Interactions of hydrophobic metal complexes and their constituents with aquatic humic substances

Amiel Boullemant, Jean-Pierre Gagné, Claude Fortin and Peter G.C. Campbell

Supplementary Material

Fluorescence intensity data

Derivation of the complexation constants for $\text{Cd}(\text{DDC})_n$ and $\text{Cd}(\text{XANT})_n$ complexes
Fluorescence intensity data

Table A1. Variations in peak intensities during the titration of SRHA and SRFA with Cd at pH 7.0 ([Cd1] = 0.1 nM; [Cd2] = 1.0 nM; [Cd3] = 10 nM; [Cd4] = 0.1 µM; [Cd5] = 1.0 µM; [Cd6] = 10 µM). For SRHA wavelength pairs are in nm (excitation/emission): Area A = 245/435; Area C = 295/430. For SRFA wavelength pairs are in nm (excitation/emission): Area A = 250/435; Area B = 280/438; Area C = 335/460

<table>
<thead>
<tr>
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<th>AREA A</th>
<th>AREA B</th>
<th>AREA C</th>
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<td>SRHA alone</td>
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<td>SRHA + Cd6</td>
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| SRFA alone      | 1890.4 | 1120.7 | 894.4 |
| SRFA + Cd1      | 2395.9 | 1366.1 | 865.6 |
| SRFA + Cd2      | 2813.4 | 1603.3 | 869.7 |
| SRFA + Cd3      | 3086.2 | 1765.4 | 859  |
| SRFA + Cd4      | 3200.1 | 1866  | 850.4 |
| SRFA + Cd5      | 3612.4 | 2030  | 893.9 |
| SRFA + Cd6      | 3650.8 | 2083.3 | 866.2 |
Table A2. Variations in peak intensities during the titration of SRHA or SRFA with Cd at pH 5.5 ([Cd1] = 0.1 nM; [Cd2] = 1.0 nM; [Cd3] = 10 nM; [Cd4] = 0.1 µM; [Cd5] = 1.0 µM; [Cd6] = 10 µM). For SRHA wavelength pairs are in nm (excitation/emission): Area A = 250/441; Area C = 320/442. For SRFA wavelength pairs are in nm (excitation/emission): Area A = 255/465; Area B = 295/454; Area C = 325/458.

<table>
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Table A3. Variations in peak intensities during the titration of mixtures of DDC and SRHA or SRFA with Cd at pH 7.0 ([Cd1] = 0.38 nM; [Cd2] = 2.4 nM; [Cd3] = 12 nM; [Cd4] = 62 nM; [Cd5] = 162 nM). For SRHA wavelength pairs are in nm (excitation/emission): Area A = 245/430; Area B = 280/427; Area C = 315/443. For SRFA wavelength pairs are in nm (excitation/emission): Area A = 245/437; Area B = 280/439; Area C = 330/458.

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Table A4. Variations in peak intensities during the titration of mixtures of DDC and SRHA or SRFA with Cd at pH 5.5 ([Cd1] = 0.38 nM; [Cd2] = 2.4 nM; [Cd3] = 12 nM; [Cd4] = 62 nM; [Cd5] = 162 nM). For SRHA wavelength pairs are in nm (excitation/emission): Area A = 255/462; Area C = 315/447. For SRFA wavelength pairs are in nm (excitation/emission): Area A = 250/443; Area B = 280/434; Area C = 330/461

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Table A5. Variations in peak intensities during the titration of mixtures of XANT and SRHA or SRFA with Cd at pH 7.0 ([Cd1] = 0.38 nM; [Cd2] = 2.4 nM; [Cd3] = 12 nM; [Cd4] = 62 nM; [Cd5] = 162 nM). For SRHA wavelength pairs are in nm (excitation/emission): Area A = 250/444; Area C = 315/444. For SRFA wavelength pairs are in nm (excitation/emission): Area A = 250/456; Area C = 325/451

<table>
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<th>Titration pH 7.0</th>
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Table A6. Variations in peak intensities during the titration of mixtures of XANT and SRHA or SRFA with Cd at pH 5.5 ([Cd1] = 0.38 nM; [Cd2] = 2.4 nM; [Cd3] = 12 nM; [Cd4] = 62 nM; [Cd5] = 162 nM). For SRHA wavelength pairs are in nm (excitation/emission): Area A = 255/466; Area C = 315/440. For SRFA wavelength pairs are in nm (excitation/emission): Area A = 255/482; Area C = 330/452.

<table>
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<th>Titration pH 5.5</th>
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<th>AREA C</th>
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Thermodynamic stability constants for Cd(DDC)\textsubscript{n} and Cd(XANT)\textsubscript{n} complexes

To perform speciation calculations for cadmium in the various exposure media, one needs the following thermodynamic stability constants:

\[
\begin{align*}
\log K_1 & \quad \text{Cd}^{2+} + \text{L}^{-} \leftrightarrow \text{CdL}^{+} \\
\log K_2 & \quad \text{CdL}^{+} + \text{L}^{-} \leftrightarrow \text{CdL}_2^0 \\
\log \beta_2 & \quad \text{Cd}^{2+} + 2\text{L}^{-} \leftrightarrow \text{CdL}_2^0 \\
\log \beta_2 & = \log K_1 + \log K_2
\end{align*}
\]

where L = diethyldithiocarbamate (DDC) or ethylxanthate (XANT). To take into account the pH of the solutions, one also needs the corresponding acidity constants:

\[
\begin{align*}
\log K_{a1} & \quad \text{H}^+ + \text{L}^{-} \leftrightarrow \text{HL} \\
\log K_{a2} & \quad \text{HL} + \text{H}^+ \leftrightarrow \text{H}_2\text{L}^+ \\
\log \beta_{a2} & \quad 2\text{H}^+ + \text{L}^{-} \leftrightarrow \text{H}_2\text{L}^+ \\
\log \beta_{a2} & = \log K_{a1} + \log K_{a2}
\end{align*}
\]

For the Cd/DDC and Cd/XANT systems, many of the primary thermodynamic data needed for speciation calculations are missing. Where possible, we used the Irving-Rossotti approach to estimate the missing complexation constants.\cite{1}

**Diethyldithiocarbamate**

For the protonation of DDC, we chose a pK\textsubscript{a} value of 3.38, this value having been reported for two studies carried out in aqueous media.\cite{2,3} No log K\textsubscript{1} values are available for the Cd-DDC system in aqueous solution; the value measured in methanol and dimethylsulfoxide (8.3)\cite{4} was adjusted to 8.0 as a conservative estimate. A log \beta_2 value of 17.44 was estimated from a regression of log \beta_2 (Cd) v. log \beta_2 (Pb) for a variety of organic ligands for which reliable constants were available:\cite{5,6} log \beta_2 (Cd) = (1.07 ± 0.06) \cdot \log \beta_2 (Pb) – (1.26 ± 0.52), r\textsuperscript{2} = 0.95, N=17. For the Pb-DDC\textsubscript{2} complex, the IUPAC database gives two log \beta_2 values, the average of which is 18.45 ± 0.12. Introducing this value into the linear regression yields a log \beta_2 value of 18.54 ± 1.10 for the Cd-DDC\textsubscript{2} complex; for our calculations we chose a value of 17.44, i.e., the most unfavourable case (18.54 minus 1.10, the latter term being the standard error).

**Ethylxanthate**

For the protonation of XANT, we could only find a single value, pK\textsubscript{a} = 2.20, obtained in a 1:1 mixture of water and dimethylformamide;\cite{7} in the absence of any other data, this value was used. To estimate the log
\( \beta_2 \) value for the \( \text{Cd(XANT)}_2 \) complex, we again used the Irving-Rossotti approach with the Cd-Pb pairing. However, data for XANT are scarce and we had to use a the literature constant of the Pb complex with butyl-ethylxanthate, i.e., a ligand with one alkyl chain containing two additional -CH\(_2\)- units. According to the IUPAC database, the log \( \beta_2 \) value for the \( \text{Pb(butylethylxanthate)}_2 \) complex is 13.29. Introducing this value into the linear regression yields a log \( \beta_2 \) value of 13.0 ± 0.81 for the \( \text{Cd(butylxanthate)}_2 \) complex. To account for the two extra alkyl groups, we reduced this value by two log units and used a conservative estimate of log \( \beta_2 \) (\( \text{Cd(XANT)}_2 \)) = 11.0. The log \( K_1 \) value for Cd-XANT was estimated from the relation \( \beta_2 = K_1^2 \).\(^8\)

![Regression of log \( \beta_2 \) (Pb) against log \( \beta_2 \) (Cd) for a variety of organic ligands (I = 0; T = 298 K).](image_url)

**Fig. A1.** Regression of log \( \beta_2 \) (Pb) against log \( \beta_2 \) (Cd) for a variety of organic ligands (I = 0; T = 298 K).
References


