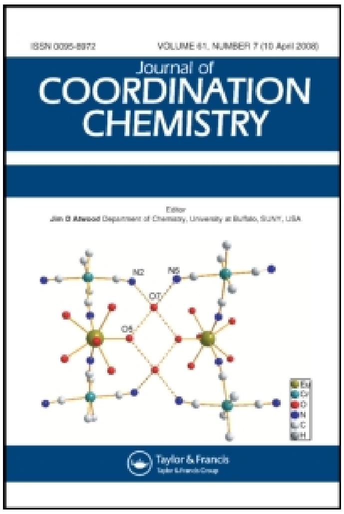

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Complexation of N-bis[2-(1,2-dicarboxyethoxy)ethyl]aspartic acid with Fe(II), Co(II), and Ni(II) in aqueous solution

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Complexation of N-bis[2-(1,2-dicarboxyethoxy)ethyl]aspartic acid with Fe(II), Co(II), and Ni(II) in aqueous solution

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In a search for environment-friendly metal chelating ligands for industrial applications, the protonation and complex formation equilibria of N-bis[2-(1,2-dicarboxyethoxy)ethyl]aspartic acid (BCA6) with Fe(II), Co(II), and Ni(II) ions in aqueous 0.1 M NaCl solution were studied at 25°C by potentiometric titration. The model for complexation and the stability constants of different complexes were determined for each metal ion using SUPERQUAD. In all cases, complex formation was dominated by stable ML^{4-} complexes.

Keywords: Chelating agent; Stability constants; N-bis[2-(1,2-dicarboxyethoxy)ethyl]aspartic acid; Fe(II); Co(II); Ni(II)

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 analysis and industry. Both 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]. Both are virtually nonbiodegradable in waste water treatment plant conditions [7–9], they are difficult to remove from bleaching effluents and they 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 been proposed [2, 3].

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

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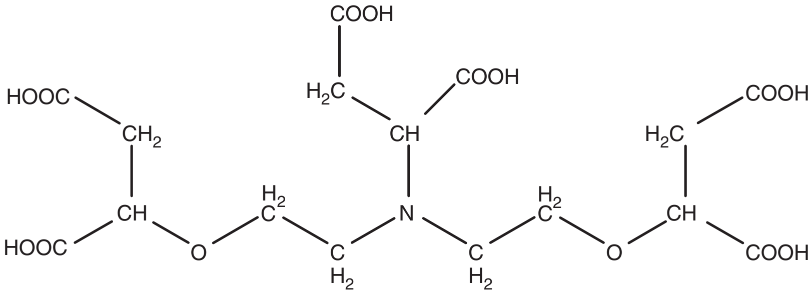
risks that EDTA continues to pose to the environment. This conclusion is based on the high levels of EDTA released to the environment through its use in industrial detergents, the pulp and paper industry, circuit board production, and during the recovery of EDTA-containing wastes. Characterization of these release scenarios shows that EDTA poses risk to aquatic organisms [12]. Since chelating agents have 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. Replacement of EDTA and DTPA by more environment-friendly chelating agents, wherever possible, would be highly desirable.

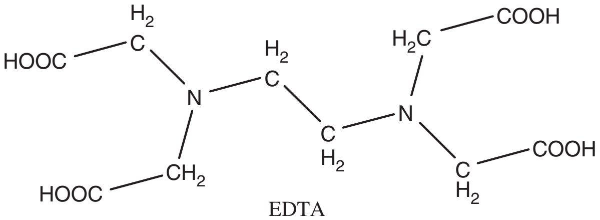
Alternative chelating agents, with complex-forming properties comparable to those of EDTA and DTPA but showing better biodegradability and having lower nitrogen content, have been tested in pulp bleaching [13–17] and detergent [18] applications. In addition, complexation studies on these potential new chelating agents have been carried out [17–23]. Pulp usually contains traces of transition metal ions, such as iron and manganese, and these catalyze the decomposition of hydrogen peroxide and peracids during bleaching [24] by increasing the chemical consumption and reducing the pulp strength. Thus, the removal of transition metal ions from pulp by chelation is an essential step when bleaching is carried out with oxygen-based chemicals. Both EDTA and DTPA are complexing agents commonly used in such chelation steps. Aspartic acid derivatives such as ethylenedisuccinic acid (EDDS), iminodisuccinic acid (ISA), and N-bis[2-(1,2-dicarboxyethoxy)ethyl]aspartic acid (BCA6) have proven suitable biodegradable alternatives in some bleaching applications for the removal of transition metal ions from pulp [13–17].

BCA6 has performed well in bleaching application tests [17], biodegradability [25–29], and complex formation with several metal ions, both as an isomeric mixture [17, 21, 22] and [S,S,S] and [R,S,R] isomers [23]. BCA6 has the advantage that its Mn complexes are inert in peracetic acid solution, in contrast to Mn-EDTA and Mn-DTPA complexes, which are capable of decomposing peroxy compounds catalytically. Thus, unlike EDTA and DTPA, BCA6 can be partly circulated back into different stages of the bleaching process [30].

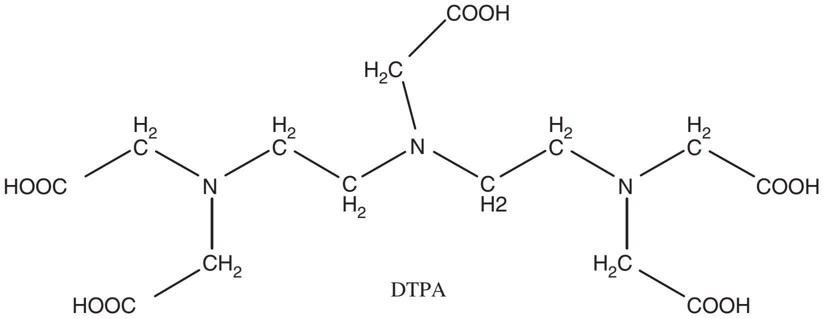
Earlier studies have examined the complexation of BCA6 with Mg(II), Ca(II), Mn(II), Fe(III), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II), and La(III) ions [17, 21, 22]. To increase the understanding of the complexation behavior of BCA6 and obtain information relevant to other potential applications of this environmental-friendly chelator, we have widened our complexation studies on BCA6 and here report on the aqueous complexation of BCA6 with Fe(II), Co(II), and Ni(II).



BCA6



EDTA



DTPA

2. Experimental

2.1. *Preparation of BCA6, stock solutions of metal ions and titration solutions*

BCA6 was produced by Kemira as a sodium salt by synthesis via a lanthanide-catalyzed Michael addition of diethanolamine to maleic acid as reported previously [31–33]. The purity of the preparation was confirmed by NMR spectroscopy and potentiometric titration. Metal chloride hydrates were of PA grade from Merck. The metal contents of the stock solutions were standardized by EDTA titration. Aqueous 0.1 M NaOH and 0.1 M HCl were prepared from Titrisol ampoules (Merck). 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 M 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 $[H^+]$ was as follows:

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

where GE denotes a glass electrode, Schott N2680, and RE is Hg, Hg_2Cl_2 || 0.1 M NaCl. Expression (2) is valid assuming the activity coefficients to be 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 the addition of 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 metal complex equilibria, aqueous 0.1 M NaOH or 0.1 M 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 were varied within the limits $0.0004\,M \leq C_M \leq 0.0032\,M$ and $0.0009\,M \leq C_L \leq 0.0027\,M$, covering metal-to-ligand ratios from 2 : 1 to 1 : 2. Five or six independent titrations were carried out for each system. The number of data points used in the calculation of the stability constants varied from 236 to 471 in the pH ranges 2.6–9.4 for Fe(II), 2.2–11.1 for Co(II) and 2.4–9.7 for Ni(II). In some titrations, the upper pH value 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 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

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

where C_H denotes the total concentration of protons calculated over the zero level HL^{5-}, H_2O, and M^{n+}.

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

$$HL^{5-} \rightleftharpoons L^{6-} + pH^+,\ p = 1;\ \beta_{-p01} \tag{4}$$

$$pH^+ + HL^{5-} \rightleftharpoons H_{p+1}L^{p-5},\ p = 1-6;\ \beta_{p01} \tag{5}$$

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

$$pH^+ + qM^{n+} + r(HL^{5-}) \rightleftharpoons (H^+)_p(M^{n+})_q(HL^{5-})_r;\ \beta_{pqr} \tag{6}$$

The hydrolysis of metal ions can be written as

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

The protonation constants of the ligand and the hydrolysis constants of the metal ions [34] 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 [35]. The sample standard deviation s and the χ^2 statistics used as criteria in the selection of complex models were given by the computer 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 BCA6*

The neutralization titrations show that the stepwise deprotonation of H_7L^+ to HL^{5-} occurs in the pH range from acidic to neutral (Z_H from 6 to 0). HL^{5-} is the major species from pH 6 to pH 8.5 when $Z_H = 0$. The negative Z_H values obtained in the pH range from neutral to 10 show that in alkaline solution one proton (from the amino nitrogen, HL^{5-} to L^{6-}) 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. The results correspond with those of earlier studies on protonation of the BCA6 mixture [17, 22] and [S,S,S] and [R,S,R] isomers [23]. For comparison with EDTA and DTPA [36], protonation of BCA6 is rewritten in the form given in table 2.

3.2. *Complexation with Fe(II), Co(II), and Ni(II)*

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 coordination of BCA6 to metal in the form of L^{6-}. In all systems, ML^{4-} is the dominant species formed. Z_H values lower than -1 were obtained for all metal ions, indicating the presence of hydroxo complex, $M(OH)L^{5-}$. Formation of the acidic species MHL^{3-}, MH_2L^{2-}, MH_3L^-, and MH_4L was also found for all metal ions. The aqueous complexation of the polydentate ligands can be characterized in terms of the formation of stable mononuclear 1 : 1 metal-to-ligand complex as the major species. This behavior is as expected and corresponds to the complexation of BCA6 with several other metal ions [17, 21–23]. In contrast to earlier studies on the complexation of BCA6 with Ca(II), Cu(II), and Zn(II) [17, 23], no binuclear species were found with Fe(II), Co(II), and Ni(II). Table 1 shows the proposed formulas of the species, with the corresponding formation constants from equation (6) found in the equilibrium analysis of different $H^+ - M^{n+} - HL^{5-}$ systems. Comparison of the findings of earlier studies carried out with EDTA and DTPA [36] was facilitated by expressing the complexation of BCA6 with Fe(II), Co(II), and Ni(II) in the form given in table 2. The stability of the complexes follows the Irving–Williams order for divalent transition metal ions: $\log K_{\mathrm{MnL}}(9.28) < \log K_{\mathrm{FeL}}(10.08) < \log K_{\mathrm{CoL}}(11.52) < \log K_{\mathrm{NiL}}(12.70) < \log K_{\mathrm{CuL}}(13.08) > \log K_{\mathrm{ZnL}}(11.34)$ [17].

The dominance of ML^{4-} 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

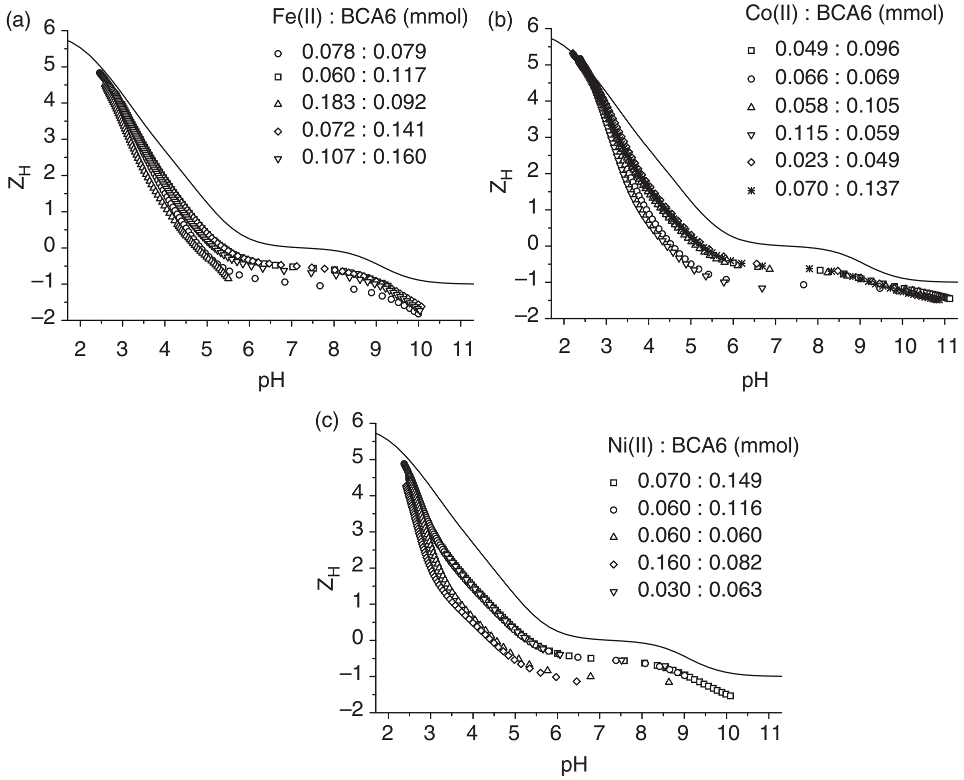


Figure 1. Z_H *vs.* pH for the complexation of (a) Fe(II), (b) Co(II), and (c) Ni(II) with BCA6 (Z_H *vs.* pH for BCA6 = solid line).

metals among different complex species is shown as a function of pH in the millimolar concentration range ($C_M = C_L = 1\,\text{mM}$). It can be concluded that, in dilute solution, BCA6 is an effective chelating agent (100% of metal is bound to the complexes) over the following pH ranges: Fe(II) 5–12, Co(II) 5–12, and Ni(II) 4–12. Dilution of the solution to the micromolar concentration area decreases the pH region of effective chelation by about two pH units in the acidic region for all metal ions and by one pH unit in the basic region for Fe(II).

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

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

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

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

Table 1. Protonation and complexation of BCA6 with Fe(II), Co(II), and Ni(II) in 0.1 M NaCl aqueous solution at 25°C.

	pqr $^{\text{eqn.(6)}}$	$\log(\beta_{pqr} \pm 3\sigma)$	Formula
H^+			
	−101	-8.89 ± 0.03	L^{6-}
	101	5.46 ± 0.03	H_2L^{4-}
	201	10.29 ± 0.02	H_3L^{3-}
	301	14.41 ± 0.03	H_4L^{2-}
	401	17.85 ± 0.03	H_5L^-
	501	20.70 ± 0.03	H_6L
	601	22.91 ± 0.04	H_7L^+
χ^2/S	34.48/1.21		
Points/titrations	166/3		
Fe(II)			
	−211	-8.27 ± 0.06	$Fe(OH)L^{5-}$
	−111	1.19 ± 0.03	FeL^{4-}
	011	6.18 ± 0.03	$FeHL^{3-}$
	111	10.55 ± 0.04	FeH_2L^{2-}
	211	14.24 ± 0.04	FeH_3L^-
	311	17.47 ± 0.06	FeH_4L
χ^2/S	16.96/1.82		
Points/titrations	425/5		
Co(II)			
	−211	-7.42 ± 0.10	$Co(OH)L^{5-}$
	−111	2.63 ± 0.05	CoL^{4-}
	011	7.17 ± 0.06	CoL^{3-}
	111	11.27 ± 0.07	CoH_2L^{2-}
	211	14.57 ± 0.10	CoH_3L^-
	311	17.56 ± 0.14	CoH_4L
χ^2/S	34.05/2.19		
Points/titrations	471/6		
Ni(II)			
	−211	-5.34 ± 0.11	$Ni(OH)L^{5-}$
	−111	3.81 ± 0.06	NiL^{4-}
	011	8.57 ± 0.05	$NiHL^{3-}$
	111	12.52 ± 0.06	NiH_2L^{2-}
	211	15.53 ± 0.08	NiH_3L^-
	311	18.21 ± 0.13	NiH_4L
χ^2/S	33.56/1.98		
Points/titrations	236/5		

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

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

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

The values of the conditional stability constants of complexes of BCA6 with Fe(II), Co(II), and Ni(II) ions, as calculated from protonation and equilibrium constants determined in this study and the binary hydrolysis constant of Fe(II), Co(II), and Ni(II) ions from reference [34] vary as a function of pH as shown in figure 3(a). Values log $K'_{\mathrm{ML}} \geq 6$ are often considered as a criterion for efficient complexation. On this

Table 2. Protonation and complexation of BCA6 with Fe(II), Co(II), and Ni(II) compared with the corresponding values of EDTA and DTPA in $\mu = 0.1$ at 25°C.

Reaction	BCA6 H_6L	EDTA H_4L [36]	DTPA H_5L [36]
H^+			
$L + H \rightleftharpoons HL$	8.89	9.52–10.37	9.90–10.79
$HL + H \rightleftharpoons H_2L$	5.46	6.13	8.40–8.60
$H_2L + H \rightleftharpoons H_3L$	4.83	2.69	4.28
$H_3L + H \rightleftharpoons H_4L$	4.12	2.00	2.70
$H_4L + H \rightleftharpoons H_5L$	3.44	(1.5)	2.0
$H_5L + H \rightleftharpoons H_6L$	2.85	(0.0)	(1.6)
$H_6L + H \rightleftharpoons H_7L$	2.21		(0.7)
$H_7L + H \rightleftharpoons H_8L$			(−0.1)
Fe(II)			
$M(OH)L + H \rightleftharpoons ML$	9.46		8.77
$M + L \rightleftharpoons ML$	10.08	14.30	16.2
$ML + H \rightleftharpoons MHL$	4.99	2.04	5.30
$MHL + H \rightleftharpoons MH_2L$	4.37		
$MH_2L + H \rightleftharpoons MH_3L$	3.69		
$MH_3L + H \rightleftharpoons MH_4L$	3.23		
$ML + M \rightleftharpoons M_2L$			2.98[b]
Co(II)			
$M(OH)L + H \rightleftharpoons ML$	10.05		
$M + L \rightleftharpoons ML$	11.52	16.45	18.8
$ML + H \rightleftharpoons MHL$	4.54	3.0	4.94
$MHL + H \rightleftharpoons MH_2L$	4.10	(1.7)[a]	
$MH_2L + H \rightleftharpoons MH_3L$	3.30		
$MH_3L + H \rightleftharpoons MH_4L$	2.99		
$ML + M \rightleftharpoons M_2L$			3.74
Ni(II)			
$M(OH)L + H \rightleftharpoons ML$	9.15	(11.9)	
$M + L \rightleftharpoons ML$	12.70	18.4	20.1
$ML + H \rightleftharpoons MHL$	4.76	3.1	5.64
$MHL + H \rightleftharpoons MH_2L$	3.95	(0.9)[a]	
$MH_2L + H \rightleftharpoons MH_3L$	3.01		
$MH_3L + H \rightleftharpoons MH_4L$	2.68		
$ML + M \rightleftharpoons M_2L$			5.59

[a] In $\mu = 1.0$, [b] at 20°C.

assumption, the approximate pH ranges suitable for the use of BCA6 as an efficient chelating agent for Fe(II), Co(II), and Ni(II) are the same as estimated from the percentage distribution curves in the millimolar concentration range. For comparison, conditional stability constants [34, 36] *versus* pH for EDTA and DTPA are added to figure 3(b) and (c). As compared with BCA6, the suitable pH range for EDTA and DTPA commences earlier in the acidic pH area by 1–2 pH units.

The stabilities of the Fe(II), Co(II), and Ni(II) chelates of BCA6 are somewhat lower than those of EDTA and DTPA. On the other hand, BCA6 shows better biodegradability than EDTA and DTPA (OECD 301B test and ISO9439 test) [25–27]. The photodegradability of BCA6, and its superiority to EDTA in terms of degradability by Fenton's process, has also been reported [28, 29]. These features make BCA6 less harm to the environment than EDTA or DTPA. Although the strength of the complexation of Mn(II) and Fe(III) ions is lower for BCA6 than for EDTA or DTPA, it appears to be high enough for practical applications in pulp bleaching [17].

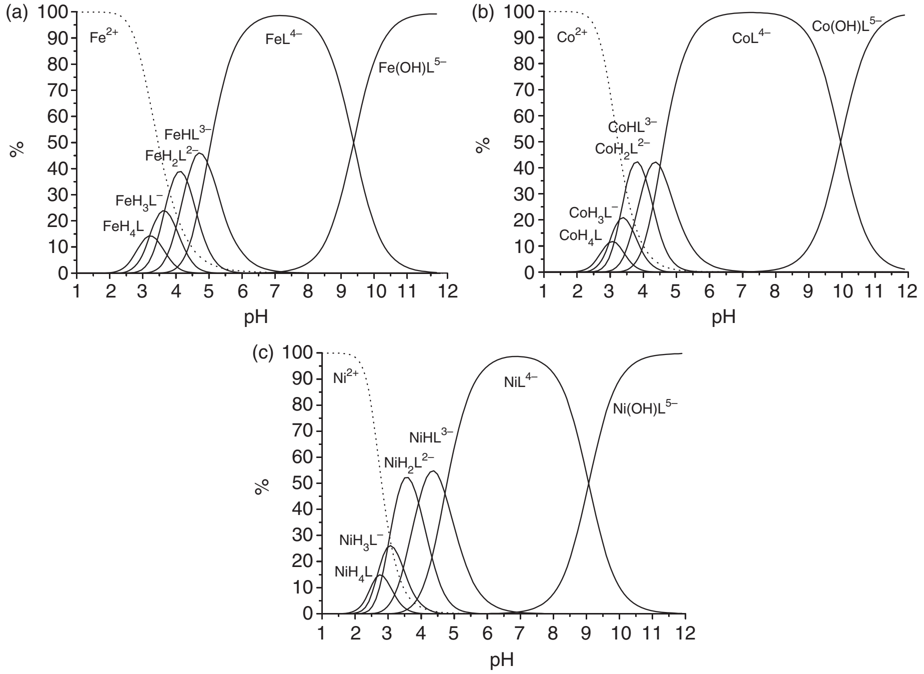


Figure 2. Percentage distribution of the different (a) Fe(II), (b) Co(II), and (c) Ni(II) complexes of BCA6 as a function of pH ($C_M = C_L = 1\,\text{mM}$).

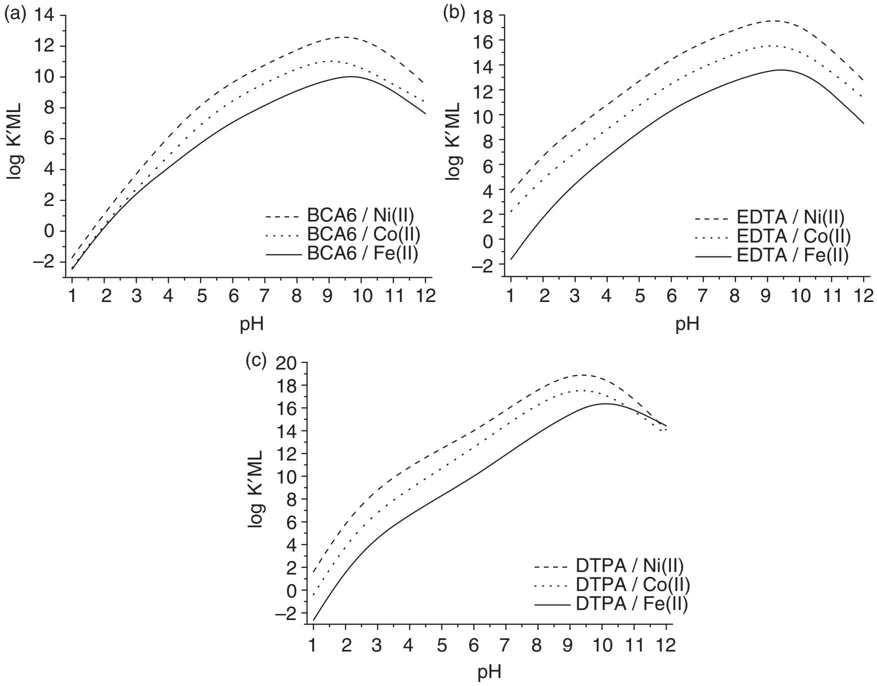


Figure 3. Conditional stability constants for ML complexes of (a) BCA6, (b) EDTA, and (c) DTPA with Fe(II), Co(II), and Ni(II) ions as a function of pH.

More importantly, the Mn–BCA6 complexes appear to be inert in hydrogen peroxide and peracetic acid solutions, whereas Mn–EDTA and Mn–DTPA complexes are capable of decomposing the peroxy compounds. The results of the present study suggest that the complexation efficiency of BCA6 is strong enough for it to be utilized as an alternative ligand in applications where Fe(II), Co(II), and Ni(II) binding is essential.

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