Formation Constants of Complexes of Manganese(II), Cobalt(II), Nickel(II), Copper(II) & Zinc(II) with 2-(Phenylhydrazino)-, 2-(p-Tolylhydrazino)- & 2-(p-Nitrophenylhydrazino)-propionic Acids

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The formation constants of complexes of 2-(phenylhydrazino)propionic acid, 2-(p-tolylhydrazino)propionic acid and 2-(p-nitrophenylhydrazino)propionic acid with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) have been determined in ethanol-water medium at different temperatures and ionic strengths, employing Calvin-Bjerrum's pH titration technique as modified by Irving and Rossotti. From the formation constants obtained at various temperatures and constant ionic strength (0.1 M) and the values of log $K$ at various pH, the stability constants have been calculated using Gibbs-Helmholtz equation from the stability constants obtained at various temperatures at constant ionic strength (0.1 M) and the values are given in Table 1. These reactions are exothermic and spontaneous as supported by the negative values of $\Delta H^\theta$ and $\Delta G^\theta$ respectively. $\Delta S^\theta$ values are positive for all the chelates indicating that entropy change is favourable for complex formation. To know the extent of ionic and covalent nature of bonding in these complexes, the $\Delta H^\theta$ and $\Delta G^\theta$ were separated into their electrostatic ($\Delta G^\theta$ and $\Delta H^\theta_e$) and cratic ($\Delta G^\theta$ and $\Delta H^\theta_c$) components as suggested by Digischer and Nancollass. Comparison of the electrostatic and cratic components for the equilibrium (1),

$$M^{2+} + 2H^- \rightleftharpoons ML^+$$

indicates that $\Delta G^\theta$ values are significantly more negative than $\Delta G^\theta_e$ values (Table 3). This trend suggests that the non-electrostatic forces are stronger than the electrostatic forces in 1:1 chelates. The difference in the electrostatic and cratic components

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>2-(Phenylhydrazino)propionic acid</th>
<th>2-(p-Tolylhydrazino)propionic acid</th>
<th>2-(p-Nitrophenylhydrazino)propionic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺</td>
<td>5.15</td>
<td>5.42</td>
<td>4.53</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>2.92</td>
<td>3.03</td>
<td>2.63</td>
</tr>
<tr>
<td>Co(II)</td>
<td>(2.54) (2.66)</td>
<td>(2.67)</td>
<td>2.82</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>3.42</td>
<td>3.72</td>
<td>3.06</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>(2.68) (2.98)</td>
<td></td>
<td>3.61</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>4.68</td>
<td>5.04</td>
<td>3.02</td>
</tr>
</tbody>
</table>

The figures in the parentheses indicate the values of log $K$; the standard deviation of stability constants is ± 0.06; the limit of error for log $K$ values is found to be ± 0.05.
decreases in the order: Cu(II) > Ni(II) > Co(II) > Mn(II). This order indicates that the ionic character of the complexes is in the order: Cu(II) < Ni(II) < Co(II) < Mn(II). Since the number of unpaired electrons also increases in the same order, it may be concluded that the ionic character of the complexes increases with the increase in the number of unpaired electrons. The data from Table 3 for the equilibrium (2)

\[ \text{ML}^+ + \text{L}^- \rightleftharpoons \text{ML}_2 \]

show a marked decrease in the ionic character of the complexes and indicate that the metal-ligand bonds in bis complexes are more covalent than those in the corresponding mono complexes.

Ligand field stabilization energies ($\delta H$) of the complexes Co(II), Ni(II) and Cu(II) have been evaluated by using the expressions of George and McClure. The values of $\delta H$ of the bivalent metal ions follow the order: Ni(II) > Cu(II) > Co(II). The low $\delta H$ value of Cu(II) is ascribed to the steric hindrance preventing the formation of four coordinated structure. The stability constants of metal chelates are strongly affected by the dielectric constant of the medium and solvating property of the solvent. An attempt has been made to investigate the effect of variation in dielectric constant on the stabilities of complexes in various ethanol-water mixtures. The results showed that the stability constant of complexes decreases as the dielectric constant increases, thereby indicating the importance of solvating property of the solvent.

The figures in the parentheses indicate the thermodynamic parameters for 1:2 complexes.
mixtures. It is seen that with increase in the organic content of the solvent the stability constants are increased. Basolo et al.\textsuperscript{19}, reported the effect of solvent on complexes containing N-metal links and concluded that the organic content of the solvent had little influence on the stabilities of complexes. Van Uitert et al.\textsuperscript{18}, observed that the stabilities of complexes, which contained O-metal links, increased by an increase in the organic content of the solvent. The present complexes contain both O-metal and N-metal links; the observed increase in the stabilities may be due to the O-metal link which is strongly affected\textsuperscript{19}.

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