Thesis

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Ion Exchange Study of the Sulphato Complexes of Zn^{2+}, Cd^{2+} and Hg^{2+}

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A STUDY OF THE SULPHATE COMPLEXES OF Zn^{2+}, Cd^{2+} and Hg^{2+}

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NOTE

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CHAPTER I

INTRODUCTION

INTRODUCTION

Inorganic salts are usually classified as simple, double or complex salts. This diffrentiation is now not significant.

A simple salt may be regarded as a complex when the metal is joined to one ligand only to form a neutral system.

In the wider sense, simple salts such as simple chlorides, sulphates, nitrates, ... etc. may be regarded as complexes. For example iron (III) combines with chlorine ion forming the following systems:

$$[FeCl]^{++}, [FeCl_2]^{+}, [FeCl_3], [FeCl_4]^{-}, [FeCl_5]^{--}, \text{and } [FeCl_6]^{---}$$

All these can be regarded as complex systems. The salt $Fe(III)Cl_3$ which is commonly regarded as a simple salt is actually a member of a complex series. This also may apply to other systems.

Stability Constants:

The most important way to characterise a complex formation in solution is to determine the equilibrium constants of the complexes formed.

The term stability is introduced to describe the amount of association that occures in solutions containing two or more component species in equilibrium in which the more stable the complex formed, the greater will be the association.

One must differentiate between two types of stability, namely "thermodynamic stability constant" and "kinetic stability constant". The former is a measure of the extent at which this species will form from, or to be transformed into other species at equilibrium conditions and the latter deals with the speed at which such transformations takes place. In the present investigation, we are dealing with thermodynamic stability constants only.

In early investigations, a great excess of ligand is usually used for complexation reactions with metal ion or atom. Thus the computation of stability constants was always based on the assumption that only one particular complex species is formed in solution, such an assumption is not always true, and in many cases may lead to erroneous results.

Bjerrum[1] was the first to emphasize, that complex formation is in general a stepwise process. This is best shown in the light of the following relationships:

Suppose a metal ion M, is introduced into a solution containing a ligand A, and suppose that conditions were chosen so that to give rise only to the formation of mononuclear species, then different equilibria will be set up. By applying the low of mass action, to those equilibria and ignoring the ionic charges for simplicity, we obtain:

$$M + A = MA \qquad K_1 = \frac{[MA]}{[M][A]}$$

$$MA + A = MA_2 \qquad K_2 = \frac{[MA_2]}{[MA][A]}$$

$$MA_2 + A = MA_3 \qquad K_3 = \frac{[MA_3]}{[MA_2][A]}$$

$$\vdots \qquad \vdots \qquad \vdots \qquad \vdots \qquad \vdots$$

$$MA_{j-1} + A = MA_j \qquad K_j = \frac{[MA_j]}{[MA_{j-1}][A]}$$

where "[ ]" referred to the activity of species in solution and K's represent the apparent or stepwise stability constants.

Generally, j is the maximum coordination number for the metal ion M, for the ligand A, j may vary from one ion to another and from one ligand to another.

The previous set of equilibria may be treated in another way as follows:

$$M + A = MA \qquad \beta_1 = \frac{[MA]}{[M][A]}$$

$$M + 2A = MA_2 \qquad \beta_2 = \frac{[MA_2]}{[M][A]^2}$$

$$M + 3A = MA_3 \qquad \beta_3 = \frac{[MA_3]}{[M][A]^3}$$

$$\vdots \qquad \vdots \qquad \vdots \qquad \qquad \vdots$$

$$M + jA = MA_j \qquad \beta_j = \frac{[MA_j]}{[M][A]^j}$$

where β_j 's denotes "overall or stoichiometric stability constant". The overall and stepwise stability constants are related by the expression

$$\beta_j = K_1 \cdot K_2 \cdot K_3 \cdots\cdots\cdots K_j$$

or

$$\beta_j = \prod^{j} K_j$$

One may take into consideration, that the above relations are based on the assumption that very dilute solutions are used in which the activity coefficients " γ's " are held constant.

Factors Affecting Stability Constants:

The relative proportions of the different metal complex species, α_j where

$$\alpha_j = \left[ML_j\right] / C_M$$

is dependent upon many factors. These may be related to the metal ion or to the ligand. The compatability between those factors will obviously control the relative values of K_1, K_2, K_3, ... K_j.

A- Correlation with Properties of the Metal Ion:

(i) Ionic charge and radius:

It is well known that the stability of complexes [formed with small ionic, highly charged, unidentate or multidentate ligands] increases as the size of the metal ion decreases.

This has been observed particularly within the lanthanide and actinide series[2,3].

The sequence La $<$ ..... Gd $<$ .... Lu (III) has been established with carboxylate[4] and aminocarboxylate ligands[5].

Also, for metal ions having the same size, stability was found to increase in the same order of increasing the charge on the metal ion[6] as found in the following series

$$K^{+} < Sr^{++} < La^{+++}$$

(ii) Ionization potential and electronegativity:

The minimum energy required to remove an electron from an atom, ion or molecule, leaving each without any kinetic energy is called the ionization potential "I" [7], zinc and cadmium have approximately the same ionization potential but mercury has a slightly higher value.

On the other hand electronegativity is the power of an atom in a molecule to attract electrons to itself[8]. Mulliken showed by theoretical arguments that the tendency of an atom in a molecule to compete with another atom to which it is bound in attracting the shared electrons should be proportional to (I+A)/2, that is the average of its ionization potential and its electron affinity.

The electronegativity will consequently expresses the energy evolved when electrons enter a vacent orbital such as a d-orbital[9,10] of a metal ion which form a complex ion, and therefore amounted for stability of the complex formed. The greater the energy evolved in the complex formation, the greater will be its stability and vice versa.

(iii) <u>Stereochemistry</u>:

The stereochemical evidence provide a more striking example for the requirement of the metal and ligand ions especially from the structural point of view.

Examples for the effects of stereochemistry upon stability constants were provided by the complexes of polyamines[11,12].

Thus the existence of an unusually large value of log K_1/K_2 within a sequence has been ascribed to a change of stereochemistry of the metal ion in which a transition in the hybrid state of the metal ion from a less to a more regular structure[13,14,15]. The large values of log K_1/K_2 may also be due to the dative π-bonding - in mono-complexes - from the metal ion to the ligand[16].

In other cases, a small negative values of log K_1/K_2 or log K_2/K_3 has been found for a number of systems. This was ascribed to the increasing in the π-acceptor properties of the ligand by the substituents[17,18].