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STUDY OF METAL-LIGAND COMPLEXES IN SOLUTION AND THEIR STABILITY CONSTANT

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Abstract:

In most cases, complex formation being a complex between metal ions and protons, it is reasonable to expect that there is some correlation between stability constant of complex and acidic dissociation constant of conjugate acid of ligand. Larson[1] found linear relationship between corresponding constants for complexes of silver(I) with organic amines. Subsequently similar correlation were found in many complex systems.[2-3] The ligand may affect chelating tendency in two possible ways - (i) It may influence the basicity of donor groups by inductive and resonance effect or and (ii) the addition of groups on ligand may be purely statistical (sterical) effects prevent the ligand ions or molecules from acquiring the orientation about central metal ions most favorable for chelation. In certain cases linear correlations was found between Hammett constant (σ) for the functional groups of the complexes. May and Jones[4] have applied Hammett's equation to complexes of substituted benzoic acids. Irving and Desilva[5]introduced stability factor "S_f" which is a measure of the stabilization due to π bonding.

Keywords: Metal, solution, stability, constant

INTRODUCTION

Considerable research work has been done on the study of complexes in solution in last five decades. The development in the field was initiated by Jannik, Bjerrum dissertation[6] published in 1941. Calvin, Bjerrum, Irving, Rossetti, Martell and Schwarzenbach have made important contribution to the rapid progress in our understanding of metal-complexes in aqueous as well as in mixed solvents.

The chelates have been extensively studied in solution as well as in solid state by many workers, because of their remarkable properties and high stability. The extensive work in co-ordination complexes has been made possible with the help of various experimental techniques and has led in a number of empirical conclusions which have been de tailed by Martell[7].

The stability of a metal complex in solution is governed by the nature of central atom and the ligands. The most important characteristics of the central atom which influence the stability of complex compound are the degree of oxidation (charge on the central ion in the case of ionic complexes) the radius and electronic structure in the case of complexes with monoatomic ligands. Stability is dependent on the same characteristics in the ligand as well as considered for the cation. The strength of binding for ligand molecules and polyatomic ions depends in addition, on the nature of the atoms, directly linked to the central atom and on the particular features of the structures of the ligand molecule or ions.

Stability of Complexes:

Stability constant of complexes have played an important tool to determine the thermodynamic parameters such as enthalpy, entropy, free energy etc. A complex formation is favoured by negative enthalpy and positive entropy changes. It is very difficult to predict the contribution of these terms because the solvation of the constituents of the complex also must be taken into consideration. According to Williams[8] the entropy term is usually favoured when the ligand is anionic and is generally favoured in case of neutral ligands. Enthalpy changes in complex formation determined by temperature coefficient and microcolorimetry method. More sensitive method is microcolorimetry and used by number of workers to determine $\Box$H of various complexes of transition metal ions and Lanthanides.[9-12]

Ring Size and Number of Chelate Rings:

The stability of complexes also depends upon the size and number of chelating rings. The size of the chelating rings and number of rings formed on chelation are determined by the structure of chelating agent. Hence the stability of chelate depends upon both the factors. Ley[13] has concluded from his work on amino acid chelates that five and six membered rings are most stable. Pfeiffer[14] observed that in general the five membered ring is more stable when the ring is entirely saturated. But when one or more double bonds are presents, the six membered ring is favoured. Schwarzenbach et al[15] have also observed that there is decrease in chelate stability with increase in the ring size.

Yutaka et al[16], Saha and Sinha[17] have studied steric influence of the ligand and reported increase in the value of formation constant with the change in the alkyl group from methyl to n-butyl possibly due to increase in the electrophilic character of metal with increase in the length of alkyl chain.

Nature of Metal:

Chelation as well as stability is governed by nature of metal. The stability order of metal complexes of transition metal ions is found by Irving and Williams[18] by comparing the ionic radius and second ionisation potential of metal ions.

In the present work especially effect of trivalent transition metal ion Nd(III), Pr(III), Lanthanide ion Sm(III) on the properties of metal complexes formed from substituted pyrazoline is studied.

Correlation between the Basicity of the Ligands and the Stability of the Complexes:

In most cases, complex formation being a complex between metal ions and protons, it is reasonable to expect that there is some correlation between stability constant of complex and acidic dissociation constant of conjugate acid of ligand.

Determination of Stability Constant:

The conjugated acids of most ligands are weak, consequently at the time of complex formation, there is a competition between protons and metal ions for the ligand. Then, stability constants can be determined by three steps as follows:

(1)   Construction of the formation curve of the system as a plot of

$$\bar{n} \quad \text{versus} \quad pL = \log \frac{1}{[L]}$$

(2)   The calculation of K_1 and K_2 values by solving the formation function of the system.

(3)   The conversion of stoichiometric constants into the thermodynamic functions.

(4)   Calvin-Bjerrum Titration :

(5)   Hearson and Gilbert[19], Wilkins and Lewis[20], Rossetti and Rossotti have described general methods for the determination of stability constants, by using the technique of Calvin and Melchior[21] [Calvin-Bjerrum titration technique]. In the present investigation, Irving and Rossetti method has been used. The experimental part contains titration of –

(6)   (1) Free acid   (2) Free acid + ligand   (3) Free acid + ligand + metal with standard solution of NaOH. The ionic strength of each solution is kept constant generally at 0.1 M by the addition of KNO_3.

(7)   In past, the number of workers[22] reported their results on metal-ligand chemistry. Many workers observed the effect of solute-solvent interactions on protonation equilibrium of organic acid and chelation equilibrium of their transition metal ion complexes.

(8)   Khadsan et al[23] carried out study of Co(II), Cu(II) and Ni(II) complexes with substituted pyrazoline and pyrazole. pH-metric study on determination of metal-ligand stability constant of some substituted isoxazolines

is carried recently by Pawar et al[24]. Transition metal complexes of substituted Schiff's bases is studied by Thakur et al[25].

Metal-ligand stability constants of the complexes of transition metal ions, Lanthanides and nuclear metal ions with dihydroxy compounds, aminohydroxy phenols, naphthols, carboxylic acids, sulphonic acids, coumarins, triazines and peptides have been reported by number of workers.

(9) Tayade et al[26] have studied stability constants of Cu(II) chelates with some substituted s-triazines. Wagh[27] carried out potentiometric studies of complex of Pyrazoline. Narwade et al[28] have studied the equilibrium constants

CONCLUSION:

In past, the number of workers reported their results on metal-ligand chemistry. Many workers observed the effect of solute-solvent interactions on protonation equilibria of organic acid and chelation equilibria of their transition metal ion complexes. Carried out study of Co(II), Cu(II) and Ni(II) complexes with substituted pyrazoline and pyrazole. pH-metric study on determination of metal-ligand stability constant of some substituted isoxazolines is carried out. Transition metal complexes of substituted Schiff's bases is studied .Metal-ligand stability constants of the complexes of transition metal ions, Lanthanides and nuclear metal ions with dihydroxy compounds, aminohydroxy phenols, naphthols, carboxylic acids, sulphonic acids, coumarins, triazines and peptides have been reported by number of workers.

REFERENCE:

1. Larson E.:*Z. Physik. Chem.*, Leipzing, **A 169**, (1934)207.
2. Laberman R. 32.Larson E.: *Z. Physik. Chem.*, Leipzing, **A 169**, (1934)207.
3. Tucci E.R., K.E., C.H. and : *J. Inorg. Nuclear Chem.*, **29**, (1967) 1957. Li N.C.
4. May W.R. and Jones M.M. : *J. Inorg. Nuclear Chem.*, **24**, (1962) 511.
5. Irving H. and *Proc. Chem. Soc.*, (1962) 250.
6. Desilva J.J. Bjerrum J.:"Metal amine formation in aqueous solution', P. Haase and Sons, Copenhagen (1941).
7. Martell, A.E. and Calvin, M.:"Chemistry of Metal Chelate Compounds", Prentice Hall, Inc., England, Cliffs, NJ (1962).
8. William R.J.P.:*J. Phys. Chem.*, **58**, (1954), 121.
9. Care R.A. and Staveley L.A.K.: *J. Chem. Soc.*, 4571 (1956).
10. Jonassen H.B., Hurst G. G.L.C., Bane R.B. and Meibohm A.W.:J. Phy. Chem., **56** (1952)
11. Izatt R.M., Fernaelius W.C. and Block B.P. :ibid - **59** (1955), 235.
12. Poulsen I. and Bjerrum J. : *Acta. Chem. Scand.*, **9** (1955), 1407.
13. Ley:*J. Electro. Chem.*, **10** (1940), 954.
14. Pfeiffer: *Angew Chim.*, **53**, (1940), 93.
15. Schwarzenbach and Ackerman K. : *Helv. Chim. Acta.*, **31**, (1948), 1029.
16. Yutaka F., Reiko M. and Kozo S.: *Bull. Chem. Soc. Japan*, **49(4)** (1976). 1017.
17. Saha N. and Sinha S. : *Ind. J. Chem.*, **24** (1985), 203.
18. Irving H. and Williams R.J.P.: *J. Chem. Soc.*, **75** (1953), 3192.
19. Hearson J.Z. and Gilbert J.B.: *J. Am. Chem. Soc.*, **77** (1955) 2594.
20. Lewis J. and Wilkins R.G. : "Modern Coordination Chemistry", Inter Sci. Pub. Co., New York (1960).
21. Calvin M. and Melchior N.C. : *J. Am. Chem. Soc.*, **70** (1948) 3270.
22. Martell, A.E. and Calvin, M.: "Chemistry of Metal Chelate Compounds", Prentice Hall, Inc., England, Cliffs, NJ (1962).
23. Khadsan, Kadu M.V., Doshi A.G.: *Oriental J. Chem.*, **21(1)** (2005), 137-140.
24. Pawar N.N., Doshi A.G. : *Asian J. Chem.*, **18(1)** (2006), 750.
25. Thakur C.D., Shankarwar A.G., Deshpande Y.H. : *Acta Ciencia Indica*, **XXXI(4)** (2005), (2005), 317.

26.   Tayade D.T., Patil S.U. Shelke Y.B., Dhakite S.P., : *Asian J. Chem.*, **15(1)** (2003),

27.   Wagh S.P.: Ph.D. Thesis, Amravati University (2004).
28.   Narwade, M.L., Chincholkar, M.M. and Sathe, S.W.:*J. Chem. Soc.*, **72**, (1987) 260.