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Helena Hyvönen^a & Reijo Aksela^b

^a Department of Chemistry, Laboratory of Inorganic Chemistry, University of Helsinki, PO Box 55, FIN-00014 Helsinki, Finland

^b Kemira Oyj, Espoo Research Centre, PO Box 44, FIN-02271 Espoo, Finland

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Complexation of some environmentally friendly carboxylic acid ligands with La^{3+} ion 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 search for environmentally friendly metal chelating ligands for industrial applications, protonation, and complex-formation equilibria of iminodisuccinic acid (IDS), 3-hydroxy-2,2'-iminodisuccinic acid (HIDS), N,N'-ethylenediaminedisuccinic acid (EDDS), and oxydisuccinic acid (ODS) with La^{3+} 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 using the computer program SUPERQUAD. Complex formation was dominated by stable LaL^- complexes for all tested ligands.

Keywords: Chelating agent; Stability constants; Iminodisuccinic acid (IDS); 3-Hydroxy-2,2'-iminodisuccinic acid (HIDS); N,N'-Ethylenediaminedisuccinic acid (EDDS); Oxydisuccinic acid (ODS); La^{3+}

1. Introduction

Aminopolycarboxylates, such as ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA), form strong metal complexes and have therefore been widely utilized as chelating agents for a variety of large-scale industrial applications for decades. However, they are non-biodegradable. The persistence of EDTA and DTPA and their metal complexes in nature as determined by their accumulation in the environment has been a source of considerable concern during the past few years [1–6]. For example, both EDTA and DTPA are virtually non-biodegradable under waste water treatment plant conditions [7–9]. They are also difficult to remove from bleaching effluents and may be capable of remobilizing toxic heavy metal ions from sediments [10, 11]. Moreover, due to their property of forming strong complexes with iron they may increase eutrophication through the liberation of phosphates. EDTA is found in drinking water and is present in almost all anthropogenically impacted surface water molecules in industrialized countries. Mechanisms that describe the effect of aminocarboxylate chelating agents on the aquatic environment have been proposed [2, 3].

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

EDTA is on the EU priority list of substances for risk assessment. In accord 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 into the environment through its manifold uses which include industrial detergents, pulp and paper industry applications, circuit board production and during the recovery of EDTA-containing wastes. Characterization of these release scenarios shows that EDTA poses a risk to aquatic organisms [12]. Chelating agents are a plentiful source of nitrogen, *inter alia* in the effluents of a pulp mill; therefore, the nitrogen content of the ligands should be as low as possible. Replacement of EDTA and DTPA by more environmentally benign chelating agents wherever possible would therefore be highly desirable.

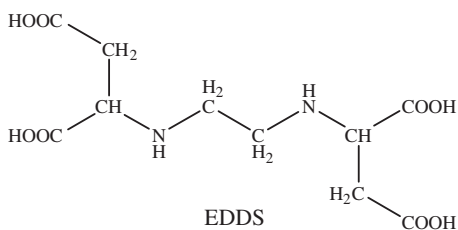
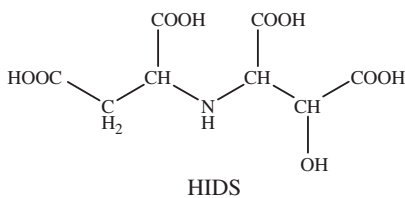
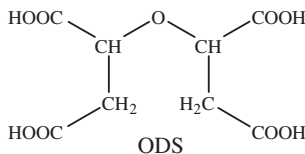
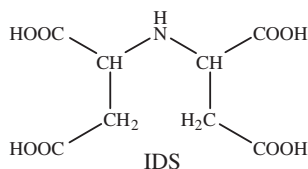
Several alternative chelating agents, that have complex-forming properties comparable to those of EDTA and DTPA but which have better biodegradability characteristics and lower nitrogen contents, have been tested in the following uses: pulp bleaching [13–17], detergent [18], and plant growth [19–24]. In addition, complexation studies on these potential new chelating agents have been carried out [17, 18, 25–32]. Ethylenediaminedisuccinic acid (EDDS) and iminodisuccinic acid (IDS) have been found to be suitable alternatives with better biodegradable properties in some bleaching applications than both EDTA and DTPA which are commonly used for the removal of transition metal ions from pulp [13, 15]. Moreover, EDDS, IDS, and 3-hydroxy-2,2'-iminodisuccinic acid (HIDS) have been reported to be potential alternatives to environmentally persistent EDTA for the increase of Fe uptake and plant growth [19–23] and EDDS and IDS also as fixing agents for seed coatings [24].

Chelating agents have also been used to solubilize heavy metals in polluted soils. Although most of the chelating agent is removed from the soil before returning the rehabilitated soil to the field, residual amounts are always left. The formation of metal complexes with this residual complexing agent is possible and must therefore be taken into consideration. EDTA metal complexes may be leached deep into the soil and contaminate groundwater. An investigation into the degradation of residual EDDS from the washing of polluted soil has shown that EDDS degrades in the soil [33]. Recently, the readily biodegradable isomer [S,S]-EDDS has been used as a replacement for EDTA in soil washing and phyto-extraction processes [34–37]. Phyto-extraction through the use of high-biomass extraction plants has been proposed as an alternative method to remove metals from contaminated soil. However, this process is generally considered to be very slow. Therefore, EDTA and EDDS have been investigated and compared for their chemically enhanced phyto-extraction properties. Heavy metals were strongly mobilized by both chelators. However, the persistence of EDTA makes it unsuitable for use in phyto-extraction under normal field conditions [37–40]. IDS has also been evaluated as a biodegradable alternative to EDTA in soil washing tests, but was found to be less effective than EDDS [36]. In the studies of arsenic phyto-extraction, HIDS has been recently reported to be more efficient than EDDS, IDS, and EDTA [21].

The complexation characteristics of IDS, HIDS, EDDS, and oxydisuccinic (ODS) acid for several metal ions have been studied previously [25, 26, 31, 32, 41]. Interest in studying the complexation of lanthanum has arisen because it is used as a catalyst in the synthesis of these aminosuccinates via Michael addition [42]. When lanthanum is used as a catalyst in the synthesis of such ligands, the complexation of the reaction product with lanthanum deactivates the catalyst. Therefore, it is important to know the stability

and pH dependency of these lanthanum complexes. At first, the disappearance of the La catalyst during the synthesis caused a problem, which was solved by recycling the catalyst by ion exchange [43]. As part of the search for the deactivated La, the complexation of N-bis[2-(1,2-dicarboxyethoxy)ethyl] glycine, N-bis[2-(1,2-dicarboxyethoxy)ethyl] aspartic acid, and N-tris[(1,2-dicarboxyethoxy)ethyl] amine with La^{3+} in aqueous 0.1 M NaCl solution was studied [27]. The capability of these ligands to chelate La^{3+} caused solvable problems in the synthesis. Although the first motive for lanthanum studies was to find the reason for problems in the synthesis, another result from our previous studies on lanthanum complexation was that, on the other hand, this chelating property can be utilized in applications for which strong La^{3+} binding is essential [27]. This has led to studies on the complexation of La^{3+} ion with the other environmentally friendly ligands IDS, HIDS, EDDS, and ODS to find out if also their complexation capability could be strong enough for applications. Although ODS has not been reported to be readily biodegradable, it was included in studies for comparison as a nitrogen free ligand suggestive of IDS.

We have widened our complexation studies on the environmentally friendly chelating agents and report here on the aqueous complexation with La^{3+} for IDS, HIDS, EDDS, and ODS to obtain information on their respective potentials as biodegradable chelators and to increase our understanding of their complexation behavior in terms of basic research as well as applications.



2. Experimental

2.1. Reagents: ligands, stock solution of metal ion, and titration solutions

IDS, ODS, and EDDS were produced by Kemira Finland and HIDS was produced by Nippon Shokubai Japan. ODS was prepared in its acid form and the other ligands as their sodium salts. Aqueous La^{3+} solution was prepared by dissolving p.a. grade $\text{La}(\text{NO}_3)_3$ hydrate in distilled water. The metal content of the stock solution 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). 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} 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 measurement of the hydrogen ion concentration $[\text{H}^+]$ was as follows:

$$-\text{RE} | \text{equilibrium solution} | \text{GE} + \quad (1)$$

where RE is Hg, $\text{Hg}_2\text{Cl}_2 || 0.1 \text{ mol L}^{-1}$ NaCl, and GE denotes a glass electrode, Schott N2680. Expression (2) is valid assuming the activity coefficients to be constant.

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

The cell parameter E_0 and the liquid junction coefficient j_{H} , which is valid in acidic solutions, were determined for each titration by addition of known amounts of HCl to the background electrolyte. The value of the liquid junction coefficient j_{OH} , which is valid in basic solutions, was determined periodically. Only stable emf readings were used in the calculations.

Aqueous 0.1 mol L^{-1} NaOH or 0.1 mol L^{-1} HCl was added to the solution during measurements of the metal complex equilibria. 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 $0.4 \text{ mmol L}^{-1} \leq C_{\text{M}} \leq 2.8 \text{ mmol L}^{-1}$ and $0.9 \text{ mmol L}^{-1} \leq C_{\text{L}} \leq 3.5 \text{ mmol L}^{-1}$, covering metal-to-ligand ratios from 2:1 to 1:5. Five to nine independent titrations were carried out for each system. The number of data points used in the calculation of the stability constants varied from 316 to 464 over the pH ranges of 2.2–10.9 for IDS, 2.1–10.8 for HIDS, 2.5–11.0 for EDDS, and 2.1–11.1 for ODS. The reproducibility and reversibility of the equilibria were tested by performing forward (increasing pH) and backward (decreasing pH) titrations.

2.3. Data treatment

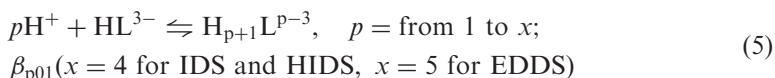
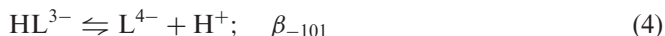
Protonation and deprotonation of the ligands were controlled by addition of HCl or NaOH. Curves of Z_{H} versus pH were drawn to visualize the experimental data sets. Z_{H} describes the average number of H^+ ions added or liberated per mole of ligand and is given by the equation

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

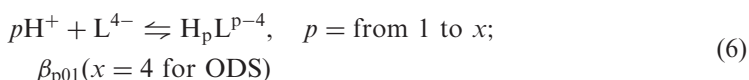
where C_{H} denotes the total concentration of protons calculated over the zero level HL^{3-} for IDS, HIDS, and EDDS and zero level L^{4-} for ODS. When an alkaline ligand solution was titrated against aqueous HCl or an acidic ligand solution was titrated against aqueous NaOH, there was an easily detected inflection point at pH 7. At that pH, the major species is HL^{3-} for IDS, HIDS, and EDDS and L^{4-} for ODS. Thus data were analyzed by using HL^{3-} as the zero level for the ligands IDS, HIDS, and EDDS

and L^{4-} for ODS. By this choice of the zero level in the calculations the accumulation of errors of protonation constants in different pH ranges could be avoided.

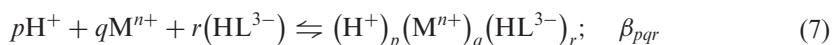
In evaluating the equilibrium constants, the following two-component equilibria were considered for IDS, HIDS, and EDDS



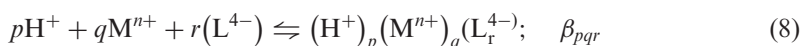
and for ODS



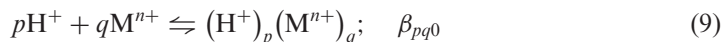
Metal complex-formation can be characterized by the general three-component equilibria for IDS, HIDS, and EDDS



and for ODS



The hydrolysis of metal ion can be written as



Protonation constants of the ligands and the hydrolysis constants of the metal ion [44] were considered as known parameters in evaluation of the three-component system (7 or 8).

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 run on the computer program SUPERQUAD [45]. 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. The error limits for $\log \beta$ values determined in this study are reported as three standard deviations given by the program in order to improve the confidence level.

3. Results and discussion

3.1. Protolytic properties of IDS, HIDS, EDDS, and ODS

Neutralization titrations for IDS and HIDS show that stepwise deprotonation of carboxylic acid groups from H_5L^+ to HL^{3-} occurs in the pH range from acidic to neutral (Z_H from 4 to 0, see figure 1, the curves for ligands alone) and for ODS from H_4L to L^{4-} , which is a major species for ODS when pH is over 7. The major species from pH 6 to 9 for IDS and HIDS is HL^{3-} when $Z_H = 0$. The negative Z_H values obtained for IDS and HIDS in the pH range from neutral to 11 show that in alkaline

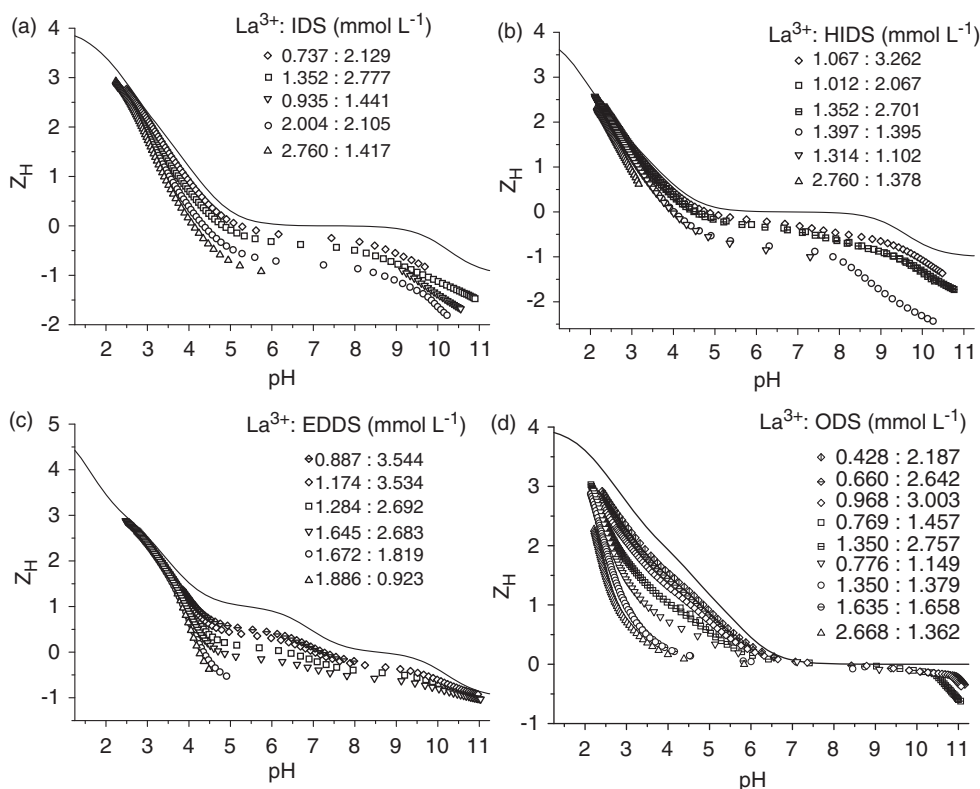


Figure 1. Z_H vs. pH for complexation of La^{3+} with (a) IDS, (b) HIDS, (c) EDDS, and ODS (d) (Z_H vs. pH for ligands = solid line).

solution one proton (from the amino nitrogen, HL^{3-} to L^{4-}) can leave the ligands (figure 1, the curves for ligands alone). Stepwise deprotonation of carboxylic acid groups from H_6L^{2+} to H_2L^{2-} for EDDS occurs in the acidic pH range up to 4 (Z_H from 5 to 1). The major species from about pH 4 to 7 is H_2L^{2-} ($Z_H = 1$) and from about pH 7 to 10 is HL^{3-} ($Z_H = 0$, proton is leaving the first amino nitrogen). The negative Z_H values obtained in the pH range from 10 up to about 11 show that in an alkaline solution another 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) or (6) obtained in the final refinements are listed in table 1. The results correspond with those of earlier studies on the protonation of IDS [26], EDDS [25], and ODS [41]. The protonation of HIDS was obtained from literature [31]. The protonation of IDS, HIDS, EDDS and ODS is rewritten in the form given in table 2 for comparison with EDTA and DTPA [46].

3.2. Complexation with La^{3+} ion

Analysis of the data was initiated by drawing curves of Z_H versus pH (figure 1). In all systems, where the zero level is HL^{3-} (IDS, HIDS, and EDDS), Z_H reaches a value of -1 and in the case of ODS (zero level L^{4-}) Z_H reaches a value of 0 with increasing pH,

Table 1. Protonation and complex formation of IDS, HIDS, EDDS, and ODS with La^{3+} in aqueous 0.1 M NaCl at 25°C.

pqr	IDS, HL^{3-} $\log(\beta_{pqr} \pm 3\sigma)$	HIDS, HL^{3-} $\log(\beta_{pqr} \pm 3\sigma)$	EDDS, HL^{3-} $\log(\beta_{pqr} \pm 3\sigma)$	Formula (IDS, HIDS, EDDS)	ODS, L^{4-} $\log(\beta_{pqr} \pm 3\sigma)$	Formula (ODS)
H^+		[31]				
-101	-10.26 ± 0.02	-9.60 ± 0.01	-10.22 ± 0.02	L^{4-}		
101	4.58 ± 0.02	4.06 ± 0.01	6.93 ± 0.01	H_2L^{2-}	5.87 ± 0.03	HL^{3-}
201	8.33 ± 0.02	7.10 ± 0.01	10.81 ± 0.02	H_3L^-	10.46 ± 0.03	H_2L^{2-}
301	11.14 ± 0.03	9.19 ± 0.03	13.93 ± 0.02	H_4L	13.67 ± 0.03	H_3L^-
401	13.16 ± 0.03	10.78 ± 0.06	15.70 ± 0.03	H_5L^+	15.93 ± 0.04	H_4L
501			17.13 ± 0.07	H_6L^{2+}		
χ^2/S	20.01/1.53	40.33/1.61	10.53/1.21		11.63/1.11	
Points/titrations	330/3	289/4	395/6		167/4	
La^{3+}						
-311	-21.01 ± 0.16	-20.49 ± 0.12		$\text{La}(\text{OH})_2\text{L}^{3-}$		
-211	-10.13 ± 0.09	-10.03 ± 0.11	-9.76 ± 0.12	$\text{La}(\text{OH})\text{L}^{2-}$	-12.97 ± 0.06	$\text{La}(\text{OH})_2\text{L}^{3-}$
-111	-0.30 ± 0.05	-1.21 ± 0.10	1.99 ± 0.03	LaL^-	-1.89 ± 0.12	$\text{La}(\text{OH})\text{L}^{2-}$
011	4.56 ± 0.04	3.71 ± 0.09	6.07 ± 0.07	LaHL	8.91 ± 0.02	LaL^-
111	8.04 ± 0.04	7.13 ± 0.04	10.05 ± 0.05	LaH_2L^+	12.13 ± 0.02	LaHL
211	10.87 ± 0.11		13.32 ± 0.10	$\text{LaH}_3\text{L}^{2+}$		
-312	-16.39 ± 0.13			$\text{La}(\text{OH})\text{L}_2^{6-}$		
-212	-6.27 ± 0.13	-6.71 ± 0.14		LaL_2^{2+}		
012			11.28 ± 0.12	$\text{La}(\text{HL})_2^{5-}$		
-121	2.81 ± 0.16	3.66 ± 0.09		La_2L^{2+}		
χ^2/S	25.62/1.80	22.63/2.05	35.31/1.67		40.48/2.04	
Points/titrations	316/5	461/6	357/6		464/9	

Protonation of HIDS from ref. [31].

Table 2. Protonation and complex formation of IDS, HIDS, EDDS, and ODS with La^{3+} in aqueous 0.1 mol L⁻¹ NaCl ($\mu=0.1$) at 25°C compared to corresponding values of EDTA and DTPA. Charges are omitted for clarity.

Reaction	IDS H_4L	HIDS H_4L	EDDS H_4L	ODS H_4L	EDTA H_4L	DTPA H_5L
Protonation		[31]			[46]	[46]
$\text{L} + \text{H} \rightleftharpoons \text{HL}$	10.26	9.60	10.22	5.87	9.52–10.37	9.90–10.79
$\text{HL} + \text{H} \rightleftharpoons \text{H}_2\text{L}$	4.58	4.06	6.93	4.59	6.13	8.40–8.60
$\text{H}_2\text{L} + \text{H} \rightleftharpoons \text{H}_3\text{L}$	3.75	3.04	3.88	3.21	2.69	4.28
$\text{H}_3\text{L} + \text{H} \rightleftharpoons \text{H}_4\text{L}$	2.81	2.09	3.12	2.26	2.00	2.70
$\text{H}_4\text{L} + \text{H} \rightleftharpoons \text{H}_5\text{L}$	2.02	1.59	1.77		(1.5)	2.0
$\text{H}_5\text{L} + \text{H} \rightleftharpoons \text{H}_6\text{L}$			1.43		(0.0) ^a	(1.6)
$\text{H}_6\text{L} + \text{H} \rightleftharpoons \text{H}_7\text{L}$						(0.7)
$\text{H}_7\text{L} + \text{H} \rightleftharpoons \text{H}_8\text{L}$						(-0.1)
Complexation, $\text{M} = \text{La}^{3+}$					[46]	[46]
$\text{M}(\text{OH})_2\text{L} + \text{H} \rightleftharpoons \text{M}(\text{OH})\text{L}$	10.88	10.46		11.08		
$\text{M}(\text{OH})\text{L} + \text{H} \rightleftharpoons \text{ML}$	9.83	8.82	11.75	10.80		
$\text{M} + \text{L} \rightleftharpoons \text{ML}$	9.96	8.39	12.21	8.91	15.36	19.49
$\text{ML} + \text{H} \rightleftharpoons \text{MHL}$	4.86	4.92	4.08	3.22	2.24	2.60 ^b
$\text{MHL} + \text{H} \rightleftharpoons \text{MH}_2\text{L}$	3.48	3.42	3.98			
$\text{MH}_2\text{L} + \text{H} \rightleftharpoons \text{MH}_3\text{L}$	2.83		3.27			
$\text{M}(\text{OH})\text{L}_2 + \text{H} \rightleftharpoons \text{ML}_2$	10.12					
$\text{ML} + \text{L} \rightleftharpoons \text{ML}_2$	4.29	4.10				
$\text{MHL} + \text{HL} \rightleftharpoons \text{M}(\text{HL})_2$			5.21			
$\text{ML} + \text{M} \rightleftharpoons \text{M}_2\text{L}$	3.11	4.87				

^a $\mu = 1.0$.^b20°C, protonation of HIDS [31], protonation and complexation of EDTA and DTPA [46].

indicating coordination of ligands to metal in the form of L^{4-} . In all systems, LaL^- is the dominant species formed. Z_H values lower than -1 for IDS, HIDS, and EDDS and lower than 0 for ODS were obtained, indicating the presence of hydroxo complex species, $La(OH)L^{2-}$. This species begins to form at pH 8 for IDS, HIDS, and ODS, but not until pH 10 for EDDS. The Z_H values still continue to decrease for IDS, HIDS, and ODS and $La(OH)_2L^{3-}$ was also found for these ligands. Formation of the acidic species $LaHL$ was found for all ligands, LaH_2L^+ for IDS, HIDS, and EDDS and LaH_3L^{2+} for IDS and EDDS. As expected aqueous complexation of the polydentate ligands can be characterized in terms of formation of stable mononuclear 1:1 metal-to-ligand complexes as the major species. The complexation model for IDS and HIDS was complemented by the binuclear species La_2L^{2+} and by the bis complex LaL_2^{2+} . Moreover, the bis complex species $La(OH)L_2^{6-}$ was found for IDS. The complexation model for EDDS was complemented by the bis complex species $La(HL)_2^{5-}$. That kind of species has been found in earlier studies for EDDS also with Mn^{2+} , Cu^{2+} , and Zn^{2+} ions [25]. Table 1 shows the proposed formulas of the species, with the corresponding formation constants from equations (7) or (8) found in equilibrium analysis of the different $H^+ - La^{3+} - HL^3/L^{4-}$ systems. Comparison with the findings of earlier studies carried out with EDTA and DTPA [46] was facilitated by expressing the complexation of IDS, HIDS, EDDS, and ODS with La^{3+} in the form given in table 2.

Stability of the major LaL^- complex species follows the order of $\log K_{ML}$ values: EDDS (12.21) > IDS (9.96) > ODS (8.91) > HIDS (8.39). Nitrogen is usually considered to be a strong donor, as can be seen in the case of EDDS, EDTA, and DTPA, each of which have several nitrogens. However, it is noteworthy that the stability of LaL^- for ODS is somewhat higher than for HIDS and only one logarithm unit lower than for IDS. The absence of nitrogen atoms in ODS seems not to create any significant disadvantage for the large oxygen donor favoring La^{3+} ion.

The dominance of LaL^- 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 metal 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, HIDS, EDDS, and ODS are effective chelating agents for La^{3+} ion (100% of the metal is bound to the complexes) over the following pH ranges: HIDS 8–12, IDS 7–12, EDDS 6–12, and ODS 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 ligands and for ODS also in the basic region.

In industrial applications, complexation efficiency is commonly estimated by using conditional stability constants. The conditional stability constant, $\log K'_{ML}$, for the major complex species ML^{n-x} is given by equation (10)

$$K'_{ML} = \frac{\alpha_{ML}}{\alpha_M \cdot \alpha_L} \cdot K_{ML} \quad (10)$$

where the side-reaction coefficients α_M , α_L , and α_{ML} are defined as in equations (11), (12), and (13) and K_{ML} as in equation (14):

$$\alpha_M = \frac{\Sigma(H^+)_p (M^{n+})_q}{[M^{n+}]} \quad (11)$$

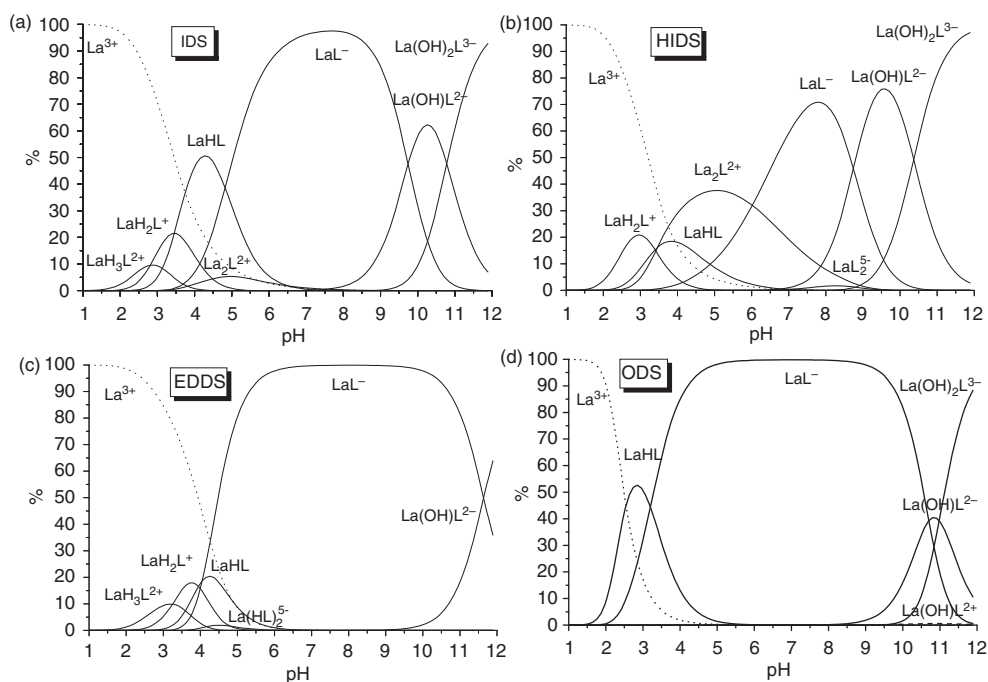


Figure 2. Percentage distribution of the different La³⁺ complexes of (a) IDS, (b) HIDS, (c) EDDS, and ODS (d) as a function of pH ($C_M = C_L = 1 \text{ mmol L}^{-1}$).

$$\alpha_L = \frac{\Sigma(H^+)_p(L^{x-})}{[L^{x-}]} \quad (12)$$

$$\alpha_{ML} = \frac{\Sigma(H^+)_p(M^{n+})(L^{x-})_r}{[ML^{n-x}]} \quad (13)$$

$$K_{ML} = K(M^{n+} + L^{x-} \rightleftharpoons ML^{n-x}) \quad (14)$$

Values of the conditional stability constants for the complexes of IDS, HIDS, EDDS, and ODS with La³⁺, as calculated with the aid of the protonation and equilibrium constants determined in this study (protonation of HIDS [31]) and the binary hydrolysis constant of La³⁺ from reference [44], vary as a function of pH as shown in figure 3. The values of $\log K'_{ML} \geq 6$ are often considered as a criterion for efficient complexation. On this assumption, the approximate pH ranges suitable for use of IDS, HIDS, EDDS, and ODS as an efficient chelating agent for the La³⁺ are about the same as estimated from the percentage distribution curves in the millimolar concentration range. Conditional stability constants *versus* pH for EDTA and DTPA [44, 46] were added to figure 3 for comparison. The suitable pH range for EDTA and DTPA commences earlier in the acidic pH area by 1–4 pH units as compared with IDS, HIDS, EDDS, and ODS.

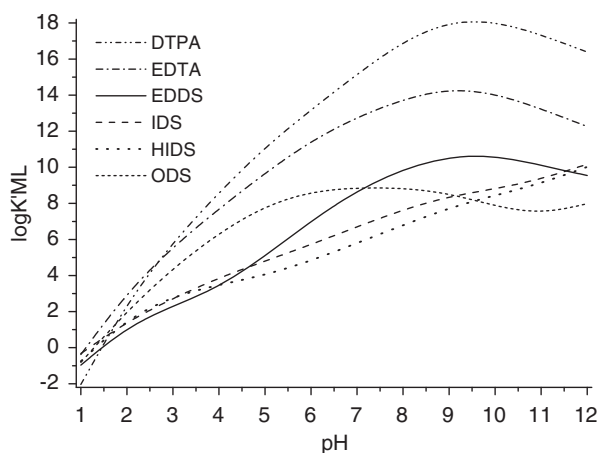


Figure 3. Conditional stability constants for ML complexes of IDS, HIDS, EDDS, ODS, EDTA, and DTPA with La^{3+} ions as a function of pH.

4. Conclusion

Stabilities of the La^{3+} chelates of IDS, HIDS, EDDS, and ODS are somewhat lower than those of EDTA and DTPA. The suitable pH range is also narrower for IDS, HIDS, EDDS, and ODS than for EDTA and DTPA. On the other hand, IDS, HIDS, and EDDS show better biodegradability characteristics [47–52] and EDDS has better photo-degradability than EDTA and DTPA [53] (IDS has been evaluated by OECD 301F and ISO 9439 tests, HIDS by modified MITI (II) method, EDDS by OECD 301B and ISO 9439 tests). IDS and HIDS have lower nitrogen contents than EDTA and DTPA, EDDS has a lower nitrogen content compared to DTPA and ODS is a nitrogen-free ligand. These factors make them less harmful to the environment than EDTA or DTPA. Results of the present study suggest that the complexation efficiencies of IDS, HIDS, EDDS, and ODS are strong enough for them to be utilized as alternative ligands in applications for which La^{3+} binding is essential and a suitable pH range can be used. When comparing the stability constants of lanthanide complexes of DTPA, EDTA, and EDDS, it appears that ML complexes of DTPA have similar stabilities regardless of the size of the lanthanide cation, while the stability of EDTA and EDDS complexes increases with increasing atomic number along the lanthanide series [46, 54]. The studies on the complexation of the other biodegradable chelators with the series of lanthanide ions, which are also used in industrial applications, will be a subject for further studies.

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