# Stability Constants of Lanthanide(III) Chelates of 8-Quinolinol-5-Sulfonate

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The stability constants of complexes of 8-quinolinol-5-sulfonate with scandium(III), yttrium(III) and lanthanum(III) were determined potentiometrically in 0.1 M sodium chloride solution at 25°C. Along with the ordinary first complexes, second and third complexes ($ML^+$, $ML_2^-$, $ML_3^{3-}$) were also observed in solutions of 8-quinolinol-5-sulfonate that contains metal ions. The stoichiometries of formed complexes were defined by Job's method. The results showed that the values of the stability constants of the first, second and third complexes increase [Sc(III) > Y(III) > La(III)] with decreasing metal ionic radius.

Key Words: Stability constant, Scandium, Yttrium, Lanthanum, Potentiometry.

## INTRODUCTION

Scandium(III), as the first member of group 3, has the smallest ionic radius (0.89 Å), so that its chemical behaviour is intermediate between that of aluminium(III) and of lanthanum(III). Yttrium lies above lanthanum in group 3 of the periodic table and has a similar 3+ ion with a noble gas core. Yttrium and lanthanum are highly electropositive elements and their chemistry is largely ionic and determined by the size of the lanthanum(III) ion. The size of the ionic radius of yttrium(III) (0.89 Å) is close to those of terbium(III) (0.92 Å) and dysprosium(III) (1.05 Å). It generally occurs with the lanthanides in nature and its chemical properties resemble to holmium(III) and dysprosium(III) in its compounds. Ionic radii of actinides (Ac), for the commonest oxidation state of (IV) are smaller than the radii of lanthanum(III) ions and they are in the region of 0.96–1.08 Å. The radius of thorium(IV), as the first element of actinides, is 1.08 Å and is very close to yttrium(III) ion. The lanthanum(III) ion (1.17 Å) has a radius of *ca.* 0.13 Å, that is larger than of yttrium(III). If the next 14 elements would not intervene (if, in other words, La is with $[Xe]5d^26s^2$ configuration) we should expect that element, standing where hafnium does, to have radii *ca.* 0.13 Å which become larger than those of zirconium. Instead, there is a steady shrinkage whose cumulative effect is to make the hafnium atom almost exactly of the same size as the zirconium atom[1].

The aqua ions of scandium(III), yttrium(III) and lanthanum(III) polarize solvated water molecules, giving rise to several hydrolytic species. The constants of the hydrolytic equilibria have been calculated extensively for Sc(III), Y(III) and Th(IV) ions in previous studies[2-13]. Because of its small ionic radius,

scandium(III) ion is more readily hydrolyzed than the lanthanum(III) ions in perchlorate solutions; the main species are $[Sc(OH)]^{2+}$, $[Sc_2(OH)_2]^{4+}$, $[Sc_3(OH)_4]^{5+}$ and $[Sc_3(OH)_5]^{4+}$. Y(III) also gives hydrolytic species, predominantly $[Y(OH)]^{2+}$ and also $[Y_2(OH)_2]^{4+}$ ions. Thorium(IV) ion is more resistant to hydrolysis than other ions of Ac(IV), but it also undergoes extensive hydrolysis in aqueous solution at pH higher than 3.0.[3] The hydrolysis species of thorium(IV) are more complicated than the species of scandium(III) and ytrium(III). The hydrolysis equilibria of the lanthanum(III) ion have been studied at 60°C by measuring with a glass electrode, in a series of lanthanum perchlorate solution at different $H^+$ concentrations. They have been interpreted in terms of $[La(OH)]^{2+}$, $[La_2(OH)]^{5+}$, $[La_5(OH)_9]^{6+}$ and $[La_6(OH)_{10}]^{8+}$.[14]

In view of the relatively high stabilities of some transition and rare-earth metal chelates of pyrocatechol-3,5-disulfonate (tiron) the interaction of these and other metal ions with 8-quinolinol-5-sulfonate (HQSA) were investigated in this study. Both of these ligands form five-membered rings with metals, the main difference between the two being that tiron contains two phenolic groups as donors, while the latter ligand contains one phenolic group and one heterocyclic nitrogen atom. Both ligands would be expected to form chelates solubilized by sulfonate groups. The soluble 8-quinloniol-5-sulfonate is of further interest as a ligand because of the well-known affinity of the parent compound, 8-quinoline itself, for the thorium(IV) ion and for many other metal ions.

The stabilities of the chelate compounds formed by this ligand and some of the metals studied in the present investigation have been reported by Nasanen and others for somewhat different reaction conditions[15, 16-19].

The bidentate ligand HQSA has been reported to form only 1 : 1 complexes with Th(IV)[19], Ca(II)[15], Sr(II)[15] and Ba(II)[15] to form 1 : 1 and 1 : 2 complexes with Mn(II)[19], Fe(III)[19], Cu(II)[19], Zn(II)[19], Mg(II)[19], UO_2(II)[19], Cd(II)[20] and Pb(II)[21] and to form 1 : 1, 1 : 2 and 1 : 3 complexes with Co(II)[19], Ni(II)[19], Al(III)[22], VO(IV)[23], Mn(II)[2] and Ga(II)[25].

## EXPERIMENTAL

All the chemicals were of analytical reagent grade and were used as received. All solutions were made with bi-distilled, deionized and $CO_2$-free water. For potentiometric measurements, the stock solution Sc(III) was prepared by dissolving $Sc_2O_3$ (Aldrich, 99.9% purity) in a known quantity of HCl (37%, d = 1.19 $g/cm^3$) to prevent hydrolysis. The stock solution of Y(III) was prepared by dissolving $Y_2O_3$ (Sigma, 99.9% purity) in a known quantity of HCl (37%, d = 1.19 $g/cm^3$) to prevent hydrolysis. The stock solution of La(III) was also prepared by dissolving $La_2O_3$ (Fluka, 99.9% purity) in a known quantity of HCl (37%, d = 1.19 $g/cm^3$) to prevent hydrolysis. The stock solutions of metals were standardized with $Na_2EDTA$ ($EDTA^{2-}$: anion of ethylenediaminetetraacetic acid)[26].

In potentiometric titrations, constant ionic media were produced by 0.1 M NaCl (Merck) for all potentiometric systems. HQSA (Aldrich, 98%) was used without further purification, since its Gran[27] plot indicated its high purity. Analytical grade $Na_2EDTA$ (Merck, proanalyse product) was used without recrystallization. The molecular weights of HQSA and $Na_2EDTA$ were checked by potentiometric

titrations. 0.1 M sodium hydroxide (Merck, proanalyse) solution was prepared as carbonate-free solution and was standardized against potassium hydrogen phthalate (Merck, 99.9%).

**Potentiometric titrations:**  Measurements were made in a 100 mL jacketed titration cell, the inner compartment of which was maintained at a constant temperature by circulating water from a constant temperature bath. The cell equipped with a magnetic stirrer and a tightly fitting rubber stopper, through which nitrogen inlet and outlet tubes, automatic titrator delivery tube and combined pH-electrode were inserted. The electrodes were calibrated with an acetic acid buffer system by converting pH-meter readings to hydrogen ion concentrations determined from data tabulated by Harned and Owen.[28] In the pH region below 3.5, between 3.5–10.5 and above 10.5, the pH-meter was calibrated with measured concentrations of hydrochloric acid, acetic acid and sodium hydroxide, respectively.

The calculation of the pH values for each point of the titration requires the knowledge of $E_0$ and $E_j$ in the equation

$$E = E_0 + RT/S \ln 10pH + E_j \qquad (1)$$

$E_j$ (junction potential) is negligible under our experimental conditions. Because Schott model automatic titrator fitted with a combined pH electrode (Schott) containing a filling solution of 0.1 M NaCl was used for titrations of the HQSA and M(III) complexes. $E_0$ can be calculated directly from the strong acid-base titration in two ways:

(a)  by using the points in the acid range only for the calculations of slope and intercept (and using the points in alkaline range for calculating $pK_w$);

(b)  by using a least squares computer program for calculating simultaneously $E_0$ and $pK_w$. We chose (a) in our research and the $pK_w$ value calculated in our ionic medium is 13.79. The potentiometric measurements were made 25.01 ± 0.1°C and at an ionic strength of 0.1 M regulated with NaCl.

Solutions containing 1 : 1, 1 : 2, 1 : 3, 1 : 4 and 1 : 10 molar ratios of metal ion to ligand were introduced into the titration cell, so that 50 mL final solution containing approximately $1.924–2.886 \times 10^{-3}$ M of metal ion. After thermal equilibrium was reached, the hydrogen ion concentration was determined by a number of successive readings after each addition of small increments of standard 0.1 M NaOH solution.

**Spectrophotometric measurements:**  Electronic absorption spectra of the samples were taken by a Schimadzu UV-2100 spectrophotometer (Kyoto, Japan) in order to determine the stoichiometries of the complexes by Job's method[29].

Spectrophotometric measurements were applied to the Sc(III) : HQSA, Y(III): HQSA and La(III) : HQSA systems in different molar ratios. The solutions were allowed to attain equilibrium for approximately 24 h in the nitrogen atmosphere at 25°C. In order to apply the continuous variation method and to draw Job's plot for all the titration systems, this procedure was prepared for solutions in which Sc(III), Y(III) or La(III) molar fractions were different and the pH value was constant.

## Calculations

The stability constants ($\beta_{pqr}$) are defined by eqn. (2) (charges are omitted for simplicity):

$$pM + qH + rL \rightleftharpoons M_pH_qL_r \qquad (2)$$

were refined by least-squares methods employing the BEST computer pro-gramme. The computations of the acid dissociation constants of HQSA and the stability constants of M(III) : HQSA complexes from potentiometric data were carried out with BEST computer programme. The programme BEST was used to minimize the standard deviation of the fit ($\sigma_{fit}$) between the observed and calculated pH values for the overall titration data[30]. Two groups of equilibria were treated in this work: first group of equilibria included the acid dissociation constants of $H_2L$ and $HL^{2-}$ ligands, second groups were M(III) : HQSA complex formation equilibria; thus log K and log β values were defined for these equilibria.

## RESULTS AND DISCUSSION

**8-Quinolinol-5-sulfonic Acid (HQSA):**　Potentiometric titration of 8-quino-linol-5-sulfonic acid produces two sharp inflections which probably correspond to the separate neutralization reactions
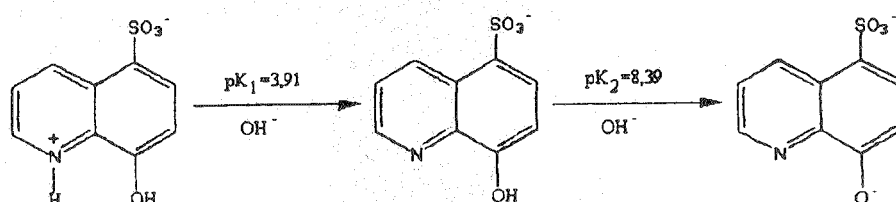


The pK values of 3.91 and 8.39 may be compared to the corresponding values of 3.84 and 8.35 obtained for HQSA by Richard *et al.*[19] Also the pK values of 3.91 and 8.39 may be compared to the corresponding values of 5.02 and 9.81 obtained for 8-quinolinol by Nasanen *et al.*[31] The lower basicity of the sulfonate derivative may be considered as the result of electronic interaction of the sulfonate group with the aromatic ring. Although the group itself is negative, the nature of the interaction is such that negative charge is withdrawn from the ring.

**Interaction of metal ions with HQSA:**　Titration curves are illustrated in Figs. 1–3 for the HQSA chelates of Sc(III), Y(III) and La(III) for 1 : 1, 1 : 2, 1 : 3, 1 : 4 and 1 : 10 ratios of metal to ligand.

**Sc(III) chelates:**　The complex species in the Sc(III)-HQSA system were ascertained by selection of three chemical models composed of computer-simu-lated $ScL^+$, $ScL_2^-$, $ScL_3^{3-}$ complexes. The stability constants for scandium(III) complexes with HQSA were obtained by computer analysis of the potentiometric titration data, and are listed in Table-1. No indications of $ScL_4^{5-}$ chelate formation are apparent in 1 : 4 and 1 : 10 molar ratio of titrations Sc(III) ion. Hence, it can be proposed that $ScL^+$, $ScL_2^-$ and $ScL_3^{3-}$ type species formation can be proposed. (Fig. 1).

**Y(III) Chelates:**　Titration of solutions containing 1 : 1, 1 : 2 and 1 : 3 ratios of ligand to metal ion results in pronounced inflection at m = 2.0, 4.0 and 6.0 corresponding to the formation of chelates having the compositions $YL^+$, $YL_2^-$ and $YL_3^{3-}$, respectively (Fig. 2). The 1 : 4 and 1 : 10 curves given in Fig. 2 indicate normal but not the combination of four moles of ligand with the Y(III) ion.

The data obtained from different mole ratios (1 : 1, 1 : 2, 1 : 3, 1 : 4 and 1 : 10) were applied to BEST programme, so that they were introduced into the equations
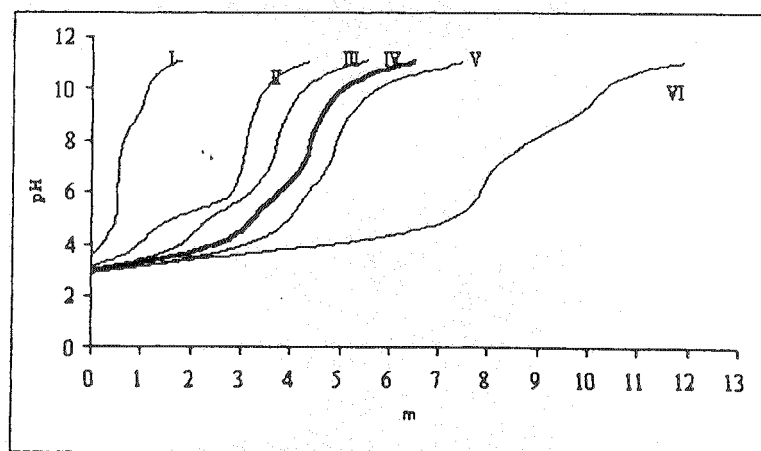
Fig. 1. Potentiometric titration curves of Sc(III) complexes of HQSA in 0.1 M NaCl at 25°C:
I. HQSA alone ($T_L = 9.620 \times 10^{-2}$ M). II. (1 : 1) Sc(III) : HQSA ($T_{Sc} = 9.620 \times 10^{-2}$ M,
$T_L = 9.620 \times 10^{-2}$ M). III. (1 : 2) Sc(III) : HQSA ($T_{Sc} = 9.620 \times 10^{-2}$M, $T_L = 1.924$
$\times 10^{-1}$ M). IV. (1 : 3) Sc(III) : HQSA ($T_{Sc} = 9.620 \times 10^{-2}$ M, $T_L = 2.886 \times 10^{-1}$ M).
V. (1 : 4) Sc(III) : HQSA ($T_{Sc} = 9.620 \times 10^{-2}$M, $TL = 3.848 \times 10^{-1}$ M). VI. (1 : 10)
Sc(III) : HQSA ($T_{Sc} = 9.620 \times 10^{-2}$ M, $TL = 9.620 \times 10^{-1}$ M).

for equilibrium to calculate the formation constants of $YL^+$, $YL_2^-$ and $YL_3^{3-}$
complexes (see rows 2, 3, 4 in Table-1).

TABLE-1

ACID DISSOCIATION CONSTANTS (log K) OF 8-QUINOLINOL-5-SULFONIC ACID
(HQSA) AND FORMATION CONSTANTS (log $\beta_{pqr}$) OF Sc(III), Y(III) AND La(III)
HQSA COMPLEXES ($25 \pm 0.1C°, I = 0.1$ M NaCl).

| Row | pqr | Equilibrium | Const. | HQSA | Sc(III) | Y(III) | La(III) |
|---|---|---|---|---|---|---|---|
| 1. | | $H_2L \rightleftharpoons HL^- + H^+$ | log $K_1$ | $3.91\pm0.01$ $3.84^{19}$ | | | |
| 2. | | $HL^- \rightleftharpoons L^{2-} + H^+$ | log $K_2$ | $8.39\pm0.01$ $8.35^{19}$ | | | |
| 3. | 110 | $M^{3+} + L^{2-} \rightleftharpoons ML^+$ | log $\beta_{110}$ | | $8.31\pm0.04$ | $7.29\pm0.03$ | $5.90\pm0.02$ |
| 4. | 120 | $M^{3+} + 2L^{2-} \rightleftharpoons ML^{2-}$ | log $\beta_{120}$ | | $15.07\pm0.04$ | $13.14\pm0.03$ | $10.81\pm0.02$ |
| 5. | 130 | $M^{3+} + 3L^{2-} \rightleftharpoons ML_3^{3-}$ | log $\beta_{130}$ | | $21.99\pm0.04$ | $18.60\pm0.04$ | $14.29\pm0.04$ |

$\beta_{pqr} = [M_pH_qL_r]/[M]^p[H]^q[L]^r$

**La(III) chelates:** Titration of equimolar amounts of ligand and La(III) ion
resulted in a steep inflection m = 2.0 corresponding to the formation of $LaL^-$
(Fig. 3). The observed inflection at m = 2.0 is the indication of the binding of the
aromatic nitrogen and phenolic oxygen to form a five-membered ring. Preparation
of a solution containing a 1 : 2 molar ratio of ligand to La(III) ion results in the
formation of a chelate of the type $LaL_2^-$. Titration of 1 : 3 molar ratio of ligand to
metal ion resulted in a steep inflection at m = 6.0 corresponding to the formation of
the completely coordinated La(III) chelate $LaL_3^{3-}$.

It can be proposed that the titration of a solution with a 1 : 4 and 1 : 10 molar ratio
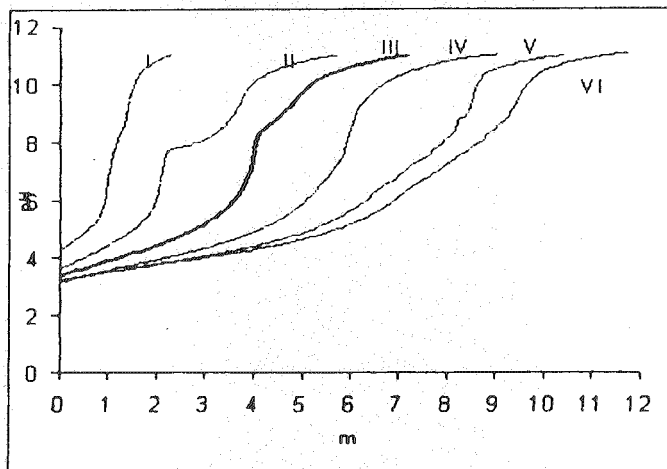of metal ion to ligand resulted in only $LaL^+$, $LaL_2^-$ and $LaL_3^{3-}$ species. Thus the data

Fig. 2   Potentiometric titration curves of Y(III) complexes of HQSA in 0. 1 M NaCl at 25°C:
I. HQSA alone ($T_L = 1.040 \times 10^{-2}$ M). II. (1 : 1) Y(III) : HQSA ($T_Y = 1.040 \times 10^{-2}$ M,
$T_L = 1.040 \times 10^{-2}$ M). III. (1 : 2) Y(III) : HQSA ($T_Y = 1.040 \times 10^{-2}$ M, $T_L = 2.080 \times 10^{-1}$
M). IV. (1 : 3)  Y(III) : HQSA ($T_Y = 1.040 \times 10^{-2}$ M, $T_L = 3.120 \times 10^{-1}$ M). V. (1 : 4)
Y(III) : HQSA ($T_Y = 1.040 \times 10^{-2}$ M, $T_L = 4$. VI. (1 : 10) Y(III) : HQSA ($T_Y = 1.040 \times$
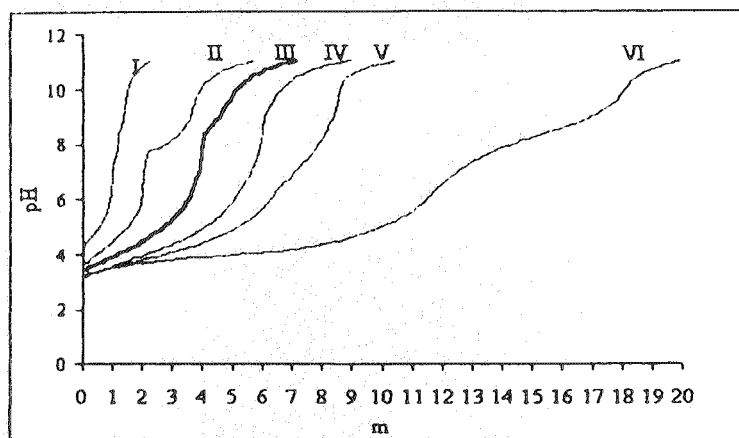$10^{-2}$ M, $T_L = 1.040 \times 10^{-1}$)



Fig. 3   Potentiometric titration curves of La(III) complexes of HQSA in 0.1 M NaCl at 25°C.
I. HQSA alone ($T_L = 9.620 \times 10^{-2}$ M). II. (1 : 1) La(III) : HQSA ($T_{La} = 9.180 \times 10^{-2}$ M,
$T_L = 9.180 \times 10^{-2}$ M). III. (1 : 2) La(III) : HQSA ($T_{La} = 9.180 \times 10^{-2}$M, $T_L = 1$. 836 ×
$10^{-1}$M). IV. (1 : 3)La(III) : HQSA($T_{La}$- $9.180 \times 10^{-2}$M, $T_L = 2.754 \times 10^{-1}$M). V. (1 : 4)
La(III) : HQSA($T_{La} = 9.180 \times 1^{0-2}$M, $T_L = 3.672 \times 10^{-1}$M). VI. (1 : 10) La(III) : HQSA
($T_{La} = 9. 180 \times 10^{-2}$M, $T_L = 9. 180 \times 10^{-1}$ M).

obtained from different mole ratios (1 : 1, 1 : 2, 1 : 3, 1 : 4 and 1 : 10) were applied
BEST programme, so that they were introduced into the equations for equilibrium
to calculate the formation constants of $LaL^+$, $LaL_2^-$ and $LaL_3^{3-}$ complexes (Rows 2,
3, 4 in Table-1).

    **Spectrophotometric measurements:**   The interactions between M(III) and
HQSA were also investigated by spectrophotometry. For that reason, the electronic
absorption spectra of solutions in which M(III) : HQSA ratios were 1 : 1, were
taken at specific pH value (for example, pH = 4.2 for Sc(III) : HQSA chelate). The

maximum absorbance was observed at $\lambda = 360$ nm (for Sc(III) : HQSA system) for 1 : 1 molar ratio. The solutions have M(III) molar fractions ($X_M$) in 0.0–1.0 range and pH was adjusted to 4.2 (Sc(III) : HQSA), their absorbance was measured at $\lambda = 360$nm. The Job's plot showed maximum absorbance at $X_M = 0.25$ (Fig. 7). Thus Job's plot confirms the formation of $ScL_3^{3-}$ type complex ion at pH = 4.2. Application of the method of Job for determination of the stoichiometry of these interactions also demonstrates the presence of a complex with 3 mol of chelating agent per mole in both Y(III) and La(III) systems.

The species distributions for M(III) : HQSA systems are depicted in Figs. 4–6. They are drawn for 1 : 10 mole ratios. The complex formation starts with $H_2L$ ligands at the $(N,O^-)$ sites, the resulting major species have a stoichiometry $ML^+$, $ML_2^-$ and $ML_3^{3-}$ that lie in the acidic pH range. From the distribution diagrams one can see that the complexes $ML_3^{3-}$ are dominant over the pH region of 3.8–7.0 for the all the metal-HQSA systems (Figs. 4–6).
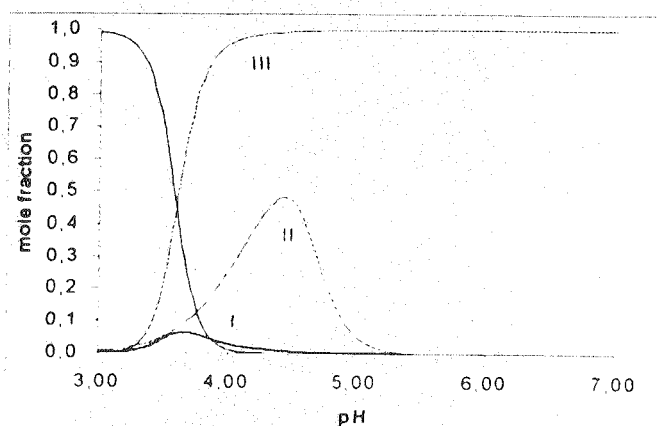


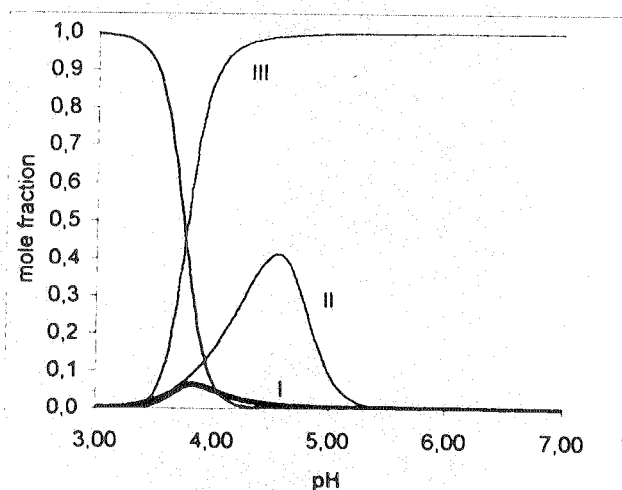Fig. 4.   Species distribution curves of the Sc(III) ion and HQSA system as a function of $-\log[H^+]$:



Fig. 5.   Species distribution curves of the Y(III) ion and HQSA system as a function of $-\log[H^+]$:
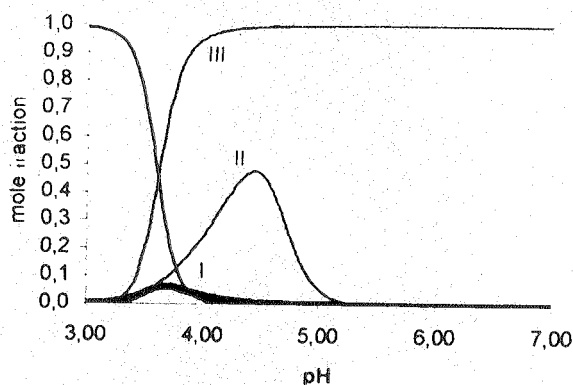I. $YL^+$, II. $YL_2^-$, III. $YL_3^{3-}$.

Fig. 6.   Species distribution curves of the Y(III) ion and HQSA system as a function of $-\log [H^+]$:
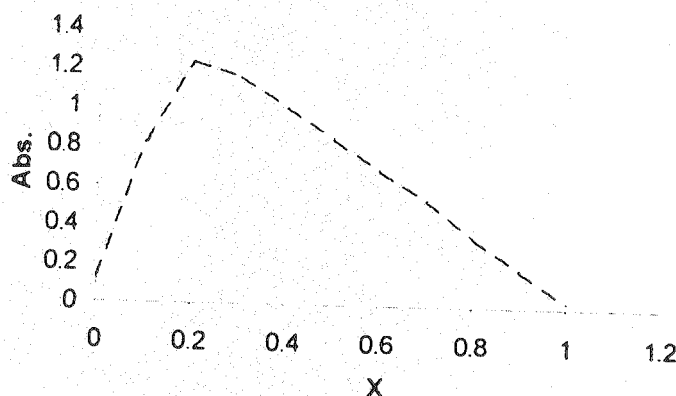I. $LaL^+$, II. $LaL_2^-$, III. $LaL_3^{3-}$

Fig. 7.   Job's plot for Sc(III) : HQSA in pH = 4.2 at $\lambda = 360$

## Conclusion

In this study, the stability constants of HQSA chelates of three metals in aqueous solutions were determined. The Sc(III), Y(III) and La(III) ions can coordinate to bidentate HQSA through the aromatic nitrogen and phenolic oxygen in molar ratio 1 : 1 and higher. The existence of $ML^+$, $ML_2^-$ and $ML_3^{3-}$ type complexes was verified by pH measurements. Since the ionic radius of Sc(III) is the smallest one in the below mentioned metals, the stability order obtained for HQSA is Sc(III) > Y(III) > La(III) (Table–1). In Sc(III), Y(III) or La(III) and HQSA systems, a model including $MLH_{-1}$ was proposed; however, the BEST program rejects the $MLH_{-1}$ complex for the system M(III)/HQSA. Furthermore, in the M(III)/HQSA system, only 1 : 1, 1 : 2 and 1 : 3 type complexes are consistent with the potentiometric titrations.

## ACKNOWLEDGEMENT

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