JOURNAL OF CHEMICAL & ENGINEERING DATA

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pubs.acs.org/jced

Stability of Metal Chelates of Some Hydroxamic Acid Ligands

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ABSTRACT: The binary−ligand complexes formed between acetohydroxamic acid (Aha) and benzohydroxamic acid (Bha) ligands and selected transition metals (Sc(III), Y(III), and La(III)) were investigated potentiometrically in aqueous solution at (25 ± 0.1) °C and $I = 0.10$ M NaCl to determine the protonation constants of the free ligands and stability constants of the binary complexes. The complexation model for each metal−ligand system was established from the potentiometric data using the software program BEST. The concentration distributions of the various metal−ligand complexes formed in solution were also evaluated. The complex stability was found to follow the trend Sc(III) > Y(III) > La(III) based on the ionic radius of the metal ions.

INTRODUCTION

Scandium (Sc) is the first member of the group III elements, and Sc(III) has the smallest ionic radius (0.83 Å). Its behavior in chemical reactions is intermediate between that of aluminum (Al(III)) and the trivalent lanthanides. Similarly, yttrium has a 3+ ion (Y(III)) with a noble gas core, and yttrium is located above lanthanum (La) in group III of the periodic table. Yttrium and lanthanum are highly electropositive elements. The ionic radius of Y(III) is 0.89 Å, which is closer to that of terbium(III) (0.92 Å), and the ionic radius of La(III) is 1.17 Å. In general, yttrium is present with the lanthanides in nature. The chemical properties of yttrium in its compounds resemble those of holmium(III) and dysprosium(III). The aqua ions of Sc(III), Y(III), and La(III) generate several hydrolytic species by polarizing solvated water molecules. The equilibrium constants for Sc(III), Y(III), and Th(IV) for some ligands in aqueous solutions have been reported previously.[1−12]

The Sc(III) ion is more readily hydrolyzed than lanthanide(III) ions in perchlorate solution due to the small ionic radius of Sc(III). The major ionic species of this reaction are $[Sc(OH)]^{2+}$, $[Sc_2(OH)_2]^{4+}$, $[Sc_3(OH)_4]^{5+}$, and $[Sc_3(OH)_5]^{4+}$. Y(III), another member of the lanthanides in group III, yields $[Y(OH)]^{2+}$ and $[Y_2(OH)_2]^{4+}$ ions as the major hydrolytic species in its reactions. The reaction products of La(III) have been identified in different perchlorate solutions under a range of pH conditions at 60 °C using a glass electrode.[13] The reaction products of La(III) under these conditions were determined to be $[La(OH)]^{2+}$, $[La_5(OH)_9]^{6+}$, and $[La_6(OH)_{10}]^{8+}$.

There is significant interest in the coordination chemistry of the lanthanides and earlier 3d transition elements. Sc(III) is frequently used in the determination of the stability of the various coordination complexes; due to its chemical nature, Sc(III) exhibits certain similarities to the lanthanides and the trivalent transition elements titanium, vanadium, and chromium. The lanthanides have been reported to form the most stable complexes with oxygen donating ligands, although they can also form coordination complexes with nitrogen donors.[14]

Hydroxamic acids [RC(=O)NH(OH)] are quite abundant and well-known ligands in biological areas, including medicine, pharmacology, and different agricultural fields.[15] These ligands have an inhibiting effect on certain metalloenzymes. Derivatives of hydroxamic acid are involved in the microbial iron transport system as siderophores.[16] Siderophores are low molecular weight compounds with iron (Fe) chelating activities.[17,18] However, siderophores can also form metal ion complexes with different metals, such as Al(III). The complexation ability of siderophores with Al(III) is used in the clinical treatment of Al(III) intoxication with desferrioxamine, which is a naturally occurring siderophore.[19] Siderophores have an additional function in molybdenum uptake in nitrogen fixing bacteria.[20,21] In addition, derivatives of hydroxamic acid are present in different plant species involved in pathogen resistance and metal ion uptake from soil. Hydroxamic acid derivatives have been developed to prepare iron and related metal ion chelation compounds as therapeutic chemicals.[22,23] Hydroxamic acids are also used in different fields of chemistry, especially in the analysis of trace metals like Fe(III) and some trivalent elements.[24,25] Hydroxamic acid garners significant attention due to its affinity to form complexes with Fe-containing compounds in biological systems.[26,27]

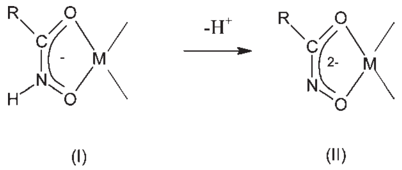
Hydroxamate species have been selected and studied as ligands in coordination compounds. In general, metal ion binding to hydroxamic acids occurs by deprotonation of the OH group on this ligand, and subsequent (O, O) coordination takes place between the metal and the carbonyl oxygen and deprotonated OH group. In a benzenohydroxamate complex of Fe(III), X-ray diffraction analysis showed that chelate formation occurs between oxygens belonging to the carbonyl and NHOH groups. In addition to X-ray studies, structures of coordination complexes of different hydroxamic acid compounds have also been studied in solution and the solid state.

In most of these studies, complexes of Fe(III) and some other metal ions, such as Co(II), Co(III), Ni(II), Zn(II), Cu(II), and V(IV), were investigated. The results and significance of these studies with respect to siderophore-mediated iron uptake by microorganisms have been examined in different reviews.[18,22] Previous studies on complex formation with simple primary hydroxamic ligands in aqueous solutions indicates that two (O, O) bonding modes of relevant ligands are accessible to metal ions like Cu(II) and V(IV) depending on pH. The hydroamato (1−)

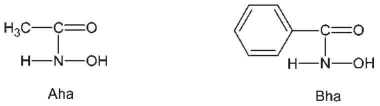
Received: December 14, 2010
Accepted: April 15, 2011
Published: April 27, 2011

dx.doi.org/10.1021/je1013119 | J. Chem. Eng. Data 2011, 56, 2337–2342

Scheme 1



Scheme 2



type species results from the first deprotonation step and involves the coordination of the (CO)NHO$^-$ moiety (See I in Scheme 1). Subsequently, metal-induced deprotonation of NHO produces the hydroximato (2−) form of the ligand (See II in Scheme 1).

Coordination complexes of hydroxamic acids have generally been analyzed in binary systems; a few studies on hydroxamic acid complexes in ternary systems have also been reported.[28] There are also many studies on the metal chelating, antifungal, and antimicrobial activities of benzohydroxamic acid and its nuclear-substituted derivatives.[15,29−32]

To study the involvement of hydroxamic acid in analytical chemistry and in biological systems, gathering a large amount of data on the stabilities of its chelates with various metal ions is essential. Thus, the stability constants for trivalent Sc(III), Y(III), and La(III) with hydroxamic acid have been determined in an aqueous medium at 25 °C in 0.1 M ionic strength. In addition, this study obtains further information on the complex formation of these metals with acetohydroxamic acid (Aha) or benzohydroxamic acid (Bha) in ML, ML_2, and ML_3 type complexes in an aqueous system. Another aim of the present study is to identify the structures of the binary complexes formed in the reaction medium using potentiometric titration techniques. A literature survey of the complex formation equilibria of Aha and Bha revealed that there is no study on this aspect of equilibria with hydroxamic acid in aqueous systems except for the formation of La-Aha (20 °C, 0.1 M) complexes in a binary system.[33] The structures of the ligands used in this study are shown in Scheme 2.

■ MATERIALS AND METHODS

Materials. All of the chemicals used in this study were of analytical grade and were used without further purification. Sodium hydroxide solutions were prepared with freshly boiled, doubly deionized water under a nitrogen atmosphere. The concentration of the sodium hydroxide solution was periodically checked by pH-metry using the appropriate Gran function against oven-dried potassium hydrogen phthalate as the primary standard.[34,35] HCl (Merck; 37 %, d = 1.19 g·cm^{-3}) solution were titrated against standardized potassium hydroxide.[34,35] Potassium chloride, used as a background electrolyte, was a Merck (p.a.) reagent. The ionic strength of each solution was adjusted to 0.1 M by the addition of NaCl as the supporting electrolyte.

Acetohydroxamic acid (Aha) and benzohydroxamic acid (Bha) were purchased from Sigma. The purity of the ligand solutions was checked, and the molecular weights of the ligands were determined by the Gran method with standardized NaOH. Stock solutions of the metal ions (Sc(III), Y(III), and La(III)) were prepared from analytical grade oxides (Merck). The solutions were kept acidic by the addition of small amounts of HCl. The excess acid in the stock metal solutions was determined by a Gran function.[34] The metal(III) stock solutions were standardized complexometrically according to Schwarzenbach and Flaschka.[36]

Potentiometric Equilibrium Measurements. All of the measurements were carried out in 0.1 M ionic strength and 25 °C. The automatic titration apparatus (Schott-Hofheim, Germany) equipped with a combined glass electrode was used for the pH measurements. The precision of the pH meter was ± 0.002 pH units. The meter was calibrated using buffer solutions at pH = 4.0 and pH = 7.0. The temperature of the solutions in the titration vessel was maintained at (25 ± 0.1) °C with a thermostatic arrangement. The potentiometric method was carried out via titrations of the ligands (Aha and Bha) in the absence and presence of the M(III) (Sc(III), Y(III), and La(III)) ion in a standardized NaOH solution.

The pH-metric measurements were carried out at an ionic strength of 0.1 M using NaCl. NaOH solutions of known concentration (ca. 0.1 M) were used as titrant. The pH-metric titrations were performed over the approximate pH range 2.0 to 11.00. The ligand concentration was varied in the range of ($4.9 \cdot 10^{-3}$ to $1.5 \cdot 10^{-2}$) M. The metal:ligand ratios were 1:1 to 1:10. Measurements were made with samples at four or five different ratios, and a pK_w value of 13.76 was determined in the present study. The pH-metric results were used to establish the stoichiometry of the species and to calculate the stability constants. The pH-metric measurements were carried out with a Schott pH meter equipped with a Schott combined electrode, and the titrant was added from a Schott automatic titrator. The electrode system was calibrated by the method of Irving et al.[37] so that the pH-meter readings could be converted into hydrogen ion concentrations. The calculations were done with the BEST computer program.

The specific details of the applied procedures were described in a previous publication.[38] The potentiometric titrations were carried out in a jacketed cell with a 100 mL capacity under a nitrogen atmosphere and at an ionic strength of 0.1 M NaCl. All of the potentiometric titrations were performed in triplicate. The data obtained from the potentiometric titrations were analyzed with the BEST computer program.[39] The BEST program calculates the set of known and estimated equilibria constants that involve the formation of H^+ and metal-complexes of Aha and Bha and computes concentrations of H^+ ion for each equilibrium and quantity of added base. The corresponding equilibrium constants that "best" fit the experimental data were determined by minimizing the squares sum.

To apply the BEST program to each M(III)−ligand system, 300 to 350 experimental titration points were introduced into BEST. Thus, the mathematical analysis of the data, comprising 27 titrations, was performed, and the averages of the constants obtained from the BEST program are tabulated in Tables 1 and 2. Two groups of equilibria were treated in this work; the first group of equilibria included the acid dissociation constants of HL and L^- (ligands), and the second group included the M(III):ligand complex formation equilibria. The log K and log β_{pqr} values were subsequently defined for these equilibria.

Table 1. Protonation Constants of Acetohydroxamic Acid (Aha) and Stability Constants of Sc(III), Y(III), and La(III) Aha Complexes at (25 ± 0.1) °C, I = 0.1 M NaCl

row	equilibrium	constant	Aha	Sc(III)	Y(III)	La(III)
1	$HL^- + H^+ \rightleftharpoons H_2L$	$\log K_{H_2L}$	9.36 ± 0.01 9.27[44]			
3	$M^{3+} + L^{2-} \rightleftharpoons ML^+$	$\log \beta_{110}$		7.60 ± 0.04	6.31 ± 0.02	5.54 ± 0.03 5.16[33a]
4	$M^{3+} + 2L^{2-} \rightleftharpoons ML_2^-$	$\log \beta_{120}$		16.96 ± 0.03	11.89 ± 0.02	9.65 ± 0.02 9.33[33a]
5	$M^{3+} + 3L^{2-} \rightleftharpoons ML_3^{3-}$	$\log \beta_{130}$		20.36 ± 0.04	15.81 ± 0.04	12.95 ± 0.03 11.88[33a]

[a] (20 °C, I = 0.1 M).

Table 2. Protonation Constants of Benzohydroxamic Acid (Bha) and Stability Constants of Sc(III), Y(III), and La(III) Bha Ccomplexes at (25 ± 0.1) °C, I = 0.1 M NaCl

row	equilibrium	constant	Bha	Sc(III)	Y(III)	La(III)
1	$HL^- + H^+ \rightleftharpoons H_2L$	$\log K_{H_2L}$	8.83 ± 0.01 8.696[45]			
3	$M^{3+} + L^{2-} \rightleftharpoons ML^+$	$\log \beta_{110}$		6.87 ± 0.04	6.39 ± 0.02	5.87 ± 0.03
4	$M^{3+} + 2L^{2-} \rightleftharpoons ML_2^-$	$\log \beta_{120}$		13.02 ± 0.03	12.51 ± 0.02	11.05 ± 0.02
5	$M^{3+} + 3L^{2-} \rightleftharpoons ML_3^{3-}$	$\log \beta_{130}$		18.12 ± 0.04	17.99 ± 0.04	16.19 ± 0.03

RESULTS AND DISCUSSION

Potentiometry Study. The equilibria in the M(III)-Aha and M(III)-Bha systems, where M is Sc(III), Y(III), or La(III), and the corresponding notations for the protonation constants of Aha and Bha and the stability constants of the M(III)-complexes with Aha or Bha are given as follows:

$$pM + qL + rH \rightleftharpoons M_pL_qH_r$$

and

$$\beta_{pqr} = [M_pL_qH_r]/[pM]^p[qL]^q[rH]^r$$

where p, q, and r represent the chemical stoichiometric coefficients of the M(III) ion (Sc(III), Y(III), or La(III)), ligand (L), and proton (H) in the coordination complex, respectively. The charges of the ions are omitted for the sake of clarity.

Proton–Ligand Stability Constants. Hydroxamic acids are very weak acids, although they are several times stronger than phenol. The suppression of acid character may be attributed to the intramolecular hydrogen bonding in these compounds. Evidence in support of the intramolecularly hydrogen-bonded structure has been presented in several infrared studies.[40,41] Hydroxamic acids have a carboxylic acid functional group, and their acidity has been attributed essentially to the OH group. Thus, as in amides, the suppression of the nitrogen's basic character is observed in hydroxamic acids.[42,43]

The acid–base behavior of the Aha and Bha ligands was studied by potentiometry. A representative pH titration curve for these ligands is presented in curve I of Figure 1. Acetohydroxamic acid and benzohydroxamic acid (Scheme 2) can each release one proton in the measured range, and the log K_{HL} values measured by pH-metry are listed in Tables 1 and 2. The values in Tables 1 and 2 are consistent with hydroxamic acid acidity in general, and they are also in good agreement with previously reported results. The log K_{HL} value for Aha is significantly lower than that of Bha. This difference is probably due to increased electron donation from the alkyl chain in Aha and electron withdrawal of the phenyl moiety in Bha.

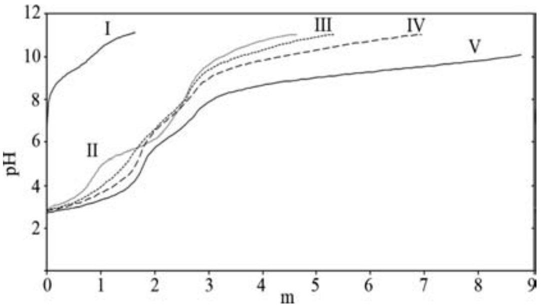


Figure 1. Potentiometric titration curves of Sc(III) complexes of Aha in 0.1 M NaCl at 25 °C (m = mmole base/mmole ligand). I. Aha alone ($T_L = 9.620 \cdot 10^{-2}$ M). II. (1:1) Sc(III):Aha ($T_{Sc} = 9.620 \cdot 10^{-2}$ M, $T_L = 9.620 \cdot 10^{-2}$ M). III. (1:2) Sc(III):Aha ($T_{Sc} = 9.620 \cdot 10^{-2}$ M, $T_L = 1.924 \cdot 10^{-1}$ M). IV. (1:3) Sc(III):Aha ($T_{Sc} = 9.620 \cdot 10^{-2}$ M, $T_L = 2.886 \cdot 10^{-1}$ M). V. (1:10) Sc(III):Aha ($T_{Sc} = 9.620 \cdot 10^{-2}$ M, $T_L = 9.620 \cdot 10^{-1}$ M).

The acid dissociation character of hydroxamic acids in ionizing solvents can be represented by the following equilibria:

$$H_2L^+ \rightleftharpoons HL + H^+$$

$$HL \rightleftharpoons L^- + H^+$$

Protonation constants for the hydroxamic acids in this study were calculated with the FORTRAN program BEST by finding the algebraic solution of the mass balance and charge balance equations evaluated at each equilibrium point on the titration curves. All of the models converged at $(0.02)^{1/2}$ pH units from the observed pH values, which is considered to be an acceptable fit.

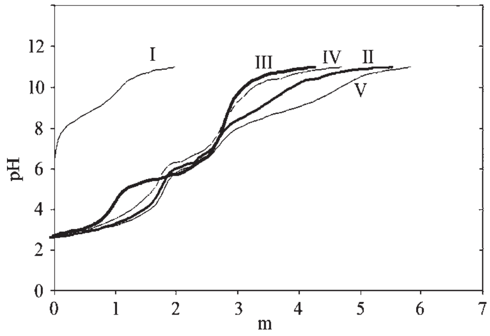


Figure 2. Potentiometric titration curves of Sc(III) complexes of Bha in 0.1 M NaCl at 25 °C. (m = mmole base/mmole ligand). I. Bha alone ($T_L = 9.620 \cdot 10^{-2}$ M). II. (1:1) Sc(III):Bha ($T_{Sc} = 9.620 \cdot 10^{-2}$ M, $T_L = 9.620 \cdot 10^{-2}$ M). III. (1:2) Sc(III):Bha ($T_{Sc} = 9.620 \cdot 10^{-2}$ M, $T_L = 1.924 \cdot 10^{-1}$ M). IV. (1:3) Sc(III):Bha ($T_{Sc} = 9.620 \cdot 10^{-2}$ M, $T_L = 2.886 \cdot 10^{-1}$ M). V. (1:10) Sc(III):Bha ($T_{Sc} = 9.620 \cdot 10^{-2}$ M, $T_L = 9.620 \cdot 10^{-1}$ M).

On the basis of the data in Tables 1 and 2, the protonation of the ligands, represented by K_a, is most likely due to the protonation of the phenolic hydroxyl group. The K_a values in Tables 1 and 2 are consistent with hydroxamic acids in general, and they are also in good agreement with those found in the literature.[44,45]

Metal−Ligand. The complexation behavior of Aha and Bha toward M(III) ions in aqueous solution was studied by potentiometry. A representative pH-metric titration curve of this binary system ($T_{Sc} = 9.620 \cdot 10^{-2}$ M, $T_L = 9.620 \cdot 10^{-2}$ M, T_L/T_M = 1:1) is shown in Figures 1 and 2. Analysis of the complexes and ligand curves (Figure 1 and 2) indicates that the addition of metal ion to the free ligand solutions shifts the buffer region of the ligand to lower pH. This result indicates that complex formation reactions proceed by release of protons from such ligands. A representative set of experimental titration curves obtained for the Sc(III)-Aha and Sc(III)-Bha systems are shown in Figures 1 and 2. The global formation constants (Tables 1 and 2) were calculated from fitting analysis of the titration curves using the BEST computer program.

Complex formation with hydroxamic acids is believed to occur via replacement of the hydroxylamine hydrogen by the metal ion, and closure of the chelate occurs through the carbonyl oxygen. This simple picture of complex formation shows similarity between HL and the first metal ligand complex formed (ML^+). In other words, the complex formed between a proton and the ligand ion L^- can be considered to be HL. This analogy is further exemplified by the order of the stabilities of the ligand proton complexes.

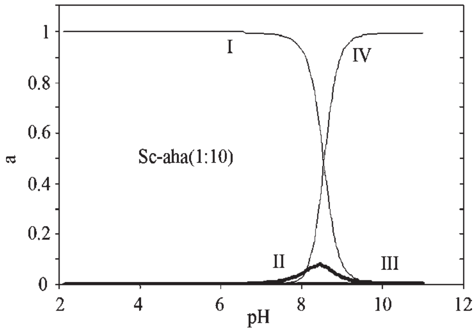


Figure 3. Species distribution curves of the Sc(III) ion and Aha system as a function of $-\log[H^+]$. I. Sc(III). II. ScL^+ III. ScL_2^-. IV. ScL_3^{3-}.

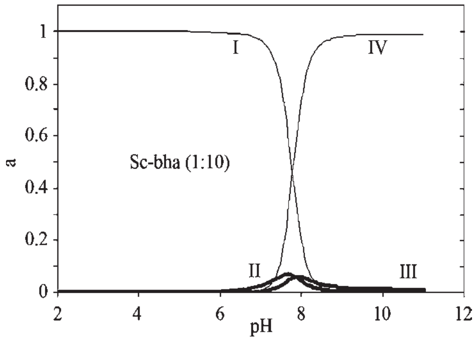


Figure 4. Species distribution curves of the Sc(III) ion and the Bha system as a function of $-\log[H^+]$. I. Sc(III). II. ScL^+. III. ScL_2^-. IV. ScL_3^{3-}.

Iron(II) and cobalt(III) complexes of monohydroxamic acids (aceto-, propiono-, steareo-) have been reported.[46] Spectral and magnetic properties of these complexes indicate that they exist in an octahedral coordination environment via the oxygen atoms of the deprotonated hydroxamic acid ligand. Both complex series are relatively unstable; the former undergoes rapid oxidation to Fe(III), and the latter reduces to Co(II) with concomitant oxidation of the ligand to acetate. Complexes of Fe(III), Co(II), Cu(II), and Zn(II) have also been reported.[46] In addition to complexes with the well-known hydroxamate type chelate(s), 1:2 metal:ligand complex species containing one or both of the coordinated ligands in the hydroximato (R_C-$CONO^{-2}$) form have been found in Cu(II)-Aha and Cu(II)-Bha systems. Complex formation with Fe(III) starts at a very acidic pH, and if the ligand is in high enough excess, the 1:3 species solely exists in the pH range ca. 4 to 8. Hydroxo complexes are generally formed above pH = 8.0 to 8.5.[47]

Interaction of Metal Ions with Aha. Titration curves are illustrated in Figure 1 (for simplicity only the Sc(III)-Aha system is shown) for the Aha chelates of Sc(III), Y(III), and La(III) at 1:1, 1:2, 1:3, and 1:10 mol ratios of metal to ligand. The concentration of the metal chelate was varied from ($4.88 \cdot 10^{-2}$ to $1.46 \cdot 10^{-1}$) M. Samples at five or six different ratios were measured. The potentiometric titration curves of all of the M(III)-Aha systems (in the present study) exhibited steep inflections at m = 1.0 and m = 2.0 for the 1:1 molar ratio (Figure 1, curve II). At a molar ratio of 1:2, these inflections were observed at m = 2.0 and m = 3.0. (Figure 1, curve III). At molar ratios of 1:3 and 1:10, these inflections were observed at m = 2.0 and m = 3.0. (Figure 1, curves III and IV). These titration results for solutions with 1:1, 1:2, 1:3, and 1:10 molar ratios of metal ion to ligand are consistent with the conclusion that only ML, ML_2, and ML_3 species were present. The data obtained for the different molar ratios (1:1, 1:2, 1:3, and 1:10) were supplied into the BEST program and introduced into equilibrium equations (Rows 2, 3, and 4 in Table 1) to calculate the stability constants of the ML, ML_2, and ML_3 complexes (Table 1). Concentration distribution curves in Figure 3 show the dominance of the ScL_3^{3-} species at ca. pH 8.

Interactions of Metal Ions with Bha. The complex species in the Sc(III)-Bha, Y(III)-Bha, and La(III)-Bha systems were ascertained by the selection of several chemical models composed of computer-simulated ML, ML_2, and ML_3 complexes. The titration of a solution with 1:1, 1:2, 1:3, and 1:10 molar ratios of metal ion to ligand resulted in only ML, ML_2, and ML_3 species.

The data obtained for the different molar ratios (1:1, 1:2, 1:3 and 1:10) were supplied into the BEST program and introduced into equilibrium equations (Rows 2, 3, and 4 in Table 2) to calculate the stability constants of the ML, ML_2, and ML_3 complexes (Table 2). Concentration distribution curves in Figure 4 show the dominance of the ScL_3^{3-} species at ca. pH 8.

CONCLUSION

(1) We conclude that Aha and Bha are coordinated as bidentate ligands, and the metal(III) ion has a coordination number of 6.

(2) The complex stability of the binary complexes with respect to the metal ion present follows the order: Sc(III) > Y(III) > La(III). The results of this study show that the superposition of different effects, that is, the number of chelating moieties in the ligand and the length and structure of the connecting chain and the ionic radius and oxidation state of the metal, is reflected in the stabilities of the complexes.

(3) Aha and Bha ligands were found to be good metal ion sequestering agents. The observed order of stability for binary systems with respect to the hydroxamic acid is Aha > Bha. Aha, which has more basic donor atoms, generally forms more stable complexes than Bha.

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