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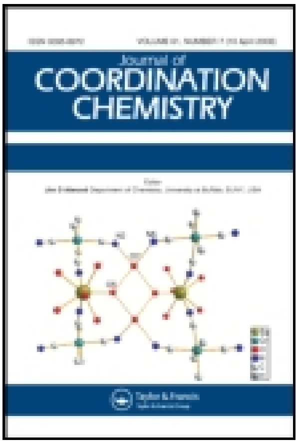

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Complexation of iminodisuccinic acid (IDS) and 3-hydroxy-2,2′-iminodisuccinic acid (HIDS) with Cd^{2+}, Hg^{2+}, and Pb^{2+} in aqueous solution

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Published online: 10 Mar 2011.

To cite this article: Helena Hyvönen, Laura Svärd & Reijo Aksela (2011) Complexation of iminodisuccinic acid (IDS) and 3-hydroxy-2,2′-iminodisuccinic acid (HIDS) with Cd^{2+}, Hg^{2+}, and Pb^{2+} in aqueous solution, Journal of Coordination Chemistry, 64:6, 1091-1103, DOI: 10.1080/00958972.2011.562895

To link to this article: http://dx.doi.org/10.1080/00958972.2011.562895

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Journal of Coordination Chemistry
Vol. 64, No. 6, 20 March 2011, 1091–1103

Complexation of iminodisuccinic acid (IDS) and 3-hydroxy-2,2′-iminodisuccinic acid (HIDS) with Cd^{2+}, Hg^{2+}, and Pb^{2+} in aqueous solution

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(*Received 12 November 2010; in final form 24 January 2011*)

In a search for environmentally friendly metal-chelating ligands for industrial applications, the protonation and complex formation equilibria of iminodisuccinic acid (IDS) and 3-hydroxy-2,2′-iminodisuccinic acid (HIDS) with Cd^{2+}, Hg^{2+}, and Pb^{2+} in aqueous $0.1\,mol\,L^{-1}$ $NaNO_3$ solution were studied at 25°C by potentiometric titration. Models for complexation and stability constants of the different complexes were determined for each metal ion using the computer program SUPERQUAD. In all cases, complex formation was dominated by stable ML^{2-} complexes.

Keywords: Iminodisuccinic acid; 3-Hydroxy-2,2′-iminodisuccinic acid; Stability constants; 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 analytic chemistry and industry. Both of these ligands have been used for decades as chelating agents for a variety of large-scale industrial applications. However, the persistence of EDTA and DTPA and their metal complexes in nature may cause environmental harm. During the past few years, the nonbiodegradability of these ligands and their consequent accumulation in the environment have been a source of considerable concern [1–6]. Both are virtually nonbiodegradable in waste water treatment plant conditions [7–9], are difficult to remove from bleaching effluents, and may be capable of remobilizing toxic heavy metal ions from sediments [10, 11]. They form strong complexes with iron and may increase eutrophication through the liberation of phosphates. EDTA is found in drinking water and is present in almost all anthropogenically influenced surface waters in industrialized countries. Mechanisms describing the effect of aminocarboxylate chelating agents on the aquatic environment have also been proposed [2, 3].

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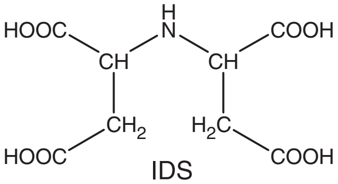
Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2011.562895

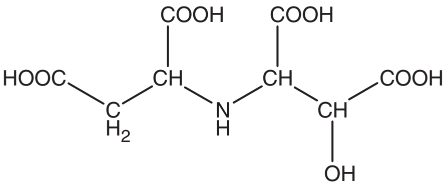
EDTA is on the EU priority list of substances for risk assessment. In accordance with the conclusions of the EU Risk Assessment Report [12], there is a need to limit the risks that EDTA continues to pose to the environment. This conclusion is based on high levels of EDTA released into the environment through its use in industrial detergents, the pulp and paper industry, circuit board production, and during the recovery of EDTA-containing wastes. The characterization of these release scenarios shows that EDTA poses a risk to aquatic organisms [12]. Since chelating agents are a plentiful source of nitrogen, for example, in the effluents from pulp mills, the nitrogen content of ligands should be as low as possible. The replacement of EDTA and DTPA by more environmentally friendly chelating agents wherever possible would be highly desirable.

Iminodisuccinic acid (IDS) and 3-hydroxy-2,2′-iminodisuccinic acid (HIDS) are candidates for alternative chelating agents possessing complex-forming properties comparable to those of EDTA and DTPA, but with better biodegradability and lower nitrogen content. IDS has been tested in a pulp bleaching application where both EDTA and DTPA are commonly used for the removal of transition metal ions from pulp [13] and in a plant growth application [14]. In addition, complexation studies on both of these potential new chelating agents have been carried out with several metal ions [15–17].

When planning the use of IDS and HIDS for possible applications, it is important to know their complexation with toxic heavy metal ions compared to conventional chelating agents. The complexation of IDS and HIDS with several metal ions has been studied earlier. Due to concern about their possible ability to mobilize heavy metals, to deepen our understanding of their complexation behavior and to obtain information relevant to potential applications of these biodegradable chelators, we extended our complexation studies on IDS and HIDS and report here on their aqueous complexation with Cd^{2+}, Hg^{2+}, and Pb^{2+}.



IDS



HIDS

2. Experimental

2.1. *Reagents: ligand, stock solutions of metal ions, and titration solutions*

IDS was produced by Kemira and HIDS by Nippon Shokubai as sodium salts. Both products were water solutions, IDS 40 wt% and HIDS 45.3 wt%. HIDS contained 2.0 wt% disodiumtartarate and 1.8 wt% disodiummaleate as by-products, which were taken into account in the calculation as explained in data treatment. Aqueous $Cd(NO_3)_2$ and $Hg(NO_3)_2$ solutions were prepared by dissolving $Cd(NO_3)_2$ in distilled water and $Hg(NO_3)_2$ in aqueous nitric acid. $Pb(NO_3)_2$ solution was prepared from a Titrisol ampoule (Merck). The metal salts were p.a. grade from Merck.

The metal content of the stock solutions was standardized by EDTA titration. The acid content of the metal solutions were determined by titration with 0.1 mol L^{-1} NaOH solution after liberation of H^+ by cation exchange. Aqueous 0.1 mol L^{-1} NaOH was prepared from Titrisol ampoules (Merck) and 0.1 mol L^{-1} HNO_3 from Convol ampoules (BDH). The water used in the dilutions and titration solutions was purified with Milli-RO and Milli-Q water purification systems (Millipore).

2.2. *Potentiometric measurements*

Protonation and complex formation equilibria were studied in aqueous 0.1 mol L^{-1} $NaNO_3$ 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 5.02. The cell arrangement for the measurement of the hydrogen ion concentration $[H^+]$ was as follows:

$$-\mathrm{RE}\,|\,\text{equilibrium solution}\,|\,\mathrm{GE}+, \tag{1}$$

where GE denotes a glass electrode (Schott N2680) and RE is Hg, $Hg_2Cl_2\,||\,0.01$ mol L^{-1} NaCl, 0.09 mol L^{-1} $NaNO_3$. Equation (2) is valid assuming that the activity coefficients are constant.

$$E = E_0 + 59.157\ \log[\mathrm{H}^+] + j_\mathrm{H}[\mathrm{H}^+] + j_\mathrm{OH}[\mathrm{OH}^-]. \tag{2}$$

The cell parameter E_0 and the liquid junction coefficient j_H, valid in acidic solutions, were determined for each titration by adding a known amount of HNO_3 to the background electrolyte. The value of the liquid junction coefficient j_{OH}, valid in basic solutions, was determined periodically. Only stable EMF readings were used in the calculations.

During measurements of the metal complex equilibria, aqueous 0.1 mol L^{-1} NaOH or 0.1 mol L^{-1} HNO_3 was added to the solution. The ratio of the total concentrations of metal (C_M) to ligand (C_L) was held constant. The initial concentrations varied within the limits $0.0004\ \mathrm{mol\,L^{-1}} \le C_M \le 0.0032$ and $0.0004\ \mathrm{mol\,L^{-1}} \le C_L \le 0.0039\ \mathrm{mol\,L^{-1}}$, covering metal-to-ligand ratios from 2 : 1 to 1 : 5 for IDS and from 2 : 1 to 1 : 4 for HIDS. Five to seven independent titrations were carried out for each system. The number of data points used in the calculation of the stability constants varied from 116 to 397 in the pH ranges 3.0–10.5 for Cd^{2+}, 3.5–5.7 for Hg^{2+}, and 2.2–10.6 for Pb^{2+} in the case of IDS and 2.6–9.8 for Cd^{2+}, 3.1–7.7 for Hg^{2+}, and 2.0–9.4 for Pb^{2+} in the case of HIDS. In some titrations, the pH range was limited by the appearance of a precipitate. The reproducibility and reversibility of the equilibria were tested by performing forward (increasing pH) and backward (decreasing pH) titrations.

2.3. *Data treatment*

Protonation and deprotonation of the ligand were controlled by the addition of HNO_3 or NaOH. Curves of Z_H *versus* pH were plotted to visualize the experimental data sets. Z_H describes the average number of H^+ ions added or liberated per mole of ligand and is given by the relation

$$Z_\mathrm{H} = (C_\mathrm{H} - [\mathrm{H}^+] + k_\mathrm{w}[\mathrm{H}^+]^{-1})/C_\mathrm{L}, \tag{3}$$

where C_H denotes the total concentration of protons calculated over the zero level HL^{3-}, H_2O, and M^{2+}.

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

$$HL^{3-} \rightleftharpoons L^{4-} + H^+; \quad \beta_{-101}, \tag{4}$$

$$pH^+ + HL^{3-} \rightleftharpoons H_{p+1}L^{p-3}, \quad p = 1 - 4; \quad \beta_{p01}. \tag{5}$$

Metal complex formation can be characterized by the general three-component equilibrium

$$pH^+ + qM^{2+} + r(HL^{3-}) \rightleftharpoons (H^+)_p(M^{2+})q(HL^{3-})_r; \quad \beta_{pqr}. \tag{6}$$

The hydrolysis of metal ions can be written as

$$pH^+ + qM^{2+} \rightleftharpoons (H^+)_p(M^{2+})_q; \quad \beta_{pq0}. \tag{7}$$

The protonation constants of the ligands and the hydrolysis constants of the metal ions [18] were considered as known parameters in the evaluation of the three-component system (6). In evaluation of the protonation constants and the stability constants of HIDS, the protonation of tartaric acid and maleic acid and the complex formation of tartaric acid present as impurities in starting material were taken into account in the calculation as known parameters in the refinements (values of these constants from ref. [17]). Mathematical analysis of the systems involves a search for complex models (*pqr*-triplets) and equilibrium constants for the complexes that best describe the experimental data. The calculations were carried out with the computer program SUPERQUAD [19]. The sample standard deviation S and the χ^2 statistics used as criteria in the selection of the complex models were those given by the program. As a means to improve the confidence level, the error limits for log β values determined in this study are reported as three times the standard deviation given by the program.

3. Results and discussion

3.1. *Protolytic properties of IDS and HIDS*

The neutralization titrations for both ligands show that the stepwise deprotonation of H_5L^+ to HL^{3-} occurs in the pH range from acidic to neutral (Z_H from 4 to 0, the carboxylic acid groups). HL^{3-} is the major species from pH 6 to pH 9 for IDS and from pH 6 to pH 8 for HIDS when $Z_H = 0$. The negative Z_H values obtained in the pH range from neutral to 11 show that in alkaline solution one proton (from the amino nitrogen, HL^{3-} to L^{4-}) can leave the ligands (figures 1 and 2, the curves for ligands alone). The equilibrium constants for reactions (4) and (5) obtained in the final refinements are listed in table 1. The results correspond with those of earlier studies on protonation of IDS [15] and HIDS [16] in 0.1 mol L^{-1} NaCl. For comparison with EDTA and DTPA [17], the protonation of IDS and HIDS is rewritten in the form given in table 2. The titrations did not reach pH range basic enough for the deprotonation of the hydroxyl group in HIDS. The hydroxyl group may, however, decrease the basicity of nitrogen in

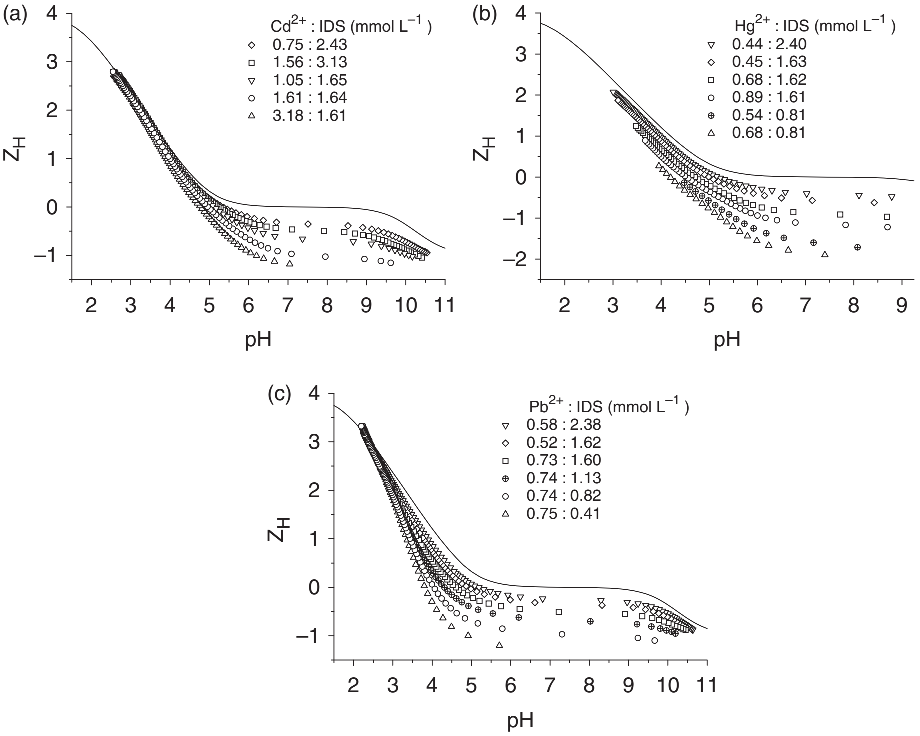


Figure 1. Z_H *vs*. pH for complexation of (a) Cd^{2+}, (b) Hg^{2+}, and (c) Pb^{2+} with IDS (Z_H *vs*. pH for IDS = solid line).

HIDS relative to the basicity of nitrogen in IDS ($\log K$ value for IDS 10.25 and for HIDS 9.54) in analogy with the relationship between, for example, nitrilotriacetic acid (NTA, $\log K$ 9.46–9.84) and triethanolamine (TEA, $\log K$ 7.85). When the hydroxyl group is located near the carboxylic acid groups, the protonation constants decrease to some extent (table 2) in analogy with, for example, the $\log K$ values of the carboxylic acid groups of succinic acid (3.99 and 5.24), malic acid (3.24 and 4.68), and tartaric acid (2.82 and 3.97) [17].

3.2. *Complexation with Cd^{2+}, Hg^{2+}, and Pb^{2+}*

Analysis of the data was initiated by plotting Z_H *versus* pH (figures 1 and 2). In all systems, Z_H reaches a value of -1 with increasing pH, indicating coordination of IDS and HIDS to metal in the form of L^{4-}. In all systems, ML^{2-} is the dominant species formed. Z_H values below -1 were obtained in the basic pH range for Cd^{2+} and Pb^{2+}, indicating the presence of hydroxo complex species, $M(OH)L^{3-}$. For Hg^{2+} a hydroxo species was not found because of the competitive hydrolysis of the metal ion, which overcomes the complexation in the basic pH range. The formation of the acidic species MHL^{-} and MH_2L was found for all metal ions. As expected, the aqueous complexation of the polydentate ligands can be characterized in terms of the formation of a stable

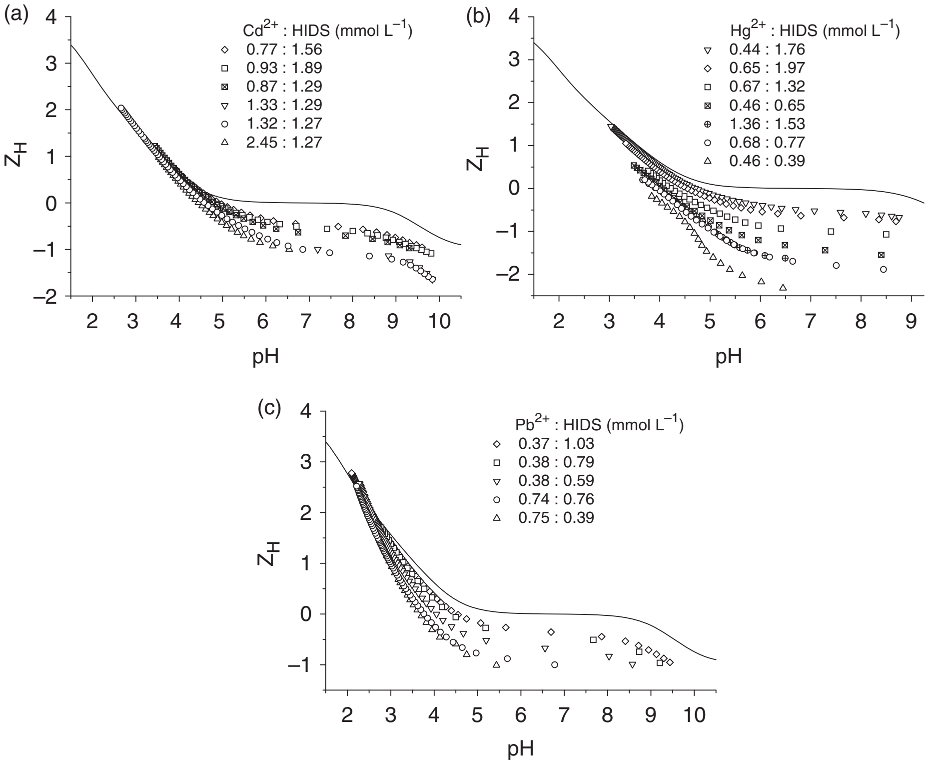


Figure 2. Z_H *vs.* pH for complexation of (a) Cd^{2+}, (b) Hg^{2+}, and (c) Pb^{2+} with HIDS (Z_H *vs.* pH for HIDS = solid line).

mononuclear 1 : 1 metal-to-ligand complex as the major species. For Cd^{2+}, the complexation model was complemented by the binuclear species M_2L and bis complex species ML_2^{6-}. Table 1 shows the proposed formulae of the species, with corresponding formation constants from equation (6) found in the equilibrium analysis of the different $H^+ - M^{2+} - HL^{3-}$ systems. Comparison with the findings of earlier studies carried out with EDTA and DTPA [17] was facilitated by expressing complexation of IDS and HIDS with Cd^{2+}, Hg^{2+}, and Pb^{2+} in the form given in table 2. For all metal ions studied here the stability of the major species ML^{2-} formed with IDS is 0.5–1.1 log units higher than the corresponding complex formed with HIDS. This might be due to decreased basicity of the nitrogen in HIDS compared to that in IDS.

The dominance of ML^{2-} complexes over a wide pH range in solutions where the metal-to-ligand ratio is 1 : 1 is illustrated in figures 3 and 4. The percentage distribution of the metals among the different complex species is shown as a function of pH in the millimolar concentration range ($C_M = C_L = 1\,\text{mmol}\,L^{-1}$). It can be concluded that, in dilute solution, IDS and HIDS are effective chelating agents (about 100% of metal is bound to the complexes) for Cd^{2+} and Pb^{2+} over the following pH ranges: Cd^{2+} 8–12 for both ligands and Pb^{2+} 5–11 for IDS and 5–12 for HIDS. For Hg^{2+} a chelation efficiency of 100% is not reached with either ligand. Dilution of the solution to the micromolar concentration range decreases the pH region of effective chelation to 8–10

Table 1. Protonation and complexation of IDS and HIDS with Cd^{2+}, Hg^{2+}, and Pb^{2+} in 0.1 mol L^{-1} $NaNO_3$ aqueous solution at 25°C.

	pqr[a]	IDS (H_4L) log ($\beta_{pqr} \pm 3\sigma$)	HIDS (H_4L) log ($\beta_{pqr} \pm 3\sigma$)	Proposed formula
H^+				
	−101	-10.25 ± 0.01	-9.54 ± 0.01	L^{4-}
	101	4.62 ± 0.02	4.06 ± 0.01	H_2L^{2-}
	201	8.35 ± 0.01	7.11 ± 0.01	H_3L^-
	301	11.25 ± 0.02	9.20 ± 0.02	H_4L
	401	13.27 ± 0.03	10.81 ± 0.02	H_5L^+
χ^2/S		19.72/1.86	9.81/0.65	
Points/titrations		469/5	441/5	
Cd^{2+}				
	−211	-12.49 ± 0.10	-11.58 ± 0.10	$Cd(OH)L^{3-}$
	−111	2.22 ± 0.04	-1.96 ± 0.08	CdL^{2-}
	011	3.12 ± 0.04	2.89 ± 0.12	$CdHL^-$
	111	7.15 ± 0.09	6.76 ± 0.19	CdH_2L
	−212	-9.17 ± 0.14	-7.92 ± 0.33	CdL_2^{6-}
	−121	0.60 ± 0.12	0.76 ± 0.31	Cd_2L
χ^2/S		23.01/1.32	6.09/1.64	
Points/titrations		278/5	176/6	
Hg^{2+}				
	−111	2.49 ± 0.12	2.16 ± 0.06	HgL^{4-}
	011	6.86 ± 0.08	6.55 ± 0.06	$HgHL^-$
	111	10.39 ± 0.13	9.74 ± 0.09	HgH_2L
χ^2/S		16.00/1.05	9.39/1.13	
Points/titrations		116/6	184/7	
Pb^{2+}				
	−211	-9.74 ± 0.11	-7.98 ± 0.08	$Pb(OH)L^{3-}$
	−111	1.11 ± 0.04	0.69 ± 0.05	PbL^{2-}
	011	5.06 ± 0.05	4.78 ± 0.03	$PbHL^-$
	111	8.63 ± 0.04	7.61 ± 0.06	PbH_2L
χ^2/S		13.78/1.22	36.34/0.71	
Points/titrations		397/6	280/5	

[a] Equation (6).

for Pb^{2+} with HIDS. For the Pb^{2+}–IDS system and for Cd^{2+} with both ligands the chelation efficiency decreases to less than 100%. In the case of Hg^{2+}, the competitive hydrolysis of the metal ion fully overcomes the complexation in the micromolar concentration range.

In industrial applications, complexation efficiency is commonly estimated with conditional stability constants. The conditional stability constant, $\log K'_{\mathrm{ML}}$, for the major complex species ML^{n-x} is given by equation (8)

$$K'_{\mathrm{ML}} = \frac{\alpha_{\mathrm{ML}}}{\alpha_{\mathrm{M}} \cdot \alpha_{\mathrm{L}}} \cdot K_{\mathrm{ML}}, \tag{8}$$

where the side-reaction coefficients α_{M}, α_{L}, and α_{ML} are defined as in equations (9–11), and K_{ML} as in equation (12)

$$\alpha_{\mathrm{M}} = \frac{\Sigma(\mathrm{H}^+)_p(\mathrm{M}^{n+})_q}{[\mathrm{M}^{n+}]}, \tag{9}$$

Table 2. Protonation and complexation of IDS and HIDS with Cd^{2+}, Hg^{2+}, and Pb^{2+} compared to corresponding values of EDTA and DTPA in $\mu = 0.1$ at 25°C.

Reaction ($x = 4$ for IDS, HIDS, and EDTA, $x = 5$ for DTPA)	IDS (H_4L)	HIDS (H_4L)	EDTA (H_4L) [17]	DTPA (H_5L) [17]
H^+				
$L^{x-} + H^+ \rightleftharpoons HL^{1-x}$	10.25	9.54	9.52–10.37	9.90–10.79
$HL^{1-x} + H^+ \rightleftharpoons H_2L^{2-x}$	4.62	4.06	6.13	8.40–8.60
$H_2L^{2-x} + H^+ \rightleftharpoons H_3L^{3-x}$	3.73	3.05	2.69	4.28
$H_3L^{3-x} + H^+ \rightleftharpoons H_4L^{4-x}$	2.90	2.09	2.00	2.70
$H_4L^{4-x} + H^+ \rightleftharpoons H_5L^{5-x}$	2.02	1.61	(1.5)	2.0
$H_5L^{5-x} + H^+ \rightleftharpoons H_6L^{6-x}$	–	–	(0.0)	(1.6)
$H_6L^{6-x} + H^+ \rightleftharpoons H_7L^{7-x}$	–	–	–	(0.7)
$H_7L^{7-x} + H^+ \rightleftharpoons H_8L^{8-x}$	–	–	–	(−0.1)
Cd^{2+}				
$Cd(OH)L^{1-x} + H^+ \rightleftharpoons CdL^{2-x}$	10.27	9.62	(13.2)[a]	–
$Cd^{2+} + L^{x-} \rightleftharpoons CdL^{2-x}$	8.03	7.58	16.5	19.0
$CdL^{2-x} + H^+ \rightleftharpoons CdHL^{3-x}$	5.34	4.85	2.9	4.17
$CdHL^{3-x} + H^+ \rightleftharpoons CdH_2L^{4-x}$	4.03	3.87	(1.6)[a]	–
$CdL^{2-x} + L^{x-} \rightleftharpoons CdL_2^{2-2x}$	3.30	3.58	–	–
$CdL^{2-x} + Cd^{2+} \rightleftharpoons Cd_2L^{4-x}$	2.82	2.72	–	2.3
Hg^{2+}				
$Hg(OH)L^{1-x} + H^+ \rightleftharpoons HgL^{2-x}$	–	–	8.9	–
$Hg^{2+} + L^{x-} \rightleftharpoons HgL^{2-x}$	12.74	11.70	21.5	26.4
$HgL^{2-x} + H^+ \rightleftharpoons HgHL^{3-x}$	4.37	4.39	3.2	4.24[b]
$HgHL^{3-x} + H^+ \rightleftharpoons HgH_2L^{4-x}$	3.53	3.19	2.1[a]	–
Pb^{2+}				
$Pb(OH)L^{1-x} + H^+ \rightleftharpoons PbL^{2-x}$	10.85	8.67	–	–
$Pb^{2+} + L^{x-} \rightleftharpoons PbL^{2-x}$	11.36	10.23	18.0	18.8
$PbL^{2-x} + H^+ \rightleftharpoons PbHL^{3-x}$	3.95	4.09	2.4[a]	4.52[b]
$PbHL^{3-x} + H^+ \rightleftharpoons PbH_2L^{4-x}$	3.57	2.83	(1.7)[a]	–
$PbH_2L^{4-x} + H^+ \rightleftharpoons PbH_3L^{5-x}$	–	–	(1.2)[a]	–
$PbL^{2-x} + Pb^{2+} \rightleftharpoons Pb_2L^{4-x}$	–	–	–	3.41[b]

[a] In $\mu = 1.0$.
[b] At 20°C.

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

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

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

Equations (9)–(12) give, for example, for Pb^{2+} ($=M^{2+}$)/IDS ($=L^{4-}$) system as follows:

$$\begin{aligned}\alpha_M &= ([M^{2+}] + [M(OH)^+] + [M(OH)_2] + [M(OH)_3^-])/[M^{2+}] \\ &= 1 + 10^{-7.86}[H]^{-1} + 10^{-17.27}[H]^{-2} + 10^{-28.06}[H]^{-3},\end{aligned} \tag{13}$$

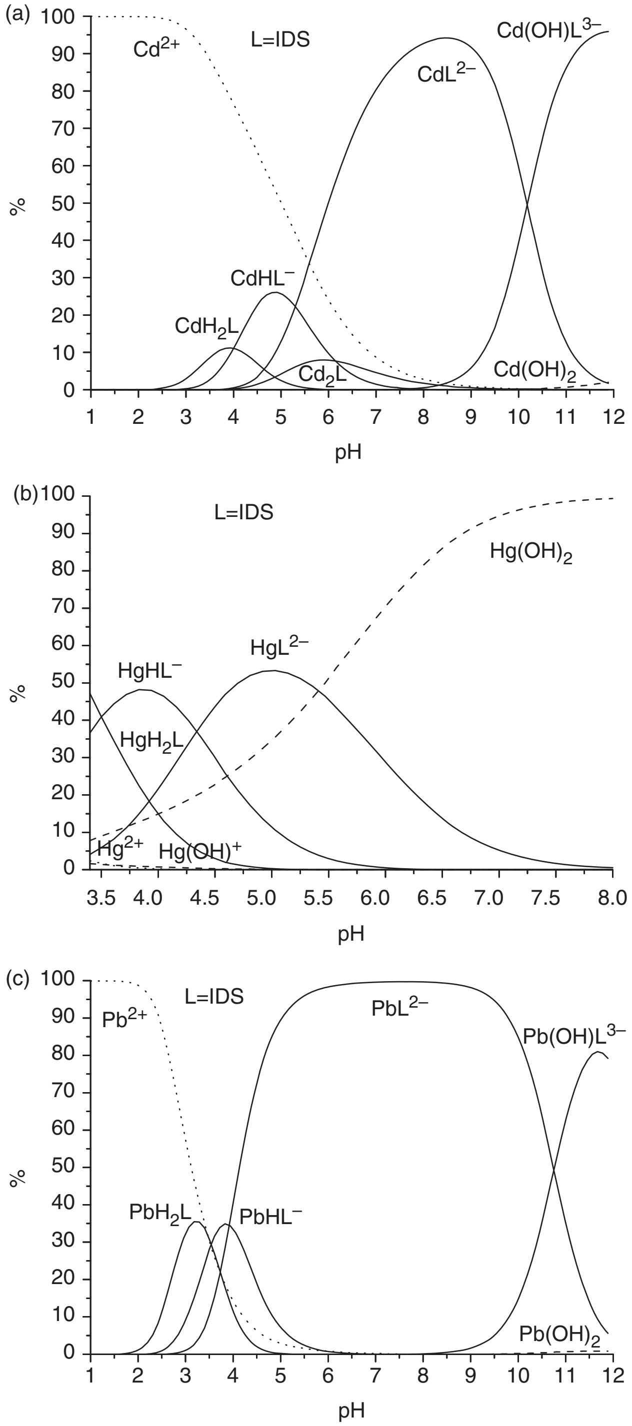


Figure 3. Percentage distribution of the different (a) Cd^{2+}, (b) Hg^{2+}, and (c) Pb^{2+} complexes of IDS *vs.* pH ($C_M = C_L = 1\,mmol\,L^{-1}$).

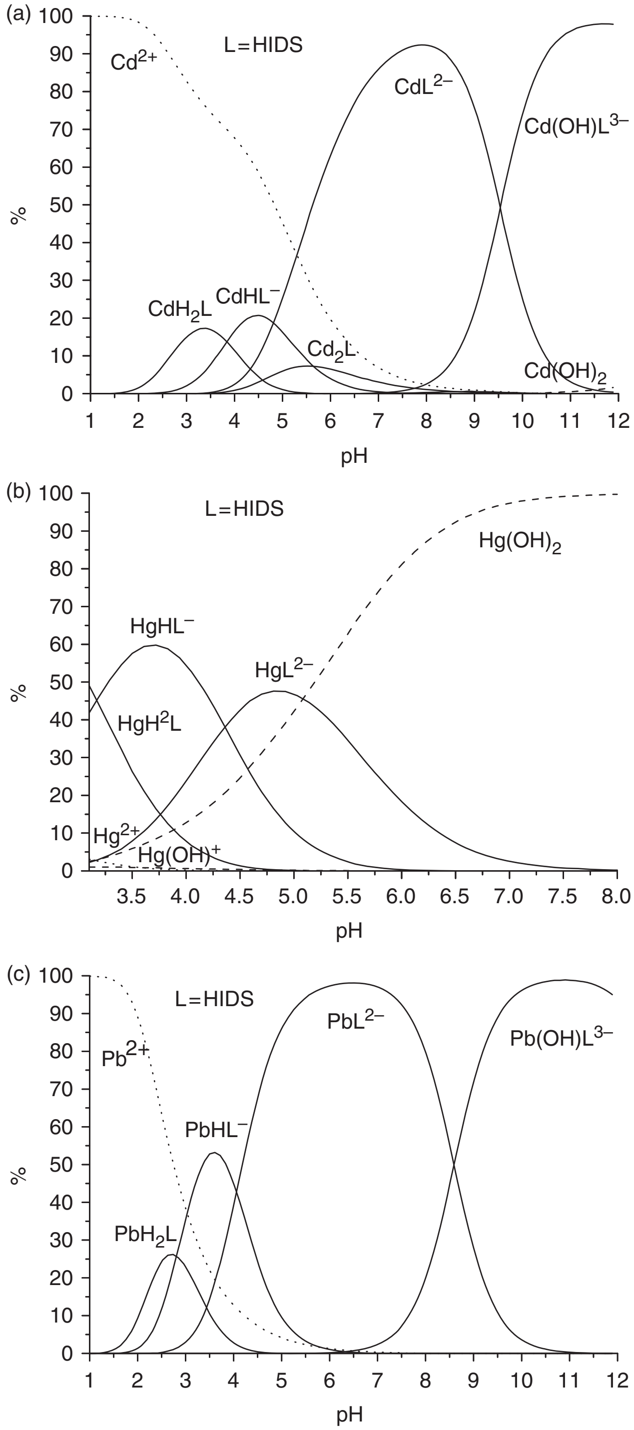


Figure 4. Percentage distribution of the different (a) Cd^{2+}, (b) Hg^{2+}, and (c) Pb^{2+} complexes of HIDS *vs.* pH ($C_M = C_L = 1\,\mathrm{mmol\,L^{-1}}$).

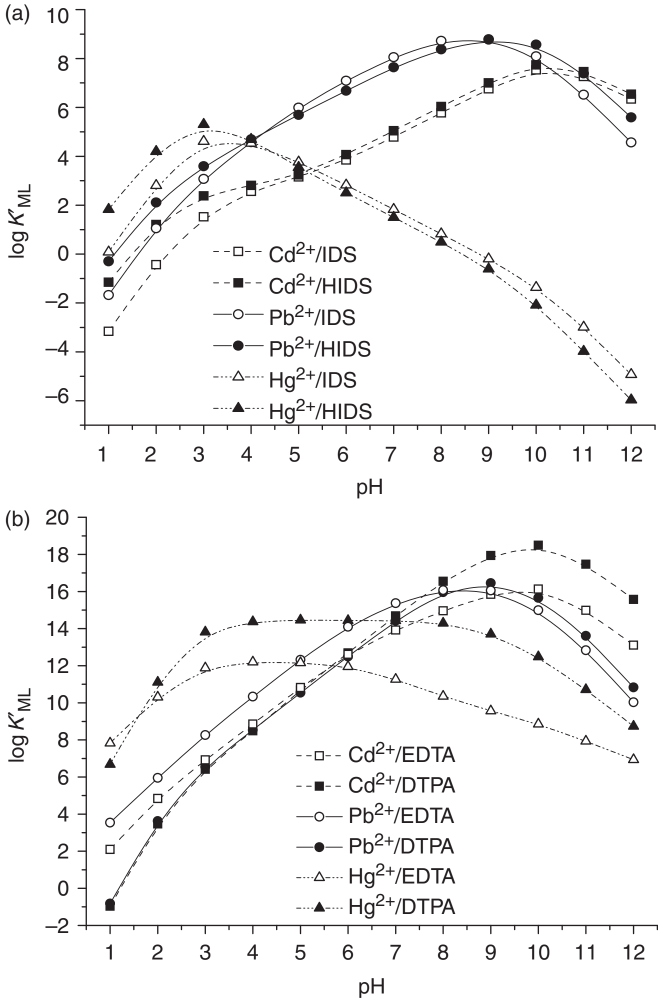


Figure 5. Conditional stability constants for ML complexes of (a) IDS and HIDS and (b) EDTA and DTPA with Cd^{2+}, Pb^{2+}, and Hg^{2+} ions as a function of pH.

$$\begin{aligned}\alpha_L &= ([L^{4-}]+[HL^{3-}]+[H_2L^{2-}]+[H_3L^-]+[H_4L]+[H_5L^+])/[L^{4-}]\\ &= 1+10^{10.25}[H]+10^{14.87}[H]^2+10^{18.60}[H]^3+10^{21.50}[H]^4+10^{23.52}[H]^5, \end{aligned}\tag{14}$$

$$\begin{aligned}\alpha_{ML} &= ([ML^{2-}]+[MHL^-]+[MH_2L]+[M(OH)L^{3-}])/[ML^{2-}]\\ &= 1+10^{3.95}[H]+10^{7.52}[H]^2+10^{-10.85}[H]^{-1}, \end{aligned}\tag{15}$$

K_{ML} for reaction $M^{2+}+L^{4-} \rightleftharpoons ML^{2-}(Pb^{2+}+IDS^{4-} \rightleftharpoons PbIDS^{2-})$ is 11.36 (table 2). (16)

The values of the conditional stability constants of complexes of IDS and HIDS with Cd^{2+}, Hg^{2+}, and Pb^{2+}, as calculated with the aid of the protonation and equilibrium constants determined in this study and the binary hydrolysis constants of Cd^{2+}, Hg^{2+}, and Pb^{2+} ions from reference [18], vary as a function of pH as shown in figure 5(a). A value $\log K'_{\mathrm{ML}} \geq 6$ is often considered as a criterion for efficient complexation. On this assumption, the approximate pH ranges suitable for the use of IDS and HIDS as efficient chelating agents for Cd^{2+} and Pb^{2+} are the same as those estimated from the percentage distribution curves in the millimolar concentration range. In the case of Hg^{2+}, $\log K'_{\mathrm{ML}}$ does not reach a value of 6 for either ligand at any pH value. Thus the conclusion is the same as can be seen using the percentage distribution curves: neither ligand forms complexes with Hg^{2+} that are strong enough for practical applications. For comparison, conditional stability constants *versus* pH for EDTA and DTPA have been included in figure 5(b). Compared with IDS and HIDS, the suitable pH range for EDTA and DTPA is much broader, and especially for Hg^{2+}, the difference is huge.

4. Conclusion

The stabilities of the Cd^{2+}, Hg^{2+}, and Pb^{2+} chelates of IDS and HIDS are somewhat lower than those of EDTA and DTPA. When complexation of Cd^{2+} or Pb^{2+} is needed, the suitable pH range is also narrower for IDS and HIDS than for EDTA and DTPA. For Hg^{2+}, the applicability of IDS and HIDS is poor. On the other hand, when these ligands are used for chelation of metal ions other than Cd^{2+}, Hg^{2+}, and Pb^{2+}, it is noteworthy that IDS (ISO9439 test, OECD 301 F test) and HIDS (MITI (II) method) show better biodegradability [20–23] than EDTA and DTPA. When this is considered along with the lower stability constants of metal complexes for Cd^{2+} or Pb^{2+} and especially for Hg^{2+} it can be concluded that IDS and HIDS are less harmful to the environment than EDTA or DTPA. On the other hand, the results of this study suggest that the complexation efficiency of IDS and HIDS can be sufficiently high for them to be utilized as alternative ligands in applications where Cd^{2+} and Pb^{2+} binding is essential and a suitable pH range can be used.

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