Stabilities of Complexes of Scandium(III) and Yttrium(III) With Salicylic Acid

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The interactions of Sc(III) and Y(III) ions with salicyclic acid, SA (H_2L), were studied in aqueous solution by means of potentiometric and spectroscopic methods. The binding of SA occurs in Y(III):SA system, either in (1:1) or (1:2) mole ratios. The stability constants of the mono protonated complex, YHL^{2+}, and $Y(HL)_2^+$ type complex were calculated. The coordination of Sc(III) to SA was defined by means of Job's plot and its formation curve. The stability constants of ScL^+ and Sc(HL)L type complexes were determined by analysis of the potentiometric data; the coordination of SA to Sc(III) occurred through carboxylate and phenolic oxygens. The existence of hydrolytic reactions of Sc(III) and Y(III) complexes of SA were defined from potentiometric data and related equilibrium constants were also defined.

Introduction

Scandium and yttrium are the first and the second members of the Sc, Y, La, Ac group. The ionic radius of Sc(III) is 0.745Å and is smaller than the ionic radius of yttrium(III) (0.90 Å). Scandium(III) is the congener of aluminum(III) and also a typical first transition series metal rather than a lanthanide[1]. Although yttrium is always found in nature with rare earths and its chemical properties are very similar to lanthanium[2]. Sc(III) and Y(III) have strong tendencies to form hydroxo species in aqueous solution[3−9]. Although the complexing behaviours of Sc(III) and Y(III) indicate that they have a strong preference for phenolate oxygens[10−19]; namely, catechol[10−17] and salicylic acid (SA, it is represented as H_2L in this study) systems[18−19] have been studied, in these complexes. The formation of ML, ML_2, ML_3 type complexes of Al(III)-SA and 5-sulphosalicylic acid (5SSA, H_2L) ligands were reported[20−21]. Although formation of MHL type complex of La(III)-5SSA and some rare earth ions were also explained[22]; but there is no current data on the stability constants of Sc(III) and Y(III) complexes formed with SA and its derivatives[23]. SA is the simplest representative of the phenolic ligands, provided with an anchoring carboxylate, and it can act as a mono or bidentate ligand; the prevelance of one of the two possibilities depends on the pH values of the solution and the charge/radius ratio of the metal ion[24].

In the present study, the formation equilibria of complexes of Sc(III) and Y(III) with SA, were investigated and their stability constants were calculated[25−26], in aqueous solution, by means of potentiometric and spectrophotometric measurements[27].

Experimental

Chemicals

SA, (Merck, p.a. product) was used without further purification; since Gran's[28] plot of it indicated its high purity.

The stock solution of Sc(III) was prepared for potentiometric measurements, by dissolving $Sc(NO_3)_3$ (Aldrich, 99.9% purity) in a known quantity of HNO_3 (Merck, 100% purity, d=1.52). For spectrophotometric studies, Sc_2O_3 was dissolved in concentrated HCl (36%, d=1.19, Merck). Stock solution of Y(III) was prepared in $HClO_4$ (60%, d=1.53) by dissolving Y_2O_3 (K&K and Sigma, 99.9% purity). All stock solutions and NaOH (Merck, 97%, purity) solution were standardized as described elsewere[29].

In potentiometric titrations, constant ionic medium was 0.1M KNO_3 for Sc(III) and 0.1M $NaClO_4$ for Y(III) solutions. The potentiometric titrations were performed in at least three different concentrations at $25.0\pm 0.1°C$, by bubbling purified nitrogen through the solution.

Instrumentation

In potentiometric titrations, the free hydrogen ion concentrations, $[H^+]$, were measured with a combined electrode, attached to a Schott-pH meter; the electrode system was calibrated by the method of Harned and Owen[30], in a water jacketed titration cell, $(100cm^3)$ by keeping the temperature constant by means of B. Braun Termomix UB Thermostat. In all three components (metal-ligand-NaOH) of the potentiometric titrations, the ratios of C_M/C_L were held constant (C_M is total concentration of yttrium(III) or scandium(III) and C_L is total concentration of ligand). The measurements were performed within the following concentration limits:

$2.00\leq$-$\log[H^+]\leq 10.00$; $1.5\times 10^{-3} \leq C_M \leq 4.5\times 10^{-3}$; $1.5\times 10^{-3} \leq C_L \leq 9.0\times 10^{-3}$ and the C_M/C_L ratios were 1.0 and 2.0.

Absorption spectra for Sc(III)-SA and Y(III)-SA systems were recorded on a Shimadzu UV-2100 spectrophotometer to define the existence of complexes at different pH values as a function of wavelengths. Furthermore, results of potentiometric studies were validated by Job's method[31] to determine the stoichiometries of some complexes, by taking UV/VIS spectra of Sc(III)-SA or Y(III)-SA systems in definite mole ratios.

Data Treatment

The first proton dissociation constant of SA (K_{a1}) was determined by potentiometric titrations within the concentration range 0.10-0.40 mmol/ml, by the procedure explained previously[32], but the second proton dissociation constant was the value found by Agreen[33]; they are given in Table 1.

The SA complexes of Sc(III) and Y(III), that formed in different stoichiometries, were taken into account, in order to calculate their stability constants, β, by introducing the experimental data into the related equilibrium equations, according to the procedure developed by Chaberek and Martell[34]. The stability constants of the complexes formed in Sc(III)-Sa and Y(III)-SA systems are listed in Table 1. The mathematical analysis of potentiometric data comprising 12 titrations and 960 experimental points[25−26] and the calculations of standard deviations of defined values in Table 1, were performed with a special computer program. The computations were performed on a Pentium 120 computer.

The average number of ligands which attached to metal ions ($\bar{n}$) were found with the help of the

computer program as a function of $(\bar{n})$ values versus log (L)[35]. $(\bar{n})$ is the number of ligands per metal ion and L is the free concentration of ligand.

Table 1. The dissociation constants of SA and the stability constants of yttrium(III) and scandium(III) complexes of SA

Equilibrium	-log K_a	logβ	-logK_{hyd}.
$H_2L \rightleftharpoons H^+ + HL^-$	2.83		
$HL^- \rightleftharpoons H^+ + L^{-2}$	13.12[32]		
$Y^{3+} HL^- \rightleftharpoons YHL^{+2}$		3.07±0.03	
$YHL^{+2} + OH^- \rightleftharpoons YHL(OH)^-$			7.20±0.05
$Y^{3+} 2HL^- \rightleftharpoons Y(HL)_2^+$		5.50±0.04	
$Y(HL)_2^+ + OH^- \rightleftharpoons Y(HL)_2(OH)$			6.99±0.04
$Sc^{3+} + L^{-2} \rightleftharpoons ScL^+$		13.09±0.05	
$ScL^+ + OH^- \rightleftharpoons ScL(OH)$			5.62±0.08
$Sc^3 + HL^- + L^{-2} \rightleftharpoons Sc(HL)L$		15.02±0.05	
$Sc(HL)L + OH^- \rightleftharpoons Sc(HL)L(OH)^-$			5.61±0.03
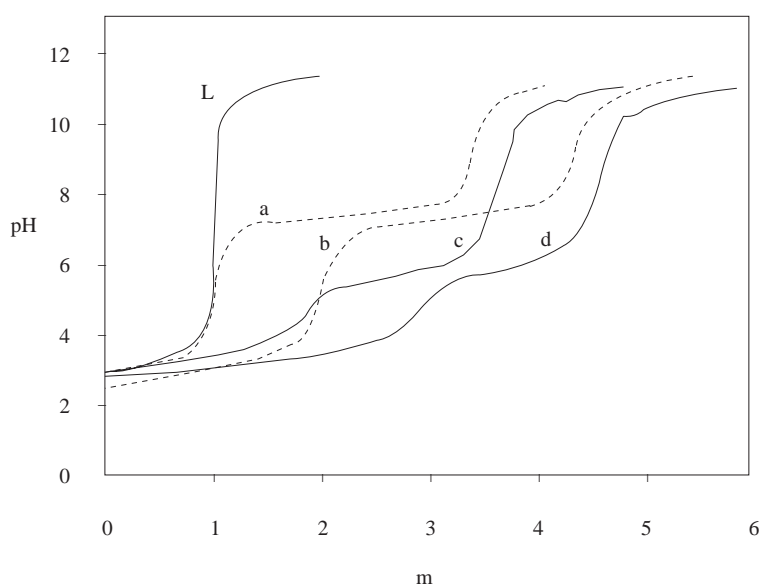
Figure 1. Potentiometric titrations of Y(III)-SA and Sc(III)-SA systems in 0.1 M KNO$_3$ or NaClO$_4$ at 25°C with following molar ratios of SA to metal ion, L: ligand alone, a: Y(III)-SA (1:1), b: Y(III)-SA (1:2), c: Sc(III)-SA (1:1), d: Sc(III)-SA(1:2)

Results and Discussion

Y(III)-SA systems

Potentiometric titrations of SA solutions, as well as of solutions containing three different molar ratios of C_M/C_L were performed, but for the sake of brevity, only the curves obtained for one concentration are shown in Figure 1. The titration curves of Y(III)-SA system in (1:1) mole ratio (curve a, b) appear to

be practically superimposed upon the curve for SA in the pH=2.00-6.00 range (curve L); corresponding to the neutralization of carboxylic proton at m=1.00 (m is mmole base/mmole ligand). This means that between m=0.00 and 1.00 proton dissociates from the carboxylic acid group, not from the phenolic group and formation of $Y(HL)^{2+}$ type protonated complex might be considered and it was shown by equilibrium (1). In fact, the formation of a very labile mono protonated complex, like lanthanium[36], was assumed, in the Y(III)-SA system; it means that SA acted as monadentate ligand through carboxylate oxygen.

$$Y^{3+} + H_2L \rightleftharpoons Y(HL)^{2+} + H^+ \tag{1}$$

Since the potentiometric titration data were fitted well only by assuming the formation of monopro-tonated $Y(HL)^{2+}$ type complexes, then its equilibrium constant $\log \beta$ value was calculated by introducing -log[H$^+$] values in related equations for equilibrium (2); and they are shown in Table 1.

$$Y^{3+} + HL^- \rightleftharpoons Y(HL)^{2+} \tag{2}$$

The observable deviations of pH values in Y(III):SA systems, after m=1.00 (pH=5.80), might be attributed to a possible hydrolytic reaction of Y(III) ion. This possibility was considered, since some rare earth ions have shown similar hydrolytic behaviours[37−38]. Furthermore, the formation of mixed-hydroxo complex by equilibrium (3) was assumed and its related constant was calculated by introducing the titration data, between m=1.00 and m=2.00. It is given in Table 1.

$$Y(HL)^{2+} + H_2O \rightleftharpoons Y(HL)(OH)^+ + H^+ \tag{3}$$
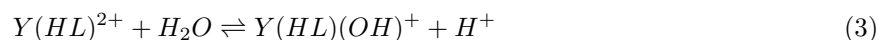
The coordination of the phenolate oxygen was somewhat hindered, for the case of Y(III)-SA system in (1:2) mole ratio; the inflections of potentiometric titration curves appeared at m=2.00 and m=4.00, and in pH values from 2.50 up to 7.00 (Figure 1, curve b); then the equilibrium constant for equilibrium (4), by assuming the coordination of two carboxylate oxygens of two moles of SA, was calculated.

$$Y^{3+} + 2H_2L \rightleftharpoons Y(HL)_2^+ + 2H^+ \tag{4}$$

The potentiometric data fitted well in m=0.00-2.00 range; the calculated stability constant for $Y(HL)_2^+$ is given in Table 1. The ratio of calculated equilibrium constants $\log(\beta(YHL^{2+}))$ / $\log\beta((Y(HL)_2^+))$=0.56 indicated that coordination of the second SA was rather hindered. The titration data above pH=6.10 could be fitted only by assuming the formation of mixed hydroxo complex by equilibrium (5). The related calculations were supported by the hydrolysis reaction and the calculated equilibrium constant is given in Table 1.

$$Y(HL)_2^+ + H_2O \rightleftharpoons Y(HL)_2(OH) + H^+ \tag{5}$$
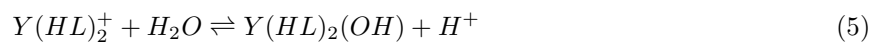
The application of Job's plot to Y(III)-SA system, was impossible since the working wavelength could not be defined. In the equilibrium calculations, another way to support potentiometric and spectrophoto-metric studies was the investigation of the formation curve[15]; but the formation curve of Y(III)-SA system could not be drawn, since it has behaved like rara earths- SA system[22].

Sc(III)-SA systems

The appearance of potentiometric titrations curves of Sc(III)-SA system in (1:1) and (1:2) mole ratios, were entirely different from in Y(III)-SA systems. The formation of ScL$^+$ complex, according to equilibrium

was (6), was assumed and its stability constant in pH range 3.20-5.00 was calculated by introducing 240 experimental data. The results supported ScL^+ being formed between m=0.00 and m=2.00.

$$Sc^{3+} + H_2L \rightleftharpoons ScL^+ + H^+ \tag{6}$$

The deviations of pH values beyond 5.00 might be attributed to hydrolytic reaction (7). This assumption was evaluated in the pH=5.00-6.25 range and equilibrium constant for mixed hydroxo complex formation (5.62±0.08) verified this assumption (Table 1).

$$ScL^+ + H_2O \rightleftharpoons ScL(OH) + H^+ \tag{7}$$

In (1:2) mole ratio of Sc(III):SA system, the inflection points of potentiometric titration curves were observed at m=3.00 and 4.60 (Figure 1d). The occurrence of equilibria (8) and (9) was considered.

$$Sc^{3+} + 2H_2L \rightleftharpoons Sc(HL)L + 3H^+ \tag{8}$$

$$Sc(HL)L + H_2O \rightleftharpoons Sc(HL)L(OH) + H^+ \tag{9}$$
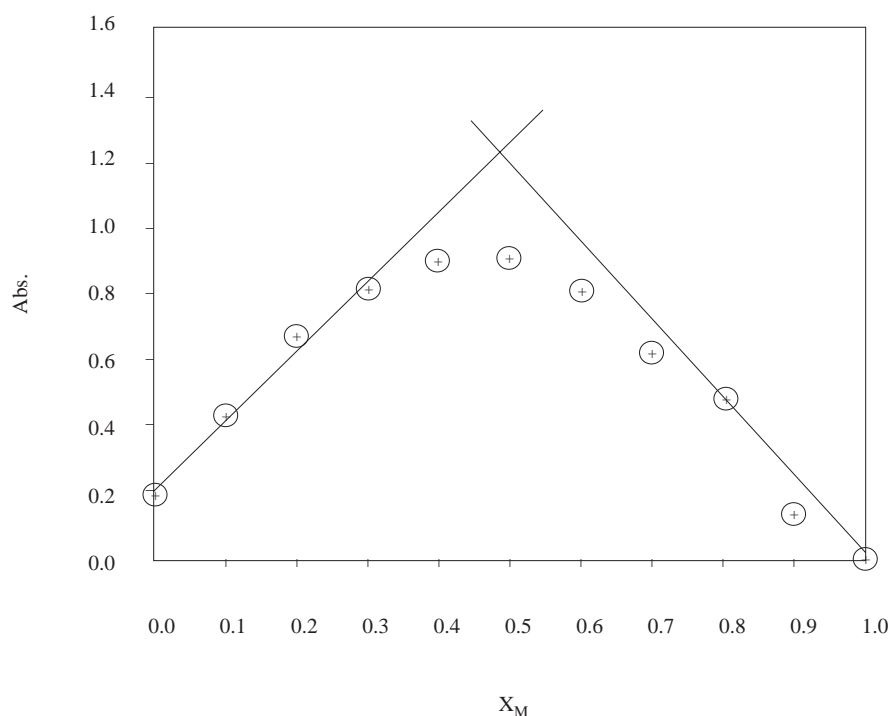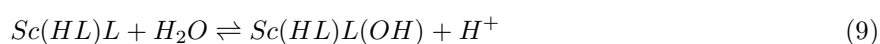
Figure 2. Job's plot for Sc(III)-SA system in pH=3.77 at λ=326 nm.

The stability constant for Sc(HL)L complex was calculated by introducing 210 related data and the existence of this type monoprotonated complex was verified (Table 1). Then the hydrolytic behaviour of Sc(HL)L complex was taken into account. The hydrolysis Sc(HL)L occurred by equilibrium (9) and the stability constant of mixed hydroxo complex Sc(HL)L(OH) was calculated, by introducing 110 points into the related equations (Table 1).

Job's method was applied to Sc(III)-SA system at λ=326 nm and pH=3.77 (Figure 2); Job's plot reflected the formation of ScL^+ type complex which was also defined by means of potentiometric results. The formation curve was drawn for Sc(III)-SA system, $\bar{n}$ values raises up to 1.00 (Figure 3) that indicated one mole Sc(III) was coordinated to one mole SA.
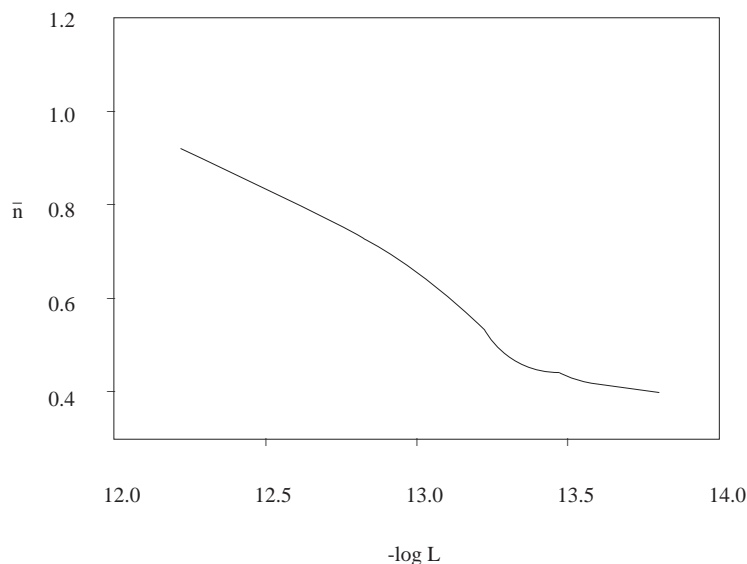
Figure 3. Degree of formation, $\bar{n}$, as a function of -logL in Sc(III)-SA system.

Conclusion

SA contains phenolate and carboxylate groups that can bind Sc(III) and Y(III) ions; these two transition metal ions can form binary, ternary, monoprotonated and mixed hydroxo complexes with SA. The salicylate set has two effective binding sites in the acidic pH range, depending on the charge/radius of the metal ion; as a result of this structure of SA, the simultaneous coordinations of both binding sites of SA are possible for Sc(III) and Y(III); but it occurs only for Sc(III); then rather strong ScL^+ complex forms Sc(III) and Y(III); but it occurs only for Sc(III); then rather strong ScL^+ complex forms and its stability constant is rather high (Table 1); since the ionic potential of Sc(III) is bigger than that of Y(III). Moreover, Y(III) can not form YL^+ type complex; the coordination of Y(III) to SA occurs only through deprotonated carboxylate oxygen of SA, either in (1:1) or (1:2) mole ratios. The existence of protonated complexes, YHL^{2+} and $Y(HL)_2^+$ were verified by calculations (Table 1). Sc(III) forms only Sc(HL)L type complex in higher concentration ratios of SA, but Y(III) forms only $Y(HL)_2$ type complex. In Spite of strong hydrolysis tendencies of Sc(III) and Y(III) that complicate the complex equilibria, the existence of hydroxo complexes formed in basic media either in (1:1) and (1:2) metal to ligand ratios, were verified by potentiometric measurements. Their related stability constants also reflect their tendencies to hydrolysis.

Acknowledgements

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