APPENDIX C

Derivation of Model for Cationic Interferent Study

We consider calcium as our example to derive this model. We start with the equilibrium described in [1], which has the corresponding equilibrium expression written in [2].

$$\mathrm{Tb(DO2A)(DPA)^{-}} + \mathrm{Ca^{2+}} \underset{}{\overset{K_{cation}}{\rightleftharpoons}} \mathrm{Tb(DO2A)^{+}} + \mathrm{CaDPA} \qquad [1]$$

$$K_{cation} = \frac{[\mathrm{Tb(DO2A)^{+}}]_{eq}[\mathrm{CaDPA}]_{eq}}{[\mathrm{Tb(DO2A)(DPA)^{-}}]_{eq}[\mathrm{Ca^{2+}}]_{eq}} \qquad [2]$$

Since $K_{Tb(DO2A)} >> K_{Ca(DO2A)}$,[1] we assume negligible formation of Ca(DO2A) or $TbDPA^{+}$. As $Tb(DO2A)^{+}$ and CaDPA form in a ratio of 1:1 from the dissociation of one $Tb(DO2A)(DPA)^{-}$, we obtain equation [3].

$$[\mathrm{Tb(DO2A)^{+}}]_{eq} = [\mathrm{CaDPA}]_{eq} \qquad [3]$$

The total concentration of Tb^{3+} is expressed in [4], and similarly the total concentration of Ca^{2+} is given in [5].

$$[\mathrm{Tb^{3+}}]_{Tot} = [\mathrm{Tb(DO2A)(DPA)^{-}}]_{eq} + [\mathrm{Tb(DO2A)^{+}}]_{eq} \qquad [4]$$

$$[\mathrm{Ca^{2+}}]_{Tot} = [\mathrm{Ca^{2+}}]_{eq} + [\mathrm{CaDPA}]_{eq} \qquad [5]$$

Rearranging, we have [6] and [7]:

$$[\mathrm{Tb(DO2A)^{+}}]_{eq} = [\mathrm{Tb^{3+}}]_{Tot} - [\mathrm{Tb(DO2A)(DPA)^{-}}]_{eq} \qquad [6]$$

$$[\mathrm{Ca^{2+}}]_{eq} = [\mathrm{Ca^{2+}}]_{Tot} - [\mathrm{CaDPA}]_{eq} = [\mathrm{Ca^{2+}}]_{Tot} - [\mathrm{Tb(DO2A)^{+}}]_{eq} \qquad [7]$$

Substituting [3], [6] and [7] into [2], we have expression [8].

$$K_{cation} = \frac{\left\{[Tb]_{Tot} - [Tb(DO2A)(DPA)^{-}]_{eq}\right\}^2}{[Tb(DO2A)(DPA)^{-}]_{eq}\left([Ca^{2+}]_{Tot} - [Tb]_{Tot} + [Tb(DO2A)(DPA)^{-}]_{eq}\right)} \quad [8]$$

After some rearranging, we have:

$$(1 - K_{cation})\left\{[Tb(DO2A)(DPA)^{-}]_{eq}\right\}^2 + \begin{pmatrix} K_{cation}[Tb^{3+}]_{Tot} \\ - K_{cation}[Ca^{2+}]_{Tot} \\ - 2[Tb^{3+}]_{Tot} \end{pmatrix}[Tb(DO2A)(DPA)^{-}]_{eq} + \left\{[Tb^{3+}]_{Tot}\right\}^2 = 0 \quad [9]$$

Solving for $[Tb(DO2A)(DPA)^{-}]_{eq}$, we have equation [10].

$$[Tb(DO2A)(DPA)^{-}]_{eq} = \frac{-A + \sqrt{A^2 - 4B\left\{[Tb^{3+}]_{Tot}\right\}^2}}{2B} \quad [10]$$

where $A = (K_{cation} - 2)[Tb^{3+}]_{Tot} - K_{cation}[Ca^{2+}]_{Tot}$
$B = 1 - K_{cation}$

In terms of intensity, we need an expression in the form of [11], as only the terbium-containing species will be observable via luminescence measurements.

$$I_{obs} = c_1 I_1 + c_2 I_2 \quad [11]$$

where $I_1 =$ intensity of $[Tb(DO2A)(DPA)^{-}]_{eq}$
$I_2 =$ intensity of $[Tb(DO2A)^{+}]_{eq}$
$c_1 = \frac{[Tb(DO2A)(DPA)^{-}]_{eq}}{[Tb(DO2A)(DPA)^{-}]_{Tot}}$
$c_2 = \frac{[Tb(DO2A)^{+}]_{eq}}{[Tb(DO2A)(DPA)^{-}]_{Tot}} = 1 - c_1$

Substituting in eq [10], we finally end with eq [12].

$$I_{obs} = \left(\frac{[Tb(DO2A)(DPA)^{-}]_{eq}}{[Tb(DO2A)(DPA)^{-}]_{Tot}}\right) I_1 + \left(1 - \frac{[Tb(DO2A)(DPA)^{-}]_{eq}}{[Tb(DO2A)(DPA)^{-}]_{Tot}}\right) I_2 \quad [12]$$

where

$$[\mathrm{Tb(DO2A)(DPA)^-}]_{eq} = \frac{-\left\{\left(10^{-7} - [\mathrm{Ca}^{2+}]_{Tot}\right)K_{cation} - 2\left(10^{-7}\right)\right\} + \sqrt{\left\{\left(10^{-7} - [\mathrm{Ca}^{2+}]_{Tot}\right)K_{cation} - 2\left(10^{-7}\right)\right\}^2 - 4\left(1 - K_{cation}\right)\left\{[\mathrm{Tb}^{3+}]_{Tot}\right\}^2}}{2\left(1 - K_{cation}\right)}$$

This equation was used in the Matlab® Curve-Fit Toolbox to fit the calcium competition experiment data and calculate the competition constants.

References

1. Chang, C. A.; Chen, Y.-H.; Chen, H.-Y.; Shieh, F.-K., Capillary electrophoresis, potentiometric and laser excited luminescence studies of lanthanide(III) complexes of 1,7-dicarboxymethyl-1,4,7,10-tetraazacyclododecane (DO2A). *Journal Of The Chemical Society-Dalton Transactions* **1998**, (19), 3243-3248.