

# Stabilities of Complexes of Scandium(III) and Yttrium(III) With Catechol Derivatives

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The interactions of scandium(III) and yttrium(III) ions with catechol derivatives; catechol(H<sub>2</sub>L, CAT), 4-nitrocatechol(H<sub>2</sub>L, 4NCAT) and 2,3-dihydroxynaphthalene-6-sulphonic acid(H<sub>2</sub>L, DHN) were investigated in different metal ion:ligand mole ratios, by potentiometry and spectrophotometry. The stoichiometries of formed complexes have been defined by Job's method and formation curves have been drawn for some complexes, whenever possible. The stability constants of the fourteen formed complexes in definite stoichiometries have been determined, in an ionic medium of 0.1M KNO<sub>3</sub> or NaClO<sub>4</sub> at a temperature of 25 °C.

Noticeably, complexes of scandium(III) ion formed at much lower pH values than complexes of yttrium(III) ion, and its catechol complexes were more stable than complexes formed with yttrium(III) ion. The dependence on ionic strength of stability constants of Sc(III) and Y(III) were defined by comparing them with values from the literature whenever possible. The stabilities of complexes of Sc(III) or Y(III) with catechol derivatives in (1:1), (1:2) and (1:3) mole ratios were compared by considering their possible structures.

## Introduction

Scandium and yttrium have been known for almost one hundred years. Scandium is the first member of the Sc, Y, La, Ac group with electronic configuration [Ar]3d<sup>1</sup> 4s<sup>2</sup> and is the congener of Al in group III. Its ionic radius (0.745 Å) is considerably smaller than the radii of Y(III): 0.90 Å and La(III): 1.045 Å; hence its chemistry more closely resembles that of its congener aluminium<sup>1</sup>. In many respects, scandium is also a typical first transition series metal rather than a lanthanide<sup>2</sup>. Yttrium is always found in nature with rare earths and its chemical properties are very similar to lanthanum. Most of the chemistry of yttrium has been investigated in connection with studies on the rare earths<sup>3-8</sup>. The aqua ions of Y(III) and Sc(III) both undergo significant hydrolysis, giving rise to OH-bridged dimers and trimers<sup>9,10</sup>.

Only a few stability constants of Sc(III) and Y(III) coordination compounds have been reported<sup>3-14</sup>. The most stable and common of Sc(III) and Y(III) complexes are those with catechol(H<sub>2</sub>L, CAT) and 2,3-dihydroxynaphthalene-6-sulphonic acid(H<sub>2</sub>L, DHN); CAT and DHN are typical oxygen donor ligands. The stability constants of CAT and DHN complexes of Sc(III) and Y(III) in (1:1) stoichiometry have been determined previously<sup>11-14</sup>; these were individual studies either with Sc(III) or Y(III) and with one of the catechol derivatives.

This research deals mainly with three catechol derivatives and their interactions with Sc(III) and Y(III) ions in aqueous solution. Since it has been noted that the above-mentioned researches were carried out in different ionic mediums at different temperatures, our first aim was to investigate the interaction of catechol derivatives of catechol derivatives with Sc(III) and Y(III) in 0.1 M  $\text{KNO}_3$  and  $\text{NaClO}_4$  ionic medium. Thus the dependence on the ionic strength of stability constants would be defined. The second aim was to compare the stabilities of the Sc(III) and Y(III) complexes that were formed with different phenolic ligands. The investigation of other phenolic ligands will be the subject of future papers. The selected catechol derivatives were CAT, 4NCAT and DHN. Their related equilibrium constants were calculated by potentiometry and spectrophotometry.

## Experimental

### Materials

CAT, 4NCAT and DHN have been used as the ligands. The ligands (Fluka puriss or Merck p.a. products) were used without further purification; their purities were checked by alkalimetric titrations; they were always > 99.5%. The ligands were introduced into the reaction cell, in definite stoichiometries<sup>15</sup>.

The stock solutions of Sc(III) and Y(III) were prepared in doubly distilled  $\text{CO}_2$ -free water; for potentiometric studies, scandium(III) nitrate was prepared by dissolving  $\text{Sc}_2\text{O}_3$  in a known quantity of  $\text{HNO}_3$  to avoid hydrolysis and the ionic medium was 0.1 M  $\text{KNO}_3$ . For spectrophotometric studies,  $\text{Sc}_2\text{O}_3$  was dissolved in concentrated HCl; since  $\text{NO}_3^-$  ion absorbs strongly in the UV/VIS region of the spectrum<sup>16</sup>. For that reason, ionic strength was maintained constant by 0.1 M KCl. Yttrium(III) perchlorate was prepared in a known quantity of  $\text{HClO}_4$ , by dissolving  $\text{Y}_2\text{O}_3$ . The ionic medium for Y(III) equilibrium studies was 0.1 M  $\text{NaClO}_4$ . The stock solutions of Sc(III) and Y(III) were standardized against EDTA solution<sup>17</sup>.

### Instrumentation

The free hydrogen-ion concentration,  $[\text{H}^+]$ , was measured to within 0.001 pH units with a Schott-pH meter. The combined glass electrode was systematically calibrated in  $-\log[\text{H}^+]$  (pH) units, by direct titration of acetic acid with standard NaOH under the same conditions as the solution under study, in the pH range 3.50-10.50. The observed pH meter readings were compared with the actual hydrogen ion concentrations that were determined from the data tabulated by Harned and Owen<sup>18</sup>. The pH readings, which were below 3.50 and above 10.50, were calibrated by measurements in HCl and NaOH solutions, respectively.

### Procedure

For potentiometric measurements, stock solution of metal ion, in a known volume, and weighed ligands, were introduced into the water jacketed cell ( $1000\text{ cm}^3$ ) by circulating thermostated water that had a constant temperature of  $25.00 \pm 0.1^\circ\text{C}$ . The molar ratios of metal ion to ligand were (1:1), (1:2) and (1:3). The volume of the solution was completed to  $50 \pm 0.1\text{ mL}$  by  $\text{KNO}_3$  or  $\text{NaClO}_4$  solutions, in order to maintain a relatively constant ionic strength. The final solution contained approximately  $1.10^{-3}$ - $5.10^{-3}$  mole of metal ion/L. Presaturated pure nitrogen was passed through the solution throughout the course of a titration. After thermal equilibrium was reached, the hydrogen ion concentrations were determined by a number of successive readings after each addition of small increments of standard 0.1 M NaOH. An excess of strong acid

(HCl or HClO<sub>4</sub>) was titrated with standard NaOH up to the pH corresponding approximately to neutralize it.

The stoichiometries of the complexes involved were determined by Job's Method<sup>19</sup>, in which UV/VIS spectra were taken in definite mole ratios of metal ions and ligands as a function of pH, in the range 4.0-10.0. The absorbance measurements were performed on metal ion: ligand systems that were definite in pH values and molar ratios. Job's plots were then drawn for each metal ion and ligand system.

## Calculations

### The calculations of Stability Constants of Complexes and Acid Dissociation Constants of Ligands:

A computer program<sup>23-24</sup> to calculate the stability constants of complexes from potentiometric data has three parts: the first and second parts of the program solve the stability constants of Sc(III) and Y(III) complexes that are in different stoichiometries of catechol derivatives to metal ion. The criterion used for which species were present in equilibria was simply model best fit the potentiometric data. The available models then tested only those containing the species ML, ML<sub>2</sub>, ML<sub>3</sub> and MHL<sub>3</sub>, which are explained below. The calculations relating to the determination of stability constants were then performed with the derived equations. The mathematical analysis of potentiometric data comprised 9 titrations and 920 experimental points. The standard deviations of the values in Table 1 were obtained by a special computer program. The computations were performed on a Pentium 120 computer. All thermodynamic parameters were expressed in the molar scale. The acid dissociation constants were determined with the appropriate computer program<sup>20</sup>.

**Table 1.** The stability constants of Sc(III) and Y(III) complexes of ligands studied in this research and their dissociation constant

Ligands	Equilibrium	-log K <sub>a</sub>	log β		log β (Lit.)	
			Sc(III)	Y(III)	Sc(III)	Y(III)
CAT (H <sub>2</sub> L)HL <sup>-</sup> ⇌ H <sup>+</sup> +L <sup>-2</sup>	H <sub>2</sub> L ⇌ H <sup>+</sup> +HL <sup>-</sup>	9.23	-	-	-	-
	13.00 <sup>22</sup>	-	-	-	-	-
	M+L ⇌ ML	-	16.54±0.05	11.35±0.03	17.13 <sup>11,a</sup> 14.2 <sup>12,b</sup>	9.81 <sup>12,b</sup>
4NCAT (H <sub>2</sub> L)HL <sup>-</sup> ⇌ H <sup>+</sup> +L <sup>-2</sup>	H <sub>2</sub> L ⇌ H <sup>+</sup> +HL <sup>-</sup>	6.62 <sup>20</sup>	-	-	-	-
	10.75 <sup>20</sup>	-	-	-	-	-
	M+L ⇌ ML	-	13.58±0.01	9.83±0.01	-	-
	M+2L ⇌ ML <sub>2</sub>	-	27.35±0.03	18.39±0.03	-	-
	M+2L+HL ⇌ MHL <sub>3</sub>	-	-	24.39±0.05	-	-
	M+3L ⇌ ML <sub>3</sub>	-	40.14±0.05	-	-	-
DHN (H <sub>2</sub> L <sup>-</sup> )	H <sub>2</sub> L <sup>-</sup> ⇌ H <sup>+</sup> +HL <sup>-2</sup>	8.16	-	-	-	-
	HL <sup>-2</sup> ⇌ H <sup>+</sup> +L <sup>-3</sup>	11.75 <sup>14</sup>	-	-	-	-
	M+L ⇌ ML	-	15.92±0.03	12.32±0.03	14.15 <sup>13,b</sup>	10.14 <sup>14,c</sup> 10.09 <sup>13,b</sup>
		-	-	-	-	18.22 <sup>14,c</sup>
	M+2L ⇌ ML <sub>2</sub>	-	29.48±0.04	21.12±0.05	-	-
	M+2L+HL ⇌ MHL <sub>3</sub>	-	—	24.35±0.07	-	-
	M+3L ⇌ ML <sub>3</sub>	-	34.65±0.05	—	-	24 <sup>14,c</sup>

(In this research temperature at 25 °C, I=0.1 M KNO<sub>3</sub> for Sc(III), I=0.1M NaClO<sub>4</sub> for Y(III).)

(a: 25 °C, I=0.1, b:30 °C, I=0.2, c: 25 °C, I=0.5)

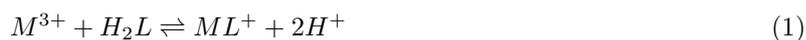
### The calculation of average number of ligands attached to a metal ion:

The third part of the computer program calculates the average number of ligands attached to a metal ion. It gives the results in a graphical form known as the complex formation curve of the metal ion-ligand system,

as a function of ( $\bar{n}$ ) values versus  $(-\log L)^{21}$ .  $n$  is the number of ligands per metal ion, and  $L$  is the free concentration of ligands.

### Model 1. Formation of ML Type Complexes of Catechol Derivatives:

Catechol and its derivatives act as diprotic acids. The diprotic acid  $H_2L$  forms only a complex species  $ML$  with a metal ion,  $M^{3+}$ , according to the equilibrium (1) in the 1:1 metal ion: ligand mole ratio



The related equilibrium constant  $K_1$  is then given as

$$K_1 = \frac{[ML^+][H^+]^2}{[M^{3+}][H_2L]} \quad (2)$$

The related mass balance equations can be described by equations (3)-(5), where  $T_M$  and  $T_{H_2L}$  are the total concentrations of metal ion and ligand, respectively; the corresponding free equilibrium concentrations of metal ion, ligand and complexes are given in brackets to denote their molar concentrations.

$$T_M = [ML^+] + [M^{3+}] \quad (3)$$

$$T_{H_2L} = [ML^+] + [H_2L] \quad (4)$$

$$[H^+] = 2[ML^+] - m.T_M \quad (5)$$

Solving equations (2-5) simultaneously, equation (6) is obtained.

$$K_1 = \frac{2([H^+] + mT_m)[H^+]^2}{((T_M(2 - m))[H^+])^2} \quad (6)$$

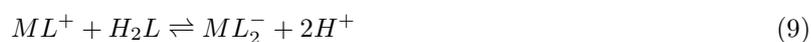
The stability constant of  $ML$  complex species ( $\beta_1$ ), which is the equilibrium constant for equilibrium (7), can be calculated in terms of the dissociation constants of diprotic acid,  $K_{a1}$  and  $K_{a2}$  and  $K_1$ , by equation (8)



$$\beta_1 = \frac{[ML^+]}{[M^{3+}][L^{2-}]} = \frac{K_1}{(K_{a1}.K_{a2})} \quad (8)$$

### Model 2. Formation of $ML_2$ Type Complexes of Catechol Derivatives:

In order to explain the results of potentiometric titrations of metal ion: ligand system in which mole ratios were (1:2); the existence of equilibria (1) and (8) can be suggested for ligands that were DHN and 4NCAT. A different approach can then be followed for these stoichiometries. The formation of  $ML$  by equilibrium (1) and then the formation of  $ML_2$  by equilibrium (9) step by step are taken into consideration.  $K_2$  (10) as a function of free equilibrium concentrations of related species (11-13) is found by



The equilibrium constant  $K_2$  is given as

$$K_2 = \frac{[ML_2^-][H^+]^2}{[ML^+][H_2L]} \quad (10)$$

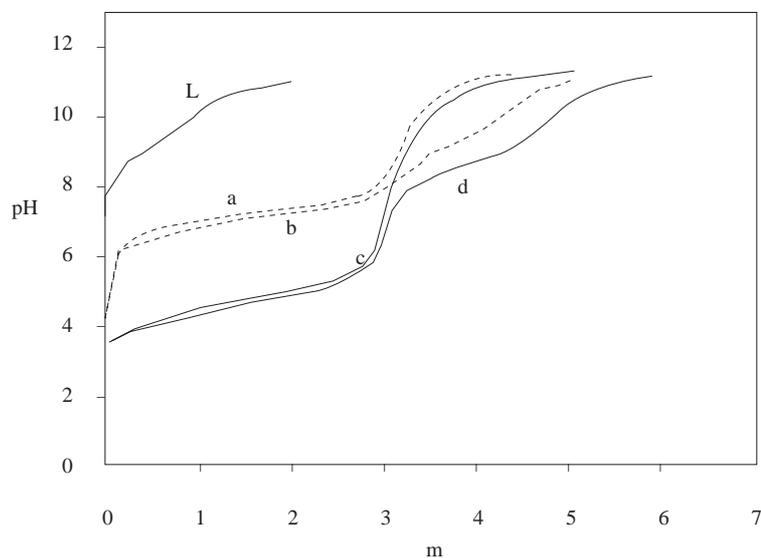
The mass balance equations are given by (10)-(11)

$$T_M = [ML^+] + [ML_2^-] \quad (11)$$

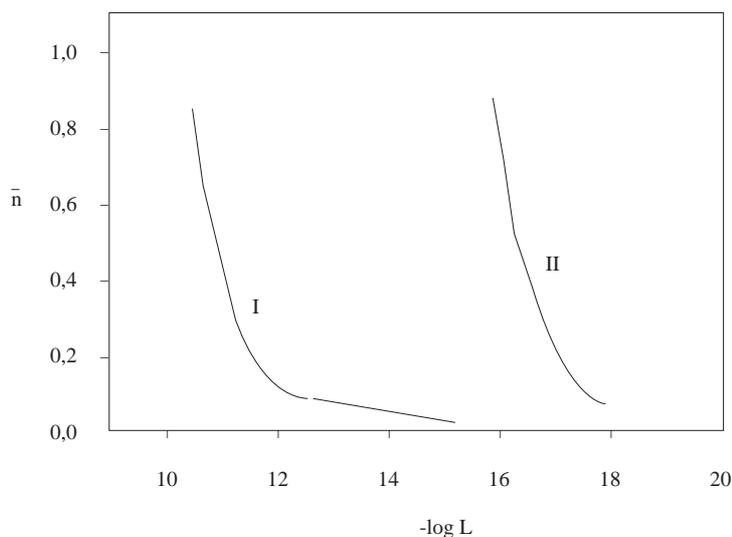
$$T_{H_2L} = [H_2L] + [ML^+] + 2[ML_2^-] \quad (12)$$

$$[H^+] = 2[ML_2^-] - mT_M \quad (13)$$

solving the equations simultaneously, equation (14) is obtained



**Figure 1.** Potentiometric titration of Sc(III) and Y(III) complexes of catechol in 0.1 M  $KNO_3$  or  $NaClO_4$  at 25 °C with the following molar ratios of ligand to metal ion, **L**- Ligand alone, **a**- Y(III): CAT (1:1), **b**- Y(III): CAT (1:2), **c**- Sc(III): CAT (1:1), **d**- Sc(III): CAT (1:2)



**Figure 2.** Degree of formation,  $\bar{n}$ , as a function of  $-\log L$ :

**curve I-** Y(III):CAT complex,

**curve II-** Sc(III): CAT complex

$$K_2 = \frac{2([H^+] + mT_M)[H^+]^2}{((T_M(2 - m))[H^+]) \cdot ((T_M(4 - m))[H^+])} \quad (14)$$

The stability constant of  $ML_2^-$ , ( $\beta_2$ ), the equilibrium constant for equilibrium (15) can be given in terms of dissociation constants of the diprotic ligands,  $K_{a1}$  and  $K_{a2}$  and the equilibrium constants  $K_1$ ,  $K_2$ , for equilibrium (1) and (9), respectively.



Then  $\beta_2$  can be solved by equation (16)

$$\beta_2 = \frac{[ML_2^-]}{[M^{3+}][L^{2-}]^2} = \frac{K_1 K_2}{(K_{a1})^2 (K_{a2})^2} \quad (16)$$

### Model 3. Formation of $MHL_3$ Type Complexes of Catechol Derivatives:

When dealing with a diprotic ligand  $H_2L$  (DHN and 4-NCAT) for which the existence of equilibriums (1), (9) and (17) can be also considered in the (1:3) mole ratio of metal ion to ligand.



The equilibrium constant  $K_3$  is given as

$$K_3 = \frac{[MHL_3^{2-}][H^+]}{[ML_2^-][H_2L]} \quad (18)$$

The mass balance equations are given by (19-20)

$$T_M = [ML_2^-] + [MHL_3^{2-}] \quad (19)$$

$$T_{H_2L} = [H_2L] + 2[ML_2^-] + 3[MHL_3^{2-}] \quad (20)$$

$$[H^+] = [MHL_3^{2-}] - mT_M \quad (21)$$

solving the equations simultaneously, equation (22) is obtained

$$K_3 = \frac{([H^+] + mT_M)[H^+]}{(T_M(1 - m))[H^+]^2} \quad (22)$$

The stability constant of  $MHL_3^{2-}$ , ( $\beta_3^H$ ), which is the equilibrium constant of equilibrium (23), can be given in terms of dissociation constants of the diprotic ligands  $K_{a1}$  and  $K_{a2}$  and the equilibrium constants  $K_1$ ,  $K_2$ ,  $K_3$



$$\beta_3^H = \frac{[MHL_3^{2-}]}{[M^{3+}][L^{2-}]^2[HL^-]} = \frac{K_1K_2K_3}{(K_{a1})^3(K_{a2})^2} \quad (24)$$

#### Model 4. Formation of $ML_3$ Type Complexes of Catechol Derivatives:

When dealing with a diprotic ligand,  $H_2L$ , for which the existence of equilibria (1), (9) and (25) can also be taken into the consideration in a (1:3) mole ratio of metal ion to ligand.



The equilibrium constant  $K_3$  can be given by equation (26)

$$K_3 = \frac{[ML_3^{3-}][H^+]^2}{[ML_2^-][H_2L]} \quad (26)$$

The mass balance equations can be calculated by (27)-(28)

$$T_M = [ML_2^-] + [ML_3^{3-}] \quad (27)$$

$$T_{H_2L} + 2[ML_2^-] + 2[ML_2^-] + 3[ML_3^{3-}] \quad (28)$$

$$[H^+] = 2[ML_3^{3-}] - mT_M \quad (29)$$

solving the equations simultaneously, the  $K_3$  equilibrium constant can be found by equation (30)

$$K_3 = \frac{2([H^+] + mT_M)[H^+]^2}{(T_M(2 - m) - [H^+])^2} \quad (30)$$

The stability constant of  $ML_3^{3-}$ , ( $\beta_3$ ), which is valid for equilibrium (31), can be given in terms of dissociation constants of the diprotic ligand,  $K_{a1}$  and  $K_{a2}$  and the equilibrium constants  $K_1$ ,  $K_2$ ,  $K_3$ , by equation (32)



$$\beta_3 = \frac{[ML_3^{3-}]}{[M^{3+}][L^{2-}]^3} = \frac{K_1 K_2 K_3}{(K_{a1})^3 (K_{a2})^3} \quad (32)$$

## Results

### Potentiometric Studies

#### Interaction of Sc(III) and Y(III) Ions with CAT:

When Sc(III) and Y(III) ions and CAT were present either in (1:1) or in (1:2) mole ratios, inflection points on the potentiometric titration curves were observed at  $m=3.0$ , where  $m$  is the ratio of the number of moles of the base to metal ion (Figure 1). Comparisons of the potentiometric titration curves of Sc(III):CAT and Y(III):CAT systems with CAT alone showed that there decreases in pH values for the buffer regions of them. These might indicate the interactions between these metal ions and CAT, but drifts in pH values after  $m=2.0$  were observed, which could be due to the hydrolysis of the formed complexes of CAT with Sc(III) and Y(III) ions. The degree of formation,  $\bar{n}$  values were calculated, in order to find the number of ligands bound to Sc(III) and Y(III) ions; then  $\bar{n}$  values were plotted versus  $-\log L$  values that were found from potentiometric titration results (Figure 2); however, it is known that  $\bar{n}$  can not be deduced unless it reaches a limiting value metal: ligand system. The existence of model 1 and the formation of the ML type complex, between  $m=0.0-2.0$  and  $pH=3.2-5.1$  ranges in the Sc(III):CAT system, has been suggested, since  $(\bar{n}-\log L)$  plot reaches the limiting value  $\bar{n}=1.0$  (Figure 2). The existence of the ML-type complex has been verified by the introduction of experimental values into equation (8). On the other hand,  $(\bar{n}-\log L)$  plot did not reach limiting value due to the occurrence of the hydrolysis after  $pH=7.00$  values.

#### Interaction of Sc(III) and Y(III) Ions with 4NCAT:

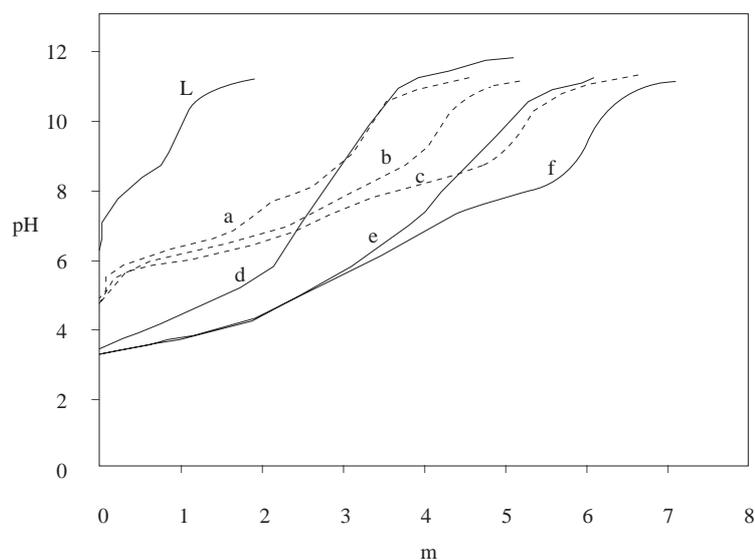
The potentiometric titration curves of Sc(III):4NCAT and Y(III):4NCAT in (1:1) mole ratio exhibited inflection points at  $m=2.0$  and at  $m=3.0$  values, respectively (Figure 3, curves a and d). The formation of ML type complex of Sc(III) and Y(III) ions with 4NCAT might be suggested by considering the inflection points of titration curves. The presence of ML complexes has been verified by taking into consideration model 1 and by solving equation (18) in the ranges  $pH=3.20-4.50$  and  $pH=4.04-5.93$  respectively. But the Sc(III) and Y(III) complexes of 4NCAT entered hydrolysis in (1:1) mole ratios, between the values  $m=2.0-3.0$  values; when Sc(III) or Y(III) metal ions and 4NCAT were present at (1:2) mole ratios, inflection points on potentiometric titration curves were observed at  $m=4.0$  (Figure 3, curves b and e). Under these conditions, the formation of  $ML_2$  type complexes of Sc(III) or Y(III) ions with 4NCAT may be inferred by applying model 2. In fact, their existence has been proved by equation (16) in the range  $pH=2.80-5.60$  for the Sc(III):4NCAT system in a 1:2 mole ratio and in the range  $pH=5.04-7.27$  for Y(III):4NCAT system in (1:2) mole ratio. The potentiometric titration curve of the Y(III):4NCAT system in (1:3) mole ratio was exhibited inflection at  $m=5.0$  (Figure 3, curve c). Then the formation of the  $MHL_3$  type complex was assumed and the existence of model 3 was shown in this system; the related equilibrium (23) and equation (24) were considered and solved. In the case of Sc(III):4NCAT in the (1:3) mole ratio, the inflection points were observed at  $m=4.0$  and  $m=6.0$ ; for that reason, the occurrence of model 4 was considered and then the validity of this model was verified by equation (32) for the equilibrium (31) to this system.

The degree of formation values,  $(\bar{n})$ , were evaluated either for systems of Sc(III):4NCAT or Y(III):4NCAT that were in (1:3) mole ratios; then the formation curves were drawn (Figure 4) for them. It was noted that

the ( $\bar{n}$ ) value approaches 3.0 in the Sc(III):4NCAT system, and 2.5 in the Y(III):4NCAT system. Hence, the formation of the  $ML_3$  type complex with the Sc(III) and  $MHL_3$ -type complex with Y(III), in (1:3) metal-to-ligand mole ratios was determined.

### Interaction of Sc(III) and Y(III) Ions with DHN:

The potentiometric titration curves of Sc(III):DHN and Y(III):DHN in different mole ratios are given in Figure 5. The mole ratios of metal ions to ligands were (1:1), (1:2) and (1:3). When these curves were analyzed, it was clear that they were compatible with curves that were observed for the 4-NCAT systems. Therefore, the existences of different models were considered for the (M(III):DHN) systems, as for Sc(III) and Y(III):4-NCAT systems that were in (1:1), (1:2), (1:3) mole ratios. The occurrence of related equations were assumed and the calculations of their equilibrium constants were then performed to solve their stability constants. The results verified these assumptions.

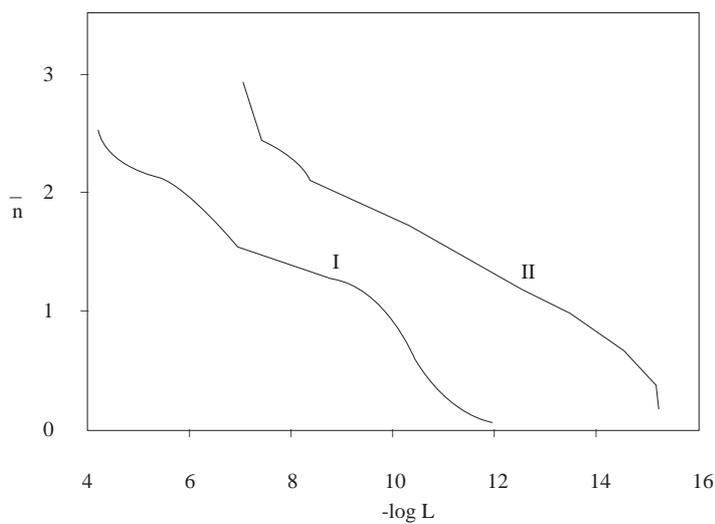


**Figure 3.** Potentiometric titration of Sc(III) and Y(III) complexes of 4-nitrocatechol in 0.1 M  $KNO_3$  or  $NaClO_4$  at 25 °C with the following molar ratios of ligand to metal ion,

**L** Ligand alone,

**a-** Y(III):4NCAT (1:1), **b-** Y(III):4NCAT (1:2), **c-** Y(III):4NCAT (1:3),

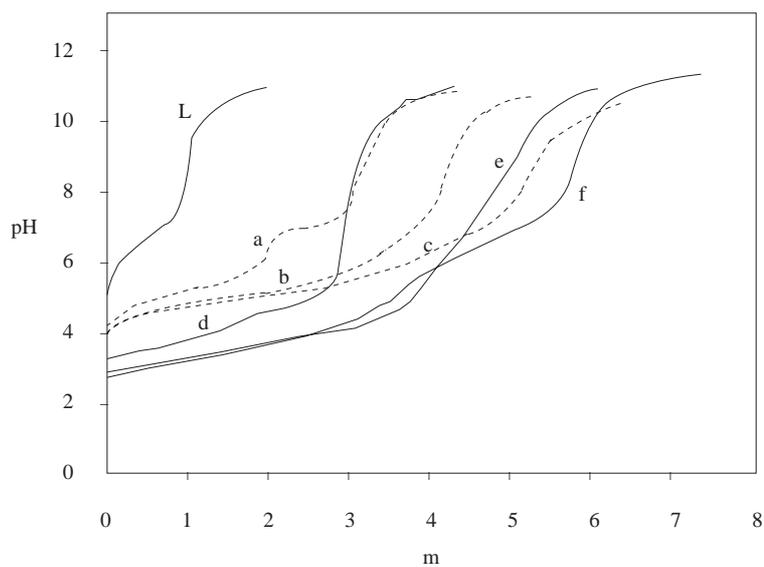
**d-** Sc(III):4NCAT (1:1), **e-** Sc(III):4NCAT (1:2), **f-** Sc(III): 4NCAT (1:3),



**Figure 4.** Degree of formation,  $\bar{n}$ , as a function of  $-\log L$ :

**curve I-** Y(III):4NCAT complex

**curve II-** Sc(III):4NCAT complex



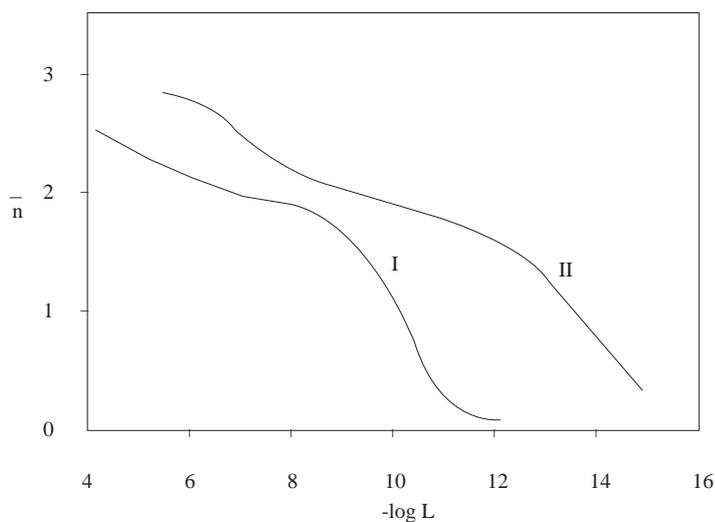
**Figure 5.** Potentiometric titration of Sc(III) and Y(III) complexes of 2,3-dihydroxynaphthalene-6-sulphonic acid in 0.1 M  $\text{KNO}_3$  or  $\text{NaClO}_4$  at  $25^\circ\text{C}$  with the following molar ratios of ligand to metal ion,

**L** Ligand alone,

**a-** Y(III):DHN (1:1), **b-** Y(III):DHN (1:2), **c-** Y(III):DHN (1:3),

**d-** Sc(III):DHN (1:1), **e-** Sc(III):DHN (1:2), **f-** Sc(III):DHN (1:3),

Formation curves were drawn for Sc(III):DHN and Y(III):DHN systems that were in (1:3) mol ratios, and the ( $\bar{n}$ ) values approached 3.0 and 2.5, respectively (Figure 6). The appearance of these kinds of formation curves support the existence of the assumed complexes.



**Figure 6.** Degree of formation,  $\bar{n}$ , as a function of  $-\log L$ :  
**curve I-** Y(III):DHN complex  
**curve II-** Sc(III):DHN complex

## Spectrophotometric Studies:

### Sc(III)-Complexes:

The formation of  $ML$ ,  $ML_2$  and  $ML_3$  type complexes were defined from the results of potentiometric measurements. The stoichiometries of formed complexes were also investigated by spectrophotometry. The spectra of 4-NCAT and Sc(III):4NCAT solutions were compared. The shifts of  $\lambda_{max}$  to higher values were indications of complex formation between Sc(III) and 4NCAT; the the working pH values were then defined from potentiometric titration curves, and they were pH=3.50, 4.50 and 6.60, with maximum absorbances occurring at a at wavelength of 500 nm. The absorbances of solutions that have a Sc(III):4NCAT system in different mole ratios were higher than those of 4NCAT alone, at three selected pH values. Therefore, Job's diagrams were drawn for different solutions; maximum absorbance was observed at  $x_M=0.5$  for a solution at pH=3.50. These results indicate the formation of an  $ML$ -type complex. Similarly, the maximum absorbance value was found at  $x_M=0.33$  for a solution with pH=4.50; it has indicated the formation of  $ML_2$  type complex. On the other hand, the Job's diagram drawn for solutions at pH=6.60, suggests the formation of an  $ML_3$ -type complex.

Formation of  $ML$ -,  $ML_2$ - and  $ML_3$ -type complexes were determined from the potentiometric titration curves of DHN alone and in different mole ratios of Sc(III) and DHN, at pH ranges 4.80-5.20, 5.50-7.00-8.50, respectively. Then, the spectrum of DHN alone and solutions of Sc(III):DHN that were at defined pH values, and in different mole ratios of Sc(III) and DHN, were compared. The maximum absorbance values were then defined for each species at a wavelength of 348 nm and formation of  $ML$ ,  $ML_2$  and  $ML_3$  type complexes were demonstrated with the aid of Job's diagram, in Sc(III) and DHN solutions.

### Y(III)- Complexes:

As in the Sc(III):4NCAT solutions, the absorbance values of solutions that contain Y(III) and 4NCAT in different stoichiometries in various pH ranges, at 500nm, were much higher than the absorbances of 4NCAT alone. Maximum absorbance values were determined as  $x_M=0.5$ ,  $x_M=0.33$  and  $x_M=0.25$ , from the Job's diagram, prepared at pH=6.00, pH=7.50 and pH=8.00, respectively. Hence, formation of ML type complex in pH=6.00, ML<sub>2</sub> type in pH=7.50 and MHL<sub>3</sub> type at pH=8.00 values were defined by spectrophotometry. The results of calculations carried out by assuming their existences and introducing potentiometric measurements were in accordance with the spectrophotometric results. Job's diagrams were drawn at 342 nm for pH values of 7.00 and 8.00; the maximum absorbances determined from the Job's diagrams were  $x_M=0.33$  and  $x_M=0.25$  for pH values of 7.00 and 8.00, respectively. As a result of Job's diagrams, it was determined that the Y(III) ion also formed ML-, ML<sub>2</sub>- and MHL<sub>3</sub>-type complexes with DHN-like 4NCAT. In fact, their formation and occurrence were also shown by potentiometric measurements.

## Discussion

CAT is the first member of the catechol derivatives, and its acid dissociation constants were found to be smaller than the acid dissociation constants of DHN and 4NCAT (see Table 1). While there is no functional group in the CAT ring, 4NCAT is the most acidic of the three ligands used, since it contains one electron withdrawing -nitro group at the 4- position. Hence, the protons of 4NCAT dissociate from 4NCAT relatively easily, compared with DHN and CAT. In DHN, there is a naphthamene ring and it contains electron withdrawing -sulphonato group on one of its rings, and neighboring -OH groups the other ring. Since the -sulphonato group on DHN is located on the other ring, it is not as effective as the -nitro group on 4NCAT. Hence, DHN is a less acidic ligand than 4NCAT.

The stability constants of the Sc(III):CAT complex in the ML type has measured by Usherenko et al. in 25 °C and 0.1 M ionic medium; their values were very close to the constants in the present study. The stability constant values in Makhijani and Sangal<sup>12</sup> for Sc(III) and Y(III):CAT complexes in ML form, were lower than the values of the present study, since their ionic medium was 0.2 M and the temperature was 30 °C. Makhijani and Sangal<sup>13</sup> have also determined the stability constants of DHN complexes of Sc(III) and Y(III) in ML form for the same working conditions. They were again lower than the values of the present study for CAT complexes. On the other hand, Lajunen<sup>14</sup> has investigated Y(III):DHN complexes in (1:1) stoichiometry and determined their stability constants; the ionic medium was 0.5 M and temperature was 25 °C. These were lower than the values of the present study.

It is clear that catechol derivatives have two dissociable protons; these protons can dissociate even at lower pH values due to the complex formation (Figure 1, 3, 5). potentiometrically determined stability constants of complexes that were formed between Sc(III), Y(III) ions and catechol derivatives, and acid dissociation constants of ligands, are given in Table 1.

When the stability constants of complexes formed between Sc(III) or Y(III) ions and catechol derivatives were compared with each other, it was observed that the stability constants of ML type complexes that were formed between Sc(III) or Y(III) and 4NCAT were lower than the others. The reason for that might be the -nitro group, on the 4NCAT ring, since it withdraws the electrons on the ring and weakens the M-O bond.

The sulpho group on DHN is also a strong electron withdrawing group, but because it is located on the other ring, it is rather difficult to weaken the M-O bond by electron withdrawing from the ring. For that

reason, the stability constants of  $ML_2$  type complexes formed between Sc(III) or Y(III) ions and DHN were greater than the stability constants of the complexes formed by 4NCAT. The stability constants of  $ML_3$ -type complexes formed between the Sc(II) ion and DHN were expected to be greater than the stability constants of 4NCAT complexes, but they were found to be lower than those. This may be related to the bulkier structure of DHN. Hence, the binding of the bulkier DHN to the metal ion is rather difficult. However, stability constants of  $MHL_3$ -type complexes formed between Y(III) and DHN or 4NCAT were near each other. This may be explained by the bigger ionic radius of Y(III) and competition of  $H^+$  and Y(III) for the third  $H_2L$  ligand in Y(III):DHN or 4NCAT in (1:3) mole ratios; the formation of  $MHL_3$  type complexes occurred instead of  $ML_3$  in with Y(III)

Generally, the complex formation tendency of Sc(III) was greater than the Y(III), since the ionic radius of Sc(III) is smaller than the Y(III). Then, the stability constants of complexes formed between Sc(III) ion and catechol derivatives were greater than the stability constants of complexes of Y(III) ions.

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