CHAPTER V

RESULTS AND DISCUSSION
GENERAL CONSIDERATION

The valency system of an element in the transition series consists of the following orbitals:

penultimate shell  cutermost shell

3d  4s, 4p, 4d, 4f

In the ground state the 4s orbital is filled by one electron pair and the 3d orbital is occupied from 1 to 10 electrons according to the atomic number of the element; the 4p, 4d and 4f orbitals are unoccupied.

The transition element of the lowest atomic number, that is scandium has the electron configuration in ground state as:

\[
\begin{array}{cccccc}
1s & 2s & 2p & 3s & 3p & 3d & 4s \\
2 & 2 & 6 & 2 & 6 & 1 & ?
\end{array}
\]

The configurations of the succeeding elements are obtained by the further addition of the electrons to the 3d orbital, so that when the zinc atom is reached the 3d orbital contains 10 electrons; whereas, vanadium which comes to be second after scandium contains 3 electrons in 3d orbital. The atom due to partially filled d shell and small ionic radius may readily form stable complexes in which four or six monodentate ligands surround the metal atom or ion. When electron rich ligands are symmetrically disposed about a transition
element, the high-energy d-orbitals are just the ones needed for covalent bonding while the low energy d-orbitals serve to drain off excess of non-bonding electrons.

1 Jones has shown that vanadyl ion can form complexes of tetrahedral as well as square configuration by undergoing sp³ and dsp² hybridization respectively. Whereas, zinc ion has been shown to form tetrahedral complexes by sp³ hybridization. Distribution of the electrons and orbitals available for bond formation can be shown as follows:

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Coordination number</th>
<th>Hybridization</th>
<th>Orbitals Available</th>
<th>Types of complexes for bond formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO⁺⁺</td>
<td>4</td>
<td>sp³</td>
<td>3d 4s 4p</td>
<td>tetrahedral</td>
</tr>
<tr>
<td>WO⁺⁺</td>
<td>4</td>
<td>dsp²</td>
<td>3d 4s 4p</td>
<td>square</td>
</tr>
<tr>
<td>Zn⁺⁺</td>
<td>4</td>
<td>sp³</td>
<td>3d 4s 4p</td>
<td>tetrahedral</td>
</tr>
</tbody>
</table>

Since dsp² bonds are stronger than sp³ bonds, the planar square arrangement would be the preferred one for WO⁺⁺.

The stability of the WO⁺⁺ complexes may be explained thus; the combination of a p orbital of oxygen atom of vanadyl
ion with one of the $t_{2g}$ orbitals of the vanadium atom produces a molecular orbital of lower energy than that of the original $t_{2g}$ orbital and hence the complex is stabilized.

Durrant and Durrant have shown that in planar vanadyl complexes, the vanadyl group is perpendicular to the plane, with the vanadium atom slightly above it.

The ligands chosen for the present investigations are azo-salicylic acid dyes. We know that these contain two types of functional groups $-\text{OH}$ and $-\text{COOH}$ which are responsible for chelate formation. The primary functional group here is carboxylic group. The ease with which the hydrogen is displaced by the metal depends upon the electronegativity of the atom to which hydrogen is attached. In the present case the hydrogen atom is attached to oxygen, which is highly electronegative. Higher the electronegativity, greater is the ease with which combination occurs. Again, the second type of group responsible for the coordinate bond formation between the group and the metal is one with surplus electronic activity; and we have the phenolic group having surplus electronic activity. Due to the presence of these two functional groups, these dyes behave as strong chelating agents resulting in remarkably stable complexes.

'A' Composition of the complexes:

It has been shown conclusively by Vosburgh and Cooper method that only one complex is formed in each system.
under the experimental conditions. In a particular system, the curves are those of ligand blank and of metal and ligand solutions mixed in possible stoichiometric proportions. These curves are obtained by plotting absorption versus wavelength of all these solutions. The systems studied here (fig. 1-16) clearly show that there is a shift in the absorption maxima, confirming the chelation of the system. The identical nature of various curves is again a positive proof for the presence of only one complex in the system.

After having the clear indication that only one chelate is formed in each system, the Job's method of continuous variation has been applied for the determination of the stoichiometry of the complexes. With the application of this method, each of the systems have been found to give 1:1 (M:L) complex with Zn(II) as well as with Cu(II). The conclusions have been drawn from the figs. 17 - 32.

The composition of the chelates was further confirmed by monovariation method of Nayar and Pande by taking conductance as index property, and again the same results showing 1:1 (M:L) complex formation were revealed (fig. 63 - 70). The results thus, obtained by the above methods also agreed with those by potentiometric method. The points of the maximum slope of the curves (figs. 71 - 78) at 1:1 ratio of the reactants show the formation of 1:1 (M:L) complex in all the systems.
For confirming the results further, ratio titrations were carried out. 7n(II) and VO(II) ions were taken in different ratios of ligands e.g. 1:1, 1:2 and 1:3 and each mixture titrated against alkali. The neutralization curves (Fig. 33 - 38) obtained by neutralization of hydrogen ion liberated in the chelation reaction indicate that only one hydrogen ion is liberated in the process, thus conclusively showing that only 1:1(M:L) complex is being formed in the system.

It is also worth noting that in calculation of the values of stability constants of the 1:1 complexes, the values of \( \log K \) could not have remained constant over the whole range of series, had any higher complex formed.

The chelates formed in the above systems are quite stable, and even after keeping for 48 hours, there is no appreciable change in the optical density of the chelate solutions.

'B' Stabilities of the complexes :-

The stability of the transitional metal complexes is greater as compared to non-transitional metals. Pauling\(^5\) in order to account for the enhanced stability of cyanide complexes of transitional metals introduced the concept of \( \pi \)-bonding in metal complexes. Later on Orgel\(^6\) emphasized the same concept of \( \pi \)-bonding for the enhanced stability of the transition state rather than the ease of approach of the incoming group.
The crystal field theory requires for the maximum stability of a given geometric configuration, that the d-electrons of the metal ion avoid the region of maximum concentration of the ligand electrons. Making use of this criterion, it is apparent that the stability of the transition state increases, and hence the lability of the original complex increases, for any process which reduces the electron density along the M-X and M-Y directions.

When we come to enquire why some ligands stabilize low vacant states and others high vacant states we find that two ideas prevail:

1. That the stabilization of low valent states is essentially a π-bond effect (dative π-bonding, etc).

2. That the stabilization of high valency states is essentially a σ-bond effect associated with the electronegativity of the ligand atom, and that the more highly electronegative the ligand atom, the better it is in stabilising high valency states.

All evidence at present available points to the π-components of the coordinate bonds being the deciding factor in the valency stabilization. When the ligand atoms have suitable π-type orbitals (i.e. atomic π-, d-, dp-hybrid, aromatic π orbitals, etc.) these orbitals interact in the manner discussed by Orgel, with the d-orbitals in the nemul-
timate shell of the metal atom and umusula valency states can
become more stable. The essential point is, however, that when the \( \pi \) -type orbitals on the ligand atoms are vacant, low valency states are stabilized, but when they are filled, the high valency states are stabilized.

Under the present investigations, stability constant values of the complexes have been determined by Job's method of continuous variation using optical density as index property and by Bjerrum's method using pH as index property. The results obtained by these method have been tabulated below:

<table>
<thead>
<tr>
<th>Ligand of the complex</th>
<th>Composition</th>
<th>pH</th>
<th>Bjerrum's method</th>
<th>Job's method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Zn(II) (II)</td>
<td>Zn(II) (I)</td>
</tr>
<tr>
<td>Unsubstituted dye</td>
<td>1:1</td>
<td>7.0</td>
<td>1.9338x10^4</td>
<td>1.7250x10^4</td>
</tr>
<tr>
<td>2-methyl dye</td>
<td>1:1</td>
<td>7.0</td>
<td>5.7111x10^5</td>
<td>5.6979x10^5</td>
</tr>
<tr>
<td>3-methyl dye</td>
<td>1:1</td>
<td>9.5</td>
<td>2.8919x10^5</td>
<td>2.8694x10^5</td>
</tr>
<tr>
<td>4-methyl dye</td>
<td>1:1</td>
<td>7.5</td>
<td>1.6324x10^5</td>
<td>1.4630x10^5</td>
</tr>
<tr>
<td>2-methoxy dye</td>
<td>1:1</td>
<td>6.5</td>
<td>2.6631x10^5</td>
<td>2.6582x10^5</td>
</tr>
<tr>
<td>4-methoxy dye</td>
<td>1:1</td>
<td>6.5</td>
<td>2.2722x10^5</td>
<td>2.1186x10^5</td>
</tr>
<tr>
<td>3-chloro dye</td>
<td>1:1</td>
<td>8.5</td>
<td>9.9002x10^4</td>
<td>9.0100x10^4</td>
</tr>
<tr>
<td>4-chloro dye</td>
<td>1:1</td>
<td>7.0</td>
<td>6.4103x10^4</td>
<td>6.3291x10^4</td>
</tr>
</tbody>
</table>

The difference in stability constants obtained by the two methods, are due to (i) the application of different methods, (ii) different media used for determination of stability constants - in the first method water and in the second method
30% alcohol, (iii) large difference in pH values of the solutions at which stability constants were determined by these two methods, (iv) different metal salts used - in the first method, zinc sulphate and vanadyl sulphate and in the second method metal perchlorates, and (v) the ionic strength being maintained constant in the second method whereas no consideration for it has been taken in first method.

The above mentioned stability constant values of the complexes clearly indicate that zinc complexes are stronger than those of vanadyl complexes. Similarly, methyl and methoxy substitutions in the dyes form more stable complexes than those of unsubstituted and chloro substituted dye complexes. The relative stability of the methyl and methoxy dye complexes over unsubstituted and chloro complexes can be explained by the fact, that, these groups apart from being 6-donor substituents in ligands are also strong \( \pi \) -donors, and this \( \pi \) -donor activity increases the stability of the complexes formed. Whereas, chloro group on one hand being a \( \pi \) -donor substituent is a 6-acceptor on the other hand. The latter tendency neutralizes the stabilizing effect caused by the former, and thus rendering the stability of the chloro complexes more or less equal to those of unsubstituted dye complexes. Similarly, in all the cases the stability of the complexes was found to decrease in the order \( o > m > p \).
Structure of the complexes:

Ligands taken under present investigations are all azo salicylic acid dyes, with a common salicylic acid residue in them. These ligands can be represented as having the following common structure:

\[
\begin{array}{c}
\text{N=N} \\
\text{O} \\
\text{C}_{\text{oo}}^{-}
\end{array}
\]

In the above structure the chelating groups are undoubtedly hydroxyl and carboxylic groups. Thus, the ligands can be shown to combine with metallic ions in two different ways:

(a) By removal of hydrogen ion of phenolic group along with the hydrogen ion of carboxylic group in complex formation.

\[
\begin{array}{c}
\text{N=N} \\
\text{O} \\
\text{C}_{\text{oo}}^{-}
\end{array}
+ M^{++} \rightarrow
\begin{array}{c}
\text{N=N} \\
\text{O} \\
\text{C}_{\text{oo}}^{-}
\end{array}
\]

(b) And secondly, without displacing the hydrogen ion of phenolic group during the complex formation.

\[
\begin{array}{c}
\text{N=N} \\
\text{O} \\
\text{C}_{\text{oo}}^{-}
\end{array}
+ M^{++} \rightarrow
\begin{array}{c}
\text{N=N} \\
\text{O} \\
\text{C}_{\text{oo}}^{-}
\end{array}
\]

Out of above two proposed structures, (ii) is ruled out; because it has been shown by replaceable hydrogen
titrations that only one hydrogen ion is replaced in chelate formation. This assumption is further supported by the work of a number of workers who have studied the complexes of salicylic acid and sulphosalicylic acid by different methods, such as, solubility product, ion-exchange, kinetic, extraction, pH-metric, enzymatic and spectrophotometric studies.

The ion exchange method shows that the sulphosalicylic acid complexes of beryllium have a net zero charge, giving the structure:

\[
\begin{align*}
\text{(iv)}
\end{align*}
\]

The above structure is analogous to the structure (iii) proposed by the author.

The same type of structure has been confirmed by Hok - Bernstrom by extraction studies. Whereas spectrophotometric studies by Foly, Turner and Anderson have revealed both the types of structures. This controversy has been solved by Varma and Mehrotra. According to their views the beryllium complex of salicylic acid acts as an acid with a \( pK_a \) value of 3.4, and in strongly alkaline medium, the phenolic hydrogen will be completely removed.
A similar structure for copper salicylate complex has been given by Babko, in which a higher pH of solution tends to remove the hydrogen ion of phenolic group.

\[
\begin{array}{c}
\text{alkali} \\
\end{array}
\]

It has already been shown in the preceding pages that the composition of the complexes formed in the present investigations is 1:1 (M:1) in the case of zinc as well as vanadyl ion. By analogy from the similar structures, which have been mentioned above, the following structure can be proposed for the complexes formed:

\[
\begin{array}{c}
\text{(vi)} \\
\end{array}
\]

As the coordination numbers of both the ions in the present investigations is 4, the remaining coordination positions can be said to be occupied by water molecules.

In the light of the above, the author proposes the following structures for the Zn(II) and VO(II) complexes with azo-dyes:
1. 5-phenyl azo salicylic acid:

2. 2-methyl phenyl azo salicylic acid:

3. 3-methyl phenyl azo salicylic acid:

4. 4-methyl phenyl azo salicylic acid:

5. 2-methoxy phenyl azo salicylic acid:
6. 4-methoxy phenyl azo salicylic acid :

\[
\begin{array}{c}
\text{CH}_3 \\
\text{N} = \text{N} \\
\text{N} \\
\text{O} \\
\text{C} - \text{O} \\
\text{H}_2 \text{O} \\
\text{H}_2 \text{O}
\end{array}
\]

7. 3-chloro phenyl azo salicylic acid :

\[
\begin{array}{c}
\text{Cl} \\
\text{N} = \text{N} \\
\text{N} \\
\text{O} \\
\text{C} - \text{O} \\
\text{H}_2 \text{O} \\
\text{H}_2 \text{O}
\end{array}
\]

8. 4-chloro phenyl azo salicylic acid :

\[
\begin{array}{c}
\text{Cl} \\
\text{N} = \text{N} \\
\text{N} \\
\text{O} \\
\text{C} - \text{O} \\
\text{H}_2 \text{O} \\
\text{H}_2 \text{O}
\end{array}
\]

In each of the above M stands for Zn(II) or VO(II).

The composition and structure of the complexes have been further confirmed by isolation and I.R. studies (next chapter).
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SUMMARY AND CONCLUSION

Eight azo-salicylic acid dyes have been synthesized by the author. The stoichiometry of the complexes formed by them with zinc and vanadyl ions has been established by:

1. Vosburgh and Cooper method.
2. Job's method of continuous variation using absorbance as index property.
3. Ratio titrations using pH as index property.
4. Replaceable hydrogen titrations.
5. Mono variation method of Pande and Nayar using conductance as index property.
6. Potentiometric method using E.M.F. as index property.

The composition of the complexes of both Zn(II) and VO(II) with each of the azo dyes is found to be 1:1 (M:L) (chapter - V).

The stability constants of the chelates have been calculated by Bjerrum-Calvin method and by Job's method of continuous variation using pH and absorbance respectively as index properties. It is found that Zn(II) complexes have greater stability than VO(II) complexes. Similarly complexes of methyl and methoxy substituted dyes have been found to be more stable than complexes of unsubstituted and chloro substituted dyes. These and the differences in the stability constant values by the two methods have been explained (chapter - V).
The possible structures of the complexes have been suggested from theoretical considerations and by analogy with earlier work (chapter - V).

The structures have been further confirmed by isolation of the complexes and I.R. studies (chapter-VI).

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