Studies on mixed ligand complexes of Cu(II), Ni(II), Zn(II) and Cd(II) with 8-hydroxyquinoline-5-sulphonic acid & anthranilic acid/nicotinic acid

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pH-metric studies on the interaction of Cu(II), Ni(II), Zn(II) and Cd(II) with 8-hydroxyquinoline-5-sulphonic acid (HQSA) in the presence of anthranilic acid (AnthA) or nicotinic acid (NicoA) indicate the simultaneous formation of 1:1 mixed ligand chelates; however, no complex formation occurs in the systems Zn(II)/Cd(II)-HQSA-NicoA.

8-Hydroxyquinoline-5-sulphonic acid (HQSA) is an excellent chelating agent and has been reported\(^1\) to be a biologically and physiologically active compound. Although the binary chelates of HQSA have been studied quite extensively, only a few studies on the mixed ligand chelates are recorded\(^5\) - \(^12\). We report here pH-metric studies on the mixed ligand chelates of Cu(II), Ni(II), Zn(II) and Cd(II) with HQSA and anthranilic acid (AnthA)/nicotinic acid (NicoA).

Experimental
Preparation of the solutions (5 \(\times\) 10\(^{-3}\) M) of metal nitrates and HQSA, and pH-metric titration techniques have been described earlier\(^8\). The solutions of anthranilic acid (BDH) and nicotinic acid (BDH) were prepared by direct weighing and their strengths were checked pH-metrically. The formation constant data are given in Table 1.

Results and discussion
The dissociation constant values of HQSA \((pK_1 = 4.06\) & \(pK_2 = 8.49\)) were taken from the literature\(^6\) and those of anthranilic acid \((4.88 \pm 0.04)\) and nicotinic acid \((4.75 \pm 0.03)\) were calculated by the method of Chaberek and Martell\(^14\).

The pH-metric titration curves 4, 5, 7, 8, 10, 11, 13, 14, 16 and 18 (Fig. 1) of the solutions containing equimolar quantities of metal nitrates and HQSA/AnthA/NicoA may be explained on the basis of the formation of 1:1 binary chelates and their conversion into the corresponding hydroxo derivatives. The curve for Cu(II)-NicoA system indicates that the reactions for the formation of 1:1 binary complex and its hydroxo derivative overlap with each other whereas in other systems stepwise formation of 1:1 binary complex and hydroxo derivative takes place. No complex formation tendency is observed in the case of Cd(II)/Zn(II) with nicotinic acid under present conditions. The formation constants of 1:1 Cu(II)/Ni(II)/Zn(II)/Cd(II)-HQSA \((\log K_{MA} = 11.92, 9.02, 7.54 \text{ and } 7.70\) respectively) were taken from the literature\(^5\) - \(^6\). The equilibrium and forma-

<table>
<thead>
<tr>
<th>System</th>
<th>(\log K_{MA})</th>
<th>(\log K_{MAL})</th>
<th>(\log K_{MAL}^{-})</th>
<th>(\log K_{MAL}^{+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)-AnthA</td>
<td>5.00 ± 0.04</td>
<td>15.00 ± 0.07</td>
<td>1.79 ± 0.08</td>
<td>2.43 ± 0.07</td>
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<tr>
<td>Ni(II)-AnthA</td>
<td>2.19 ± 0.03</td>
<td>12.11 ± 0.06</td>
<td>1.80 ± 0.06</td>
<td>5.32 ± 0.06</td>
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<tr>
<td>Zn(II)-AnthA</td>
<td>1.99 ± 0.08</td>
<td>11.45 ± 0.09</td>
<td>1.97 ± 0.09</td>
<td>5.98 ± 0.09</td>
</tr>
<tr>
<td>Cd(II)-AnthA</td>
<td>1.89 ± 0.06</td>
<td>10.29 ± 0.11</td>
<td>2.29 ± 0.11</td>
<td>7.14 ± 0.11</td>
</tr>
<tr>
<td>Cu(II)-NicoA</td>
<td>2.52 ± 0.02</td>
<td>14.53 ± 0.05</td>
<td>2.14 ± 0.05</td>
<td>2.77 ± 0.05</td>
</tr>
<tr>
<td>Ni(II)-NicoA</td>
<td>2.03 ± 0.05</td>
<td>11.44 ± 0.08</td>
<td>2.34 ± 0.08</td>
<td>5.86 ± 0.08</td>
</tr>
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</table>

\(\log K_{MA}: M^{2+} + L^- = ML^-; \log K_{MAL}: MA + L^- = MAL^-; \log K_{MAL}^{-}: M^{2+} + A^{2+} + L^- = MAL^{+}; \log K_{MAL}^{+}: MA + HL = MAL^{-} + H^+; \log K^{+}: M^{2+} + H_2A + HL = MAL^{-} + 3H^+\)
Potentiometric titration curves of mixed ligand chelates: Cu(II)/Ni(II)/Zn(II)/Cd(II)-HQSA-AnthA/NicoA: curve 1, HQSA; 2, AnthA; 3, NicoA; 4, Cu(II)-HQSA; 5, Cu(II)-AnthA; 6, Cu(II)-HQSA-AnthA; 7, Ni(II)-HQSA; 8, Ni(II)-AnthA; 9, Ni(II)-HQSA-AnthA; 10, Zn(II)-HQSA; 11, Zn(II)-AnthA; 12, Zn(II)-HQSA-AnthA; 13, Cd(II)-HQSA; 14, Cd(II)-HQSA-AnthA; 15, Cd(II)-HQSA-AnthA; 16, Cu(II)-NicoA; 17, Cu(II)-HQSA-NicoA; 18, Ni(II)-NicoA; 19, Ni(II)-HQSA-NicoA. Arrow indicates appearance of a solid phase.

Ternary formation constants of 1:1 M(II)-AnthNNicoA complexes were calculated by algebraic method as described earlier. Constant values were found up to $m = 1$, except in the Cu(II)-NicoA system, where the values were constant up to $m = 0.5$ (Table 1).

Curves 6, 9, 12, 15, 17 and 19 (Fig. 1) represent the pH-metric titrations of solutions containing copper(II), nickel(II), zinc(II) or cadmium(II) nitrate in the presence of equimolar concentrations of HQSA and AnthNNicoA respectively. These curves exhibit a sharp inflection at $m = 3$ except for the Cu(II)-NicoA system, which shows a poor inflection at $m = 3$ followed by a sharp inflection at $m = 4$. Initially, all these curves run slightly above the corresponding binary titration curves due to zwitter-ion formation tendency of anthranilic and nicotinic acids in solution, indicating that in the beginning 1:1 M(II)-HQSA binary complexes are formed. The lowering of the curves for the ternary systems, Cu(II)/Ni(II)/Zn(II)/Cd(II)-HQSA-AnthA/NicoA in comparison with the curves for binary systems M(II)-HQSA after $m = 1.8, 1.3, 0.8, 0.2, 1.8$ and $1.2$ respectively, indicates the simultaneous formation of 1:1:1 mixed ligand complexes, MAL, in these systems. Further, an inflection at $m = 4$ in the case of the system Cu(II)-HQSA-NicoA and buffer regions after $m = 3$ in other systems, except in Cu(II)-HQSA-AnthA, indicate the conversion of ternary complexes into the corresponding hydroxo derivatives in the high pH-range. The values of the formation constants of the ternary complexes were determined by algebraic method as described earlier (Table 1).

Anthranilic acid forms stronger ternary complexes than nicotinic acid because the former ligand is coordinated to the metal ion in such a way that the benzene ring is coplanar with the rest of the complex molecule since the amino and COOH groups are in the ortho-positions. In the latter case, the pyridine ring of nicotinic acid is probably perpendicular to the plane of the rest of the molecule as the COOH group is in the meta-position with respect to nitrogen atom.

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References