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Studies on Mixed Ligand Complexes of Th^{4+} with some Oxygen Donor Ligands

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The complexation reactions of Th^{4+} with oxygen donor ligands, 2-hydroxybenzoic acid (sa), 3-carboxy-4-hydroxybenzenesulphonic acid (ss) and 1,2-dihydroxybenzene (ca) have been studied by pH-metric methods. Formation constant values of the various binary, hydroxo and ternary complexes including $Th(sa)^{2+}$, $Th(sa)_2$, $Th(sa)_3^{2-}$, $Th(sa)_4^{4-}$, $Th(sa)(OH)^+$, $Th(ss)^+$, $Th(ss)_2^{2-}$, $Th(ss)_3^{5-}$, $Th(ss)_4^{8-}$, $Th(ss)(OH)$, $Th(ss)(OH)_2^-$, $Th(ss)_2(OH)^{3-}$, $Th(ca)^{2+}$, $Th(ca)_2$, $Th(ca)(OH)^+$, $Th(ca)(OH)_2$, $Th(sa)(ss)^-$, $Th(sa)(ca)$, $Th(ss)(ca)^-$, $Th(sa)(ss)_2^{4-}$, $Th(ss)(sa)_2^{3-}$, $Th(ca)(sa)_2^{2-}$, $Th(ca)(ss)_2^{4-}$ and $Th(sa)_2(ss)_2^{6-}$ liable to exist in mixtures containing corresponding metal-ligand/pair of ligand ratio have been determined at 25°C and at an ionic strength of 0.1 M KNO_3 and the results have been discussed.

INTRODUCTION

The oxygen donor ligands have a great importance in kinetic studies[1, 2] and many analytical methods based on complex formation reaction in solution[3, 4]. The problems related to equilibrium measurements have been solved by means of various experimental techniques[5–8] and methods of evaluation of equilibrium constant. The oxygen donor ligands, 2-hydroxybenzoic acid (sa), 3-carboxy-4-hydroxybenzenesulphonic acid (ss) and 1,2-dihydroxybenzene (ca) have excellent chelating tendencies. But, most of their complexation reactions studied involve either simple binary species or the mixed ligand species formed in steps due to attachment of primary and bidentate secondary ligands[9–12]. Very little work is available concerning the formation constants of the ternary systems containing the two ligands of comparable basicity capable of binding the metal ion in a single step[13, 14]. These systems generally include the transition metal ion (coordination number 4) and the bidentate ligands containing both the oxygen and nitrogen donors. Rare informations have been reported on mixed complexes of metal ions with coordination number six[15–17]. More interesting results could be expected in the interaction between metal ions of high coordination number and pairs of bi-, tri-, tetra- etc. dentate ligands[18]. A metal ion with coordination number eight (Th^{4+}) may involve up to four bidentate ligand units in the mixed complexes.

Thus, in the present investigation simultaneous coordination of two different types of ligands, chosen from sa, ss and ca, expecting the formation of mixed ligand species (i) Th^{4+}-sa-ss, Th^{4+}-sa-ca and Th^{4+}-sa-ca; (ii) Th^{4+}-sa_2-ss, Th^{4+}-sa-ss_2, Th^{4+}-sa_2-ca, Th^{4+}-sa-ca_2, Th^{4+}-ss_2-ca, Th^{4+}-ss-ca_2; (iii) Th^{4+}-sa_2-ss_2, Th^{4+}-sa_2-ca_2, Th^{4+}-ss_2-ca_2; (iv) Th^{4+}-sa_3-ss, Th^{4+}-sa-ss_3, Th^{4+}-sa_3-ca, Th^{4+}-sa-ca_3, Th^{4+}-ss_3-ca and Th^{4+}-ss-ca_3 has been investigated at 25°C and $\mu = 0.1$ M KNO_3 by pH-metric techniques described earlier[19, 20]. Equilibrium constants of these mixed ligand complexes along with the binary and some hydroxo complexes existing in solution have been reported.

EXPERIMENTAL

Material

Standard solutions of 1.0 M potassium nitrate and 0.0387 N HNO_3 were prepared using analytical grade reagents. Aqueous solution (5.0×10^{-3} M) of thorium nitrate (SISCO) was prepared and metal content was determined by the gravimetric method (ignition to oxide)[21]. 5.0×10^{-3} M aqueous solution of each 3-carboxy-4-hydroxybenzenesulphonic acid (CDH) and 1,2-dihydroxybenzene (BDH) were prepared by direct weighing. 2-Hydroxybenzoic acid (BDH) was dissolved in known amount of alkali and the volume was raised to get 5.0×10^{-3} M solution of the ligand. Excess of alkali present in titration mixtures containing the ligand was neutralized by adding known amount of nitric acid solution before titration.

Procedure

A number of mixtures: (i) HNO_3; (ii) 5.0×10^{-4} M ligand + (i); (iii) 5.0×10^{-4} M metal nitrate + (ii); (iv) 2.5×10^{-4} M metal nitrate + (ii); (v) 1.66×10^{-4} M metal nitrate + (ii); (vi) 1.25×10^{-4} M metal nitrate + (ii) were prepared for studying the equilibrium reactions involving proton-ligand dissociation and simple complex formation. Six types of titration mixtures for mixed ligand complex systems containing pair of ligand H_nA-H_lB and metal nitrate, were prepared keeping metal nitrate: H_nA:H_lB ratio 1:1:1, 1:2:1, 1:1:2, 1:2:2, 1:3:1, 1:1:3, and adding the mineral acid as in (i) (total metal ion initial concentration, $C_{M^\circ} = 5.0 \times 10^{-4}$ M in each case). The pH-metric titrations were carried out in an inert atmosphere of nitrogen (by bubbling oxygen free nitrogen gas, through the solution, in the titrating vessel) keeping the initial volume of each mixture 50 cm^3 at an ionic strength of 0.10 M KNO_3 and temperature 25°C.

From the experimental data pH *vs.* volume of alkali curves were plotted and were utilized to calculate moles of alkali used per mole metal/ligand (*a*) at different pH[19]. Further, *a* values were plotted against pH and the existing complex equilibria were analysed. A scientific calculator CASIO fx-910 was used for calculation work.

RESULTS AND DISCUSSION

1. Proton-ligand dissociation constants

A sharp inflection in pH *vs. a* curve (Fig. 1 shown only up to pH 11.0) of sa system shows that protons from the —COOH and —OH groups are dissociated in two distinct steps above pH *ca.* 2.4 (below pH *ca.* 4.6) and 11.8, respectively. The titration mixture, however, remains colourless throughout the titration. The calculated proton-ligand dissociation constants are: $K_1^H = 10^{-2.91 \pm 0.01}$, $K_2^H = 10^{-13.50 \pm 0.02}$.

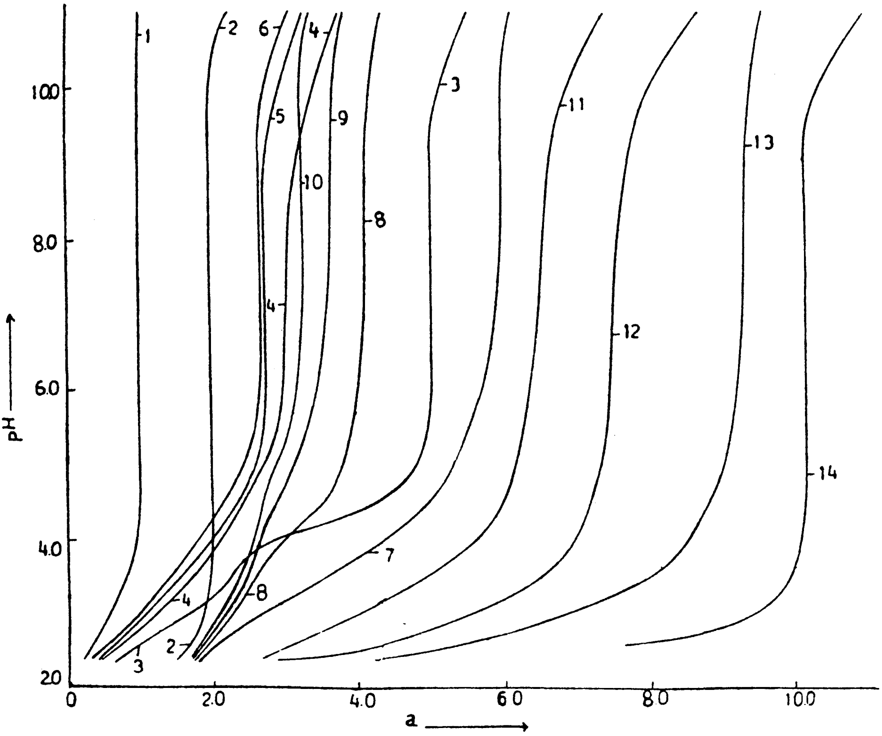

Fig. 1. pH *vs.* *a* curves of binary and mixed ligand complexes of Th^{4+} with sa and ss: (1) sa, (2) ss, (3) Th^{4+}-sa, (4) Th^{4+}-2sa, (5) Th^{4+}-3sa, (6) Th^{4+}-4sa ($C_{ss^\circ} = 5.0 \times 10^{-4}$ M), (7) Th^{4+}-ss, (8) Th^{4+}-2ss, (9) Th^{4+}-3ss, (10) Th^{4+}-4ss ($C_{ss^\circ} = 5.0 \times 10^{-4}$ M), (11) Th^{4+}-sa-ss, (12) Th^{4+}-2sa-ss, (13) Th^{4+}-sa-2ss, (14) Th^{4+}-2sa-2ss ($C_{M^\circ} = 5.0 \times 10^{-4}$ M), [where C_{sa°, C_{ss° and C_{M° are initial concentration of sa, ss and Th^{4+} in the titration mixtures, respectively; *a* = moles of alkali used per mole of ligand/metal for ligand, binary complex/ternary complex systems, respectively].

The proton of —SO_3H group in ss is dissociated at very low pH value, and the ligand mixture remains colourless under the experimental range of pH. The steep inflection in the titration curve at *a* = 2.0 shows that the two proton-ligand dissociation equilibria corresponding to proton dissociation from —COOH and —OH groups exist independently. The proton-ligand dissociation constant values for these steps are $K_2^H = 10^{-2.36 \pm 0.07}$ and $K_3^H = 10^{-11.52 \pm 0.03}$. The higher value of dissociation constant for the phenolic group than that of sa is probably due to electron withdrawing nature of —SO_3H group.

Proton-ligand equilibria, corresponding to dissociation of protons from the two phenolic gorups of ca is evident from the titration curve (figure omitted). The dark reddish-brown colour of the netural ligand molecule gradually turns yellowish-brown (at pH ~ 8.6), and subsequently the mixture appears reddish-brown beyond pH ~ 10.0. Proton-ligand dissociation constants, $K_1^H = 10^{-9.40 \pm 0.03}$ and $K_2^H = 10^{-11.58 \pm 0.02}$ evaluated as earlier, can be compared with those reported by Martell *et al.*[9]

2. Binary complexes

(a) 1 : 1 *metal-ligand systems*: Analysis of the titration curve and the calculations carried out for evaluation of equilibrium constant indicate that in 1 : 1 metal-sa, colourless mixture formation of $Th(sa)^{2+}$ takes place below pH ~ 3.25 (below $a = 2.0$). A further increase in a value indicates coordination of OH^- ion between pH ~ 3.25 and 4.05. Beyond $a = 3.0$ the titration mixture appears turbid and the turbidity gradually turns into a thick precipitate at $a = 4.0$, probably due to existence of the neutral $Th(sa)(OH)_2$ species. The precipitate does not dissolve up to pH ~11.00. The equilibrium constants for the soluble species are given in Table 1.

Colourless $Th(ss)^+$ complex is formed between $a = 0$ and 3.0. Further, between $a = 3.0$ and 4.0, formation of soluble and neutral species Th(ss)(OH) is indicated by the related titration curve (Fig. 1). The equilibrium constants of the simple and hydroxy complexes are given in Table 1. Existence of turbidity between pH 4.2 and 11.0 did not allow any further calculations.

In 1 : 1 metal-ca system, a gradual colour change, from reddish-brown to dark yellow at $a = 2.0$ (pH ~ 3.90), supports the formation of $Th(ca)^{2+}$ complex concluded on the basis of comparison of pH *vs.* a curves (ca and 1 : 1 metal-ca). The colour of the mixture further does not change between pH 3.90 and 5.50 (a ~ 3.77). Thus, the complex $Th(ca)^{2+}$ and both the hydroxo species $Th(ca)(OH)^+$ and $Th(ca)(OH)_2$, expected to be formed between $a = 2.0$ and 4.0 are identical in colour. Appearance of a steep inflection at $a = 4.0$ in pH *vs.* a curve and turbidity in the mixture at $a = 3.80$ is perhaps due to formation of neutral $Th(ca)(OH)_2$ species free from coexistence of other higher hydroxo complexes.

(b) 1:2 *metal-ligand systems*: Involving the formation of $Th(sa)_2$ and $Th(ss)_2^{2-}$ related metal-ligand equilibria exist, respectively, below $a = 2.0$ (pH ~ 3.84) and 3.0 (pH ~ 4.05) in 1:2 metal-ligand mixtures. Turbidity exists in titration mixtures of sa and ss systems from pH 4.34 and 4.68, respectively. However, in ss systems, formation of monohydroxo complex species between pH 4.01 and 4.47 is indicated by the pH *vs.* a curves. The equilibrium constants of the soluble species are given in Table-1. The titration mixture of ca system is precipitated at pH ~ 5.66. In the corresponding titration curve there is a steep inflection at $a = 2.0$ (pH ~ 5.75) which may be expected due to existence of neutral and yellow $Th(ca)_2$ complex. Amount of the precipitate, initially appearing at lower pH, decreases from pH ~ 9.50 (a = 2.07) leaving behind a turbid solution.

(c) 1:3, *metal-ligand systems*: The titration curves of sa and ss systems indicate formation of 1 :3 metal-ligand complexes in solution, respectively, below pH 4.05 ($a = 2.0$) and 4.55 ($a = 3.0$). The titration mixtures of both the ligand systems turn turbid from pH ~ 5.4 and 4.70, respectively. Equilibrium constants of the soluble species are given in Table-1. In ca system below pH ~ 5.80, where 1:3, metal-ligand titration mixture is in solution form, the composite ligand and 1:2, metal-ligand pH *vs.* *a* curve coincides with that of 1:3, metal-ca composition. Thus, $Th(ca)_3^{2-}$ complex does not exist in solution. However, no calculation could be made above pH ~ 5.80, due to the existence of turbidity.

TABLE-1

EQUILIBRIUM CONSTANTS OF BINARY AND HYDROXO COMPLEXES OF Th^{4+} WITH sa, ss and ca (25°C, $\mu = 0.1$ M KNO_3)

Reaction		log K
$Th^{4+} + sa^{2-}$	$\rightleftarrows Th(sa)^{2+}$	14.71 ± 0.06
$Th(sa)^{2+} + sa^{2-}$	$\rightleftarrows Th(sa)_2$	13.96 ± 0.28
$Th(sa)_2 + sa^{2-}$	$\rightleftarrows Th(sa)_3^{2-}$	13.55 ± 0.16
$Th(sa)_3^{2-} + sa^{2-}$	$\rightleftarrows Th(sa)_4^{4-}$	13.26 ± 0.28
$Th(sa)^{2+} + OH^-$	$\rightleftarrows Th(sa)(OH)^+$	10.20
$Th^{4+} + ss^{3-}$	$\rightleftarrows Th(ss)^+$	12.25 ± 0.11
$Th(ss)^+ + ss^{3-}$	$\rightleftarrows Th(ss)_2^{2-}$	11.65 ± 0.10
$Th(ss)_2^{2-} + ss^{3-}$	$\rightleftarrows Th(ss)_3^{5-}$	11.00 ± 0.09
$Th(ss)_3^{5-} + ss^{3-}$	$\rightleftarrows Th(ss)_4^{8-}$	10.73 ± 0.08
$Th(ss)^+ + OH^-$	$\rightleftarrows Th(ss)(OH)$	10.55
$Th(ss)(OH) + OH^-$	$\rightleftarrows Th(ss)(OH)_2^-$	9.85
$Th(ss)_2^{2-} + OH^-$	$\rightleftarrows Th(ss)_2(OH)^{3-}$	9.73
$Th^{4+} + ca^{2-}$	$\rightleftarrows Th(ca)^{2+}$	17.45 ± 0.02
$Th(ca)^{2+} + ca^{2-}$	$\rightleftarrows Th(ca)_2$	16.79 ± 0.06
$Th(ca)^{2+} + OH^-$	$\rightleftarrows Th(ca)(OH)^+$	10.03
$Th(ca)(OH)^+ + OH^-$	$\rightleftarrows Th(ca)(OH)_2$	9.16

(d) 1:4 *metal-ligand systems*: Formation of $Th(sa)_4^{4-}$ and $Th(ss)_4^{8-}$ is also evident, below *a* = 2.0 (pH ~ 4.24) and *a* = 3.0 (pH ~ 5.19) respectively from their titration curves (Fig. 1). Turbidity formations beyond pH ~ 4.97 and 4.89 have been observed in the titration of 1:4 metal-ligand titration mixtures of sa and ss, respectively. As expected, from the study of 1:3 metal-ca system where 1:3 metal-ligand species is not formed, $Th(ca)_4^{4-}$, also, does not exist in solution as the composite curve of the ligand and 1:3 metal-ligand systems, coincides with that of 1:4 Th-ca system in solution range below pH 6.33, and beyond this pH the reaction mixture remains in turbid form.

Comparing the values of equilibrium constants given in Table 1, it is concluded that the complexing tendency of the ligand follows the order: ca > sa > ss. As expected, the equilibrium constants K_1 and K_2 for 1,2-dihydroxybenzene are greater than those of 2-hydroxybenzoic acid containing —COOH group in place of one phenolic group. Smaller values of equilibrium constants, K_1, K_2, K_3 and K_4 for 3-carboxy-4-hydroxybenzenesulphonic acid complexes than the corresponding value for 2-hydroxybenzoic acid complexes, may be regarded as a result of its poor electron donating property due to larger size of the ligand and electron withdrawing nature of sulphonic acid group.

Table-1 shows that association of OH^- ion with 1 : 1 metal-ligand complexes follows the order: $Th(ss)^+ > Th(sa)^{2+} > Th(ca)^{2+}$. Here, it would not be unreasonable to say that the coordination of OH^- ion is favoured in the complexes with low electron density around the central atom. Tendency of coordination of OH^- ion with $Th(ss)(OH) > Th(ca)(OH)^+$ and $Th(ss)_2^{2-}$ can again be explained on the similar grounds.

Mixed ligand complexes

(a) 1 : 1 : 1 *systems*: The titration mixtures of Th^{4+} systems containing pair of ligands, sa-ss, sa-ca and ss-ca (in 1 : 1 :1 ratio) turn turbid at pH ~ 3.80, 4.37 and 4.01, respectively. In all the systems, the mixture remains colourless under the experimental range of mixed ligand complex formation in solution. Existence of turbidity did not permit further analysis. On comparing the pH *vs. a* curves of each mixed system with the corresponding ligand, 1 : 1 and 1:2 metal-ligand systems[16, 19], it has been concluded that MAB type complex is formed in solution:

$$M + A + B \rightleftarrows MAB; \quad K_{AB} = \frac{[MAB]}{[M][A][B]}$$

Equilibrium constant K was calculated (Table-2), considering the existence of free M, MA, MA_2, MB, MB_2 and MAB in solution, as described earlier[19].

Formation constant value for the addition of ss to 1 : 1 Th^{4+} complex with sa is almost comparable in magnitude with the value for aqua-ion. A parallel effect is noted on addition of sa to 1 : 1 Th^{4+}-ss complex. These informations are in agreement with those of Perrin and coworkers[14] reported earlier on ternary complexes of some biologically important ligands, ethylenediamine, histamine, serine and salicylic acid with Cu^{2+}. But, for the reaction $CuA^{2+} + B \rightleftarrows CuAB$ (where A = 2,2′-bipyridyl and B is the anion of salicylic acid, catechol or tiron), Martell *et al.*[9] reported higher values of the stepwise formation constants (from 0.9 to 1.5 logarithm units) than for the addition of B to the hydrated Cu^{2+} ion. Earlier findings[16, 22] on mixed ligand complexes of adenine, xanthine and hypoxanthine involving tripositive rare earth ions can also be compared with the latter results. In both the remaining systems of the present study, the formation constants for addition of one of the ligands to 1 : 1 metal complex with the other ligand are higher (from 0.89 to 3.33 logarithm units) than K_1 values for the addition of the ligand to aqua-ion.

(b) 1 : 1 :2 *or* 1 :2 : 1 *systems*: Formation of 1 : 1 :2 or 1 :2 : 1 complexes of sa and ss is indicated by comparison of pH *vs. a* curve of the system taken, with those of the corresponding 1 : 1 : 1 complex and the ligand (Fig. 1) introduced twice of the metal ion. The system Th^{4+}-2sa-ss, Th^{4+}-ss-2ss, Th^{4+}-2sa-ca and Th^{4+}-2ss-ca remain colourless under the experimental condition of pH. Analysis of the corresponding titration curves was not possible from pH ~ 3.91, 4.06, 3.99 and 4.21, respectively due to precipitation of the reaction mixtures. The equilibrium constants of the mixed ligand complexes calculated in the solution range by the methods described earlier[19] are given in Table-2. Comparison of the pH *vs. a* curves for ligand pair systems with double amount of ca (figure ommited) show that Th^{4+}-sa-ca_2 and Th^{4+}-ss-ca_2 species do not exist in solution.

TABLE-2

EQUILIBRIUM CONSTANTS OF TERNARY COMPLEXES OF Th^{4+} WITH POSSIBLE PAIRS OF sa, ss AND ca (25°C, $\mu = 0.10$ M KNO_3)

Reaction		log K
$Th^{4+} + sa^{2-} + ss^{3-}$	$\rightleftarrows Th(sa)(ss)^{-}$	27.26 ± 0.20
$Th(sa)^{2+} + ss^{3-}$	$\rightleftarrows Th(sa)(ss)^{-}$	12.55
$Th(ss)^{+} + sa^{2-}$	$\rightleftarrows Th(sa)(ss)^{-}$	15.01
$Th^{4+} + sa^{2-} + ca^{2-}$	$\rightleftarrows Th(sa)(ca)$	34.29 ± 0.42
$Th(sa)^{2+} + ca^{2-}$	$\rightleftarrows Th(sa)(ca)$	19.58
$Th(ca)^{2+} + sa^{2-}$	$\rightleftarrows Th(sa)(ca)$	16.84
$Th^{4+} + ss^{3-} + ca^{2-}$	$\rightleftarrows Th(ss)(ca)^{-}$	30.72 ± 0.34
$Th(ss)^{+} + ca^{2-}$	$\rightleftarrows Th(ss)(ca)^{-}$	18.47
$Th(ca)^{2+} + ss^{3-}$	$\rightleftarrows Th(ss)(ca)^{-}$	13.27
$Th^{4+} + sa^{2-} + 2ss^{3-}$	$\rightleftarrows Th(sa)(ss)_2^{4-}$	40.02 ± 0.46
$Th(sa)^{2+} + 2ss^{3-}$	$\rightleftarrows Th(sa)(ss)_2^{4-}$	25.31
$Th(sa)(ss)^{-} + ss^{3-}$	$\rightleftarrows Th(sa)(ss)_2^{4-}$	12.76
$Th(ss)_2^{2-} + sa^{2-}$	$\rightleftarrows Th(sa)(ss)_2^{4-}$	16.12
$Th^{4+} + ss^{3-} + 2sa^{2-}$	$\rightleftarrows Th(ss)(ca)_2^{3-}$	41.41 ± 0.17
$Th(ss)^{+} + 2sa^{2-}$	$\rightleftarrows Th(ss)(sa)_2^{3-}$	29.16
$Th(ss)(sa)^{-} + sa^{2-}$	$\rightleftarrows Th(ss)(sa)_2^{3-}$	14.15
$Th(sa)_2 + ss^{3-}$	$\rightleftarrows Th(ss)(sa)_2^{3-}$	12.94
$Th^{4+} + ca^{2-} + 2sa^{2-}$	$\rightleftarrows Th(ca)(sa)_2^{2-}$	50.58 ± 0.38
$Th(ca)^{2+} + 2sa^{2-}$	$\rightleftarrows Th(ca)(sa)_2^{2-}$	33.13
$Th(ca)(sa) + sa^{2-}$	$\rightleftarrows Th(ca)(sa)_2^{2-}$	16.29
$Th(sa)_2 + ca^{2-}$	$\rightleftarrows Th(ca)(ss)_2^{2-}$	21.91
$Th^{4+} + ca^{2-} + 2ss^{3-}$	$\rightleftarrows Th(ca)(ss)_2^{4-}$	44.11 ± 0.28
$Th(ca)^{2+} + 2ss^{3-}$	$\rightleftarrows Th(ca)(ss)_2^{4-}$	26.66
$Th(ca)(ss)^{-} + ss^{3-}$	$\rightleftarrows Th(ca)(ss)_2^{4-}$	13.39
$Th(ss)_2^{2-} + ca^{2-}$	$\rightleftarrows Th(ca)(ss)_2^{4-}$	20.21
$Th^{4+} + 2sa^{2-} + 2ss^{3-}$	$\rightleftarrows Th(sa)_2(ss)_2^{6-}$	55.36 ± 0.69
$Th(sa)_2(ss)^{3-} + (ss)^{3-}$	$\rightleftarrows Th(sa)_2(ss)_2^{6-}$	13.95
$Th(sa)_2 + 2ss^{3-}$	$\rightleftarrows Th(sa)_2(ss)_2^{6-}$	26.69
$Th(sa)(ss)_2^{4-} + sa^{2-}$	$\rightleftarrows Th(sa)(ss)_2^{6-}$	15.34
$Th(ss)_2^{2-} + 2sa^{2-}$	$\rightleftarrows Th(sa)(ss)_2^{6-}$	31.46

Formation constants, in all the systems, of mixed complexes for the addition of ligand B to ThA_2 are greater than the constants for addition of this ligand to aqua-ion. A similar information is also obtained when ss^{3-} and sa^{2-} combine with $Th(sa)(ss)^{-}$, $Th(ss)(ca)^{-}$ and $Th(sa)(ca)$, respectively. But, a reverse trend is followed on coordination of sa^{2-} with $Th(sa)(ss)^{-}$.

(c) 1:2:2 *and* 1:1:3 *or* 1:3:1 *systems*: None of the three composite pH *vs. a* curves (Fig. 1) for sa and ss systems, of Th^{4+}-$2H_nA$-H_lB and H_lB or Th^{4+}-H_nA-$2H_lB$ and H_nA or Th^{4+}-H_nA-H_lB, H_nA and H_lB systems, separately coincides with the corresponding curve of Th^{4+}-$2H_nA$-$2H_lB$ mixtures in the pH range where ThA_2B_2 species is expected to exist. Deviation of the two curves indicates the formation of ThA_2B_2 mixed complex in solution. In the Th^{4+}-2sa-2ss mixture, which remains colourless, throughout the titration range, the turbidity formation has been noted from pH ~ 4.05.

For evaluation of equilibrium constant of the mixed complex, $Th(sa)_2(ss)_2^{6-}$ the calculation method described earlier[19] for MAB, MA_2B or MAB_2 complexes has been further extended here to MA_2B_2 complex systems using mass and charge balance relations. Considering the existence of MA, MA_2, MA_3, MA_4, MB, MB_2, MB_3, MB_4, MAB, MA_2B, MAB_2, MA_2B_2 species in solution, expressions for [A], [B], [M], $[MA_2B_2]$ (eqns. 1–4) were obtained. [A] was, thus, calculated by Newton's method with the help of eqn. (1):

$$R_1[A]^5 + R_2[A]^4 + R_3[A]^3 + R_4[A]^2 + R_5[A] - R_6 = 0$$

Further, the Eqns. (2)–(4) were used to obtain the concentration of free ligand B, free metal ion and $[MA_2B_2]$.

$$\begin{aligned}[B] &= \frac{C_M(2n + 2l - a)}{b_1} - \frac{a_1}{b_1}[A] \\ &= e - d[A] \end{aligned} \tag{2}$$

$$\begin{aligned}[M] &= a_2[A]/(2 + K_{1A}[A] - K_{1A}K_{2A}K_{3A}[A]^3 - 2K_{1A}K_{2A}K_{3A}K_{4A}[A]^4 \\ &\quad + 2K_{1B}[B] + 2K_{1B}K_{2B}[B]^2 + 2K_{1B}K_{2B}K_{3B}[B]^3 + 2K_{1B}K_{2B}K_{3B}K_{4B}[A]^4 \\ &\quad + K_{AB}[A][B] + K_{AB_2}[A][B]^2) \\ &= b_2[B]/(2 + K_{1B}[B] - K_{1B}K_{2B}K_{3B}[B]^3 - K_{1B}K_{2B}K_{3B}K_{4B}[A]^4 \\ &\quad + 2K_{1A}[A] + 2K_{1A}K_{2A}[A]^2 + 2K_{1A}K_{2A}K_{3A}[A]^3 + 2K_{1A}K_{2A}K_{3A}K_{4A}[A]^4 \\ &\quad + K_{AB}[A][B] + K_{A_2B}[A]^2[B] \end{aligned} \tag{3}$$

$$\begin{aligned}[MA_2B_2] &= C_M - [M] - [MA] - [MA_2] - [MA_3] - [MA_4] - [MB] - [MB_2] \\ &\quad - [MB_3] - [MB_4] - [MAB] - [MA_2B] - [MAB_2] \end{aligned} \tag{4}$$

where

$$R_1 = 2K_{1A}K_{2A}K_{3A}K_{4A}(a_2 - b_2d) + 2d^4K_{1B}K_{2B}K_{3B}K_{4B}(b_2d - a_2)$$

$$\begin{aligned}R_2 &= K_{1A}K_{2A}K_{3A}(2a_2 - b_2d) + 2b_2eK_{1A}K_{2A}K_{3A}K_{4A} + K_{1B}K_{2B}K_{3B}(a_2d^3 - 2b_2d^4) \\ &\quad + ed^3K_{1B}K_{2B}K_{3B}K_{4B}(8a_2 - 10b_2d) - a_2dK_{A_2B} + b_2d^3K_{AB_2}\end{aligned}$$

$$\begin{aligned}R_3 &= 2a_2K_{1A}K_{2A} + b_2eK_{1A}K_{2A}K_{3A} + 2b_2d^3K_{1B}K_{2B} + K_{1B}K_{2B}K_{3B}ed^2(8b_2d - 3a_2) \\ &\quad + K_{1B}K_{2B}K_{3B}K_{4B}e^2d^2(20b_2d - 12a_2) - a_2dK_{AB} + a_2eK_{A_2B} \\ &\quad - 3b_2ed^2K_{AB_2} - b_2d^2K_{AB}\end{aligned}$$

$$\begin{aligned}R_4 &= -K_{1B}d(a_2 + 2b_2d) - 6b_2ed^2K_{1B}K_{2B} + K_{1B}K_{2B}K_{3B}e^2d(3a_2 - 12b_2d) \\ &\quad + K_{1B}K_{2B}K_{3B}K_{4B}e^3d(8a_2 - 20b_2d) + K_{1A}(2a_2 + b_2d) + K_{AB}e(a_2 + 2b_2d) \\ &\quad + 3b_2e^2 + dK_{AB_2}\end{aligned}$$

$$R_5 = K_{1B}e(a_2 + 4b_2d) + 6b_2e^2dK_{1B}K_{2B} + K_{1B}K_{2B}K_{3B}e^3(8b_2d - a_2)$$
$$+ K_{1B}K_{2B}K_{3B}K_{4B}e^4(10b_2d - 2a_2) - b_2eK_{1A} + 2a_2 + 2b_2d - b_2e^2K_{AB}$$
$$- b_2e^3K_{AB_2}$$

$$R_6 = 2b_2e(1 + eK_{1B} + e^2K_{1B}K_{2B} + e^3K_{1B}K_{2B}K_{3B} + e^4K_{1B}K_{2B}K_{3B}K_{4B})$$

$$a_1 = \frac{n[H^+]^n}{K^H_{1A}K^H_{2A}K^H_{3A}\ldots K^H_{nA}} + \frac{(n-1)[H^+]^{n-1}}{K^H_{2A}K^H_{3A}\ldots K^H_{nA}} + \ldots + \frac{[H^+]}{K^H_{nA}}$$

$$a_2 = \frac{[H^+]^n}{K^H_{1A}K^H_{2A}K^H_{3A}\ldots K^H_{nA}} + \frac{[H^+]^{n-1}}{K^H_{2A}K^H_{3A}\ldots K^H_{nA}} + \ldots + \frac{[H^+]}{K^H_{nA}} + 1$$

$$b_1 = \frac{l[H^+]^l}{K^H_{1B}K^H_{2B}K^H_{3B}\ldots K^H_{lB}} + \frac{(l-1)[H^+]^{l-1}}{K^H_{2B}K^H_{3B}\ldots K^H_{itlaiclb}} + \ldots + \frac{[H^+]}{K^H_{lB}} + 1$$

$$b_2 = \frac{[H^+]^l}{K^H_{1B}K^H_{2B}K^H_{3B}\ldots K^H_{lB}} + \frac{[H^+]^{l-1}}{K^H_{2B}K^H_{3B}\ldots K^H_{lB}} + \ldots + \frac{[H^+]}{K^H_{lB}}$$

$(n/l) = 2$ and 3 for sa and ss, respectively

$$e = \frac{C_M(2n + 2l - a)}{b_l}$$

$$d = \frac{a_l}{b_l}$$

All the Th^{4+}-$3H_nA$-H_lB or Th^{4+}-H_{nA}-$3H_lB$ type mixtures remain in turbidity form above pH ~ 3.0 where calculation for mixed complexes is not possible. But, below this pH the composite pH *vs. a* curves of Th^{4+}-$2H_nA$-H_lB and H_nA or Th^{4+}-H_nA-$2H_lB$ and H_lB mostly coincide with the corresponding Th^{4+}-$3H_nA$-H_lB or Th^{4+}-H_nA-$3H_lB$ curves (figure omitted), respectively. Also, the calculations carried out using the expressions (1), (5), (6) and (7) for [A], [B], [M] and $[MA_3B]$, respectively derived from mass and charge balance relations similar to 1:2:2 system, indicate that ThA_3B does not exist in significant amount in Th^{4+}-$3H_nA$-H_lB mixture.

$$[B] = \frac{C_M(3n + l - a)}{b_l} - \frac{a_l}{b_l}[A]$$
$$= e - d[A] \qquad (5)$$

$$[M] = a_2[A]/(3 + 2K_{1A}[A] + K_{1A}K_{2A}[A]^2 - K_{1A}K_{2A}K_{3A}K_{4A}[A]^4 + 3K_{1B}[B]$$
$$+ 3K_{1B}K_{2B}[B]^2 + 3K_{1B}K_{2B}K_{3B}[B]^3 + 3K_{1B}K_{2B}K_{3B}K_{4B}[B]^4$$
$$+ 2K_{AB}[A][B] + K_{A_2B}[A]^2[B] + K_{A_2B_2}[A]^2[B]^2)$$
$$= b_2[B]/(1 + K_{1A}[A] + K_{1A}K_{2A}[A]^2 + K_{1A}K_{2A}K_{3A}[A]^3$$
$$+ K_{1A}K_{2A}K_{3A}K_{4A}[A]^4 - K_{1B}K_{2B}[B]^2 - 2K_{1B}K_{2B}K_{3B}[B]^3$$
$$- 3K_{1B}K_{2B}K_{3B}K_{4B}[B]^4 - K_{A_2B_2}[A]^2[B]^2 \qquad (6)$$

$$
\begin{aligned}
[MA_3B] = C_M - [M] - [MA_2] - [MA_3] - [MA_4] - [MB] - [MB_2] - [MB_3] \\
[MB_4] - [MAB] - [MA_2B] - [MA_2B_2]
\end{aligned} \tag{7}
$$

where

$$
\begin{aligned}
R_1 &= K_{1A}K_{2A}K_{3A}K_{4A}(a_2 - b_2d) + 3d^4K_{1B}K_{2B}K_{3B}K_{4B}(b_2d - a_2) \\
&\quad + d^2K_{A_2B_2}(b_2d - a_2) \\
R_2 &= d^3K_{1B}K_{2B}K_{3B}(2a_2 - 3b_2d) + ed^3K_{1B}K_{2B}K_{3B}K_{4B}(12a_2 - 15b_2d) \\
&\quad + a_2K_{1A}K_{2A}K_{3A} + b_2eK_{1A}K_{2A}K_{3A}K_{4A} - b_2d^2K_{A_2B} \\
&\quad + edK_{A_2B_2}(2a_2 - 3b_2d) \\
R_3 &= K_{1A}K_{2A}(a_2 + b_2d) + d^2K_{1B}K_{2B}(3b_2d - a_2) \\
&\quad + ed^2K_{1B}K_{2B}K_{3B}(12b_2d - 6a_2) + K_{1B}K_{2B}K_{3B}K_{4B}e^2d^2(30b_2d - 18a_2) \\
&\quad + e^2K_{A_2B_2}(3b_2d - a_2) - 2b_2d^2K_{AB} + 2b_2edK_{A_2B} \\
R_4 &= K_{1A}(2b_2d + a_2) - b_2eK_{1A}K_{2A} - 3b_2d^2K_{1B} + K_{1B}K_{2B}ed(2a_2 - 9b_2d) \\
&\quad + e^2dK_{1B}K_{2B}K_{3B}(6a_2 - 18b_2d) + e^3dK_{1B}K_{2B}K_{3B}K_{4B}(12a_2 - 30b_2d) \\
&\quad + 4b_2edK_{AB} - b_2e^2K_{A_2B} - b_2K_{A_2B_2}e^3 \\
R_5 &= a_2 - 2b_2eK_{1A}3b_2d + 6b_2edK_{1B} + e^2K_{1B}K_{2B}(9b_2d - a_2) \\
&\quad + e^3K_{1B}K_{2B}K_{3B}(12b_2d - 2a_2) + e^4K_{1B}K_{2B}K_{3B}K_{4B}(15b_2d - 3a_2) \\
&\quad - 2b_2e^2K_{AB} \\
R_6 &= 3b_2e(1 + eK_{1B} + e^2K_{1B}K_{2B} + e^3K_{1B}K_{2B}K_{3B} + e^4K_{1B}K_{2B}K_{3B}K_{4B}) \\
e &= \frac{C_M(3n + l - a)}{b_l}
\end{aligned}
$$

Equilibrium constant of ThA_2B_2 type of mixed complex is given in Table-2. Higher value of constants is indicated in coordination of ss^{3-}, sa^{2-} with $Th(ss)(sa)_2^{3-}$, $Th(sa)(ss)_2^{4-}$, respectively than the K_1 values of their aqua complexes. Experiments on mixed complex systems containing two or three molecules of ca were not performed as their lower mixed species (1:2:1) with two ca molecules do not exist in solution.

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