Salicylic Acid Derivatives Form Stable Complexes with Scandium(III) Ion in Aqueous Solution

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The stability constants of 5-nitrosalicylic acid (5-NSA) and 5-sulfosalicylic acid (5-SSA) complexes of Sc(III) were determined by potentiomeric pH titration. ML and ML_2 type first and second complexes were observed in the solutions of 5-NSA and 5-SSA with Sc(III) at 25 °C in $I=0.1$ M ionic medium. The stability constants of Sc(III)–5NSA and Sc(III)–5SSA systems were also investigated by spectrophotometry to determine the stoichiometries of the complexes formed in the reactions. Our results showed that Sc(III)–5SSA complexes are more stable than the Sc(III)–5NSA complexes in aqueous solutions.

Key words salicylic acid; scandium; stability constant; potentiometry

Scandium's chemical and physical features are similar to those of lanthanides. But it was suggested that scandium is a typical first transition series metal rather than being a lanthanide.[1] Sc(III) is the first member of the Sc, Y, La, Ac group. Transition metals have a very high tendency to form metal–ligand complexes with various mono and dihydroxy phenolic compounds. The formation of ML, ML_2 and ML_3 type complexes of Al(III)–5NSA and Al(III)–5SSA were reported previously.[2,3]

Sc(III) has a strong tendency to form hydroxo species in aqueous solution.[4] The complex forming tendency of Sc(III) with various ligands such as disodium 1,2-dihydroxy benzene 3,5-disulfonic acid (TIRON), 2,3-dihydroxy benzoic acid (2,3-DHBA) and salicylic acid (SA) was analyzed previously.[5,6] The complex formation between 5-NSA (H_2L), 5-SSA (H_2L^-) and Sc(III) has not been investigated so far.

We have analysed the formation and the stabilities of the 5-NSA and 5-SSA complexes of Sc(III) at t=25 °C in $I=$ 0.1 M ionic medium in this study. The formation of complexes of Sc(III) with 5-NSA and 5-SSA, together with the dissociation constants of the ligand, were investigated using potentiometric and spectrophotometric methods.[6—8] The effects of electron attracting groups such as -nitro and -sulfo groups of the ligands on the stabilities of the Sc(III) complexes have not been reported previously. Hence 5-NSA and 5-SSA were used in our studies as ligands.

The potentiometric titration curves of the Sc(III)–5NSA system in 1 : 1 mol ratio exhibit inflection points at m (mmol base/mmol metal)=2.0 and $m=3.25$ (Fig. 1-II). The formation of an ML type complex of Sc(III) with 5-NSA may be suggested from the drops in the buffer regions of the titration curves, from inflection points at $m=2.0$ and from hydrolysis of the Sc(III) complex of 5-NSA in 1 : 1 mol ratio, between $m=3.0$—4.0. Inflection points on potentiometric titration curves were observed at $m=4.0$ and $m=5.0$ for the Sc(III)–5NSA system in 1 : 2 mol ratio (Fig. 1-III). The formation of an ML_2 type complex of Sc(III) with 5-NSA is one of the possibilities. Moreover, continued drops on pH readings after $m=4.0$ suggest that hydrolysis of an ML_2 type complexes is initiated in the system.

The potentiometric titration curve of Sc(III)–5SSA in 1 : 1 mol ratio exhibits inflection points at $m=3.0$ and $m=4.0$ (Fig. 2-II). The formation of an ML type complex of Sc(III)–

5SSA was assumed. A drop in the pH values in the buffer regions and inflection points at $m=3.0$ were observed between $m=3.0$ and $m=4.0$; this reflects the formation of a 1 : 1 Sc(III)–5SSA complex.

When Sc(III) metal ion and 5-SSA are present at 1 : 2 mol ratio, inflection points on the potentiometric titration curves were observed at $m=5.0$ and $m=6.0$, respectively (Fig. 2-III). This result suggests that an ML_2 type complex formed gradually in the $m=0.0$—6.0 range. At the beginning, two moles of titrated protons are dissociated from the sulfo groups between $m=0.0$ and 2.0 while the other titrated protons dissociated between $m=2.0$ and $m=4.0$ are from the carboxylate groups. Two moles of protons which are dissociated between $m=4.0$ and $m=6.0$ at the final stage are from the phenolic groups.

The degree of formation, ($\bar{n}$) values, were evaluated both for Sc(III)–5NSA and Sc(III)–5SSA complexes that are present in 1 : 2 mol ratios. Then the formation curves were drawn (Figs. 3 and 4). It has been noticed that, the number of ligands per Sc(III) ion ($\bar{n}$) is approximately equal to 1.85.

The formation of an ML and an ML_2 type complex was assumed from the potentiometric titrations curves. In order to validate these assumptions, the stoichiometries of the formed complexes were investigated by the spectrophotometric method. For the potentiometric titration curves of 5-NSA alone, 1 : 1 and 1 : 2 mol ratios of Sc(III) and 5-NSA were prepared at pH ranges 2.40—3.98 and 2.20—5.00 respectively. Then, the spectrum of 5-NSA alone and solutions of Sc(III)–5NSA that are present at defined pH values and in different mol ratios were compared. After that, maximum absorbance values were determined for each species, at OD_{395}. The formation of ML and ML_2 type complexes was demonstrated using Job's diagram of Sc(III) and 5-NSA solutions in different mol ratios. In order to identify the stoichiometries of complexes formed between Sc(III) ion and the 5-SSA ligand, spectra were recorded at different pH values, as in the Sc(III)–5SSA solutions. Job's diagrams were drawn at OD_{260} for pH=3.5 and pH=4.5 and maximum absorbances were observed at $X_M=0.5$ and $X_M=0.3$ values in Job's diagram respectively.

It was concluded that Sc(III) ions form ML, ML_2 type complexes with 5-NSA and 5-SSA. The results obtained from the potentiometric data (β) are given in Table 1. The
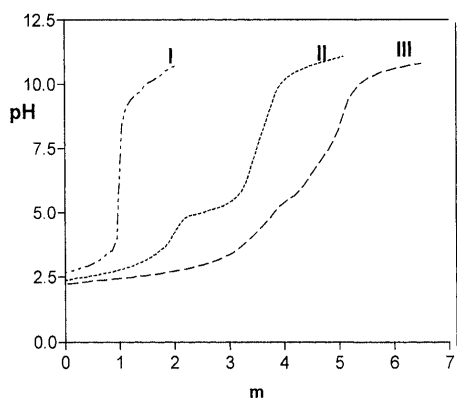
Fig. 1. Potentiometric Titrations of Sc(III)–5NSA System in 0.1 M KNO$_3$ at 25 °C with Different Molar Ratios of 5-NSA to Metal Ion

I, ligand alone; II, Sc(III)–5NSA (1 : 1); III, Sc(III)–5NSA (1 : 2).

Fig. 3. Degree of Formation, $\bar{n}$, as a Function of $-\log L$ of Sc(III)–5NSA Complex
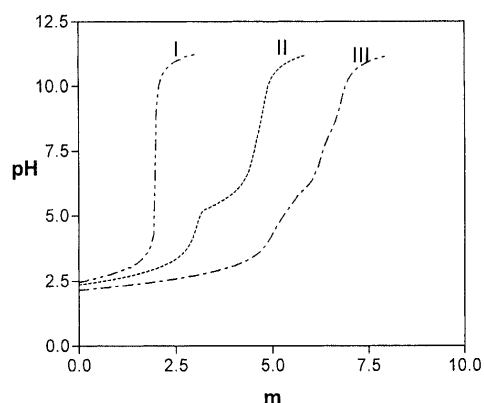

Fig. 2. Potentiometric Titrations of Sc(III)–5SSA system in 0.1 M KNO$_3$ at 25 °C with Different Molar Ratios of 5-SSA to Metal Ion

I, ligand alone; II, Sc(III)–5SSA (1 : 1); III, Sc(III)–5SSA (1 : 2).
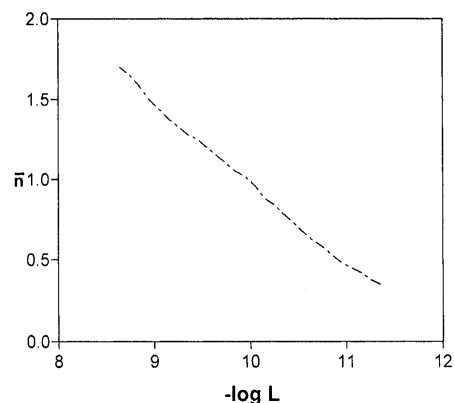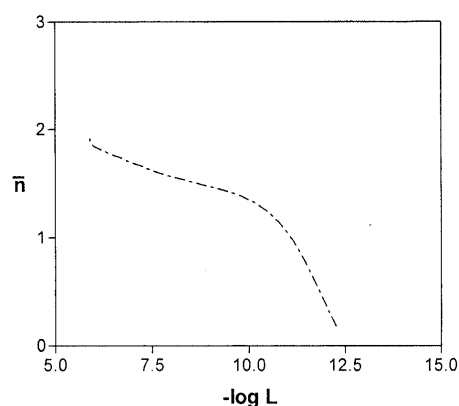

Fig. 4. Degree of Formation, $\bar{n}$, as a Function of $-\log L$ of Sc(III)–5SSA Complex

Table 1. Stability Constants of the Complexes ML, ML$_2$ and the Dissociation Constants of 5-NSA and 5-SSA at 25 °C and $I=0.1$

Ligands	Equilibrium	$-\log K_a$ [a]	$\log \beta$ [b]	$-\log K_{hyd.}$ [c]
5-NSA (H$_2$L)	H$_2$L $\rightleftharpoons$ H$^+$+HL$^-$	2.20		
	HL$^-$ $\rightleftharpoons$ H$^+$+L^{2-}	10.10		
	Sc^{3+}+L^{2-} $\rightleftharpoons$ ScL$^+$		10.93±0.05	
	ScL$^+$+OH$^-$ $\rightleftharpoons$ ScL(OH)			5.10±0.09
	Sc^{3+}+2L^{2-} $\rightleftharpoons$ ScL$_2^-$		16.47±0.05	
	ScL$_2^-$+OH$^-$ $\rightleftharpoons$ ScL$_2$(OH)$^{2-}$			6.65±0.03
5-SSA (H$_2$L$^-$)	H$_2$L$^-$ $\rightleftharpoons$ H$^+$+HL^{2-}	2.42		
	HL^{2-} $\rightleftharpoons$ H$^+$+L^{2-}	11.90		
	Sc^{3+}+L^{3-} $\rightleftharpoons$ ScL		12.23±0.03	
	ScL+OH$^-$ $\rightleftharpoons$ ScL(OH)$^-$			5.21±0.03
	Sc^{3+}+2L^{3-} $\rightleftharpoons$ ScL$_2^{3-}$		18.06±0.03	
	ScL$_2^{3-}$+OH$^-$ $\rightleftharpoons$ ScL$_2$(OH)$^{4-}$			3.18±0.05

a) $-\log K_a$ is calculated as described previously.[7] Numbers show the acidity constants of the ligands. *b*) $-\log \beta$ is calculated as described previously.[6] It shows the stability constants of the formed complexes in the reaction. *c*) $-\log K_{hyd.}$ is the hydrolysis constant of Sc(III)–5NSA(1 : 1, 1 : 2) and Sc(III)–5SSA (1 : 1, 1 : 2).[6]

dissociation constants of the ligands were determined under the same experimental conditions as described previously[7] and are also given in Table 1.

5-NSA is more acidic than 5-SSA when their acidities are compared with each other. The reason for this is that the -nitro and -sulfo groups weaken the O–H bond by attracting electrons with inductive and resonance effects which results in the dissociation of a proton in a relatively easy way. It is also known that -nitro groups are more a electron attracting group than -sulfo group. These results suggest that the stabil-

ities of complexes of Sc(III) formed with 5-SSA is higher than the stabilities of complexes of Sc(III)–5NSA.

Experimental

All the chemicals used in this study were of analytical reagent grade. 5-NSA (Aldrich, 99% purity) and 5-SSA (Merck) used in this study, were used as received, since Gran's plot of the ligand potentiometric study requires high purity.[9] The determination of acid dissociation constants of these ligands was explained previously.[7] Three different stock solutions of scandium(III) (7.2×10^{-3}, 1.44×10^{-3} and 2.88×10^{-3} M, respectively) were prepared from Sc(NO$_3$)$_3$ (Aldrich, 99% purity) for potentiometric studies. A known quantity of HNO$_3$ (Merck, 100% purity, $d=1.52$) was added to the

stock solution of Sc(III) to avoid hydrolysis. The stock solutions of scandium(III) (1×10^{-3}—1×10^{-4} M) were prepared from Sc_2O_3 (Aldrich, 99.9% purity) for spectrophotometric studies since the nitrate ion absorbs in the UV/VIS region of the spectrum.[4] The concentrations of the stock solutions were then checked by EDTA titration.[10]

CO_2 free 0.1 M NaOH stock solution was prepared with NaOH purchased from Merck Co. and was standardized with potassium hydrogen phthalate.[4] In order to maintain the ionic strength at constant level, 0.1 M KNO_3 was added at definite amount. All solutions were prepared under CO_2 free, nitrogen atmosphere and in double distilled water, at 25.0 ± 0.10 °C, in a water jacketed titration cell. At least three different titrations were carried out for each Sc(III)–L system.

Instrumentation The pH was measured by a Schott-pH meter instrument, equipped with combined electrode. The titration solution was kept free from carbon dioxide and oxygen by continious bubbling of purified nitrogen and was presaturated by passing nitrogen through the titration cell. The electrode system was calibrated by the method of Harned and Owen,[11] so the pH-meter readings could be converted into hydrogen concentrations. In all cases the temperature was kept constant, at 25.0 ± 0.10 °C, by means of a B. Braun Termomix UB Termostat.

Absorption spectra of the samples were measured using a Shimadzu UV-2100 Spectrophotometer. The stoichiometry of these complexes was determined by Job's method.[12] This allows the stoichiometry of the complexes to be defined by taking UV/VIS spectra of the metal ion and ligand system in definite mol ratios of metal ions and ligands. Thus, the results of the potentiometric studies were also validated by Job's method.

Calculations A computer program was devised for the computation and refinement of the formation constants using previously described equations.[8] First, the stability constants of Sc(III)–5NSA and Sc(III)–5SSA complexes that are in 1 : 1 and 1 : 2 stoichiometries of 5-NSA and 5-SSA to metal ion were determined using the part I and II of the program.[6] Then the stability constants of the complexes were determined using the derived equations. The twelve possible titrations were analysed mathematically (Table 1). All thermodynamic parameters are expressed in molar scale.

The values of $\bar{n}$, (the average number of ligand(s) bound per mole of metal ion)[13] and a log L (a free concentration of anionic form of the ligand) were computed in the third part of the computer program for the analysed two systems.

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