Thermodynamic stabilities and thermodynamic parameters of metal-substituted thiosemicarbazide complexes

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The stability constants of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes with 2-amino-4-benzimidothiosemicarbazide have been found to be proportional to their ionic strengths and inversely proportional to the temperature. Negative values of $\Delta G^\circ$ and $\Delta H^\circ$ show spontaneous and exothermic reactions respectively between the metals and the ligand. Positive $\Delta S^\circ$ values have been observed in all the cases except in case of Fe(III).

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In continuation of our earlier studies on the synthesis and characterization of 3d metal complexes with 2-amino-4-benzimidothiosemicarbazide, the thermodynamic stability constants and thermodynamic parameters of 3d metal complexes with 2-amino-4-benzimidothiosemicarbazide (ABTSC) are presented in this note.

### Experimental

ABTSC was synthesized as reported already. Fresh solution of ABTSC, prepared in double-distilled air-free water, was always used. Stock solutions of metal salts (manganese chloride, ferric chloride, cobaltous chloride, nickel chloride and copper acetate) were prepared in double distilled air-free water and their strengths were determined by usual methods. AnalR grade reagents were used.

The following mixtures of solutions (keeping total volume 30 mL in each case) were titrated against carbonate-free 0.1 M KOH at two different temperatures (30°C/40°C ± 0.1°C). pH of the resulting solutions was measured using Deluxe pH meter, fitted with manual temperature controlled device and a combined glass and saturated calomel electrode: (i) 20 mL of 0.02 M ABTSC + X mL of 0.1 M KCl; and, (ii) 20 mL of 0.02 M ABTSC + X mL of 0.1 M KCl + Y mL of 0.02 M metal salt solution (X = 0.5, 1.0 and 1.5 mL; Y = 1 and 2.0 mL).

For each set (metal-ligand system), pH titration of ABTSC + KCl alone and in presence of different concentrations of metal ions at different ionic strengths (0.0016/0.0033/0.005 M) and at different temperatures (30/40°C) were performed following the method reported by Calvin and Melchior. From the titration curves at different pH values, different sets of $\bar{n}$ values were determined and the corresponding free ligand [L] was calculated. The formation curves were drawn and found to be normal. The values of stepwise stability constant $\log K_1$ and $\log K_2$ of these complexes were determined at $\bar{n} = 0.5$ and $\bar{n} = 1.5$ from the formation curves. At each temperature, average values of overall stability constant ($\log K$) were plotted against ionic strength for each metal-ligand system and the values of thermodynamic stability constant ($\log K$) at zero ionic strength were calculated by extrapolation.

From the knowledge of thermodynamic stability constants, the values of the changes in free energy ($\Delta G^\circ$) were calculated at 30°C using the relation $\Delta G^\circ = -2.303 RT \log K^\circ$; enthalpy was calculated using the relation $\Delta H^\circ[1/T_2-1/T_1] = -2.303 R [1(\log K^\circ)T_2 - (\log K^\circ)T_1]$ and entropy were calculated at 30°C by using the relation:

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

### Results and discussion

The pH titration curves of ligand alone and metal-ligand mixtures showed a lowering of pH indicating the release of protons. Moreover, maximum lowering in the case of 1:2 metal-ligand mixtures and the inflection both corresponded to 1:2 stoichiometric ratio. Conductometric studies and elemental analysis also supported the pH metric results.

The pH titrations of ligand alone at different temperatures and different ionic strengths showed almost identical nature of the curves. The $pK_1$ value was thus found to be 8.7. The average values of overall stability constants were found to increase with increasing ionic strengths in all the cases and exhibited a decreasing trend with increasing temperature. The values of thermodynamic stability constants ($\log K^\circ$) followed Mellor and Maley and
<table>
<thead>
<tr>
<th>System</th>
<th>Temp (°C)</th>
<th>Log $K$ at 30°C</th>
<th>Log $K^\circ$</th>
<th>$\Delta G^\circ$ at 30°C (kJ mol$^{-1}$)</th>
<th>$\Delta H^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\circ$ (J K$^{-1}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-ABTSC</td>
<td>30</td>
<td>6.66</td>
<td>8.47</td>
<td>5.7</td>
<td>-33.07</td>
<td>-18.15</td>
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<tr>
<td></td>
<td>40</td>
<td>6.62</td>
<td>8.23</td>
<td>5.6</td>
<td>-55.12</td>
<td>-254.23</td>
</tr>
<tr>
<td>Fe-ABTSC</td>
<td>30</td>
<td>10.1</td>
<td>9.3</td>
<td>8.10</td>
<td>-45.25</td>
<td>-18.15</td>
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<tr>
<td></td>
<td>40</td>
<td>8.7</td>
<td>9.90</td>
<td>7.7</td>
<td>-48.15</td>
<td>-7.26</td>
</tr>
<tr>
<td>Co-ABTSC</td>
<td>30</td>
<td>8.38</td>
<td>8.23</td>
<td>8.26</td>
<td>-53.61</td>
<td>-52.66</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>8.33</td>
<td>8.40</td>
<td>8.30</td>
<td>-53.61</td>
<td>-52.66</td>
</tr>
<tr>
<td>Ni-ABTSC</td>
<td>30</td>
<td>9.46</td>
<td>9.71</td>
<td>8.95</td>
<td>-53.61</td>
<td>-52.66</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>9.17</td>
<td>9.38</td>
<td>8.95</td>
<td>-53.61</td>
<td>-52.66</td>
</tr>
<tr>
<td>Cu-ABTSC</td>
<td>30</td>
<td>8.83</td>
<td>9.96</td>
<td>9.24</td>
<td>-53.61</td>
<td>-52.66</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>8.30</td>
<td>8.45</td>
<td>8.26</td>
<td>-53.61</td>
<td>-52.66</td>
</tr>
</tbody>
</table>

Irving-William$^4$ order, viz., Fe (III) > Cu (II) > Ni (II) > Co (II) > Mn(II). Moreover, iron complex was found to have the highest value of stability constant due to higher charge on the central metal ion. The negative values of $\Delta G^\circ$ in all the cases showed spontaneous reaction between the metals and the ligand. Negative values of $\Delta H^\circ$ showed the exothermic nature of the metal-ligand interaction. Positive values of $\Delta S^\circ$ were observed in all the cases except in case of iron. Large negative values of entropy in case of iron complex is associated with large negative values of enthalpy. For this, the solvent and ligand field-central ion interactions$^6$ and also $\pi$ interactions$^7$ may be the possible contributing factors. The data (Table 1) further showed that $\Delta G^\circ$ values followed the order Fe(III) > Cu(II) > Ni(II) > Co(II) > Mn(II) which suggested a decrease in the reaction rate in the same order$^8$. It is clear from the pH measurements that values of $\bar{n}$ increase with increasing pH, showing thereby, that the anionic form of the ligand takes part in the formation of the complexes.

References