The stability constants for simple and mixed-ligand complexes of uranyl ion with carboxylic acids at 30° ± 0·1° and $p = 0·1$ (NaClO$_4$) have been determined pH-metrically. Uranyl ion forms both 1:1 and 1:2 complexes with quinolinic and dipicolinic acid and only 1:1 complexes with aspartic, glutamic, thiomalic, thiodiglycolic and thiodipropionic acids individually. Ternary complexes of uranyl ion-aspartic/glutamic acids with (i) pyridine dicarboxylic and (ii) thiodicarboxylic acids have also been investigated. It is observed that the mixed-ligand chelate is stable when both the ligands are N-O donors. The values of $K_{2xy}$ and $\beta_{xy}$ are dependent on acid dissociation constants of secondary ligands and stabilities of their binary metal chelates respectively.

**Materials and Methods**

Uranyl nitrate (BDH, AR) was dissolved in perchloric acid to give the required concentration. The ligands such as aspartic, glutamic, quinolinic, dipicolinic, thiomalic, thiodiglycolic and thiodipropionic were obtained from Fluka (Germany) and their purity checked. All the solutions were prepared in doubly distilled water. Always fresh solutions of amino acids were used to avoid absorption of CO$_2$ by amino acids. The details of the measurement of pH are given in an earlier paper.$^{10}$

**Results and Discussion**

**Acid dissociation constants and stabilities of binary uranyl complexes** — The methods adopted to determine acid dissociation constants of the ligands and the stability constants of the simple complexes have been described earlier.$^{12}$ Quinolinic and dipicolinic acids form both 1:1 and 1:2 complexes while the remaining acids form only 1:1 with uranyl ion. The log $K_1$ and log $K_2$ values for these ligands were calculated by the method of least squares$^{12}$ and are presented in Table 1.

**Mixed-ligand systems** — The formation of the mixed-ligand chelates was concluded to be in a simultaneous equilibrium according to the procedure of Carey and Martell$^{13}$. The mixed-ligand stabilities and other equilibrium constants were calculated by the procedure$^{14}$, and these are presented in Table 2.

The possible complexation equilibria of mixed-ligand systems of uranyl ion are given in Eqs. (1-7)

\[
K_{MX_i} = K(M+X \rightleftharpoons MX) \quad \ldots (1)
\]

\[
K_{MX_i} = K(MX+X \rightleftharpoons MX_2) \quad \ldots (2)
\]

\[
K_{MY_i} = K(M+Y \rightleftharpoons MY) \quad \ldots (3)
\]

\[
K_{MY_i} = K(MY+Y \rightleftharpoons MY_2) \quad \ldots (4)
\]

\[
K_{XXY} = K(MX+Y \rightleftharpoons MXY) \quad \ldots (5)
\]

\[
K_{YXX} = K(MY+X \rightleftharpoons MXY) \quad \ldots (6)
\]

\[
\beta_{XY} = K(M+X+Y \rightleftharpoons MXY) \quad \ldots (7)
\]

The disproportionation constants, given by Eqs. (8-11)

\[
K_{DXY} = K(MX+MY \rightleftharpoons MXY+M) \quad \ldots (8)
\]

\[
K_{DXY} = K(MX_2+MY \rightleftharpoons MXY+MX) \quad \ldots (9)
\]

\[
K_{DXY} = K(MX+MY_2 \rightleftharpoons MXY+MY) \quad \ldots (10)
\]

\[
K_{DXY} = K(MX_2+MY_2 \rightleftharpoons 2MXY) \quad \ldots (11)
\]

for the corresponding systems have been calculated. All the mathematical calculations were done on Unitrich 1201M and DCM Moscal 1400 electronic calculators.

The pH of titration curves for one representative system are shown in Fig. 1. The moles of base added after the neutralization of HClO$_4$ are represented as $m$. $\text{UO}_2^{2-}$-glutamic-thiodipropionic acid — Separately, glutamic and thiodipropionic acids form only 1:1 complexes in the pH range 3-5. The pH of precipitation of the mixed ligand system was 5-5, while $\text{UO}_2^{2-}$-glutamic and $\text{UO}_2^{2-}$-thiodipropionic acid precipitated at pH 5-40 and 5-68 respectively. The mixed-ligand titration curves shifted towards right hand side of the composite curve in the pH range 3-4-5 at which $m = 0-3$. The formation of 1:1 complex is in the same pH range. Since the mixed-ligand curve did not coincide with either of the individual metal complex titration curves, the formation of 1:1:1 complex by a simultaneous
TABLE 1 — DISSOCIATION CONSTANTS OF LIGANDS AND STABILITY CONSTANTS OF URANYL COMPLEXES

<table>
<thead>
<tr>
<th>Ligand/acid</th>
<th>pK₁</th>
<th>pK₂</th>
<th>pK₃</th>
<th>log K₁</th>
<th>log K₂</th>
<th>log K₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quinolinic</td>
<td>2.35±0.03</td>
<td>2.36</td>
<td></td>
<td>4.71±0.02</td>
<td>4.72</td>
<td></td>
</tr>
<tr>
<td>Dipicolinic</td>
<td>2.11±0.02</td>
<td>2.10</td>
<td></td>
<td>4.83±0.04</td>
<td>4.76</td>
<td></td>
</tr>
<tr>
<td>Aspartic</td>
<td>3.71±0.04</td>
<td>3.68</td>
<td></td>
<td>9.63±0.02</td>
<td>9.62</td>
<td></td>
</tr>
<tr>
<td>Glutamic</td>
<td>4.05±0.02</td>
<td>4.03</td>
<td></td>
<td>9.46±0.03</td>
<td>9.54</td>
<td></td>
</tr>
<tr>
<td>Thiomalic</td>
<td>3.14±0.02</td>
<td>3.15</td>
<td></td>
<td>4.94±0.02</td>
<td>4.94</td>
<td></td>
</tr>
<tr>
<td>Thiodiglycolic</td>
<td>3.08±0.04</td>
<td>3.15</td>
<td></td>
<td>4.28±0.01</td>
<td>4.29</td>
<td></td>
</tr>
<tr>
<td>Thiodipropionic</td>
<td>3.87±0.02</td>
<td>3.84</td>
<td></td>
<td>4.93±0.01</td>
<td>4.91</td>
<td></td>
</tr>
</tbody>
</table>

Literature values are taken from ref. 15.
*The values are log K₁.
†The value is taken from ref. 1.

TABLE 2 — LOGARITHMS OF EQUILIBRIUM CONSTANTS OF TERNARY COMPLEXES OF UO₂⁺-AMINO ACIDS (H₂Y)-SECONDARY LIGAND (H₃Y)

<table>
<thead>
<tr>
<th>Systems/acid</th>
<th>βₓᵧ</th>
<th>Kₓᵧ</th>
<th>Kᵧₓ</th>
<th>Δ log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspartic-quinolinic</td>
<td>8.48</td>
<td>4.58</td>
<td>-0.23</td>
<td>3.13</td>
</tr>
<tr>
<td>Aspartic-dipicolinic</td>
<td>9.21</td>
<td>4.94</td>
<td>0.50</td>
<td>3.77</td>
</tr>
<tr>
<td>Aspartic-thiomalic</td>
<td>8.94</td>
<td>3.47</td>
<td>0.23</td>
<td>5.24</td>
</tr>
<tr>
<td>Aspartic-thiodiglycolic</td>
<td>7.96</td>
<td>5.10</td>
<td>-0.75</td>
<td>4.53</td>
</tr>
<tr>
<td>Aspartic-thiodipropionic-glutamic-quinolinic</td>
<td>9.76</td>
<td>2.99</td>
<td>1.05</td>
<td>5.72</td>
</tr>
<tr>
<td>Glutamic-quinolinic</td>
<td>8.32</td>
<td>4.46</td>
<td>-0.11</td>
<td>3.97</td>
</tr>
<tr>
<td>Glutamic-dipicolinic</td>
<td>9.35</td>
<td>4.52</td>
<td>0.92</td>
<td>3.91</td>
</tr>
<tr>
<td>Glutamic-thiomalic</td>
<td>8.81</td>
<td>4.32</td>
<td>0.38</td>
<td>5.11</td>
</tr>
<tr>
<td>Glutamic-thiodiglycolic</td>
<td>7.55</td>
<td>4.31</td>
<td>-0.88</td>
<td>4.12</td>
</tr>
<tr>
<td>Glutamic-thiodipropionic-glutamic</td>
<td>9.49</td>
<td>2.98</td>
<td>1.06</td>
<td>5.45</td>
</tr>
</tbody>
</table>

*Kₓᵧ = MX+MYeMXY+M.
†Kᵧₓ = MX+MYeMXY+MX.
The accuracy of βₓᵧ was between 0.01 and 0.10 log unit.

equilibrium was inferred. The complexation reaction is as follows:

\[
\text{UO}_2^2+ + \text{H}_2\text{X} + \text{H}_2\text{Y} \rightleftharpoons [\text{UO}_2(\text{X})(\text{HY})]^+ + 3\text{H}^+
\]

The conclusions were drawn regarding the various complexation reactions by similar considerations. *Aspartic-\text{UO}_2^2+ - secondary ligands* — The negative Δ log K values for aspartic-\text{UO}_2^2+ - secondary ligand indicate the preferential formation of ternary complexes over the binary ones. The significantly higher values for aspartic-\text{UO}_2^2+ - dipicolinic and aspartic-\text{UO}_2^2+ - quinolinic acid systems may be interpreted on the basis of the nature of coordinating atoms.

It is known that a ternary complex is more stable when donor atoms are N=N and O=O as primary and secondary ligands respectively. In the present investigation the donor atoms are N=O in the primary and N=O or O=O in secondary ligands. It is observed from the values of Δ log K that the formation of mixed-ligand chelate is relatively favoured, when the donor atoms are N=O in both the ligands. In addition to the nature of binding atoms the values of Δ log K depend on the size of the chelate ring also.

The mixed-ligand stabilities can be explained on statistical factors like steric hindrance, neutralization of charge in ternary complexes and chelate rings formed by the two ligands. Amongst the three
systems in which thioacid is one component, \(-\Delta \log K\) is maximum for aspartic-UO\(_2^+\)-thiodiglycolic acid system. The nature of complexation reaction and neutralization of charge in ternary complex are responsible for the observed highest \(-\Delta \log K\) value. The low value of \(-\Delta \log K\) for aspartic-UO\(_2^+\)-thiodipropionic acid system is due to the strain involved in the ten-membered ring.

The values of \(K_{2XY}\) are parallel to \(-\Delta \log K\) in all the systems for the equilibrium \(MX+MY \rightleftharpoons MXY+M\). A comparison of \(K_{2XY}\) and \(K_{MX}\) shows that the binary complexes are favoured over the ternary. The values of \(K_{2XY}\) follow the order: thiodipropionic \(>\) thiomalic \(>\) thiodiglycolic \(>\) quinolinic \(>\) quinolonic \(>\) dipicolinic. The plot of \(K_{2XY}\) vs \(\Sigma pK\) for series of closely related ligands gave a direct relationship between the two quantities. The stabilities of ternary chelates are in the same order as the corresponding binary chelates.

### Glutamic-UO\(_2^+\)-secondary ligands

Glutamic acid forms six-membered chelate ring around the uranyl ion. The comparison of \(pK\) values of aspartic with succinic and glutamic with glutaric acid indicate that the effect of amino group on the \(-\text{COOH}\) dissociation is almost equal in both the ligands.

\(-\Delta \log K\) is negative in all the systems and follows the order: dipicolinic \(>\) quinolinic \(>\) thiodiglycolic \(>\) thiomalic \(>\) thiodipropionic acid. The values of \(\Delta \log K\) for glutamic-UO\(_2^+\)-quinolinic and glutamic-UO\(_2^+\)-dipicolinic acid systems are almost the same. The chelate ring size formed by glutamic and quinolinic is nearly identical. The relatively higher \(-\Delta \log K\) value obtained in glutamic-UO\(_2^+\)-dipicolinic is due to the coordination through \(\text{N} - \text{O}\) in both the ligands. The lower value of \(-\Delta \log K\) observed for glutamic-UO\(_2^+\)-thiodiglycolic is due to the absence of partial neutralization of charge in ternary chelate as compared to that of aspartic-UO\(_2^+\)-thiodiglycolic acid system. The other factors utilized to explain the mixed-ligand stabilities are (i) \(K_{2XY}>0.6\) log units for all the systems. (ii) \(K_{2XY}>K_{MX}\), except in glutamic-UO\(_2^+\)-dipicolinic acid, the formation of ternary chelate is not favourable for the equilibrium \(MX+Y \rightleftharpoons MXY\). This is also justified from the negative values of \(K_{2XY}\) in glutamic-UO\(_2^+\)-quinolinic and glutamic-UO\(_2^+\)-thiodiglycolic acid systems. (iii) The plots of \(K_{2XY}\) vs \(\Sigma pK\) (Fig. 2) gave the direct relationship between these two quantities. (iv) The overall stabilities of secondary ligands for series of closely related thiodicarboxylic and pyridine-dicarboxylic acids. The plots of \(b_{XY}\) vs \(K_{MX}\) were linear.

![Fig. 2 — Relation between \(K_{2XY}\) and the product of acid dissociation constant of the ligands for uranyl-dibasic-dibasic acid systems [(a) Uranyl ion-aspartic (Y)-ligand (X), (b) Uranyl ion-glutamic (Y)-ligand (X); ligand (X): (1) thiomalic, (2) thiodiglycolic, (3) thiodipropionic acid. \(\mu=0.1M\) (NaClO\(_4\)); temp. = 30\(^\circ\)]

### Acknowledgement

The authors are grateful to Prof. D. D. Khanolkar for his keen interest and encouragement. One of the authors (D.N.S.) thanks the CSIR, New Delhi, for the award of a senior research fellowship.

### References