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## Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

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First published on: 22 September 2010

**To cite this Article** Hyvönen, Helena , Lehtinen, Päivi and Aksela, Reijo(2008) 'Complexation of *N*-bis[2-(1,2-dicarboxyethoxy)ethyl]aspartic acid with Cd(II), Hg(II) and Pb(II) ions in aqueous solution', *Journal of Coordination Chemistry*, 61: 6, 984 – 996, First published on: 22 September 2010 (iFirst)

**To link to this Article:** DOI: 10.1080/00958970701481455

**URL:** <http://dx.doi.org/10.1080/00958970701481455>

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## Complexation of *N*-bis[2-(1,2-dicarboxyethoxy)ethyl]aspartic acid with Cd(II), Hg(II) and Pb(II) ions in aqueous solution

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(Received 26 April 2007; in final form 24 May 2007)

The persistence of widely used chelating agents EDTA and DTPA in nature has been of concern and there is a need for ligands to replace them. In a search for environmentally friendly metal chelating ligands for industrial applications, complex formation equilibria of *N*-bis[2-(1,2-dicarboxyethoxy)ethyl]aspartic acid (BCA6) with Cd(II), Hg(II) and Pb(II) in aqueous 0.1 M NaNO<sub>3</sub> solution were studied at 25°C by potentiometric titration. Complexation was modeled and the stability constants of the different complexes were determined for each metal ion using the computer program SUPERQUAD. With all metal ions, stable ML<sup>4-</sup> complexes dominated the complex formation. The stabilities of Cd(II), Hg(II) and Pb(II) chelates of BCA6 are remarkably lower than those of EDTA and DTPA. Environmental advantages of the use of BCA6 instead of EDTA and DTPA are better biodegradability and lower nitrogen content with a possibility to save chemicals and process steps in pulp bleaching.

**Keywords:** Stability constants; Cd(II); Hg(II); Pb(II); *N*-bis[2-(1,2-dicarboxyethoxy)ethyl] aspartic acid; Chelating agent

### 1. Introduction

The ability of aminopolycarboxylates such as ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA) to form stable metal complexes has been widely utilized in analytical chemistry and industrial applications. Both ligands are excellent chelating agents and have been extensively used for decades as effective chelating agents in a variety of large-scale industrial applications from detergents to agrochemicals. The persistence of EDTA and DTPA and their metal complexes in nature, because of the low biodegradability of EDTA and DTPA, causes environmental harm and concern by their possible capability to remobilize toxic heavy metal ions from sediments. They form strong complexes with iron and may increase eutrophication by liberation of phosphates. EDTA is found in drinking water samples and is present in almost all anthropogenically influenced surface waters in industrialized countries. During the past few years, the low biodegradability of these ligands and their

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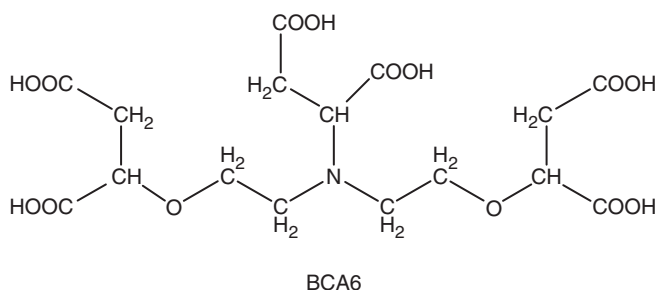
accumulation in the environment has been the cause of a great deal of concern [1–5]. Environmental chemistry of aminopolycarboxylate chelating agents, the mechanisms of how the chelating agents and metal complexes affect the environment and the study of synthetic chelating agents and compounds exhibiting complexing properties into the aquatic environment have been reported [2–3].

Because of their industrial importance, complexing agents are produced and used in large and increasing quantities. EDTA is on a priority list of substances for EU Risk Assessment. In accordance with the conclusion in the risk assessment report there is a need to limit the risks; risk reduction measures are already being applied. The high releases are due to use of EDTA in industrial detergents, by paper mills, by circuit board producers and during recovery of EDTA containing wastes. The risk characterization for these scenarios led to a risk for aquatic organisms [6].

For environmental reasons, pulp bleaching methods based on oxygen chemicals have been developed with the aim of reducing consumption of chlorine-based chemicals. Oxygen, ozone, hydrogen peroxide and peracetic acid are commonly used to replace chlorine chemicals. Pulp usually contains traces of transition metal ions, such as iron and manganese, and these catalyze the decomposition of hydrogen peroxide and peracids and other oxygen-based chemicals during bleaching [7]. The presence of these metals results in excess chemical consumption and reduced pulp strength. Thus the removal of transition metal ions from the pulp by chelation is an essential step when bleaching is done with oxygen-based chemicals. Both EDTA and DTPA are complexing agents commonly used in such chelation steps. Both are virtually nonbiodegradable in waste water treatment plant conditions [8–10] and are difficult to remove from bleaching effluents. As an extra environmental concern, they might have the capability to remobilize toxic heavy metal ions from sediments [11, 12]. Since the chelating agents are a plentiful source of nitrogen, e.g. in the effluents of a pulp mill, the nitrogen content of the ligands should be as low as possible. In short, replacement of EDTA and DTPA by more environmentally friendly chelating agents wherever possible would be highly desirable.

The complex forming properties of alternative chelating agents should be comparable to those of EDTA and DTPA. The nitrogen content of the ligands should be as low as possible. Finally, chelating agents should degrade in nature at least partially in order to lose complex forming ability. Some suitable candidates to replace EDTA and DTPA have been tested both in bleaching [13–17] or detergent [18] applications and in complexation studies [17–21]. The complexation of ethylenediaminedisuccinic acid (EDDS) and iminodisuccinic acid (ISA) with several metal ions [19, 20] and their performance in pulp bleaching [15] has been studied previously. Recently, we have discovered the metal complex chemistry of new ligands *N*-bis[2-(1,2-dicarboxyethoxy)ethyl]aspartic acid, *N*-bis[2-(1,2-dicarboxyethoxy)ethyl]-glycine and *N*-bis[2-(1,2-dicarboxyethoxy)ethyl]-methylglycine [17]. These ligands have proven suitable as chelating agents for pulp bleaching application. *N*-bis[2-(1,2-dicarboxyethoxy)ethyl]aspartic acid (BCA6) was the most suitable choice in pulp bleaching, because it is easy to prepare, more biodegradable than EDTA and DTPA, and inert in peroxy solution. [17] BCA6 has the advantage that its Mn-complexes are inert in the peracetic acid solution, in contrast to Mn-EDTA and Mn-DTPA complexes, which are capable of decomposing peroxy compounds catalytically. Although EDDS and ISA are biodegradable, their metal complexes are not inert in hydrogen peroxide or peracetic acid solution. Like the Mn-complexes of EDTA and DTPA, they decompose peroxy compounds. Thus, BCA6 can be circulated partly

back into different stages of the bleaching process. Therefore, use of BCA6 gives an environmental advantage by reducing amounts of bleaching chemical, fresh water and the number of process stages in bleaching [22]. Although BCA6 shows photodegradability and better biodegradability than EDTA and DTPA [23–27], it can be circulated in the bleaching process. The biodegradation does not occur in process circumstances, where microbes are not present in large populations. In waste water treatment plants the conditions for the biodegradation are more favourable. When planning the use of BCA6 in pulp bleaching applications it was important to know its complexation with toxic heavy metal ions, compared with conventional chelating agents. The complexation of BCA6 with Mg(II), Ca(II), Mn(II), Fe(III), Cu(II), Zn(II) and La(III) ions has been studied earlier [17, 21]. Due to the concern of the possible ability to mobilize heavy metals, the complexation studies of BCA6 is widened in this study, where we report on the aqueous complexation of BCA6 with Cd(II), Hg(II) and Pb(II) ions.



## 2. Experimental

### 2.1. Preparation of BCA6 and stock solutions of metal ions

BCA6 was prepared (Kemira) by synthesis via a lanthanide-catalyzed Michael addition of diethanolamine to maleic acid as described in references [28–30]. The purity of the preparation was checked by NMR methods and potentiometric titration. Aqueous Cd(II) and Hg(II) nitrate solutions were prepared by dissolving Cd(NO<sub>3</sub>)<sub>2</sub> in distilled water and Hg(NO<sub>3</sub>)<sub>2</sub> in aqueous nitric acid. Pb(II) nitrate solution was prepared from a Titrisol ampoule (Merck). The metal contents of the stock solutions were standardized by EDTA titration (Cd(II) 0.100 mol l<sup>-1</sup>, Hg(II) 0.120 mol l<sup>-1</sup>, Pb(II) 0.020 mol l<sup>-1</sup>). The acid contents of the metal solutions were determined by titration with 0.1 M NaOH solution after liberation of the H<sup>+</sup> ions by cation exchange.

### 2.2. Potentiometric measurements

The protonation and complex formation equilibria were studied in aqueous 0.1 M NaNO<sub>3</sub> at 25.0°C through a series of potentiometric EMF titrations carried out with a Schott-Geräte GmbH titrator TPC2000 and utilizing titration software TR600 version 5.00. The cell arrangement for measurement of the hydrogen ion concentration, [H<sup>+</sup>] was the following:



where GE denotes a glass electrode, Schott N2680, and RE is Hg, Hg<sub>2</sub>Cl<sub>2</sub> || 0.01 M NaCl, 0.09 M NaNO<sub>3</sub>. Assuming the activity coefficients to be constant, expression (2) is valid

$$E = E_0 + 59.157 \log[\text{H}^+] + j_{\text{H}}[\text{H}^+] + j_{\text{OH}}[\text{OH}^-] \quad (2)$$

The cell parameter  $E_0$  and the liquid junction coefficient  $j_{\text{H}}$ , valid in acidic solutions, were determined for each titration by addition of a known amount of HNO<sub>3</sub> to the background electrolyte. The value of the liquid junction coefficient  $j_{\text{OH}}$ , valid in basic solutions, was determined periodically. Only stable emf readings (0.2 mV/2–3 min) were used in the calculations.

During measurements of the metal complex equilibria, aqueous 0.1 M NaOH or HNO<sub>3</sub> was added to the solution. The ratio of the total concentrations of metal,  $C_{\text{M}}$ , to ligand,  $C_{\text{L}}$ , was held constant. The initial concentrations were varied within the limits  $0.0002 \text{ M} \leq C_{\text{M}} \leq 0.0010 \text{ M}$  and  $0.0004 \text{ M} \leq C_{\text{L}} \leq 0.0010 \text{ M}$ , covering metal-to-ligand ratios from 1:2 to 2:1. Four or five independent titrations were carried out for each system. The number of data points used in the calculation of the stability constants varied between 343 and 400 in the pH ranges 2.0–10.2 for Cd(II), 1.9–9.4 for Hg(II) and 2.0–10.8 for Pb(II). In some titrations the upper pH values were limited by the appearance of a precipitate or very slow attainment of equilibrium. The reproducibility and reversibility of the equilibria were tested by performing forward (increasing pH) and backward (decreasing pH) titrations. The protonation constants of BCA6 were described earlier in 0.1 M NaCl [17], but determined here in the same background electrolyte, 0.1 M NaNO<sub>3</sub>, as the complex formation with Cd(II), Hg(II) and Pb(II).

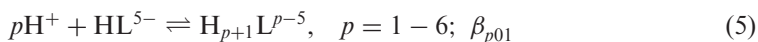
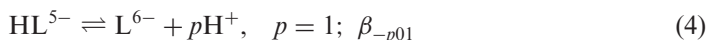
### 2.3. Data treatment

Protonation/deprotonation of the ligand was controlled with HNO<sub>3</sub>/NaOH additions. Curves of  $Z_{\text{H}}$  versus pH were drawn to visualize the experimental data sets.  $Z_{\text{H}}$  describes the average number of H<sup>+</sup> ions added or liberated per mole of ligand and is given by the relation

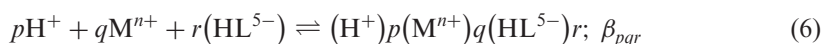
$$Z_{\text{H}} = \frac{(C_{\text{H}} - [\text{H}^+] + k_{\text{w}}[\text{H}^+]^{-1})}{C_{\text{L}}} \quad (3)$$

where  $C_{\text{H}}$  denotes the total concentration of protons calculated over the zero level HL<sup>5-</sup>, H<sub>2</sub>O and M<sup>*n*+</sup>.

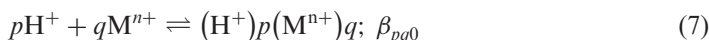
In evaluating the equilibrium constants the following two-component equilibria were considered:



The metal complex formation can be characterized by the general three-component equilibrium:



The hydrolysis of metal ions can be written



The protonation constants of the ligand determined in this study and the hydrolysis constants of the metal ions [31] were considered as known parameters in the evaluation of the three-component system (6).

The mathematical analysis of the systems involves a search for the complex models ( $pqr$ -triplets) and the equilibrium constants of the complexes that best describe the experimental data. The calculations were carried out with the computer program SUPERQUAD [32]. The sample standard deviation  $s$  and the  $\chi^2$ -statistics used as criteria in selection of the complex models were those given by the program.

### 3. Results and discussion

#### 3.1. Protolytic properties of BCA6

The neutralization titrations show the stepwise deprotonation of  $\text{H}_7\text{L}^+$  to  $\text{HL}^{5-}$  to occur in the pH range from 2 to neutral ( $Z_{\text{H}}$  from 6 to 0).  $\text{HL}^{5-}$  is the major species in the pH range 6–8 when  $Z_{\text{H}}=0$ . The negative  $Z_{\text{H}}$  values reached in the pH-range from neutral to 10 shows that one proton (from amino nitrogen,  $\text{HL}^{5-}$  to  $\text{L}^{6-}$ ) can leave the ligand in alkaline solution (figure 1, the curve for mere ligand). The equilibrium constants for reactions (4) and (5) obtained in the final refinements are listed in table 1. The results correspond with the values of earlier studies carried out in aqueous 0.1 M NaCl [17]. For comparison with EDTA and DTPA [33], the protonation of BCA6 is also rewritten in the form given in table 2.

#### 3.2. Complexation with Cd(II), Hg(II) and Pb(II)

The analysis of the data was started by drawing curves of  $Z_{\text{H}}$  versus pH (figure 1). In all systems  $Z_{\text{H}}$  obtains the value  $-1$  with increasing pH, indicating coordination of BCA6 to metal in the form of  $\text{L}^{6-}$ . The formation of  $\text{ML}^{4-}$  is dominant in all systems.  $Z_{\text{H}}$  value lower than  $-1$  was obtained for Cd(II) and Pb(II) indicating the presence of hydroxo complex species,  $\text{M}(\text{OH})\text{L}^{5-}$ , for those metal ions. The competitive hydrolysis of Hg(II) overcomes the complex formation between Hg(II) and BCA6 in the pH area where hydroxo complex could be found. The formation of acidic species  $\text{MHL}^{3-}$ ,  $\text{MH}_2\text{L}^{2-}$ ,  $\text{MH}_3\text{L}^-$  and  $\text{MH}_4\text{L}$ , was found in all systems. In addition, the acidic species  $\text{MH}_5\text{L}^+$  was found for Hg(II), with complexation starting in very acidic solution. Aqueous complexation of the polydentate ligand can be characterized by formation of stable mononuclear 1 : 1 metal to ligand complex as the major species. For Pb(II) the complexation model was complemented by binuclear species  $\text{M}_2\text{L}^{2-}$ ,  $\text{M}_2\text{HL}^-$  and  $\text{M}_2\text{H}_2\text{L}$ , which gave significant improvement to the fit ( $\chi^2/s$ : from 81.37/2.61 to 23.16/1.25). The proposed formulas of the species, with the corresponding formation constants from equation (6) found in the equilibrium analysis of the different  $\text{H}^+ - \text{M}^{n+} - \text{HL}^{5-}$  systems, are shown in table 1. Comparison with the findings of earlier studies carried out with EDTA and DTPA [33] was facilitated by

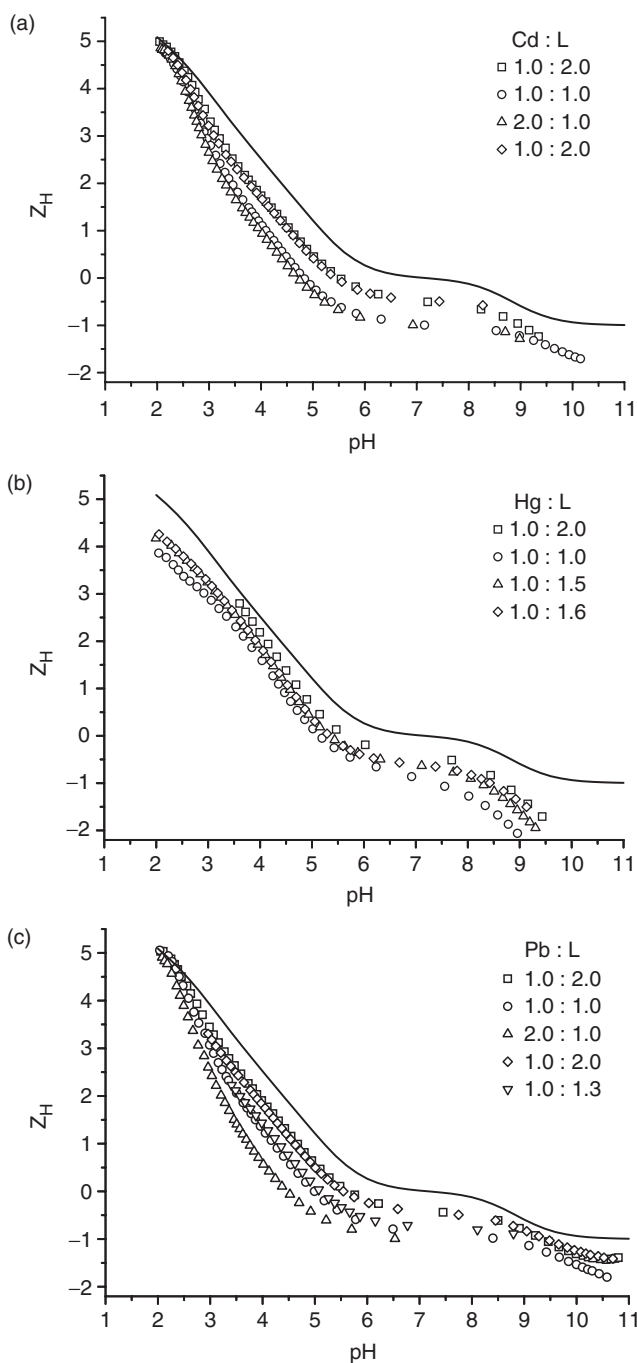


Figure 1. (a)  $Z_H$  vs. pH for complexation of Cd(II) with BCA6 (solid line:  $Z_H$  vs. pH for BCA6). (b)  $Z_H$  vs. pH for complexation of Hg(II) with BCA6 (solid line:  $Z_H$  vs. pH for BCA6). (c)  $Z_H$  vs. pH for complexation of Pb(II) with BCA6 (solid line:  $Z_H$  vs. pH for BCA6).

Table 1. The protonation and complexation of BCA6 with Cd(II), Hg(II) and Pb(II) in 0.1 M NaNO<sub>3</sub> aqueous solution at 25°C (the value of ionic product of water 13.75, the hydrolysis constants of the metal ions from ref. [31]).

	$pqr^{eqn.(6)}$	$\log(\beta_{pqr} \pm 3\sigma)$	Formula
H <sup>+</sup>	-101	-8.84 ± 0.03	L <sup>6-</sup>
	101	5.50 ± 0.05	H <sub>2</sub> L <sup>4-</sup>
	201	10.29 ± 0.04	H <sub>3</sub> L <sup>3-</sup>
	301	14.30 ± 0.05	H <sub>4</sub> L <sup>2-</sup>
	401	17.55 ± 0.05	H <sub>5</sub> L <sup>-</sup>
	501	20.19 ± 0.05	H <sub>6</sub> L
	601	21.79 ± 0.09	H <sub>7</sub> L <sup>+</sup>
$\chi^2/S$	49.79/0.86		
Points/titrations	349/4		
Cd(II)	-211	-7.37 ± 0.10	Cd(OH)L <sup>5-</sup>
	-111	2.25 ± 0.05	CdL <sup>4-</sup>
	011	7.33 ± 0.05	CdHL <sup>3-</sup>
	111	11.69 ± 0.04	CdH <sub>2</sub> L <sup>2-</sup>
	211	15.26 ± 0.03	CdH <sub>3</sub> L <sup>-</sup>
	311	17.74 ± 0.09	CdH <sub>4</sub> L
$\chi^2/S$	16.64/0.80		
Points/titrations	400/4		
Hydrolysis of Cd(II)	-110	-10.31	Cd(OH) <sup>+</sup>
	-404	-32.36	Cd <sub>4</sub> (OH) <sub>4</sub> <sup>4+</sup>
Hg(II)	-111	6.01 ± 0.06	HgL <sup>4-</sup>
	011	11.29 ± 0.09	HgHL <sup>3-</sup>
	111	15.79 ± 0.08	HgH <sub>2</sub> L <sup>2-</sup>
	211	19.95 ± 0.09	HgH <sub>3</sub> L <sup>-</sup>
	311	23.25 ± 0.08	HgH <sub>4</sub> L
	411	25.80 ± 0.08	HgH <sub>5</sub> L <sup>+</sup>
$\chi^2/S$	37.99/0.75		
Points/titrations	355/4		
Hydrolysis of Hg(II)	-110	-3.60	Hg(OH) <sup>+</sup>
	-210	-6.34	Hg(OH) <sub>2</sub>
	-330	-6.42	Hg <sub>3</sub> (OH) <sub>3</sub> <sup>3+</sup>
Pb(II)	-211	-7.90 ± 0.11	Pb(OH)L <sup>5-</sup>
	-111	1.98 ± 0.08	PbL <sup>4-</sup>
	011	7.22 ± 0.07	PbHL <sup>3-</sup>
	111	11.58 ± 0.08	PbH <sub>2</sub> L <sup>2-</sup>
	211	15.32 ± 0.07	PbH <sub>3</sub> L <sup>-</sup>
	311	18.07 ± 0.12	PbH <sub>4</sub> L
	-121	6.76 ± 0.16	Pb <sub>2</sub> L <sup>2-</sup>
	021	11.52 ± 0.13	Pb <sub>2</sub> HL <sup>-</sup>
	121	15.20 ± 0.21	Pb <sub>2</sub> H <sub>2</sub> L
$\chi^2/S$	23.16/1.25		
Points/titrations	343/5		
Hydrolysis of Pb(II)	-110	-7.86	Pb(OH) <sup>+</sup>

rewriting the complexation of BCA6 with Cd(II), Hg(II) and Pb(II) in the form given in table 2.

Figure 2 shows the percentage distribution of the metals among the different complex species as a function of pH in the millimolar concentration area ( $C_M = C_L = 1$  mM). It can be concluded that, in dilute solution, BCA6 is an effective chelating agent



Table 2. The protonation and complexation of BCA6 compared to corresponding values of EDTA and DTPA in  $\mu=0.1$  at 25°C (<sup>a</sup> in  $\mu=1.0$ ; <sup>b</sup> at 20°C).

Reaction	BCA6 (H <sub>6</sub> L)	EDTA (H <sub>4</sub> L) [33]	DTPA (H <sub>5</sub> L) [33]
H <sup>+</sup>			
L + H $\rightleftharpoons$ HL	8.84	9.52–10.37	9.90–10.79
HL + H $\rightleftharpoons$ H <sub>2</sub> L	5.50	6.13	8.40–8.60
H <sub>2</sub> L + H $\rightleftharpoons$ H <sub>3</sub> L	4.79	2.69	4.28
H <sub>3</sub> L + H $\rightleftharpoons$ H <sub>4</sub> L	4.01	2.00	2.70
H <sub>4</sub> L + H $\rightleftharpoons$ H <sub>5</sub> L	3.25	(1.5)	2.0
H <sub>5</sub> L + H $\rightleftharpoons$ H <sub>6</sub> L	2.64	(0.0)	(1.6)
H <sub>6</sub> L + H $\rightleftharpoons$ H <sub>7</sub> L	1.60		(0.7)
H <sub>7</sub> L + H $\rightleftharpoons$ H <sub>8</sub> L			(–0.1)
Cd(II)			
M(OH)L + H $\rightleftharpoons$ ML	9.62	(13.2) <sup>a</sup>	
M + L $\rightleftharpoons$ ML	11.09	16.5	19.0
ML + H $\rightleftharpoons$ MHL	5.08	2.9	4.17
MHL + H $\rightleftharpoons$ MH <sub>2</sub> L	4.36	(1.6) <sup>a</sup>	
MH <sub>2</sub> L + H $\rightleftharpoons$ MH <sub>3</sub> L	3.57		
MH <sub>3</sub> L + H $\rightleftharpoons$ MH <sub>4</sub> L	2.48		
ML + M $\rightleftharpoons$ M <sub>2</sub> L			2.3
Hg(II)			
M(OH)L + H $\rightleftharpoons$ ML		8.9	
M + L $\rightleftharpoons$ ML	14.85	21.5	26.4
ML + H $\rightleftharpoons$ MHL	5.28	3.2	4.24 <sup>b</sup>
MHL + H $\rightleftharpoons$ MH <sub>2</sub> L	4.50	2.1 <sup>a</sup>	
MH <sub>2</sub> L + H $\rightleftharpoons$ MH <sub>3</sub> L	4.16		
MH <sub>3</sub> L + H $\rightleftharpoons$ MH <sub>4</sub> L	3.30		
MH <sub>4</sub> L + H $\rightleftharpoons$ MH <sub>5</sub> L	2.55		
Pb(II)			
M(OH)L + H $\rightleftharpoons$ ML	9.88		
M + L $\rightleftharpoons$ ML	10.82	18.0	18.8
ML + H $\rightleftharpoons$ MHL	5.24	2.4 <sup>a</sup>	4.52 <sup>b</sup>
MHL + H $\rightleftharpoons$ MH <sub>2</sub> L	4.36	(1.7) <sup>a</sup>	
MH <sub>2</sub> L + H $\rightleftharpoons$ MH <sub>3</sub> L	3.74	(1.2) <sup>a</sup>	
MH <sub>3</sub> L + H $\rightleftharpoons$ MH <sub>4</sub> L	2.75		
ML + M $\rightleftharpoons$ M <sub>2</sub> L	4.78		3.41 <sup>b</sup>
MHL + M $\rightleftharpoons$ M <sub>2</sub> HL	4.30		
MH <sub>2</sub> L + M $\rightleftharpoons$ M <sub>2</sub> H <sub>2</sub> L	3.62		

(over 90% of metal is bound to the complexes) over the following pH ranges: Cd(II) and Pb(II) 4–12 and Hg(II) 1–7. Dilution of the solution to micromolar concentration increases the lower pH limit of the effective chelation region to more basic direction. The region is limited also from the basic direction slightly for Pb(II) and strongly for Hg(II). The binary hydrolysis of Hg(II) is so dominant at micromolar concentrations that complexation is limited to very narrow pH area.

In industrial applications, conditional stability constants are often used for estimation of complexation efficiency. The conditional stability constant,  $\log K'_{ML}$  for the major complex species  $ML^{n-x}$  is given by equation (8):

$$K'_{ML} = \frac{\alpha_{ML}}{\alpha_M \cdot \alpha_L} \cdot K_{ML} \quad (8)$$

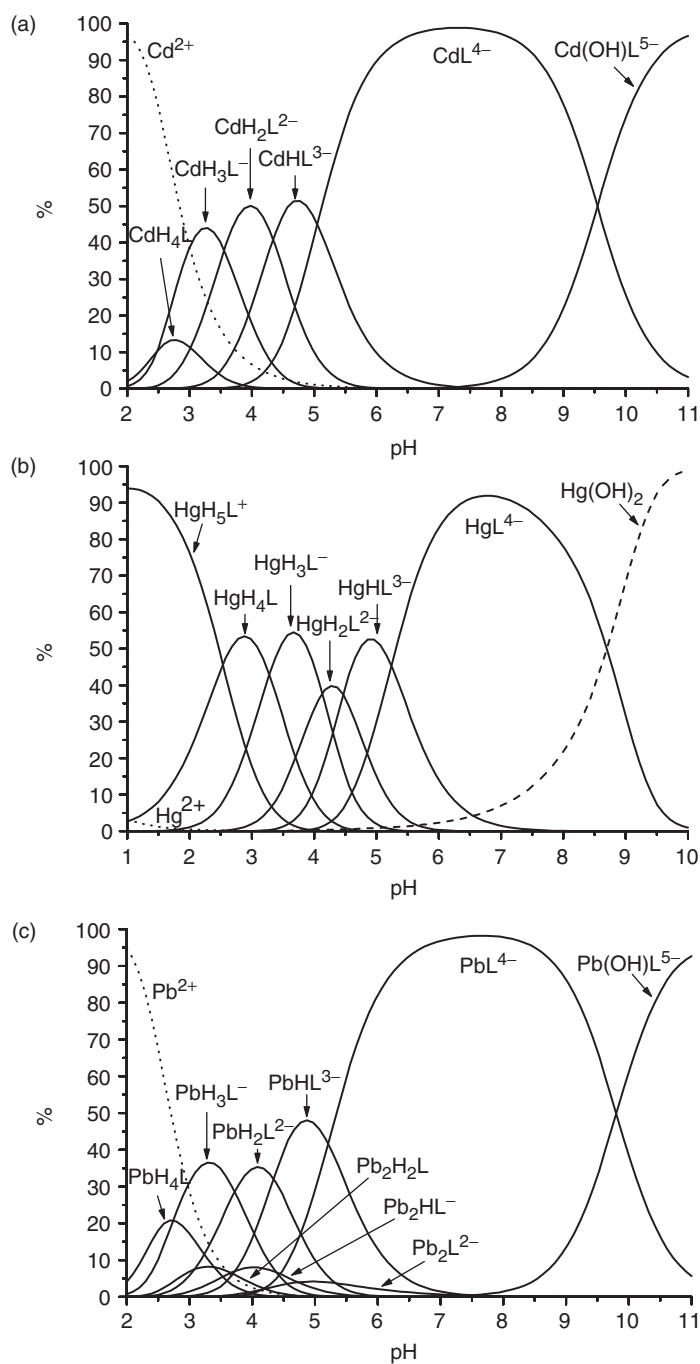


Figure 2. (a) Percentage distribution of the different Cd(II) complexes of BCA6 vs. pH ( $C_M = C_L = 1 \text{ mM}$ ). (b) Percentage distribution of the different Hg(II) complexes of BCA6 vs. pH ( $C_M = C_L = 1 \text{ mM}$ ). (c) Percentage distribution of the different Pb(II) complexes of BCA6 vs. pH ( $C_M = C_L = 1 \text{ mM}$ ).

where the side reaction coefficients  $\alpha_M$ ,  $\alpha_L$  and  $\alpha_{ML}$  are defined as in equations (9), (10) and (11) and  $K_{ML}$  as in equation (12):

$$\alpha_M = \frac{\Sigma(H^+)_p (M^{n+})_q}{[M^{n+}]} \quad (9)$$

$$\alpha_L = \frac{\Sigma(H^+)_p (L^{x-})}{[L^{x-}]} \quad (10)$$

$$\alpha_{ML} = \frac{\Sigma(H^+)_p (M^{n+})(L^{x-})_r}{[ML^{n-x}]} \quad (11)$$

$$K_{ML} = K(M^{n+} + L^{x-} \rightleftharpoons ML^{n-x}) \quad (12)$$

The values of conditional stability constants of complexes of BCA6 with Cd(II), Hg(II) and Pb(II) ions vary as a function of pH as shown in figure 3. They were calculated by utilizing protonation and equilibrium constants determined in this study and the binary hydrolysis constant of Cd(II), Hg(II) and Pb(II) ions [31]. The values  $\log K'_{ML} \geq 6$  are often considered as a criterion for efficient complexation. According to this assumption, the approximate pH ranges suitable for use of BCA6 as efficient chelating agents for Cd(II), Hg(II) and Pb(II), are the same as estimated from the percentage distribution curves.

Besides the statistical parameters provided by SUPERQUAD, back calculations of experimental titration curves ( $M:L = 1:1$ ), made using the HYSS2006 –program [34], are added to ensure the validation of the equilibrium model (figure 4). They correspond well with experiments.

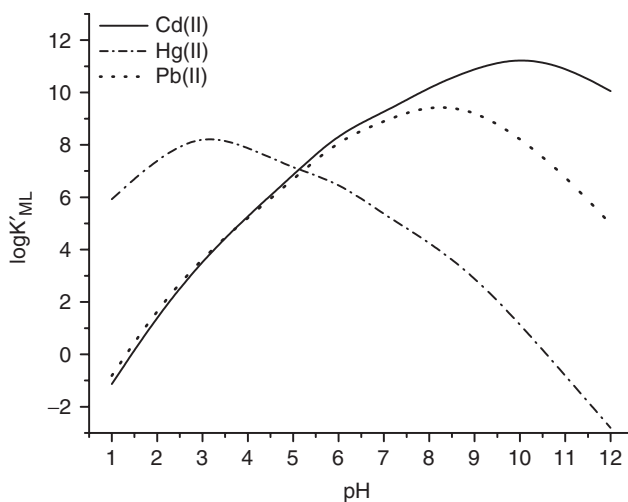


Figure 3. Conditional stability constants for ML complexes of BCA6 with Cd(II), Hg(II) and Pb(II) ions as a function of pH.

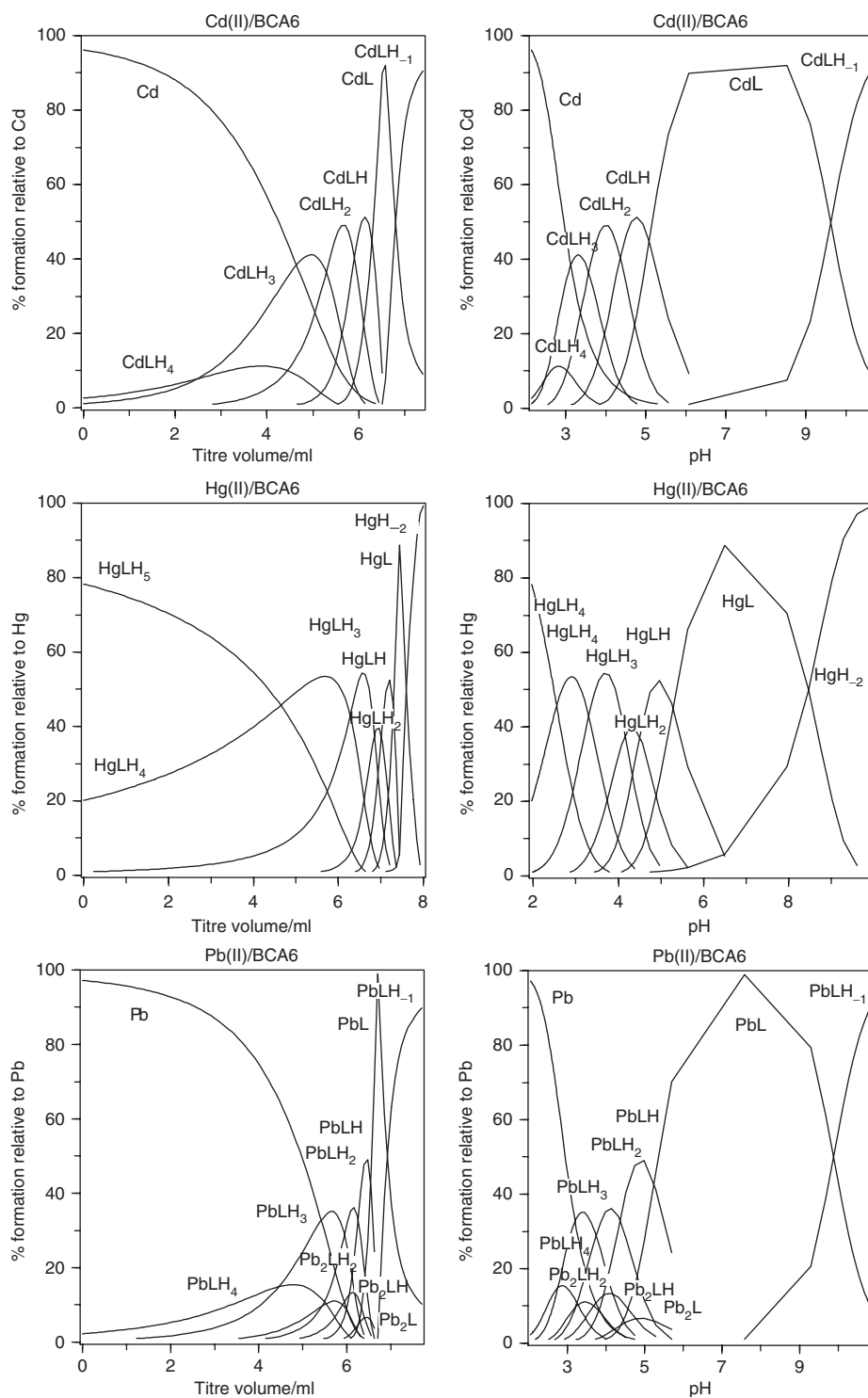


Figure 4. Back calculations (HYSS2006) of experimental titration curves (M : L = 1 : 1).

### 3.3. Conclusion

The stabilities of the Cd(II), Hg(II) and Pb(II) chelates of BCA6 are lower than those of EDTA and DTPA. On the other hand, BCA6 has shown greater biodegradability than EDTA and DTPA in ISO9439 and OECD 301B and 301F tests [23–25]. The photodegradability of BCA6 has also been reported. BCA6 is photodegraded by stepwise cleavage of malic acid yielding malic acid and diethanolamine, the degradation products photodegrade further to hydroxyacetic acid and malonic acid. [26] According to the start and end analyses of the biodegradation test liquors, the biodegradation of BCA6 proceeds in a similar manner. [35] Additionally, BCA6 has proved its superiority compared to EDTA in terms of degradability by Fenton's process [27]. Due to its lower complexing ability and higher degradability, its capability to remobilize heavy metal ions from sediments is lower than that of EDTA and DTPA. These aspects make BCA6 less harmful to nature than EDTA and DTPA. The strength of complexation of Mn(II) and Fe(III) ions is also lower than that of EDTA and DTPA, but appear to be high enough for pulp bleaching applications. More importantly, the Mn-BCA6 complexes appear to be inert in hydrogen peroxide and peracetic acid solution, whereas Mn-EDTA and Mn-DTPA complexes are capable of decomposing the peroxy compounds. This would accomplish the recycling of process waters and saving of process steps in pulp bleaching applications [17, 22]. In addition, its substantially lower nitrogen content compared to EDTA and DTPA is an advantage. On the other hand, the complexation efficiency of BCA6 could be strong enough to be utilized as alternative ligand in applications where Cd(II), Hg(II) or Pb(II) binding is essential.

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