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Stability constants of Fe(III) and Cr(III) complexes with DL-2-(2-carboxymethyl)nitrilotriacetic acid (GLDA) and 3-hydroxy-2,2´-iminodisuccinic acid (HIDS) in aqueous solution

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Abstract

The complex formation equilibria of Cr^{3+} and Fe^{3+} ions in aqueous solution with two biodegradable aminopolycarboxylate chelants (DL-2-(2-carboxymethyl)nitrilotriacetic acid (GLDA) and 3-hydroxy-2,2´-iminodisuccinic acid (HIDS)) were investigated. The potentiometric data obtained at the constant ionic strengths (I) of 0.1 and 1.0 $mol\cdot dm^{-3}$ KCl and at 25 ± 0.1°C was processed with the aid of the computer program HYPERQUAD 2008. The formation constants of the proton-chelant and metal-chelant ($\log K_{ML}$) species (M = Fe^{3+} or Cr^{3+}; L = GLDA or HIDS) were determined, and the concentration distributions of complex species in solution were evaluated for both metal ions. In various pH conditions, the interaction between the chelants (L = GLDA or HIDS) and the metal ions (M = Fe^{3+} or Cr^{3+}) leads to the formation of different complexes formulated as MH_2L^+, MHL, ML^-, $M(OH)L^{2-}$ and $M(OH)_2L^{3-}$. The $\log K_{ML}$ values at I = 0.1 $mol\cdot dm^{-3}$ KCl (T = 25 ± 0.1°C) were 15.27 ($\log K_{Fe\text{–}GLDA}$), 14.96 ($\log K_{Fe\text{–}HIDS}$), 13.77 ($\log K_{Cr\text{–}GLDA}$), 12.67 ($\log K_{Cr\text{–}HIDS}$), and at I = 1.0 $mol\cdot dm^{-3}$ KCl (T = 25 ± 0.1°C) were 14.79 ($\log K_{Fe\text{–}GLDA}$), 14.34 ($\log K_{Fe\text{–}HIDS}$), 12.90 ($\log K_{Cr\text{–}GLDA}$), 12.09 ($\log K_{Cr\text{–}HIDS}$). The conditional stability constants ($\log K'_{ML}$) of the ML complexes were calculated in terms of pH in the range of 2–12, and compared with the same for EDTA and other biodegradable chelants (NTA and EDDS).

Keywords: stability constant; biodegradable aminopolycarboxylate chelant; GLDA; HIDS; chromium(III), iron(III).

1.0 Introduction

Extractant-assisted industrial process designs,[1, 2] or the contaminated waste treatment operations[3, 4] are frequently using aminopolycarboxylate chelants (APCs) as the solvents. The ability of the APCs of forming stable and water-soluble metal complexes makes them a unique choice as the cleaning solution ingredient for inhibiting the interfering metal ions from playing their normal chemical roles.[5] Among the APCs, ethylenediaminetetraacetic acid (EDTA) is commonly utilized for its capability to form water-soluble complexes having marked stability with the majority of toxic metal ions.[2] Although cheap and convenient, the major drawback of using APCs as the extractant is the related environmental consequences upon release into the surroundings.[6] APCs exposure initiates remobilization of metal ions from soils and sediments in the aquatic environments,[2] and may intensify the threshold values of the corresponding toxic effects in some cases.[7] APCs are also blamed for enhancing eutrophication through raising the total nitrogen content and phosphate solubility in interstitial waters,[8] and their prolonged persistency owing to their poor photo–, chemo– and biodegradability.[9, 10] The eco-safety has been and continues to be an issue of concern, and increasingly stringent legislative regulations have been proposed or imposed to control the discharge of APCs in the environment.[11] Researchers are focused extensively either on the treatment and recovery of APCs from the treated wastewater[12-16] or, more recently, search for the replacement of the environmentally unsafe classical APCs with the eco-friendly biodegradable APC variants.[3, 17, 18] The usefulness of the newly developed eco-friendly chelants for specific applications can be critically evaluated based on their complexation behavior.[19, 20]

Metal pollution of soils derived from numerous anthropogenic activities, including agricultural practices, industrial activities and waste disposal is a global concern.[4, 21] Nitrilotriacetic acid (NTA), iminodisuccinic acid (IDSA), [S,S]-ethylenediaminedisuccinic acid (EDDS) and methylglycine diacetic acid (MGDA) have been proposed as the biodegradable replacement for EDTA for the remediation of metal-contaminated soils,[17, 22] and the formation and stability data of their corresponding proton-chelant and metal-chelant complexes are available.[23] Our research group is particularly interested in the usage of biodegradable APCs for in-situ or ex-situ decontamination of the soil contaminated with toxic metal ions, and we have introduced two commercially available APCs, DL-2-(2-carboxymethyl)nitrilotriacetic acid (GLDA) and 3-hydroxy-2,2´-iminodisuccinic acid (HIDS) (Figure 1), for the application in the aforementioned purpose.[3] Superior biodegradable characteristics relative to EDTA of both the chelants, GLDA[24] and HIDS,[25] have been claimed. The complexation data of these chelants have not been reported in the NIST standard reference database of critically selected stability constants of metal complexes,[23] while such fundamental fact is obligatory for considering the new biodegradable chelants in any chelant-based clean-up practices. Previously, we have reported the complexation characteristics of GLDA and HIDS with the divalent ecotoxic ions (Ni, Cu, Zn, Cd, and Pb) at the ionic strength (*I*) of 0.1 $\mathrm{mol \cdot dm^{-3}}$ and at 25 ± 0.1°C in aqueous solutions.[26] As a continuation to our ongoing study, we are reporting the same for two trivalent metal ions, chromium and iron, with GLDA and HIDS at two different ionic strengths (*I*) of 0.1 and 1.0 $\mathrm{mol \cdot dm^{-3}}$ maintaining the same temperature condition.

Chromium is one of the 100 most dangerous toxic substances as mentioned in the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA).[27] It is found in many metal-contaminated sites besides other toxic ions[28, 29] and, more precisely, in the soils that have been contaminated with electroplating wastes.[30] In accordance with the toxicity characteristic leaching procedure (TCLP), the concentration of chromium in soil leachates should not exceed 5 ppm.[27] Iron is one of the major cations that co-exists with the toxic metals in soil solid phase, competes with the toxic metals for the chelants and simultaneously extracted.[31, 32] The objective of the current study was to provide supporting information for designing eco-friendly processes for solid waste management using GLDA or HIDS. The outcome is the stability information of the binary and ternary complexes of GLDA and HIDS with Cr(III) and Fe(III), which have not been reported before.

2.0 Experimental Section

2.1 Instrumentation

Potentiometric measurements were carried out using a KEM AT-610 automatic titrator (Kyoto Electronics, Kyoto, Japan), equipped with a pH-combination electrode and a temperature probe. The electrode system was calibrated using standard buffer solutions (pH 4.0, 7.0 and 9.0) prepared from buffer powders (Horiba, Kyoto, Japan) before and after each series of pH measurements at 25 ± 0.1°C. It is worth to be noted that this calibration process is a part of the instrument maintenance protocol as recommended by the manufacturers, and the results are not used in the calculations.

The titration vessels (100 cm^3) were emerged into a water-jacket type thermostat connected to the water circulation system Eyela CCA-1111 (Tokyo Rikakakai, Tokyo, Japan), and a constant temperature condition (25 ± 0.1°C) was maintained. Magnetic stirring was employed during the titration as included within the titration vessel assembly. A special cover containing inlets for the electrode, temperature probe, and dosing nozzle for the titrator, in addition to a nitrogen gas inlet and outlet was used as a seal of the vessel. A stream of purified nitrogen gas was flowed through all the solutions and during the titrations in order to eliminate the ingress of CO_2 or O_2 and maintain an inert atmosphere.

An automated TOSOH 8020 high-performance liquid chromatography system (Tosoh, Tokyo, Japan) were used to validate the GLDA and HIDS concentrations. The ultrapure water (resistivity >18.2 MΩ·cm) that used throughout the experiments were obtained from the Arium® Pro water purification system (Sartorius Stedim Biotech GmbH, Göttingen, Germany).

2.2 Chemicals

Aqueous solutions of the sodium salt of GLDA (wt = 40%) (AkzoNobel, Amsterdam, Netherlands) and HIDS (wt = 51.5%) (Nippon Shukubai, Tokyo, Japan) were used. Both the products are commercially available and were used without any additional treatment.

All the other chemicals and solvents were of analytical reagent grade. Potassium hydrogen phthalate (Wako Pure Chemical, Osaka, Japan) was used to standardize potassium hydroxide (Carbonate-free; Kanto Chemical, Tokyo, Japan) potentiometrically. A pre-standardized hydrochloric acid (Kanto Chemical, Tokyo, Japan) solution was used. The ionic strength of the system was adjusted using the potassium chloride (Wako Pure Chemical, Osaka, Japan; >0.99 mass fraction purity). Titrisol® ampoules of chromium and iron (Merck KGaA, Darmstadt, Germany) were used to prepare the stock solutions of metals.

The working solutions were prepared from the stock solutions with ‘CO_2-free’ water, which was prepared through the boiling and cooling of the ultrapure water using a stream of nitrogen.

2.3 Procedure

Aqueous solutions (A–D) of 50 cm^3 (total volume) were titrated with 0.1 $mol\cdot dm^{-3}$ carbonate-free KOH at 25 ± 0.1°C. Solutions of two different ionic strengths (0.1 and 1.0 $mol\cdot dm^{-3}$) were used, and the conditions were maintained constant by the addition of an appropriate amount solid KCl.

Solution A: HCl (8×10^{-3} $mol\cdot dm^{-3}$) + GLDA (1.0×10^{-3} $mol\cdot dm^{-3}$)

Solution B: HCl (8×10^{-3} $mol\cdot dm^{-3}$) + GLDA (1.0×10^{-3} $mol\cdot dm^{-3}$) + M(III) ions (Cr^{3+} or Fe^{3+}) (1.0×10^{-3} $mol\cdot dm^{-3}$)

Solution C: HCl (8×10^{-3} $mol\cdot dm^{-3}$) + HIDS (1.0×10^{-3} $mol\cdot dm^{-3}$)

Solution D: HCl (8×10^{-3} $mol\cdot dm^{-3}$) + HIDS (1.0×10^{-3} $mol\cdot dm^{-3}$) + M(III) ions (Cr^{3+} or Fe^{3+}) (1.0×10^{-3} $mol\cdot dm^{-3}$)

It should be noted that the formation rate of Cr(III)-chelant complexes at room-temperature is known to be low because of the inertness of the Cr(III) ion, which create difficulties in determining the equilibria in aqueous solutions.[33, 34] The slow interaction problem between the Cr(III) and chelants can be minimized either by refluxing the reaction mixture for 10 to 20 min[35] or by aging the solution mixtures at a certain temperature.[36] We have followed the aging process to ensure the formation of Cr(III) complexonates. The mixtures of Cr(III) and the chelants (GLDA or HIDS) at different molar ratios were aged for

45 days at 25 ± 0.1°C before subjecting to the potentiometric measurements. There was no such observation reported for the complexation behavior of Fe(III) with the chelants.

Prior to the titration, each solution was allowed to stand for at least 30 minutes at 25 ± 0.1°C. A constant volume increment at pre-fixed intervals was set in the auto-titrator operating software, and a real-time titration curve was obtained from the recorded data. At least, three replicates of each titration and more than 100 points of potentiometric measurements were used for data analysis.

2.4 Calculation

The results of strong acid-strong base titrations were used for the calculations of the concentration of the base, the percent of carbonate contamination, the pK_w value (pK_w = 13.78, I = 0.1 mol·dm^{-3}; pK_w = 13.75, I = 1.0 mol·dm^{-3} at 25 ± 0.1°C), electrode potential (E^0) and slope factor (S) with the computer program GLEE[37] before and after each of the titrations. The experimental conditions, *e.g.* temperature, ionic strength and ionic medium, were maintained same as the solution under study. Prior to the real titrations, the titration conditions were simulated with the HySS2009 program.[38] The protonation and metal-chelant stability constants were calculated by analyzing the potentiometric data using the HYPERQUAD 2008 program.[39] The visual interpretation of the refinement process was obtained by the HYPERQUAD program in addition to the best fit for the titration data.

3.0 Results and Discussion

3.1 Protonation constants

Potentiometric pH profiles of the GLDA- and HIDS-fortified aqueous solutions in the absence of metal ions were used to compute the protonation constants of GLDA and HIDS. The raw data-sets were treated with the non-linear least-squares refinement program HYPERQUAD 2008, wherein the weights of the titrant are the independent variables and the pH values are the dependent variables. The total amount of substance present initially in the titration vessel is specified in millimoles, the volume in cm^3 and the species' concentrations is in mol·dm^{-3}. The total amount of protons is the sum of the amount present in any protonated ligand that is initially present in the titration vessel plus whatever mineral acid has also been added. The unit of burette concentration is mol·dm^{-3} and hydroxide is entered with a negative sign. The product of burette concentration and titre volume is expressed in the units of millimoles.

The following relationship shows the proton-chelant (HL; L = GLDA or HIDS) constants for the overall reaction, β_n:

$$\beta_n = K_{a1} \cdot K_{a2} \cdots K_n = \frac{[\mathrm{H}_n\mathrm{L}]}{[\mathrm{H}]^n[\mathrm{L}]} \qquad (1)$$

where K_{a1}, K_{a2}….K_n define the stepwise acid dissociation constants.

The overall (logβ_{pqr}) and successive (log$K$) protonation constants of GLDA and HIDS were calculated with the HYPERQUAD program and listed in Tables 1 and 5. The symbols p, q and r were used as the coefficients for metal ions, protons and chelants to designate the stoichiometry associated with the possible equilibria in solution.

The percentage distribution of the various protonation stages of GLDA and HIDS at 25 ± 0.1°C in the aqueous medium at I = 1.0 mol·dm^{-3} is provided in Figure 2, while the same at I = 0.1 mol·dm^{-3} were reported elsewhere.[26] The species distribution curves of GLDA and HIDS (Figure 2) showed the occurrence of the first protonation of L^{4-} to HL^{3-} at the amino nitrogen atoms in the alkaline conditions. The HL^{3-} remains as the dominant species at pH 5.5–8.5 for HIDS (90–99.5%) and pH 6.0–8.4 (90–98.5%) for GLDA (I = 0.1 mol·dm^{-3})[26] or at pH 4.7–8.3 for HIDS (90–99.2%) and pH 6.0–8.1 (90–97.8%) for GLDA (I = 1.0 mol·dm^{-3}). In the range of neutral to acidic pH, the next protonations of GLDA (H_2L^{2-} to H_4L) and HIDS (H_2L^{2-} to H_5L^+) occur at the oxygen atoms of the carboxylate groups. The association of the last proton in GLDA occurs at pH ~2, the lowest pH limit used for calculation, and, hence, excluded from the consideration. The predicted schemes of the protonation equilibria of GLDA and HIDS are shown in Figures 3 and 4.

The log$K$ data of GLDA at I = 0.1 mol·dm^{-3} (25 ± 0.1°C) were reported in the NIST database [23], and shown in the parentheses of Table 5. There are no Log$K$ data for GLDA at I

= 1.0 mol·dm^{-3} and HIDS at I = 0.1 and 1.0 mol·dm^{-3}, and at 25 ± 0.1°C in the standard NIST database.

3.2 Metal-chelant stability constants

The overall formation constants (logβ_{pqr}) for the systems containing the metal ion (M = Fe^{3+} or Cr^{3+}) and chelant (L = GLDA or HIDS) were computed from the potentiometric titration data (Tables 2 and 3). The hydrolytic behavior of each metal species was taken into account when calculating the ML stability constants. The following general equation can represent the overall reaction:

$$p\mathrm{M} + q\mathrm{H} + r\mathrm{L} \Leftrightarrow \mathrm{M}_p\mathrm{H}_q\mathrm{L}_r \qquad \beta_{pqr} = \frac{[\mathrm{M}_p\mathrm{H}_q\mathrm{L}_r]}{[M]^p[H]^q[L]^r} \tag{2}$$

where p, q and r are the coefficients for metal ions, protons and chelants, respectively, which indicate the stoichiometry associated with the possible equilibria in solution.

The differences between the logβ values were used to calculate the stepwise formation constant (log$K$) for each of the species of GLDA and HIDS (Table 5), and compared with those reported for NTA, EDDS and EDTA in the NIST database.[23] In any ML systems, the equations (3)–(5) describe the stepwise formation equilibria while the equations (6)–(7) define the additional deprotonation reactions involving the coordination of water molecules:

$$\mathrm{M} + \mathrm{L} \Leftrightarrow \mathrm{ML} \qquad K_{\mathrm{ML}} = \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]} \tag{3}$$

$$\mathrm{ML} + \mathrm{H} \Leftrightarrow \mathrm{MHL} \qquad K_{\mathrm{MHL}}^{\mathrm{H}} = \frac{[\mathrm{MHL}]}{[\mathrm{ML}][\mathrm{H}]} \tag{4}$$

$$\mathrm{MHL} + \mathrm{H} \Leftrightarrow \mathrm{MH_2L} \qquad K_{\mathrm{MH_2L}}^{\mathrm{H}} = \frac{[\mathrm{MH_2L}]}{[\mathrm{MHL}][\mathrm{H}]} \tag{5}$$

$$\mathrm{ML(H_2O)} \Leftrightarrow \mathrm{M(OH)L} + \mathrm{H} \qquad K_{\mathrm{M(OH)L}} = \frac{[\mathrm{M(OH)L}][\mathrm{H}]}{[\mathrm{ML(H_2O)}]} \tag{6}$$

$$\mathrm{ML(OH)} \Leftrightarrow \mathrm{M(OH)_2L} + \mathrm{H} \qquad K_{\mathrm{M(OH)_2L}} = \frac{[\mathrm{M(OH)_2L}][\mathrm{H}]}{[\mathrm{ML(OH)}]} \tag{7}$$

The stoichiometries and stability constants of the binary and ternary ML complexes (M = Fe^{3+} or Cr^{3+}; L = GLDA or HIDS) were determined from a composition model that was consistent with the titration data, made sense from a chemical point of view, and offered a better statistical fit in comparison with other possible compositions.

The distributions of the actual metal-chelant species in the aqueous systems at varying equilibrium conditions are controlled by the solution pH, and regulate the corresponding bioavailability, physiological and toxicological behavior of the metals.[40] The pH dependent species distribution curves drawn in the range of pH 2.0 to 11 for each ionic strength (I = 0.1 and 1.0 mol·dm^{-3}) were shown in the Figure 5. For each of the ionic strengths, the complexation were observed to start from the initial pH ~2.0 with the formation of MH_2L^+ in the Fe(III)–HIDS, Cr(III)–GLDA and Cr(III)–HIDS systems, while it was from pH ~3.0 for the Fe(III)–GLDA systems. The first species MH_2L^+ was expected to form by the coordination of weakly basic imine nitrogen atom and the deprotonated carboxylic group in GLDA or the hydroxyl group in HIDS, where the four remaining coordination sites of the metal ions may be occupied by the water molecules. As the pH increases, coordinated water molecules are replaced by the deprotonated carboxylic groups in GLDA or HIDS which leads to the formation of the MHL, ML^-, $M(OH)L^{2-}$ and $M(OH)_2L^{3-}$complexes (M = Fe^{3+} or Cr^{3+}; L = GLDA or HIDS).

In the titration curves obtained for the ML systems (M = Fe^{3+} or Cr^{3+}; L = GLDA or HIDS), a second inflection can be observed at higher pH values accompanied by a visible color change of the aqueous medium. The comparative titration curves for the ML systems at I = 0.1 mol·dm^{-3} is shown in Figure 6, and the experimental potentiometric titration data-sets for all the systems are available as the supplementary information file. The color of the aqueous medium changed from colorless to yellow in the Fe(III)–L systems while the initial violet color changed to dark green in the Cr(III)–L systems, and such changes indicate the formation of hydrolyzed ML complexes.[41]

In Table 4, a list of the dominant species formed within the ML systems (M = Fe^{3+} or Cr^{3+}; L = GLDA or HIDS) and the corresponding pH ranges are provided. Above 50% formation of all the dominant species were occurred virtually in whole pH range (pH 5–8).

The $M(OH)L^{2-}$ remain the common dominant species at I = 0.1 and 1.0 mol·dm^{-3} with the exception for Cr(III)–HIDS system where $CrHIDS^{2-}$ was appeared as the dominant species.

In the ML systems (M = Fe^{3+} or Cr^{3+}; L = GLDA or HIDS), formation of the hydrolytic species $M(OH)^{2+}$, $M(OH)_2^{+}$, $M(OH)_3$, $M(OH)_4^{-}$ were observed with some exceptions. The formations of the $M(OH)^{2+}$ were not occurred in the systems of M(III)–GLDA (M = Fe^{3+} or Cr^{3+}; I = 1.0 mol·dm^{-3}) and Fe(III)–HIDS (I = 0.1 and 1.0 mol·dm^{-3}), and $M(OH)_2^{+}$ was not appeared in the Fe(III)–HIDS (I = 1.0 mol·dm^{-3}) system. A notable increase in the distribution of $Fe(OH)_3$ was observed in the Fe(III)–L systems (L = GLDA or HIDS) when the ionic strength was increased from 0.1 to 1.0 mol·dm^{-3}. A similar occurrence was also noticed for $Cr(OH)^{2+}$ formation in the Cr(III)–HIDS system.

There is no stability constant data for the GLDA or HIDS complexation with Fe^{3+} or Cr^{3+} in the NIST database[23] at I = 0.1 and 1.0 mol·dm^{-3} (25 ± 0.1°C) with which we can compare the data from our current work.

Iron is marked as a potential competing ion during the application of chelant for the treatment of solid wastes containing divalent ecotoxic ions (*e.g.* Ni, Cu, Zn, Cd, and Pb) or trivalent chromium. The $\log K_{ML}$ values for Ni, Cu, Zn, Cd, and Pb (L = GLDA or HIDS; I = 0.1 mol·dm^{-3}, 25 ± 0.1°C) in the aqueous medium was reported elsewhere,[26] while the same for Cr(III) and Fe(III) are reported in the current work. The comparative stability of the ML complexes was in the order of $\log K_{FeL} > \log K_{CrL} > \log K_{CuL} > \log K_{NiL} > \log K_{PbL} > \log K_{ZnL} > \log K_{CdL}$ for both GLDA (15.27 > 13.77 > 13.03 > 12.74 > 11.60 > 11.52 > 10.31) and HIDS (14.96 > 12.67 > 12.63 > 11.30 > 10.21 > 9.76 > 7.58). The stability constants of greater magnitude were observed for the metal-GLDA complexes than the corresponding values for the metal-HIDS complexes. Furthermore, the comparisons indicate the formation of the ML complexes having higher stability with the trivalent ions than those with the divalent ions. The tendency may be attributable to the comparatively stronger ionic binding of the trivalent ions than the divalent ions with the chelants.[42, 43] The comparative ML complex stability characteristics can be predicted in a general sense by the hard and soft acids and bases (HSAB) principle which assigns the terms 'hard' or 'soft', and 'acid' or 'base' to chemical species.[44, 45] According to the HSAB approach, both the Fe^{3+} and Cr^{3+} ions are belong to the ‘hard acid’ class while Cd^{2+} ion is belonged to the ‘soft acid’ class and the other ions (Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+}) are categorized as the ‘borderline (hard-soft)’.[44] GLDA has O (of the carboxylic group), and HIDS has N (of the amino group) and O (of the carboxylic group) as the donor atoms, and are considered as ‘hard base’.[46] The most preferable and stable interactions are occurred between the hard acid and hard bases, and the soft acids and soft bases.[46-48] The comparative higher stability of the Fe^{3+} or Cr^{3+} complexes with GLDA or HIDS than the Cu^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+} or Cd^{2+} is, therefore, attributable to the more-preferred interaction between the hard acid and hard base. The comparative stability order of the ML complexes can also be assumed using the solution-phase electronegativity scale which includes the oxidation state and coordination number of the metal ions. The approach considers that the stability of the ML complexes depends on the nature of the corresponding bonding character between metal and chelant, which is related to the electronegativities of metal ions for complexes with a given ligand. The solution-phase electronegativity values of the ions include in the discussion decrease in the following order: Cr^{3+} (4.026) > Fe^{3+} (3.835) > Cu^{2+} (2.952) > Ni^{2+} (2.891) > Zn^{2+} (2.796) > Cd^{2+} (2.660) > Pb^{2+} (2.478),[49] and confirm the superior stability character of the M(III)-L complexes than that of the M(II)-L complexes. The formation constants of the Cr(III) complexes with GLDA or HIDS have been found to be a litter lower than those of the corresponding Fe(III) complex, which is opposite to the order predicted from the solution-phase electronegativity scale. The difference in stability can be explained by considering the greater contribution of Racah’s electrostatic parameter upon the crystal-field stabilization in the Fe(III) complex with the chelant (GLDA or HIDS) than in the Cr(III) complex.[50] A longer treatment time or operation at a higher temperature is suggested if the Cr(III) ion is a target ion in a chelant-based clean-up process due to the slow formation rate of the corresponding ML complexes. The $\log K_{\mathrm{ML}}$ values of Fe(III) is higher than all the toxic ions considered in the comparison. Therefore, it is recommended to examine the Fe(III) content of the waste before the chelant application, and an excess of chelant is required to be added for minimizing the interfering effect of higher Fe(III) content.

3.3 Conditional metal-chelant stability constants

The stability of the metal-chelant complexes depends on the nature of the bond between the metal and chelant, which may be electrostatic or covalent based on the oxidation state and coordination number of the metal ion and/or the electronic structure and character of the chelant.[51] The fundamental stability characteristics of a metal–chelant complex in solution can be assumed from the stepwise or overall formation constant.[52] Since the factors, those are likely to affect the system, *e.g.* pH or interfering effects from other species, are ignored while the values are derived, the applications of these values are of limited significance for practical use. Therefore, the term 'conditional stability constant' is defined considering the effect of the side reactions that may occur during the metal-chelant complexation reactions.[53] The most frequently used equation for defining the conditional stability constant ($\log K'_{\mathrm{ML}}$) is the following:[53]

$$\log K'_{\mathrm{ML}} = \log K_{\mathrm{ML}} - \log \alpha_{\mathrm{HL}} - \log \alpha_{\mathrm{M}} \tag{8}$$

where $\log K_{\mathrm{ML}}$ is the formation constant of the metal–chelant species at a molar ratio of 1:1. The term α_{HL} expresses the side reactions involving chelant protonation. The term α_{M} denotes the other interfering reactions, which include the formation of metal hydroxides and the effect of buffers. Equation 8 can be expanded with the inclusion of the term α_{ML} for considering the formation of metal-chelant-proton species (MLH) or the metal-chelant-hydroxide species (MLOH):

$$\log K'_{\mathrm{ML}} = \log K_{\mathrm{ML}} - \log \alpha_{\mathrm{HL}} - \log \alpha_{\mathrm{M}} + \log \alpha_{\mathrm{ML}} \tag{9}$$

The form of the equation used for the calculation of the $\log K'_{\mathrm{ML}}$ depends on the inclusion of the necessary metal hydroxide species, MLH species or MLOH species in the computation on a set pH. Accordingly, eq 8 is the more frequently used than eq 9.[53]

The $\log K'_{\mathrm{ML}}$ values of the ML complexes (M = $\mathrm{Fe^{3+}}$ or $\mathrm{Cr^{3+}}$; L = GLDA, HIDS, NTA, EDDS or EDTA) in the aqueous medium at the ionic strength, I = 0.1 and 1.0 mol·dm^{-3} and at 25 ± 0.1°C as a function of pH (2–12) were calculated using HySS2009 program,[38] and illustrated in Figure 7. In the Fe(III)–L system at I = 0.1 mol·dm^{-3}, the stability of the corresponding complexes at pH 7 was as follows: EDTA > EDDS > NTA > HIDS > GLDA, and it was at the same order at $I = 1.0$ mol·dm^{-3} excluding the EDDS (data is not available). The Cr(III)–L complexes of EDTA possess superior stability than those of GLDA or HIDS, and GLDA ($\log K'_{ML} = 5.62$) has the ability to form more stable complexes than that of HIDS ($\log K'_{ML} = 4.37$) at pH 7 ($I = 0.1$ mol·dm^{-3}). The stability of the Cr(III)–L complexes (GLDA or HIDS) at $I = 1.0$ mol·dm^{-3} were comparable when solution is neutral or pH ≈ 7, and there was no other data to compare. The $\log K'_{ML}$ values of the GLDA and HIDS can be summarized into their corresponding ranges irrespective of the pH: Fe(III)–L at $I = 0.1$ mol·dm^{-3} (0.3–5.5, GLDA; 1.4–6.8, HIDS) and at $I = 1.0$ mol·dm^{-3} (0.6–6.0, GLDA; 1.3–8.7, HIDS); Cr(III)–L at $I = 0.1$ mol·dm^{-3} (1.9–5.8, GLDA; 0.2–5.8, HIDS) and at $I = 1.0$ mol·dm^{-3} (1.6–7.0, GLDA; 0.5–4.9, HIDS). The summary data shows that the overall stability of the Fe(III) and Cr(III) complexes with the GLDA or HIDS is not that high compare to the other biodegradable chelants, and much lower than the frequently used EDTA for solid waste treatment.

4.0 Conclusions

In the current work, the metal-chelant (ML) stability constants of GLDA and HIDS with Fe(III) and Cr(III) at different ionic strengths (0.1 and 1.0 mol·dm^{-3} KCl) and at 25 ± 0.1°C was calculated from the potentiometric titration data, and the experimental findings are expected to contribute significantly to the understanding of the complexation behavior of corresponding biodegradable chelants. The formations of mono-protonated, di-protonated, mono-hydroxo and di-hydroxo ML complexes were observed at 1:1 component ratio. The stability constants of the studied trivalent metal complexes were found to be higher for Fe(III)–L than that of Cr(III)–L. A lower complexation aptitude was observed for GLDA and HIDS than that of EDTA or other biodegradable options. Since the post-operation eco-toxicity of GLDA or HIDS is low, it can be considered as an option to minimize the consumption of EDTA. However, the chelants (GLDA or HIDS) cannot be considered as a replacement of NTA or EDDS for the removal of Fe(III) at $I = 0.1$ mol·dm^{-3}. There is not enough data in literature to conclude about the Cr(III) removal performance of GLDA or HIDS. In this respect, it could be important to gain more data about the complexation of transition metal ions with the biodegradable APCs due to a widespread interest in the chelant-based waste treatment processes.

Supporting Information

The experimental potentiometric titration data-sets and information about the titration conditions for all the systems. This material is available free of charge via the Internet at http://pubs.acs.org.

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Table 1. The overall protonation constants (logβ_{pqr}) for the HL systems (L = GLDA or HIDS) in the aqueous medium at the ionic strengths (I, mol·dm^{-3}) of 0.1 and 1.0 and at 25 ± 0.1°C[a]

Protonation equilibria	p	q	r	I = 0.1 mol·dm^{-3}		I = 1.0 mol·dm^{-3}	
				logβ_{pqr}	SD	logβ_{pqr}	SD
$GLDA^{4-} + H^+ \rightleftharpoons HGLDA^{3-}$	0	1	1	9.39	0.04	9.08	0.06
$HGLDA^{3-} + H^+ \rightleftharpoons H_2GLDA^{2-}$	0	2	1	14.40	0.03	14.06	0.08
$H_2GLDA^{2-} + H^+ \rightleftharpoons H_3GLDA^-$	0	3	1	17.89	0.03	17.52	0.07
$H_3GLDA^- + H^+ \rightleftharpoons H_4GLDA$	0	4	1	20.45	0.03	20.02	0.08
$HIDS^{4-} + H^+ \rightleftharpoons HHIDS^{3-}$	0	1	1	9.61	0.02	9.23	0.06
$HHIDS^{3-} + H^+ \rightleftharpoons H_2HIDS^{2-}$	0	2	1	13.68	0.02	13.01	0.04
$H_2HIDS^{2-} + H^+ \rightleftharpoons H_3HIDS^-$	0	3	1	16.76	0.02	15.96	0.06
$H_3HIDS^- + H^+ \rightleftharpoons H_4HIDS$	0	4	1	18.90	0.03	18.02	0.06
$H_4HIDS + H^+ \rightleftharpoons H_5HIDS^+$	0	5	1	20.50	0.04	19.68	0.08

[a] All the values were calculated from the potentiometric data using HYPERQUAD 2008 (n = 3). The symbols p, q and r are the coefficients for metal ions, protons and chelants, respectively, indicating the stoichiometry associated with the possible equilibria in solution.

Table 2. The overall formation constants (logβ_{pqr}) for the ML systems (M = Fe^{3+} or Cr^{3+}; L = GLDA) in the aqueous medium at the ionic strengths (I, mol·dm^{-3}) of 0.1 and 1.0 and at 25 ± 0.1°C[a]

Protonation equilibria	p	q	r	I = 0.1 mol·dm^{-3}		I = 1.0 mol·dm^{-3}	
				logβ_{pqr}	SD	logβ_{pqr}	SD
Fe^{3+}							
$Fe^{3+} + 2H^+ + GLDA^{4-} \rightleftharpoons FeH_2GLDA^+$	1	2	1	22.64	0.02	22.21	0.08
$Fe^{3+} + H^+ + GLDA^{4-} \rightleftharpoons FeHGLDA$	1	1	1	19.36	0.02	18.98	0.08
$Fe^{3+} + GLDA^{4-} \rightleftharpoons FeGLDA^-$	1	0	1	15.27	0.02	14.79	0.06
$Fe^{3+} + OH^- + GLDA^{4-} \rightleftharpoons Fe(OH)GLDA^{2-}$	1	–1	1	10.49	0.02	10.11	0.06
$Fe^{3+} + 2OH^- + GLDA^{4-} \rightleftharpoons Fe(OH)_2GLDA^{3-}$	1	–2	1	2.37	0.01	2.14	0.06
$Fe^{3+} + OH^- \rightleftharpoons Fe(OH)^{2+}$	1	–1	0	–1.19 (–2.56)	0.10	–	–
$Fe^{3+} + 2OH^- \rightleftharpoons Fe(OH)_2^+$	1	–2	0	–4.08 (–6.20)	0.04	–4.36 (–6.42)	0.11
$Fe^{3+} + 3OH^- \rightleftharpoons Fe(OH)_3$	1	–3	0	–11.87 (–12.50)	0.04	–11.77 (–12.67)	0.08
$Fe^{3+} + 4OH^- \rightleftharpoons Fe(OH)_4^-$	1	–4	0	–21.93 (–21.88)	0.04	–22.48 (–21.95)	0.08
Cr^{3+}							
$Cr^{3+} + 2H^+ + GLDA^{4-} \rightleftharpoons CrH_2GLDA^+$	1	2	1	21.86	0.09	21.18	0.04
$Cr^{3+} + H^+ + GLDA^{4-} \rightleftharpoons CrHGLDA$	1	1	1	18.36	0.09	17.64	0.04
$Cr^{3+} + GLDA^{4-} \rightleftharpoons CrGLDA^-$	1	0	1	13.77	0.09	12.90	0.04
$Cr^{3+} + OH^- + GLDA^{4-} \rightleftharpoons Cr(OH)GLDA^{2-}$	1	–1	1	7.28	0.09	6.20	0.04
$Cr^{3+} + 2OH^- + GLDA^{4-} \rightleftharpoons Cr(OH)_2GLDA^{3-}$	1	–2	1	–1.91	0.06	–3.31	0.04
$Cr^{3+} + OH^- \rightleftharpoons Cr(OH)^{2+}$	1	–1	0	–1.65 (–4.41)	0.06	–	–
$Cr^{3+} + 2OH^- \rightleftharpoons Cr(OH)_2^+$	1	–2	0	–7.66 (–10.35)	0.08	–7.48 (–10.83)	0.07
$Cr^{3+} + 3OH^- \rightleftharpoons Cr(OH)_3$	1	–3	0	–18.17 (–18.65)	0.09	–19.30 (–19.33)	0.12
$Cr^{3+} + 4OH^- \rightleftharpoons Cr(OH)_4^-$	1	–4	0	–27.82 (–27.81)	0.04	–28.91 (–28.32)	0.05

[a] All the values were calculated from the potentiometric data using HYPERQUAD 2008 (n = 3). The symbols p, q and r are the coefficients for metal ions, protons and chelants, respectively, indicating the stoichiometry associated with the possible equilibria in solution. The data in the parentheses are the literature values of equilibrium constants for reactions of Fe(III) and Cr(III) ions with hydroxide ions.[54]

Table 3. The overall formation constants ($\log\beta_{pqr}$) for the ML systems (M = Fe^{3+} or Cr^{3+}; L = HIDS) in the aqueous medium at the ionic strengths (I, $mol\cdot dm^{-3}$) of 0.1 and 1.0 and at 25 ± 0.1°C[a]

Protonation equilibria	p	q	r	$I = 0.1\ mol\cdot dm^{-3}$		$I = 1.0\ mol\cdot dm^{-3}$	
				$\log\beta_{pqr}$	SD	$\log\beta_{pqr}$	SD
Fe^{3+}							
$Fe^{3+} + 2H^+ + HIDS^{4-} \rightleftharpoons FeH_2HIDS^+$	1	2	1	20.74	0.09	20.27	0.04
$Fe^{3+} + H^+ + HIDS^{4-} \rightleftharpoons FeHHIDS$	1	1	1	18.43	0.08	17.76	0.03
$Fe^{3+} + HIDS^{4-} \rightleftharpoons FeHIDS^-$	1	0	1	14.96	0.08	14.34	0.03
$Fe^{3+} + OH^- + HIDS^{4-} \rightleftharpoons Fe(OH)HIDS^{2-}$	1	–1	1	10.00	0.08	9.57	0.03
$Fe^{3+} + 2OH^- + HIDS^{4-} \rightleftharpoons Fe(OH)_2HIDS^{3-}$	1	–2	1	1.23	0.08	0.69	0.02
$Fe^{3+} + OH^- \rightleftharpoons Fe(OH)^{2+}$	1	–1	0	–	–	–	–
$Fe^{3+} + 2OH^- \rightleftharpoons Fe(OH)_2{}^+$	1	–2	0	–5.07 (–6.20)	0.11	–	–
$Fe^{3+} + 3OH^- \rightleftharpoons Fe(OH)_3$	1	–3	0	–12.53 (–12.50)	0.06	–12.05 (–12.67)	0.03
$Fe^{3+} + 4OH^- \rightleftharpoons Fe(OH)_4{}^-$	1	–4	0	–22.22 (–21.88)	0.06	–22.74 (–21.95)	0.03
Cr^{3+}							
$Cr^{3+} + 2H^+ + HIDS^{4-} \rightleftharpoons CrH_2HIDS^+$	1	2	1	18.5	0.04	17.8	0.06
$Cr^{3+} + H^+ + HIDS^{4-} \rightleftharpoons CrHHIDS$	1	1	1	16.17	0.02	15.80	0.02
$Cr^{3+} + HIDS^{4-} \rightleftharpoons CrHIDS^-$	1	0	1	12.67	0.02	12.09	0.02
$Cr^{3+} + OH^- + HIDS^{4-} \rightleftharpoons Cr(OH)HIDS^{2-}$	1	–1	1	5.99	0.02	5.17	0.04
$Cr^{3+} + 2OH^- + HIDS^{4-} \rightleftharpoons Cr(OH)_2HIDS^{3-}$	1	–2	1	–2.75	0.01	–3.64	0.02
$Cr^{3+} + OH^- \rightleftharpoons Cr(OH)^{2+}$	1	–1	0	–3.05 (–4.41)	0.1	–2.1 (–4.60)	0.12
$Cr^{3+} + 2OH^- \rightleftharpoons Cr(OH)_2{}^+$	1	–2	0	–7.83 (–10.35)	0.08	–8.42 (–10.83)	0.10
$Cr^{3+} + 3OH^- \rightleftharpoons Cr(OH)_3$	1	–3	0	–16.38 (–18.65)	0.02	–17.66 (–19.33)	0.04
$Cr^{3+} + 4OH^- \rightleftharpoons CrOH)_4{}^-$	1	–4	0	–26.95 (–27.81)	0.02	–28.16 (–28.32)	0.02

[a] All the values were calculated from the potentiometric data using HYPERQUAD 2008 ($n = 3$). The symbols p, q and r are the coefficients for metal ions, protons and chelants, respectively, indicating the stoichiometry associated with the possible equilibria in solution. The data in the parentheses are the literature values of equilibrium constants for reactions of Fe(III) and Cr(III) ions with hydroxide ions.[54]

Table 4. The dominant species in the ML systems (M = Fe^{3+} or Cr^{3+}; L = GLDA or HIDS) in the aqueous medium at the ionic strengths (*I*, mol·dm^{-3}) of 0.1 and 1.0 and at 25 ± 0.1°C[a]

ML system	Dominant Species	$I = 0.1$ mol·dm^{-3}		$I = 1.0$ mol·dm^{-3}	
		pH range	% formation	pH range	% formation
Fe(III) + GLDA	$Fe(OH)GLDA^{2-}$	5.0–8.0	50–91	4.8–7.9	50–90
Fe(III) + HIDS	$Fe(OH)HIDS^{2-}$	5.0–8.6	50–94	4.8–8.5	50–94
Cr(III) + GLDA	$Cr(OH)GLDA^{2-}$	6.5–9.2	50–89	6.8–9.3	50–80
Cr(III) + HIDS	$CrHIDS^{-}$	3.5–6.5	50–90	3.8–6.7	50–86

[a] All the values were calculated from the potentiometric data using HYPERQUAD 2008 ($n = 3$).

Table 5. The stepwise protonation and complexation constants of the ML systems (M = Fe^{3+} or Cr^{3+}; L = GLDA or HIDS) compared with the corresponding values of NTA, EDDS and EDTA in the aqueous medium at the ionic strengths (I, mol·dm^{-3}) of 0.1 and 1.0 at 25 ± 0.1°C

Equilibria	GLDA (H_4L)[a]		HIDS (H_4L)[a]		NTA (H_3L)[b]		EDDS (H_4L)[b]		EDTA (H_4L)[b]	
Log*K*										
	$I = 0.1$	$I = 1.0$	$I = 0.1$	$I = 1.0$	$I = 0.1$	$I = 1.0$	$I = 0.1$	$I = 1.0$	$I = 0.1$	$I = 1.0$
$[HL]/[H][L]$	9.39 (9.36[b])	9.08	9.61	9.23	9.46–9.84	8.95–9.34	10.01	–	9.52–10.37	8.73-10.2
$[H_2L]/[HL][H]$	5.01 (5.03[b])	4.98	4.07	3.78	2.52	2.28	6.84	6.65	6.13	6.19
$[H_3L]/[H_2L][H]$	3.49 (3.49[b])	3.46	3.08	2.95	(1.81)	(1.81)	3.86	3.81	2.69	2.52
$[H_4L]/[H_3L][H]$	2.56 (2.56[b])	2.5	2.14	2.06	(1.0)	(1.0)	2.95	–	2	2.02
$[H_5L]/[H_4L][H]$	–	–	1.6	1.68	–	–	–	–	(1.5)	1.4
$[H_6L]/[H_5L][H]$	–	–	–	–	–	–	–	–	(0.0)	00
Fe^{3+}										
$[M(OH)L]/[M(OH)_2L][H]$	8.12	7.97	8.77	8.88	7.58	–	–	–	–	–
$[ML]/[MOHL][H]$	4.78	4.68	4.96	4.77	4.36	5.00	–	–	7.39	7.53
$[ML]/[M][L]$	15.27	14.79	14.96	14.34	16	14.78	22.00[e]	–	25.1	23.8
$[MHL]/[ML][H]$	4.09	4.19	3.47	3.42	–	(0.9)	–	–	(1.3)	–
$[MH_2L]/[MHL][H]$	3.28	3.23	2.31	2.51	–	–	–	–	–	–
$[ML_2]/[M][L]^2$	–	–	–	–	24	–	–	–	–	–
Cr^{3+}										
$[M(OH)L]/[M(OH)_2L][H]$	9.19	9.51	9.43	10.86	8.45[e]	–	–	–	–	–
$[ML]/[MOHL][H]$	6.49	6.7	6.68	6.92	6.23[e]	–	–	–	7.37	–
$[ML]/[M][L]$	13.77	12.90	12.67	12.09	–	–	–	–	23.4[e]	–
$[MHL]/[ML][H]$	4.59	4.74	3.5	3.71	–	–	–	–	1.7	–
$[MH_2L]/[MHL][H]$	3.5	3.54	2.33	2.05	–	–	–	–	–	–
$[ML_2]/[M][L]^2$	–	–	–	–	–	–	–	–	–	–

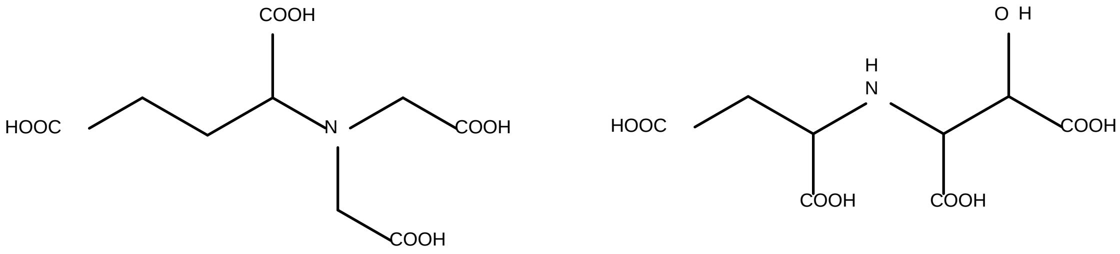
[a] Calculated values from the experimental potentiometric data using HYPERQUAD 2008 ($n = 3$).

[b] From the NIST database of critically selected stability constants of metal complexes [23].

[c] $I = 1$ mol·dm^{-3}

[d] $I = 0.5$ mol·dm^{-3}

[e] At 20°C.



GLDA HIDS

Figure 1. Chemical structures of DL-2-(2-carboxymethyl)nitrilotriacetic acid (GLDA) and 3-hydroxy-2,2´-iminodisuccinic acid (HIDS).

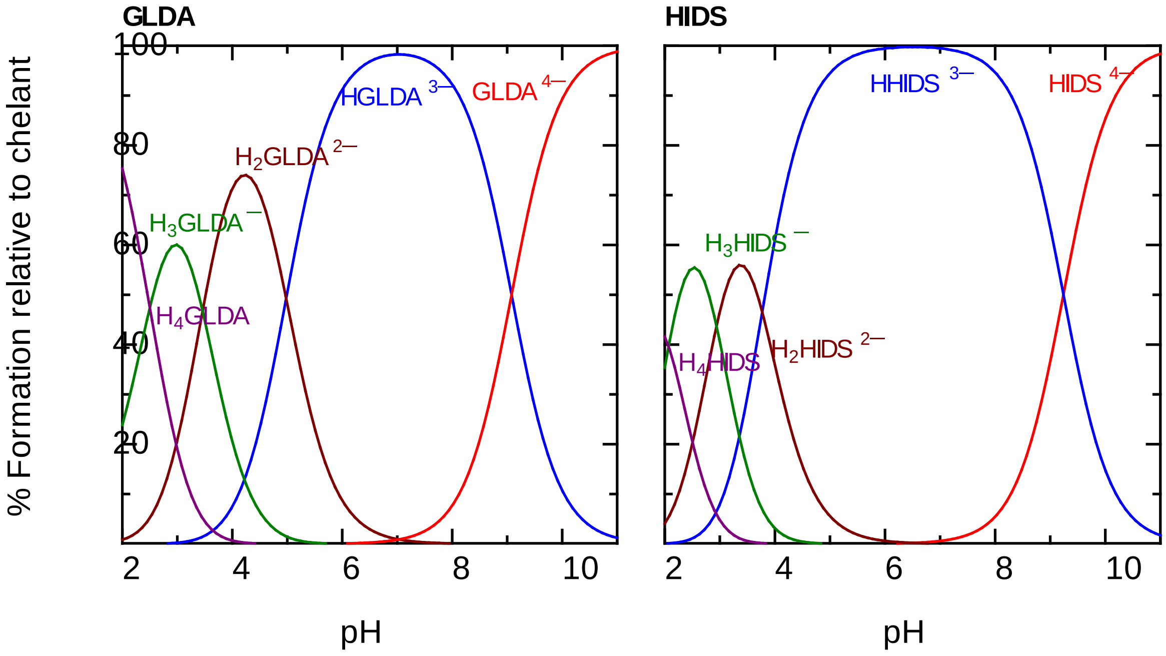


Figure 2. The percentage distribution of different protonation stages of GLDA and HIDS in the aqueous medium at the ionic strength, I = 1.0 mol·dm^{-3} and at 25 ± 0.1°C.

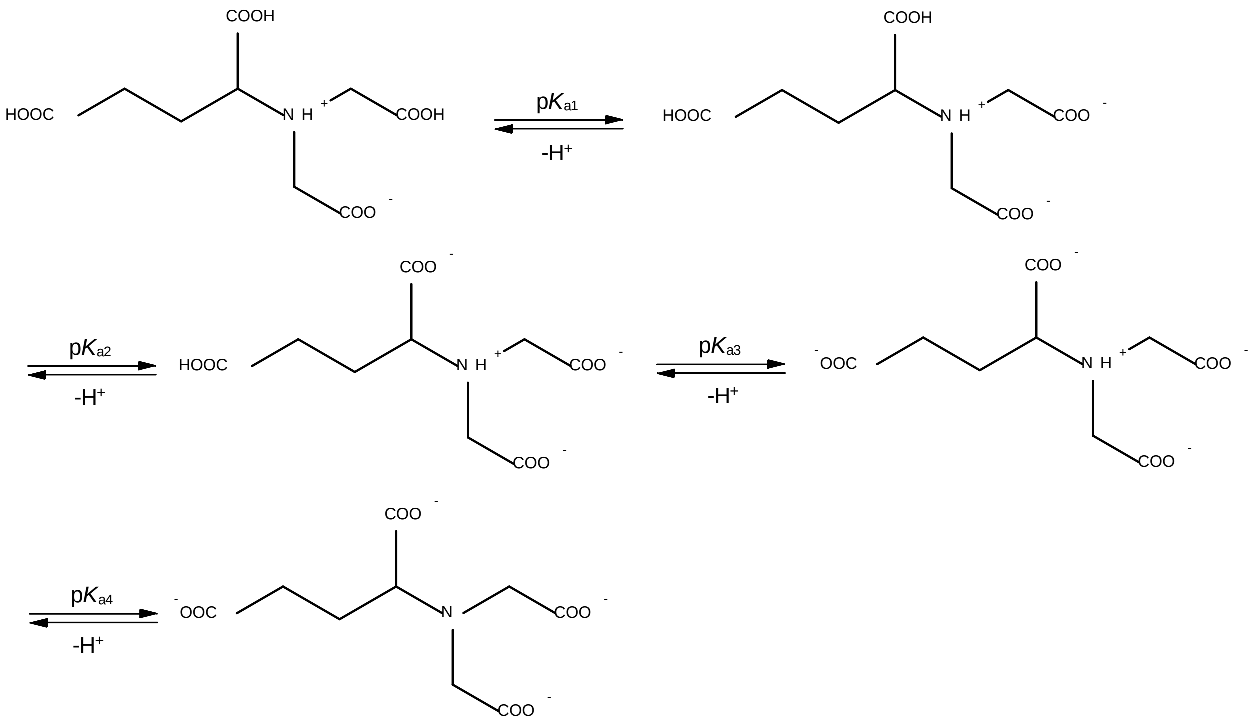


Figure 3. The predicted scheme of the protonation equilibria for GLDA in aqueous medium at ionic strength, $I = 1.0$ mol·dm^{-3} and at 25 ± 0.1°C.

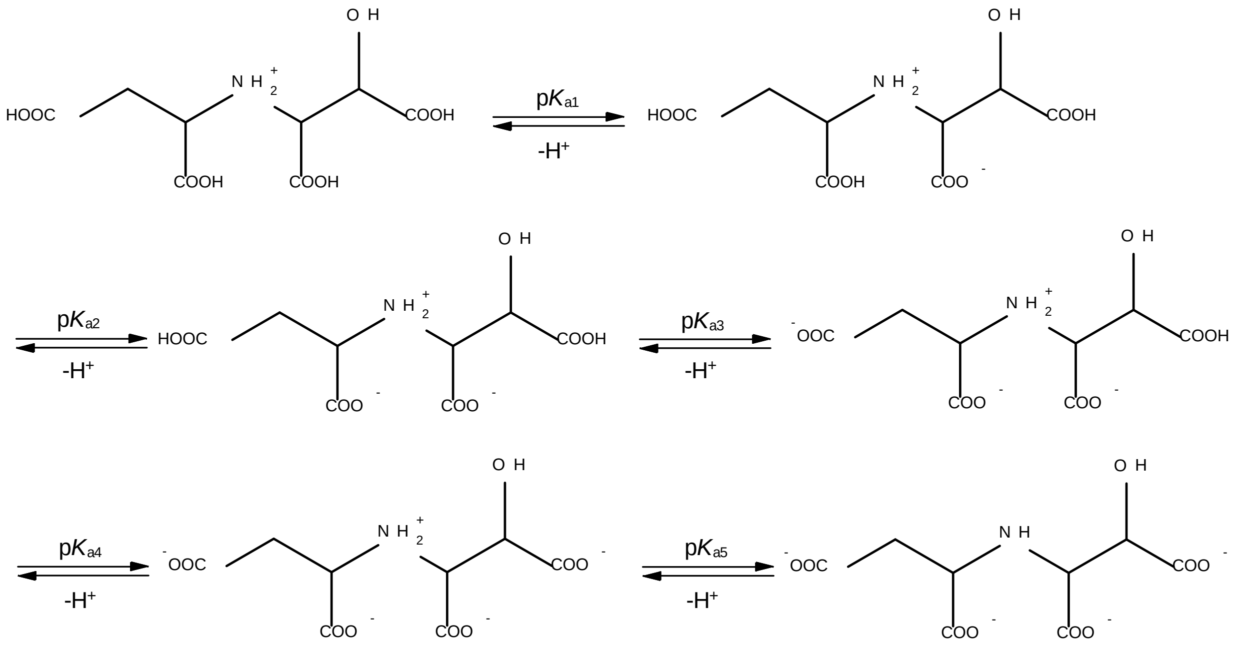


Figure 4. The predicted scheme of the protonation equilibria for HIDS in aqueous medium at ionic strength, I = 1.0 mol·dm^{-3} and at 25 ± 0.1°C.

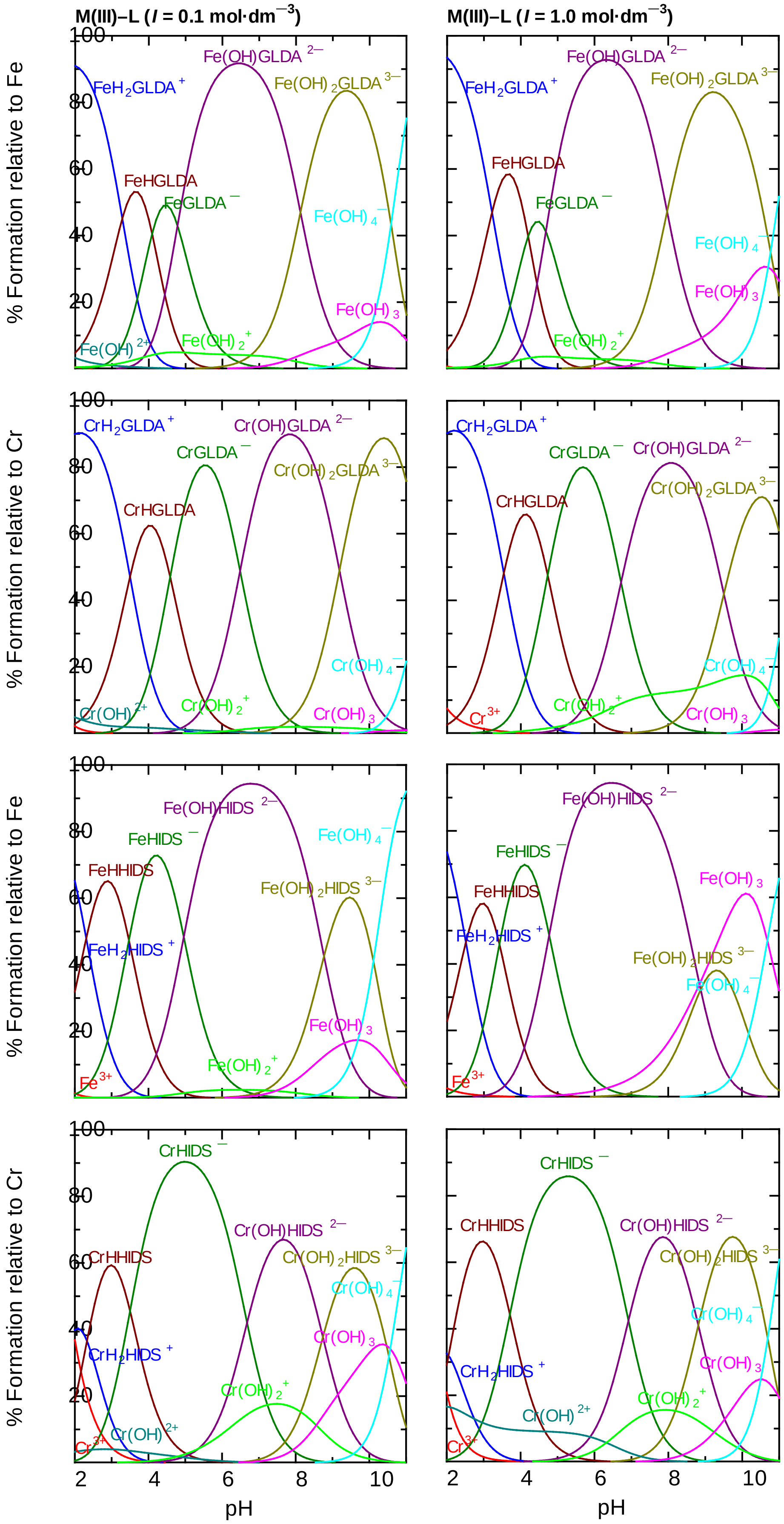


Figure 5. The species distribution curves for ML systems (M = Fe^{3+} or Cr^{3+}; L = GLDA or HIDS) in aqueous medium at ionic strength, I = 0.1 and 1.0 mol·dm^{-3} and at 25 ± 0.1°C.

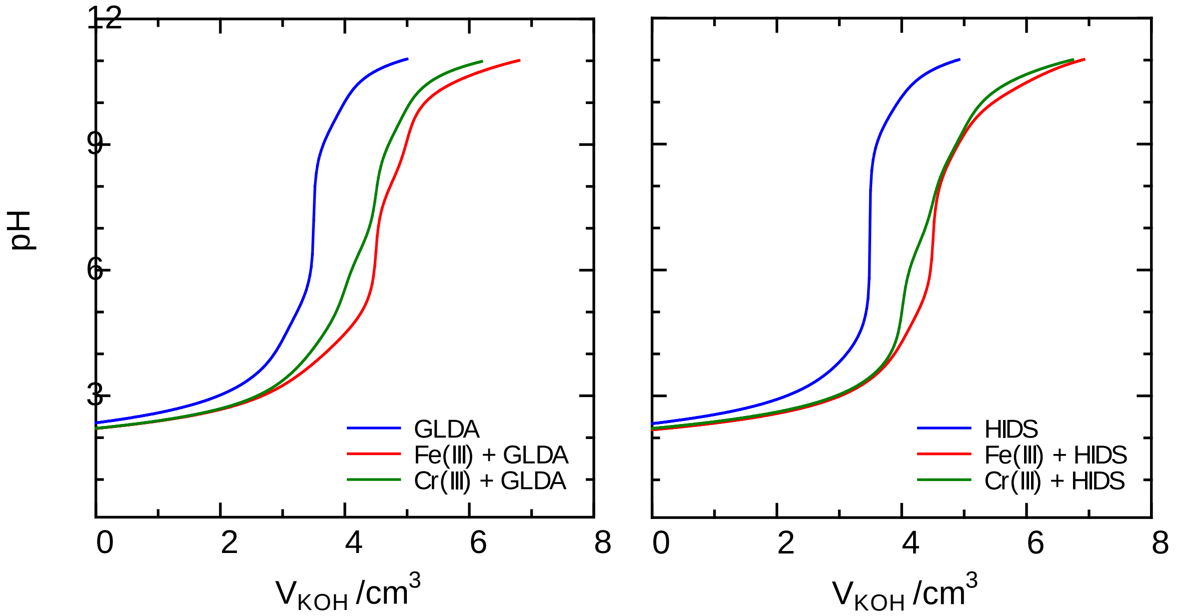


Figure 6. Potentiometric titration curves for the ML systems (M = Fe^{3+} or Cr^{3+}; L = GLDA or HIDS) in the aqueous medium at the ionic strength, $I = 0.1$ mol·dm^{-3} and at 25 ± 0.1°C.

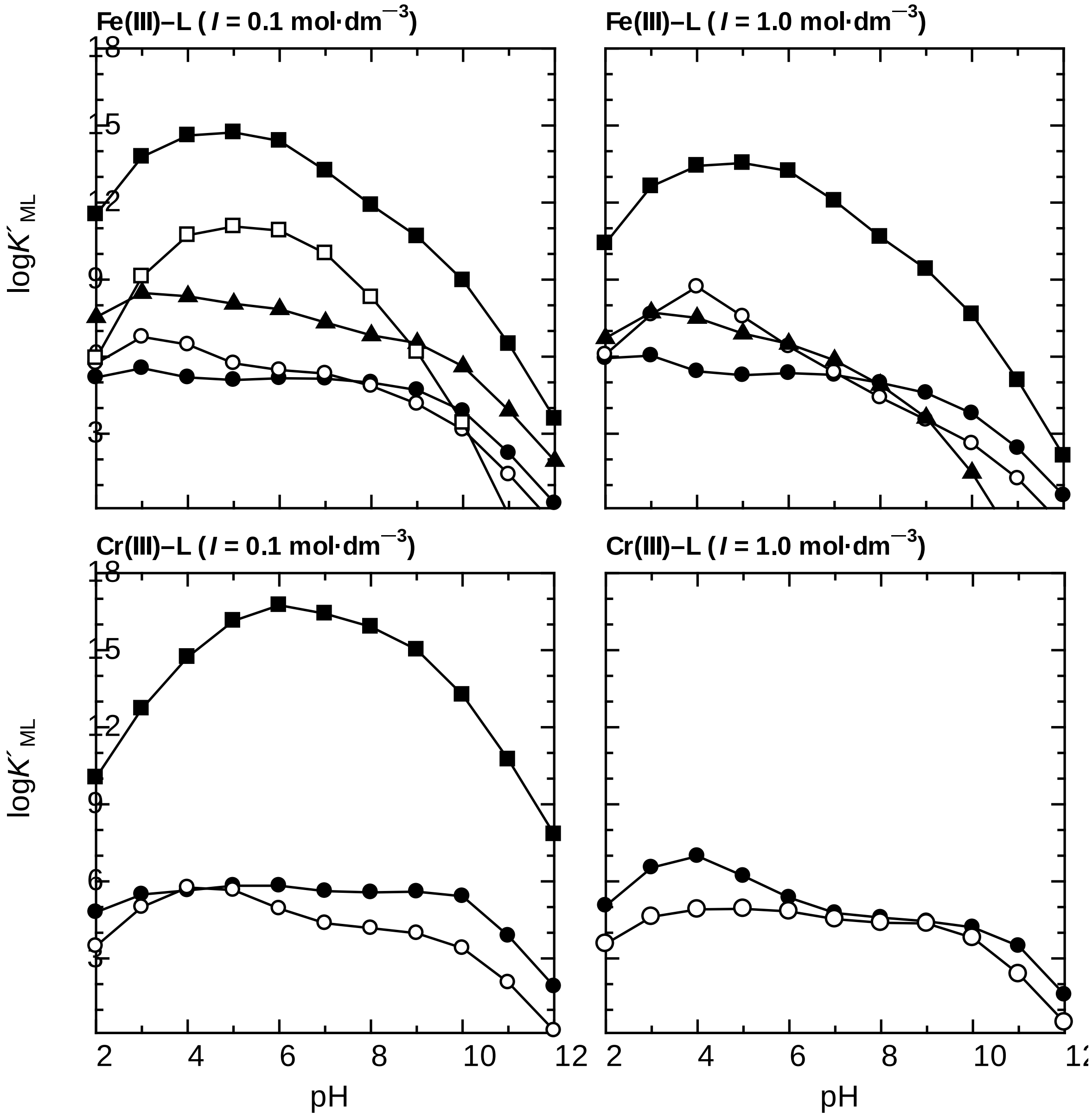


Figure 7. The conditional stability constants for the ML systems (M = Fe^{3+} or Cr^{3+}; L = GLDA, HIDS, NTA, EDDS or EDTA) in the aqueous medium at the ionic strength, I = 0.1 and 1.0 mol·dm^{-3} and at 25 ± 0.1°C as a function of pH: ●, M(III)–GLDA; ○, M(III)–HIDS; ▲, M(III)–NTA; □, M(III)–EDDS; ■, M(III)–EDTA.