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CHAPTER - VI

SUMMARY

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CHAPTER - VISUMMARY

It is obvious that an important finding in connection with in chemical reaction is the identification of the resultant products that can be isolated. Equally important aspect is to know how the reaction proceeds. A detail kinetic investigation through light on the nature of involvement of species of transient existence and a succession of stepwise formation of species. The mechanism of the chemical reaction is therefore an important aspect. Next question which confronts a researcher is "why do chemical reaction occur?" The answer for this question must be sought in the thermodynamic of reactions. This includes the quantitative investigation of species in solution and the energetics of formation of the various species. Solution chemistry is regarded as difficult and complicated because of involvement of large number of species and very complicated relations between them with respect to charge, composition, concentration and energetics. It is, therefore, considered that a study of chemical equilibria is the most challenging field in inorganic chemistry.

Substituted vic-hydroxy aldehydes and their derivatives are gaining importance because of their applications in reactions of interest to analytical chemists and also because of the structural flexibility these compounds have acquired an important

place in structural chemistry of coordination compounds. Interesting bio-inorganic chemistry is now coming up and metal complexes of this group of ligands are being investigated with respect to their activity in biological systems. Hence the solution chemistry of complex ions involving metal ions and these ligands must be studied in order to have proper understanding of chemical aspects in relation with structure and reactivity. The present project is related to the thermodynamic aspects of complex formation between nitrosalicylaldehydes, resorcyaldehyde oxime and substituted salicylaldehyde thiosemicarbazones.

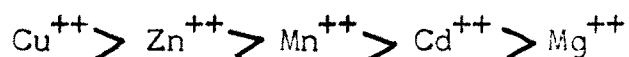
The classical Calvin-Bjerrum technique as modified by Irving and Rossotti was used for determination of the stability constants.

Series of titrations were carried out with standard NaOH solution at three different temperatures  $25^{\circ}$ ,  $35^{\circ}$  and  $45^{\circ}\text{C}$ . In all these titrations solvent compositions and final volumes were kept constant. The temperatures were controlled within  $\pm 0.1^{\circ}\text{C}$ . The proton-ligand stability constants and metal-ligand stability constants were determined by using half integral and graphical methods. Thermodynamic parameters were determined by using temperature coefficient and Gibbs Helmholtz equation.

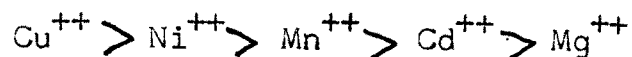
On the basis of experimental results and analysis we arrive at the following conclusions:

- 1) The substituents in the ligand aromatic ring alter the electron density at various sites, affect the proton-ligand and metal-ligand stability constants and affect the chelation. Due to electron withdrawing - NO<sub>2</sub> group in position 3 and 5 there is decrease in log K<sub>1</sub><sup>H</sup> and log K<sub>1</sub> values for salicylaldehyde.
- 2) 3-Nitro salicylaldehyde and 5-Nitro-salicylaldehyde form fairly stable 1:1 complexes in solution.
- 3) The stability constants of divalent ions of first transition series increases with increase in atomic number except in zinc. The zinc chelates are less stable than copper chelates.
- 4) The stability constant increases with increase in second ionisation potentials.
- 5) Thiosemicarbazones gives quite stable 1:1 complexes. 1:2 complexes are precipitated at high pH range so they are not studied.
- 6) Irving and Williams stability order is obeyed by all ligands. The stability orders observed in present work are as follows:

3-Nitrosalicylaldehyde



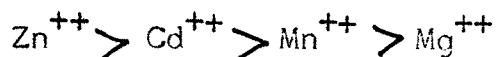
5-Nitrosalicylaldehyde



3-Resorcyaldehyde oxime



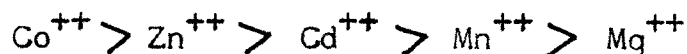
Salicylaldehyde thiosemicarbazone



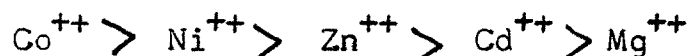
4-Methyl salicylaldehyde thiosemicarbazone



5-Nitrosalicylaldehyde thiosemicarbazone



Resorcyaldehyde thiosemicarbazone



7) The reversal of order of  $\text{Ni}^{++}$  and  $\text{Co}^{++}$  from Irving and Rossottis order for 3-Resorcyaldehyde oxime having N, O donors lead to conclude that the order of log K values depends on nature of the metal ion and nature of the donor atoms.

8)  $\log K_1^H$  and  $\log K_2^H$  values for proton-ligand stability constants and  $\log K_1$  values for metal-ligand stability constants increases with increase in temperature except for Resorcyaldehyde thiosemicarbazone.

9) All thiosemicarbazones have high -ve value for  $\Delta H$ , hence these ligands form most stable complexes and involved formation of stronger metal-ligand bonds.

10) The enthalpy change and entropy change may supporting or opposing the formation of the complex formation as seen for 3-Resorcyaldehyde oxime.

The logical extension of the present work will be the extension of applications of ligands with varying structural features, choice of several other metal ions including ~~rare~~ earths and biologically significant metal ions, use of ligands with structures comparable to molecules of life i.e. ligands responsible for various physiological activities of animals and plants. Application of more penetrating experimental techniques, comprehensive review of the work being done in bioinorganic studies pertaining to equilibria and also a look at whatever has been done from different angles so as to know more about the chemical reactions. The candidate intends to continue his studies in this area, which had fascinated him during the course of this investigation and will continue to attract his mind in future also.

Appendix - A

VALUES OF THE CONSTANT  $\delta \equiv E_j - \log m_{rH}$  in  
METHANOL-WATER AND ETHANOL-WATER IN pH UNITS. (at 25°C)

Wt. per cent Alcohol	Methanol-water solvents		Ethanol-water solvents		
	Ref. 2	Ref. 1	Ref. 4	Ref. 1	Ref. 3
0	0	0	0	0	0
20	0.01	0.01	- 0.03	0.02	-
30	-	-	-	-	0.07
35	0.05	0.06	+ 0.07	0.10	-
50	0.13	0.13	0.17	0.21	0.23
65	0.15	0.14	0.19	0.24	-
71.89	-	-	-	-	0.29
80	- 0.06	-	0.11	0.11	-
90	- 0.51	-	- 0.40	-0.40	-
100	- 2.34	-	- 2.36	-2.91	-2.77

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