

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

NACIYE TÜRKEL

*Department of Chemistry, Faculty of Arts and Sciences, Uludağ University
16059 Bursa, Turkey*

Fax: (90)(224)4428136; E-mail: nturkel@uludag.edu.tr

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^{2-}) 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]5d²6s² 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 atom¹.

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 $[\text{Sc}(\text{OH})]^{2+}$, $[\text{Sc}_2(\text{OH})_2]^{4+}$, $[\text{Sc}_3(\text{OH})_4]^{5+}$ and $[\text{Sc}_3(\text{OH})_5]^{4+}$. Y(III) also gives hydrolytic species, predominantly $[\text{Y}(\text{OH})]^{2+}$ and also $[\text{Y}_2(\text{OH})_2]^{4+}$ 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 yttrium(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 $[\text{La}(\text{OH})]^{2+}$, $[\text{La}_2(\text{OH})]^{5+}$, $[\text{La}_5(\text{OH})_9]^{6+}$ and $[\text{La}_6(\text{OH})_{10}]^{8+}$.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-quinolinol-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, $\text{UO}_2(\text{II})$ 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%, $d = 1.19 \text{ g/cm}^3$) 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%, $d = 1.19 \text{ g/cm}^3$) 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%, $d = 1.19 \text{ g/cm}^3$) 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 Gran²⁷ 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

$$E = E_0 + RT/S \ln 10 \text{pH} + E_j \quad (1)$$

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:

- 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);
- 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 $25.01 \pm 0.1^\circ\text{C}$ 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 $1.924\text{--}2.886 \times 10^{-3}$ 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 Shimadzu UV-2100 spectrophotometer (Kyoto, Japan) in order to determine the stoichiometries of the complexes by Job's method²⁹.

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

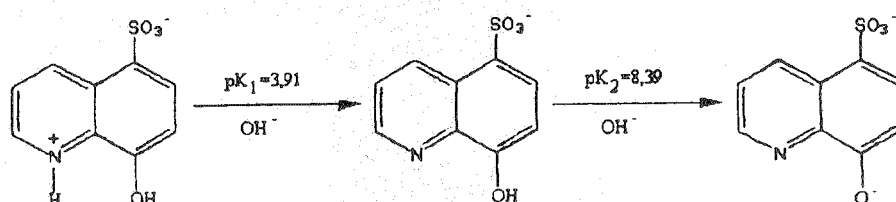
The stability constants (β_{pqr}) are defined by eqn. (2) (charges are omitted for simplicity):



were refined by least-squares methods employing the BEST computer programme. The computations of the acid dissociation constants of HQSA and the stability constants of $M(\text{III}) : \text{HQSA}$ complexes from potentiometric data were carried out with BEST computer programme. The programme BEST was used to minimize the standard deviation of the fit (σ_{fit}) between the observed and calculated pH values for the overall titration data³⁰. 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 $M(\text{III}) : \text{HQSA}$ complex formation equilibria; thus $\log K$ and $\log \beta$ values were defined for these equilibria.

RESULTS AND DISCUSSION

8-Quinolinol-5-sulfonic Acid (HQSA): Potentiometric titration of 8-quinolinol-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 $\text{Sc}(\text{III})$, $\text{Y}(\text{III})$ and $\text{La}(\text{III})$ 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 $\text{Sc}(\text{III})$ -HQSA system were ascertained by selection of three chemical models composed of computer-simulated 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 $\text{Sc}(\text{III})$ 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 $\text{Y}(\text{III})$ 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

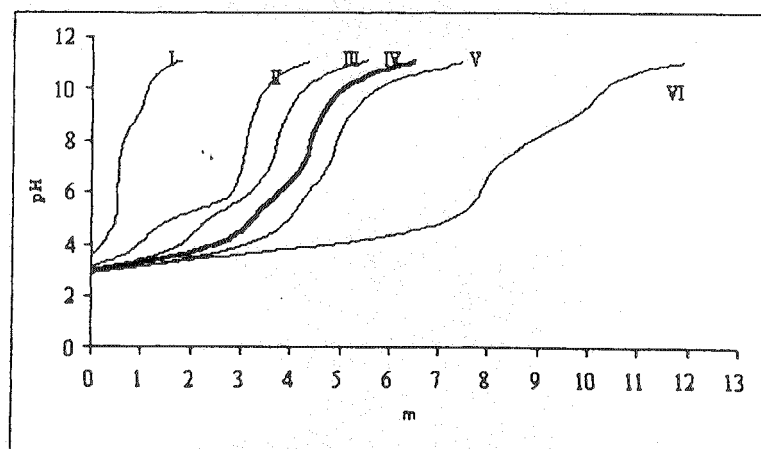


Fig. 1. Potentiometric titration curves of Sc(III) complexes of HQSA in 0.1 M NaCl at 25°C: I. HQSA alone ($T_L = 9.620 \times 10^{-2}$ M). II. (1 : 1) Sc(III) : HQSA ($T_{Sc} = 9.620 \times 10^{-2}$ M, $T_L = 9.620 \times 10^{-2}$ M). III. (1 : 2) Sc(III) : HQSA ($T_{Sc} = 9.620 \times 10^{-2}$ M, $T_L = 1.924 \times 10^{-1}$ 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, $T_L = 3.848 \times 10^{-1}$ M). VI. (1 : 10) Sc(III) : HQSA ($T_{Sc} = 9.620 \times 10^{-2}$ M, $T_L = 9.620 \times 10^{-1}$ 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 β_{pqr}) OF Sc(III), Y(III) AND La(III) HQSA COMPLEXES ($25 \pm 0.1^\circ\text{C}$, $I = 0.1$ M NaCl).

Row	pqr	Equilibrium	Const.	HQSA	Sc(III)	Y(III)	La(III)
1.		$H_2L \rightleftharpoons HL^- + H^+$	log K_1	3.91±0.01 3.84 ¹⁹			
2.		$HL^- \rightleftharpoons L^{2-} + H^+$	log K_2	8.39±0.01 8.35 ¹⁹			
3.	110	$M^{3+} + L^{2-} \rightleftharpoons ML^+$	log β_{110}		8.31±0.04	7.29±0.03	5.90±0.02
4.	120	$M^{3+} + 2L^{2-} \rightleftharpoons ML_2^-$	log β_{120}		15.07±0.04	13.14±0.03	10.81±0.02
5.	130	$M^{3+} + 3L^{2-} \rightleftharpoons ML_3^{3-}$	log β_{130}		21.99±0.	18.60±0.04	14.29±0.04

04

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

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

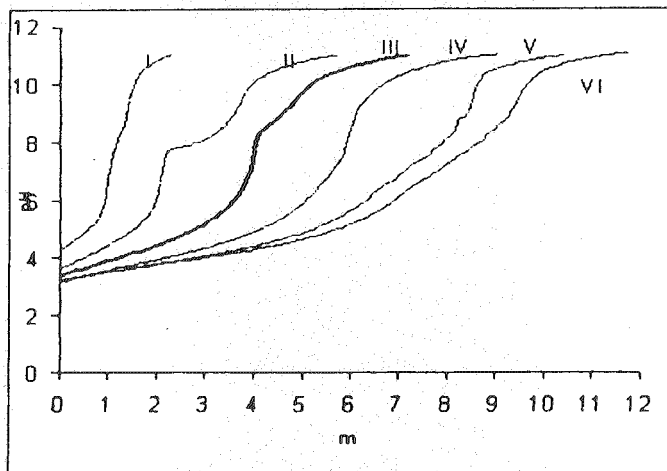


Fig. 2 Potentiometric titration curves of Y(III) complexes of HQSA in 0.1 M NaCl at 25°C: I. HQSA alone ($T_L = 1.040 \times 10^{-2}$ M). II. (1 : 1) Y(III) : HQSA ($T_Y = 1.040 \times 10^{-2}$ M, $T_L = 1.040 \times 10^{-2}$ M). III. (1 : 2) Y(III) : HQSA ($T_Y = 1.040 \times 10^{-2}$ M, $T_L = 2.080 \times 10^{-1}$ 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, $T_L = 1.040 \times 10^{-1}$)

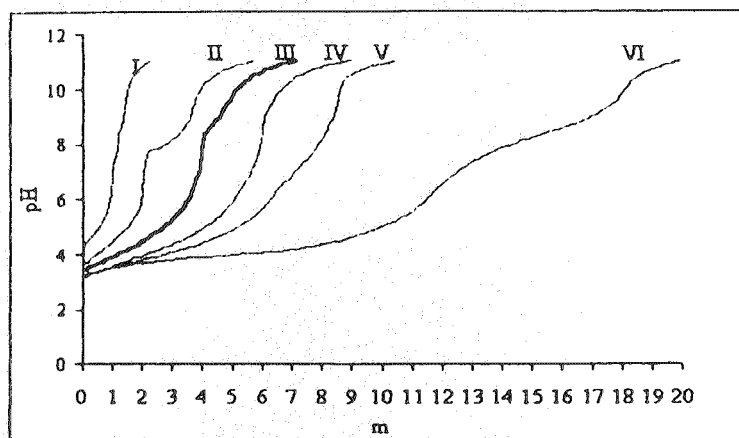


Fig. 3 Potentiometric titration curves of La(III) complexes of HQSA in 0.1 M NaCl at 25°C. I. HQSA alone ($T_L = 9.620 \times 10^{-2}$ M). II. (1 : 1) La(III) : HQSA ($T_{La} = 9.180 \times 10^{-2}$ M, $T_L = 9.180 \times 10^{-2}$ M). III. (1 : 2) La(III) : HQSA ($T_{La} = 9.180 \times 10^{-2}$ M, $T_L = 1.836 \times 10^{-1}$ 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 ($T_{La} = 9.180 \times 10^{-2}$ 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).

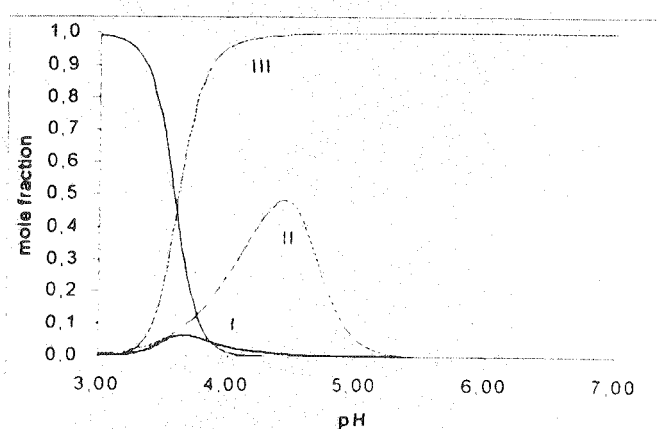


Fig. 4. Species distribution curves of the Sc(III) ion and HQSA system as a function of $-\log [H^+]$:

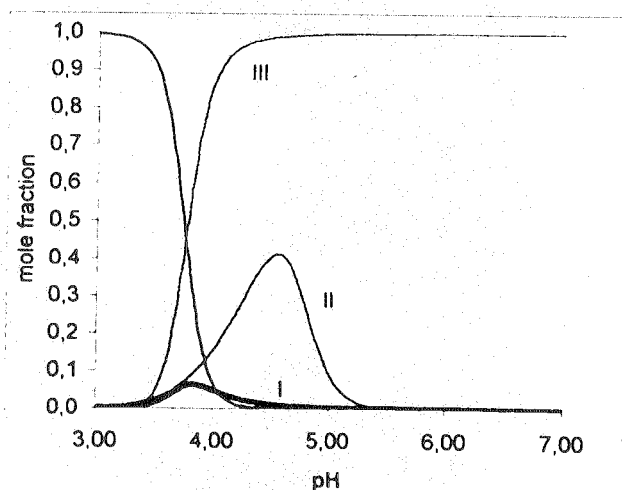


Fig. 5. Species distribution curves of the Y(III) ion and HQSA system as a function of $-\log [H^+]$:
I. YL^+ , II. YL_2 , III. YL_3^{3-}

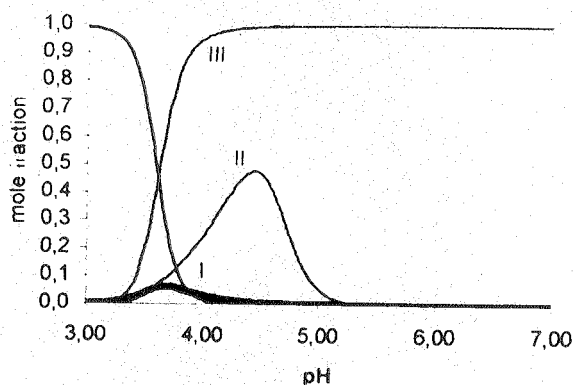


Fig. 6. Species distribution curves of the Y(III) ion and HQSA system as a function of $-\log [H^+]$: I. LaL^+ , II. LaL_2^- , III. LaL_3^{3-}

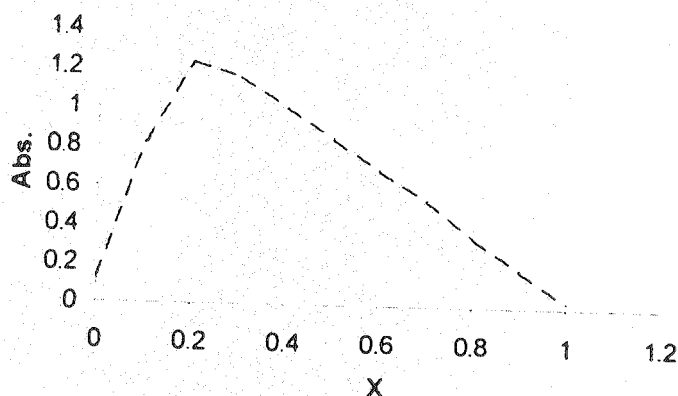


Fig. 7. Job's plot for Sc(III) : HQSA in pH = 4.2 at $\lambda = 360$

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

The instruments used in this research were supplied by the Alexander Von Humbolt Foundation, to whom the author wishes to express their sincere thanks.

REFERENCES

1. F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 6th Edn., Wiley-Interscience, New York (1999).
2. D.L. Cole, L.D. Rich., J. D. Owen and E.N. Eyring, *Inorg. Chem.*, **8**, 682 (1969).
3. Y. Murakami and A.E. Martell, *J. Am. Chem. Soc.*, **82**, 5605, (1960).
4. M. Kilpatrick and L. Pokras, *J. Electrochem. Soc.*, **101**, 39 (1954).
5. L.G. Sillen, *Acta Chem. Scand.*, **8**, 299 (1954).
6. ———, *Acta Chem. Scand.*, **8**, 318 (1954).
7. G. Biederman and L. Ciavatta *Arkivfor Kemi.*, **22**, 253 (1964).
8. V.P. Antonovich and V.A. Nazerenko, *Russ. J. Inorg. Chem.*, **13**, 7, 940, (1968).
9. J. Aveston, *Inorg. Phys. Theo.*, 1599 (1966).
10. L.D. Shtenke, N.A. Skorik and V.N. Kumak, *Russ. J. Inorg. Chem.*, **15**, 623 (1970).
11. S. Akalm and U. Özer, *J. Inorg. Nucl. Chem.*, **33**, 4171 (1971).
12. C.T. Horowitz, K.A. Schneidner, J.R.G.A. Melson, D.N. Joughblood and H.H. Scheck, *Scandium*, Acad. Press, New York (1975).
13. P.L. Brown., J. Ellis and R.N. Sylva, *J. Chem. Soc., Dalton Trans.*, **35** (1983).
14. L. Ciavatta, M. Iuliano and R. Porto, *Polyhedron*, **6**, 1283 (1987).
15. R. Nasanen and E. Uisatalo, *Acta Chem. Scand.*, **8**, 112 (1954).
16. A. Albert, *Biochem. J.*, **54**, 646 (1953).
17. L.E. Maley and D.P. Mellor, *Austral. J. Sci. Res.*, **2A**, 579 (1949).
18. A. Albert and A. Hampton, *J. Chem. Soc.*, 505 (1954).
19. C.F. Richard, R.L. Gustafson and A.E. Martell, *J. Am. Chem. Soc.*, **81**, 1033 (1959).
20. O. Makitie, L.H.J. Lajunen and A. Laokkonen, *Finn. Chem. Lett.*, 31 (1977).
21. S.S. Mujumber and B.I. Nemade, *J. Electrochem. Soc. India*, 39 (1990).
22. K. Hayashi, T. Ohsawa, K. Okamoto, J. Hidaka and H. Einaga, *J. Coord. Chem.*, **12**, 243 (1983).
23. G.E. Mont and A.E. Martell, *J. Am. Chem. Soc.*, **88**, 1387 (1966).
24. J.P. Scharff and R. Genin, *Anal. Chim. Acta*, **78**, 201 (1975).
25. P. Letkeman, A.E. Martell and R.J. Motekaitis, *J. Coord. Chem.*, **10**, 47 (1980).
26. G. Schwarzenbach and H. Flaschka., *Complexometric Titrations*, Interscience, New York (1969).
27. G. Gran, *Analyst*, **77**, 661 (1952).
28. H.S. Harned and B.B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold, New York (1950).
29. H.H. Willard, L.L. Merritt and J.R.A. Dean, *Instrumental Methods of Analysis*, Van Nostrand, New York (1981).
30. A.E. Martell and R.J. Motekaitis, *The Determination and Use of Stability Constants*, VCH Publishers, New York (1989).
31. R. Nasanen, P. Lumme and A. Mukula, *Acta Chem. Scand.*, **5**, 1199 (1951).