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Formation of Yttrium(III) Complexes with Salicylic Acid Derivatives in Aqueous Solution

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Complexes of yttrium(III) formed with 5-sulphosalicylic acid, 5-SSA (H_3L), and 5-nitrosalicylic acid, 5-NSA (H_2L), were investigated in 0.1 mol.dm^{-3} sodium perchlorate ionic medium at 25.0 ± 0.1 °C potentiometrically for various molar ratios of Y(III) to these salicylic acid, SA (H_2L), derivatives. Y(III) forms YL and YL_2^{3-} type complexes with 5-SSA that have rather high stabilities (log β_1= 7.91 ± 0.01 and log β_2= 14.56 ± 0.06). In the Y(III):5-NSA system, YL^+ and YL_2^- type complexes appear with high stabilities (log β_1= 7.39 ± 0.02 and log β_2= 13.50 ± 0.07). Y(III):5-SSA and Y(III):5-NSA complexes exist over a very wide pH range (pH 2.50-11.0) and these SA derivatives are coordinated from salicylate sites (COO^-, O). The stabilities of Y(III) complexes formed with 5-NSA and 5-SSA are higher than its SA and 5-hydroxysalicylic acid, 5-HSA (H_3L), complexes due to the existences of electron withdrawing groups at the fifth position. The formation constants of Y(III) complexes of SA and SA derivatives are lower than those of their Sc(III) complexes as a result of the smaller ionic potential of Y(III). Due to the higher charge on yttrium Y(III) complexes of SA, 5-NSA and 5-SSA are more stable than Ca(II):SA complex. This result may be utilized for in vitro and in vivo studies, since the ionic radia of Ca(II) and Y(III) are roughly equal.

Introduction

It is well established that yttrium is always found in nature with lanthanides, and its ionic radius is 1.04 Å for coordination number 6[1] and its chemical properties are very similar to the later lanthanides (1.00-1.17 Å). In our previous papers the binary and mixed ligand complexes of Y(III) and their equilibria between Y(III) and the title ligands were reported[2−6]. Although Martell et al.[7,8] studied La(III) complexes of 5-sulphosalicylic acid, 5-SSA(H_3L), they did not examine Y(III). On the other hand, the complex formation equilibria of 5-SSA with lanthanides by potentiometry were investigated[9,10], but they did not consider 5-nitrosalicylic acid, 5-NSA (H_2L). We have already investigated the behaviors of Y(III) and Sc(III) towards SA (H_2L)[3]; it was observed that Sc(III) forms ScL^+ and Sc(HL)L type complexes in 1:1 and 1:2 mole ratios, respectively.

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The stoichiometries of SA complexes of Y(III) are different, since the coordination of SA occurs only from one side to Y(III); as a result the occurrence of YHL^{2+} and $Y(HL)_2^+$ type complexes resulted.

We now continue to study the complexes of Y(III) formed with SA derivatives: 5-SSA and 5-NSA. 5-Sulfosalicylate (L^{3-}) ion has a higher charge than salicylate ion (L^{2-}) and the effects of substituents at the fifth position to the carboxylic groups, $-SO_3H$ and $-NO_2$, on their stabilities can be elucidated, by considering the basicities of these ligands. The present work was undertaken for the following reasons: in order to (i) obtain precise information on formation constants for the systems of Y(III):5-SSA and Y(III):5-NSA; (ii) correlate the formation constants of complexes formed between Sc(III), Y(III) and SA derivatives, since we have already defined the stabilities of Sc(III) complexes of 5-SSA[4], 5-NSA[4] and 5-hydroxysalicylic acid[6]; (iii) compare the behavior of Y(III) with Ca(II). It is well established that in the periodic table there is the diagonal relation between Na^+, Ca^{2+} and Y^{3+}, like the similar relation between Li^+ and Mg^{2+}. Although lithium is not an essential element, its action as a major psychotherapeutic drug is in part based on the possibility of its interaction with the phosphate compounds of Mg^{2+} as a result of the diagonal relation with Mg(II)[11]. Therefore, one can expect similar behavior for Y(III) compounds, being useful while interacting with Ca(II) sites. Due to the importance of Ca(II) (ionic radius 0.95 Å for coordination number 6) for biological media, we are interested in its coordination tendencies. It has been defined that Ca(II) is strongly bound by ligands with carboxylate and phenolate ions[1,7]. Therefore, we decided to compare the stabilities of complexes for SA derivatives formed with Ca(II) and Y(III), although the only complex of Ca(II) formed with SA was investigated, since they may be valuable for in vitro and vivo studies of Ca(II).

Experimental

Reagent, apparatus and procedure

Yttrium oxide (99.9%, Sigma) in $HClO_4$ (60%, d = 1.53) was dissolved in order to prepare its stock solution, which was standardized by EDTA titration[12]. The ligands 5-SSA (Merck, p.a) and 5-NSA (Aldrich, p.a.) were used without further purification; their purities were determined periodically by Gran titrations[13,14]. The sodium hydroxide stock solution was standardized against potassium hydrogen phthalate. All solutions were prepared using twice distilled water and protected from atmospheric CO_2 by soda lime traps.

The potentiometric titrations were carried out in a jacketed cell at 25.0 ± 0.1 °C. Calvin-Bjerrum titration was adopted[13–16]. The free hydrogen ion concentrations were measured with a combined glass electrode attached to a Schott model pH-meter (Hofheim, Germany); the accuracy of the pH-meter was ±0.002 pH unit. Before each experiment the potentiometric cell was standardized in 10^{-2}mol.dm^{-3} $HClO_4$, acetic acid buffer (Merck) and 10^{-1} mol.dm^{-3} solution of NaOH for measurement of the hydrogen ion concentration rather than its activity according to Irving et al.[12]. In the calibration step of the pH-meter pH reproducibility is < 0.005 units in the acidic pH region and < 0.010 units in the basic pH region. The potentiometric titrations were performed within the limits $3 \leq pH \leq 11$ under a purified nitrogen (99.99%, BOS, Turkey) atmosphere to prevent oxidation of the ligands. At least 4 different potentiometric titrations were performed for each ligand studied; the first was carried out with the ligand alone; the others were for Y(III):H_2L^{2-} (or H_2L) systems in which Y(III) concentrations were in the 1.2 x 10^{-3}- 3.7 x 10^{-3} mol.dm^{-3} range and in different mole ratios of Y(III) to ligands. During each titration the ionic strength was maintained

at 0.1 mol.dm^{-3} $NaClO_4$ and pH readings were taken after a suitable period (2-3 min) for equilibrium to be reached.

Calculations

The potentiometric titration curves of SA derivatives and Y(III) complexes of these ligands were analyzed mathematically to determine their formation constants (log β) at various pH values by the special computer program RANA, which was written by our research group[3,15]. The previously determined[15] protonation constants (K) of 5-SSA and 5-NSA were introduced into the necessary equations and then the formation constants of the Y(III) complexes of 5-SSA and 5-NSA were calculated by introducing at least 50 experimental points of each titration according to Martell's method[16,17]. The criterion of RANA is log K and log β values obtained by point-wise calculations for each system, which are presented in Tables 1 and 2, respectively. Non-linear least-square analysis of the data in terms of assumed reactions gave a satisfactory fit in the buffer regions of complexes in different mole ratios of Y(III) and SA derivatives.

The species distribution diagrams and the formation function, $\overline{n}$, the average number of ligands attached per Y(III) were also drawn by RANA.

Results and Discussion

Potentiometric investigations

The protonation constants of 5-SSA and 5-NSA

The protonation constants of 5-SSA and 5-NSA were reported by previous authors[4,7–10,15]. We determined the protonation constants of L^{3-} and HL^{2-} ions for 5-SSA and L^{2-} and HL^{-} ions for 5-NSA. Our previous[15] and new results obtained in this work for the protonation constants of 5-SSA and 5-NSA were equal; they are tabulated in Table 1 (rows 1-5).

Table 1. Log K values for protonation equilibria of salicylate derivatives at 25.0 ± 0.1 °C and at I = 0.1 mol.dm^{-3} $NaClO_4$. *This work, pK_W = 13.79.

Row	Equilibrium	SA	5-HSA	5-NSA	5-SSA
1	$L^{3-} + H^+ \rightleftharpoons HL^{2-}$	–	12.74[6]	-	11.90[15,*]
2	$HL^{2-} + H^+ \rightleftharpoons H_2L^-$	–	10.18[6]	-	2.48[15,*]
3	$H_2L^- + H^+ \rightleftharpoons H_3L$	-	2.73[6]	-	-
4	$L^{2-} + H^+ \rightleftharpoons HL^-$	13.12[3]	–	10.11[15,*]	–
5	$HL^- + H^+ \rightleftharpoons H_2L$	2.83[3]	–	1.95[15,*]	–

The complexes of Y(III) and 5-SSA

This system was investigated potentiometrically at various concentrations of 5-SSA, as well as in solutions containing different molar ratios of the Y(III) and 5-SSA. In 1:1 mole ratio of Y(III):5-SSA system the inflection points of the potentiometric titrations were observed at m = 2.0, m = 3.0 and m = 4.0 [m is mmoles of base per mmole of Y(III)], but for simplicity only the curve obtained for one concentration is given in Figure 1, curve II. The occurrence of YL type complex with 5-SSA is suggested, due to the deprotonation of 3 protons from 5-SSA, since drops in the buffer regions of the titration curves of the 1:1 Y(III):5-SSA system were noted with respect to the titration curves of 5-SSA alone. The neutralization

of one proton from the sulpho group occurs between m = 0.0 and 1.0, while the other titrated proton is dissociated between m = 1.0 and m = 2.0 from the carboxylate group; the third mole of proton is dissociated from the phenolic group between m = 2.0 and m = 3.0. The continued drifts in pH readings were recorded in the 1:1 Y(III):5-SSA system after pH 7.34 in the m = 3.0-4.0 range; it could be related to the hydrolysis of the YL type complex. The occurrence of hydroxo complexes was encountered in several Y(III):ligand systems, like 1:1 and 1:2 Y(III):SA[3] and Y(III):HSA[6] systems. Inflection points on potentiometric titration curves were shifted to m = 4.0, 5.0 and 6.0 for the Y(III):5-SSA system in 1:2 mole ratio (Figure 1, curve III). The observed drops and shifts of inflection points on the buffer regions of potentiometric titration curves suggest that YL_2^{3-} type complex formed gradually in the m = 0.0-6.0 range for the 1:2 Y(III):5-SSA system. The measurements were also carried out in higher mole ratios like 1:3, 1:4 and 1:5 (Figure 1, curves IV, V and VI). The coordination of 5-SSA from the carboxylate and phenolate sides may be proposed and the existence of YL and YL_2^{3-} type complexes was assumed.

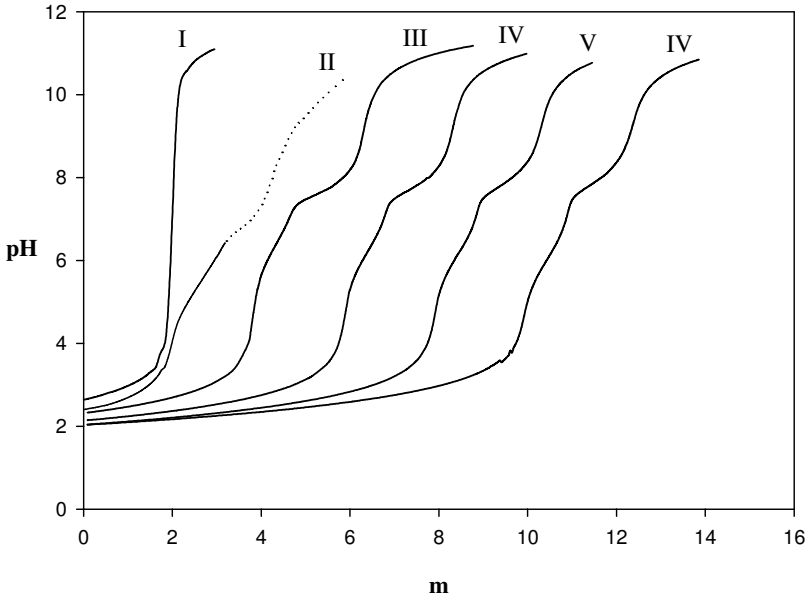

Figure 1. Potentiometric titration curves of Y(III) complexes of 5-SSA in 0.1 mol.dm^{-3} at 25.0 ± 0.1 °C. **I.** 5-SSA alone (T_L = 1.5 x 10^{-3} mol.dm^{-3}); **II.** (1:1) molar ratio of Y(III) to 5-SSA (T_L= T_Y= 1.5 x 10^{-3} mol.dm^{-3}); **III.** (1:2) molar ratio of Y(III) to 5-SSA; **IV.** (1:3) molar ratio of Y(III) to 5-SSA; **V.** (1:4) molar ratio of Y(III) to 5-SSA; **VI.** (1:5) molar ratio of Y(III) to 5-SSA.

The formation constant of YL complex species was calculated by introducing 95 pH values in the pH 5.40-7.50 range that were obtained from 1:2 and higher mole ratio of Y(III):5-SSA (Table 2, row 1). The assumed, YL_2^{3-} complex species and its formation constant was defined by introducing 90 pH values in the pH 7.56-8.50 range that were read in 1:2 and higher mole ratios of Y(III):5-SSA system (Table 2, row 2). The formation constants of YL(OH) type complex was also defined by introducing 50 pH values that were taken from 1:1 Y(III):5-SSA system in the pH 7.34-7.74 range (m = 3.1-3.9) into the related formation constant equation (Table 2, row 3). It is worth indicating that the occurrence of hydrolytic reactions was not observed in mole ratios higher than 1:1.

Table 2. Log β values for complex formation equilibria of Y(III) and Sc(III) ions with salicylate derivatives at 25.0 ± 0.1 °C and at I = 0.1 mol.dm^{-3} $NaClO_4$.

Row	Equilibrium	SA	5-HSA	5-NSA	5-SSA
1	$Y^{3+} + L^{3-} \rightleftharpoons YL$				7.91 ± 0.01*
2	$Y^{3+} + 2L^{3-} \rightleftharpoons YL_2^{3-}$				14.59 ± 0.06*
3	$YL + OH^- \rightleftharpoons YL(OH)^-$				6.90 ± 0.06*
4	$Y^{3+} + L^{2-} \rightleftharpoons YL^+$			7.39 ± 0.02*	
5	$Y^{3+} + 2L^{2-} \rightleftharpoons YL_2^-$			13.50 ± 0.07*	
6	$YL^+ + OH^- \rightleftharpoons YL(OH)$			6.86 ± 0.06*	
7	$Y^{3+} + HL^- \rightleftharpoons YHL^{2+}$	3.07[3]			
8	$Y^{3+} + 2HL^- \rightleftharpoons Y(HL)_2^+$	7.20[3]			
9	$YHL^{2+} + OH^- \rightleftharpoons YHL(OH)^+$	6.59[3]			
10	$Y^{3+} + H_2L^- \rightleftharpoons Y(H_2L)^{2+}$		4.49[6]		
11	$Y^{3+} + 2H_2L^- \rightleftharpoons Y(H_2L)_2^+$		5.34[6]		
12	$Y(H_2L)^{2+} + OH^- \rightleftharpoons Y(H_2L)(OH)^+$		6.76[6]		
13	$Y(H_2L)_2^+ + OH^- \rightleftharpoons Y(H_2L)_2(OH)$		6.79[6]		
14	$Sc^{3+} + L^{3-} \rightleftharpoons ScL$				12.23[4]
15	$Sc^{3+} + 2L^{3-} \rightleftharpoons ScL_2^{3-}$				18.06[4]
16	$Sc^{3+} + L^{2-} \rightleftharpoons ScL^+$	13.09[3]		10.93[4]	
17	$Sc^{3+} + HL^- + L^{2-} \rightleftharpoons Sc(HL)L$	15.02[3]			
18	$Sc^{3+} + 2L^{2-} \rightleftharpoons ScL_2^-$			16.47[4]	
19	$Sc^{3+} + HL^{2-} \rightleftharpoons ScHL^+$		12.37[6]		
20	$Sc^{3+} + HL^{2-} + H_2L^- \rightleftharpoons Sc(HL)(H_2L)$		15.73[6]		
21	$Ca^{2+} + HL^- \rightleftharpoons CaHL$	0.14[7]			

*This work

The complexes of Y(III) and 5-NSA

The potentiometric titrations of 5-NSA alone and in 1:1 mole ratio of the Y(III):5-NSA system were carried out; inflections were observed at m = 1.0, m = 2.0 and m = 3, but drops in the pH readings were noted due to the hydrolysis at higher than m = 2.0 value (Figure 2, curves I and II). As a result of the neutralization of 2 protons of 5-NSA, the coordination of 5-NSA is assumed through carboxylate and phenolate groups to Y(III) in the m = 0.0-2.0 range; thus the occurrence of YL^+ type complex was proposed. The further potentiometric titrations were performed in 1:2 and 1:3 mole ratios of Y(III):5-NSA, their inflections were recorded at m = 2.0, m = 3.0 and m = 4.0 for 1:2 mole ratio and at m = 3.0, m = 4.0 and m = 5.0 for 1:3 mole ratio (Figure 2, curves III and IV). As a result of these potentiometric titrations, the occurrences of YL^+ and YL_2^- type complexes were assumed. In order to calculate the formation constants of YL^+ type complex species, 96 pH values that were obtained from 1:2 and 1:3 systems in the pH 4.40-6.50 range were introduced into the related equation (Table 2, row 4). The formation constant of YL_2^- complex species were calculated by means of 62 pH values that were observed in 1:2 and 1:3 Y(III):5-NSA systems in the pH 6.60-7.40 range (Table 2, row 5). Due to the observation of continuous drifts on pH values in the 1:1 Y(III):5-NSA system, after pH 6.50 in the m = 2.0-3.0 range the formation of YL(OH) type complex was suggested. Then its formation constant was calculated (Table 2, row 6).

Further investigations for the complexes of Y(III):5-SSA and Y(III):5-NSA systems

The species distribution curves were drawn for Y(III):5-SSA and Y(III):5-NSA systems in different mole ratios; in the acidic pH range for all mole ratios of Y(III) to 5-SSA, 5-NSA the major species are YL and YL^+ type mono complex, respectively (Figures 3 and 4). The major species in the neutral and basic pH ranges of Y(III):5-SSA and Y(III):5-NSA systems are YL_2^{3-} or YL_2^- type complexes for 1:2 and higher mole ratios.

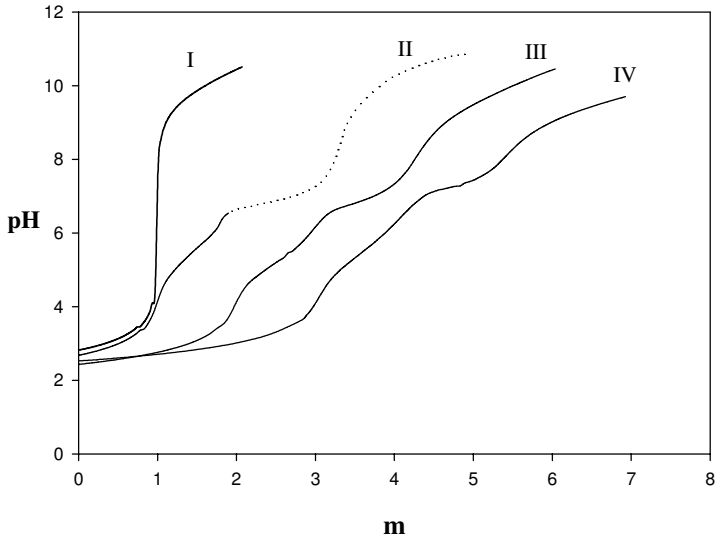

Figure 2. Potentiometric titration curves of Y(III) complexes of 5-NSA in 0.1 mol.dm^{-3} at 25.0 ± 0.1 °C. **I.** 5-NSA alone (T_L= 3.0 x 10^{-3} mol.dm^{-3}); **II.** (1:1) molar ratio of Y(III) to 5-NSA (T_L= T_Y= 3.0 x 10^{-3} mol.dm^{-3}); **III.** (1:2) molar ratio of Y(III) to 5-NSA; **IV.** (1:3) molar ratio of Y(III) to 5-NSA.

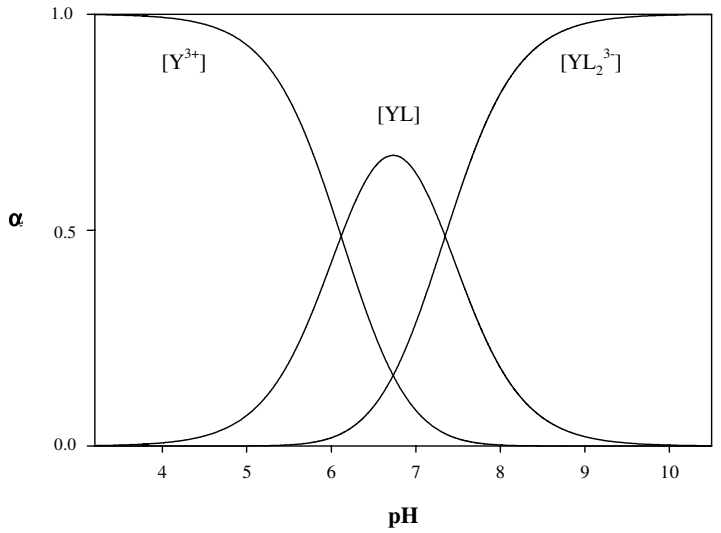

Figure 3. Species distribution curves of the 5-SSA system and the metal ion Y(III) as a function of –log[H^+], for a solution initially containing 7.50 x 10^{-2}mol.dm^{-3} 5-SSA and 1.50 x 10^{-3} mol.dm^{-3} Y(III); T = 25.0 ± 0.1°C and I = 0.1 mol.dm^{-3} $NaClO_4$.

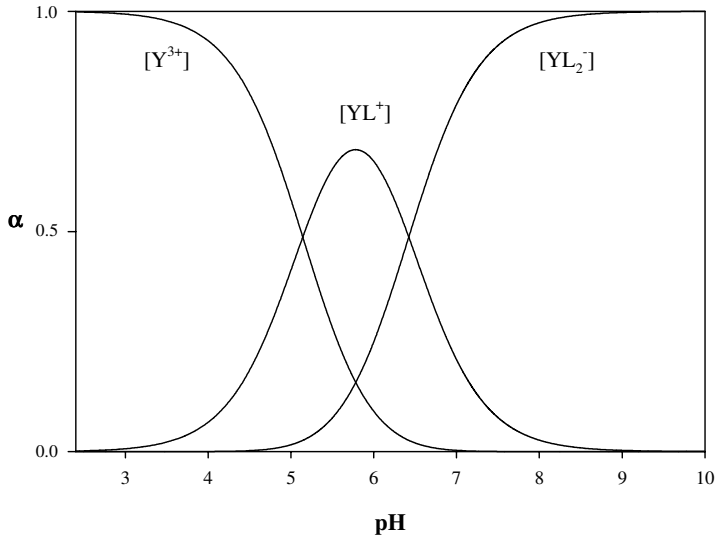

Figure 4. Species distribution curves of the 5-NSA system and the metal ion Y(III) as a function of –log[H^+], for a solution initially containing 1.78 x 10^{-2}mol.dm^{-3} 5-NSA and 1.26 x 10^{-3} mol.dm^{-3} Y(III); T = 25.0 ± 0.1°C and I = 0.1 mol.dm^{-3} $NaClO_4$.

The degree of formation values ($\overline{n}$) were also determined in order to verify the potentiometric data of Y(III):5-SSA and Y(III):5-NSA systems; then the $\overline{n}$ values were plotted versus –log ligand concentration (Figure 5). The formation curves have plateaus at $\overline{n} \cong 1.00$ and then they reach up to $\overline{n} = 2.0$; they reflect the coordination of 5-SSA and 5-NSA in L^{3-} and L^{2-} forms, respectively, and they indicate the coordinations of 2 moles of 5-SSA or 5-NSA.

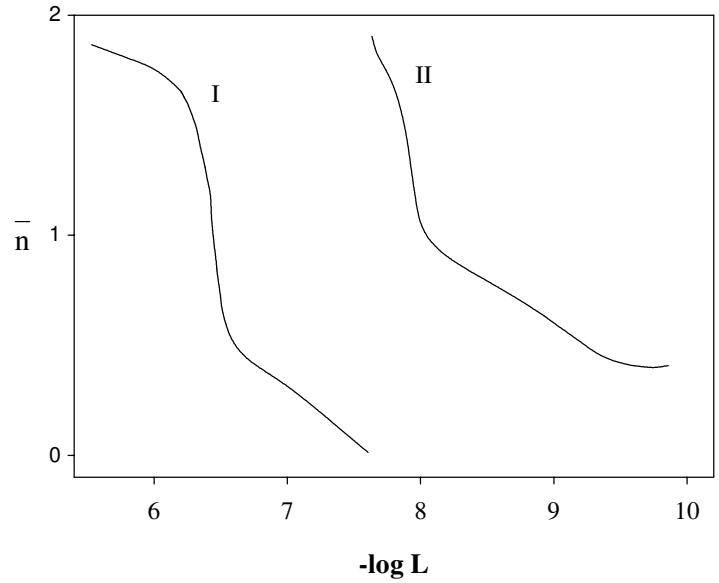

Figure 5. Degree of formation, $\overline{n}$, as a function of –log L in Y(III):salicylate derivatives system **I:** Y(III):5-SSA system; **II:** Y(III):5-NSA system.

Conclusion

1. In acidic and neutral pH ranges, the coordination of Y(III) to 5-SSA and 5-NSA occurs either in 1:1 or higher mole ratios, presumably via salicylate sites (COO^-, O^-) to form YL and YL^+ type complexes, respectively. In neutral and basic pH ranges, Y(III) forms YL_2^{3-} and YL_2^- type complexes either in 1:2 or higher ratios of Y(III):5-SSA and Y(III):5-NSA, respectively.

2. Due to the existence of electron withdrawing groups, –sulpho and –nitro at the fifth position, the stabilities of complexes formed between Y(III) and 5-SSA, 5-NSA are higher than its SA^3 and 5-HSA^6 complexes.

3. As a result of the smaller ionic radius of Sc(III) than Y(III), 5-SSA and 5-NSA complexes of Sc(III) are stronger than corresponding Y(III) complexes.

4. Only YL and YL^+ type complexes of Y(III) formed with 5-SSA and 5-NSA, respectively, have tendencies to form mixed hydroxo complexes in neutral pH range; but the hydrolsis tendencies of YL_2^{3-} and YL_2^- type complexes were not observed for 5-SSA and 5-NSA complexes, respectively.

5. Although Y(III) can form YL and YL^+ type complexes with 5-SSA and 5-NSA respectively, the complex formation equilibria of Y(III) with SA^3 and 5-HSA^6 are rather more complicated than Sc(III) complex equilibria, whereas the coordination of Y(III) to SA^3 and 5-HSA^6 takes place only through deprotonated carboxylate oxygen of ligands, either in 1:1 or 1:2 mole ratios. It may be related to the bigger ionic radius of Y(III).

6. As a result of the different type of coordinations of Y(III) with SA, 5-SSA and 5-NSA bigger ionic potential of Y(III), its complexes are more stable than Ca(II):SA complex. This result may be utilized for in vitro and in vivo studies, since the ionic radia of Ca(II) and Y(III) are roughly equal.

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