DETERMINATION OF STABILITY CONSTANTS OF 5-METHYLSALICYLIDENE-P-NITROANILINE COMPLEXES WITH Pr³⁺, Nd³⁺, Sm³⁺, Gd³⁺ AND Dy³⁺

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In the present communication the successive stability constants of the complexes of 5-methylsalicylidene-p-nitroaniline with various trivalent metal ions have been determined potentiometrically following the Calvin-Bjerrum pH titration technique as adopted by Irving and Rossotti.

The Corning Model 12, a precision research pH meter with a combined glass electrode and a calomel reference electrode was used for measuring 'B' values (pH meter readings) of the solutions. The change in 'B' can be measured with an accuracy of 0.005 unit.

Experimental

The ligand 5-methylsalicylidene-p-nitroaniline (M.P. 167°C) was prepared by the method described in literature.

The dioxan used for experimental work was purified by the method described by Vogel. The medium of titration was 75:25% dioxan-water (v/v) mixture. Sodium perchlorate was added to maintain a constant ionic strength. The reagents were standardised complexometrically by EDTA titrations. The experimental details and computational methods were the same as described in the earlier communication. The experimental method of Irving and Rossotti was applied to find out the values of \( \tilde{n} \) and pL.

Results and Discussion

The reagent does not undergo hydrolysis under the experimental conditions described. This was indicated by the T.L.C. taken from time to time of a sample of titration mixture.

In the ligand it is the phenolic (OH) group which takes part in the complex formation and the proton is replaced from it by metal ions during chelation. Since only one proton per ligand molecule is liberated during complexation, 'Y', the number of dissociable protons attached to each ligand molecule is one.

\( \tilde{n}_A \) values at various 'B' values were calculated and a curve between 'B' and the corresponding \( \tilde{n}_A \) values was plotted. The formation curve extends over a range 0.135 < \( \tilde{n}_A \) < 0.995 and is wave-like. The value of pK₄ was evaluated from the half integral point at \( \tilde{n}_A = 0.5 \). This was further corroborated from the plot of

\[
\log \left( \frac{\tilde{n}_A}{(1 - \tilde{n}_A)} \right) \quad \text{vs.} \ B.
\]

\( \tilde{n} \) and pL values were calculated and \( \tilde{n} \) values were plotted against the corresponding pL values to get the formation curves of the metal complex-ion equilibria. From these formation curves, the values of stability constants log \( K_4 \) were evaluated which correspond to pL value at \( \tilde{n} = 0.5 \). This was further corroborated from the plot of

\[
\log \left( \frac{\tilde{n}}{(1 - \tilde{n})} \right)
\]

against pL. The log \( K_4 \) for metals could not be evaluated due to precipitation probably due to metal ion hydrolysis.

The most representative values are recorded in Table I. The order of stability of the trivalent metal chelates was found to be Dy³⁺ > Nd³⁺ > Gd³⁺ > Sm³⁺ > Pr³⁺

<table>
<thead>
<tr>
<th>Cations</th>
<th>H⁺</th>
<th>Pr³⁺</th>
<th>Nd³⁺</th>
<th>Sm³⁺</th>
<th>Gd³⁺</th>
<th>Dy³⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>log ( K_4 )</td>
<td>10.62</td>
<td>7.44</td>
<td>7.7</td>
<td>7.47</td>
<td>7.6</td>
<td>7.8</td>
</tr>
</tbody>
</table>

* For proton association (H⁺), \( K_4 \) corresponds to the species LH while for metal ions \( K_4 \) corresponds to the species ML₄.

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