

Complex formation reactions of Scandium(III), Yttrium(III) and Lanthanum(III) complexes with 8-Hydroxyquinoline

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Abstract: This study aims to investigate the nature and types of complexes formed in aqueous solution between 8-Hydroxyquinoline (HQ) and the ions of Sc^{+3} , Y^{+3} , and La^{+3} . Potentiometric titration was used to follow the formation of complexes. The coordination compounds formed were studied through the determination of stability constants of these complexes in aqueous solution at $25,0 \pm 0,1^\circ\text{C}$ and ionic strength of 0,1 M KNO_3 . The basicity of the ligand was also assessed by the determination of the dissociation constants of the ligand. All of the constants were determined by computer refinement of pH-volume data using the BEST computer program. Distribution diagrams for the species were drawn showing the concentrations of individual species as a function of pH by the SPE software program.

Keywords: Stability constants, 8-Hydroxyquinoline, Sc(III), Y(III), La(III)

1. Introduction

Scandium(Sc(III)), yttrium(Y(III) and lanthanum(La(III)) are elements of the group 3B in the periodic table. Being in the main group, these elements lose all their 3 valence electrons and form a well-defined cationic aqueous chemistry. For this reason, each member of the group have similar chemistry with the transition elements. Differing sizes of M(III) ions lead to differences in chemical behavior within the group. The ionic radii of La(III) :1,17 Å; Y(III): 0,89 Å and Sc(III): 0,83 Å, which decreases from La to Sc. Therefore, it is expected that the thermodynamic stability of their complexes should increase in the order La-Y-Sc. Scandium has the smallest ionic radius and it is the lightest of these elements. Its properties are quite similar to aluminum. It has an appreciably hydrolyzed aqueous solution and an oxide with acidic properties. Lanthanum and actinium show basic properties similar to Calcium. Sc, Y and La have poorly developed coordination chemistries and form weaker coordinate bonds compared to later elements in their transition series. La is even less inclined to form strong coordinate bonds than Sc[1]. The stability constants of a number of relevant 1:1, 1:2 and 1:3 metal-some oxygen and nitrogen donor ligands- complexes reflects this[2-8]. This might be unexpected in view of the charge of +3 ions, but it is complexed with greater electropositivity which inhibits covalent contribution to

their bonding. La, of course, shows these characteristics more clearly than Sc. While La and Y are similar to the lanthanide elements, Sc has more similarity with Al[1].

Interest in the coordination chemistry of Sc has increased in the last decade. G. A. Melson and R. W. Stotz are concerned only with the coordination chemistry of Sc[2]. J. A. Mc Cleverty has compared the chemistry of Sc, Y, the lanthanides, the actinides and some of their complexes in this review[3].

Several authors have investigated the complexes formed between oxygen and nitrogen donating ligands and metal ions of Sc, Y and La using potentiometric methods[5, 6, 8, 9]. Complexes formed between 8-Hydroxyquinoline 5-sulfonic acid and Sc, Y and La have also been investigated in 0,1 M potassium nitrate ionic medium at $25,0^\circ\text{C}$ [7].

8-Hydroxyquinoline, HQ and its derivatives have an important place in analytical chemistry, separation techniques, absorption spectrophotometry, fluorometry and partition chromatography because they can form complexes with many metal ions. These ligands are excellent reagents for gravimetric analysis due to their extraordinary coordinating abilities. They can also be used to extract metal ions. More recently, they became an interesting chelating agent used in light emitting devices or in sensors/diagnostics because they form luminescent coordination compounds. Their derivatives are also used in insecticides, bactericides, fungicides and amoebicides[10-

12].

The 8-Hydroxyquinoline unit is also important in metallosupramolecular chemistry. Its unique coordinating features leads to its usage in molecular recognition of metal ions. The self-assembly of specific oligomeric complexes with certain emitting properties can be induced in approximate derivatives. Application of 8-Hydroxyquinoline derivatives to obtain new supramolecular sensors, emitting devices or self-assembled aggregates have been described in the review of [13-25].

Very little attention has been paid to the Sc, Y and La complexes of 8-Hydroxyquinoline in aqueous ionic medium. The stability constants of the complexes formed between HQ and Ag(I)[10], Zn(II)[11], Al(III)[23], Ca(II)[26], Ba(II)[27], Mg(II)[27], Sr(II)[27], Be(II)[28], Fe(III)[28], Ga(III)[28], Co(II)[28], Ni(II)[28], Cu(II)[28], In(III)[28], Th(IV)[29], Hf(III)[29], (UO₂)²⁺[29], Pb(II)[30], Ge(IV)[31], Cd(II)[32], Sm(III)[33], Mn(II)[34] have been determined in aqueous or organic solvents ionic medium by several authors, using potentiometric or different methods.

They described a method for determining the formation constants of the 8-Hydroxyquinoline with a number of transition metals (Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)) from potentiometric titration data. They determined the formation constants, solubility products, and molecular solubilities of these compounds in the temperature range 25-80°C [35]. La:8-Hydroxyquinoline complexes were investigated in chloroform with in NaClO₄, ionic medium by solvent extraction data. It has been found that the stability constants (B) of La:8-Hydroxyquinoline complexes are 5,9, 11,5 and 17,0 for LaL, LaL₂ and LaL₃ respectively [36]. In the present study, complexation equilibria of Sc, Y and La with 8-Hydroxyquinoline were determined in potassium nitrate in ionic medium.

2. Result and Discussion

2.1. Solution Equilibria

The acid dissociation constants 8-Hydroxyquinoline were determined under the same experimental conditions of ionic strength and temperature (See Table 1) and compared with the values reported in the literature [11]. These constants should be taken into consideration during the evaluation of the pH-metric data (Fig 1, curve I).

2.2. Sc(III): 8-Hydroxyquinoline Complexes

The displaced titration curves for the complex solutions with (1:1, 1:2, 1:3 and 1:10) metal to ligand mole ratio clearly indicates the formation of different kinds of complexes (Fig 1, curve II, III, IV and V). The best fit of the titration curves were obtained when complexes ScL⁺, ScL₂⁻ and ScL₃⁻³ (model 1) were expected. The calculations are shown in Table 1.

The distribution diagrams were drawn in the titration where the metal to ligand mole ratio was 1:3. They were obtained with the aid of SPE program [37] and the

concentration of total metal ion present $\sim 2,0 \times 10^{-3}$ M was set at 100 %. In Fig 2 the species ScL⁺ for the system 8-Hydroxyquinoline and metal ion Sc(III) reaches a maximum of 95 % at pH 4.0. The second species ScL₂⁻ reaches a maximum of 10 % at pH 5.0 and ScL₃⁻³, the complex species in the ratio of 3 moles of ligand to one mole metal, presents a maximum of 98 % near pH 8.0.

Table 1. The acid dissociation constants of 8-Hydroxyquinoline (HQ) and the stability constants of the Sc(III), Y(III) and La(III):HQ complexes (25,0 \pm 0,1 °C, I=0,1 M KNO₃). Standard deviations (σ); (a1=0,02, a2=0,03, a3=0,03, b1=0,05, b2=0,06, b3=0,04, c1=0,04, c2=0,02, c3=0,05).

Equilibrium	Constant	HQ	Sc(III)	Y(III)	La(III)
H2L \rightleftharpoons HL- + H+	logKH2L	4,96 \pm 0,05 (5,11)[11]			
HL- \rightleftharpoons L-2 + H+	logKHL	9,64 \pm 0,05 (9,65)[11]			
M 3+ + L2- \rightleftharpoons ML+	log β 1		10,30 ^{a1}	8,23 ^{b1}	6,25 ^{c1}
M3+ + 2L2- \rightleftharpoons ML2-	log β 2		17,44 ^{a2}	15,52 ^{b2}	11,48 ^{c2}
M3+ + 3L2- \rightleftharpoons ML3-3	log β 3		25,50 ^{a3}	20,24 ^{b3}	16,84 ^{c3}

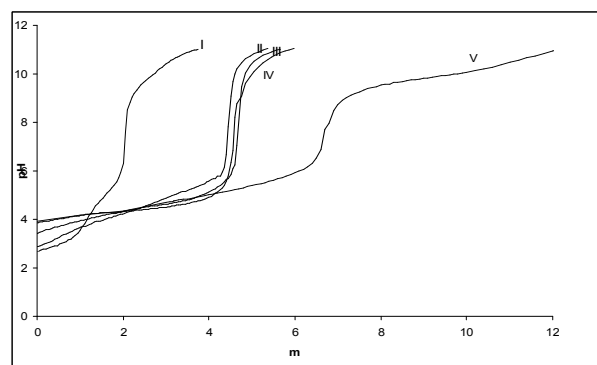


Fig 1. Potentiometric titration curves of Sc(III): HQ system at ionic strength 0,1 M KNO₃ at 25,0 \pm 0,1 °C I) HQ, alone II) 1:1 mole ratio of Sc(III) to HQ III) 1:2 mole ratio of Sc(III) to HQ IV) 1:3 mole ratio of Sc(III) to HQ V) 1:10 mole ratio of Sc(III) to HQ 1:10.

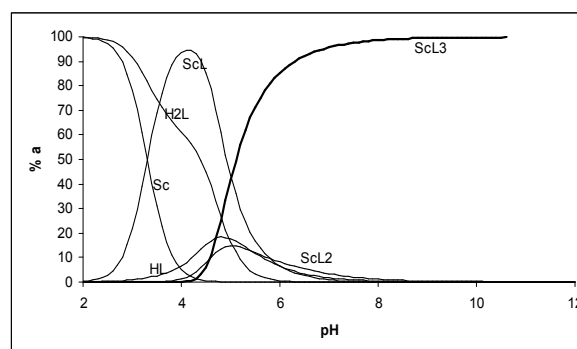


Fig 2. Species distribution curves of the metal ion Sc(III) and the HQ as a function of pH, for a solution initially containing $1,924 \times 10^{-3}$ M metal ion and $5,772 \times 10^{-3}$ M HQ. T=25,0 \pm 0,1 °C and I=0,1 M KNO₃. % a is the percentage of a species present, with the concentration of the metal set at 100%. HL and H₂L are mono- and diprotonated species; Sc: non-hydrolyzed metal; ScL, ScL₂, ScL₃ are the complexed species with one, two and three ligand molecules.

2.3. Y(III): 8-Hydroxyquinoline Complexes

As the starting model, we considered the presence of the species YL^+ , YL_2^- , YL_3^{-3} (model 1). No other species involving metal and ligand ions were retained, thus the hydrolytic products ($YL(OH)$, $YL_2(OH)$, $YL_2(OH)_2$, $YL_3(OH)$ and $YL_3(OH)_2$) were allowed to vary systematically. By adding the species hydrolytic products, the standard deviation (σ) increased by more than 50 % (model 2). As no other species lowered the minimum, model 1 was assumed as the best describing the data, also in consideration that the standard deviation(σ) is comparable with the experimental uncertainty. The stability constants calculated for the Y(III): 8-hydroxyquinoline system at varying molar ratios are presented in Table 1.

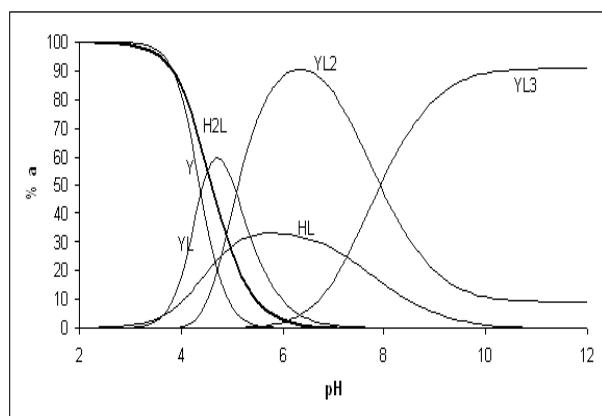


Fig 3. Species distribution curves of the metal ion Y(III) and the HQ as a function of pH, for a solution initially containing $2,08 \times 10^{-3} M$ metal ion and $6,240 \times 10^{-3} M$ HQ. $T = 25,0 \pm 0,1^\circ C$ and $I = 0,1$ MKNO₃. % a is the percentage of a species present, with the concentration of the metal set at 100%. HL and H₂L are mono- and diprotonated species; Y: non-hydrolyzed metal; YL, YL₂, YL₃ are the complexed species with one, two and three ligand molecules.

The determined equilibrium constants permitted the build up of distribution curves for all of the species present in these systems. In Fig 3 the free metal ion predominates only at acidic pH values, i.e. below 4, whereas upon increasing the pH sequential formation of YL^+ , YL_2^- and YL_3^{-3} is observed. The complex that contains one mole metal to one mole ligand YL^+ , reaches its maximum (58 %) at pH 5.0 and a minimum at a pH near 6.2. The complex species YL_2^- starts to be formed at pH 4.0 reaches a maximum (90 %) at 6.0 and the species by YL_3^{-3} three moles of ligand to one of metal reaches maximum of 80 % at pH 10. YL_3^{-3} is the predominant Y(III) species in a very wide range of pH, metal and ligand concentrations and metal-to ligand ratios.

2.4. La(III): 8-Hydroxyquinoline Complexes

The displayed titration curves for the complex solutions with (1:1, 1:2, 1:3 and 1:10) metal to ligand mole ratio clearly indicate the formation of different kind of complexes. Model 1 considers only the presence of LaL^+ , but the standard deviation was considerably high. The

introduction of the hydrolytic products $LaL(OH)$, $LaL_2(OH)_2$, $LaL_3(OH)_2$, LaL_2^- and LaL_3^{-3} (model 2) increases (σ) about three times of model 1(σ). A still better agreement was achieved by adding also LaL_3^{-3} (model 4). On adding other species, the minimum (σ) could be lowered so that model 4 (LaL^+ , LaL_2^- , LaL_3^{-3}) was assumed as the best describing the data. The values of the logarithms of the formation constants for the complexed species are shown in Table 1. To visualize the amounts of the different species, the distribution diagram, given in Fig 4, was constructed.

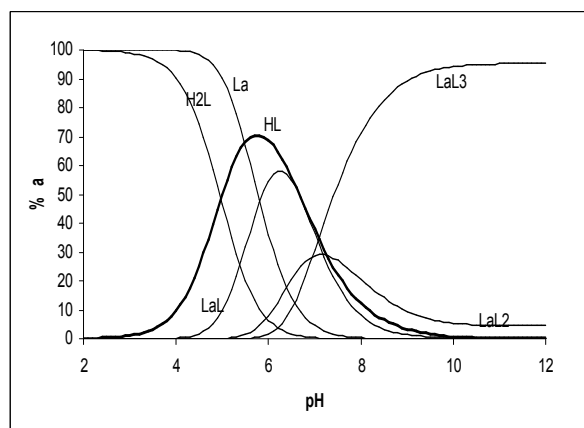


Fig 4. Species distribution curves of the metal ion La(III) and the HQ as a function of pH, for a solution initially containing $1,836 \times 10^{-3} M$ metal ion and $5,508 \times 10^{-3} M$ HQ. $T = 25,0 \pm 0,1^\circ C$ and $I = 0,1$ MKNO₃. % a is the percentage of a species present, with the concentration of the metal set at 100%. HL and H₂L are mono- and diprotonated species; La: non-hydrolyzed metal; LaL, LaL₂, LaL₃ are the complexed species with one, two and three ligand molecules.

In Fig 4, the complex which contains one metal to one mole ligand LaL^+ , reaches its maximum (55 %) at pH 6.0 and a minimum at pH near 9.0. The complex species LaL_2^- starts to be formed at pH 5.0 reaches a maximum (25 %) at pH 7.0 and the species by LaL_3^{-3} three moles of ligand to one of metal starts to be formed at pH 6.0 and reaches a maximum (90 %) at pH 10.0.

3. Conclusion

The stability constants values reported in Table 1 for the different Sc (III), Y(III) and La(III), 8-Hydroxyquinoline complexes (ML, ML₂ and ML₃) indicate that the Sc(III) complexes are relatively more stable than the corresponding ones of Y(III) and La(III). This is in line with the expectation of relatively high tendency of Sc(III) towards complex formation, when compared to Y(III) and La(III) due to its lowest ionic radius.

4. Experimental

4.1. Materials and Reagents

Scandium(III) nitrate and yttrium trioxide, lanthanum

trioxide were received from Aldrich, Sigma and Fluka, respectively. These solutions of metal ions were standardized[38] with ethylenediaminetetraacetic acid (EDTA from Merck). 8-Hydroxyquinoline was supplied from Aldrich. The molecular weights of the 8-Hydroxyquinoline were determined by the Gran[39] method with standardized NaOH. Carbonate free sodium hydroxide stock solutions were prepared from Merck and standardized[38] by titration against primary standard potassium hydrogen phthalate(KHP from Merck). All solutions were prepared with distilled, deionized and boiled water and maintained at 0,1 M ionic strength with potassium nitrate(from Merck). A stream of nitrogen (99,99 %, B.O.S) passing through the reaction system maintained the required inert atmosphere for the potentiometric titrations.

4.2. Potentiometric Equilibrium Measurements

pH titrations were performed on solutions in 100 mL double-walled glass vessel using the automatic titration apparatus (Schott-Hofheim, Germany) equipped with a combined glass electrode was used for the pH measurements. The precision of the pH meter was $\pm 0,0002$ pH units. At constant increments of volume of titrant ($0,1 \pm 0,02$ mL), the corresponding pH was read and plotted vs. m (number of millimoles of NaOH per number of millimoles of ligand or milimoles of metal) to calculate the values of the acid dissociation and stability constants of the system with the aid of the BEST computer program[37]. The input for the BEST program consists of millimoles of each component, the titration variables, the initial equilibrium constant estimates of each species to be formed from the solutions components and the experimentally determined profiles of pH vs. base added. The temperature was controlled at $25,0 \pm 0,1^\circ\text{C}$ by thermostatic arrangement. The cell was equipped with a magnetic stirrer and a tightly fitting cap, which contained three holes for the combined electrode, nitrogen gas and automatic burette. The pH was measured between 2.0-11.0 under a nitrogen flow to avoid carbon dioxide contamination. The weight of the ligand was approximately one tenth the concentration of the titrant, and when with the metal, five titrations were carried out the one the ligand alone and four others with a metal to ligand mole ratios of 1:1, 1:2, 1:3 and 1:10. Each titration was repeated at least 3 times under carefully controlled experimental conditions. About 80 to 100 points (data points of potentiometric measurements) were collected for each titration, and the equilibrium state during titrations was checked by monitoring the time necessary to reach equilibrium (several titrations were carried out with different equilibration periods ranging between (10 and 60)s per data point)and by performing back-titrations. All of the solutions were maintained at 0,1 M ionic strength with potassium nitrate.

The formed species in the studied systems were characterized by the general equilibrium processes (1),

while the stability constants for these generalized species are given by Eq.(2).



$$\beta = [M_pL_q] / [M]^p [L]^q \quad (2)$$

The calculations were performed using the computer program BEST installed on a personal computer. The stoichiometries and the stability constants of the complexes formed were determined by trying various possible composition models for the system studied. The model selected gave the best statistical fit and was chemically consistent with the titration data without giving any systematic drifts in the magnitudes of various residuals, as described elsewhere[37]. The concentration distribution diagrams were obtained using the program SPE[37].

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