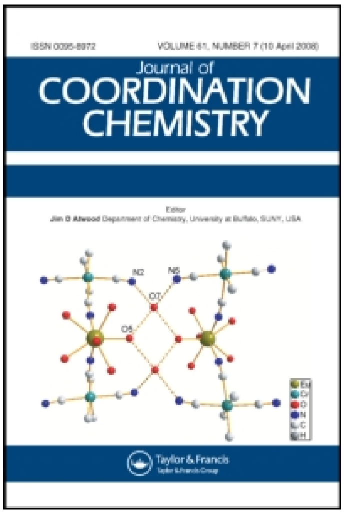

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Helena Hyvönen[a]; Reijo Aksela[b]
[a] Department of Chemistry, Laboratory of Inorganic Chemistry, University of Helsinki, FIN-00014 Helsinki, Finland [b] Kemira Oyj, Espoo Research Centre, FIN-02271 Espoo, Finland

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Complexation of 3-hydroxy-2,2′-iminodisuccinic acid (HIDS) with Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions in aqueous solution

HELENA HYVÖNEN*† and REIJO AKSELA‡

†Department of Chemistry, Laboratory of Inorganic Chemistry, University of Helsinki,
PO Box 55, FIN-00014 Helsinki, Finland
‡Kemira Oyj, Espoo Research Centre, PO Box 44, FIN-02271 Espoo, Finland

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In a search for environmental-friendly metal chelating ligands for industrial applications, the protonation and complex formation equilibria of 3-hydroxy-2,2′-iminodisuccinic acid with Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions in aqueous 0.1 mol L^{-1} NaCl solution were studied at 25°C by potentiometric titration. The model for complexation and the 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^{n-4} complexes.

Keywords: Chelating agent; Stability constants; 3-hydroxy-2,2′-iminodisuccinic acid (HIDS)

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 analytics 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 has been a source of considerable concern [1–6]. They are virtually nonbiodegradable in waste water treatment plant conditions [7–9], are difficult to remove from bleaching effluents, and are 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 been proposed [2, 3].

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*Corresponding author. Email: helena.hyvonen@helsinki.fi

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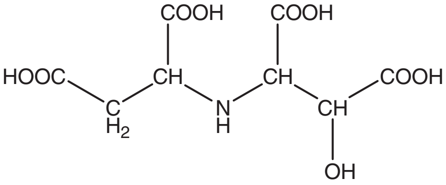
EDTA is on the EU priority list of substances for risk assessment. In accordance with the conclusions of the EU Risk Assessment Report [12], there is a need to limit the risks that EDTA continues to pose to the environment. This conclusion is based on the high levels of EDTA released to the environment through its use in industrial detergents, 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]. As the chelating agents are a plentiful source of nitrogen for example, in the effluents of a pulp mill, the nitrogen content of ligands should be as low as possible. The replacement of EDTA and DTPA by more environmental-friendly chelating agents wherever possible would be highly desirable.

Alternative chelating agents possessing complex-forming properties comparable to those of EDTA and DTPA, but with better biodegradability and lower nitrogen content, have been tested in pulp bleaching [13–17], detergent [18], and plant growth [19–21] applications. In addition, complexation studies on these potential new chelating agents have been carried out [17, 18, 22–27]. Aspartic acid derivatives, such as ethylenedisuccinic acid (EDDS), iminodisuccinic acid (ISA), and *N*-bis[2-(1,2-dicarboxyethoxy)ethyl]aspartic acid (BCA6) [13–17] have been proved as suitable biodegradable alternatives in some bleaching applications, where both EDTA and DTPA are commonly used for the removal of transition metal ions from pulp.

To deepen our understanding of the complexation behavior of 3-hydroxy-2,2′-iminodisuccinic acid (HIDS) and to obtain information relevant to the potential applications of this biodegradable chelator, we extended our complexation studies on environmental-friendly chelating agents to include HIDS and report here on its aqueous complexation with Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}.



HIDS

2. Experimental

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

HIDS was produced by Nippon Shokubai as a sodium salt. Metal chloride hydrates were p.a. grade from Merck. The metal content of the stock solutions was standardized by EDTA titration. Aqueous 0.1 mol L^{-1} NaOH and 0.1 mol L^{-1} HCl were prepared from Titrisol ampoules (Merck). 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 $\mathrm{mol\,L^{-1}}$ NaCl 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 $[H^+]$ is as follows:

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

where GE denotes a glass electrode (Schott N2680), and RE is Hg, Hg_2Cl_2 || 0.1 $\mathrm{mol\,L^{-1}}$ NaCl. Expression (2) is valid assuming that the activity coefficients are constant.

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

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 HCl to the background electrolyte. The value of the liquid junction coefficient j_{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 $\mathrm{mol\,L^{-1}}$ NaOH or 0.1 $\mathrm{mol\,L^{-1}}$ HCl 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 $0.0008\,\mathrm{mol\,L^{-1}} \le C_M \le 0.0039\,\mathrm{mol\,L^{-1}}$ and $0.0011\,\mathrm{mol\,L^{-1}} \le C_L \le 0.0056\,\mathrm{mol\,L^{-1}}$, covering metal-to-ligand ratios from 3 : 1 to 1 : 4. Four to six independent titrations were carried out for each system. The number of data points used in the calculation of the stability constants varied from 83 to 393 in the pH ranges 5.2–10.5 for Mg^{2+}, 5.1–10.6 for Ca^{2+}, 1.9–10.1 for Fe^{3+}, 2.8–9.2 for Fe^{2+}, 4.0–10.4 for Mn^{2+}, 2.4–10.1 for Co^{2+}, 1.9–10.1 for Ni^{2+}, 2.0–9.5 for Cu^{2+}, and 2.3–9.4 for Zn^{2+}. 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 addition of HCl or NaOH. Curves of Z_H *versus* pH were drawn 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:

$$Z_H = \left(C_H - [H^+] + k_w[H^+]^{-1}\right)/C_L, \tag{3}$$

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

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

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

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

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

$$pH^+ + qM^{n+} + r(HL^{3-}) \leftrightarrows (H^+)p(M^{n+})q(HL^{3-})_r;\ \beta_{pqr}. \qquad (6)$$

The hydrolysis of metal ions can be written as

$$pH^+ + qM^{n+} \leftrightarrows (H^+)p(M^{n+})_q;\ \beta_{pq0}. \qquad (7)$$

The protonation constants of the ligand and the hydrolysis constants of the metal ions [28] were considered as known parameters in the evaluation of the three-component system (6). 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 [29]. The sample standard deviation (SD) S and the χ^2 statistics used as criteria in 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 SD given by the program.

3. Results and discussion

3.1. *Protolytic properties of HIDS*

The neutralization titrations 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 8, when $Z_H = 0$. The negative Z_H values obtained in the pH range from neutral to 10.5 show that in alkaline solution one proton (from the amino nitrogen, HL^{3-} to L^{4-}) can leave the ligand (figure 1, the curve for ligand alone). The equilibrium constants for reactions (4) and (5) obtained in the final refinements are listed in table 1. For comparison with EDTA and DTPA [30], the protonation of HIDS is rewritten in the form given in table 2.

3.2. *Complexation with Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions*

Analysis of the data was initiated by drawing curves of Z_H *versus* pH (figure 1). In all systems, Z_H reaches a value of -1 with increasing pH, indicating the coordination of HIDS to metal in the form of L^{4-}. In all systems, ML^{n-4} is the dominant species formed. Z_H values below -1 were obtained for all metal ions, indicating the presence of hydroxo species, $M(OH)L^{n-5}$. For Fe(III), $M(OH)_2L^{3-}$ was also found. Formation of the acidic species MHL^{n-3} was also found for Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}, and MH_2L^{n-2} for Fe^{3+}, Ni^{2+}, and Cu^{2+} ions. As expected, the aqueous complexation of the polydentate ligands can be characterized in terms of the formation of a stable mononuclear 1 : 1 metal-to-ligand complex as the major species. For Fe^{2+}, the complexation model was complemented by the binuclear species M_2L. Table 1 shows the proposed formulae of the species, with the corresponding formation constants from equation (6) found in the equilibrium analysis of the different H^+–M^{n+}–HL^{3-} systems.

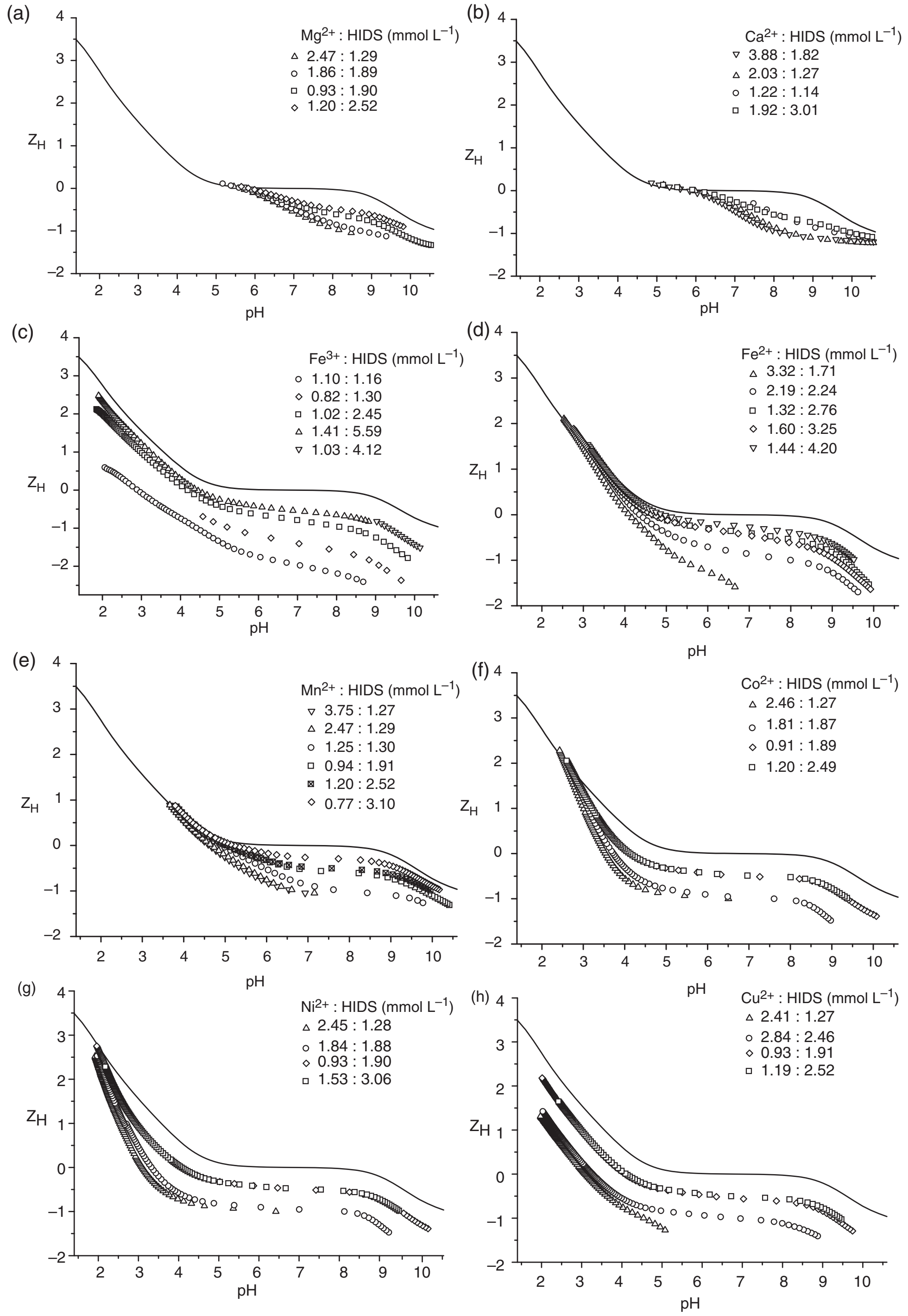


Figure 1. Z_H *vs.* pH for complexation of (a) Mg^{2+}, (b) Ca^{2+}, (c) Fe^{3+}, (d) Fe^{2+}, (e) Mn^{2+}, (f) Co^{2+}, (g) Ni^{2+}, (h) Cu^{2+}, and (i) Zn^{2+} with HIDS (Z_H *vs.* pH for HIDS = solid line).

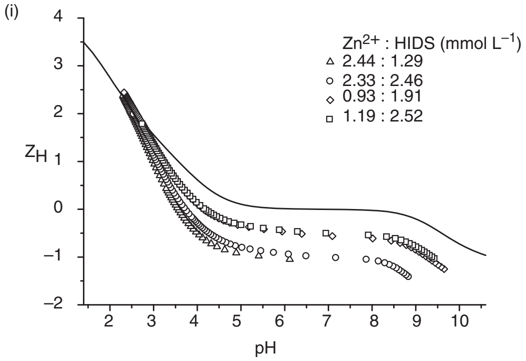


Figure 1. Continued.

Table 1. Protonation and complexation of HIDS with Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} in 0.1 mol L^{-1} NaCl aqueous solution at 25°C.

	pqr^{a}	$\log(\beta_{pqr} \pm 3\sigma)$	Formula
H^+			
	−101	−9.60 ± 0.01	L^{4-}
	101	4.06 ± 0.01	H_2L^{2-}
	201	7.10 ± 0.01	H_3L^{-}
	301	9.19 ± 0.03	H_4L
	401	10.78 ± 0.06	H_5L^{+}
χ^2/S	40.33/1.61		
Points/titrations	289/4		
Mg^{2+}			
	−211	−13.85 ± 0.14	$Mg(OH)L^{3-}$
	−111	−4.04 ± 0.07	MgL^{2-}
χ^2/S	7.31/2.24		
Points/titrations	83/4		
Ca^{2+}			
	−211	−15.44 ± 0.16	$Ca(OH)L^{3-}$
	−111	−4.48 ± 0.05	CaL^{2-}
χ^2/S	6.15/2.50		
Points/titrations	87/4		
Mn^{2+}			
	−211	−12.85 ± 0.09	$Mn(OH)L^{3-}$
	−111	−2.78 ± 0.05	MnL^{2-}
χ^2/S	19.02/1.93		
Points/titrations	180/6		
Fe^{3+}			
	−311	−8.47 ± 0.10	$Fe(OH)_2L^{3-}$
	−211	−0.43 ± 0.14	$Fe(OH)L^{2-}$
	−111	4.76 ± 0.17	FeL^{-}
	011	8.23 ± 0.17	FeHL
	111	10.38 ± 0.18	FeH_2L^{+}
χ^2/S	12.53/2.12		
Points/titrations	158/5		
Fe^{2+}			
	−211	−11.61 ± 0.10	$Fe(OH)L^{3-}$
	−111	−2.62 ± 0.09	FeL^{2-}
	011	2.67 ± 0.06	$FeHL^{-}$
	−121	1.60 ± 0.05	Fe_2L

(*Continued*)

Table 1. Continued.

	pqr[a]	$\log(\beta_{pqr} \pm 3\sigma)$	Formula
χ^2/S	9.59/1.74		
Points/titrations	191/5		
Co^{2+}			
	−211	-8.93 ± 0.04	$Co(OH)L^{3-}$
	−111	0.13 ± 0.02	CoL^{2-}
	011	3.82 ± 0.03	$CoHL^{-}$
χ^2/S	24.10/1.59		
Points/titrations	290/4		
Ni^{2+}			
	−211	-7.68 ± 0.06	$Ni(OH)L^{3-}$
	−111	1.69 ± 0.04	NiL^{2-}
	011	5.23 ± 0.02	$NiHL^{-}$
	111	7.67 ± 0.06	NiH_2L
χ^2/S	23.31/2.22		
Points/titrations	393/4		
Cu^{2+}			
	−211	-6.03 ± 0.09	$Cu(OH)L^{3-}$
	−111	2.93 ± 0.07	CuL^{2-}
	011	6.51 ± 0.05	$CuHL^{-}$
	111	9.09 ± 0.08	CuH_2L
χ^2/S	35.96/2.19		
Points/titrations	380/4		
Zn^{2+}			
	−211	-8.87 ± 0.04	$Zn(OH)L^{3-}$
	−111	0.08 ± 0.02	ZnL^{2-}
	011	3.92 ± 0.02	$ZnHL^{-}$
χ^2/S	18.38/1.42		
Points/titrations	296/4		

[a] Equation (6).

Table 2. Protonation and complexation of HIDS with Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} compared with corresponding values of EDTA and DTPA in $\mu = 0.1$ at 25°C.

Reaction ($x = 4$ for HIDS and EDTA, $x = 5$ for DTPA)	HIDS (H_4L) log K	EDTA (H_4L) log K [30]	DTPA (H_5L) log K [30]
$L^{x-} + H^+ \rightleftharpoons HL^{1-x}$	9.60	9.52–10.37	9.90–10.79
$HL^{1-x} + H^+ \rightleftharpoons H_2L^{2-x}$	4.06	6.13	8.40–8.60
$H_2L^{2-x} + H^+ \rightleftharpoons H_3L^{3-x}$	3.04	2.69	4.28
$H_3L^{3-x} + H^+ \rightleftharpoons H_4L^{4-x}$	2.09	2.00	2.70
$H_4L^{4-x} + H^+ \rightleftharpoons H_5L^{5-x}$	1.59	(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)
Mg^{2+}			
$Mg(OH)L^{1-x} + H^+ \rightleftharpoons MgL^{2-x}$	9.81		
$Mg^{2+} + L^{x-} \rightleftharpoons MgL^{2-x}$	5.56	8.79	9.27
$MgL^{2-x} + H^+ \rightleftharpoons MgHL^{3x}$		4.0	6.85
$MgL^{2-x} + Mg^{2+} \rightleftharpoons Mg_2L^{4-x}$			2.07[a]

(*Continued*)

Table 2. Continued.

Reaction ($x = 4$ for HIDS and EDTA, $x = 5$ for DTPA)	HIDS (H_4L) log *K*	EDTA (H_4L) log *K* [30]	DTPA (H_5L) log *K* [30]
Ca^{2+}			
$Ca(OH)L^{1-x} + H^+ \rightleftharpoons CaL^{2-x}$	10.96		
$Ca^{2+} + L^{x-} \rightleftharpoons CaL^{2-x}$	5.12	10.65	10.75
$CaL^{2-x} + H^+ \rightleftharpoons CaHL^{3-x}$		3.1	6.11
$CaL^{2-x} + Ca^{2+} \rightleftharpoons Ca_2L^{4-x}$			1.6
Mn^{2+}			
$Mn(OH)L^{1-x} + H^+ \rightleftharpoons MnL^{2-x}$	10.07		
$Mn^{2+} + L^{x-} \rightleftharpoons MnL^{2-x}$	6.82	13.89	15.2
$MnL^{2-x} + H^+ \rightleftharpoons MnHL^{3-x}$		3.1	4.45
$MnL^{2-x} + Mn^{2+} \rightleftharpoons Mn_2L^{4-x}$			2.09[b]
Fe^{3+}			
$Fe(OH)_2L^{1-x} + H^+ \rightleftharpoons Fe(OH)L^{2-x}$	8.04		
$Fe(OH)L^{2-x} + H^+ \rightleftharpoons FeL^{3-x}$	5.19	7.39	9.66
$2\ Fe(OH)L^{1-x} \rightleftharpoons Fe_2(OH)_2L_2^{4-2x}$		2.8[c]	
$Fe^{3+} + L^{x-} \rightleftharpoons FeL^{3-x}$	14.36	25.1	28.0
$FeL^{3-x} + H^+ \rightleftharpoons FeHL^{4-x}$	3.47	(1.3)	3.56
$FeHL^{4-x} + H^+ \rightleftharpoons FeH_2L^{5-x}$	2.15		
Fe^{2+}			
$Fe(OH)_2L^{1-x} + H^+ \rightleftharpoons Fe(OH)L^{1-x}$			9.41
$Fe(OH)L^{1-x} + H^+ \rightleftharpoons FeL^{2-x}$	8.99		8.77
$Fe^{2+} + L^{x-} \rightleftharpoons FeL^{2-x}$	6.98	14.30	16.2
$FeL^{2-x} + H^+ \rightleftharpoons FeHL^{3-x}$	5.29	2.04	5.30
$FeL^{2-x} + Fe^{2+} \rightleftharpoons Fe_2L^{4-x}$	4.22		2.98[b]
Co^{2+}			
$Co(OH)L^{1-x} + H^+ \rightleftharpoons CoL^{2-x}$	9.06		
$Co^{2+} + L^{x-} \rightleftharpoons CoL^{2-x}$	9.73	16.45	18.8
$CoL^{2-x} + H^+ \rightleftharpoons CoHL^{3-x}$	3.69	3.0	4.94
$CoHL^{3-x} + H^+ \rightleftharpoons CoH_2L^{4-x}$		(1.7)[c]	
$CoL^{2-x} + Co^{2+} \rightleftharpoons Co_2L^{4-x}$			3.74
Ni^{2+}			
$Ni(OH)L^{1-x} + H^+ \rightleftharpoons NiL^{2-x}$	9.37	(11.9)	
$Ni^{2+} + L^{x-} \rightleftharpoons NiL^{2-x}$	11.29	18.4	20.1
$NiL^{2-x} + H^+ \rightleftharpoons NiHL^{3-x}$	3.54	3.1	5.64
$NiHL^{3-x} + H^+ \rightleftharpoons NiH_2L^{4-x}$	2.44	(0.9)[c]	
$NiL^{2-x} + Ni^{2+} \rightleftharpoons Ni_2L^{4-x}$			5.59
Cu^{2+}			
$Cu(OH)L^{1-x} + H^+ \rightleftharpoons CuL^{2-x}$	8.96	(11.4)	
$Cu^{2+} + L^{x-} \rightleftharpoons CuL^{2-x}$	12.53	18.78	21.2
$CuL^{2-x} + H^+ \rightleftharpoons CuHL^{3-x}$	3.58	3.1	4.80
$CuHL^{3-x} + H^+ \rightleftharpoons CuH_2L^{4-x}$	2.58	2.0	2.96
$CuL^{2-x} + Cu^{2+} \rightleftharpoons Cu_2L^{4-x}$			6.79
Zn^{2+}			
$Zn(OH)L^{1-x} + H^+ \rightleftharpoons ZnL^{2-x}$	8.95	(11.6)	
$Zn^{2+} + L^{x-} \rightleftharpoons ZnL^{2-x}$	9.68	16.5	18.2
$ZnL^{2-x} + H^+ \rightleftharpoons ZnHL^{3-x}$	3.84	3.0	5.60
$ZnHL^{3-x} + H^+ \rightleftharpoons ZnH_2L^{4-x}$		(1.2)[c]	
$ZnL^{2-x} + Zn^{2+} \rightleftharpoons Zn_2L^{4-x}$			4.48

[a] At 37°C and in $\mu = 0.15$.
[b] At 20°C.
[c] In $\mu = 1.0$.

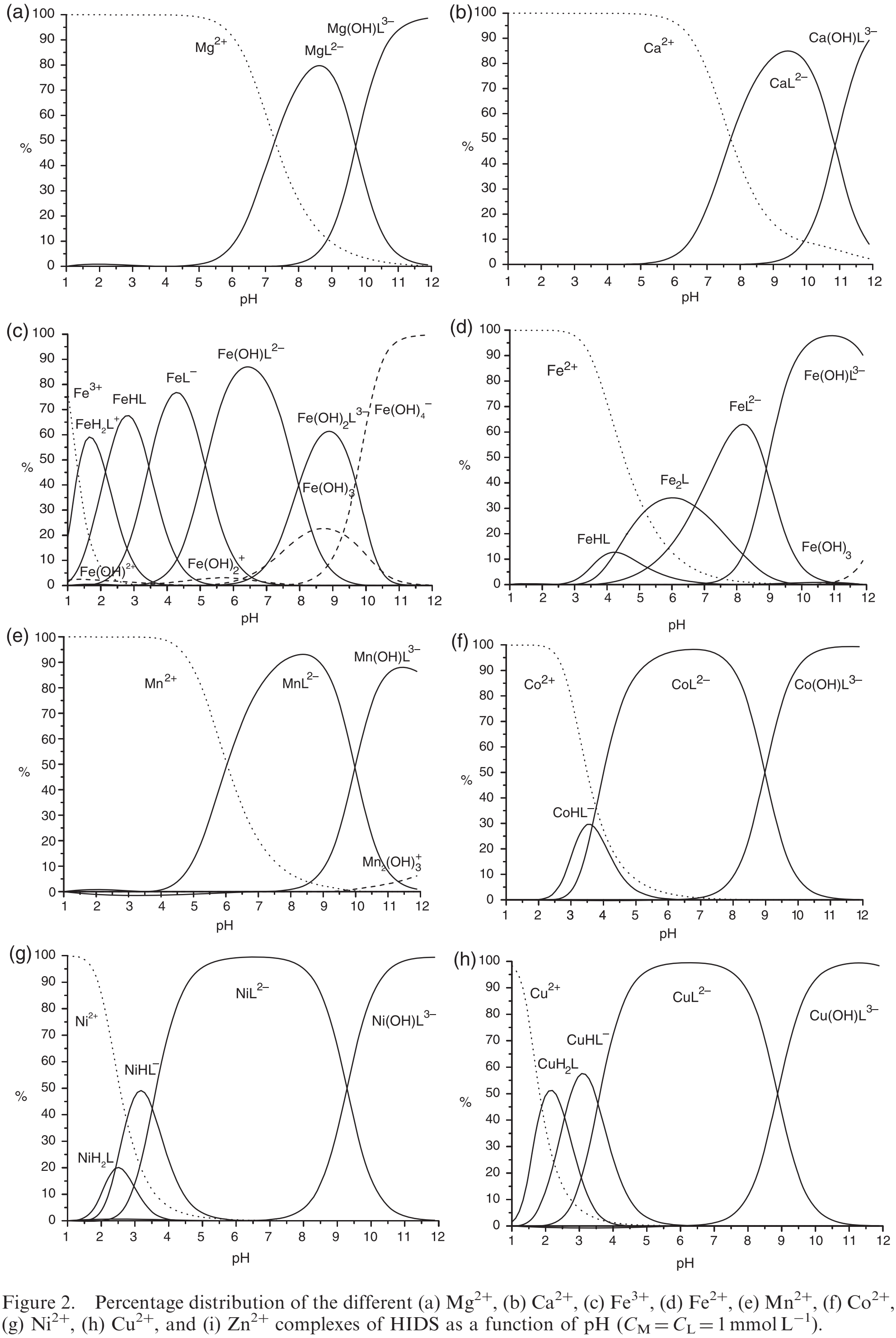


Figure 2. Percentage distribution of the different (a) Mg^{2+}, (b) Ca^{2+}, (c) Fe^{3+}, (d) Fe^{2+}, (e) Mn^{2+}, (f) Co^{2+}, (g) Ni^{2+}, (h) Cu^{2+}, and (i) Zn^{2+} complexes of HIDS as a function of pH ($C_M = C_L = 1\,\mathrm{mmol\,L^{-1}}$).

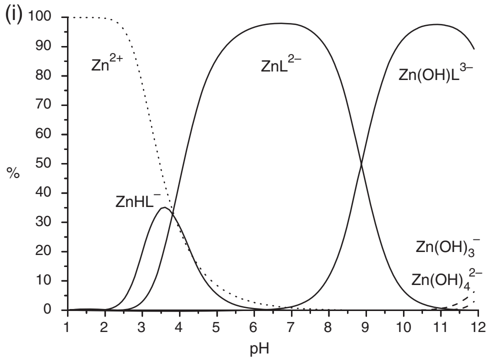


Figure 2. Continued.

Comparison with the findings of earlier studies carried out with EDTA and DTPA [30] was facilitated by expressing the complexation of HIDS with Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} in the form given in table 2. Stability of the complexes follows the Irving–Williams order for divalent transition metal ions: $\log K_{\mathrm{MnL}}(6.82) < \log K_{\mathrm{FeL}}(6.98) < \log K_{\mathrm{CoL}}(9.73) < \log K_{\mathrm{NiL}}(11.29) < \log K_{\mathrm{CuL}}$ $(12.53) > \log K_{\mathrm{ZnL}}(9.68)$.

The dominance of ML complexes over a wide pH range in solutions, where the metal-to-ligand ratio is 1 : 1 is illustrated in figure 2. The percentage distribution of the metals among the different complex species is shown as a function of pH in the millimolar concentration range ($C_{\mathrm{M}} = C_{\mathrm{L}} = 1\,\mathrm{mmol\,L^{-1}}$). It can be concluded that, in dilute solution, HIDS is an effective chelating agent (100% of metal is bound to the complexes) over the following pH ranges: Mg^{2+} 10–12, Ca^{2+} 11–12, Mn^{2+} 9–11, Fe^{3+} 3–6, Fe^{2+} 9–11, Co^{2+} 6–12, Ni^{2+} 5–12, Cu^{2+} 4–12, and Zn^{2+} 6–11. Dilution of the solution to micromolar concentration decreases the pH region of effective chelation by about three pH units in the acidic region and by about one pH unit in the basic region for Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. For all other metal ions, the chelation efficiency decreases below 100%, and in the case of Fe^{3+}, the competitive hydrolysis of the metal ion begins to overcome 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

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

where the side-reaction coefficients α_{M}, α_{L}, and α_{ML} are defined as in equations (9), (10), and (11), and K_{ML} as in equation (12):

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

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

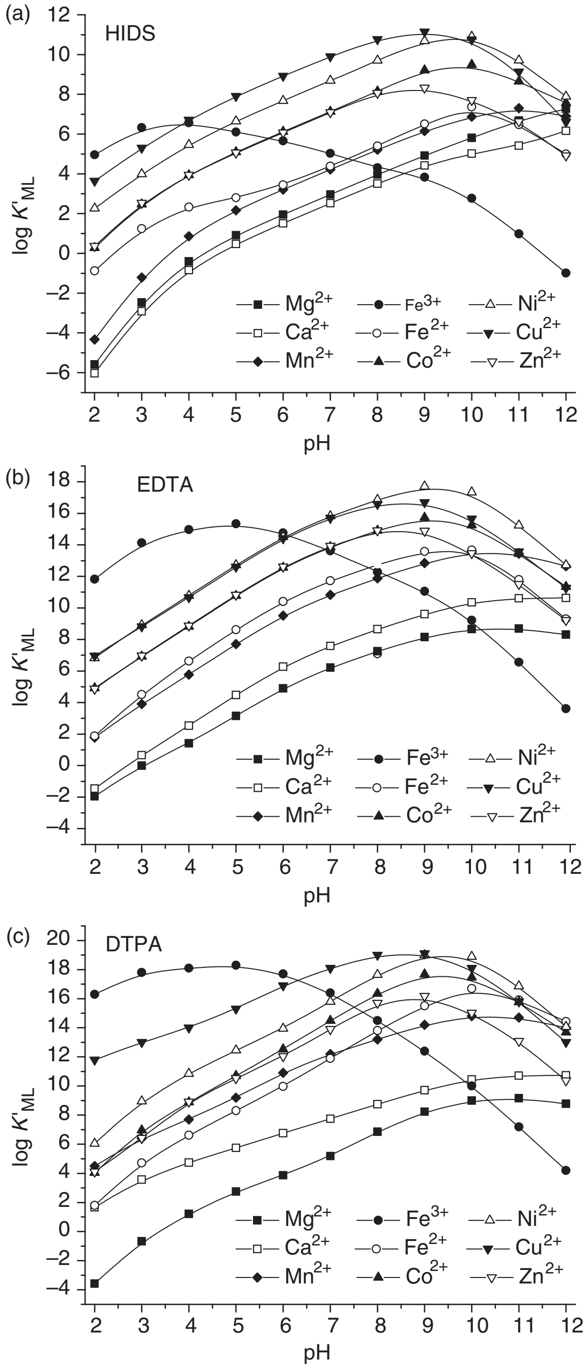


Figure 3. Conditional stability constants for ML complexes of (a) HIDS, (b) EDTA and (c) DTPA with Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions as a function of pH.

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

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

The values of the conditional stability constants of complexes of HIDS with Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}, as calculated with the aid of the protonation and equilibrium constants determined in this study and the binary hydrolysis constant of Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} from reference [28], vary as a function of pH as shown in figure 3(a). The values log $K'_{\mathrm{ML}} \geq 6$ are often considered as a criterion for efficient complexation. On this assumption, the approximate pH ranges suitable for the use of HIDS as an efficient chelating agent for Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} are about the same as those estimated from the percentage distribution curves in the millimolar concentration range. For comparison, conditional stability constants *versus* pH for EDTA and DTPA have been included in figure 3(b) and (c). Compared with HIDS, the suitable pH range for EDTA and DTPA commences earlier in the acidic pH area by 1–3 pH units in the case of Mg^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} and by 5–6 pH units in the case of Ca^{2+}, Mn^{2+}, and Fe^{2+}. For Fe^{3+}, the suitable pH range is narrower for HIDS also in the basic pH range.

4. Conclusion

The stabilities of the Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} chelates of HIDS are somewhat lower than those of EDTA and DTPA. The suitable pH range is also narrower for HIDS than for EDTA and DTPA. On the other hand, HIDS shows better biodegradability than EDTA and DTPA (according to the producer, HIDS is easily degradable with modified MITI (II) method), which makes HIDS less harmful to the environment than EDTA or DTPA. The results of the present study suggest that the complexation efficiency of HIDS is strong enough for it to be utilized as an alternative ligand in applications where Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} binding is essential and a suitable pH range can be used.

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