SYMBOLISM

The symbolism used in the present work is given below. For the sake of simplicity charges on the metal ions, ligands and complexes have been omitted. The terms 'stability constant', 'association constant' and 'formation constant' are synonyms. The latter term has been generally used in the present case. Similarly, the terms 'biligand complex', 'mixed ligand complex' and 'ternary complex' have the same meaning.

\[ B \ldots \]  observed pH meter reading

\[ \bar{\eta}_H \ldots \]  formation function of the ligand

\[ \bar{\eta} \ldots \]  formation function of the complex

\[ pL \ldots \]  free ligand exponent

\[ T_0^M \ldots \]  total metal concentration (molar)

\[ T_0^A \ldots \]  total ligand (primary) concentration (molar)

\[ T_0^L \ldots \]  total ligand (secondary) concentration (molar)

\[ E^0 \ldots \]  total concentration of reference acid (molar)

\[ N \ldots \]  concentration of alkali used (molar)

\[ I \text{ or } \mu \ldots \]  ionic strength

\[ \text{Temp} \ldots \]  temperature (in °C)

\[ H_n^A \ldots \]  protonated primary ligand

\[ A_n^- \ldots \]  deprotonated primary ligand

\[ H_n^L \ldots \]  protonated secondary ligand

\[ L_n^- \ldots \]  deprotonated secondary ligand

\[ K_n^H \ldots \]  stepwise proton-ligand formation constants

\[ (K_1^H, K_2^H \ldots K_n^H) \]

\[ \beta_n^H \ldots \]  'overall' or 'cumulative' proton-ligand formation constants

\[ \log \beta_n^H = \log K_1^H + \log K_2^H + \ldots + \log K_n^H \]

\[ MA \ldots \]  1:1 binary complex with primary ligand
$K_{MA}^M$ metal-ligand formation constant of 1:1 MA complex

\[
\begin{align*}
(M + A & \xrightarrow{K_{MA}^M} MA
\end{align*}
\]

$ML$ 1:1 binary complex with secondary ligand

$K_{ML}^M$ metal-ligand formation constant of 1:1 ML complex

\[
\begin{align*}
(M + L & \xrightarrow{K_{ML}^M} ML
\end{align*}
\]

$ML_2$ 1:2 binary complex with secondary ligand

$K_{ML_2}^M$ metal-ligand formation constant of 1:2 $ML_2$ complex

\[
\begin{align*}
(ML + L & \xrightarrow{K_{ML_2}^M} ML_2
\end{align*}
\]

$MAL$ 1:1:1 ternary complex (mixed ligand complex)

$K_{MAL}^M$ metal-ligand formation constant of 1:1:1 $MAL$ complex

\[
\begin{align*}
(MA + L & \xrightarrow{K_{MAL}^M} MAL
\end{align*}
\]

$K_{mix}$ or $K_M$ mixing constant  $(= \beta_{11}/\sqrt{\beta_{20}\beta_{02}})$, where $\beta_{20}$ and $\beta_{02}$ are the formation constants of stronger (A) & weaker (L) ligands, respectively

\[
\begin{align*}
(\beta_{11} = K_{MAL}^M \text{ or } K_{MAL}^M, \beta_{20} = K_{MA2}^M, \beta_{02} = K_{ML2}^M)
\end{align*}
\]

$\beta_{MAL}^M$ or $K_{MAL}^M$ overall formation constant of $MAL$

\[
\begin{align*}
(log\beta_{MAL}^M = logK_{MA}^M + logK_{MAL}^M)
\end{align*}
\]

$\Delta logK_1$ stability quantifying factor of ternary $MAL$ complex with respect to binary $ML$ complex

\[
\begin{align*}
= logK_{MAL}^M - logK_{ML}^M (MA + ML \xrightarrow{\Delta logK_1} MAL + M)
\end{align*}
\]

$K_{rep}$ reproporation or antidisproportionation constant; a stability quantifying factor of ternary $MAL$ complex

\[
\begin{align*}
= 2 log\beta_{MAL}^M -(log\beta_{MA2}^M + log\beta_{ML2}^M)
\end{align*}
\]

\[
\begin{align*}
= (logK_{MAL}^M - logK_{ML2}^M) + (logK_{ML}^M - logK_{MA2}^M)
\end{align*}
\]

\[
\begin{align*}
(MA_2 + ML_2 \xrightarrow{K_{rep}} 2 MAL)
\end{align*}
\]
\[ K_{\text{dis}} \]

Disproportionation constant

\[
(2 \text{ MAL} \xrightarrow{K_{\text{dis}}} \text{MA}_2 + \text{ML}_2)
\]

\[ \Delta \log K_2 \]

Logarithmic change in the equilibrium constant

\[
\Delta \log K_2 = \log K_{\text{MA}} - \log K_{\text{ML}}
\]

\[ \Delta \log K_L \]

Logarithmic change in the equilibrium constant

\[
\Delta \log K_L = \log K_M - \log K_{\text{ML}}
\]

Mathematically,

\[
\Delta \log K_L = \Delta \log K_2 - \Delta \log K_1
\]

\[ \Delta G \]

Free energy change accompanying the formation of 1:1 binary ML and 1:1:1 ternary MAL complex in accordance with the equilibria

\[
\text{M} + \text{L} \xrightarrow{} \text{ML}, \quad \Delta G_{\text{ML}}^M = -2.303 \text{ RT} \log K_{\text{ML}}^M
\]

\[
\text{MA} + \text{L} \xrightarrow{} \text{MAL}, \quad \Delta G_{\text{MAL}}^{\text{MA}} = -2.303 \text{ RT} \log K_{\text{MAL}}^{\text{MA}}
\]

\[ \Delta H \]

Enthalpy change in the complex formation

\[ \Delta S \]

Entropy change in the complex formation

\[ S_{\text{M}} \]

Standard entropy of Ln(III) cation

\[ 4f^n \]

Number of 4f electrons in a Ln(III) metal ion

\[ r (\text{Å}) \]

Ionic radius of the metal ion

\[ L \]

Total orbital angular momentum of lanthanide

\[ \text{C.N.} \]

Coordination number

\[ \text{H.N.} \]

Total hydration number

\[ \text{HSAB} \]

Hard and soft acid base scale

\[ \text{Ln(III)} \]

Tervalent lanthanide metal ion

\[ \sigma^- \]

Standard deviation

\[ r (\text{statistical}) \]

Correlation coefficient