SYNTHESIS AND STUDY
OF
QUINALIZARIN COMPLEXES
WITH
La(III), Ce(III), Sm(III) and Tb(III)

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Dedicated to the memory of
Endale Nisserie, Embibel Masresha, Nigussie Zenebe
and Biruk Wondaferash.

ADDIS ABABA UNIVERSITY
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CONTENTES

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Abstract

The complexation of 1,2,5,8-tetrahydroxyanthraquinone (quinalizarin) with some trivalent lanthanide ions: Sm(III), Tb(III), Ce(III), and La(III) has been studied spectrophotometrically and potentiometrically. The methods of continuous variation and mole ratio indicate the metal to ligand ratio is 1:1. The stability of the complexes were found to be in the order Sm > Tb > Ce > La.

Solid lanthanide-quinalizarin complexes were also isolated. The solid complexes are fine dark powders,insoluble in water and common organic solvents. From elemental analysis, thermal analysis and infrared spectra the complexes are characterized as chelate polymers, with a formula of $[Ln(C_{14}H_5O_6)XH_2O]_n$ (X = 5 when Ln = Sm, Ce and X = 6 when Ln = La, Tb). The relative thermal stability of three of the complexes were determined from differential thermal analysis, and are in the order: Sm > Ce≈La.

1 Introduction

Quinones, hydroxyquinones (Appendix), and their substituted derivatives form an extended class of compounds and has attracted the interest of chemists and has been studied thoroughly. The investigations reported covered practically every topic of synthetic and experimental chemistry, including isolation from natural products, total synthetics,and biological significant properties[1-6]. Thus, quinones and their derivatives, either synthetic or naturally occurring have been extensively utilized as acid-base indicators, pigments and drugs[6]. Also they found important applications in electrochemistry[7], analytical and coordination chemistry. In the field of biology the interest has been focused on their antimicrobial and antitumour activity and some drugs based on quinones are now in use. For example 5-hydroxy-1,4-naphtolenedione (juglone) has been used as antitubercular and antibacterial agent as well as for the determination of nickel(11)[5]. 1,2- Dihydroxy-9,10- anthracenedione (alizarin) and its derivatives have been used as analytical agents for the determination of molybdenum[8]. 1,2,5,8-tetrahydroxy-9,10-anthracenedione (quinalizarin) was used for determination of molybdenum in some alloys and steel[9], and it was also recommended for the detection and determination of small amounts of beryllium[10] and magnesium[11]. Spectrophotometric study and analytical applications of 9,10-anthraquinone derivatives in the presence of cationic surfactants and their complexes with vanadium was conducted[12]. Study of the dyeing of polyamide and

1-hydroxyanthraquinone; 1,8- dihydroxyanthraquinone and 1,4,5,8-polyester fibbers with nickel complexes of tetrahydroxyanthraquinone were also reported[13].

1.1 Metal - Anthraquinone Complexes

In most of the above applications of hydroxyquinones their chelating ability plays an important role, thus the study of their metal chelates would be of great value in understanding the mechanism of their chemical and biological activity[5,6]. In fact, in the last few years a number of papers concerning the synthesis, characterization and thermal stability of some metal chelates of hydroxybenzoquinone, hydroxynaphtoquinones, and hydroxyanthraquinones have been published[2-8,10-18]. The structure of the studied chelate complexes afford to form mononuclear, homobinuclear, bridging,or polymeric depending on the number and position of the hydroxy group in the ligand, nature of the metal ions or/and reaction conditions.

1.1.1 Mononuclear and Homobinuclear Complexes.

5-hydroxynaphtoquinone ($C_{10}H_6O_3$) with Cu(II), Ni(II), Fe(II), Pt(II), Pd(II) and 1,2- dihydroxyanthraquinone ($C_{14}H_8O_4$) with Ni(II), Mn(II), Zn(II) form fine powders or microcrystalline materials[5] which are stable in air, do not melt up to 300°C, insoluble in DMF and DMSO and slightly soluble in methylene chloride and/or ethanol. They are characterized as mononuclear chelates $[M(C_{10}H_5O_3)_2(OH_2)_n$,n=o when

M = Fe, Pt, n = 2 when M = Cu, Ni; $M(C_{10}H_5O_3)_2(NH_3)_2$, M = Pd; $M(C_{14}H_7O_4)_2(OH_2)_2$, M = Ni, Mn; $M(C_{14}H_7O_4)_2$ $2H_2O$, M=Zn].

The chelating ability of 1,8-dihydroxyanthraquinone ($C_{14}H_8O_4$) with the divalent metal ions: Cu(II), Ni(II), Mn(II) and Zn (II) has been studied[6]. The Cu(II) and Ni (II) metal ions gave both mononuclear $[M(C_{14}H_7O_4)_2]$ and homobinuclear $[M_2(C_{14}H_6O_4)_2]$ chelates, while Mn(II) and Zn(II) gave only the mononuclear chelates. It is therefore evident that 1,8-dihydroxyanthraquinone ($C_{14}H_8O_4$) can coordinate to the divalent metal ions either through its monoanionic $(C_{14}H_7O_4)^-$ form as a chelating bidentate ligand or through its dianionic $(C_{14}H_6O_4)^{2-}$ form as a chelating tridentate ligand. The mononuclear and homobinuclear chelates of Cu(II) and Ni(II) gave on reaction with pyridine, adducts $[M(C_{14}H_7O_4)_2(py)$ and $M_2(C_{14}H_6O_4)_2(py)$, where M = Cu, Zn].

Homobinuclear metal chelate complexes having 1,4-dihydroxyanthraquinone (quinizarin) as a bridging unit have been prepared with four bivalent first row transition elements[3], namely cobalt, nickel, copper and zinc. The coordination spheres of the metal ions consist of two nearly equivalent six-membered rings with oxygen donor atoms derived from the quinizarin and the terminal ligands which are either ß-diketones or salicylic aldehyde. The complexes are microcrystalline substances of deep colour, stable in air, and insoluble in water and most common organic solvents, but slightly soluble in hot DMF and $CHCl_3$.

1.1.2. Polymeric Complexes of Anthraquinones.

The ligands: 2,5-dihydroxy-p-benzoquinone; 5,8-dihydroxy-1,4-naphtoquinone; 1,4-dihydroxyanthraquinone; 1,5-dihydroxyanthraquinone; 1,2,5,8-tetrahydroxyanthraquinone, and 6,11-dihydroxynaphthacenequinone capable of being tetrafunctional form linear polymers when allowed to react with suitable metals. Each of which reacts with copper(II)ion to produce a linear uncharged polymer[14]. Metal chelate polymers have been prepared from 5,8-dihydroxy-1,4-naphtoquinone (naphtazin) and the divalent metal ions of cobalt, nickel, copper, zinc, and beryllium[15]. The divalent metal chelates of 2,5-dihydroxy-p-benzoquinone with cobalt, nickel, zinc and copper were also investigated[16]. Coordination polymers of 1,4-dihydroxyanthraquinone with some non-transition metal ions, namely aluminium (II), indium (II), beryllium (II) and magnesium (II) were synthesized and characterized[17]. The polymeric complexes are dark coloured powders, and are not soluble in water and common organic solvents, but sparingly soluble in DMF and DMSO.

Most of the isolated complexes of the hydroxyanthraquinones contain molecules of water either as coordinated and/or as crystalline water. The structure and bonding of the chelates were determined by spectroscopic [uv-vis, IR, spr (for some)], thermal and magnetic measurements.

1.2 The Lanthanides

1.2.1. Electronic Configurations

The studied metals: Lanthanum (^{57}La), Cerium (^{58}Ce), Samarium (^{62}Sm) and Terbium (^{65}Tb) belong to a group known as rare earth metals[18]. The rare earth metal group consists of the elements lanthanum, lanthanides/lanthanones (Ce - Lu, atomic numbers 58 - 71) together with scandium (^{21}Sc) and yttrium (^{39}Y). The ground state outer electronic configuration of scandium is $3d^1\ 4s^2$, yttrium $4d^1\ 5s^2$ and lanthanum $5d^1\ 6s^2$. The electronic structure of the lanthanide metals are not known for certain[20]. Since lanthanum, the element preceding this series, has the electronic structure: xenon core $5d^1\ 6s^2$, it may be assumed that fourteen f electrons are filled in from cerium to lutenium. An alternative electronic structure involves moving the single 5d electrons into the 4f shell, except where this destroys the symmetry of a half full f shell, therefore the ground state electronic configuration of cerium is $4f^1\ 5d^1\ 6s^2$ or $4f^2\ 6s^2$, samarium $4f^5\ 5d^1\ 6s^2$ or $4f^6\ 6s^2$, and terbium $4f^8\ 5d^1\ 6s^2$ or $4f^9\ 6s^2$, with the xenon core. Which of the two arrangements is true is of little importance because the lanthanides typically form compounds which are ionic and trivalent, and the electronic structures of the ions are $Ce^{3+}\ f^1$, $Sm^{3+}\ f^5$, and $Tb^{3+}\ f^8$. The 4f electrons in the antepenultimate shell are very effectively screened from effects at the outside of the atom by the 5s and 5p electrons. Consequently the 4f electrons are not involved in the normal chemistry of these elements nor do they take part in bonding, though they do affect their spectra and magnetic properties.

In addition to the characteristic +3 oxidation state, cerium with +2 and +4, samarium with +2 and terbium with +4 are known[20,21].

1.2.2. Occurrence and Uses

The principal source of the rare earths is the mineral monazite, which is essentially a complex phosphate, containing as much as 70% cerium. Other important mineral sources are basthaesite (carbonate), gadolinite (a silicate), fergusonite (a columbate and tantalate), samarskite (a tantalate and uramate), xenotine and allanite (a silicate)[22,23]. It may be of some interest to mention that it has been shown that all the rare earths except Pm, Ho, Tb and Lu are present in small amounts in a number of plants[22]. The percentage composition of the studied metals in the lithosphere is given in Table 1.

Table 1. Mean percentage composition of Ce,La,Sm and Tb in the outer 10 miles of the lithosphere

Element	Lithosphere atomic %	Composition mass %
Cerium	6.0×10^{-4}	4.5×10^{-3}
Lanthanum	2.5×10^{-4}	1.8×10^{-3}
Samarium	9.0×10^{-5}	7.0×10^{-4}
Terbium	1.0×10^{-5}	1.5×10^{-4}

The pure metals of the lanthanides have little use in their own, but alloys (known as mischmetals) containing predominantly cerium (30-50%), together with smaller quantities of the other cerium group metals and non-lanthanide impurities have sufficiently strong reducing power for metallurgical applications. Mischmetals is an excellent scavenger for oxygen or sulphur in many metal systems[22,23].

Magnesium alloys containing ca 3% mischmetal and 1% zirconium have sufficiently high strength and creep resistance at 450-600 °F to be useful in jet engine parts. Mischmetal imports high temperature strength to aluminium, oxidation resistance to nickel alloys, hardness to copper, and workability to stainless steel and vanadium. The pyrophoric properties of cerium alloys have made them in tracer bullets and luminescent shells which show their path by the light evolved on ignition of the alloy, in cigarette and gas lighters.

The lanthanide compounds have ceramic applications[23]. These include as high efficient glass and soft metal polishing; lanthanum oxide in the preparation of low-dispersion, high refraction optical glasses; cerium (iv) oxide to improve the stability and discoloration resistance of glass to gamma of electron-beam radiation, and to opacify in enamels.

Known uses of these compounds as catalysts include the oxides in the hydrogenation, dehydrogenation, and oxidation of various organic compounds; the anhydrous chlorides in polyesterification process; and the chlorides and cerium phosphate in petroleum cracking. In the sense that heterogenous catalysts are commonly characterized by unpaired electrons, paramagnetism, defect structures, or variability in oxidation state, catalysis is a promising practical area[23].

Extensive uses of the lanthanides have always been limited by commercial scarcity and high cost. The problems of availability have not been solved completely, but they have been reduced substantially. Costs have been decreased almost exponentially since the development of ion exchange techniques. As continuing research reveals new and unique potentialities, cost may be expected to decrease until ultimately they will reach levels where the lanthanides can become competitive with some of the more common elements[23].

1.2.3. Lanthanide Complexes

In recent years the complexing tendencies of trivalent lanthanide ions towards a variety of chelating agents have been investigated, and there has been a rapid accumulation of information regarding stepwise formation constants and factors influencing the formation of the chelates[24]. The coordination number of a Ln^{x+} (Ln = La to Lu, atomic numbers 57-71) is only rarely 6, and large coordination numbers (7-10,12) are the rule rather than the exception[21,24,25]. Large coordination numbers are, of course, a consequence of the increased space available around these larger cations. The most common and stable complexes are those with chelating oxygen ligands such as citric acid, oxalic acid, EDTA and acetylacetone. These complexes frequently have water or solvent molecules attached to the central metal, and the coordination numbers of 7,8, and 9 are very common[20].

Oxalic acid precipitates lanthanum and the lanthanides from weak acid solutions and is therefore used for their isolation[19]. The composition of a white crystalline precipitate of lanthanum oxalate is described by the formula $La_2(C_2O_4)_3$ $10H_2O$. Dihydroxytartaric acid precipitates the ions of all lanthanides from weak acid or neutral solutions. The composition of the precipitate is approximately described by the formula $4La_2O_3.5C_4H_4O_8.24H_2O)$[19].ß-Diketones react with the ions of tervalent lanthanides to form chelate complexes $Ln(diket)_3(H_2O)_x$ (where Ln = lanthanides, diket = diketonate, $x = 1-3$)[19,21,26,27]. Dibenzoylmethane, $C_6H_5COCH_2COC_6H_5$, in methyl alcohol precipitates $Ce(C_6H_5CO.CH{=}COC_6H_5)_4$ from methanol solution of Ce(IV) salt if the pH of the solution is adjusted to 8 by NH_3 solution in methyl alcohol[19,21].

The macrocyclic polyether benzo-15-crown-5 reacts with the hydrated lanthanide (III) nitrates in acetone solution to form complexes of the type $Ln(NO_3)_3.C_{14}H_{20}O_5$ (Ln= La,Ce,Pr,Nd and Sm) with lighter (i.e larger) lanthanides and of the type $Ln(NO_3)_3.C_{14}H_{20}O_5.3H_2O.(CH_3)_2CO$ (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and with the heavier (i.e smaller) lanthanides. The macrocyclic dibenzo-18-crown-6 formes complexes of the type $Ln(NO_3)_3.C_{20}H_{24}O_6$ (Ln = La, Pr and Nd) in acetonitrile solution with lighter lanthanides but fails to form stoichiometric complexes under these conditions with heavier lanthanides[28]. Lanthanide nitrates formed solid complexes with several polyether glycols $HO(CH_2CH_2CH_2O)nH$ (EOn), and polyethylene glycol dimethyl ethers, $CH_3O(CH_2CH_2O)nCH_3$ (meEOnme, glymes)[29]. The composition of the complexes were 1:1 (Ln:ligand), i.e. $Ln(NO_3)_3EOn$ or $Ln(NO_3)_3meEOnme$, for triethylene glycol (EO3), tetraethylene glycol (EO4), pentaethylene glycol (EO5) and tetraglyme (meEO4me); 1:2 (Ln:ligand), i.e. $Ln(NO_3)_3(EO2)_2$, for diethylene glycol (EO2); 2:1, i.e. $[Ln(NO_3)_3]_2EO7$, for heptaethylene glycol and 4:3 ($[Ln(NO_3)_3]_4(meEOnme)_3$) for pentaglyme (meEO5me) and hexaglyme (meEO6me). The solid complexes obtained were all deliquescent. The deposition of the solid complexes were generally interfered by water in the solution, and was not observed for some heavier lanthanides when a small amount of water was present in the solution. The solubility, stability constants and other properties of the lanthanoide nitrate complexes with polyethylene glycols and glymes were also determined[29,30].

Complexes with monodentate oxygen ligands are much less stable than the chelates, and tends to dissociate in aqueous solution[20]. The ammoniates, or amines, $LnCl_3.XNH_3$ are decomposed upon addition of water with the formation of the difficultly soluble hydrous oxides or hydroxides[21]. Amines or diamines that are strongly basic, i.e. excellent donors, give the same precipitates when added to aqueous Ln^{3+} salt solution. More weakly basic amines do not react under comparable conditions, However, ethylenediamine reacts with solutions of the anhydrous salts in anhydrous acetonitrile to form solid compounds of the stoichiometric compositions $Ln(en)_3X_3$ and $Ln(en)_4X_3$ where X= NO_3, Cl, Br, or ClO_4[31], with variation of coordination number of the cation from 9 to 8. The ultimate stable ions $[Ln(en)_4]^{3+}$ with an overall average enthalpy change averaging about 61 Kcal mol^{-1}, indicating the Ln-N bond is one of reasonable strength and forms in the absence of water as a competing oxygen donor[32]. Furthermore, the formation of 1,10-phenanthroline (O-phen) and 2,2'-bipyridyl (bipy) chelates, e.g. $Ln(O\text{-}phen)_2X_3$, $Ln(O\text{-}phen)(C_2H_5OH)X_3$, $Ln(bipy)_3X_3$ (X = Cl, SCN, NO_3, CH_3CO_2- but not in all possible combinations described), from ethanolic solutions, or of terpyridyl (terpy), Ln(terpy)$X_3(H_2O)_n$ (X = Cl, NO_3, n = 0 - 3)[21,33-35] indicat that the nitrogen atom can be a donor of some significance. A series of lanthanide amine cages were also synthesized and characterized[36-38]. Recently the possibility of rare earth chelates be considered as laser materials[39,40] due to the low pumb power necessary to excite the complexes via IMET process, relatively high quantum efficiency[41], long life time and narrow band width. The diminished lattice coupling of the rare earth ion in the chelate may be very important in liquid laser where quenching is normally quite serious. However, the quantum efficiency for these chelates are somewhat greater than ruby.

1.3. Aim and scope of the Present Investigation

In the last few years a number of papers concerning the synthesis, characterization, thermal stability, and biological function of some metal chelates of hydroxyanthraquinones and their derivatives have been published[2-8,10-18], including the formation of chelate complexes of some lanthanoids with quinizarin[42]. However, the literature survey reveals the lanthanide-anthraquinone complexes are not studied in detail.

The present investigation presents the spectroscopic study of complexation of 1,4,5,8-tetrahydroxyanthraquinone, quinalizarin (QA), with trivalent ions of Ln, namely: lanthanum, cerium, samarium, and terbium, in ethanolic solution. The isolation, characterization and thermal stabilities of solid Ln-QA chelate complexes were also conducted.

1.4. Spectrophotometric Methods for the Determination of the Composition of Complexes

Various methods have been applied to the investigation of the empirical formulas of coloured complexes in solution. In the present investigation, attempts to determine the stoichiometry of the Ln-QA complexes in solution were made by continuous variation[43], molar ratio[44,45], and Bent and French[45,46] methods. Hence, a brief review on their theoretical back grounds are given below.

1.4.1. Method of Continuous Variation

The formation of many complexes can be represented by the equation

$$A + nB = ABn \qquad (1)$$

in which A is a metallic ion and B a ligand. To determine n, solutions of A and B of the same molar concentration are mixed in varying proportions, and the absorption of monochromatic light is measured. The difference (Y) between each value found and the corresponding value of the absorbance calculated for no reaction is plotted against the composition. The resulting curve (Y against composition) should have a maximum if the absorbance has a large value for the complex than A or B, or a minimum if smaller. The composition at which the difference Y is a maximum/minimum bears a simple relation to 'n' of Equation 1 and is independent of the equilibrium constant.

$$n = \frac{x_{max}}{1 - x_{max}} \qquad (2)$$

where the mixture is made by the addition of x litter of B to (1 - x) litter of A (x<1).

1.4.2. The Mole Ratio Method

This method is also applicable for deducing the stoichiometry of complexes in solution, for situations in which several complexes exist under a given set of experimental conditions. For the ideal case, the absorbance of the solution as a function of concentration of variable component is a continuous curve made up of straight line segments. Change of slope may be observed at any mole ratio of the complexes formed, except for very unusual relations between absorptivities, at restricted wavelengths, of adjacent complexes. While this relationship may be found at some wavelengths, it is unlikely to hold over a wide wavelength region. The absence of change of slope over a given wavelength region indicates that the existence of the complex cannot be established directly by spectrophotometric measurements in this region, and the absence of change of slope over the entire measurable spectrum is strong evidence that a complex of such ratio does not exist.

1.4.3. Bent and French Method

This method is applicable only to solutions in which the complex is highly dissociable. If we write as a general expression for a reaction to be considered, the equation:

$$mA + nB = A_mB_n \qquad (3)$$

(the charge on the complex being determined by the value of m and n), then the expression for equilibrium constant for the reverse reaction will be

$$K = \frac{[A]^m[B]^n}{[A_mB_n]} \qquad (4)$$

If we now take the logarithm of both sides of this expression we may write

$$\log[A_mB_n] = m\log[A] + n\log[B] - \log k \qquad (5)$$

If we keep the concentration of one of the components constant, we then have the equation for a straight line if we plot the logarithm of the optical density, which is proportional to the concentration of the coloured complex, against the logarithm of the concentration of the other component. The slope of this straight line then gives the value of n or m.

2 Experimental

2.1 Apparatus and Reagents

Apparatus: uv-vis. spectra were recorded using a Beckman DU-65 spectrophotometer. IR-spectra were recorded by FI-IR 1600. The pH meter used was Beckman Chem-Meter. Thermal analysis and elemental analysis for carbon, hydrogen and nitrogen were carried in Cairo University, Egypt.

Reagents: The solvents (absolute ethanol, diethylether, DMF, DMSO, etc) were reagent grade (BDH).

Stock Solutions: A stock solution of $2x10^{-3}M$ of quinalizarin (QA) in absolute ethanol was prepared by dissolving 0.272g (10^{-3} moles) of QA (from Hopkin and Williams LTD) in absolute ethanol to the final volume of 500mL. Working solutions were prepared by diluting a suitable aliquot of the stock solution to a known volume with absolute ethanol. Different universal buffer systems were also prepared[47]

Stock solutions of $10^{-4}M$ lanthanide (Ln^{3+}) salts in absolute ethanol were prepared by dissolving appropriate weights of $SmCl_3.6H_2O$, $TbCl_3.6H_2O$, $Ce(NO_3)_3.6H_2O$ and $La(NO_3)_36H_2O$ (from Fluka Chem. A.G) in a known volume of solutions, and the concentrations were determined by EDTA titration.

For digestion of isolated solid complexes conc. H_2SO_4, HNO_3 and $HClO_4$ (BDH, A.R) were used. For the determination of the metal ions disodium EDTA solution was prepared[46] from EDTA (from Hopkin and Williams LTD) and NaOH pellets[48] (BDH, A.R). To standardize the disodium EDTA solution, primary standard 0.01M solution of $ZnSO_4$ was prepared from Zn pellets[48,49] (BDH). For

EDTA titration , the indicator Eriochrom Black T (BDH) solution was prepared[50].

2.2 Isolation of solid Complexes:

The Ln-QA complexes were prepared as follows: To a 200 mL of ethanolic solution of QA, that contains 0.5 m.mol. (0.1361 gm) QA a 50 mL of aqueous lanthanide salt solution that contain 0.5 m.mol. of $SmCl_3.6H_2O$, $TbCl_3.6H_2O$, $Ce(NO_3)_3.6H_2O$ or $La(NO_3)_3.6H_2O$ was added and stirred for half an hour. The mixture was refluxed for two hours, and a dark precipitate was separated by centrifugation for each metal ion. The separated precipitates were washed several times with water, ethanol and finally with diethyl ether, dried in air, and kept in a desiccator over KCl. The purity of the complexes were checked by TLC.

3. Results and Discussion

3.1. Spectrophotometric Studies.

3.1.1. UV-vis. Spectrum of Quinalizarin in Absolute Ethanol

The UV-vis spectrum of QA in ethanol in the range 300 to 700 nm at different concentrations are illustrated in Fig.1(a-c). 10^{-4}M QA solution show absorbtion maxima at ca. 494 nm (ϵ=2.6 X 10^{4}l $mol^{-1}cm^{-1}$) and 516 nm(sh). On dilution two additional inflection points appearing at 340 nm and 570 nm, with the resolution of the absorption maxima at 494 and 516 nm. The band at 340 nm may be attributed to $n-\pi^*$ (L.E) transition of the C=O groups while the intense bands at 494 nm and 516 nm may due to the benzenoid and quinonoid electron transfer (E.T.) while the shoulder around 570 nm may be assigned to $n-\pi^*$ (E.T) transition[51,52].

Based on quantum mechanical calculations, the spectrum of alizarin (analogous compound with quinalizarin), in contrast to the observed spectra of alizarin in solution, does not contain resolved electronic transitions in the visible region. The experimentally observed spectrum of a solution of alizarin was explained by assuming a superposition or overlap of spectra of two corresponding tautomeric forms[12], Fig.14. By the same talken the appearance of resolved absorption maxima at 494 nm and 516 nm in the spectra of QA solution indicate the presence of different tautomers of the studied chromopher.

3.1.2. UV-vis Spectrum of Ln-QA Systems

The addition of excess amount of 10^{-4}M Ln^{3+} solutions to equimolare solution of the QA show instantaneous shift in λ_{max} to ca. 580 nm (Fig.1,2). The red shift in λ_{max} of the ligand by the addition of Ln^{3+} solutions may due to charge transfer[52-54] caused by the formation of complexes with the lanthanoids

Effect of water: As the QA is essentially solubilize in ethanol, and in order to study the behaviour of QA and the formed complexes in universal buffer systems, different spectras were taken by the addition of increasing portions of water till no precipitation occurs.

The intensity of the band at 580 nm (which is due to the complex) enhanced by the presence of 10% and 20% water (Fig.3), but the presence of higher percentage, >40%, of water decreased the intensities, while the intensity of the characteristic band of the ligand at 494 nm. increased. This illustrates complexation reaches maximum in 10% or 20% water (v/v) solutions but decreases at higher percentage; and the effect of water is more pronounced for Ce-QA complex.

Effect of pH: The pH of $4x10^{-5}$M QA was 5.6, whereas the pH of 1:1 (Ln:QA) mixtures range from 3.4 to 4.5. The absorption band of the reaction mixtures around 580 nm due to complexation was affected by the addition of acid, or a buffer system (Fig.4).

The pH dependence of the formation of different dissociated forms of QA was also investigated. The appearance of two isobestic points were observed in the spectra of QA that were taken at different pHs (Fig.4); which demonstrates the presence of different species of QA in solution.

From the effect of pH on the absorption spectra of the ligand(QA), Fig.4, its pK_a values were determined using limiting absorbance and Colleter methodes[55,56], and the values amount to 4.6 and 6.1.

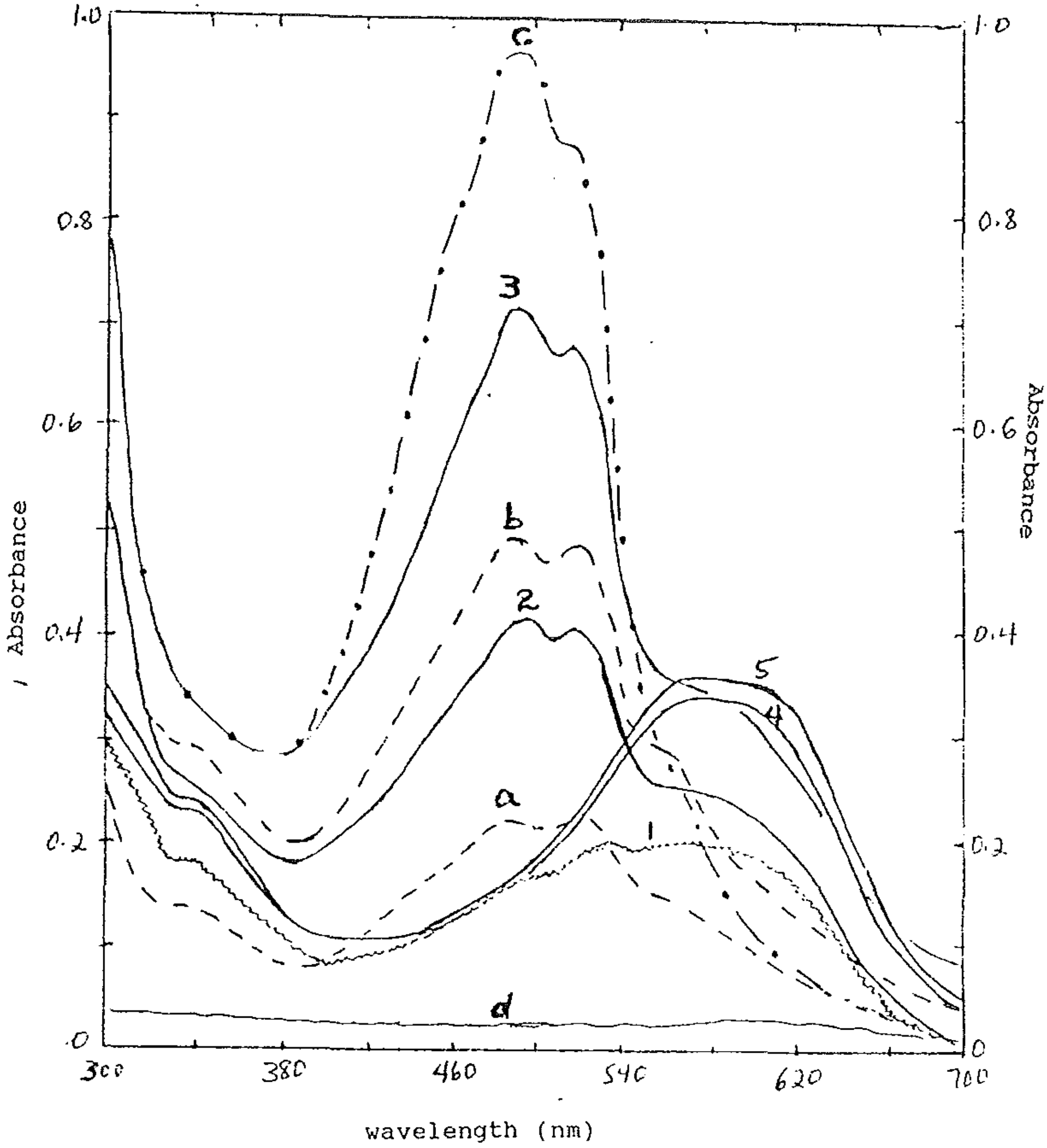


Fig.1. Absorption spectra of QA and its terbium complaxes (in ethanol) :
a-c) $2.5\text{x}10^{-5}$M, $5\text{x}10^{-5}$M, and 10^{-4}M QA, respectively; d) 10^{-4}M $TbCl_3$

1) $2.5\text{x}10^{-5}$M QA + $2.5\text{x}10^{-5}$M $TbCl_3$
2) $5.0\text{x}10^{-5}$M QA + $2.5\text{x}10^{-5}$M $TbCl_3$
3) $7.5\text{x}10^{-5}$M QA + $2.5\text{x}10^{-5}$M $TbCl_3$
4) $2.5\text{x}10^{-5}$M QA + $5.0\text{x}10^{-5}$M $TbCl_3$
5) $2.5\text{x}10^{-5}$M QA + $7.5\text{x}10^{-5}$M $TbCl_3$

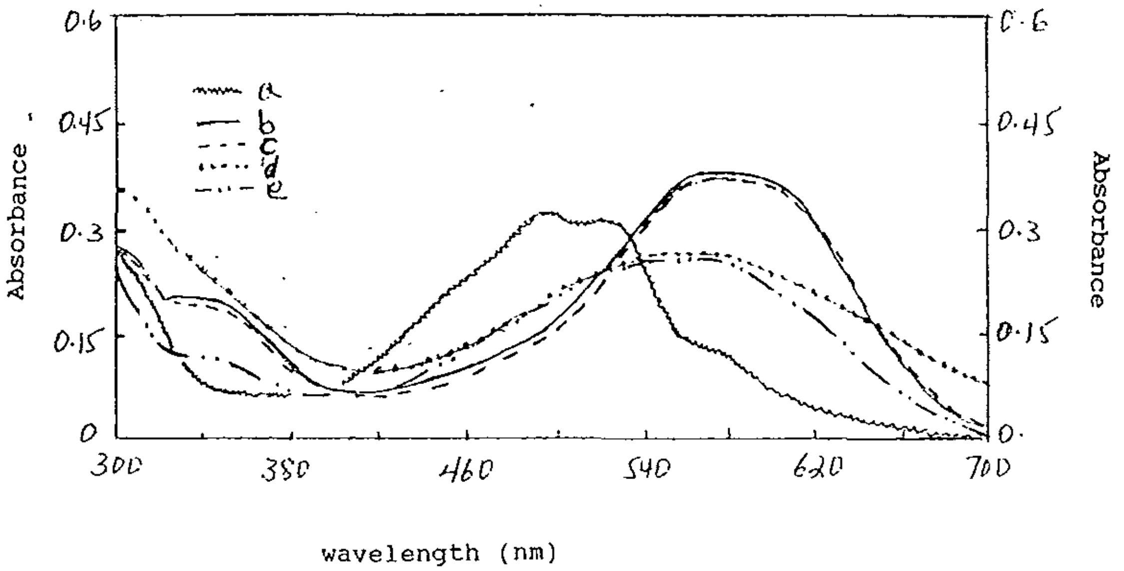


Fig.2. Absorption spectra of ethanolic QA and its Ln complexes :

a) 2.5×10^{-5}M QA
b) 2.5×10^{-5}M QA + 5×10^{-5}M $TbCl_3$
c) 2.5×10^{-5}M QA + 5×10^{-5}M $SmCl_3$
d) 2.5×10^{-5}M QA + 5×10^{-5}M $Ce(NO_3)_3$
e) 2.5×10^{-5}M QA + 5×10^{-5}M $La(NO_3)_3$

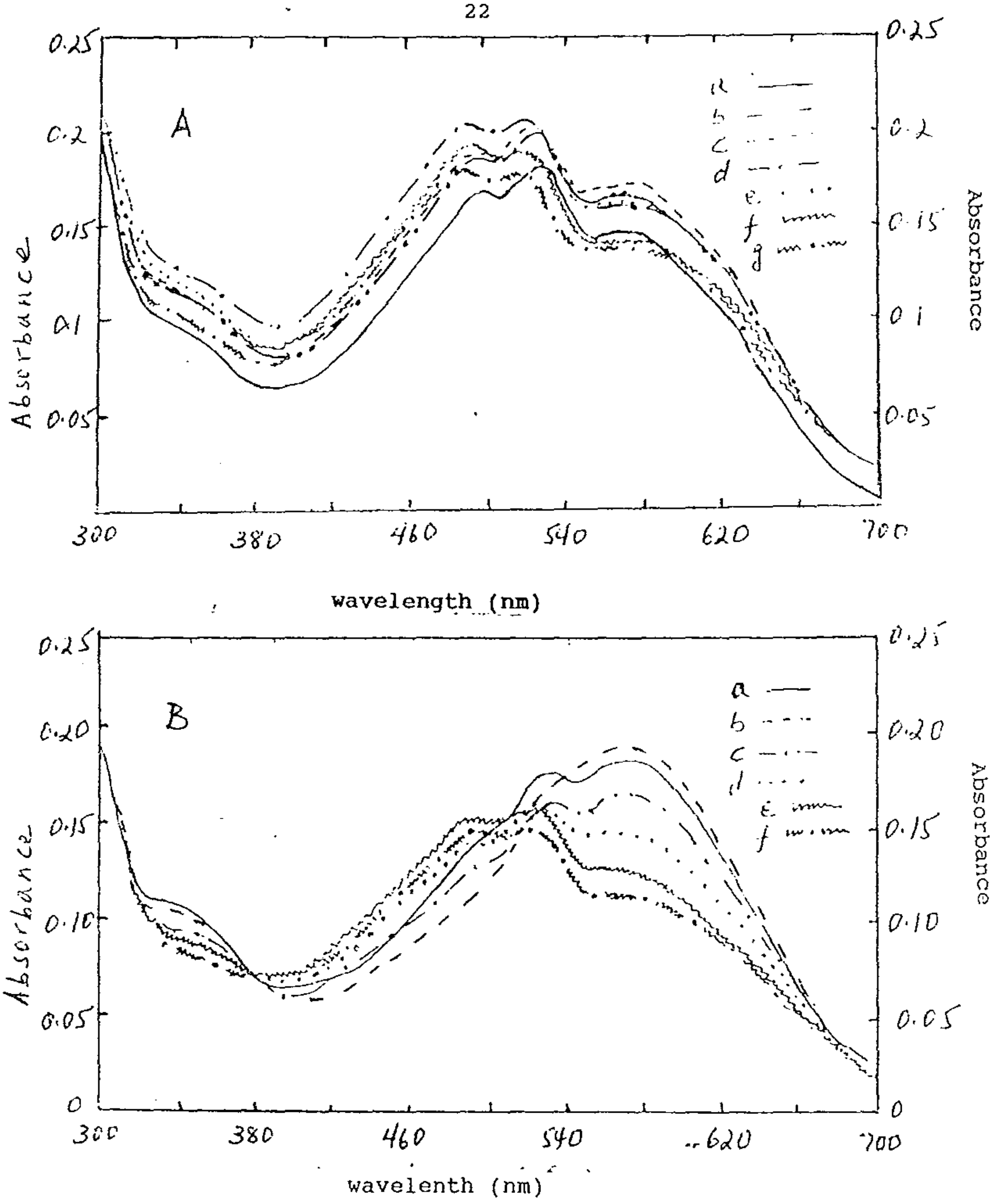


Fig.3. Effect of solvent on the absorption specra of
A)Sm-QA B)Ce-QA at:
a) 0% b) 10% c) 20% d) 30% e) 40%
f) 50% g) 60% water(V/V)

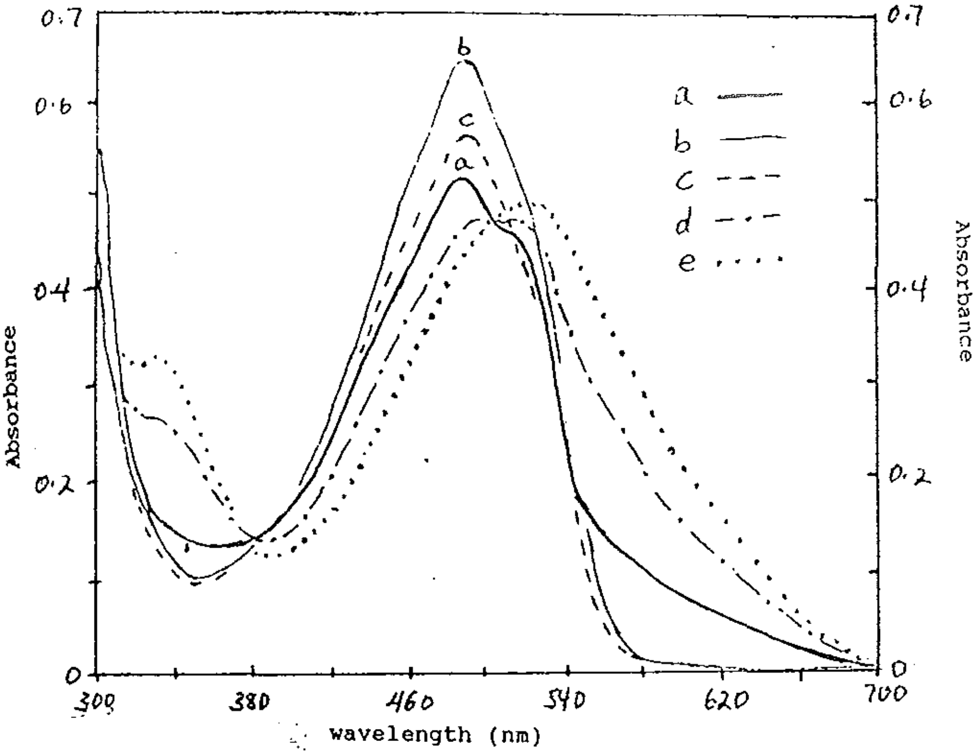


Fig.4. Effect of pH on the absorption spectra of 4x10^{-5}M QA; at pH :
a) 5.6 (without buffer)
b) 3.1 c) 3.5 d) 7.2 e) 8.2

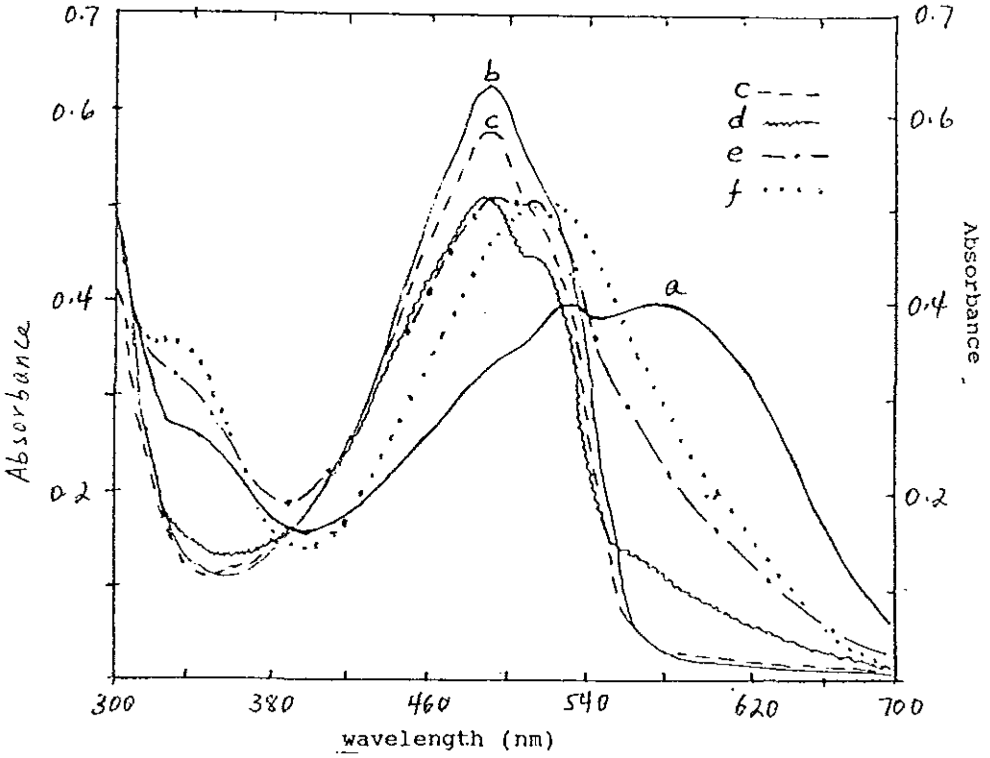


Fig.5. Effect of pH on the absorbtion specra of mixtures of 4x10^{-5}M SmCl$_3$ and 4x10^{-5}M QA;
at pH : a) 3.9 (without buffer)
b)3.1 c)3.5 d)5.7 e) 7.1 f)8.2

3.1.3 Stoichiometry of the complexes.

The composition of Ln-QA complexes have been determined using continuous variation[43], and mole ratio[44,45] methods, also attempts were made to use the Bent and French method[45,46].

In the method of continuous variation the resulting curves, Y against composition had maxima at mole fractions of 0.5 in all the systems. These results indicate the ratio of the lanthanides (La, Ce, Sm, or Tb) to QA to be 1:1. The curves are shown in Fig. 6-9.

The formulas of Ln-QA complexes were further investigated by the mole ratio method. Two series of solutions (in 80% v/v ethanol) were prepared by varying the mole ratio of Ln to constant concentration of QA ($2x10^{-5}$M). The absorbances of the solutions at 580 nm as a function of [Ln]/[QA] are represented in Fig.10 -13.

The investigation of the mole ratio curves Fig.10-13 indicate the formed complexes are in 1:1 mole ratio (M:L). The assymetrical nature of continuous variation curves of La-QA and Ce-QA systems (Fig. 8,9), and the flactuation of the mole ratio curves in the same region (Fig. 12,13) may indicat the formation of 2:1 complexes in adition to the 1:1 complexes in these cases. The attempt to apply the Bent and French method gave no conclusive result. This could be due to the high stability of the formed complexes[45,46].

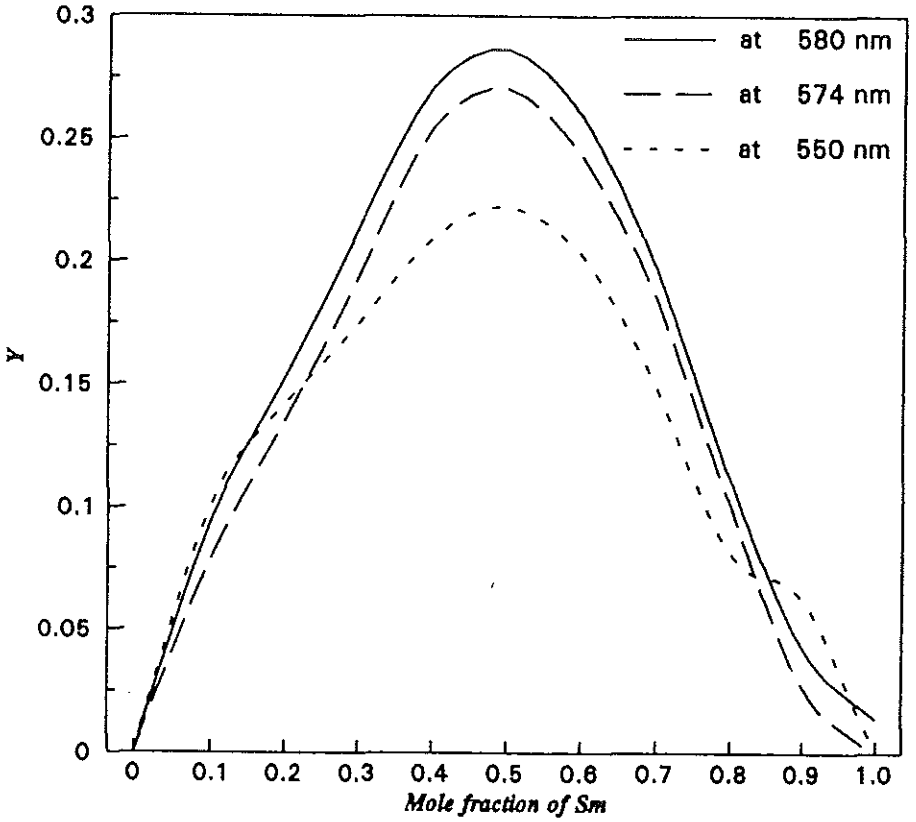


Fig. 6. Continuous Variation Curves for Sm - QA System

[Sm] + [QA] = 10^{-4} M

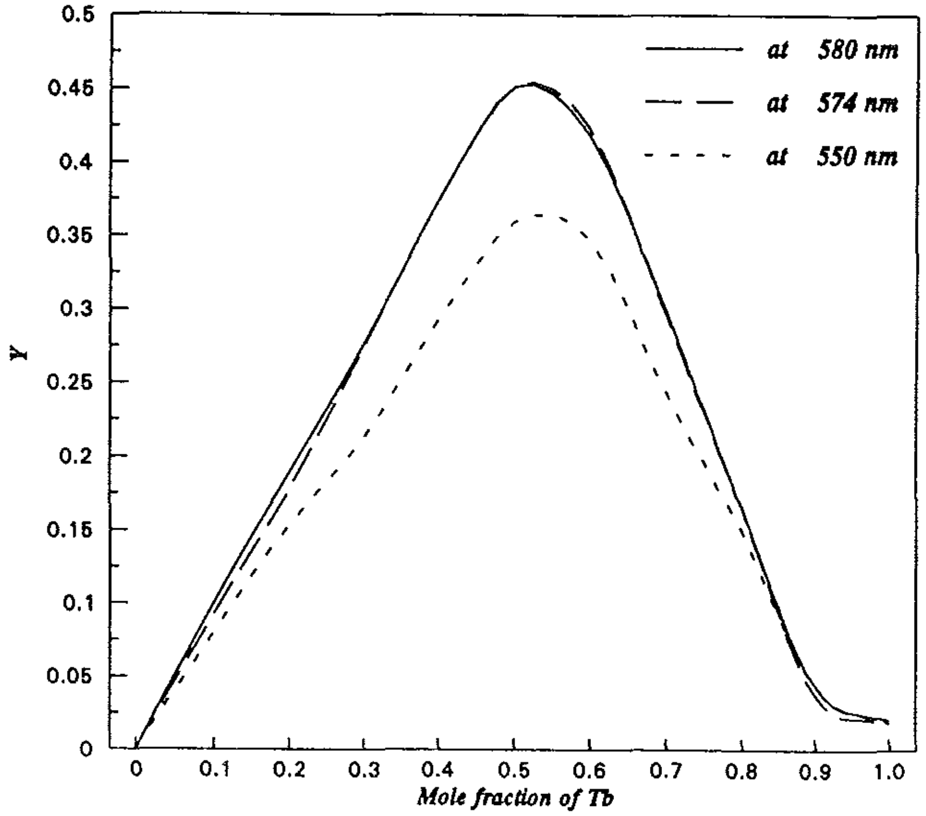


Fig. 7. Continuous Variation Curves for Tb - QA System

[Tb] + [QA] = 10^{-4} M

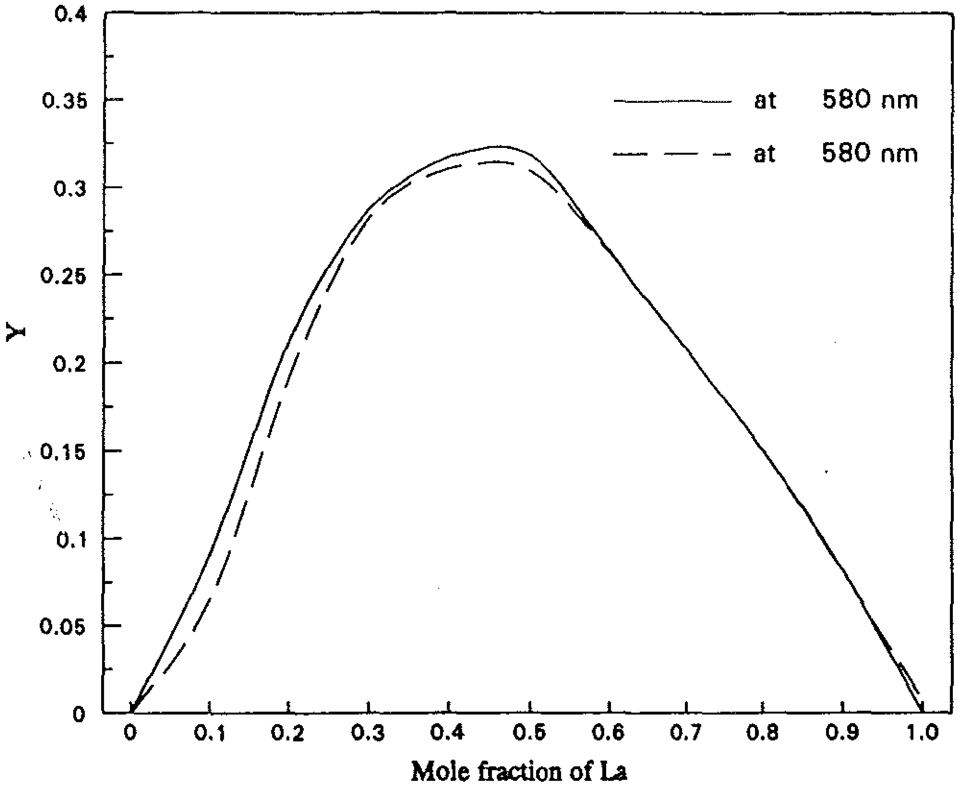


Fig. 8. Continuous Variation Curves for La - QA System

[La] + [QA] = 10^{4} M

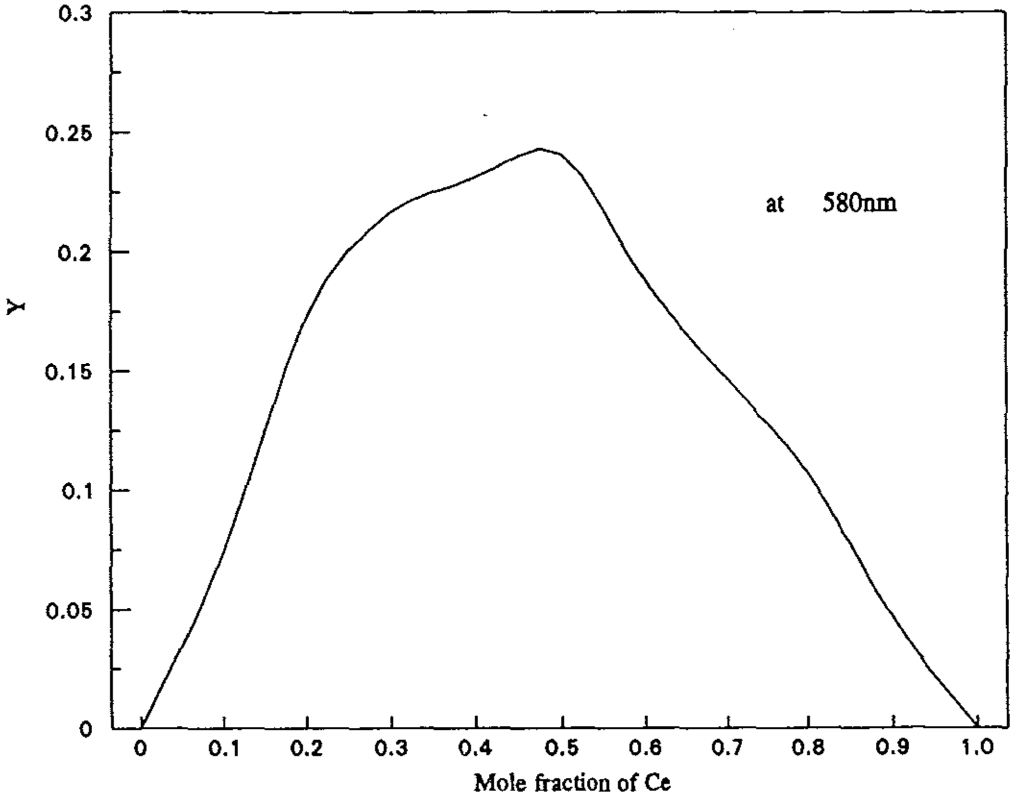


Fig. 9. Continuous Variation Curve for Ca-QA System

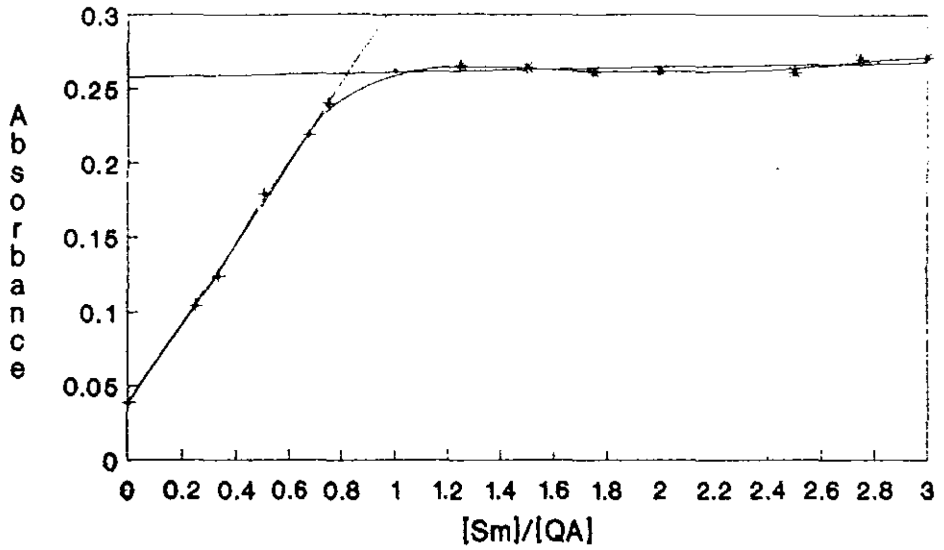


Fig. 10. Mole ratio method curve for
Sm-QA system, at 580 nm;
constant component [QA] = 0.2 mM

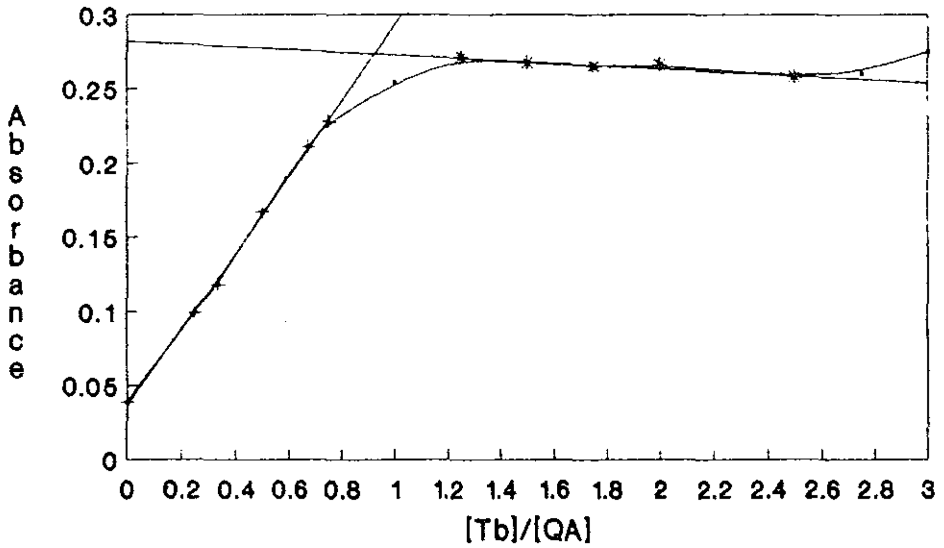


Fig. 11. Mole ratio method curve for
Tb-QA system, at 580 nm;
constant component [QA] = 0.2 mM

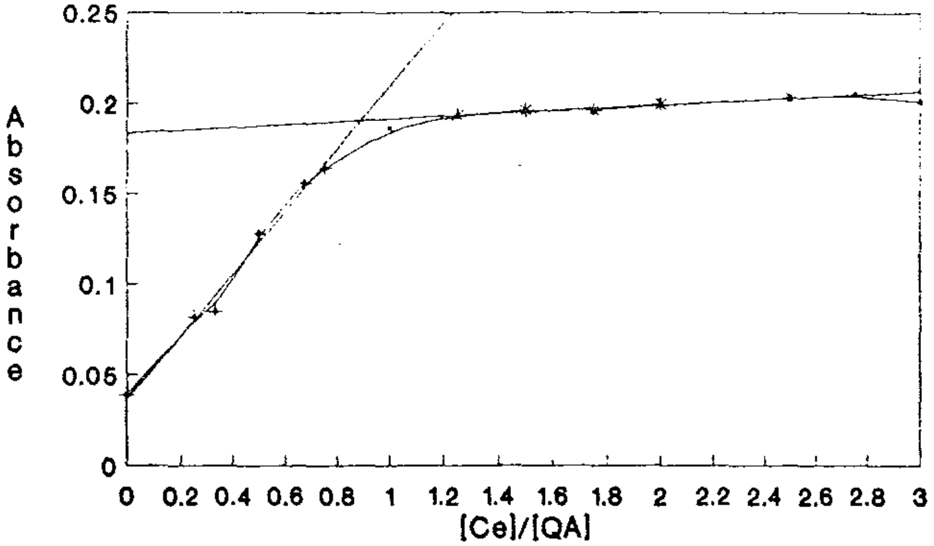


Fig. 12 Mole ratio method curve for Ce-QA system, at 580 nm; constant component [QA] = 0.2 mM

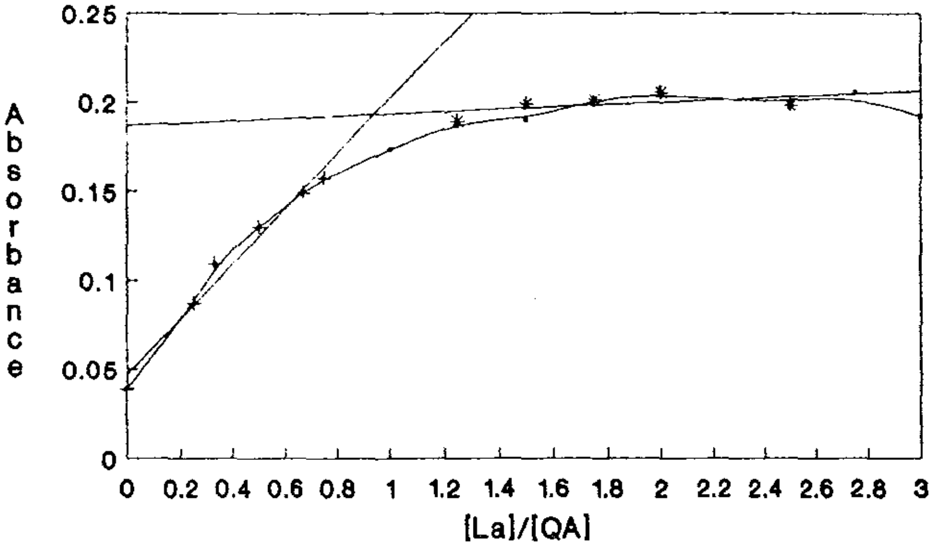


Fig. 13. Mole ratio method curve for La-QA system, at 580 nm; constant component [QA] = 0.2 mM

3.1.4 Evaluation of Equilibrium Constants from the Mole Ratio Curves

If only one complex of high stability is formed, the mole ratio graph consists of two linear intersecting parts. The ratio of the total concentration of metal and ligand at the intersection gives directly the ligand to metal ion ratio in the complex[57]. The stability constant in this case cannot be obtained. If the complex is moderately stable a steep curve is obtained and the intersection of the slopes of the two linear parts of the curves gives the ratio. However, there is an increasing uncertainty with decreasing stability. In favourable cases the stability constants can simply be derived from the difference between the measured curves and that constracted from the slopes. In the case of weak complexes this simple method fails to give any reliable information[57].

For the Ln-QA complexes, consider the dissociation to be expressed as:

Ln_mQA	=	m Ln	+	n QA	(6)	
C		0		0		initial concentration
C (1-α)		mαC		nαC		equilibrium concentration

C is the total concentration of the complex in mol l^{-1} assuming no dissociation, and α is the degree of dissociation. The equilibrium constant may be written as:

$$K=\frac{(m\alpha C)^{m}(n\alpha C)^{n}}{C(1-\alpha)} \qquad (7a)$$

Or

$$K=\frac{\alpha^{2}C}{1-\alpha} \qquad (7b)$$

The values m, n for each complex having been established, values of α and C may be obtained from the curves in Fig.10-13 by the following relationship[45]

$$\alpha = \frac{(E_m - E_s)}{E_m} \qquad (8)$$

where E_m is the maximum absorbance obtained from the horizontal portion of the curves indicating that all the QA is present in the form of the complex. E_s is the absorbance at the stoichiometric molar ratio of Ln-complex, the total concentration of the complex being equal to the concentration of the QA. The results are given in Table 2. The α value for SmQA complex have not been calculated, since the curve brakes sharply, i.e the complex is of high stability[57].

Table 2. The degree of dissociation, α, and the equilibrium constant, K, calculated from mole ratio curves.

Compound	E_n	E_s	α	K X 10^8
TbQA	0.26	0.25	0.038	2.88
CeQA	0.20	0.19	0.050	5.26
LaQA	0.20	0.17	0.150	52.90

The values in the above table and the fact that the curve break sharply for SmQA serve to show the relative stability of the complexes as Sm > Tb > Ce > La.

3.2 Potentiometric Studies

In order to examine complexation as a possible mode of action, the complexation of QA with the studied lanthanide ions have been studied potentiometrically. The following mixtures were prepared for each lanthanide ion and titrated against standard 0.001N NaOH[54].

a) 5 mL KCl (0.01M) + 10 mL HCl (0.001M) + 15 mL ethanol

b) 5 mL KCl (0.01M) + 10 mL HCl (0.001M) + 10 mL QA (10^{-4}) + 5 mL ethanol

c) 5 mL KCl (0.01M) + 10 mL HCl (0.001M) + 10 mL QA (10^{-4}) + 5 mL Ln^{+3} (10^{-4})

Representative potentiometric titration curves are shown in Fig.14.

The average number of protons associated with a ligand, $\bar{n}_A$, was calculated using the formula of Irrving and Rossotti[57,58], Equation 9. And the average number of ligands associated with the metal ions, $\bar{n}$, was calculated using Equation 10.

$$\bar{n}_A = Y + \frac{(V_1 - V_2)(N^0 + E^0)}{(V_0 + V_1)\,T_L} \qquad (9)$$

$$\bar{n} = \frac{(V_3 - V_2)(N^0 + E^0)}{(V_0 + V_1)\,\bar{n}_A T_M^0} \qquad (10)$$

[Where V_1, V_2, and V_3 denote the volume of alkali required to reach the same pH in titration of acid, ligand, and the metal ion: respectively, T_L the total concentration of the ligand, Y the total number of dissociable protons attached to the ligand (4), N^0 The normality of alkali, V_0 total volume of mixture, E^{0} the initial concentration of free ligand and T^{n}_{o} is the total concentration of metal ion.] The results were as follow :

$\bar{n}_A = 2.1$; $\bar{n} = 0.90$ for Sm

$\bar{n} = 0.95$ for Tb

$\bar{n} = 0.82$ for Ce

$\bar{n} = 1.25$ for La

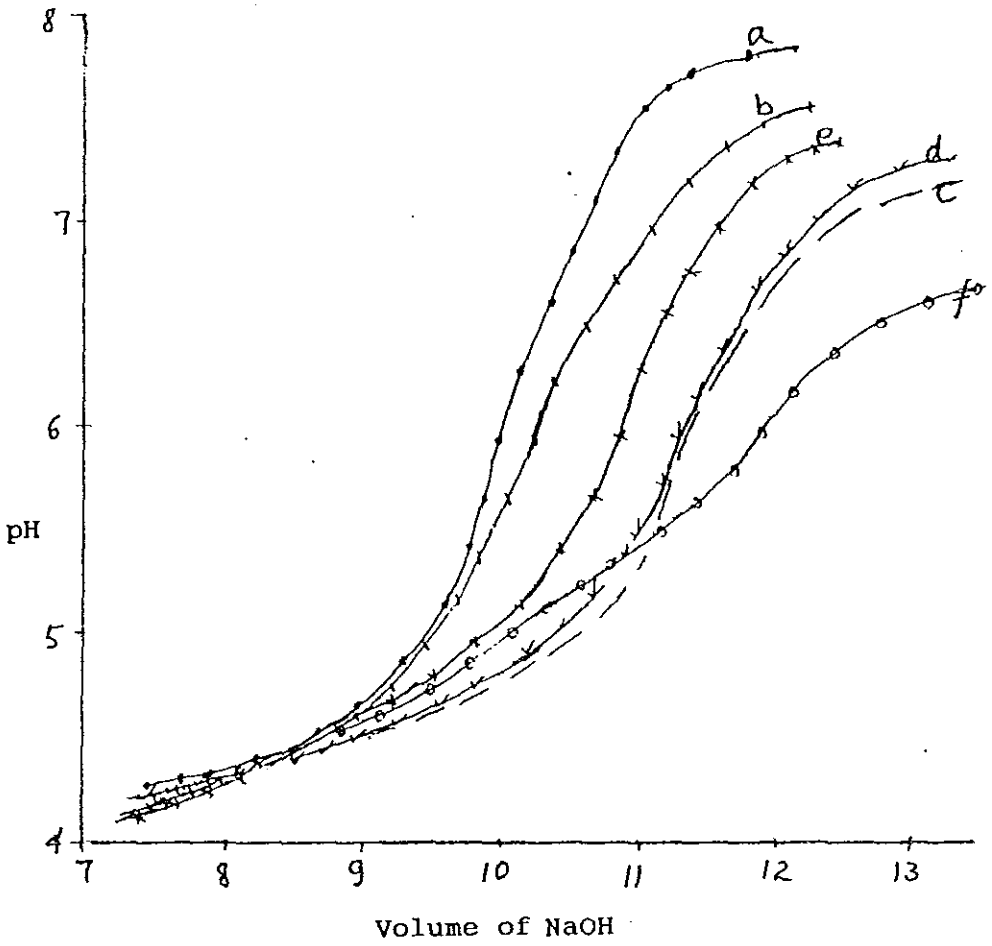


Fig.14. Potentiometric titration curves
a) Free acid b) Ligand (QA) c) Sm-QA
d) Tb-QA e) Ce-QA f)La-QA

3.3 Isolation and Characterization of Solid Ln-QA Complexes

The Ln-QA solid complexes were isolated and purified as per the procedure given in section 2.2.

3.3.1 Physical Properties of the Complexes

All of the compounds are dark powders, stable in air which did not melt up to 280°C. They are found to be insoluble in water, ethanol, acetone, chloroform, diethyl ether, bromobenzene, 1,2-dichloroethanol, etc. but slightly soluble in DMSO and DMF.

3.3.2 UV-vis spectra of Ln-QA in DMSO

The uv-vis spectrum of DMSO solutions of the ligand and the isolated complexes scanned in the range 350 - 900 nm. absorption maxima of the ligand and the complexes are shown in Table 3.

Table 3. λ_{max} of Ln-QA complexes in DMSO

Substance	λ_{max} (nm)
QA	452, 520
Sm-QA	538, 590
Tb-QA	526, 590
La-QA	544, 590
Ce-QA	567

3.3.3 Elemental Analysis

The composition of the metal in each Ln-Q complex was determined by complexometric EDTA titration using Eriochrom Black T indicator, after digestion[55]. Carbon and hydrogen analysis were carried out in cairo University, Egypt. The results of the analyses are presented in Table 4.

Table 4. Analytical data of La-QA complexes

	Experimental (Calculated)		
Complexes	%Ln	%C	%H
$C_{14}H_8O_6$	--	60.27(61.07)	2.69 (2.97)
$Sm(C_{14}H_5O_6).3H_2O$	29.87(31.74)	35.84(35.50)	2.4 (2.35)
$Ce(C_{14}H_5O_6).4H_2O$	28.30(29.11)	33.82(34.93)	2.6 (2.31)
$La(C_{14}H_5O_6).3H_2O$	28.25(30.06)	37.26(36.38)	2.42 (2.40)
$Tb(C_{14}H_5O_6).3H_2O$	32.10(32.96)	34.15(34.87)	2.27 (2.30)

3.3.4 Thermal Analysis

Thermogravimetric (TG) and differential thermogravimetric (DTG) analysis were also carried for Sm-QA, Ce-QA and La-QA complexes. The thermoanalytical curves are given in Fig.15 and 16.

The TG and dTG curves showed that the thermal decomposition of the complexes is a rather complicated phenomenon, taking place in several steps and is affected by the central metal ion. The temperature range, percent mass loss (observed and theoretically predicted) are summarized in Table 5[1*].

Table 5. The most relevant data obtained from the TG and DTG Measurements

Compounds	Temperature range (°C)	% Mass loss obs. (cal)	Fragment
Sm($C_{14}H_2O_8$).$5H_2O$)	46 -180	8.23 (7.07)	$2H_2O$
	180 -286	7.35 (7.07)	$2H_2O$
	286 -500	44.34 (44.58)	$C_{13}H_8O_4$
	residue at 500	40.08 (41.28)	$1/2Sm_2O_2C_2O_4$
Ce($C_{14}H_5O_6$).$6H_2O$	80 -120	7.08 (6.96)	$2H_2O$
	120 -249	9.13 (10.45)	$3H_2O$
	249 -447	45.4 (43.91)	$C_{13}H_7O_4$
	residue at 447	38.39 (38.68)	$1/2(Ce_2O_2O_4)$
La($C_{14}H_5O_6$).$6H_2O$	40 -120	8.01 (8.73)	$2.5H_2O$
	120 -249	8.05 (8.73)	$2.5H_2O$
	249 -500	35.32 (35.49)	$C_{12}H_7O_2$
	residue at 500	48.62 (46.97)	$1/2La_2O_2C_4O_8$

As can be seen in the thermal analysis data, Table 5, the mass loss of 7 to 8.23% in the range 40 to 120/180 °C may be due to water of crystallization, and the mass loss of 7 to 9.13% from 120/180 to 287 °C could be that of coordinated water molecules. The presence of water molecules in the complexes were also confirmed by their I.R. spectra.

The decomposition of the ligand in all the complexes took place in two steps, but at different temperature ranges: 300 - 400 °C for Sm-QA, 250 - 340 °C for Ce-QA and from 250 - 390 °C for La-QA complexes.

[1*] Samples were not dried at 120°C as the case it was in the

400 °C for Sm-QA, 250 - 340 °C for Ce-QA and from 250 - 390 °C for La-QA complexes.

Residue: The residues at 500 °C were 40.08%, 38.59% and 48.62% for Sm-QA, Ce-QA and La-QA complexes, respectively. These values indicate the residues were not the end products of the decomposition, but intermediate products that could lead to their oxides; because, during thermal decomposition of lanthanide compounds their oxides are formed above 600°C.[62,63]

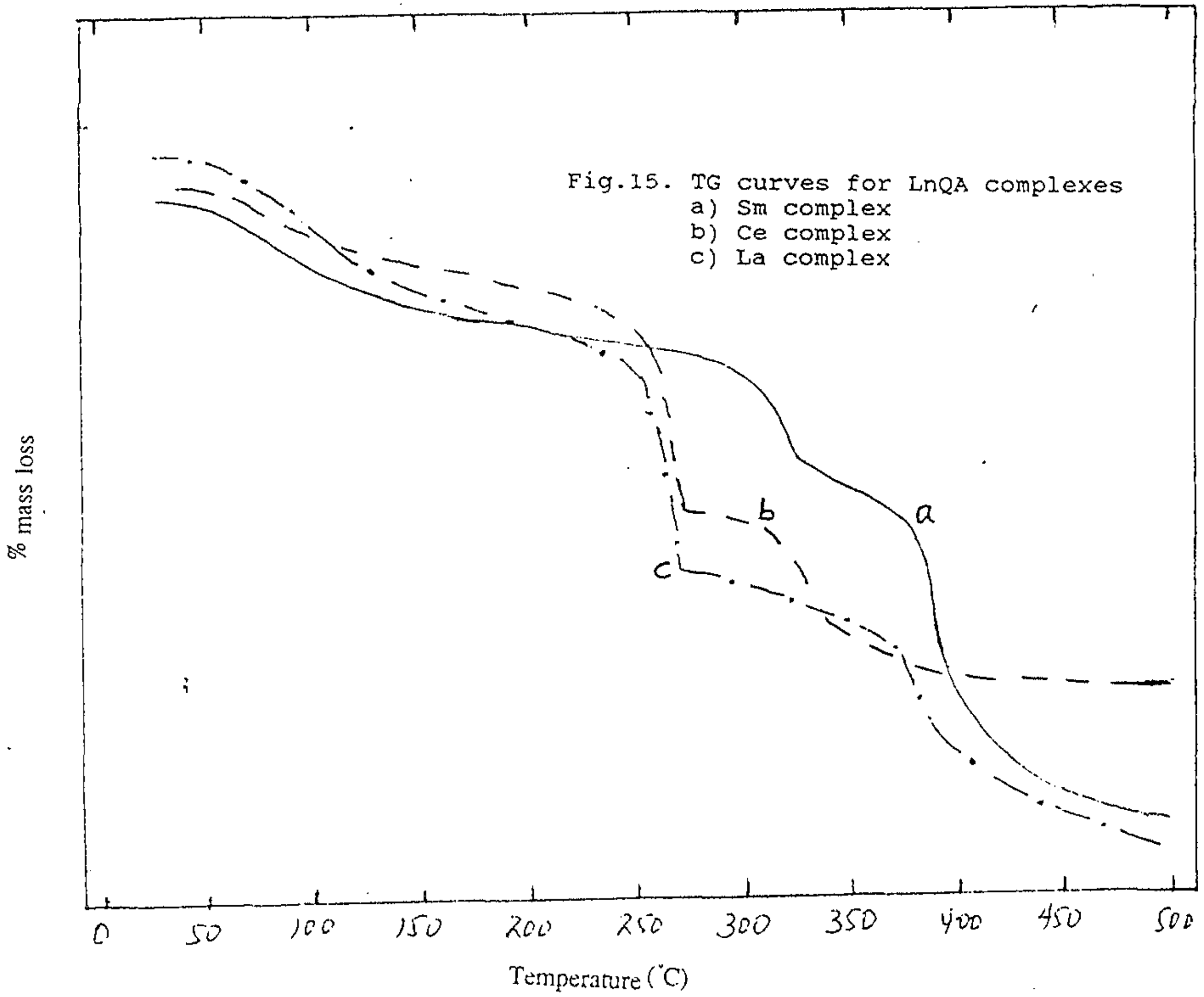


Fig.15. TG curves for LnQA complexes
a) Sm complex
b) Ce complex
c) La complex

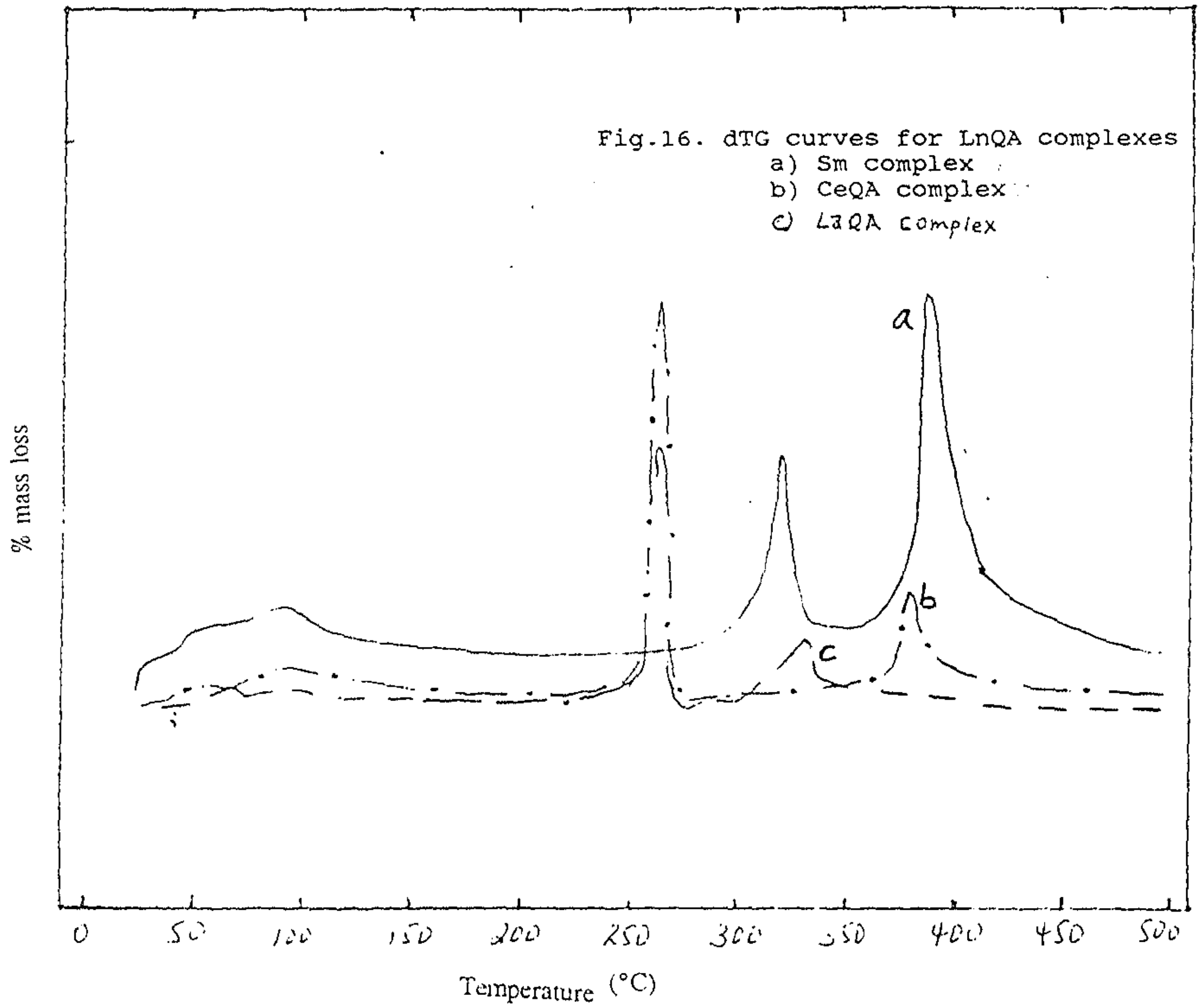


Fig.16. dTG curves for LnQA complexes
a) Sm complex
b) CeQA complex
c) LaQA complex

3.3.5 Infrared Spectra

Infrared spectra of the ligand, QA and the Ln-QA complexes were taken after dehydration both in KBr, Fig.16, and Nujol mull,Fig.17. The most relevant absorption bands in the IR spectra of the Ln-QA chelates and their tentative assignments are shown in Table 6. Band assignments were based on the comparison method by considering the IR spectra of the new chelates and the free ligand, as well as related compounds[3,5,6,8,14-18,64,65].

IR spectra of the ligand exhibits a band at 3345 cm^{-1} assignable to the ν(OH) phenolic[66]. In all the complexes a broad band is observed in the region 3500 - 3100 cm^{-1}; this could be attributed to the ν(OH) of the uncoordinated phenolic or to coordinated water molecules[18,66].

All the compounds show a number of intense bands in the region 1200 - 1700 cm^{-1}, which are due to normal modes of vibration of the ligand affect by its coordination and hence are of great importance for the elucidation of its coordination mode[5,6]. The strong bands of the ligand at 1607 cm^{-1} and 1577 cm^{-1}, due to ν(C=O) of the ketonic groups shifted to lower frequencies ($\Delta\nu \approx 35$ - 70 cm^{-1}) in the complexes, Table 7. This pronounced change in the carbonyl absorption occurs on chelation[18,66], which is due to the delocalization of the π electrones.

Special attention should be paid to the region 1200 to 1280 cm^{-1} in the IR spectra of the studied chelates, since some bands related to the bonding mode of the ligand occur in this region[6]. It is well known[67,68] that in hydroxyanthraquinones the (C-O) bands occur in the region 1200 - 1250 cm^{-1}. The position of these bands indicate that the C-O bonds have a fractional double bond character. The very strong and broad bands in the region 1180 - 1225 cm^{-1} in the ligand, that could be due to the overlap of the different phenolic C-O absorptions became more or less sharper in the complexes at 1254 cm^{-1} (except at 1258 cm^{-1} for Ce-QA). This suggests coordination of oxygen of the phenolic groups with the metal ions forming chelated rings. These rings are expected to be stabilized by a considerable delocalization of the π - electron density.

The chelates show no absorption in the region where carbonyl absorption occurs in the free ligand, indicating that both carbonyl are acting as coordinating groups to form polymers[16,17].

Table 6. Relevant IR frequencies (cm^{-1}) of QA chelates with La (III) ions and their assignments

QA	SmQA	TbQA	CeQA	LaQA	
3345	3423	3419	3425	3433	**ν**(OH) Phenolic or water of crystallization
1607	1558	1558	1551	1561	**ν**$(C=O)_1$
1577	1508	1508	1541	1541	**ν**$(C=O)_2$
1251	1254	1254	1258	1251	**ν**$(C-O)_{3,4,5,6}$overlap
	1154	1154	1158	1158	$(OH)_{DEF}$

Table 7. Carbonyl frequencies and their peak shifts for the metal chelate polymers.

Compound	νC=O (cm^{-1}	$\Delta\nu$C=O (cm^{-1})
QA	1607	
	1577	
SmQA	1558	-49
	1508	-69
TbQA	1558	-49
	1508	-69
CeQA	1551	-56
	1541	-36
LaQA	1561	-46
	1541	-36

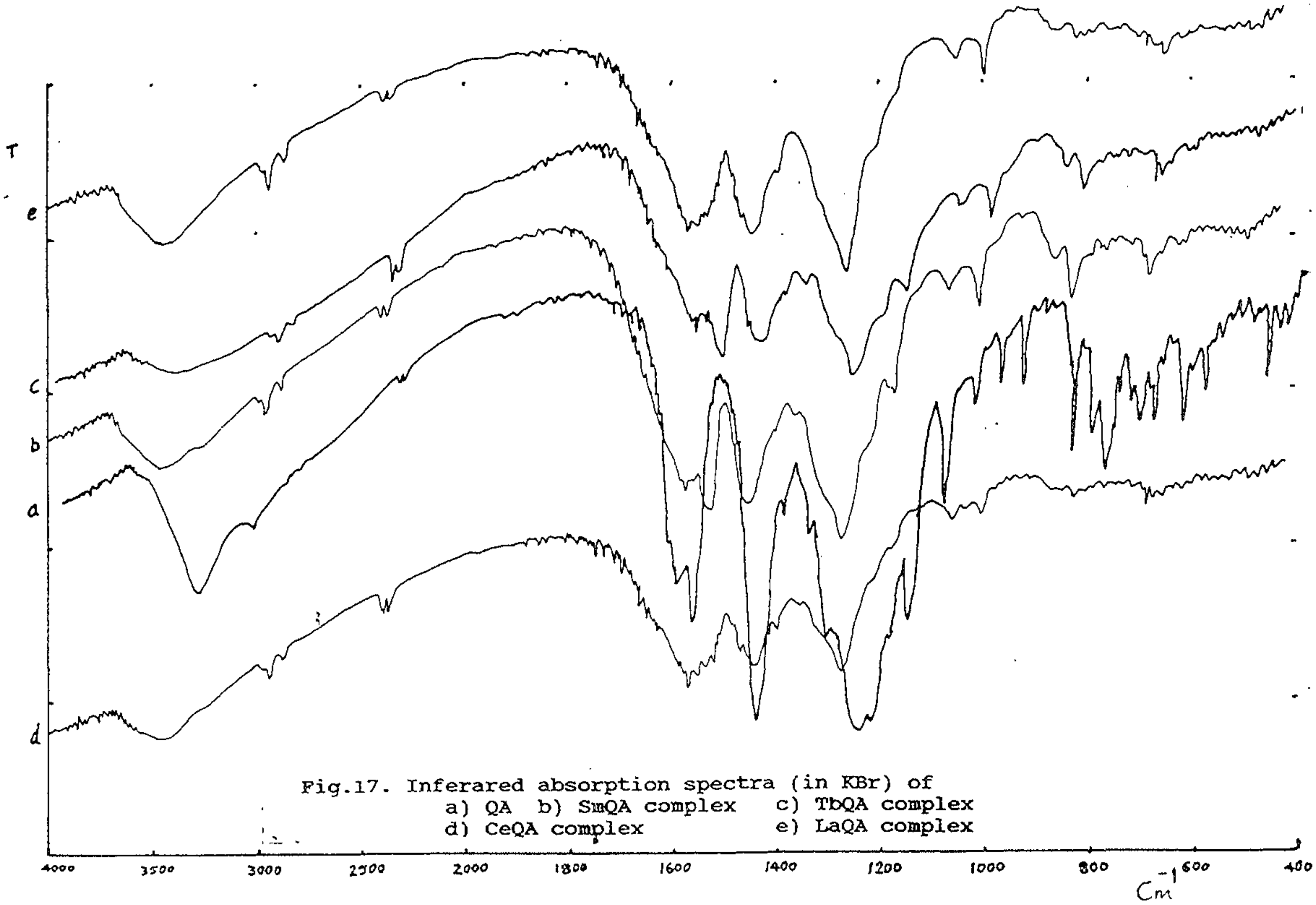


Fig.17. Inferared absorption spectra (in KBr) of
a) QA b) SmQA complex c) TbQA complex
d) CeQA complex e) LaQA complex

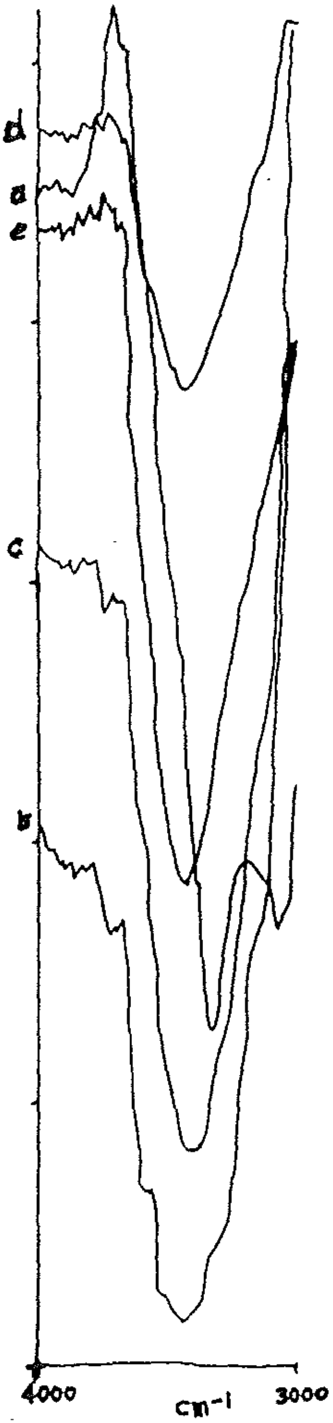


Fig.18. Infrared absorption spectra (in Nujol mull) of :

a) QA b) SmQA complex c)TbQA complex
d) CeQAcomplex e)LaQA complex

4. Mode of Interaction

In the study of the dissociation characteristics of α-as well as ß-substituted hydroxyanthraquinone derivatives it was found that ß-hydroxy derivatives dissociate in more acidic media[12], which leads to the presence of tautomers in solution. For instance 1,2-dihydroxyanthraquinone generate an ana-quinoid structure II, Fig.19, via hydrogen transfer from the first hydroxy group to the oxygen atom in adjacent carbonyl group.

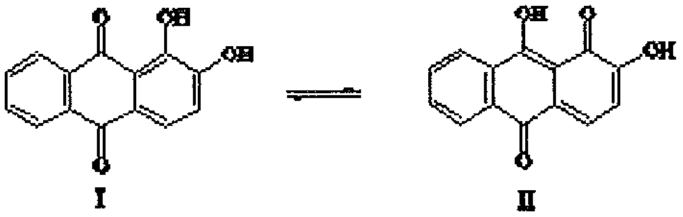


Fig. 19 Tautomer of 1,2-dihydroxyanthraquinone[12].

Taking into account the existence of an ana-quinoid structure for reagent (II), a hypothetical structure for two - component complexes involving both ß-hydroxy and C=O groups and the formation of a five-membered ring metallocycle with vanadium

ion was proposed[12].

Like the 1,2-dihydroxyanthraquinone, quinalizarin (1,2,5,8-tetrahydroxyanthraquine) has ß-hydroxy group that could form tautomer II,Fig. 20 in solution. Therefore, interaction or complex formation of the lanthanoids with QA could involve participation of ß-hydroxy group.

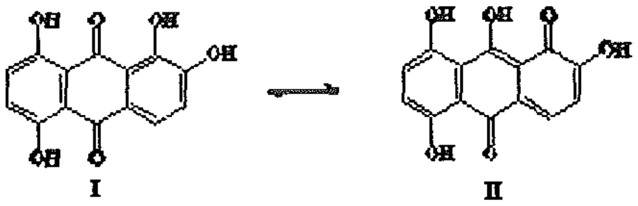


Fig. 20 Tautomer of quinalizarin.

Physical properties, elemental analysis, thermal analysis, and i.r. data provide good evidence that the LnQA complexes are polymeric. And we propose their structures as given in Fig.21. The stability of the complexes being in the order : Sm > Tb > Ce ≥ La.

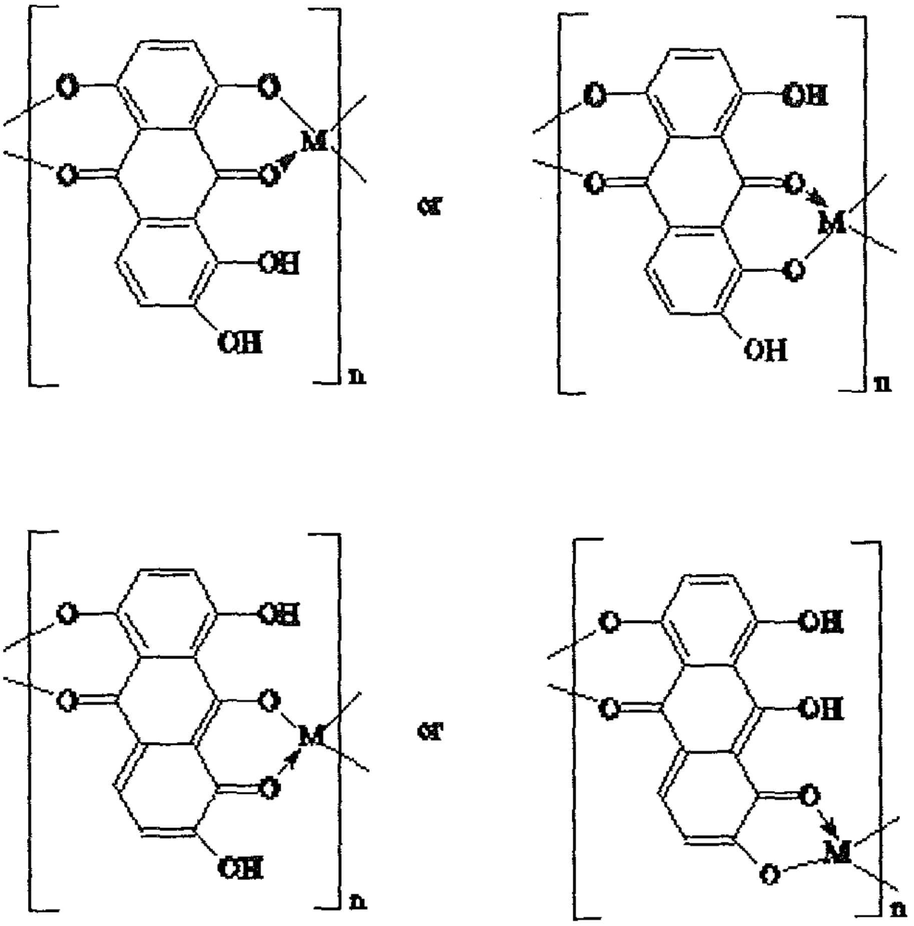


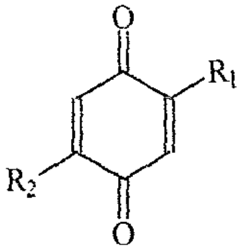
Fig. 21. Proposed structures of LnQA chelate polymers where M = Sm, Tb, La and Ce.

5. Conclusion

Quinalizarin formes stable complexes with samarium, terbium, cerium and lanthanum ions in 1:1 (M:L) ratios. Both spectroscopic and potentiometric studies reveal that the ligand dissociates with liberation of two protons, the pK values amount to 4.1 and 6.1, in the studied pH range, such protons are due to the phenolic substituents. The infrared studies give evidence that chelation occurs through carbonyl (C=O) and phenoxy groups. The stability constant calculations as well as the termograms of the complexes illustrate the stability sequence as follow : Sm > Tb > Ce ≥ La.

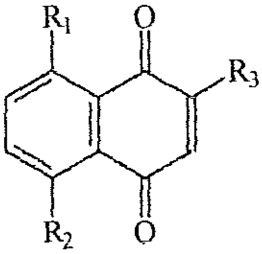
Appendix

1. Benzoquinones



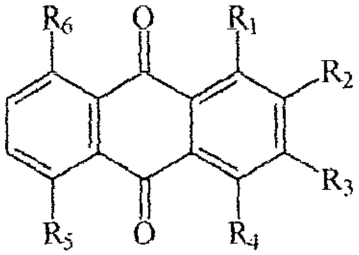
$R_1 = R_2 = H$	p-benzoquinone
$R_1 = OH, R_2 = H$	2-hydroxy-p-benzoquinone
$R_1 = R_2 = OH$	2, 5-dihydroxy-p-benzoquinone

2. Naphtoquinones



$R_1 = R_2 = R_3 = H$	1,4-naphtoquinone
$R_1 = OH, R_2 = R_3 = H$	5-hydroxy-1,4-naphtoquinone
$R_1 = R_2 = H, R_3 = OH$	2-hydroxy-1,4-naphtoquinone
$R_1 = R_2 = OH, R_3 = H$	5,8-dihydroxy-1,4-naphtoquinone

3. Anthraquinones



$R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = H$

anthraquinone (9,10-anthracenedione)

$R_1 = R_4 = OH, R_2 = R_3 = R_5 = R_6 = H$

1,4-dihydroxyanthraquinone (quinizarin)

$R_1 = R_6 = OH, R_2 = R_3 = R_4, = R_5 = H$

1,8-dihydroxyanthraquinone

$R_1 = R_2 = R_5 = R_6 = OH, R_4 = R_5 = H$

1,2,5,8-tetrahydroxyanthraquinone
(quinalizarin)

Fig. 22 Structures of some hydroxyquinones.

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Declaration

I, the undersigned, declare that this thesis is my work, has not been presented for a degree in any universty and all sources of material used for the thesis have been duly acknowledged.

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The thesis has been submitted for examination with my approval as a universty advisor.

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