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Scandium(III) and Yttrium(III) Complexes of Hydroxysalicylic Acid Ligands

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Interactions of scandium(III) and yttrium(III) with 2,X-dihydroxybenzoic acids (2,X-DHBA, X = 4–6) (H_3L) have been investigated in aqueous solution by potentiometric method at 25°C and at an ionic strength of 0.1 M (KNO_3 for Sc(III) and $NaClO_4$ for Y(III)). It has been observed that at low pH, the coordination of 2,X-DHBA ligands to Sc(III) occurs through salicylate sites; while Y(III) binds it only from carboxylate. In more basic media the hydrolytic equilibria take place, either in 1 : 1 or in 1 : 2 mole ratios of Sc(III) or Y(III) : H_3L systems. The stability constants of the formed $Sc(LH)^+$, $Sc(LH)(H_2L)$, $Y(H_2L)^{2+}$, $Y(H_2L)_2^+$ type complexes and their mono hydroxo complexes have been determined.

Key Words: Scandium(III), Yttrium(III), Diydroxybenzoic acid, Potentiometric method, Stability constant.

INTRODUCTION

2,X-dihydroxybenzoic acids, (2,X-DHBA, X = 4–6, H_3L) are reported as salicylic acid (SA) derivatives with an extra separate phenolic hydroxy group within the molecule. Due to the existence of carboxylate and phenolate oxygens, they are very effective ligands, especially for metal ions that have strong affinities to the hydroxy groups like aluminum(III)[1, 2], oxovanadium(IV)[3], cupper(II)[4], iron(III)[5] and manganese(II)[5] ions. 2,X-DHBA ligands are all regarded as dibasic by some researchers[1, 2, 4] or tribasic acids by others[5, 6]. Although they have three acidic protons, only two of these protons dissociate in the measurable pH-range. It has been observed by pH-metric and spectrophotometric measurements that the OH groups *ortho* to the carboxylate in the 2,X-DHBA ligands do not dissociate until pH *ca.*13.4, due to the strong intermolecular hydrogen bond between the COO^- and O^- groups.

Martell *et al.*[1] have analyzed and classified the stabilities of Al(III) complexes of hydroxyaliphatic and hydroxyaromatic ligands. Kiss *et al.*[2] have explained the binding modes of 2,X-DHBA ligands in Al(III) complexes in various pH media. The chelating of 2,4-DHBA to Fe(III) occurs in acidic and neutral media through salicylate type (COO^-, O^-) coordination. The formation of $Fe(LH)^+$ and $Fe(LH)_3^{3-}$ type complexes have been defined[5] in more basic media (pH = 8–12) deprotonation of $Fe(LH)_3^{3-}$ takes place. The formation of $Fe(LH)^+$ type complex

has been considered for 2,6-DHBA, but they haven't been proved. On the other hand Mn(II), despite its similar electronic configuration, does not give complexes with 2,4-DHBA. Cadmium(II) has special affinity to 2,3-DHBA, but the formation of complexes in Cd(II) solution with 2,4-DHBA and 2,6-DHBA has not been observed[6]. Comparison of their results shows that Fe(III) and Cu(II) favour the salicylate mode of coordination whereas Cd(II) favours the catecholate mode. Chromium(III) has formed with 2,X-DHBA (X = 4, 5, 6), $Cr(LH)^{+}$and Cr(LH)(OH), $Cr(LH)(H_2L)(OH)^{-}$ type complexes[7].

Scandium(III) is the first transition element of the first row, but it is the congener of Al(III)[8] and its ionic radius for coordination number = 6 is 0.89 Å. Yttrium is always found in nature with rare earths and its chemical properties are very similar to lanthanides[9, 10] and its ionic radius for coordination number 6 is 1.04 Å. The aqua ions of Y(III) and Sc(III) both take place in various hydrolytic equilibria[11, 12]. They have investigated the stabilities of complexes of Sc(III) and Y(III) with catechol[13] and some salicylic acid[14, 15] derivatives. They reported that the complexes of Sc(III) with catechol or salicylic acid derivatives have higher stabilities than Y(III) complexes. While Y(III) forms $Y(LH)^{2+}$ and $Y(LH)_2^{+}$ type complexes with salicylic acid (SA, H_2L), Sc(III) forms ScL and $ScL(LH)^{2-}$ type complexes[14]. The complex formation tendencies of Sc(III) and Y(III) ions with 2,X-DHBA (X = 4, 5, 6) have not been investigated so far.

EXPERIMENTAL

All the chemicals including the scandium nitrate and yttrium oxide, sodium hydroxide, nitric acid, perchloric acid, potassium nitrate, potassium hydrogen phthalate, ethylenediaminetetraacetic acid-disodium salt (EDTA) and sodium perchlorate etc. used were of analytical reagent grade. Sodium hydroxide free from carbonate was prepared and standardized with potassium hydrogen phthalate. 2,4-DHBA was purchased from Fluka and 2,5-DHBA and 2,6-DHBA were purchased from Aldrich. These ligands were used without further purification; their molecular weights were periodically checked by Gran titrations[14]. The stock solutions of Sc(III) and Y(III) were prepared by dissolving appropriate amounts of scandium nitrate (Aldrich, 99.9%) in a small excess of HNO_3 and of yttrium oxide (Sigma, 99.9%) in a small excess of $HClO_4$. Then they were standardized by EDTA titration by the method of Schwarzenbach, as previously described[14]. The concentrations of free acids in the Sc(III) and Y(III) solutions were systematically checked by potentiometric titrations before each series of experiments. All solutions were prepared in carbon dioxide-free double distilled water.

A Schott-pH meter (accuracy ±0.05) fitted with combined electrode was calibrated with acetic acid buffer as well as with standard HCl and NaOH to give hydrogen ion concentrations directly. Measurements were made at 25.0 ± 0.05°C and the ionic strength was maintained at approximately 0.1 M. Purified nitrogen was circulated through the jacketed titration cell under slight pressure to exclude carbon dioxide. All potentiometric titrations were carried out in triplicate. Complexations were investigated within pH interval; at least 1–3 min time intervals were necessary between additions of successive aliquots of sodium hydroxide to reach constancy of pH.

RESULTS AND DISCUSSION

The acid-base chemistry of 2,X-DHBA (X = 4–6) was studied earlier by Kiss *et al.*[2,3] and Aydin *et al.*[16] The protonation constants of HL^{2-} and H_2L^- ion of above mentioned ligands were determined by Aydin *et al.*[16]. But, they could not find the protonation constant of L^{3-} ion of these ligands. They are tabulated with literature values in Table-1.

TABLE-1
PROTONATION CONSTANTS (log K) OF 2,X-DHBA (X = 4,5,6) AND STABILITY CONSTANTS OF Y(III) AND SC(III) COMPLEXES (LOG β) WITH 2,X-DHBA (X = 4, 5, 6) at 25.0 ± 0.1C AND I = 0.1 M

Row	Equilibrium	2,4-DHBA	2,5-DHBA	2,6-DHBA
	Proton complexes		log K	
1.	2-OH($L^- + H^+ \rightleftharpoons HL^{2-}$)	13.37[18]	12.74[18]	13.28[18]
2.	X-OH($HL^{2-} + H^+ \rightleftharpoons H_2L^-$)	8.80 ± 0.01[16]	10.18 ± 0.02[16]	11.03 ± 0.04[16]
3.	COOH($H_2L^- + H^+ \rightleftharpoons H_3L$)	3.12 ± 0.02	2.73 ± 0.03	1.20 ± 0.06
	Sc(III) Complexes		log β	
4.	$Sc^{3+} + HL^{2-} \rightleftharpoons Sc(HL)^+$	13.43 ± 0.03	12.37 ± 0.04	11.78 ± 0.04
5.	$Sc^{3+} + HL^{2-} + H_2L^- \rightleftharpoons Sc(HL)(H_2L)$	15.85 ± 0.02	15.73 ± 0.05	13.15 ± 0.03
6.	$Sc(HL)^+ + OH^- \rightleftharpoons Sc(HL)(OH)$	5.14 ± 0.11	5.20 ± 0.07	5.39 ± 0.07
7.	$Sc(HL)(H_2L) + OH \rightleftharpoons Sc(HL)(H_2L)(OH)^-$	5.48 ± 0.01	5.46 ± 0.07	5.26 ± 0.06
	Y(III) Complexes		log β	
8.	$Y^{3+} + H_2L^- \rightleftharpoons Y(H_2L)^{2+}$	3.64 ± 0.03	4.49 ± 0.06	2.58 ± 0.03
9.	$Y^{3+} + 2H_2L^- \rightleftharpoons Y(H_2L)_2^+$	5.36 ± 0.04	5.34 ± 0.03	4.52 ± 0.05
10.	$Y(H_2L)^{2+} + OH^- \rightleftharpoons Y(H_2L)(OH)^+$	6.63 ± 0.03	6.76 ± 0.04	6.60 ± 0.03
11.	$Y(H_2L)_2^+ + OH^- \rightleftharpoons Y(H_2L)_2(OH)$	6.61 ± 0.03	6.79 ± 0.02	6.63 ± 0.02

Scandium(III) Complexes

The potentiometric titrations were carried out in (1 : 1) and (1 : 2) mole ratios of Sc(III) to 2,X-DHBA over the pH range 2.5–10.0. They have two distinct end-points at m = 2.0 (where m is the mmoles of base per mmol of Sc(III) ion) and at m = 3.0 for 1 : 1 mole ratio of Sc(III) to ligand. They have shifted to m = 3.0 and m = 4.0 for 1 : 2 mole ratio (Fig. 1–3, curves IV and V). The potentiometric data indicate the formation of complexes by coordination equilibria (4) and (5) for 1 : 1 and 1 : 2 mole ratios of Sc(III) : 2,X-DHBA systems, respectively. The neutralization curves of 2,X-DHBA (H_3L) alone and in the presence of Sc(III) are not superimposable in the acidic region, corresponding to the deprotonations of two protons, first one from carboxyl group and second one from —OH group *ortho-* to it and as a result the salicylate type coordination of ligands to Sc(III) has been taken into account. But in the case of 1 : 2 mole ratio, the coordination of second mole of 2,X-DHBA can be considered only from one

of salicylic sites. The potentiometric titration data that are at pH = 2.60–6.00 range have been introduced into the computer program RANA. When Sc(III) : ligand titration data were evaluated, it was found that the assumption of monomeric salicylate-type complex, $Sc(LH)^+$, was enough for a fit to the titration curve, either in 1 : 1 or 1 : 2 mole ratios in m = 0.0–2.00 range. Then the occurrence of $Sc(LH)(H_2L)$ type complex formation has taken place through mono and diprotonated forms of L^{3-} ion. The formation constants for $Sc(LH)^+$ and $Sc(LH)(H_2L)$ type complexes gave a satisfactory fit in the first buffer regions between m = 0.0–2.0 and m = 0.0–3.0; for 1 : 1 and 1 : 2 mole ratios, respectively. The formation constants are tabulated in Table-1. Thus —OH group in position X (X = 4, 5 or 6) is protonated, but the less acidic phenolic —OH of the salicylic function is deprotonated; in other words; 2,X-DHBA type ligands are coordinated from COO^- and O^- sides of salicylic acid to Sc(III) ion. For this reason the complex formation constants of salicylic acid and 2,X-DHBA derivatives can be compared directly[14, 15] in acidic region. The deprotonation of the unbound hydroxyl at positions four, five or six would take place only at higher pH. The occurrence of hydrolytic equilibria (6) and (7) evidently have been assumed and the formation of mixed hydroxo complexes Sc(LH)(OH), $Sc(LH)(H_2L)(OH)^-$ has been suggested and their formation constants have been determined (Table-1). If the stability constants of salicylic acid (H_2L^-) complexes of Sc(III) with its 2,X-DHBA complexes in 1 : 1 and 1 : 2 mole ratios are compared; the corresponding values of salicylic acid complexes are (13.05 ± 0.05)[14] and (15.02 ± 0.05)[14], respectively. Evidently the existence of salicylate type binding in 2,X-DHBA complexes can be considered.

The average number of ligands attached to Sc(III) ions ($\bar{n}$) was defined with the help of RANA as a function of ($\bar{n}$) values versus log L (L is the free concentration of ligand). The degree of formation ($\bar{n}$) was evaluated for Sc(III) :

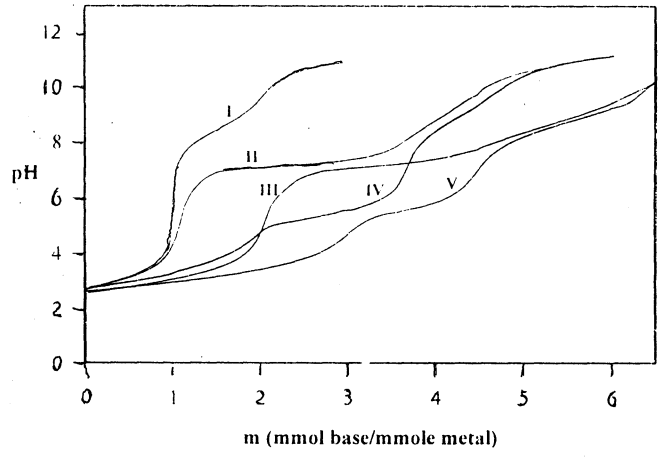

Fig. 1. Titration curves of Y(III) : 2,4-DHBA and Sc(III) : 2,4-DHBA system at ionic strength 0.1 M at 25°C, **I:** 2,4-DHBA alone; **II:** 1 : 1 mole ratio of Y(III) to 2,4-DHBA; **III:** 1 : 2 mole ratio of Y(III) to 2,3-DHBA; **IV** : 1 : 1 mole ratio of Sc(III) to 2,4-DHBA; **V:** 1 : 2 mole ratio of Sc(III) to 2,4-DHBA.

2,X-DHBA complexes present in 1 : 2 mole ratios. Then the formation curves were drawn; all of them are similar in appearance up to $\bar{n} = 1.25$. This indicates that 1 mole of 2,X-DHBA is coordinated to Sc(III) and the second one is partly coordinated (Fig. 3)

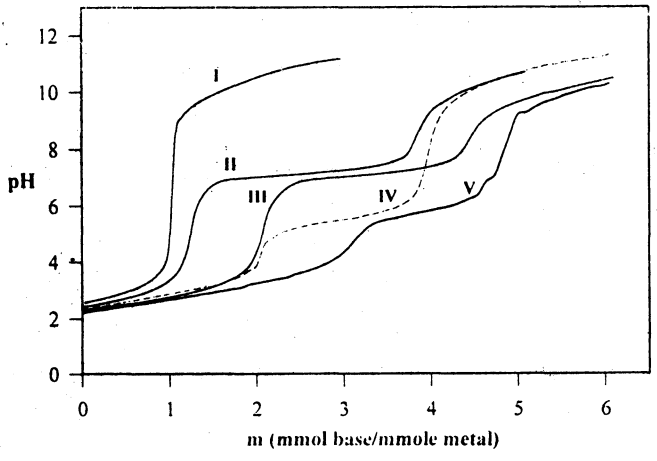

Fig. 2. Titration curves of Y(III) : 2,5-DHBA and Sc(III) : 2,5-DHBA system at ionic strength 0.1 M at 25°C. **I:** 2,5-DHBA alone; **II:** 1 : 1 mole ratio of Y(III) to 2,5-DHBA; **III:** 1 : 2 mole ratio of Y(III) to 2,5-DHBA; **IV:** 1 : 1 mole ratio of Sc(III) to 2,5-DHBA; **V:** 1 : 2 mole ratio of Sc(III) to 2.5-DHBA.

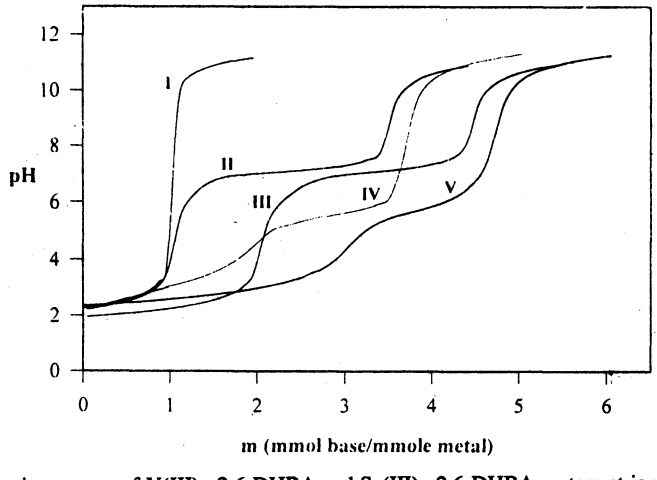

Fig. 3. Titration curves of Y(III) : 2,6-DHBA and Sc(III) : 2,6-DHBA system at ionic strength 0.1 M at 25°C. **I:** 2,6-DHBA alone; **II:** 1 : 1 mole ratio of Y(III) to 2,6-DHBA; **III:** 1 : 2 mole ratio of Y(III) to 2,6-DHBA; **IV:** 1 : 1 mole ratio of Sc(III) to 2,6-DHBA; **V:** 1 : 2 mole ratio of Sc(III) to 2,6-DHBA.

Yttrium(III) Complexes

The titration curves of yttrium(III) : 2,X-DHBA system at different mole ratios have been submitted in Figs. 1–3, curves II and III. They exhibited sharp pH

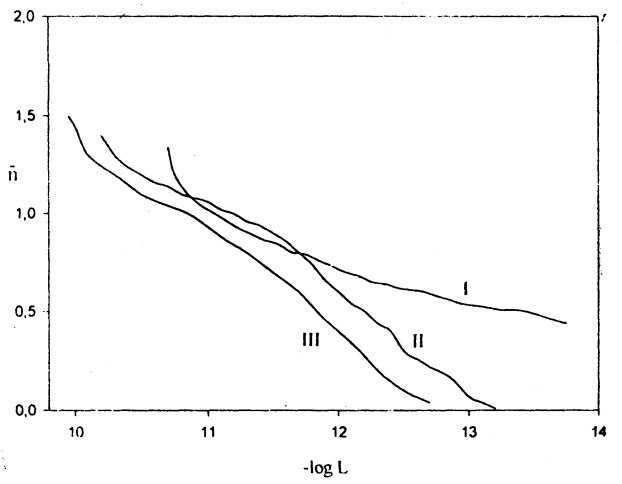

Fig. 4. Degrees of formation in the Sc(III) ion with 2,4-DHBA, 2,5-DHBA and 2,6-DHBA systems, $\bar{n}$, as a function of log L. **I**: Sc(III) : 2,4-DHBA, **II:** Sc(III) : 2,5-DHBA, **III:** Sc(III) : 2,6-DHBA.

jumps (from pH *ca.*3.5 to 7.0), since one and two protons have been released per Y(III) ion for 1 : 1 and 1 : 2 mole ratios, respectively. The results of potentiometric titrations have been introduced in the pH range from pH = 2.12 to pH = 3.74. The comparison of titration curves of 2,X-DHBA ligands and Y(III) : 2,X-DHBA systems and their evaluation have been performed like Sc(III) : 2,X-DHBA systems that was discussed under the "Sc(III) complexes" title. Thus the formation of $Y(H_2L)^{2+}$ and $Y(H_2L)_2^+$ complexes in the acidic pH range could be considered by equilibria (8) and (9). In 1 : 1 and 1 : 2 mole ratios of Y(III) : 2,X-DHBA, as a major species, mono and bis-complexes of H_2L^- ion have been considered. Well only assuming 2,X-DHBA ligands acted as monodentate ligand through carboxylate oxygen, fit the potentiometry data. Since the same behaviour has been noticed for oxovanadium(IV) ion[3] and has been defined that a carboxylate group can act as an anchoring site. The coordination of 2,X-DHBA ligands to Y(III) can occur through COO^- ion; the stability constants of $Y(H_2L)^{2+}$ type complexes are higher than the protonation constants of carboxylate group for each 2,X-DHBA ligand. In fact the formation of very labile monoprotonated complexes of La(III)[17] and Y(III)[14] with salicylic acid in which the occurrence of COO^- coordination have been indicated. The formation of hydroxo complexes of Y(III) has been assumed according to equilibria (10) and (11). The stability constants of hydroxo complexes of Y(III) are very close to each ligand (Table-1).

Conclusion

Hydroxy salicylic acid ligands contain two phenolates and one carboxylate groups that can bind Sc(III) and Y(III) ions effectively; but the coordination abilities of Sc(III) and Y(III) ions towards 2,X-DHBA (X = 4–6) ligands are different; since Sc(III) has smaller ionic radius than Y(III) ion. As a result, Sc(III) complexes are stronger than Y(III) complexes, since the coordination of Y(III) to 2,X-DHBA occurs only through deprotonated carboxylate oxygen either in 1 : 1

or 1 : 2 mole ratios. In the acidic pH range, simultaneous coordination from salicylate sites (COO^-, O^-) occurs only for Sc(III). Thus Sc(III) ion forms $Sc(LH)^+$, $Sc(LH)(H_2L)$ type complexes; while Y(III) ion forms $Y(H_2L)^{2+}$ and $Y(H_2L)_2^+$ type complexes. The stabilities of salicylic acid and 2,4-DHBA complexes of Sc(III) and Y(III) are very close to each other; it has been decided that the binding modes of Sc(III) and Y(III) complexes of SA and 2,X-DHBA are equal for each metal ion. The stability constants of mono-hydroxo complexes, that are products of hydrolytic equilibria in basic media, have been determined by potentiometric measurements.

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