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USE OF CADMIUM TO DETERMINE COMPLEXING CAPACITIES AND CONDITIONAL STABILITY CONSTANTS OF OTHER METAL–LIGAND SYSTEMS *VIA* ANODIC STRIPPING VOLTAMMETRY

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Abstract—Quantification of the binding of metal ions which strongly complex with the organic components in natural waters is very difficult or impossible to measure directly. This paper shows that using competition *via* Cd^{2+} and the differential pulse stripping voltammetric technique provides an indirect route to quantifying organic ligand complexation by e.g. lanthanide metal ions.

The complexation of metal ions by organic compounds in natural waters is of both bio- and geochemical importance.[1,2] Quantification of this complexation is, however, extremely difficult because of the low concentration (e.g. 10^{-9} M or less) and because of the often unknown nature of the organic components. Indirect competitive methods can be used,[3] principally involving the addition of another metal ion which can also complex with the organic component(s).

This method requires an analytical technique which is specific for the competing metal and which can distinguish between free and complexed forms of the metal. The electrochemical methods of polarography and voltammetry provide these requirements as well as high sensitivity. The metal ion of choice has been Cu^{2+} because of its strong complexing properties and ease of detection. However, controversy has arisen over the ability of the electrochemical reduction methods to distinguish different Cu species; aqueous Cu^{2+} and $[Cu(EDTA)]^{2-}$ are prime examples.[4,5]

The Cd^{2+} ion appears to be a worthwhile alternative; it can readily be determined by electrochemical methods and its organocomplexes, e.g. $[Cd(EDTA)]^{2-}$ and $[Cd(NTA)]^{-}$, are reported to be electrochemically inactive[6,7] i.e. can be distinguished from the aqueous Cd^{2+} ion. We report here results on the Cd–EDTA system (at 25°C and 0.70 M ionic strength) using differential pulse stripping voltammetric (DPASV) measurements which show that Cd^{2+} can be an effective competitor for lanthanide ions and for determining their complexing intensities in sea-water. In fact, Schwarzenbach *et al.*[8] in an earlier classical study also used Cd as a competing metal to determine the stability constants of lanthanide–EDTA complexes; these studies, however, were carried out at 20°C and 0.1 M ionic strength and used the less sensitive differential pulse polarographic method. For determination of speciation at environmental concentrations, more sensitive methods such as stripping voltammetry are needed. Finally, our

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results confirm the earlier reports that $[Cd(EDTA)]^{2-}$, but not $[Cu(EDTA)]^{2-}$, is electrochemically inactive towards reduction at the mercury drop electrode.

EXPERIMENTAL

A Princeton Applied Research polarograph analyser model 384 was used together with a model 303 electrode assembly (Hg drop electrode, Ag/AgCl reference electrode and Pt counter electrode) and a Houston Instrument Hiplot digital plotter. The instrument was run in DPASV mode with optimum conditions: 4 min initial N_2 gas purge, stripping potential −0.9 V, deposition time 60 s, equilibrium time 30 s, pulse height 50 mV, scan rate 1 mV s^{-1}, scan range −0.90 to −0.40 V. The large Hg drop size was used. Because of some variation in size, all scans were repeated at least three times and the average taken.

All chemicals used were of the purest grades available. Each solution for DPASV measurements contained 0.70 M NaCl to mimic sea-water; 10.0 cm^3 aliquots were pipetted into the electrode compartment which was thermostated at 25.0 ± 0.05°C. Solutions containing lanthanides and EDTA were left to equilibrate at 25.0 ± 0.5°C overnight before measurement. Reference solutions contained Cd^{2+} in 0.70 M NaCl solution at the appropriate pH. Blank solutions were also 0.70 M NaCl solutions with appropriate amount of EDTA. The stock Cd solution (*ca* 1×10^{-4} M) was prepared from $Cd(NO_3) \cdot 4H_2O$ and calibrated using the DPASV signal as compared with that from a commercial Cd reference solution. The stock Cd solution was then used to calibrate the stock EDTA solution (prepared from $Na_2H_2EDTA \cdot 2H_2O$) by DPASV titration until further addition of EDTA reduced the Cd^{2+} signal to zero. The *ca* pH 5 solutions were buffered with 1×10^{-3} M acetate and those at *ca* pH 8 were buffered with 1×10^{-3} M Tris buffer. The pH values were determined using a Ross combination electrode and a Corning pH/ion meter calibrated with standard buffers.

RESULTS AND DISCUSSION

Optimum instrument conditions and linearity of response

All instrument parameters were altered in order to produce the maximum signal to noise ratio; the optimum conditions found are those listed above. Variation of the deposition potential between −0.8 V and −1.0 V had little effect. A scan rate of either 1 or 2 mV s^{-1} produced good sharp peaks in the current (I) *vs* voltage (V) scans; however, above about 5 mV s^{-1} peak distortions occurred. Using the optimum conditions an excellent linear response between the peak height (I) and the Cd concentration was found (Fig. 1) over the concentration range 1.0×10^{-6}–2.0×10^{-5} M.

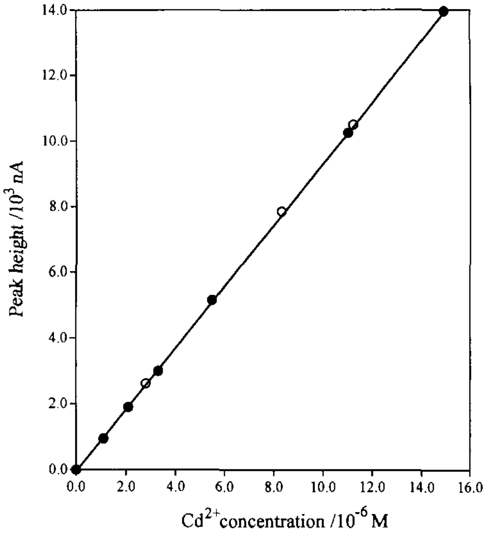

Fig. 1. Linearity of DPASV response to Cd^{2+} concentration: (●) in 0.7 M NaCl solution; (○) in 0.7 M KNO_3 solution; both at 25°C.

The above linear response was the same for both 0.7 M KNO_3 and 0.7 M NaCl media, although the measured oxidation potentials differed (−0.678 V and −0.714 V, respectively). This difference in potentials can be attributed to the presence of the chloro complexes, $CdCl_n$ (n = 1–4), in the NaCl media. Byrne *et al.*[9] calculate that over 97% of the inorganic Cd in sea-water is in the forms $CdCl^+$ and $CdCl_2$. The significance of these observations is that all the inorganic forms of Cd^{2+} are reduced at the Hg electrode at the deposition potential and, hence the peak heights in the I *vs* V plot is proportional to the total inorganic Cd present.

Addition of EDTA to the Cd solutions reduced the Cd signal in direct proportion to the EDTA concentration, thus indicating the non-reduction (electrochemical inactivity) of the $CdEDTA^{2-}$ species. In contrast, no conditions could be found under which Cu^{2+} and $CuEDTA^{2-}$ were not both reduced at the same potential. As noted above, these observations have been reported previously by others. Lack of reducibility is often attributed to the kinetic inertness of the chelated species. This is insufficient to explain the difference in behaviour between the Cd and Cu chelates.

Cd–EDTA *complexation*

The voltammograms of the Cd–EDTA solutions thus give a direct measure of the non-chelated forms of Cd, i.e. Cd^{2+} and $CdCl_n$, collectively referred to as inorganic Cd. From this, by mass balance, the concentrations of $CdEDTA^{2-}$ and free EDTA are obtained and hence, the conditional stability constant K_c.

$$K_c = [CdL]/[Cd][L] \qquad (1)$$

where

$$[Cd] = [Cd^{2+}] + \Sigma[CdCl_n] \qquad (2)$$

and

$$[L] = [L^{4-}] + \Sigma[H_nL] \qquad (3)$$

L = EDTA, n = 1 to 4.

From eqs (2) and (3) it is clear that K_c is a function of solution conditions, such as chloride and hydrogen ion concentrations, as well as the more usual ionic strength and temperature. It is useful here to define factors A_{Cd} and A_L[10,11] where:

$$\begin{aligned} A_{Cd} &= [Cd_{inorg}]/[Cd^{2+}] \\ &= 1 + {}_{Cl}\beta_1[Cl^-] + {}_{Cl}\beta_2[Cl^-]^2 \\ &\quad + {}_{Cl}\beta_3[Cl^-]^3 + {}_{Cl}\beta_4[Cl^{-1}]^4 \qquad (4) \end{aligned}$$

and

$$\begin{aligned} A_L &= [H_nL]/[L^{4-}] \\ &= 1 + {}_{H}\beta_1[H^+] + {}_{H}\beta_2[H^+]^2 \\ &\quad + {}_{H}\beta_3[H^+]^3 + {}_{H}\beta_4[H^+]^4 \qquad (5) \end{aligned}$$

where β_n values are the stability (formation) constants of each species relative to the free concentrations of Cd^{2+} and L^{4-}, respectively. The relationship between the stability constant (β) for the formation of $CdEDTA^{2-}$ and K_c is given by:

$$\beta(CdL) = [CdL]/[Cd^{2+}][L^{4-}] = K_c A_{Cd} A_L. \qquad (6)$$

The use of K_c rather than β is of particular value in complex systems like sea-water.[10,11]

Determination of K_c at pH *ca* 8 (as in sea-water) was found to be impossible because of the strong complex formation. Therefore the pH was lowered to approximately 5 to reduce the amount of EDTA in non-protonated form ($A_L = 10^6$). Buffering was achieved by addition of acetic acid/sodium acetate at a concentration of 10^{-3} M, a low enough concentration to limit complex formation with the acetate ion but sufficient to give adequate buffering. Insignificant complex formation between acetate ions and Cd^{2+} was confirmed by computer simulation using program NUTRIENT[12] and literature stability constants.[13,14]

The results obtained at the lower pH are shown in Table 1. The mean log $K_c = 6.88 \pm 0.11$. Using the best available literature values[13,14] for the stability constants in eqs (4) and (5) for 0.70 M ionic strength, 25°C and pH 4.93 we calculate $A_{Cd} = 41$ and $A_L = 2.7 \times 10^6$, and hence from eq. (6) a log β for $CdEDTA^{2-}$ formation of 14.94. This value of β must be regarded as an approximate one because of the range of values of the stability constants in the literature for $CdCl_n$ and H_nEDTA species (none at 0.7 M ionic strength and those reported at 0.5 M ionic strength are highly variable). We have also made the assumption that other species such as $Cd(HEDTA)^-$, $CdCO_3$ and $CdOH^+$ are not formed. This assumption is justified by taking literature values of the relevant stability constants and simulating the equilibria (using NUTRIENT) at the conditions used here; none of these species were of significance (< 1% of total Cd). Literature values of log β at 25°C range from 14.27 to 16.49 over an ionic strength range of 0.1 to 1.0 M (none at 0.7 M).

Table 1. DPASV results for Cd–EDTA solutions at pH 4.93, 25°C and 0.70 M NaCl ionic strength

$[L_t]^{a,b}$	I/I_o	[Cd]	log $K_c\{CdEDTA^{2-}\}$
2.520	0.795	9.608	6.73
3.780	0.684	8.270	6.87
5.040	0.590	7.127	6.90
6.300	0.492	5.948	6.79
7.560	0.389	4.703	6.93
8.820	0.287	3.465	7.08

[a] See text for meaning of symbols.

[b] Concentrations/10^{-6} M. All solutions contained 1.208×10^{-5} M total Cd.

Ternary Cd–La–EDTA *system: determination of the conditional stability constant for* LaEDTA *formation*

Solutions containing near equimolar amounts of Cd^{2+} and La^{3+} (*ca* 1×10^{-5} M) to which variable amounts of EDTA had been added were left to equilibrate at 25°C before the inorganic Cd concentration was determined by DPASV as above. This measurement, together with the known total concentrations $[Cd_t]$, $[La_t]$ and $[L_t]$, and K_c value for CdEDTA, allows the determination of a K_c value for $LaEDTA^-$ formation:

$$[Cd] = [Cd_t](I/I_o) \qquad (7)$$

where I is the measured peak height and I_o is the peak height for $[Cd_t]$ (i.e. no added EDTA), then:

$$[\mathrm{CdL}] = [\mathrm{Cd_t}]-[\mathrm{Cd}] = [\mathrm{Cd_t}](1-I/I_o) \quad (8)$$

$$[\mathrm{L}] = [\mathrm{CdL}]/K_c[\mathrm{Cd}] = (I_o-I)/K_cI. \quad (9)$$

From the law of mass action:

$$[\mathrm{LaL}] = [\mathrm{L_t}]-[\mathrm{L}]-[\mathrm{CdL}] \quad (10)$$

and

$$[\mathrm{La}] = [\mathrm{La_t}]-[\mathrm{LaL}] \quad (11)$$

$$K_c\{\mathrm{LaL}\} = [\mathrm{LaL}]/[\mathrm{La}][\mathrm{L}]. \quad (12)$$

As with [Cd], the [La] term refers to all (inorganic) non-chelated forms of La.

The results obtained are given in Table 2, the mean log $K_c\{\mathrm{LaEDTA}\} = 7.16 \pm 0.22$. As before this is related to the formation constant β ($= K_c A_{La}A_L$). These measurements were made at the same pH as before (4.93), hence, $A_L = 2.7 \times 10^6$. From data on inorganic complexation in sea-water[11] only $\mathrm{La(CO_3)^+}$ is likely to be of significance but, not under the conditions of our experiments. Using the data of Byrne *et al.*,[9] $A_{La} = 1.56$ giving a log β for $\mathrm{LaEDTA^-}$ formation of 13.84. This value is lower than those reported in the literature (14.48–15.04 at 25°C and 0.5 M ionic strength). Again it must be emphasized that the log β value must be taken as an approximate one for the reasons outlined above.

For complexation of the lanthanides in natural water, knowledge of complexing capacities and relative binding affinities can be of more value than absolute β values (A coefficients may not be known or undeterminable for the organic ligand). One advantage of this competitive approach is the ability to obtain relative binding affinities and K_c values without having to determine free ligand concentrations; this is illustrated in the following section.

Table 2. DPASV results for the ternary Cd–La–EDTA solutions at pH 4.93, 25°C and 0.70 M NaCl ionic strength

$[\mathrm{EDTA_t}]^a$	I/I_o	$[\mathrm{Cd}]^b$	$[\mathrm{L}]^b$	log $K_c\{\mathrm{LaEDTA}\}$
3.15	0.875	10.57	8.39	7.03
6.30	0.688	8.32	7.53	6.76
7.87	0.655	7.91	6.37	6.93
9.45	0.617	7.45	5.27	7.06
11.02	0.595	7.18	3.97	7.24
12.60	0.507	6.12	3.49	7.18
14.17	0.409	4.94	1.95	7.43
15.75	0.392	4.74	1.80	7.37
6.18	0.839	9.93^c	5.56^c	7.50
11.70	0.594	6.95^d	4.76^d	7.08

[a] Concentrations/10^{-6} M.
[b] $[\mathrm{Cd_t}] = 1.208 \times 10^{-5}$ M, $[\mathrm{La_t}] = 1.001 \times 10^{-5}$ M.
[c] $[\mathrm{Cd_t}] = 1.184 \times 10^{-5}$ M, $[\mathrm{La_t}] = 9.80 \times 10^{-6}$ M.
[d] $[\mathrm{Cd_t}] = 1.170 \times 10^{-5}$ M, $[\mathrm{La_t}] = 9.77 \times 10^{-6}$ M.

Relative binding affinities and critical stability constants of La, Pr *and* Nd *with* EDTA

The above experiments were repeated at a pH of 7.89 using 1.0×10^{-3} M Tris buffer (insignificant buffer complexing expected). The perchlorate salts of the three lanthanides were used. Our preliminary experiments had shown that because of the strong complexing of EDTA at this pH, within the limitations of the technique, no free ligand was detectable, i.e. $[\mathrm{L_t}] = [\mathrm{CdL}]+[\mathrm{LnL}]$ (Ln = lanthanide ion), provided that $[\mathrm{Ln_t}]+[\mathrm{Cd_t}] > [\mathrm{L_t}]$. As before the DPASV measurements gave the free Cd concentration and hence [CdL] [eqs (7) and (8) above], from which:

$$[\mathrm{LnL}] = [\mathrm{L_t}]-[\mathrm{CdL}] \quad (13)$$

$$[\mathrm{Ln}] = [\mathrm{Ln_t}]-[\mathrm{LnL}]. \quad (14)$$

For any one solution the ratio of critical constants is given by:

$$K_c\{\mathrm{LnL}\}/K_c\{\mathrm{CdL}\} = [\mathrm{LnL}][\mathrm{Cd}]/[\mathrm{Ln}][\mathrm{CdL}] \quad (15)$$

$$= \{([\mathrm{LnL}]/[\mathrm{Ln}])(I/I_o-1)\}. \quad (16)$$

Equation (16) shows that the K_c ratio can be obtained without knowing the free ligand concentration. The results of these measurements are shown in Table 3. Knowing the K_c value for CdEDTA at one pH enables the calculation of K_c values at any other pH and hence *via* eq. (6) β values, since it follows from eq. (6):

Table 3. DPASV results on the ternary Cd–Ln–EDTA solutions at pH 7.89, 25°C and 0.70 M NaCl ionic strength

$[\mathrm{Ln_t}]^a$	$[\mathrm{Cd_t}]$	$[\mathrm{EDTA_t}]$	I/I_o	$K_c\{\mathrm{LnL}\}/$ $K_c\{\mathrm{CdL}\}$
		Ln = $\mathrm{Ln^{3+}}$		
1.001	1.244	1.080	0.527	1.12
1.001	1.244	2.002	0.134	1.92
1.001	2.428	1.080	0.719	1.68
		Ln = $\mathrm{Pr^{3+}}$		
1.000	6.040	1.080	1.904	9.5
		Ln = $\mathrm{Nd^{3+}}$		
1.000	12.13	1.080	0.958	28.6

[a] Concentrations/10^{-6} M.

$$K_c A_{Cd} A_L = K_{c'} A_{Cd'} A_{L'} \tag{17}$$

or

$$K_{c'} = K_c A_{Cd}/A_{Cd'} \tag{18}$$

where K_c and $K_{c'}$ refer to solutions of different pH. The A_{Cd} value is independent of pH over the range studied. Equation (18) also holds for the lanthanide complexes. Furthermore, it can be shown that if the A coefficients for the metal ions are independent of the pH (e.g. no hydroxy species form) then the ratio $K_c\{LnL\}/K_c\{CdL\}$ should also be independent of pH, since:

$$K_c\{LaL\}/K_c\{CdL\} = \beta\{LaL\}/\beta\{CdL\}(A_{Cd}A_L/A_{La}A_L). \tag{19}$$

At pH 4.93 the ratio $K_c\{LaL\}/K_c\{CdL\} = 1.64 \times 10^7/7.94 \times 10^6 = 2.0$, which is very close to the ratio found (Table 3) at the higher pH confirming our expectation.

Even if the K_c or β values are not known for the Cd complex the relative complexing abilities of other metal ions can be obtained. Thus from the K_c ratios in Table 3 the relative complexing constants for La^{3+}, Pr^{3+} and Nd^{3+} with EDTA is seen to be 1/6.3/19.1; this is close to ratio of stability constants in the literature[12,13] which is of the order 1/8–10/20–50.

CONCLUSIONS

The competitive method for quantifying metal complexation in difficult media is well established.[3] The results presented here demonstrate that Cd is a viable alternative to Cu and by using the sensitive anodic stripping voltammetry technique has certain advantages over Cu. If a solid-state electrode is employed rather than the mercury electrode used in this work then the detection limit for free Cd ions can be substantially lowered; we hope to explore this later. One limitation of the competitive method is that the affinity of the competing metal for the ligand must be similar to that of the metal being probed, so it is important to have the choice of more than one metal competitor. Finally, the results of this study show that a stability constant for the metal competitor need not be known if the relative binding abilities of a number of other metals is required; this is a particular advantage for a series such as the lanthanides and where the nature of the organic ligand is unknown—as is the case in sea-water.

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