Tetrad Effect in the Solution Stabilities of Mixed Ligand Complexes of Lanthanides

SANGEETA VERMA & M C SAXENA
Department of Chemistry, Dr. Harisingh Gour Vishwavidyalaya, Sagar (M.P.) 470003

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The occurrence of tetrad effect in the solution stabilities of mixed ligand complexes of lanthanides has been studied for the ternary systems of the type [Ln(III).A.L], where Ln(III)=La3+, Ce3+, Pr3+, Nd3+, Eu3+, Gd3+, Tb3+ or Dy3+; A=HEDTA, CDTA or DTPA; and L=IMDA. The formation constants \(\log K_{\text{ML}}\), \(\log K_{\text{MA}}\) and \(\log K_{\text{ML}}^{\text{MA}}\) have been determined by potentiometric pH-titrations using Irving-Rossotti approach at 25°C and at ionic strength, \(I=0.2\) (mol dm\(^{-3}\), NaClO\(_4\)). The formation constants of the mixed ligand complexes follow the sequence: HEDTA > CDTA > DTPA, reflecting mainly the electrostatic effect. The \(\Delta \log K\) values are negative. The stability data indicate the occurrence of tetrad effect at Gd(III). A differential plot method has been used to locate the occurrence of tetrad effect at the one-fourth and three-fourths filled 4f-shells also. The so-called inclined - W plots have been obtained on correlating the formation constants with the total orbital angular momentum quantum number, \(L_{\text{t}}\), of the lanthanides. The implications of periodicity in \(\Delta \log K\) have been discussed with reference to the inclined-W plots.

Some properties of tervalent lanthanides, when studied as a function of 4f electrons (4f\(^n\)), have been found to show a discontinuity at Gd(III) corresponding to the half-filled 4f-shell. These properties are separation coefficients\(^1\), free energy changes of binary complex formation\(^2\) and extraction\(^3\), enthalpies and entropies of extraction\(^4,5\), free energies of crystallisation\(^6\) and hydration of lanthanide ions\(^7\), unit cell volumes of lanthanide compounds\(^8\), IR stretching frequencies\(^9\), deprotonation constants of lanthanide complexes\(^10\) and Racah parameters of lanthanide(III) ions\(^11\). The discontinuity may be observed less prominently at the 4f\(^0\) - 4f\(^1\) (quarter filled 4f-shell) and 4f\(^{10}\) - 4f\(^{11}\) (three-fourths filled 4f-shell) stages also, has been variously termed as Gd-break\(^12\), double-double effect\(^13,14\) and tetrad effect\(^15\).

The present work aims at studying the possible occurrence of tetrad effect in the solution stabilities of mixed ligand Ln(III) complexes. The ternary systems investigated are of the type [Ln(III).A.L], where Ln(III)=La3+, Ce3+, Pr3+, Nd3+, Sm3+, Eu3+, Gd3+, Tb3+ or Dy3+; A=N'-(2-hydroxyethyl)ethylenediamine NNN'-triacetate (HEDTA), 1,2-diaminocyclohexane NNN'N'-tetraacetate (CDTA) or diethylenetriamine NNN'N*N*N*pentaaacetate (DTPA), and L=iminodiacetic acid (IMDA).

Materials and Methods

The Ln(III) nitrates (99.9% purity) were supplied by M/s Indian Rare Earths Ltd. Other chemicals used were standard reagents (Sigma/Merck GR/BDH Analar). The Ln(III) solutions were standardised by EDTA titrations\(^16\). The final metal and ligand concentrations were maintained at [M]=[A]=[L]=1 \times 10^{-3} \text{ mol dm}^{-3}. The metal-ligand formation constants \(\log K_{\text{ML}}\), \(\log K_{\text{MA}}\) and \(\log K_{\text{ML}}^{\text{MA}}\) (in which case the secondary ligand concentration was kept at five-fold excess) were determined by potentiometric pH-titrations using the Irving-Rossotti approach\(^17,18\) at 25°C and at an ionic strength, \(I=0.2\) (mol dm\(^{-3}\), NaClO\(_4\)). An Elico digital pH-meter (model LI-120) with an accuracy of 0.01 pH units, a micro-burette reading upto 0.02 ml and a carbonate-free (0.2 mol dm\(^{-3}\) NaOH solution were used for the pH titrations. Reproducibility of pH data was ascertained by repeating the titrations. The values of formation constants were refined by the method of linear plots\(^19\) and were subjected to statistical refinement also using ‘Q-test\(^20\)’, which is a powerful tool for testing a statistically suspect observed value. The refined formation constant values are presented in Table 1. Figures in parentheses indicate standard deviations. The values of \(\Delta \log K_{\text{f}}\) (= \(\log K_{\text{MA}} - \log K_{\text{ML}}\)), \(\Delta \log K_{\text{p}}\) (= \(\log K_{\text{ML}}^{\text{MA}} - \log K_{\text{ML}}\)) and \(\Delta \log K_{\text{t}}\) (= \(\log K_{\text{ML}} - \log K_{\text{ML}}^{\text{MA}}\)) as derived from the formation constants, are recorded in Table 2.

Results and Discussion

A representative set of pH titration curves for the ternary system [Tb(III).CDTA.IMDA] is repro-
Table 1 – Formation Constants of Binary (log \( K_{ML} \) & log \( K_{ML}^{A} \)) and Ternary (log \( K_{MAL}^{A} \)) Lanthanide(III) Complexes

<table>
<thead>
<tr>
<th>Formation constant</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
</tr>
</thead>
<tbody>
<tr>
<td>( log K_{ML} )</td>
<td>6.30</td>
<td>6.41</td>
<td>6.55</td>
<td>6.70</td>
<td>6.86</td>
<td>6.91</td>
<td>6.78</td>
<td>7.06</td>
<td>7.16</td>
</tr>
<tr>
<td>( (L=IMDA) )</td>
<td>( \pm 0.03 )</td>
<td>( \pm 0.02 )</td>
<td>( \pm 0.02 )</td>
<td>( \pm 0.03 )</td>
<td>( \pm 0.03 )</td>
<td>( \pm 0.02 )</td>
<td>( \pm 0.04 )</td>
<td>( \pm 0.04 )</td>
<td>( \pm 0.04 )</td>
</tr>
<tr>
<td>( log K_{MAL}^{A} )</td>
<td>4.80</td>
<td>4.88</td>
<td>4.91</td>
<td>5.09</td>
<td>5.53</td>
<td>5.58</td>
<td>5.53</td>
<td>5.68</td>
<td>5.74</td>
</tr>
<tr>
<td>( (A=HEDTA) )</td>
<td>( \pm 0.03 )</td>
<td>( \pm 0.01 )</td>
<td>( \pm 0.01 )</td>
<td>( \pm 0.03 )</td>
<td>( \pm 0.03 )</td>
<td>( \pm 0.02 )</td>
<td>( \pm 0.02 )</td>
<td>( \pm 0.02 )</td>
<td>( \pm 0.02 )</td>
</tr>
</tbody>
</table>

Values in parentheses indicate standard deviations.

Table 2 – Calculated Values of \( \Delta \log K_{i} = \log K_{MAL}^{A} - \log K_{ML} \), \( \Delta \log K_{2} = \log K_{MAL}^{A} - \log K_{ML}^{A} \), and \( \Delta \log K_{i} = \log K_{ML} - \log K_{ML}^{A} \)

<table>
<thead>
<tr>
<th>( \Delta \log K )</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta \log K_{i} )</td>
<td>-1.93</td>
<td>-1.99</td>
<td>-2.11</td>
<td>-1.64</td>
<td>-1.21</td>
<td>-1.15</td>
<td>-1.10</td>
<td>-1.20</td>
<td>-1.01</td>
</tr>
<tr>
<td>( \Delta \log K_{2} )</td>
<td>-2.13</td>
<td>-2.14</td>
<td>-2.22</td>
<td>-2.23</td>
<td>-2.18</td>
<td>-2.13</td>
<td>-2.23</td>
<td>-2.22</td>
<td>-2.05</td>
</tr>
<tr>
<td>( \Delta \log K_{i} )</td>
<td>-3.00</td>
<td>-2.69</td>
<td>-2.75</td>
<td>-2.61</td>
<td>-2.59</td>
<td>-2.48</td>
<td>-2.59</td>
<td>-2.56</td>
<td>-2.53</td>
</tr>
<tr>
<td>( \Delta \log K_{2} )</td>
<td>-0.43</td>
<td>-0.46</td>
<td>-0.47</td>
<td>-0.03</td>
<td>+0.12</td>
<td>+0.18</td>
<td>+0.15</td>
<td>+0.18</td>
<td>+0.41</td>
</tr>
<tr>
<td>( \Delta \log K_{i} )</td>
<td>-0.63</td>
<td>-0.61</td>
<td>-0.58</td>
<td>-0.62</td>
<td>-0.85</td>
<td>-0.80</td>
<td>-0.88</td>
<td>-0.84</td>
<td>-0.63</td>
</tr>
<tr>
<td>( \Delta \log K_{2} )</td>
<td>-1.20</td>
<td>-1.16</td>
<td>-1.11</td>
<td>-1.00</td>
<td>-1.26</td>
<td>-1.15</td>
<td>-1.34</td>
<td>-1.18</td>
<td>-1.11</td>
</tr>
<tr>
<td>( \Delta \log K_{i} )</td>
<td>+1.50</td>
<td>+1.53</td>
<td>+1.64</td>
<td>+1.61</td>
<td>+1.33</td>
<td>+1.33</td>
<td>+1.25</td>
<td>+1.38</td>
<td>+1.42</td>
</tr>
</tbody>
</table>

Reduced in Fig. 1. An analysis of the nature of the pH titration curves shows that the present mixed ligand complexes are formed in two steps: \( M+A \neq MA \), and \( MA+L \neq MAL \). The formation of MA chelates is over in the pH range 2-3. The secondary ligand L gets bound to MA in the pH region \( \sim 5.5-6.5 \). The formation of the MAL complexes is also evident from the non-superimposable nature of the theoretical composite curve and from the horizontal distances between the various curves. No precipitation was observed in the MAL systems up to pH 10-12.

The \( \log K_{MAL}^{A} \) values with different 'A' lie in the sequence HEDTA > CDTA > DTPA, which is opposite to the known order (DTPA > CDTA > HEDTA) with respect to these ligands for their MA chelates. The reversal seems to be brought about mainly by the electrostatic factor. The MA species formed with HEDTA, CDTA and DTPA are neutral, mono-negative and binegative, respectively. Their combination with IMDA (\( L^{-2} \)) evidently involves increasing coulombic repulsion. The stepwise complexation is shown in Eqs 1-3.

\[
\text{Ln(III) + HEDTA}^{-2} \rightarrow \text{[Ln(III).HEDTA]}^{-}; \\
[\text{Ln(III).HEDTA}]+\text{IMDA}^{2-} \rightarrow \text{[Ln(III).HEDTA.IMDA]}^{2-}.
\]

\[
\text{Ln(III) + CDTA}^{-4} \rightarrow \text{[Ln(III).CDTA]}^{-}; \\
[\text{Ln(III).CDTA}]+\text{IMDA}^{2-} \rightarrow \text{[Ln(III).CDTA.IMDA]}^{3-}.
\]

\[
\text{Ln(III) + DTPA}^{-5} \rightarrow \text{[Ln(III).DTPA]}^{2-}; \\
[\text{Ln(III).DTPA}]+\text{IMDA}^{2-} \rightarrow \text{[Ln(III).DTPA.IMDA]}^{4-}.
\]

The electrostatic repulsion involved in the second step in each case leads to the sequence \( \log K_{MAL}^{A} \leq \log K_{ML} \) and, hence, the \( \Delta \log K \) values are negative. Gradually increasing negative charge on the MA species, as shown in Eqs (1) to (3), enhances the electrostatic repulsion involved in
the formation of the mixed ligand complexes. This is reflected by the observed trend in \( \Delta \log K \) values (Table 2). The \( \Delta \log K_2 \) values are found to be comparatively less negative or even positive in some cases. This is due to the observed sequence, \( \log K_{M} > > \log K_{ML} \geq \log K_{MAL} \). A marked lowering of \( \log K_{ML} \) values seems to be a consequence of significant statistical and steric effects involved in the complexation (second step, i.e., \( ML + L = ML_2 \)) with IMDA, due to its fairly large size and tridentate character. All \( \Delta \log K_i \) values \( (\Delta \log K_i = \Delta \log K_2 - \Delta \log K_1) \) are observed to be positive due to the sequence \( \Delta \log K_2 > \Delta \log K_1 \). It has been suggested that such a trend indicates a greater contribution from nonstatistical factors (presently, electrostatic factor) during the formation of mixed ligand complexes.

The primary and secondary ligands used in the present work are similar with imino nitrogen(s) and carboxylate oxygens as the binding sites (denticities: IMDA : 3, HEDTA : 5, CDTA : 6, DTPA : 8). Assuming the usual coordination number of Ln(III) ions to be eight or nine, an expansion of coordination sphere is indicated in the formation of mixed ligand complexes.

The \( \log K_{MAL} \) (or \( \log K_{ML} \)) vs \( 4f^6 \) plots, as shown in Fig. 2, indicate a marked depression at Gd(III) which is manifestation of tetrad effect. A possible minor discontinuity at the \( 4f^5 - 4f^6 \) stage is, however, not clearly seen except with HEDTA. Plots of \( \log K_{MAL} \) (or \( \log K_{ML} \)) vs \( S_M \) (standard entropy of Ln(III) ions in cal deg\(^{-1}\) mol\(^{-1}\)) also show (Fig. 3) a prominent break at Gd(III). A general linear increase (in two segments due to the 'Gd-break') in the formation constants with the standard entropies of the Ln(III) ions may be interpreted as an evidence of entropy stabilization of these mixed ligand complexes. A 'differential plot method' has been suggested here for locating two possible minor breaks at the \( 4f^6 - 4f^7 \) and \( 4f^{10} - 4f^{11} \) stages. These plots have been drawn between \( (\Delta \log K/\Delta r) ) \) vs \( (r + \Delta r) \) or \( 4f^6 \),
where $\Delta \log K$ stands for the difference between the formation constants (or a Ln(III) property, in general) of two successive Ln(III) ions, and $\Delta r$ for the corresponding difference between the ionic radii (Goldschmidt values). The present set of representative plots (Fig. 4) show a clear dip at the $4f^0 - 4f^1$ stage also besides the much more prominent minima at the $4f^2$ stage which indicates the occurrence of tetrad effect at the ends of the first and second tetrads.

The dependence of the properties of lanthanides on their total orbital angular momentum, $L_{\text{Ln}}$, has been proposed by Sinha (the so called 'inclined-W hypothesis'). Fig. 5 shows plots of $\log K_{\text{MAI}}$ (or $\log K_{\text{MII}}$) vs $L_{\text{Ln}}$ for the present set of formation constant values. All the plots are of inclined-W type but are devoid of symmetry, and, in some cases, linearity within the segments. It is evident that the curvature in the second segment is caused by the tetrad effect. Since the $L_{\text{Ln}}$ values themselves exhibit periodicity, plots of smoothly increasing/decreasing properties over the Ln(III) series are expected to yield the so called inclined-W. Thus, on correlating $4f^n$, ionic potential, polarising power (properties increasing gradually across the Ln(III)-series), and ionic radius, standard entropy and standard oxidation potential (properties decreasing over the Ln(III)-series) inclined-W plots (figures not shown) are obtained. The only difference in these two sets of plots is that the positions of the Ln(III) ions get reversed. In either case the three vertices of the inclined-W coincide with the configurations $4f^3 - 4f^4$, $4f^0$ and $4f^{10} - 4f^{11}$, i.e., the ends of first, second and third tetrad, respectively.

Siekierski and Dzhurinskii are of the opinion that the inclined-W plots are accidental. The total dependence of the properties (showing tetrad effect) on the $L_{\text{Ln}}$ quantum number is questionable. But it may be emphasised that all the $4f$ electrons in the lanthanides have the same energy and their ground terms are characterised by $L_{\text{Ln}}$. Splitting of the terms occurs as a consequence of L-S coupling. The magnitude of splitting appears to vary periodically with the number of $4f$ electrons. It is also observed that properties (here $\log K_{\text{MAI}}$) vary rather smoothly for the terms $S (L_{\text{Ln}} = 0)$ and $I (L_{\text{Ln}} = 6)$, but discontinuity occurs corresponding to the terms $F (L_{\text{Ln}} = 3)$ and $H (L_{\text{Ln}} = 5)$.

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