been studied. All these metalions form 1:1 and 1:2 binary complexes and 1:1:1 ternary complex. The thermodynamic parameters  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  of binary complexes have been determined and discussed. The stabilities of ternary complexes are discussed on the basis of  $\Delta \log K$ .[43]

In 2010 G.B. Pethe *et al.* have studied the interaction of metal ions with pyrazoles and diketons gained much interest as these compounds have importance in antidiabetiec drugs. The physical properties such as viscosity and metal-bonding stability constant in 70% DMSO-Water and refractive index and polarazibility constant in different concentration with diketones at 300 c. The result obtained of stability constants are in good agreement. Mesurement of refractive index has also been studied by Abbe's refractometer. Molar refractivity and Polarazibility constants of ligands solution have been evaluated in the present investigation. It could be seen that Molar Refractivity and Polarazibility constants are found to be decreased with increase in density of solution. The stability constants of metal-ligand complex formation of Cu(II) with pyrazoles and diketones have been studied using Irving Rassoti's Method and titration is done by using Calvin Bjerrum Method in an inert atmosphere at 0.1M ionic strength and temp.(300 c $\pm$  0.10 c) PH metrically[44]

In 2009 A.B.Naika and M.L.Narwadeb have reported the pKa values of N-heterocyclic compounds (substituted pyrazoles) in a 70% (v/v) dioxane–water mixture have been determined using pH-metric measurements. The stability constants of the complexes of Dy(III), Nd(III), Sm(III), and Tb(III) with 3-(2-hydroxyphenyl)-5-methylpyrazole, l-phenyl-3-(2-hydroxy-4-methylphenyl)-5-methylpyrazole, and l-phenyl-3-(2-hydroxy-4-methylphenyl)-5-methylpyrazole have been determined by the pH-metric method at ( $300 \pm 0.1$ ) K. The effect of ionic strengths on the complexes of Sm3+ and Pr3+ ions with pyrazole has been investigated in the internal from 0.02 to 0.1 mol dm–3 (sodium perchlorate) in the pH range 2–3.[45]

#### Conclusion

The above mentions information about the study the interaction of transition and inner transition metal ion with ligand to study the proton-ligand and metal-ligand stability constants were determined by Calvin- Bjerrum pH titration techniques as modified by Irving and Rossitti. In this review, Study Metal Ligand Stability Constant by pH Metric Technique have been summarized from 1940-2022.

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