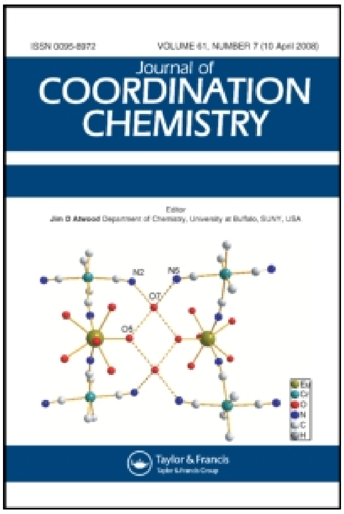

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The complexation of novel amino acid derivatives with La(III) ion in aqueous solution

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In a search for environmentally friendly metal chelating ligands the complex formation equilibria of *N-bis*[2-(1,2-dicarboxyethoxy)ethyl] glycine (BCA5), *N-bis*[2-(1,2-dicarboxyethoxy)ethyl] aspartic acid (BCA6), and *N-tris*[(1,2-dicarboxyethoxy)ethyl] amine (TCA6) with La(III) in aqueous 0.1 M NaCl solution were studied at 25°C by potentiometric titration. The models of the complexation and stability constants of the different complexes were determined using the computer program SUPERQUAD. With TCA6 and BCA6 complex formation was dominated by stable LaL^{3-} and with BCA5 by LaL^{2-} complexes.

Keywords: Chelating agent; Stability constants; *N-bis*[2-(1,2-dicarboxyethoxy)ethyl] glycine; *N-bis*[2-(1,2-dicarboxyethoxy)ethyl] aspartic acid; *N-tris*[(1,2-dicarboxyethoxy)ethyl] amine; La(III)

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 industry. The nonbiodegradability of these compounds, which are used in a variety of large-scale industrial applications from detergents to agrochemicals, has caused concern about their accumulating effects in nature [1–4] e.g. by remobilizing toxic heavy metal ions from soil [5, 6]. Being virtually nonbiodegradable in wastewater treatment conditions, EDTA and DTPA are difficult to remove from bleach plant effluents [7, 8]. EDTA is on a priority list of substances for EU Risk Assessment. In accordance with the conclusion in a risk assessment report, there is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account. This conclusion is reached because of the high releases due to the 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 [9]. Since chelating agents may be a remarkable source of nitrogen in wastewaters, the nitrogen content of the ligands should be

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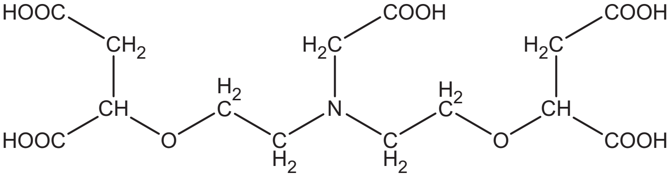
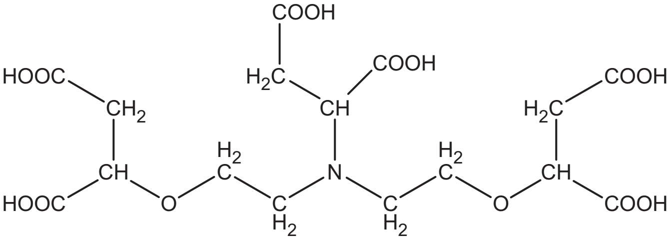
as low as possible. More environmentally friendly chelating agents, with complex forming properties comparable to the conventional ligands, but being biodegradable are desired.

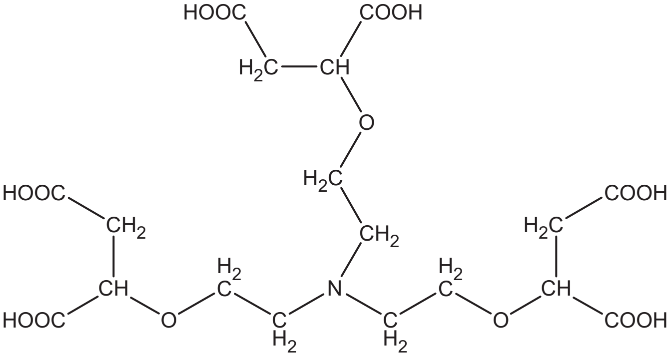


BCA5



BCA6

Alternative chelating agents such as ethylenediaminedisuccinic acid (EDDS), iminodisuccinic acid (ISA), *N*-*bis*[2-(1,2-dicarboxyethoxy)ethyl] aspartic acid (BCA6), *N*-*bis*[2-(1,2-dicarboxyethoxy)ethyl]-glycine (BCA5) and *N*-*tris*[(1,2-dicarboxyethoxy) ethyl]amine (TCA6) have been tested e.g. for pulp bleaching applications and for detergent formulation [10–15] and their complexation with several metal ions has been described [14–17]. Lanthanum was used as a catalyst in the synthesis of most of these new ligands. At first, the disappearance of the lanthanum catalyst during the synthesis caused a problem, which was solved by recycling the catalyst by ion exchange [18]. When searching for the lost lanthanum, complexation of *N*-*bis*[2-(1,2-dicarboxyethoxy) ethyl] glycine (BCA5), *N*-*bis*[2-(1,2-dicarboxyethoxy)ethyl] aspartic acid (BCA6), and *N*-*tris*[(1,2-dicarboxyethoxy)ethyl] amine (TCA6) with La(III) in aqueous 0.1 M NaCl solution was studied and is reported here.



TCA6

2. Experimental

2.1. *Preparation ofligands and stock solution of metal ion*

Isomeric mixtures of the BCA6 and BCA5 were prepared *via* a lanthanide catalyzed Michael addition of diethanolamine or *bis*-N-(2-hydroxyethyl)aspartic acid (bicine) to maleic acid. TCA6 was synthesised via a lanthanide-catalysed Michael addition of triethanolamine to maleic acid [18–21]. The purity of the preparations was checked by ^{13}C NMR and ^{1}H NMR techniques and potentiometric titrations. Aqueous La(III) solutions were prepared by dissolving $La(NO_3)_3$ hydrate in distilled water. The metal content of the stock solution was standardized by EDTA titration. The acid content of the metal solutions was determined by titration with 0.1 M NaOH solution after liberation of the H^+ ions by cation exchange.

2.2. *Potentiometric measurements*

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 5.00. The cell arrangement for the measurement of the hydrogen ion concentration, $[H^+]$ was as in equation (1)

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

where GE denotes a glass electrode, Schott N2680, and RE is Hg, $Hg_2Cl_2 \parallel$ 0.1 M NaCl. Assuming the activity coefficients to be constant, expression (2) is valid

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

The cell parameter E_0 and the liquid junction coefficient j_H, valid in acidic solutions, were determined for each titration by 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 the measurements of the metal complex equilibria, aqueous NaOH or 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 $0.0007\,\mathrm{M} \le C_M \le 0.0050\,\mathrm{M}$ and $0.0011\,\mathrm{M} \le C_L \le 0.0020\,\mathrm{M}$, covering metal-to-ligand ratios from 1 : 2 to 3 : 1. Four independent titrations were carried out for each system. The number of data points used in the calculation of the stability constants varied between 307 and 374 in the pH ($=-\log[H^+]$) range 2.7–10.8 for TCA6, 2.5–10.7 for BCA6 and 3.5–9.9 for BCA5. In some titrations the 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.

2.3. *Data treatment*

Protonation/deprotonation of the ligands was controlled with HCl/NaOH additions. 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 equation (3)

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

where C_H denotes the total concentration of protons calculated over the zero level HL^{5-}, H_2O and M^{3+} for BCA6 and TCA6 and HL^{4-}, H_2O and M^{3+} for BCA5. In evaluating the equilibrium constants the two-component equilibria (4) and (5) were considered [14, 15],

$$HL^{1-x} \leftrightharpoons L^{x-} + pH^+, \quad p = 1; \ \beta_{-p01} \quad \text{(where } x = 6 \text{ for BCA6 and TCA6, } x = 5 \text{ for BCA5)} \tag{4}$$

$$pH^+ + HL^{1-x} \leftrightharpoons H_{p+1}L^{p-x+1}, \quad p = \text{from 1 to } x; \ \beta_{p01} \\ (x = 6 \text{ for BCA6, TCA6, } x = 5 \text{ for BCA5}) \tag{5}$$

Metal complex formation can be characterized by the general three-component equilibrium (6),

$$pH^+ + qM^{n+} + r(HL^{1-x}) \leftrightharpoons (H^+)_p(M^{n+})_q(HL^{1-x})_r; \ \beta_{pqr} \\ \text{(where } x = 6 \text{ for BCA6 and TCA6, } x = 5 \text{ for BCA5)} \tag{6}$$

and hydrolysis of metal ions can be written as in equation (7)

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

The protonation constants of the ligands [14, 15] and the hydrolysis constants of the metal ions [22] were considered as known parameters in the evaluation of the three-component system (equation 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 [23]. The sample standard deviation *s* and the χ^2-statistics used as criteria in selection of the complex models were those given by the program.

3. Results and discussion

3.1. *Protolyticproperties of BCA5, BCA6 and TCA6*

The protolytic properties of BCA5, BCA6 and TCA6 were reported earlier [14, 15]. Neutralization titrations show the stepwise deprotonation of H_7L^+ to HL^{5-} for BCA6 and TCA6 and H_6L^+ to HL^{4-} for BCA5 to occur in the pH range from acidic to neutral (Z_H from 6 or 5 to 0). HL^{5-} is the major species of BCA6 and TCA6, HL^{4-} of BCA5 in the pH range 6–9 when $Z_H = 0$. The negative Z_H values reached in the pH-range from neutral to 10–11 show that one proton (from amino nitrogen, HL^{5-} to L^{6-} for BCA6 and TCA6, HL^{4-} to L^{5-} for BCA5) can leave the ligand in alkaline solution (figure 1, the curves for free ligands). For comparison with EDTA and DTP A [24],

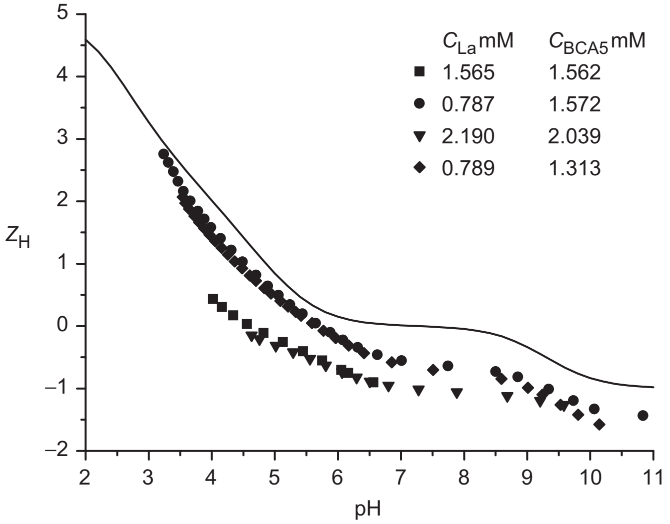


Figure 1 (a). Z_H *vs*. pH for complexation of La(III) with BCA5 (Z_H *vs*. pH for BCA5 = solid line).

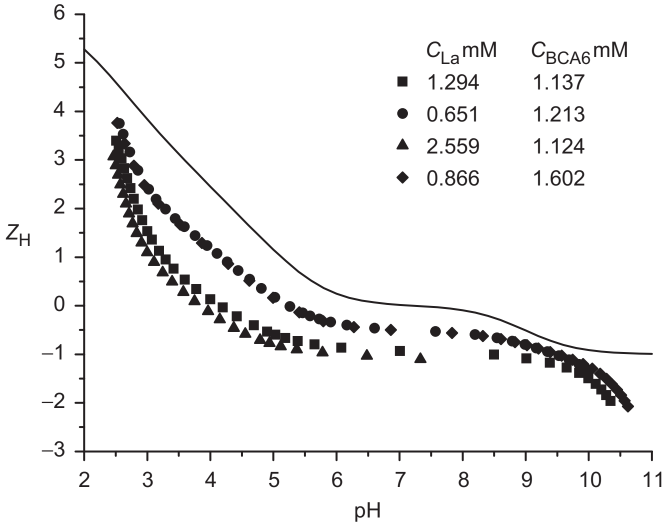


Figure 1 (b). Z_H *vs*. pH for complexation of La(III) with BCA6 (Z_H *vs*. pH for BCA6 = solid line).

the equilibrium constants for reactions (4) and (5) obtained in the final refinements [14, 15] (table 1) are rewritten in the form given in table 2.

3.2. *Complexation of BCA5, BCA6 and TCA6 with La(III)*

The analysis of the data was started by drawing curves of Z_H *versus* pH (figure 1). In TCA6, BCA6 and BCA5 systems Z_H obtains the value −1 with increasing pH,

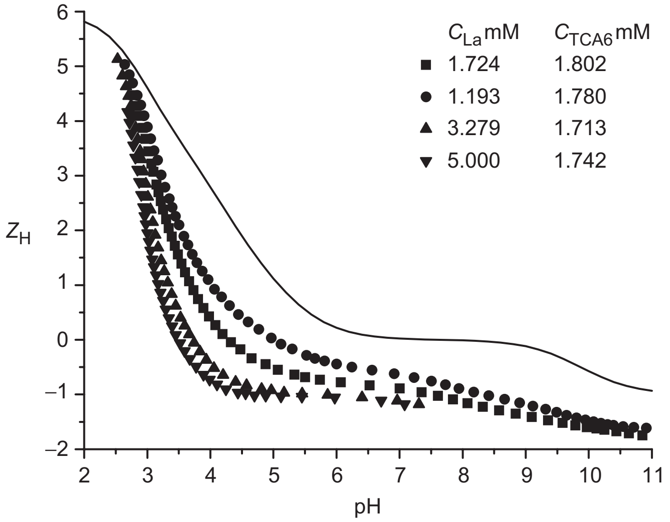


Figure 1 (c). Z_H *vs.* pH for complexation of La(III) with TCA6 (Z_H *vs.* pH for TCA6 = solid line).

Table 1. Protonation and complex formation of TCA6, BCA6 and BCA5 with La(III) in aqueous 0.1 M NaCl at 25°C.

Pqr	TCA6, HL^{5-} $\log(\beta_{pqr} \pm 3\sigma)$	BCA6, HL^{5-} $\log(\beta_{pqr} \pm 3\sigma)$	BCA5, HL^{4-} $\log(\beta_{pqr} \pm 3\sigma)$	Formula
H^+	[15]	[14]	[14]	
−101	−9.87 ± 0.05	−8.98 ± 0.03	−9.30 ± 0.04	L^{6-}/L^{5-}
101	5.40 ± 0.03	5.47 ± 0.03	5.22 ± 0.04	H_2L^{4-}/H_2L^{3-}
201	10.08 ± 0.02	10.20 ± 0.02	9.68 ± 0.04	H_3L^{3-}/H_3L^{2-}
301	14.25 ± 0.03	14.16 ± 0.03	13.24 ± 0.05	H_4L^{2-}/H_4L
401	17.87 ± 0.03	17.36 ± 0.03	16.00 ± 0.07	H_5L^-/H_5L
501	20.81 ± 0.05	19.92 ± 0.05	18.33 ± 0.07	H_6L/H_6L^+
601	23.56 ± 0.05	21.89 ± 0.06		H_7L^+
La^{3+}	This study	This study	This study	
−211	−7.88 ± 0.14	−6.60 ± 0.19	−7.10 ± 0.16	$La(OH)L^{4-}/La(OH)L^{3-}$
−111	3.15 ± 0.03	4.44 ± 0.05	2.06 ± 0.10	LaL^{3-}/LaL^{2-}
011	7.86 ± 0.02	9.19 ± 0.03	6.26 ± 0.12	$LaHL^{2-}/LaHL^-$
111	11.09 ± 0.09	12.67 ± 0.02		LaH_2L^-
211	14.63 ± 0.07	15.34 ± 0.05		LaH_3L
−121	7.26 ± 0.03	7.87 ± 0.08		La_2L
021	10.99 ± 0.05	11.61 ± 0.21		La_2HL^+
121	14.22 ± 0.09			$La_2H_2L^{2+}$
X^2/S	42.53/1.02	49.36/1.08	11.10/1.47	
Points/titrations	374/4	326/4	307/4	

indicating coordination of TCA6 and BCA6 to metal in the form of L^{6-} and BCA5 in the form of L^{5-}. The formation of LaL^{3-} for TCA6 and BCA6, and LaL^{2-} for BCA5, respectively, is dominant in these systems. Z_H value lower than −1 was obtained for all these systems, indicating the presence of hydroxo complex species, $La(OH)L^{4-}$/$La(OH)L^{3-}$. The formation of acidic species $LaHL^{2-}$/$LaHL^-$ was found in TCA6, BCA6 and BCA5 systems. The acidic species LaH_2L^- and LaH_3L were also found

Table 2. Protonation and complex formation of TCA6, BCA6 and BCA5 with La(III) in aqueous 0.1 M NaCl ($\mu = 0.1$) at 25°C compared to corresponding values of EDTA and DTPA ($^{a}\mu = 1.0$, $^{b}20°C$).

Reaction	TCA6 H_6L	BCA6 H_6L	BCA5 H_5L	EDTA [24] H_4L	DTPA [24] H_5L
$L + H \leftrightharpoons HL$	9.87	8.98	9.30	9.52–10.37	9.52–10.379
$HL + H \leftrightharpoons H_2L$	5.40	5.47	5.22	6.13	8.40–8.60
$H_2L + H \leftrightharpoons H_3L$	4.68	4.73	4.46	2.69	4.28
$H_3L + H \leftrightharpoons H_4L$	4.17	3.96	3.56	2.00	2.70
$H_4L + H \leftrightharpoons H_5L$	3.62	3.20	2.76	(1.5)	2.0
$H_5L + H \leftrightharpoons H_6L$	2.94	2.56	2.33	(0.0)^{a}	(1.6)
$H_6L + H \leftrightharpoons H_7L$	2.75	1.97			(0.7)
$H_7L + H \leftrightharpoons H_8L$					(−0.1)
La(III)					
$M(OH)L + H \leftrightharpoons ML$	11.03	11.04	9.16		
$M + L \leftrightharpoons ML$	13.02	13.42	11.36	15.36	19.49
$ML + H \leftrightharpoons MHL$	4.71	4.75	4.20	2.24	2.60^{b}
$MHL + H \leftrightharpoons MH_2L$	3.24	3.48			
$MH_2L + H \leftrightharpoons MH_3L$	3.54	2.67			
$ML + M \leftrightharpoons M_2L$	4.11	3.43			
$M_2L + H \leftrightharpoons M_2HL$	3.73	3.74			
$M_2HL + H \leftrightharpoons M_2H_2L$	3.23				

in the case of BCA6 and TCA6. The aqueous complexation of the polydentate ligands TCA6, BCA6 and BCA5 can be mainly characterized by the formation of stable mononuclear 1 : 1 metal to ligand complexes as the major species. The complexation model was complemented by binuclear species La_2L and La_2HL^+ for BCA6 and La_2L, La_2HL^+ and $La_2H_2L^{2+}$ for TCA6. The presence of binuclear species in calculations gave significant improvement to the fit. For BCA6 the improvement in χ^2/s values was from 87.15/1.90 to 49.36/1.08 and for TCA6 from 84.98/7.05 to 42.53/1.02, respectively. The proposed formulas of the species, with the corresponding formation constants from equation (6) found in the equilibrium analysis of the different $H^+ - La^{3+} - HL^{x-}$ systems, are shown in table 1. Comparison with the findings of earlier studies carried out with EDTA and DTP A [24] was facilitated by rewriting the complexation of the ligands with La(III) in the form given in table 2.

Ligands TCA6, BCA6 and BCA5 formed moderately strong LaL^{3-}/LaL^{2-} complexes with La(III). Figure 2 shows the percentage distribution of La(III) among the different complex species as a function of pH for each ligand in the millimolar concentration area ($C_M = C_L = 1$ mM). It can be concluded that, in dilute solution, ligands TCA6, BCA6 and BCA5 are effective chelating agents for La(III) (over 90% of metal is bound to the complexes) over a wide pH range: TCA6 5–12, BCA6 4–12 and BCA5 5–12. In the micromolar concentration area dilution of the solution increases the lower pH limit of the effective chelation region to more basic direction.

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)

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

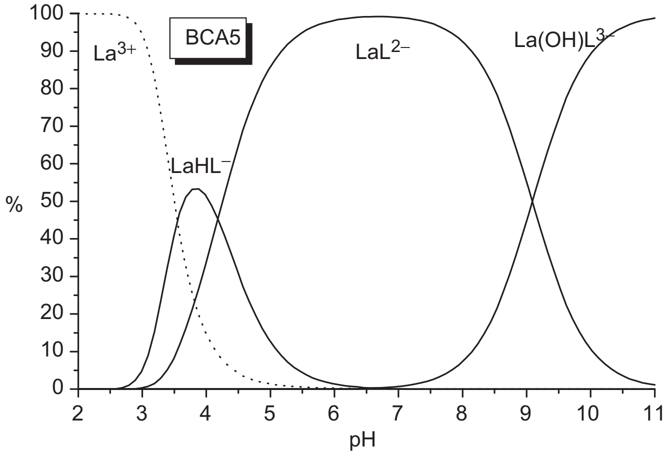


Figure 2 (a). Percentage distribution of the different La(III) complexes of BCA5 as a function of pH. ($C_M = C_L = 1$ mM).

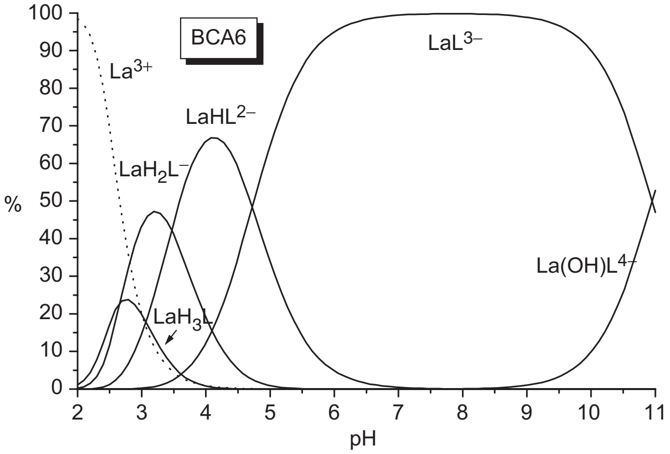


Figure 2 (b). Percentage distribution of the different La(III) complexes of BCA6 as a function of pH. ($C_M = C_L = 1$ mM).

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)

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

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

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

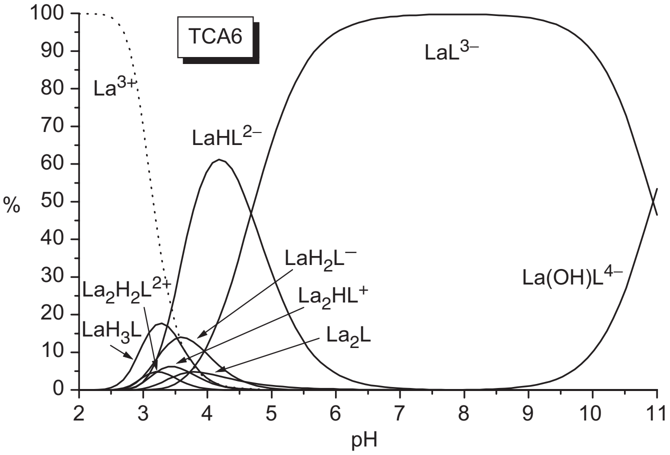


Figure 2 (c). Percentage distribution of the different La(III) complexes of TCA6 as a function of pH. ($C_M = C_L = 1$ mM).

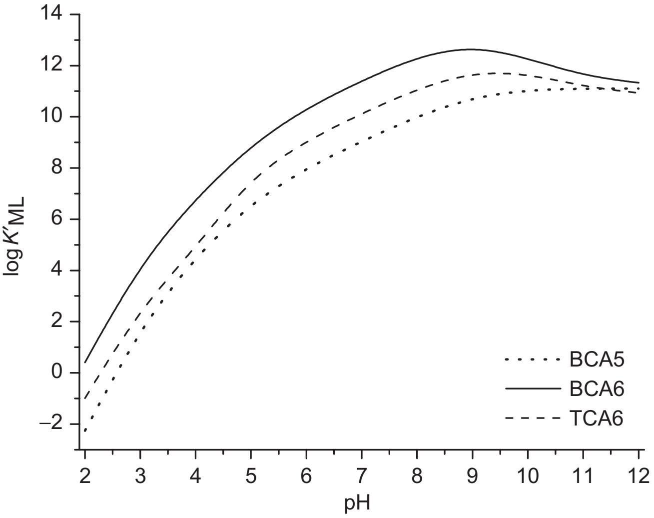


Figure 3. Conditional stability constants for ML complexes of BCA5, BCA6 and TCA6 with La(III) ion as a function of pH.

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

The values of conditional stability constants of complexes of TCA6, BCA6 and BCA5 with La(III), as calculated with the aid of the equilibrium constants determined in this study, the protonation constants from references [14, 15] and the binary hydrolysis constant of La(III)ion [22], vary as a function of pH as shown in figure 3. 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 use of TCA6, BCA6 and BCA5 as efficient chelating agents for La(III), are the same as estimated from the percentage distribution curves.

Although the stabilities of the chelates of the ligands TCA6, BCA6 and BCA5 with different metal ions are somewhat lower than those of EDTA and DTP A, they appear to be great enough for practical applications, e.g. in pulp bleaching (BCA6 and BCA5) [14] and in detergent formulations (TCA6) [15]. The capability of these ligands to chelate La(III) caused a solvable problem in the synthesis, but can be utilized in applications where strong lanthanum binding is essential.

Although these compounds have not proven to be readily biodegradable, they have shown better biodegradability than EDTA or DTPA (OECD 301B -test for BCA6 and BCA5 [25, 26] and ISO9439 -test for TCA6 [27]). The photodegradability of BCA5 and BCA6 has also been proved [28]. The lower nitrogen content of these new compounds compared to EDTA or DTPA also encourages their use to replace the conventional ligands.

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