

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

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Supplementary Material

Fluorescence intensity data

Derivation of the complexation constants for $Cd(DDC)_n$ and $Cd(XANT)_n$ 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

Titration pH 7.0	AREA A	AREA B	AREA C
SRHA alone	1727.1		1551.3
SRHA + Cd1	1808.4		1850
SRHA + Cd2	1879.4		2026.6
SRHA + Cd3	1954.6	Not present	2094.6
SRHA + Cd4	2045.7		2136.5
SRHA + Cd5	2159.6		2110.5
SRHA + Cd6	2187.3		2185.3
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

Titration pH 5.5	AREA A	AREA B	AREA C
SRHA alone	1291.2		1114.5
SRHA + Cd1	1310.1		1123.3
SRHA + Cd2	1366.9		1116.2
SRHA + Cd3	1530.6	Not present	1124.2
SRHA + Cd4	1489		1147
SRHA + Cd5	1625.4		1130.7
SRHA + Cd6	1700		1151.2
SRFA alone	1160.4	696.4	906.2
SRFA + Cd1	1172.1	709.1	904.1
SRFA + Cd2	1222.7	751.1	890.7
SRFA + Cd3	1297.7	765.4	900.9
SRFA + Cd4	1345.6	793.5	890.4
SRFA + Cd5	1401.8	832.2	879
SRFA + Cd6	1394.3	867.9	885.5

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

Titration pH 7.0	AREA A	AREA B	AREA C
SRHA alone	2771.8	1604.3	1279.7
SRHA + DDC	3137	1738.1	1266.4
SRHA + DDC + Cd1	3398.5	1913.7	1242.4
SRHA + DDC + Cd2	3829.3	2142.1	1268.4
SRHA + DDC + Cd3	3950	2240	1260
SRHA + DDC + Cd4	4113.9	2345.9	1255.3
SRHA + DDC + Cd5	4485.6	2490.4	1249.2
SRFA alone	1615.3	1011.3	1031.1
SRFA + DDC	2230.3	1279.6	985
SRFA + DDC + Cd1	2689.7	1520.6	1009.1
SRFA + DDC + Cd2	3082	1691.6	1015.8
SRFA + DDC + Cd3	3406.3	1866.9	1005.9
SRFA + DDC + Cd4	3596.3	2003.6	1025
SRFA + DDC + Cd5	4382.7	2399.1	1034.4

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

Titration pH 5.5	AREA A	AREA B	AREA C
SRHA alone	1392		1204.3
SRHA + DDC	1359.4		1181.9
SRHA + DDC + Cd1	1407		1183.6
SRHA + DDC + Cd2	1461.1	Not present	1173.1
SRHA + DDC + Cd3	1517.7		1172.9
SRHA + DDC + Cd4	1562.4		1202.9
SRHA + DDC + Cd5	1564		1200
SRFA alone	1384	837.3	953.8
SRFA + DDC	1525.7	925.7	934.6
SRFA + DDC + Cd1	1691.7	1047.8	958.7
SRFA + DDC + Cd2	1858.5	1155.2	914.3
SRFA + DDC + Cd3	1966.6	1281.7	921.3
SRFA + DDC + Cd4	2207.6	1387.2	915
SRFA + DDC + Cd5	2300.5	1528.1	917.5

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

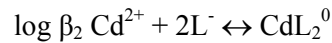
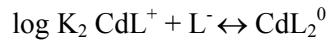
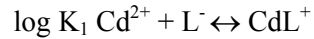
Titration pH 7.0	AREA A	AREA B	AREA C
SRHA alone	1637.8		1252.6
SRHA + XANT	1530.6		754.2
SRHA + XANT + Cd1	1650.4		755.9
SRHA + XANT + Cd2	1717.8	Not present	752.9
SRHA + XANT + Cd3	1993.4		783.7
SRHA + XANT + Cd4	2027.1		767.9
SRHA + XANT + Cd5	2066.7		779.4
SRFA alone	1365.9		1029.5
SRFA + XANT	1203.6		932.3
SRFA + XANT + Cd1	1326.3		921.3
SRFA + XANT + Cd2	1283.6	Not present	937.5
SRFA + XANT + Cd3	1339		956.1
SRFA + XANT + Cd4	1439.5		923.8
SRFA + XANT + Cd5	1442.2		928.8

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

Titration pH 5.5	AREA A	AREA B	AREA C
SRHA alone	1398.2		1198.1
SRHA + XANT	1304.7		765.1
SRHA + XANT + Cd1	1358.1		771.7
SRHA + XANT + Cd2	1433.8	Not present	784
SRHA + XANT + Cd3	1507		781.8
SRHA + XANT + Cd4	1517.1		808
SRHA + XANT + Cd5	1556.6		787.4
SRFA alone	1037.8		928
SRFA + XANT	945.9		900.7
SRFA + XANT + Cd1	943.9		874.2
SRFA + XANT + Cd2	996.5	Not present	880.4
SRFA + XANT + Cd3	1005		859.6
SRFA + XANT + Cd4	1006.2		849.2
SRFA + XANT + Cd5	1017.3		854.6

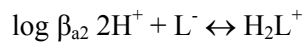
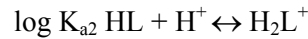
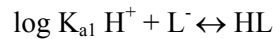
Thermodynamic stability constants for Cd(DDC)_n and Cd(XANT)_n complexes

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



$$\log \beta_2 = \log K_1 + \log K_2$$

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



$$\log \beta_{a2} = \log K_{a1} + \log K_{a2}$$

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.^[1]

Diethyldithiocarbamate

For the protonation of DDC, we chose a pK_a value of 3.38, this value having been reported for two studies carried out in aqueous media.^[2,3] No log K₁ values are available for the Cd-DDC system in aqueous solution; the value measured in methanol and dimethylsulfoxide (8.3)^[4] was adjusted to 8.0 as a conservative estimate. A log β₂ value of 17.44 was estimated from a regression of log β₂ (Cd) v. log β₂ (Pb) for a variety of organic ligands for which reliable constants were available.^[5,6] log β₂ (Cd) = (1.07 ± 0.06) · log β₂ (Pb) – (1.26 ± 0.52), r² = 0.95, N=17. For the Pb-DDC₂ complex, the IUPAC database gives two log β₂ values, the average of which is 18.45 ± 0.12. Introducing this value into the linear regression yields a log β₂ value of 18.54 ± 1.10 for the Cd-DDC₂ 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_a = 2.20, obtained in a 1:1 mixture of water and dimethylformamide,^[7] in the absence of any other data, this value was used. To estimate the log

β_2 value for the $\text{Cd}(\text{XANT})_2$ 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 $-\text{CH}_2-$ units. According to the IUPAC database, the $\log \beta_2$ value for the $\text{Pb}(\text{butylethylxanthate})_2$ complex is 13.29. Introducing this value into the linear regression yields a $\log \beta_2$ value of 13.0 ± 0.81 for the $\text{Cd}(\text{butylxanthate})_2$ complex. To account for the two extra alkyl groups, we reduced this value by two log units and used a conservative estimate of $\log \beta_2 (\text{Cd}(\text{XANT})_2) = 11.0$. The $\log K_1$ value for Cd-XANT was estimated from the relation $\beta_2 = K_1^2$.^[8]

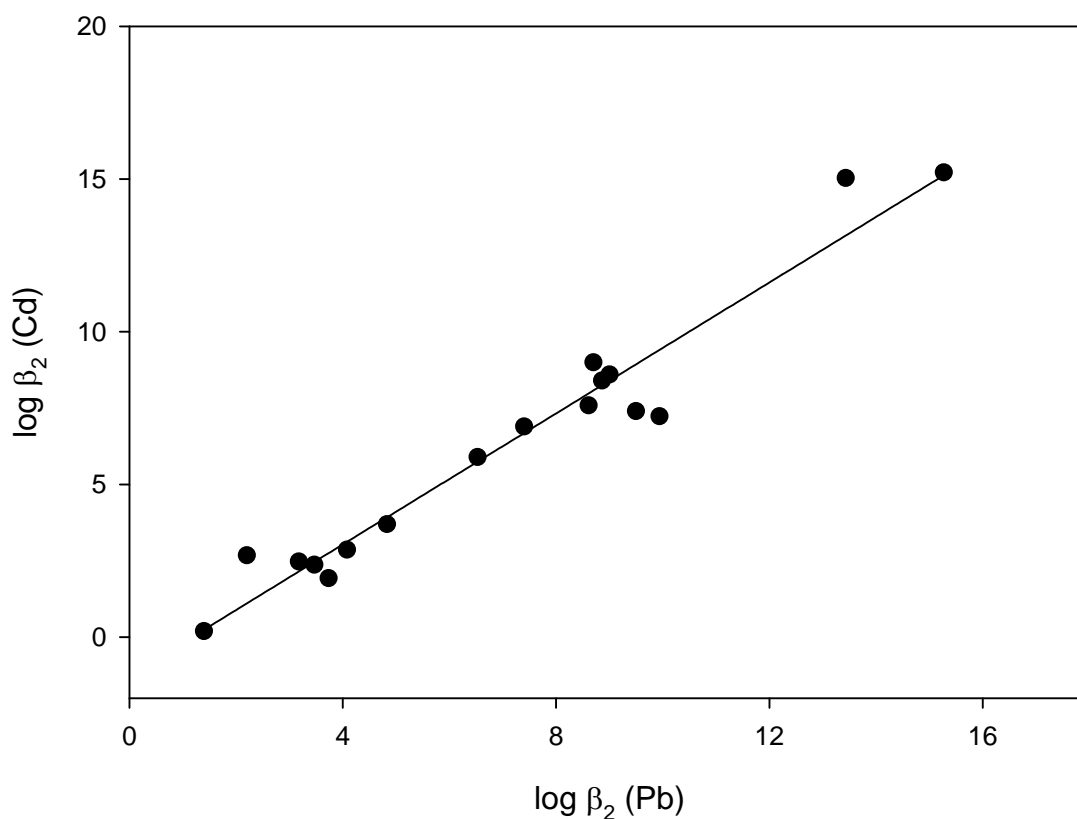


Fig. A1. Regression of $\log \beta_2$ (Pb) against $\log \beta_2$ (Cd) for a variety of organic ligands ($I = 0$; $T = 298 \text{ K}$).

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