Research Article

Study of Metal-1,10-Phenanthroline Complex Equilibria by Potentiometric Measurements

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The interaction of Sc(III), Y(III), and La(III) ions with 1,10-phenanthroline (Phen) has been investigated, using the potentiometric method at 25 ± 0.1°C and I = 0.10 M KNO3. Collected potentiometric data were processed by the “BEST” software program to establish the complexation model for each system. SPE software program was used to evaluate the concentration distributions of the species formed in solution. The stability constants for the binary complexes increased as the ionic radii of the metal cations decreased.

1. Introduction

Scandium (Sc(III)) and Yttrium (Y(III)) are the transition elements that have been known for hundreds of years. Y(III) is generally present with rare-earth elements in the nature. Hence, the chemistry of Y(III) was developed in conjunction with the chemistry of rare-earths chemistry [1]. The element above Y(III) on the periodical table is Sc(III). Like Y(III) and Lanthanum(La(III)), Sc(III) is also present as +3 state. Ionic radii of La(III), Y(III), and Sc(III) are 1.17 Å, 0.89 Å, and 0.83 Å, respectively. The thermodynamic stabilities of the various complexes of La(III), Y(III), and Sc(III) are inversely correlated to their ionic radii (e.g., increase in the thermodynamic stability results from the decreased ionic radii of these elements). The coordination compounds of Sc(III) has attracted increasing interest in recent years. Previous developments in the field of the coordination chemistry of Sc(III), Y(III), and La(III) have been reviewed [2, 3].

Previously, complexes formed between oxygen and nitrogen donating ligands and metal ions of Sc(III), Y(III), and La(III) have been investigated using potentiometric methods by several authors. The results of those previous studies suggested that Sc(III) ion forms the most stable complexes in binary ligand system in aqueous solution. The complexes of Sc(III), Y(III), and La(III) formed in different ionic mediums have been the most adequate complexes to identify the coordination number and the structure of these complexes [4–10].

1,10-Phenanthroline (Phen) (Scheme 1) and its various derivatives are widely used ligands in the different fields of chemical industry [11]. Heteroaromatic group on the Phen provides a binding site for different metal ions. Phen has a rigid structure and has two aromatic nitrogens which contains unshared electron pairs, that can bind metal ions [12, 13]. Due to its ¶-electron deficiency, Phen becomes an excellent ¶-electron acceptor. Certain derivatives of Phen contain amine groups. Due to this chemical feature, Phen is used as ligand for soft and hard sites. Most of the research on the Phen derivates focuses on their catalytic, redox, photoredox, biological activities, and their supramolecular chemistry [13–18]. Phen and its derivatives have very significant roles in the development of supramolecular chemistry [19–21]. In addition, due to their certain chemical features (e.g., luminescence emission, redox, stabilities, etc.), Phen and its derivatives play a significant function in the development of polypyridyl metal complexes of Ru(II) [22]. Being luminescent compounds, Ru-Phen derivates are also important compounds for the analysis of certain biochemical and biophysical features of biological molecules such as DNA [23–27].

The purpose of this study is to gain further information on Phen’s ability to form ML and ML2 complexes with
Sc(III), Y(III), and La(III), and to use potentiometric titration techniques to identify and characterize the structures of any binary complexes that were formed in the aqueous solution. The results on the stabilities and the structures of metal-Phen complexes analyzed in this study are presented in this article.

2. Experimental Section

2.1. Reagents. The Phen (Merck, 99.5% purity) was used without further purification. Its purity and concentration was confirmed by titration 0.1 M NaOH. Sc(NO₃)₃ (Aldrich, 99.9% purity), Y₂O₃ (Sigma, 99.9% purity), and La₂O₃ (Fluka, 99.9% purity) were standardized by EDTA titrations [28]. To adjust the ionic strength of the metal cation solutions KNO₃ (Merck, 99% purity) was used. A NaOH (Merck, 97% purity) solution was prepared from concentrated stock solution (1 M NaOH) by dilution. All of the experiments were conducted with Grade a glassware and doubly distilled water.

2.2. Potentiometric Measurements. The potentiometric titration reactions were measured with a personal computer (PC) system, as described previously [4]. The solutions were adjusted to an ionic strength of 0.1 M with KNO₃ in a 100 mL jacketed glass cell equipped with a magnetic stirrer, and a water bath was used to control the temperature to 25.0 ± 0.1°C. A slight positive pressure of purified nitrogen was maintained in the titration cell in order to exclude oxygen and carbon dioxide from the reaction solutions.

The combined electrode calibration, in terms of hydrogen ion concentration, was accomplished by adding a standardized solution of NaOH to a standardized solution of HCl (both solutions were adjusted to an ionic strength of 0.1 M). The values of $E^-$ and the response slopes from the potentiometric titrations were measured by fitting a straight line through the experimental points collected from pH 1.5 to 12. A $pK_w$ value of 13.75 was determined in the present study.

The metal stability constants of Phen with Sc(III), Y(III), and La(III) were determined directly by potentiometric titrations. Uniform volumetric additions of standardized NaOH (titrant) were made to all systems, and the potential was recorded as a function of the added volume. The pH-potentiometric titrations were measured by fitting a straight line through the experimental points collected from pH 2 to 12.

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The metal stability constants were quantified using $[M]/[L]$ ratios of 1:1, 1:2, 1:3 and 1:10 and a metal concentration of $9.668 \times 10^{-2}$ M. The experimental points were collected from pH 2 to 12. Complexation studies of the Y(III) : Phen and La(III) : Phen systems were performed using $[M]/[L]$ ratios of 1:1 to 1:10 with metal concentrations of $1.04 \times 10^{-1}$ M and $9.180 \times 10^{-2}$ M, respectively. The experimental points were collected between pH ranges 2–8 (for Y(III) : Phen) and 2–8 (for La(III) : Phen). BEST software program was used to analyze the potentiometric data collected from the titrations studies, as described previously [29]. The water and Phen acid dissociation constants, as well as all known stability constants were held constant during the refinement operations of the different metal-Phen systems studied (as defined for these equilibria.)

3. Results and Discussion

3.1. Acid Dissociation Constants of 1,10-Phenanthroline. The acid dissociation constants of Phen were determined potentiometrically in $I = 0.1$ M KNO₃ ionic medium at 25°C. A titration curve of Phen, prepared in the absence of metal cations, is shown as curve I in Figure 1. Proton ionization sites of Phen are assigned to the two ring nitrogen atoms in Phen. Previously published data supported the correspondance of these equilibria.

$$
H_2L^{2+} \rightleftharpoons HL^{+} + H^+ \\
K_{a1} = \frac{[HL^+] [H^+]}{[H_2L^{2+}]} \\
(1)
$$

$$
HL^+ \rightleftharpoons L + H^+ \\
K_{a2} = \frac{[L] [H^+]}{[HL^+]} \\
(2)
$$

Figure 1: The potentiometric titration curves of the Sc(III) : Phen complexes in 0.1 M KNO₃ at 25°C. ($m$ = mmoles of base (sodium hydroxide) added per mmole of ligand). (I) Phen alone ($T_{phen} = 9.668 \times 10^{-2}$ M). (II) (1:1) Sc(III) : Phen ($T_{Sc} = 9.668 \times 10^{-2}$ M, $T_{Phen} = 9.668 \times 10^{-2}$ M). (III) (1:2) Sc(III) : Phen ($T_{Sc} = 9.668 \times 10^{-2}$ M, $T_{Phen} = 1.934 \times 10^{-1}$ M). (IV) (1:3) Sc(III) : Phen ($T_{Sc} = 9.668 \times 10^{-2}$ M, $T_{Phen} = 2.900 \times 10^{-2}$ M).
Table 1: The Acid Dissociation Constants of 1,10-phenanthroline (Phen) and the Stability Constants of the Sc(III), Y(III) and La(III)-Phen Complexes (25 ± 0.1°C, I = 0.1 M KNO3).

<table>
<thead>
<tr>
<th>Row</th>
<th>Equilibrium</th>
<th>Constant</th>
<th>Phen</th>
<th>Sc(III)</th>
<th>Y(III)</th>
<th>La(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H2L3- = HL- + H+</td>
<td>log K_{H2L}</td>
<td>1.50 ± 0.08 (1.95) [30]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HL- = L + H+</td>
<td>log K_{HL}</td>
<td>4.92 ± 0.08 (4.77) [30]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>M^{3+} + L ⇌ ML^{3-}</td>
<td>log β_1</td>
<td>10.83 ± 0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>M^{3+} + 2L ⇌ ML^{3-}_2</td>
<td>log β_2</td>
<td>20.70 ± 0.02</td>
<td>9.47 ± 0.04</td>
<td>8.47 ± 0.03</td>
<td></td>
</tr>
</tbody>
</table>

3.2. Stability Constants of Sc(III)-Phen Complexes. Titration of solutions containing 1:1, 1:2, 1:3, and 1:10 ratios of metal ion to ligand (Figure 1, curve II, III and IV) results in marked inflection point at m = 4.0 which corresponds to the formation of chelates that have the compositions of ScL^{+3} and ScL^{2+3}, respectively. In the buffer region near the inflection point, four protons were titrated per metal ion. The following equations (3) and (4) can describe the equilibria involved in this region:

\[
\begin{align*}
\text{Sc}^{3+} + \text{H}_2\text{L}^{2+} &\rightleftharpoons \text{ScL}^{+3} + 2\text{H}^+ & \beta_1 &= \frac{[\text{ScL}^{+3}][\text{H}^+]^2}{[\text{Sc}^{3+}][\text{H}_2\text{L}^{2+}]} \\
\text{Sc}^{3+} + 2\text{H}_2\text{L}^{2+} &\rightleftharpoons \text{ScL}^{2+3} + 4\text{H}^+ & \beta_2 &= \frac{[\text{ScL}^{2+3}][\text{H}^+]^4}{[\text{Sc}^{3+}][\text{H}_2\text{L}^{2+}]^2}.
\end{align*}
\]

For the potentiometric titrations performed with various molar ratios, the presence of complexes such as ScL^{+3}, ScL^{2+3}, ScL^{3+3}, ScL(OH)^{+2}, ScL(OH)_2^{+}, ScL_{2}(OH)^{+2}, ScL_{2}(OH)_2^{+}, ScL_{3}(OH)^{+2}, ScL_{3}(OH)_2^{+}, which might occur in the ionic medium, were examined using the BEST [29] software. The software was also used to calculate the stability constants of the ScL^{+3} and ScL^{2+3} for various metal/ligand molar ratios ranging from [M]/[L] of 1:1 to 1:10. However, the software calculations rejected all species except ScL^{+3} and ScL^{2+3}. The probable structures of the corresponding ScL^{+3}, ScL^{2+3} species in aqueous solution were proposed as follows. For the ScL^{+3}, ScL^{2+3} species, Sc(III) ion coordinates with both N atoms in phenanthroline ring. The analyzed results showed that the stability constant values obtained for ScL^{+3} and ScL^{2+3} were the same at all molar ratios. Sigma fit (σ_results) was found to be lower than 0.02 in all of the stability constant calculations. Stability constants obtained in the present study for ScL^{+3} and ScL^{2+3} are given in Table 1.

The distribution diagram, computed by the SPE [29] software for a solution containing 9.668 × 10^{-2} M Sc(III) and 1.934 × 10^{-1} M Phen, is shown in Figure 3. The free metal ion predominates only at acidic pH values, that is, below 3.9, whereas upon increasing the pH the sequential formation of ScL^{+3}, ScL^{2+3} is observed. An analysis of the distribution diagram explains that at pH values close to 3.9 nearly 100% of the solution contains the ScL^{2+3} species. ScL^{+3} is not formed at detectable amount up to pH 3.9.

3.3. Stability Constants of Y(III)-Phen Complexes. Potentiometric titrations of the Y(III): Phen system were studied at various molar ratios ranging from 1:1 to 1:10 in I = 0.1 M KNO3 ionic medium at 25°C. Addition of base to a solution containing equimolar amounts of Y(III) ion and ligand results in a pronounced inflection at m = 2.0 and m = 4.0 (Figure 2).

For the potentiometric titrations performed with various molar ratios, the BEST software was used to examine complexes such as YL^{+3}, YL_{2}^{+3}, YL_{3}^{+3}, YL(OH)^{+2}, YL(OH)_2^{+}, YL_{2}(OH)^{+2}, YL_{2}(OH)_2^{+}, and YL_{3}(OH)^{+2} which might occur in the medium. The stability constants of the
YL$^{+3}$ complex were also calculated with the BEST software for various metal/ligand molar ratios ranging from [M]/[L] of 1:1 to 1:10. However, the software calculations rejected all species except YL$^{+3}$. The probable structure of the corresponding YL$^{+3}$ species in aqueous solution was proposed as follows. For the YL$^{+3}$ species, Y(III) ion coordinates with both N atoms in phenanthroline ring of one of Phen. The analyzed results showed that the stability constant values obtained for YL$^{+3}$ species same at all molar ratios. The following equation (5) can describe the equilibria involved in this region:

$$Y^{+3} + H_2L^{+2} \rightleftharpoons YL^{+3} + 2H^+ \quad \beta_1 = \frac{[YL^{+3}] [H^+]^2}{[Y^{+3}] [H_2L^{+2}]}.$$  

(5)

For all of the stability constant calculations, sigma fit ($\sigma_{\text{fit}}$) was found to be lower than 0.04. The stability constants calculated for the Y(III) : Phen system at varying molar ratios and concentrations were given in Table 1.

Based on the distribution diagram, the speciation of the major metal-ligand species was determined within the defined pH ranges by the SPE software. As shown in Figure 4, the YL$^{+3}$ species is the primary species prevalent in an aqueous solution at pH 5.0. YL$^{+3}$ constitutes ~93% of the solution’s content. The major species is YL$^{+3}$ (Figure 4).

### 3.4. Stability Constants of La(III)-Phen Complexes.

Potentiometric titrations of the La(III) : Phen system were studied at various molar ratios ranging from 1:1 to 1:10 in an 0.1 M KNO$_3$ ionic medium at 25°C. The potentiometric titration curves of a 1:1 mole ratio of La(III) to Phen exhibit inflection points at $m = 2.0$, 4.0 and 5.0 (Figure 2).

For the potentiometric titrations done at various molar ratios, the BEST software was used to examine complexes such as LaL$^{+3}$, LaL$_2^{+3}$, LaL$_3^{+3}$, LaL(OH)$_2^{+2}$, LaL(OH)$_3^{+}$, LaL$_2$(OH)$_2^{+2}$, LaL$_2$(OH)$_3^{+}$, LaL$_3$(OH)$_2^{+2}$, and LaL$_3$(OH)$_3^{+1}$ which might occur in the medium. The stability constants of the LaL$^{+3}$ species were calculated with the BEST software for various metal/ligand molar ratios changing from 1 : 1 to 1 : 10. However, the software rejected all other species except LaL$^{+3}$. The probable structure of the corresponding LaL$^{+3}$ species in aqueous solution was proposed as follows. For the LaL$^{+3}$, species, La(III) ion coordinates with both N atoms in phenanthroline ring of one of Phen. The following equation (6) can describe the equilibria involved in this region:

$$La^{+3} + H_2L^{+2} \rightleftharpoons LaL^{+3} + 2H^+ \quad \beta_1 = \frac{[LaL^{+3}] [H^+]^2}{[La^{+3}] [H_2L^{+2}]}.$$  

(6)

For all of the stability constant calculations, sigma fit ($\sigma_{\text{fit}}$) was found to be lower than 0.04. The stability constants calculated for the La(III) : Phen system at varying molar ratios and concentrations were given in Table 1.

Figure 5 displays the distribution diagram for the La(III) : Phen system as a function of pH by the SPE software. As shown in Figure 5, the LaL$^{+3}$ species is major species found in an aqueous solution at pH 4.5. The LaL$^{+3}$ species constitutes ~97% of the solution’s content.

### 4. Conclusions

In conclusion, the study of Sc(III), Y(III), and La(III)/Phen in aqueous solutions by potentiometric titrations gave the following results.

(a) Two metal/ligand complexes ScL$^{+3}$, ScL$_2^{+3}$ form at equilibrium and the relevant stability constants were determined

(b) ScL$_2^{+3}$ is the predominant metal species in a wide pH range

(c) One metal/ligand complex YL$^{+3}$ forms at equilibrium and the relevant stability constants were determined

(d) One metal/ligand complex LaL$^{+3}$ forms at equilibrium and the relevant stability constants were determined

(e) The order of stability is scandium(III) > yttrium(III) > lanthanum(III).

This pattern demonstrates that complex stability decreases as the size of the cation increases.
References


